6th QUARTERLY PROJECT STATUS REPORT

Project Title: Control of Coal Combustion SO₂ and NOₓ Emissions by In-Boiler Injection of CMA.

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Project Objectives:
The principal objectives of this research are two-fold: (A) To understand the mechanism and assess the effectiveness of sulfur capture by the chemical calcium magnesium acetate (CMA); and (B) To evaluate the NOₓ reduction capabilities of CMA by pyrolyzing the organic constituents of the chemical (the acetate) and reducing NO to stable N₂. The optimum conditions and the location of CMA introduction in the furnace will be identified.

To achieve these goals water solutions of CMA or dry powders of CMA will be injected into hot air or gases simulating the furnace exhaust (containing CO₂, SO₂, NOₓ, H₂O, O₂ etc.) and the composition of gaseous and solid products of the reaction will be monitored. The processes of burning the organic acetate as well as the calcination, sintering and sulfation of the remaining solid will be studied in detail.

The effectiveness of "homemade" CMAs containing various amounts of calcium and magnesium will be investigated to explore the role of the two chemicals in the NOₓ and mainly the SO₂ capture processes.

Finally, CMA will be introduced in the matrix of coal particles by an ion exchange technique. Upon subsequent combustion, the SO₂-NOₓ emissions will be monitored and compared to those from burning untreated coal. The composition and physical structure of the ash residues will also be examined. Both techniques (CMA pretreatment and CMA injection) may also be implemented simultaneously to assess their combined effect on SO₂-NOₓ reduction. The work reported herein pertains to these latter tasks, i.e., treating coal with CMA and measuring the reduction in SO₂ emissions and was conducted over the last few months. During the same time period more work was conducted by introducing dry and wet CMA in
the post-flame region of the furnace. Such work will be communicated upon completion in the next quarterly report.

**Project Tasks:**

**Combustion and SO$_2$-NO$_x$ Emissions of Bituminous Coal Particles Treated with CMA**

Experiments were conducted in an externally heated drop-tube furnace to assess the effectiveness of the chemical calcium magnesium acetate (CMA, CaMg$_2$(CH$_3$COO)$_6$) as a combustion catalyst and a coal pre-treatment agent for reducing SO$_2$ emissions. Bituminous coal particles of two distinct sizes, pulverized (75-90 μm) or micronized and beneficiated (mean diameter ≈ 3.5 μm) were burned. To measure the coal particle temperatures and burntimes, combustion traces were recorded for single pulverized coal particles and clusters of micronized coal particles using a three-color near-infrared optical pyrometer. The volatile and the char phase combustion temperatures of untreated pulverized-grind particles, in air at a gas temperature of 1450 K, were determined to be 2200 and 1800 K, respectively. Particles treated with CMA under the same conditions burned hotter, with the temperature of volatile and char phase being 2400 and 2000 K, respectively. SO$_2$ and NO$_x$ concentrations were measured at the exit of the furnace for both the pulverized and the micronized coals. For furnace gas temperatures between 1250 and 1450 K, in a background gas containing 10-50 ppm SO$_2$ and equivalence ratios, $\phi$, between 0.4 to 0.7, untreated micronized and pulverized bituminous coal particles produced SO$_2$ emissions in the range of 100 to 200 ppm and NO$_x$ emissions in the range of 200 to 450 ppm. In contrast, combustion of pulverized particles treated with CMA, burning under the same conditions, not only did not produce any SO$_2$ but also eliminated the background SO$_2$ concentration. The combustion of micronized coal treated with CMA produced less SO$_2$ than untreated micronized coal, but complete reduction of SO$_2$ was not achieved. Experiments with CMA-treated micronized coal in atmospheres containing 40% oxygen suggested that the primary mechanism for sulfur removal in this virtually ash-free coal was the sulfation of resulting CaO/MgO fly ash/aerosols. Experiments, where the effluent of the combustion of pulverized coal was quenched immediately after the heated furnace zone suggest that a fraction of the fuel sulfur (up to 40% of the released SO$_2$) may have been encapsulated by ash during the combustion of treated pulverized coals, with the remaining released SO$_2$...
being removed by sulfation of Ca/Mg-containing ash or submicron CaO/MgO aerosols in the cool-down region of the furnace.

1 Introduction

The combustion of fuels containing sulfur and nitrogen, such as coal, generate SO$_2$ and NO$_x$ emissions which can lead to acid rain formation. All SO$_2$ and most NO$_x$ emissions originate from the sulfur and nitrogen contents of the coal, respectively. Reduction of gaseous sulfur emissions can be achieved by physically removing the sulfur from the coal by various pretreatment techniques, or by chemically reacting the released sulfur-bearing gases (predominantly SO$_2$ and H$_2$S) with sorbents. Sorbents containing alkali and alkaline earth metals (calcium, potassium, sodium, magnesium, etc.) have been found to be effective SO$_2$ and H$_2$S scrubbing agents under various conditions[1]. The sorbent can either be introduced in the coal matrix or separately in the furnace (in-boiler injection) or in the duct (in-duct injection, wet scrubbers, etc.)[2]. This work deals with the former technique, i.e., reduction of SO$_2$ emissions through coal pretreatment with calcium and magnesium. The coal was wetted with aqueous solutions of calcium magnesium acetate (CMA), calcium acetate (CA) and magnesium acetate (MA), dried, burned and monitored for SO$_2$ emissions. While coal pretreatment with the above chemicals was not expected to affect the NO$_x$ emissions, such emissions were also monitored throughout these tests.

2 Review of Literature

In pulverized coal furnaces, efforts to mitigate SO$_2$ emissions by adding calcium-based sorbents to the coal have been met with partial success. Early attempts involved injection of ground limestone along with the coal[1] and SO$_2$ reduction efficiencies in the range of 40% were achieved. Freund and Lyon[3] and Chang et al.[4] used water-soluble calcium acetate to add calcium to the coal structure by ion-exchange. This atomic dispersion of calcium provided a more intimate association with the coal and sulfur removal as high as 90% was observed under fuel-rich conditions (at equivalence ratio$^1$ $\phi=4$), $t_{res}=1$ sec, $T_g=1300$ °C$^3$. Sulfur was retained in the ash as CaS. On the other hand Chang et al.[4] employed extremely fuel-lean conditions ($\phi=0.01-0.07$) to burn ion-exchanged coal and they found that sulfur retention in the ash (as CaSO$_4$) increased with residence time, Ca/S ratio and oxygen concentration, and

$^1$Equivalence ratio, $\phi$, is defined as the ratio of actual to stoichiometric fuel-to-air ratio.
was influenced by gas temperature. While at the optimum conditions of that study\(^2\) sulfur retentions as high as 90% were measured, the sulfur capture in more practical conditions, such as in air, \(T_w=1400\) K, \(\text{Ca}/\text{S}=2\) and \(t_{\text{res}}=1\) sec was only a few percent. Similar or lower values were obtained by Sharma et al. \([5]\) using coal treated with calcium by precipitation of \(\text{CaCO}_3\) in the pores. The strong effect of residence time in those studies, especially when the reactor temperature was greater than the \(\text{CaSO}_4\) stability limit (ca. 1350 K at 300 ppm of \(\text{SO}_2\) \([6]\)), led those authors to suggest that the sulfur was not retained in the ash during high temperature combustion. Instead, it was released during combustion and then it was captured by the \(\text{CaO}\) in the ash at a later time, as the effluent cooled. This process, however, is limited by the residence time in the post-combustion cool-down zone, the effectiveness of the particle dispersion in the gas, and by possible sintering of the \(\text{CaO}\). Thus, if heterogeneous reactions (such as \(\text{CaO} + \text{SO}_2 + 1/2 \text{O}_2 \rightarrow \text{CaSO}_4\)) at the exit of the furnace are mainly responsible for the \(\text{SO}_2\) reduction, then it may be equally (or more) effective to introduce the sorbent directly in the post combustion region of the furnace.

However, Chang et al. \([4]\) and Sharma et al. \([5]\) noticed a pronounced dependence of the sulfur capture on the oxygen partial pressure in their experiments, for which the above mechanism cannot account. Two possible explanations were offered: (i) Combustion at enhanced oxygen atmospheres increases the particle temperature by a few hundred degrees and, thus, promotes the sulfur capture efficiency through encapsulation of sulfides and sulfates in the melting ash.\(^3\) If this, however, was indeed an important mechanism it would have made residence time a parameter of lesser importance than was observed. (ii) Elevated particle temperatures, associated with high oxygen concentrations, promote vaporization of elemental calcium which, upon diffusion to the colder gas surrounding the particle, condenses to form submicron particles of \(\text{CaO}\). This \(\text{CaO}\) aerosol can provide a large surface area for heterogeneous reaction with \(\text{SO}_2\). However, based on the work of Quann and Sarofim \([8]\), Chang et al. \([4]\) calculated that even for their experiments at 40% \(\text{O}_2\), where the maximum temperatures were encountered\(^4\) the amount of calcium vaporized should only be a small percentage of that contained in the ion-exchanged coal. More recent work by Gavalas and Flagan \([10]\) showed that upon collection and examination of ash residues, the finer (submicron) particles were found to be enriched with sulfur, with their relative sulfur content increasing with \(\text{O}_2\).

\(^2\)40% \(\text{O}_2\), \(\text{Ca}/\text{S}=3.4\), \(T_w=1400\) K, \(t_{\text{res}}=16\) sec

\(^3\)Calcium has been reported to accelerate the melting of the ash between 1500 and 1700 K under oxidizing conditions \([4, 7]\).

\(^4\)Chang et al. \([4]\) calculated the char temperatures based on the model of Senior \([9]\), which for combustion of char particles, 40\(\mu\)m in size, at \(T_w = 1400^\circ\)C predicts temperatures in the range of 2500 K and 2250 K at 40% and 21% \(\text{O}_2\), respectively.
concentration, i.e., with the temperature of the burning char. Based on thermodynamic calculations, this was attributed to vaporization of CaOH ions (upon reaction of CaO with water), which has a higher vapor pressure than elemental calcium, and subsequent formation of a CaO aerosol. Given enough residence time in the post-combustion cool-down zone, these fine aerosol particles would react throughout their volume and result in high sorbent utilizations.

Toqan et al. [11] examined the in-flame sulfur capture by burning coal-water slurries containing calcium acetate or calcium hydroxide. The former sorbent was found to be more effective,\(^5\) which was attributed to the excellent solubility of calcium acetate in the slurry and the resulting fine and homogeneous distribution in the coal matrix. Those authors partly accredited the formation of sulfur-bearing calcium alumina silicates for the observed sulfur capture. The sulfur that is incorporated in the fly ash is generally stable and less prone to decomposition at high temperatures. The finer dispersion of calcium acetate makes the sulfur retention (encapsulation) in the ash more effective.

From the above investigations it becomes evident that there are three stages (regions) in furnaces where sulfur can be controlled/captured: (a) During particle combustion by encapsulation in the ash; in this stage fumes of vaporized calcium/magnesium may also be generated at high particle temperatures and may, subsequently, play an important role in the cool-down zone. The former mechanism may prevent gasification of sulfur to H\(_2\)S, SO\(_2\), etc.; in the latter mechanism sulfur will vaporize along with calcium, but no reaction is expected until lower temperatures are reached (below about 1350 K, at \(\approx 300\) ppm SO\(_2\)). (b) During the residence period of the ash (which contains calcium/magnesium oxides) in the high temperature region of the furnace, such as the isothermal cavity of the experimental drop-tube furnace of this study. Sulfur capture in this region is not likely if the temperatures are high and, thus, thermodynamically unfavorable [6, 11]. (c) In the cool-down (quenching) zone of furnaces. Capture in this region is likely and will be enhanced by residence time, degree of mixing, Ca/S ratio, and sorbent/ash particle size. Thus, any calcium/magnesium that was vaporized during the combustion stage will enhance sulfur capture in this zone because of the favorable fine size and large surface area of the subsequently condensed aerosol. Hence, sulfur can be removed in the first stage by encapsulation in the ash and in the following two stages by heterogeneous reaction. The exact role of magnesium has not been quantified yet, but at low temperatures MgO may react with SO\(_2\) and H\(_2\)O to form hydrated magnesium sulfite (such as MgSO\(_3\)•6H\(_2\)O). This is under further investigation.

This work aimed at complementing the above studies by further investigating the control of SO\(_2\) emissions by pre-treating bituminous coal with water-soluble calcium compounds. The

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\(^5\)Sulfur capture efficiencies up to 70% were recorded at Ca/S ratios of 2
calcium treatment was performed by simply wetting the coal with aqueous solutions of calcium acetate (CA), calcium magnesium acetate (CMA) and magnesium acetate (MA). This technique is much simpler than introducing calcium by either ion-exchange or by vacuum impregnation \cite{13} and/or CaCO$_3$ precipitation in the pores \cite{5} and can be adopted commercially. The effects of coal particle size and ash content were explored by using both pulverized and micronized-beneficiated coals. Since the high particle temperatures and durations encountered during the coal combustion may be of particular importance in the overall sulfur capture mechanism, such data were obtained pyrometrically and cinematographically. Time-temperature histories of single particles (both pre-treated and plain) were recorded and observations of the relevant local temperatures, both for the volatile and char combustion phase were made. Pyrolysis experiments involving pulverized-grind particles were also conducted in nitrogen to observe the char structure at the end of devolatilization for calcium-treated and plain coals. Moreover, the effects of magnesium in sulfur capture were explored and NO$_x$ emissions were monitored.

Finally, this study also aimed to contribute to the field of single particle combustion of coal, either plain or treated with the calcium-magnesium compounds. Previous studies have shown that the introduction of calcium to carbonaceous particles can alter their physical structure during the combustion process \cite{14, 15} and also the reactivity \cite{13, 16}. Calcium has also been found to catalyze the combustion of synthetic chars \cite{13} resulting in higher surface temperatures and shorter burnout times.

3 Experimental Apparatus and Procedure

3.1 Coal Properties and Preparation

A high volatile bituminous (HVAB) coal from the Pennsylvania State University coal bank, PSOC-1451, and an Otisca micronized and beneficiated bituminous coal were used throughout this study. Properties of these coals are listed in Table I. Additional physical properties of the PSOC-1451 coal and of chars produced therefrom at high temperatures have been reported by Sahu et al.\cite{17} and are highlighted in Table II. Also the reactivity of PSOC-1451 chars with oxygen has been obtained over a wide temperature range in Ref. 17 and 18. The pulverized coal was size-classified by sieving the samples in a mechanical shaker for 2 hours. The size

\footnote{To enhance the ion-exchange capability of bituminous coal, a mild thermal pretreatment at 200° C is required, which, however, causes a loss in the heating value \cite{4, 5, 12}.}

\footnote{For the case of micronized coal, observations on single burning particles were not possible, instead, traces on burning clusters of particles were obtained.}
range of 75-90 μm was used for the present set of experiments.

To impregnate the coal with calcium/magnesium, 20 wt.% solutions of calcium acetate (CA), calcium magnesium acetate (CMA) and magnesium acetate (MA) in water were prepared. These solutions were added to the pulverized and micronized coals, so as to obtain a nominal Ca/S ratio of 2, under constant stirring. In the case of the MA-treated coal an amount of magnesium equal to that in the CMA-coal was used, i.e., Ma/S ratio of 4. Thus, for every gram of the pulverized PSOC-1451 coal, 0.30 gram of CMA or 0.13 gram of CA or 0.23 gram of MA was added. The slurries were kept in a sonicator for 2 hours in order to mix uniformly. The impregnated coal was dried in an oven at ≈ 70°C for 12 hours. The sample was again sieved with a mechanical shaker to remove any agglomerated particles formed during the calcium impregnation process. SEM micrographs of the plain coal particles and those treated with CMA are shown in Fig. 1.

**TABLE I**

Properties of the coals used

<table>
<thead>
<tr>
<th>Property</th>
<th>Micronized and Beneficiated Coal</th>
<th>Pulverized Coal (PSOC-1451)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size</td>
<td>3.5 (0.5-7.5) (μm)</td>
<td>75-90 (sieved) (μm)</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>61.56 %</td>
<td>51.90 %</td>
</tr>
<tr>
<td>Volatiles</td>
<td>37.50 %</td>
<td>34.43 %</td>
</tr>
<tr>
<td>Ash</td>
<td>0.94 %</td>
<td>13.67 %</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.86 %</td>
<td>1.36 %</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.26%</td>
<td>1.36%</td>
</tr>
<tr>
<td>Calorific Value</td>
<td>32 MJ/kg</td>
<td>29.2 MJ/kg</td>
</tr>
</tbody>
</table>

3.2 Combustion Facilities

Laminar Flow Furnaces. Two externally heated, laminar flow, drop-tube furnaces of similar architecture were used for the experiments of this study. In each of these furnaces a water-cooled injector was used to introduce particles to the top of a 25 cm long radiation cavity. One furnace was sealed [19] and the effluent from the combustion of dilute clouds of particles in controlled atmospheres was monitored. The other furnace [20] was fitted with a three-color optical pyrometer [21], interfaced at the top of the injector and incorporated long slotted win-
### TABLE II
Physical Properties of the PSOC-1451 Coal and Char

<table>
<thead>
<tr>
<th>Property</th>
<th>COAL</th>
<th>CHAR (produced at 1600 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_a ) (g/cm(^3))</td>
<td>1.18</td>
<td>0.98 (cenosphere walls)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.50 (overall cenosphere [18])</td>
</tr>
<tr>
<td>( \rho_{Hg} ) (g/cm(^3))</td>
<td>1.42</td>
<td>1.81</td>
</tr>
<tr>
<td>( \rho_{He} ) (g/cm(^3))</td>
<td>-</td>
<td>1.85</td>
</tr>
<tr>
<td>( \epsilon_a ) %</td>
<td>17</td>
<td>47</td>
</tr>
<tr>
<td>Pore ( V_{Hg} ) (cm(^3)/g)</td>
<td>0.14</td>
<td>0.46</td>
</tr>
<tr>
<td>Pore ( S_{Hg} ) (m(^2)/g)</td>
<td>7.9</td>
<td>14.7</td>
</tr>
<tr>
<td>( S_{BET} ) (m(^2)/g)</td>
<td>-</td>
<td>27.8</td>
</tr>
</tbody>
</table>

Table III. Emissions of \( SO_2 \) and \( NO_x \) from Pulverized Coal

<table>
<thead>
<tr>
<th>Coal (1450 K)</th>
<th>Size ((\mu m))</th>
<th>Untreated Coal</th>
<th>Coal Treated w/ CMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulverized</td>
<td>75-90</td>
<td>0.40 SO(_2) 200 NO(_x) 430 0.34 SO(_2) 100 NO(_x) 500</td>
<td></td>
</tr>
<tr>
<td>(PSOC 1451)</td>
<td>Quench Mid-Qu</td>
<td>200 430</td>
<td>0.34 0 500</td>
</tr>
<tr>
<td>Theoretical</td>
<td>-</td>
<td>- 490 SO(_2) 220-390* NO(_x) 170-300*</td>
<td></td>
</tr>
<tr>
<td>Micronized</td>
<td>3.5</td>
<td>0.63 SO(_2) 100 NO(_x) 300 0.57 SO(_2) 50 NO(_x) 350</td>
<td></td>
</tr>
<tr>
<td>(Otisca)</td>
<td>40% ( O_2 )</td>
<td>0.57 SO(_2) 300 NO(_x) 180-310*</td>
<td></td>
</tr>
<tr>
<td>Theoretical</td>
<td>-</td>
<td>- 380 SO(_2) 220-390* NO(_x) 180-310*</td>
<td></td>
</tr>
</tbody>
</table>

* Based on 20 to 35% conversion of fuel nitrogen to \( NO_x \) and no thermal NO formation.
dows at two sides to facilitate cinematographic observations. In this furnace, single particles were burned in air and their combustion intensity was monitored by the pyrometer along the vertical path of their flight, in the manner of Timothy and Sarofim [22], and Levendis et al. [13]. A simplified schematic of the furnaces is included in Fig. 2. Gas was introduced in both furnaces through the furnace injectors and also through concentric flow straighteners, positioned in the annular space between the injectors and the alumina tubes. The main air-flow through the flow straighteners was preheated (to about 1250 K for a $T_w$ of 1500 K) before it entered the radiation cavities. The gas temperature along the centerline of each furnace was, in general, found to be lower by $\approx 50$ K than the wall temperatures of 1300 and 1500 K of the current experiments. The flow rate for the combustion experiments was kept at 1.0 lpm through the flow straightener and 2 lpm through the furnace injector. The gas temperature profile along the centerline of the furnace was rather isothermal, as shown in Fig. 2. Furnace wall temperatures were continuously monitored by type S thermocouples attached to the wall. Gas temperatures inside the furnace were measured at various axial and radial positions by an aspirated thermocouple [23]. Gas temperature and velocity profiles were also calculated through detailed numerical modelling, using the Fluent software, and gas residence times were so obtained [23].

Pyrometer and Data Acquisition. A three-color near-infrared pyrometer was used to obtain the time-temperature histories of burning particles. The details of the pyrometer are described in [21]. The interference filters used had working wavelengths of 0.64, 0.81 and 0.998 $\mu$m. Silicon photodetectors were used for recording the radiation in all three channels. The current output was converted to voltage and was then amplified by pre-amplifiers ($\times 10^9$). The time constant of the circuit was less than 1 ms. The signals were converted by a Data Translation (DT2828, 12 bit resolution) A/D high speed board and were recorded on a IBM-AT (8 MHz, 2.64 MB RAM) personal computer using the Asyst software.

SO$_2$ and NO$_x$ Detection Techniques. Emissions from the combustion of dilute clouds of coal were measured in the sealed furnace. Pulverized or micronized coals were pneumatically introduced with the aid of a coal feeding system [19] through the furnace injector. Furnace and injector air flows were regulated to provide SO$_2$, nitrogen and air to achieve a background gas concentration of 500 ppm SO$_2$ and 19.5% oxygen. It was found in earlier experiments that alumina components in the radiation cavity (furnace tube and injector insulation) absorbed SO$_2$ until a saturation point was reached. To prevent this phenomenon from biasing the results and underpredicting the SO$_2$ release during the combustion of coal, background SO$_2$ gas
was introduced in the furnace. When saturation was reached and the effluent concentration did not change any longer, coal particles were introduced and dispersed in the furnace.

The coal was introduced at the top of the furnace injector using a particle fluidizer. A glass vial containing coal particles (bed) was advanced by a constant velocity syringe pump, while a slender tube (leading to the furnace) was held inserted into the vial. A constant air flow was used to entrain the particles from the top of the bed and carry them into the tube. The entrance of the tube was beveled and was always kept half immersed in the receding surface of the particle bed. The vial and the tube were vibrated to facilitate fluidization.

Upon removing moisture with a Permapure dryer, the furnace effluent was monitored for SO$_2$ using a Rosemount Analytical 590 UV SO$_2$ analyzer and for NO$_x$ using a Beckman 951A chemiluminescent NO/NO$_x$ analyzer. The analyzer signals were recorded using a Dash-8 analog-to-digital converter interfaced with an IBM XT personal computer running Labtech Notebook and Lotus 123.

The typical experimental procedure was to saturate the furnace with SO$_2$ and let the vapors off-gas until an atmosphere of 10 to 30 ppm SO$_2$ was achieved. In the meanwhile, the furnace was brought to the desired temperature. Coal, with and without CMA, was injected to attain fuel-lean conditions ($\phi = 0.4$ to 0.5 for pulverized coal and 0.55 to 0.7 for micronized coal) in the furnace. Experiments were also performed with MA and CA treated pulverized coal.

The signals from the analyzers were recorded for the duration of the coal injection and later converted to concentration. Each experiment lasted between 20 and 25 minutes. The gas flowrate that was introduced to the furnace was constant (at STP) thus, the residence time varied between 4 to 4.5 seconds according to the temperature of the furnace.

4 Experimental Results and Discussion

4.1 Pyrolysis Behavior of Pulverized Coal

Pyrolysis of PSOC-1451 in N$_2$ at $T_g$ of 1450 K resulted in highly cenospheric particles with thin walls and occasional large blowholes, Fig. 3 a-b. Melting of coal during the formation of cenospheres is evident by close examination of the glassy surfaces of their walls, Fig. 3 b. The swelling factor$^*_{8}$ of these particles is in the range of 1.2 - 1.5. CMA treated particles also exhibited melting, swelling and cenosphere formation as the plain coal particles, Fig. 3 c.

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$^*_{8}$Swelling factor is defined as the ratio of the diameter of the char produced after pyrolysis to the diameter of the coal particle.
3c-d. They swelled, however, to a lesser degree, 1.05 -1.25. This behavior, despite their higher volatile content (because of the impregnation of organic acetate), may be attributed to inhibition of plasticity by the additional cation loading of the char, as observed elsewhere [14, 15].

### 4.2 Single Particle Combustion Observations

Combustion experiments were performed with single pulverized coal particles and groups of micronized particles in air. The wall temperature for these experiments was set at 1500 K \(T_w = 1450 \text{ K}\).

**Plain Coal Particles.** The pulverized particles (in the range of 75-90 \(\mu\text{m}\)) traveled the length of the injector at a low temperature \((\approx 300 \text{ K})\) and, upon entering the radiation cavity, they heated up and devolatilized. The volatiles burned in envelope or jet flames surrounding each particle, in agreement with earlier observations by Timothy et al., [22, 24], Zlochower et al. [25], Choi [26] and Atal and Levendis [14], where it was observed that, for particles around 100\(\mu\text{m}\) or bigger, the volatile cloud separates from the particle surface [14, 24, 25]. Fig. 4 (a-d) shows the combustion traces of single pulverized coal particles. The three curves in each intensity plot correspond to near-monochromatic radiation emitted from a burning particle that was captured by the three channels of the pyrometer. The initial peaks in all intensity traces (top rows) correspond to the homogeneous combustion of the volatiles. The long duration humps that follow the initial peaks are associated with the char combustion phase. The corresponding temperatures (bottom rows) were computed from the radiation intensity traces (pairs of wavelengths) using a Planckian approach, as described by Levendis et al. [21]. The emissivity ratio \(\varepsilon_{\text{char}} / \varepsilon_{\text{vol}}\) for both the volatile and the char burning phases was assumed equal to unity. The former assumption was based on current work which indicates that the emissivity of non-isothermal flames may be almost independent of the wavelength. If, however, the emissivity ratio is assumed to be inversely proportional to the wavelength of observation, as it can be shown for isothermal flames, then the calculated volatile flame temperatures will be lower than those presented herein by an average of 250 K.\(^9\) The volatiles burned approximately 1000 K hotter than the bulk gas temperature. The volatile combustion lasted for 4-7 ms under the conditions of the study, which is typical for bituminous coals of this size range [22, 25]. The char heated up by energy feedback from the volatile flame. In the case of plain pulverized coal particles the flame burned close to the particle surface with a maximum flame standoff (radius of flame / radius of particle) of 2.5. At the end of the volatile phase

\(^9\)It should be noted here that the volatile flame temperatures that were reported in Ref. 14 were too high because they erroneously incorporated the inverse of the wavelength ratio emissivity correction.
Combustion the charred particles are heated up to about 1800 K and then burned at nearly constant temperature until complete burnout or extinction. The char combustion lasted for 30-44 msecs. An earlier study, involving single char particles of the same coal (PSOC-1451), recorded similar trends in combustion burnout times and temperatures [18]. The observed char burnout times are compared to those predicted from a simplified diffusion control model [14, 27] (Regime III of combustion). An overall density of 0.5 g/cm³ was used for the cenospheric chars, see Table II. For char particles in this size range the calculated burnout time was 35 ms, which is in the range of experimental observations; thus, char combustion appears to be diffusion controlled under the conditions of the present study.

Previous observations on the combustion of coal agglomerates, in the size range of 150-500 μm (obtained from coal water fuel droplets [14]), have shown that as the initial agglomerate size decreases, the volatiles tend to burn closer to the resulting char surface. Hence, upon extinction of the volatile flame, the smaller char agglomerates appeared hotter [14]. This trend was verified in this study, since pulverized particles (75-90 μm) reached their highest char temperatures (1800 K) immediately after the extinction of volatiles. This indicates that the volatile flame was in close proximity to the particle surface and, as a result, effective energy feedback was achieved. A limited number of experiments with even smaller pulverized coal particles in the size range 38-45 μm, burning under the same conditions, did not reveal distinct volatile flames indicating overlap of volatile and char combustion phases. This is in agreement with previous studies which have suggested that, for burning small particles of coal, volatile flame formation is suppressed [22, 28].

Combustion traces for individual micronized particles could not be obtained either because of limitations of the pyrometer to detect low intensity signals or because of the tendency of these particles to aggregate. However, pyrometric traces of aggregates were obtained and are included in Fig. 5, along with high speed photographs.

**Coal Particles Treated with Calcium and Magnesium.** Pulverized coal particles that were treated with CMA displayed certain features, Fig. 6 (a-d) that were distinctly different from those of plain coal. The volatiles in most cases were observed to burn 200 K hotter, i.e., at ≈ 2400 K. Upon extinction of the volatile flame, the temperature was seen to dip (as indicated in Fig. 6a by an arrow), before it increased again as char combustion commenced. As mentioned before, this temperature dip at the onset of char combustion was not observed in the case of plain chars. Thereafter, the CMA-treated chars burned at fairly constant temperatures of ≈ 2000 K, which is 200 K more than the temperature of the plain chars. The observations concerning the initial dip in the char temperature can be explained on the basis

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10Large chars (ca.500μm) experienced substantial char heatup periods before they ignited.
of slightly larger volatile flames for CMA-treated coals that reduced the radiative feedback to the coal particle surface. This was clearly observed earlier in the case of bigger coal-water fuel (CWF) agglomerates, with or without CMA in Atal and Levendis [14] and was attributed to the larger mass of volatiles in CMA-containing particles, which are released abruptly. The fact that char combustion (after the initial dip) takes place at higher temperatures for CMA-treated coal may be attributed to the catalytic effects of calcium that can be significant at this temperature range. This is in agreement with earlier observations on calcium-treated synthetic and/or coal chars of similar size [14, 15] which burned at higher temperature in the presence of calcium.

Pulverized coal particles were also impregnated with calcium acetate (CA) and magnesium acetate (MA). Particles treated with CA displayed combustion behavior similar to that exhibited by CMA-treated particles. Volatile flame temperatures were calculated to be approximately 2400 K. Again, there was a dip in temperature at the end of the volatile phase combustion and, thereafter, the char temperature increased and remained at 2000 K for the rest of the burntime, Fig. 7a. The volatile phase and char phase temperatures for MA-treated coal particles were slightly lower, ≈2300 K and ≈1900 K respectively (Fig. 7 b), than the corresponding temperatures for CA- or CMA-treated particles. These temperatures though, are higher than those observed for plain coal particles. This suggests that the catalytic effects of magnesium are less than those of calcium, in agreement with earlier studies by Hengel and Walker [16] on catalytic char gasification. The effect of the additives on the burnout time of the char was not clear, since the burnout time itself was observed to vary by up to 50% from particle to particle, most likely because of size differences, in the range of 75-90μm, or morphological and structural variations.

4.3 SO₂ and NOₓ Measurements

(a) SO₂. The experimental results on emissions are summarized in Table III and are plotted in Fig. 8. The SO₂ emissions from untreated coal, either pulverized or micronized, did not depend on the gas temperature in the range of 1250 to 1450 K. The pulverized PSOC-1451 coal released approx. 200 ppm of SO₂ (ca. 40 wt.% of its sulfur content) and the micronized coal about 100 ppm of SO₂ (ca. 25 wt.% of its sulfur content). The SO₂ emissions were dramatically lowered when the pulverized coal was treated with CMA, CA or MA. Not only the treated coal did not emit any SO₂, but the background SO₂ (10-30 ppm) in the furnace was also reduced to zero (Fig. 8a). There are indications that magnesium is active at the cool-down zone of the furnace in the presence of H₂O.

The micronized and beneficiated Otisca coal emitted less SO₂ (ca. 100 ppm or 25 wt.% of its
sulfur content), which is expected since its sulfur content is lower, Fig. 8b. Upon treatment with CMA, however, this coal failed to perform as well as the pulverized coal. The SO$_2$ emissions were reduced but not eliminated (ca. 40-50 ppm were detected, i.e., 13 wt% of the sulfur content). Thus, CMA performed better in the pulverized coal inspite its, most likely, poorer penetration to the interior of the rather large (75-90µm) particles in comparison to that in the smaller (3.5µm ave.) particles of the micronized coal. Since a main difference between the pulverized and the micronized coals is that the latter was virtually ash-free, this suggests that ash-encapsulation of sulfur during the combustion of the former coal may indeed be an important mechanism of sulfur removal. However, when the CMA-treated micronized coal was burned at 40% O$_2$ in the manner of Chang et al. [4] complete sulfur removal was achieved, Fig. 8b. While single particle temperatures for micronized coal could not be measured herein, there is no doubt that at 40% O$_2$ their temperature was higher. This can be inferred from CMA-treated pulverized particles that burned at 2300 K, at 40% O$_2$, i.e., ca.300 K higher than when they burned in air. Thus, higher temperatures might have promoted vaporization of calcium and especially magnesium, whose partial pressure is higher by an order of magnitude than that of calcium [8]. Such a submicron aerosol may act as an effective sulfur capture agent in the cool-down reaction zone at the exit of the furnace.

To estimate the amount of fuel sulfur removed by ash encapsulation, a water-cooled probe was used to sample the furnace effluent isokinetically at the end of the heated zone in the furnace. This probe also introduced nitrogen to immediately quench any reactions. The results of these measurements are plotted in Fig. 8c. Untreated pulverized coal produced the same amount of SO$_2$ as before (about 200 ppm or 40 wt% of its sulfur content). However, in contrast to the earlier measurements made at the end of the cool-down zone the CMA-treated coal did not reduce SO$_2$ emissions to zero. Rather, the SO$_2$ emissions were reduced by about 100 ppm (20 wt% of its sulfur content), suggesting that up to 100/200 or about 50% of the fuel sulfur that would have released SO$_2$ in these experiments may have been removed by ash encapsulation. The remaining fraction of the released sulfur was removed by sulfation of CaO fly ash and, possibly, by submicron aerosols in the cool-down zone of the furnace, where the temperature is favorable (below 1300 K, at 120 ppm SO$_2$ [6]).

(a) NO$_x$.$^{11}$ For both coals, the NO$_x$ emissions depended on gas temperature, with the most NO$_x$ created at 1450 K and the least at 1250 K (25% less). This difference could be partly attributed to contributions from thermal NO$_x$ during combustion of the volatiles that burned

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$^{11}$The nitrogen in the coal may be released with the volatiles or during char combustion. Studies have shown the char to be slightly enriched in nitrogen [29], but to a first approximation the fraction of nitrogen in the char may be assumed to be in proportion to the char yield [30].
at 2200 K in the former case and hardly ignited in the latter case, and partly to the slow release of char nitrogen. The micronized coal - both treated and untreated - produced less NO\textsubscript{x} than the pulverized coal, possibly because of its lower nitrogen content, see Table I. Moreover, the micronized coal may have been burned under slightly more fuel-rich conditions ($\phi$ was estimated from a proximate analysis instead of an elemental analysis) than the pulverized coal (Table III) which would tend to form less NO\textsubscript{x}. Also, Abbas, et al. [31] found that under certain combustion conditions, smaller coal particles produce less NO than larger particles. This could be due to localized fuel-rich conditions surrounding the smaller particles as the volatiles and char burn together.

CMA-treated pulverized coal released on the average a similar amount of NO\textsubscript{x} as untreated coal at 1450 K.\textsuperscript{12} Similarly, CMA-treated micronized coal produced, on the average, slightly more NO\textsubscript{x} than untreated micronized coal. In part, this could be due to the extra oxygen added to the fuel by the organic acetate\textsuperscript{13}, assuming that CMA penetrated effectively these small size particles\textsuperscript{14} or to contributions from “thermal” NO\textsubscript{x}.

\section{Conclusions}

1. Impregnation of pulverized coal particles by CMA and CA (and to lesser extent MA) was found to increase the combustion temperature of both the volatile and the char phases. Effects of the additives on the burntime of either of the two phases could not be clearly detected.

2. The pre-treatment of pulverized (75-90\textmu m) and micronized (3.5\textmu m mean) and beneficiated coals with CMA, CA or MA (at a Ca/S = 2) substantially reduced the emission of SO\textsubscript{2}, at gas temperatures between 1250 to 1450 K, followed by a cool-down zone, in fuel-lean combustion ($\phi = 0.35-0.57$).

3. The combustion of CMA-, CA-, or MA-treated pulverized coal in normal air suggested that all three sulfur caption mechanisms, mentioned in the introduction, were evident in

\textsuperscript{12}Since pulverized coal treated with CMA burned 200 K hotter (both volatile and char combustion) than plain pulverized coal, the slight increase of NO\textsubscript{x} in Fig. 8a may be perceived as “thermal” NO\textsubscript{x}, but on the average no substantial changes were observed.

\textsuperscript{13}The conversion of fuel-N to NO has been found to increase with increasing (fuel-O/fuel-N) ratio [32, 33].

\textsuperscript{14}The assumption on effective penetration of CMA in micronized coal is supported by earlier observations by Atal and Levendis [22] that showed suppression of plasticity in micronized coal upon treatment with CMA, unlike the case of pulverized coal. Calcium may catalyze crosslinking in coal [14] and, thus, suppress plasticity.
the present experiments, i.e., (a) ash encapsulation of fuel sulfur during high temperature particle combustion, (b) sulfation of CaO in the ash in the cool-down region of the furnace (below ca. 1300K at 200 ppm SO$_2$) and possible sulfation of MgO at much lower temperatures, and finally (c) sulfation of CaO and MgO submicron aerosols (generated during particle combustion) in the cool-down region of the furnace as well. Experiments wherein emissions from CMA-treated pulverized coal were sampled directly at the exit of the hot zone of the furnace suggested that up to 40% of the sulfur that would be released as SO$_2$ in the present experiments was removed by ash encapsulation. The balance of the released SO$_2$ was removed by sulfation of CaO and MgO in the cooler regions of the furnace.

4. The results of experiments in normal air and in atmospheres containing 40% oxygen suggested that the release and subsequent sulfation of CaO and MgO aerosols may be the main mechanism for sulfur removal in the virtually ash-free micronized coal that was treated with CMA.

5. NO$_x$ emissions were increased with higher gas temperatures. Micronized coal produced 25% less NO$_x$ than pulverized coal. This could be due to its lower nitrogen content and slightly more fuel-rich conditions for the micronized coal combustion, as well as localized fuel-rich conditions surrounding the small particles as the volatiles and char burn together.

6. The emissions of NO$_x$ from CMA-treated pulverized coal were similar to those from untreated coal, whereas CMA-treated micronized coal released slightly more NO$_x$ than it did when untreated. The latter event may be caused by the added fuel oxygen associated with the effective penetration of the CMA additive.

6 Acknowledgements

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7 References


8 List of Figures

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2. Schematic of the furnace with the axial gas temperature profile and trajectory of burning particles.

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5. Three-color pyrometry intensity signals (top row) and two-color ratio temperature profiles (bottom row) for burning aggregates of micronized coal particles in air at $T_g$ of 1450 K. Frames from the High Speed Cinematography are attached next to the traces.

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8. $SO_2$ (-----) and $NO_x$ (- - - ) emissions from pulverized (PSOC 1451, 75-90 $\mu$m) and micronized (Otisca, 4$\mu$m) coal with and without sorbent treatment burning at 1450 K. (A) PSOC-1451 (i) plain; treated with (ii) CMA (iii) CA, (iv) MA. (B) Otisca (i) plain; treated with CMA burning in (ii) air (iii) 40% $O_2$. (C) PSOC-1451 (i) plain, sample extracted at the end of the isothermal zone; (ii) with CMA, sample extracted at the end of the isothermal zone; (iii) plain, sample extracted at the mid-height of the isothermal zone; (iv) with CMA, sample extracted at the mid-height of the isothermal zone;
Plain PSOC-1451 particles (75-90 μm)

CMA-impregnated PSOC-1451 particles (75-90 μm)
b. OPTICAL PYROMETER

R II / FURNACE INJECTOR

VOLATILE COMBUSTION

CHAR COMBUSTION

CINEMATOGRAPHY

ASH

FILTER

OPTICAL PYROMETER

VOLATILE COMBUSTION

CHAR COMBUSTION

CINEMATOGRAPHY

ASH

FILTER

GAS TEMPERATURE

VOLATILE TEMPERATURE

CHAR TEMPERATURE

EXHAUST

TEMPERATURE (K)

VERTICAL DISTANCE (cm)
A) Plain PSOC-1451 particles (75-90 µm)

B) CMA-impregnated PSOC-1451 particles (75-90 µm)
Plain PSOC-1451 particles (75-90 μm)
CMA-impregnated PSOC-1451 particles (75-90 \mu m)
PRESENT WORK and FUTURE PLANS. During the present, 7th quarter, work is being conducted on dual SO$_2$-NO$_x$ reduction with CMA, MA (magnesium acetate) and CA (calcium acetate) sorbents.

PUBLICATIONS/PRESENTATIONS FORM THIS GRANT:


6. Atal A., Steciak, J. and Levendis, A. “Combustion and SO$_2$-NO$_x$ Emissions of Bituminous Coal Particles Treated with CMA ” Submitted for publication.


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