Effectiveness of Calcium Magnesium Acetate as Dual SO_2-NO_x Emission Control Agent

Judith Steciak and Yiannis A. Levendis
Dept. of Mechanical Engineering, Northeastern University, Boston, MA 02115

Donald L. Wise
Dept. of Chemical Engineering, Northeastern University, Boston, MA 02115

Calcium magnesium acetate (CMA) is an effective dual SO_2-NO_x emission control agent. Laboratory-scale experiments with dry injected particles at a Ca/S molar ratio of 2 [or (Ca + Mg)/S ratio of 6] resulted in SO_2 and NO_x removal efficiencies of over 90% at gas temperatures of 950 – 1,250°C in atmospheres containing 12% CO_2, 3% oxygen, 2,000 ppm SO_2, and 1,000 ppm NO_x during a 1-s residence time in an isothermal cavity followed by injection of after-fire air. During the experiments, SO_2 reacted with the porous, thin-walled CaO, $CaCO_3$ and MgO cenospheres, formed when CMA calcined, while NO_x was reduced by hydrocarbon radicals from the organic acetate decomposition. While Ca was the dominant contributor to SO_2 reduction by CMA in the isothermal furnace zone, Mg also contributed to SO_2 reduction. At gas temperatures ≤ 950°C, Mg reacted directly with SO_2 in the isothermal furnace zone and was the dominant SO_2 remover in the post-furnace quenching zone while indirectly SO_2 at higher isothermal zone temperatures by precluding pore-mouth plugging when $CaSO_4$ formed. Interactions among hydrocarbons, SO_2, and NO_x are important but not fully understood.

Introduction

The control of sulfur and nitrogen oxide emissions from coal-fired power plants is generally achieved by separate processes. The most widely used flue-gas desulfurization strategies involve wet or dry low-temperature scrubbing with nonregenerated calcium compounds such as slaked lime [$Ca(OH)_2$] or limestone ($CaCO_3$) slurries. Injection of these sorbents in the high-temperature boiler gases (dry-scrubbing) has also received much attention because of the favorable kinetics of the sulfation reactions at high temperatures and the associated low capital investment. As an example of in-boiler sorbent injection, Cole et al. (1986) reported that hydrated materials (such as slaked lime) were more reactive than limestone, and also that dolomitic sorbents were more reactive than calcitic sorbents. They attributed such differences in reactivities to the higher surface area, typically smaller particle size and longer time available for sulfation of hydrated sorbents compared to carbonic sorbents, and to the higher surface area of dolomitic sorbents compared with calcitic sorbents. For example, a mean surface area of ≈ 50 m^2/g was measured for hydrated dolomitic sorbents compared with an average of ≈ 25 m^2/g for hydrated calcitic sorbents. This resulted in average Ca utilizations of $\approx 26\%$ and $\approx 16\%$, respectively, for hydrated dolomitic and calcitic sorbents exposed to 2,000 ppm SO_2 at $\approx 1{,}100$°C for 0.5 s with a Ca/S molar ratio of 2 (Cole et al., 1986). The correlation of SO_2 reduction with sorbent surface area was also reported by Greene et al. (1985) and the high surface area of dolomite was given as the reason for its high sulfur affinity. Evidence of pore structure was also reported to influence sulfation rates, with the plate-like pore structure of CaO from hydrated sorbents posing less diffusional resistance when compared with the sphere-shaped pores of CaO from calcitic sorbents (Bruce et al., 1989).

NO_x control techniques include combustion modifications (such as low-NO_x burners and staged combustion) and post-combustion treatments (such as SNCR, SCR, and injection of secondary fuel). In the past, combustion modifications alone were insufficient to meet the strictest regulations for NO_x

emissions from coal-fired boilers. For example, combustion modifications of tangential and wall-fired boilers have resulted in NO_x emissions of 220–440 ppm (at 3% oxygen) whereas NO_x emission regulations for coal-fired boilers are between ≈100–360 ppm at 6% O_2 or 80 to 300 ppm at 3% O_2 (Bowman, 1992). Hence, to further reduce NO_x, it may be necessary to use post-combustion treatment.

The major post-combustion NO_x emissions destruction methods are first selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR) wherein nitrogen-containing compounds [ammonia (Lyon, 1974) and urea (Arand et al., 1982)] are injected downstream of the boiler; and secondly, injection of secondary fuels in a fuel-rich zone downstream of the primary combustion zone (Myerson, 1975; Wendt et al., 1973). NO_x reduction efficiencies as high as 80–90% have been reported for SNCR and SCR whereas techniques using the introduction of secondary fuel have reported efficiencies of 40–70% depending on the fuel and the primary burner configuration (Bowman, 1992).

Combinations of the above techniques are used to control SO_2 and NO_x, for example, infurnace NO_x reduction modifications and lime or limestone flue-gas desulfurization (FGD). Many other combined processes have been developed, such as the Shell Flue Gas Treatment (described by Flagan and Seinfeld, 1988) that uses CuO supported on alumina. SO_2 reacts with CuO to form $CuSO_4$ and NO_x can be reduced by ammonia with CuO acting as a catalyst. Other combined processes include adding limestone or dolomite to fuel in a burner with combustion modifications to lower NO_x (Steward et al., 1992; Wang et al., 1991), Na- or Ca-based sorbent injection and SNCR (Gullett et al., 1992; Darmstaedler, 1990), or combustion modification with low-NO_x burners, dry-injection of slaked lime for SO_2 capture and dry injection of sodium bicarbonate for further SO_2 and NO_x reduction (Helfritch et al., 1992). Makansi (1990) has compiled a succinct review of these and other systems.

Removal of SO_2 and NO_x can generate new environmental problems. For example, using urea in SNCR to reduce NO_x can create emissions of ammonia and SO_3 (if SO_2 is present), and significantly increase N_2O emissions (Bowman, 1992).

Few processes exist for the simultaneous removal of SO_2 and NO_x, that is, one sorbent used for the removal of both pollutants at the same time. One process is NOXSO (Yeh et al., 1992) that uses a regenerative, dry-injection sorbent (made by spraying Na_2CO_3 on the surface of alumina spheres) that has been reported to remove 90% of SO_2 and 70 to 90% of NO_x. Greene et al. (1985) evaluated simultaneous SO_2-NO_x reduction by injecting together secondary fuel and SO_2 sorbents at 1,400°C but concluded that optimum overall reductions were obtained when the sorbents were actually injected with over-fire air at 1,150°C after the "reburning zone." They explained their conclusion based on the loss of stone reactivity due to sintering at the high temperatures of the secondary fuel injection zone (1,400°C).

This research introduces a chemical, calcium magnesium acetate [CMA, $CaMg_2(CH_2COOH)_6$], that has the potential to simultaneously sorb SO_2 and reduce NO_x (Levendis and Wise, 1994). Because CMA has a high solubility in water of 30%, it can be used as either a wet- or dry-sprayed nonregenerative dry-scrubbing agent. A single point injection at the appropriate furnace location followed by injection of over-fire air should be sufficient for the removal of both SO_2 and NO_x. This conceptual simplicity may have a major impact on retrofit projects conforming to the Clean Air Act.

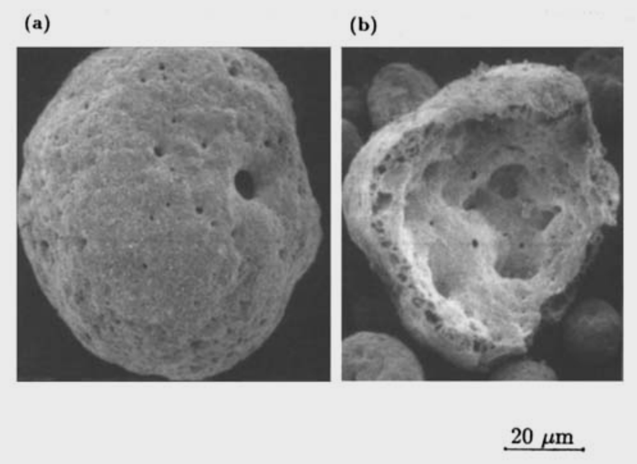

Figure 1. SEM of a calcined CMA particle.

(a) Porosity = 0.70, BET ≈ 27 m^2/g when calcined at 950°C; (b) particle cracked open to reveal interior voids and pore structure.

When CMA calcines, the acetate evaporates and leaves behind porous, thin-walled cenospheres of Ca and Mg oxides and (depending on the temperature) $CaCO_3$ (Figure 1). The organic acetate further decomposes into hydrocarbon radicals that in an oxygen-lean atmosphere can reduce NO_x to N_2. The cenospheric oxide residues remain for heterogeneous sorption of SO_2 (Levendis et al., 1993). The cenospheres' wall porosity is about 70% and the pore surface area is ≈27 m^2/g when calcination takes place at 950°C during a 4 s residence time. (The pore surface area was measured by N_2 adsorption using the Brunauer-Emmett-Teller (BET) multilayer theory.)

Commercially available CMA is expensive due to the relatively high cost of producing acetic acid from natural gas. This cost may not be offset by the ease of use and the combining of two separate processes for SO_2 and NO_x removal into one. Therefore, it appears necessary to develop processes for producing acetic acid from renewable organic or "biomass" substrates including woody biomass and wastewater treatment sludge (Wise et al., 1988, 1991; Trantolo et al., 1990). If such production becomes commercially viable, the cost of CMA could drop drastically. A recent economic study (Palasantzas and Wise, 1994) estimated that the price of CMA may change from a current *cost* of ≈ $350/ton to an estimated *revenue* of a few to several hundred dollars per ton, if appropriate "credits" for accepting and using waste biomass are taken into account.

Previous work (Levendis et al., 1993) demonstrated the superior SO_2 sorption efficiency of CMA compared at the same molar Ca/S ratio to other sorbents including $Ca(OH)_2$, $CaCO_3$, and calcium acetate (CA) (for example, CMA was 30 to 40% more effective in sulfur capture than $Ca(OH)_2$, $CaCO_3$, and CA), and the superior NO_x reduction efficiency of CMA compared to CA and calcium benzoate (CB) (Steciak et al., 1994a). This work presents the efficacy of CMA in simultaneously removing SO_2 and NO_x. Furthermore, it aims at elucidating the role of calcium, magnesium and the organic component of CMA in SO_2 and NO_x reduction.

Experimental Apparatus and Procedure

The laboratory apparatus (Levendis et al., 1993; Steciak et al., 1994a) consisted of a sealed high temperature, drop-tube laminar-flow furnace with an isothermal alumina radiation cavity (25 cm long) (Figure 3). After the isothermal radiation zone, the furnace effluent passed through a water-cooled quenching zone. In the radiation cavity, the furnace wall temperature was monitored continuously with a type S thermo-

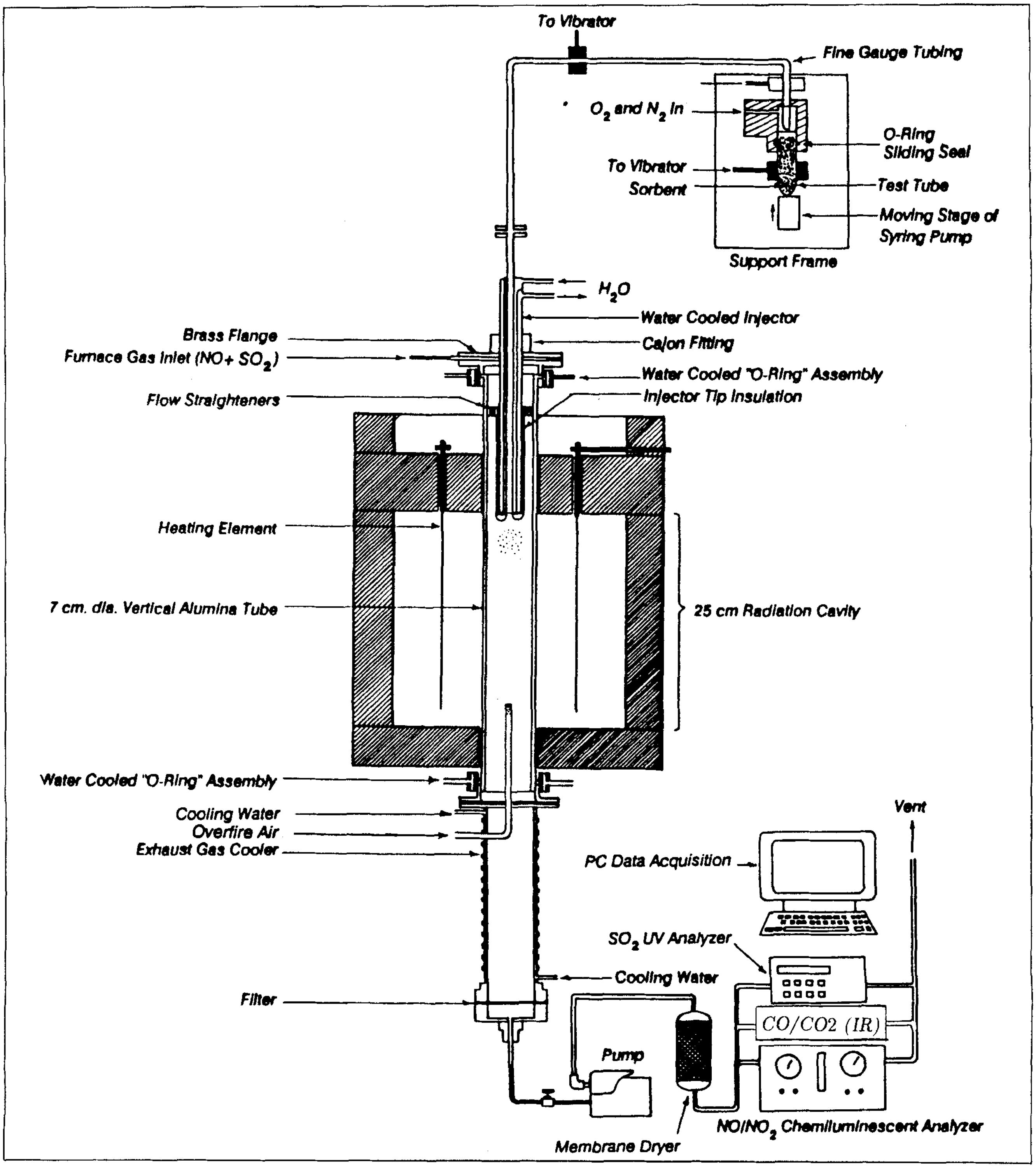

Figure 2. High-temperature furnace, particle fluidizer, and gas monitoring system.

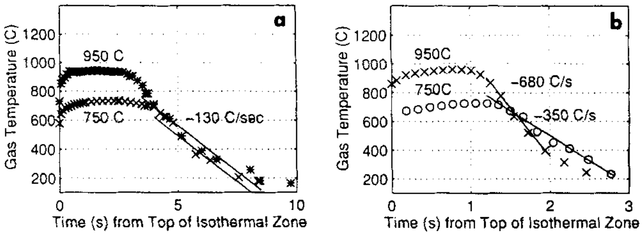

Figure 3. Typical temperature-time histories of sorbents from entry into the isothermal zone (time 0), to exit from the isothermal zone and entry into the post-furnace quenching zone.

(a) large diameter furnace, residence time 4 s; (b) small diameter furnace, residence time 1 s.

Table 1. Physical Characteristics of Sorbents and Experimental Conditions

Sorbent	Mol % of Ca Nominal	Mol % of Ca Actual	ϕ	Actual Ca/S	Actual Mg/S
Reagent-grade CA	100	100	0.67	2	0
75:25 CMA	75	95	0.68	2	0.11
50:50 CMA	50	65	0.90	2	1.08
25:75 CMA	25	57	1.0	2	1.5
Commercial CMA	33	34	1.3	2	4
Reagent-grade CA	0	0	1.1	0	4

couple. The centerline gas temperature was mapped in the radiation cavity with an aspirated type S thermocouple and in the post-furnace quenching zone by type K thermocouples. Gas flow was controlled to achieve the desired mixture of SO_2, NO, O_2, CO_2 and N_2 in the radiation cavity. Sorbent was conducted pneumatically to the furnace through a water-cooled injector. The furnace effluent was filtered before being dried with a Permapure membrane dryer and monitored for SO_2 (Rosemount Analytical UV SO_2 analyzer) and NO_x (Beckman 950A chemiluminescent NO/NO_x analyzer). For some experiments, the furnace exhaust was monitored for CO and CO_2 using Beckman 864-infrared analyzers. An STX70 detector from Industrial Scientific used an electrochemical technique to detect the presence of NH_3. Due to interference of sulfur compounds in its detection ammonia was measured only when SO_2 was not introduced to the furnace. A septum port was available to extract samples for N_2O analysis with a Varian 3400 gas chromatograph.

NO was used in these experiments because NO dominates NO_x emissions from coal combustion. However, both NO_x and NO were monitored at the furnace exhaust during the experiments in case any NO oxidized to NO_2.

Simultaneous sulfation and NO_x reduction experiments were conducted with gas temperatures in the heated zone ranging between 550 and 1,350°C. The partial pressures of SO_2, NO, and oxygen in the incoming gas were 2,000 ppm, 1,000 ppm and 3%, respectively. A few experiments were conducted with 12% CO_2 added to the incoming gas. These are typical values for the post-combustion region of coal-fired power plants. Since SO_2 was absorbed by the alumina reactor walls, sorbent was not injected until after the walls were saturated and the desired SO_2 baseline concentration attained a constant value. The gas flow rate was constant at STP (standard temperature pressure), hence the residence time in the furnace increased as the gas temperature decreased; most of the experiments were conducted with hot zone residence times of 4 to 5 s. Recent modifications to the furnace shortened the residence time in the isothermal zone to 1 s, and the results of a few experiments at this shorter residence time were included. Better dispersion of the sorbent particles in the background gases was obtained during the shorter residence time experiments. After leaving the heated zone, the gas was usually quenched at a rate of −130°C/s for the 4 s residence time experiments (exceeding −350°C/s for the 1-s residence time experiments) in the post-furnace zone (Figures 3a and 3b). This rate was not rapid enough to quench all reactions, however. Thus, in some experiments, a water-cooled, nitrogen-quenched sampling probe was inserted at the bottom of the heated zone to extract gas/particle samples. In addition, for a few experiments, a capped stainless steel tube with end perforations was inserted into the bottom of the isothermal hot zone to create an "after-fire air" zone by introducing air (Figure 2).

CMA was commercially available from Cryotech Deicing Technologies. It was ground and sieved and particles of about 50 μm in size were used. For comparative purposes, calcium acetate [CA, $Ca(CH_2COOH)_2$] and magnesium acetate [MA, $Mg(CH_2COOH)_2$] were purchased from Aldrich. In addition, CMA samples with different Ca-to-Mg molar ratios were prepared in our laboratory by dissolving appropriate amounts of CA and MA in water, sonicating the solutions, and removing the water with a vacuum pump while the solution was rotated in a sonicated, 45°C bath (Palasantzas, 1993). The sorbents were dried in an oven at 90°C, ground and sieved, and particles were subjected to EDX (Energy Dispersive X-rays) analysis to determine the actual Ca/Mg ratio (Table 1). Crystallographic analysis, conducted elsewhere (Botsaris, 1993) on similarly prepared samples, revealed that such samples do not only contain the characteristic octahedral crystals of CMA but also CA and, possibly, MA crystals.

Experimental Results and Discussion

Thermal decomposition

The thermal decomposition of CMA, CA and MA was studied by TGA with a Mettler A 400 Thermal Analysis System in air at a heating rate of 20°C/min and the results are shown in Figure 4. The sample weight was 10 mg and consisted of 45–53 μm particles. Samples were uniformly spread on the pan in thin layers in order not to impede devolatilization. (A limited number of experiments were also conducted at 10°C/min. Results showed that the TGA peaks were slightly sharper at the higher heating rate (20°C/min), that is, the devolatilization rates were faster. A slight shift of the peaks to higher temperatures was noticed when larger sorbent particles were devolatilized. Based on the above slow heating rates, it is not possible to predict whether the decomposition temperatures would be the same at the fast heating rates of the drop-tube furnace.)

Weight loss below 200°C was due to the evolution of water. MA began to decompose at 300°C when acetone evolved (Su, 1990) and $MgCO_3$ was formed. However, $MgCO_3$ was re-

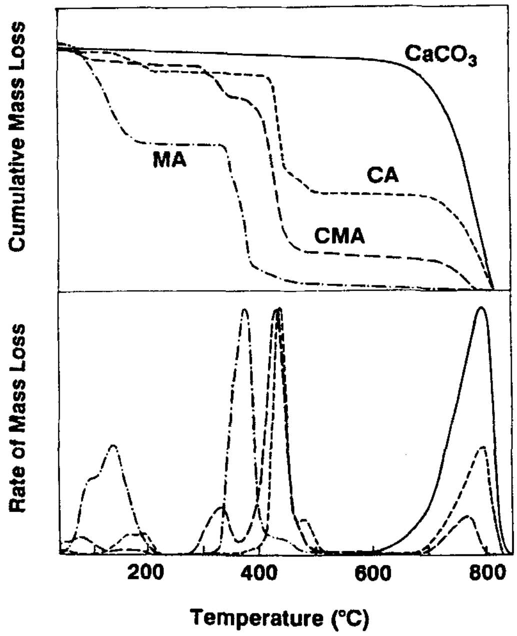

Figure 4. TGA profiles for CMA, CA and MA.

Particle size, 50 μm; heating rate, 20°C/min; rate of mass loss expressed in mg/s.

ported to decompose to MgO and CO_2 at 340°C (Su, 1990); these processes were combined into the single peak seen on the mass loss rate curve (Figure 4). CA began releasing volatiles (presumably acetone (Su, 1990)) at 400°C and forming $CaCO_3$ which began to further decompose to CaO and CO_2 above 700°C. The decomposition history of CMA was a superposition of the decompositions of MA and CA. After the initial low temperature release of water, mass evolution that coincided with the evolution of acetone and CO_2 from MA started near 300°C followed by the evolution of acetone from CA and the formation of $CaCO_3$ which peaked between 420 and 440°C (as also noted by Su, 1990). The final decomposition of $CaCO_3$ to CaO and CO_2 started at 700°C. In the drop-tube furnace, the sorbents were subjected to a rapid heating rate and higher temperatures that would further decompose acetone into hydrocarbon radicals.

Sulfur capture and NO_x reduction

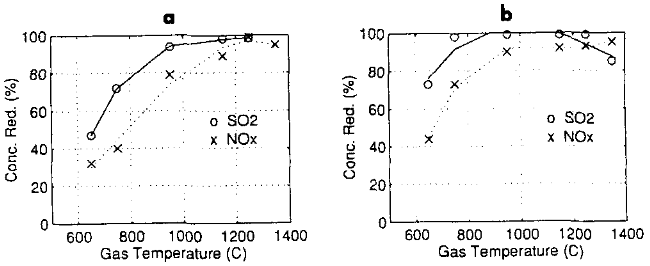

Figure 5. SO_2 and NO_x reduction by CMA as a function of temperature at Ca/S = 2 [(Ca+Mg)/S = 6] in atmospheres containing 12% CO_2, 3% O_2, 2,000 ppm SO_2, and 1,000 ppm NO at 1-s residence time in an isothermal zone.

o, SO_2 concentration reduction; x, NO_x reduction. (a) Without after-fire air; (b) with after-fire air.

At Ca/S = 2, CMA removed over 90% of SO_2 at a gas temperature ≥ 950°C and over 90% of NO_x at gas temperatures ≥ 1,150°C (Figure 5a) during 1 s residence time experiments and removed 90% of SO_2 at a gas temperature of 750°C and ≥ 70% of NO_x at gas temperatures ≥ 950°C (Figure 6) during experiments conducted with a 4-s residence. (The high NO reduction numbers at fuel lean conditions are due to the formation of nitrogen bound compounds such as HCN and NH_3. These may be partially oxidized to NO when after-fire air is added.) The reader should notice that the residence time was shortened in the new furnace by achieving higher gas velocities and, hence, better particle dispersion. This explains the paradox of getting better results at shorter residence times. The peak reduction of both SO_2 and NO_x shifted to a higher temperature at the lower residence time (1 s) since a larger fraction of the residence time was required to gasify the organic component of the CMA in these experiments. Also, upon gasification of the organics less calcium carbonate was converted to oxide at the lower residence times and sulfation most likely benefited from the faster reaction rates of carbonate (Steciak et al., 1994b). Better dispersion of CMA particles in the background gas at the shorter residence time improved SO_2 reduction but made no appreciable change in NO_x reduction. The addition of after-fire air (Figure 5b) improved SO_2 reduction (from ≈ 70% at 750°C without after-fire air to over 95% with after-fire air at the same temperature) since additional Ca sulfation could occur with the introduction of additional oxygen. Since the equilibrium temperature for stable $CaSO_4$ is ≈ 1,270°C, the measured high SO_2 reduction at gas temperatures near this value must have been due to Mg sulfation as the calcined CMA left the isothermal zone and cooled below in these slowly-quenched experiments (the role of Mg is discussed at length

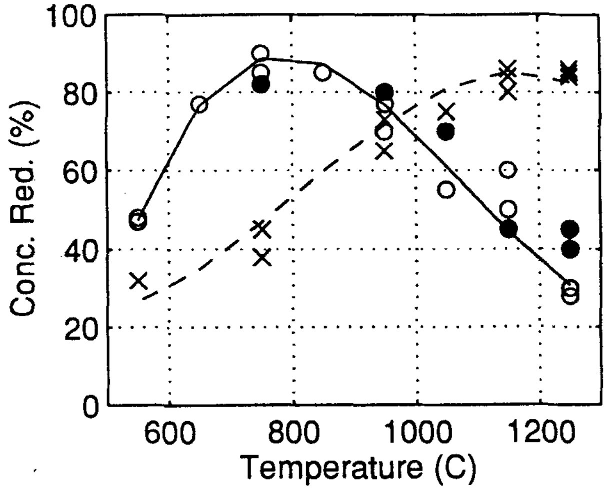

Figure 6. SO_2 and NO_x reduction by CMA as a function of temperature at Ca/S = 2 [(Ca+Mg)/S = 6] in atmospheres containing 3% O_2, 2,000 ppm SO_2, and 1,000 ppm NO.

o, SO_2 reduction at 4- to 5-s residence time; ●, SO_2 reduction at 2- to 3-s residence time; x, NO_x reduction at 2- to 3-s residence time.

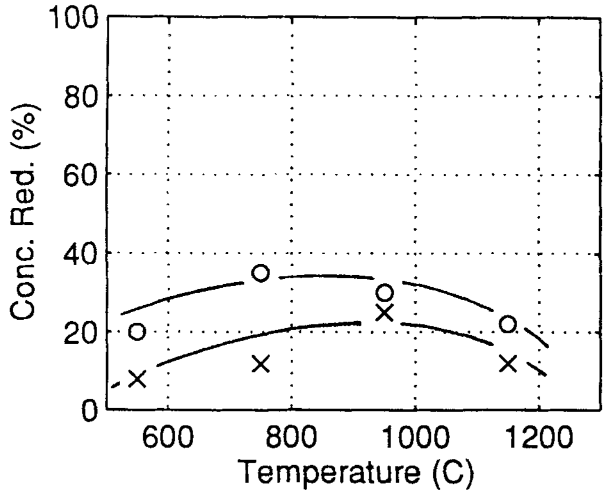

Figure 7. SO_2 and NO_x reduction by CA as a function of temperature at Ca/S = 2 in atmospheres containing 3% O_2, 2,000 ppm SO_2, and 1,000 ppm NO.

o, SO_2 reduction; *x*, NO_x reduction. Nominal furnace residence time varied between 4 to 5 s.

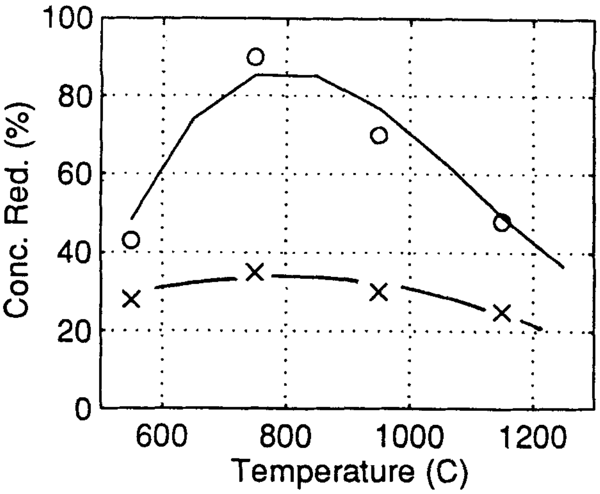

Figure 8. SO_2 and NO_x reduction by MA as a function of temperature at Mg/S = 4 in atmospheres containing 3% O_2, 2,000 ppm SO_2, and 1,000 ppm NO.

o, SO_2 reduction; *x*, NO_x reduction. Nominal furnace residence time varied between 4 to 5 s.

below). Finally, the presence of CO_2 in the furnace gas did not impede sulfation of the sorbents.

The SO_2 reduction efficiency at 4-s residence time was comparable to that measured by Levendis et al. (1993) using CMA at Ca/S = 2 in atmospheres containing 500 ppm SO_2 and 10 to 14% O_2. The NO_x reduction efficiencies measured here at an overall fuel-to-oxidizer equivalence ratio ϕ of 1.3 fell between those measured by Steciak et al. (1994a) in atmospheres with 500 ppm NO and $\phi = 0.9$ and 2.9. [The equivalence ratio ϕ is defined as the ratio of the actual fuel (acetate)-to-oxidizer ratio to the stoichiometric fuel-to-oxidizer ratio. Oxygen in SO_2, NO, the background gas, and the acetate was included in the calculation. If $\phi > 1$, the system is fuel-rich.]

The SO_2 and NO_x reduction efficiencies obtained by using CMA were well over twice those obtained with CA injected at Ca/S = 2 under the same experimental conditions (Figure 7) at a residence time of 4 s. The smaller amount of organic acetate in CA (at the above fixed molar Ca/S ratio of 2) was responsible for its less effective NO_x reduction (ϕ was 0.68 for the CA experiments).

Although the Ca/S molar ratio was kept constant for all experiments, the total alkaline metal-to-S ratio [(Ca + Mg)/S] was 6 for CMA. Hence, either the Mg in CMA or the greater amount of organic acetate was responsible for the difference in SO_2 concentration reduction between CA and CMA.

MA achieved the same SO_2 reduction efficiency of CMA at a Mg/S molar ratio of 4 (the Mg/S molar ratio of CMA is also 4 when its Ca/S molar ratio is 2) (Figure 8). The NO_x reduction efficiency of MA was lower than that of CMA, however, because of the lower amount of organic acetate (ϕ for the MA experiments was 1.06).

To study the aetiology for CMA being an excellent *dual* SO_2-NO_x reducing agent and outperforming CA at the same Ca/S ratio, an investigation was conducted targeting (a) the role of Mg in the sulfation of CMA, both in the isothermal as well as the post-furnace quenching zones; (b) the effects of a reducing atmosphere on the sulfation of CaO; (c) the effects of an afterfire oxidizing zone, following the fuel-rich sorbent injection zone, on the NO_x reduction; and, finally, (d) the interaction between SO_2, NO_x and hydrocarbons.

Role of Mg in CMA Sulfation. Results obtained from SO_2 and NO_x concentration reduction experiments by dry-spraying the different Ca-Mg-content CMA sorbents, see Table 1, in the furnace (Figure 9) showed an increasing removal of SO_2 with a decreasing fraction of Ca in the molecule with a maximum SO_2 removal of 90% obtained at a temperature of 750°C for both commercial CMA (30% Ca in the molecule) and MA (0% Ca).

The oxidative sulfation of MgO and CaO by SO_2 is not thermodynamically favored at temperatures above ≈ 840 and ≈ 1,270°C, respectively, since these temperatures correspond to a high equilibrium partial pressure of SO_2 for both reactions:

$$MgO + SO_2 + \frac{1}{2}O_2 \rightarrow MgSO_4 \qquad (1)$$

and

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

This suggests that it was thermodynamically possible for reactions with magnesium to occur at either isothermal zone temperatures below 840°C or in the cooler regions of the furnace. Kinetically, however, Kocaefe et al. (1985) reported slow reaction rates between MgO and SO_2-O_2 mixtures at temperatures between 750–780°C and no reaction at all at temperatures below 630°C.

Hence, since copious sulfation of Mg to $MgSO_4$ was not expected at the isothermal zone temperatures (Wang et al.,

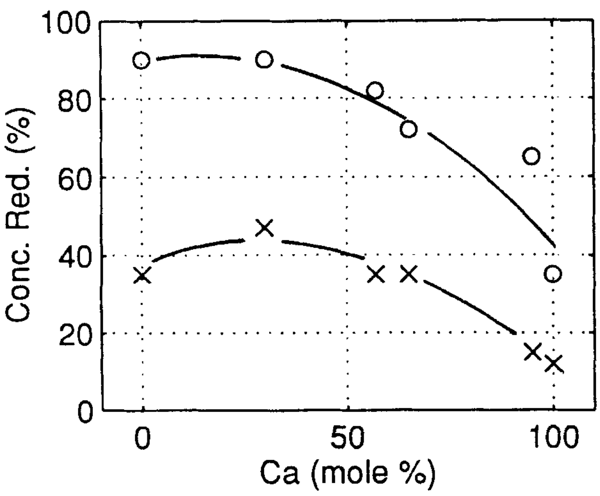

Figure 9. SO_2 and NO_x reduction by CMA with different Ca-to-Mg molar ratios at a temperature of 950°C in atmospheres containing 3% O_2, 2,000 ppm SO_2, and 1,000 ppm NO.

100°C Ca corresponds to calcium acetate, 0% Ca is 100% Mg or magnesium acetate, and commercial CMA is about 30% Ca. o, SO_2 reduction; x, NO_x reduction.

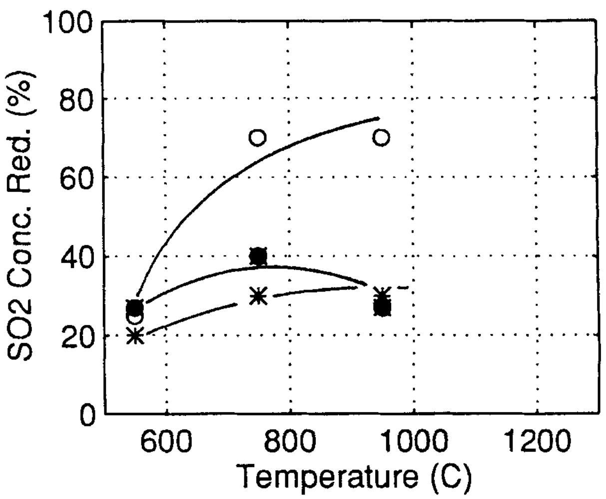

Figure 10. SO_2 reduction by rapidly quenched reactions as a function of temperature with Ca/S = 2 or Mg/S = 4 in atmospheres containing 3% O_2, 2,000 ppm SO_2, and 1,000 ppm NO.

o, CMA; *, CA; ●, MA. Nominal furnace residence time varied between 4 to 5 s. NO_x reduction was not affected by quenching.

1991; Kocaefe et al., 1985), it was determined that the sorbent residence time in the post-furnace zone (20 s) at the quenching rates of these experiments (−130°C/s in the 4-s and at least −350°C/s in the 1-s experiments) provided an environment where sulfation took place in a different path. In the presence of water vapor from the acetate decomposition, it was suspected that magnesium sulfite hydrate ($MgSO_3 \cdot 3H_2O$ or $MgSO_3 \cdot 6H_2O$) formed in the isothermal zone at the lower temperatures of this study (550–950°C) and also as the effluent was cooled before the particle collection filter. Indeed, sulfur was detected in sulfated MA residues by EDX, but no Mg compounds other than MgO were identified from XRD (X-ray diffraction) analysis. The residue filter itself was dry at the end of the experiments, reducing the likelihood of continued SO_2 sorption by residues accumulating there. Indeed, MgO has been used elsewhere in low temperature, wet, regenerative FGD processes that can recover SO_2 for sulfuric acid production (EPA, 1981; Flagan and Seinfeld, 1988). Subsequent experiments, where the effluent was sampled with a water-cooled nitrogen-quenched probe, still showed—albeit much lower—SO_2 reduction by MA, that is, 40% vs. 90% at a temperature of 750°C (Figure 10). Hence, *assuming that reactions were "frozen" in the water-cooled, nitrogen-quenched probe*, MgO must have partially reacted with SO_2 in the isothermal zone. The percentages of SO_2 removal by CMA, CA and MA in the isothermal furnace zone were estimated from experiments with the fast quenching probe. By subtracting these results from those of experiments where use of this probe was not made, the contributions of the post-furnace zone were estimated. Results are listed in Table 2.

From the data in Table 2 it is possible to estimate the percent contribution of Ca and Mg in CMA to SO_2 reduction in the isothermal furnace zone (Table 3). [As an example, in the first entry the contribution of calcium was $20/(20+28) \times 100 \approx 42\%$ or 21% per mole of Ca at Ca/S = 2. The corresponding contribution of magnesium was $28/(20+28) \times 100 \approx 58.4\%$ or 15% per mole of Mg at Mg/S = 4.] Ca contributed virtually nothing to SO_2 reduction in the post-furnace zone since the rapidly quenched experiments with CA, using the quenching probe, yielded nearly the same SO_2 reduction as the slowly quenched experiments.

The data in Table 3 show that in the isothermal zone Ca was over 3½ times more reactive than Mg at 950°C and only about 1½ times more reactive at 750 and 550°C. To the contrary, in the post-furnace zone, Mg was orders-of-magnitude more reactive than Ca (Table 2).

Table 2. SO_2 Reduction in the Isothermal Zone and in the Post-Furnace Zone*

Isothermal Zone Temp. (°C)	SO_2 Reduction (%) Isothermal Zone, 4 s			Post-Furnace Zone, 25 s		
	CMA	CA	MA	CMA	CA	MA
550	25	20	28	20	0	10
750	70	30	40	20	5	50
950	70	30	25	7	0	45

*Ca/S = 2, Mg/S = 4 and residence time of 4 s in the isothermal zone in all cases.

Table 3. Contribution of Ca and Mg in CMA to SO_2 Reduction in Isothermal Zone*

Isothermal Zone Temp. (°C)	Contrib. to SO_2 Red. (%/mol.) Ca	Mg
550	21	15
750	21	14
950	32	9

*Ca/S = 2, Mg/S = 4 and residence time of 4 s in all cases.

Table 4. Ca and Mg Utilization in the Isothermal Zone*

Isothermal Zone Temp. (°C)	Ca and Mg Util. (%) CA Ca	CMA Ca	CMA Mg	MA Mg
550	10	5	4	7
750	15	15	10	10
950	15	23	6	6

*Ca/S = 2, Mg/S = 4 and residence time of 4 s in all cases.

Table 5. XRD Analysis of Sulfated CMA Residues

Isothermal Zone Temp. (°C)	Detected Species
750	$CaCO_3$, $CaSO_4$, MgO
800	CaO, $CaCO_3$, $CaSO_4$, MgO
900	CaO, $CaCO_3$, $CaSO_4$, MgO
1,200	CaO, $CaSO_4$, MgO

Since a greater mass of calcined CMA than CA was injected for the same Ca/S molar ratio, the superior SO_2 reduction efficiency of CMA at higher temperatures could be partly due to the relatively greater total surface area for the heterogeneous sulfation of CaO and $CaCO_3$. Also, the interior surface area of CMA, accessible by pores and blowholes, could suffer less from pore-mouth plugging because of the dispersion of Ca by the relatively inert MgO sites during the sorbent's residence time at high temperatures. Ca and Mg utilization (defined as the mole fraction of Ca or Mg that reacted with SO_2) of the sorbents in the isothermal zone changes with temperature (Table 4), and the utilization data from CA and MA were used to estimate the utilization of Ca and Mg in CMA. At 950°C, the utilization of Ca in CMA improved over that in CA.

The utilization of Ca in CMA dropped from 23 to 15% as the temperature dropped from 950 to 750°C because SO_2 was reacting with a different solid. The TGA results discussed earlier showed that CMA decomposed to MgO and $CaCO_3$ near 400°C and the final decomposition of $CaCO_3$ to CaO did not start until the temperature exceeded 700°C. [These temperatures may change somewhat (most likely increase) at the high heating rates of the drop-tube furnace.] The residence time in the furnace was much shorter than that during TGA, suggesting that considerable $CaCO_3$ could remain in the calcined residues at 750°C. Indeed, XRD analysis of sulfated CMA residues indicated the presence of $CaCO_3$ at temperatures at and below 900°C (Table 5). Direct sulfation of $CaCO_3$ is thermodynamically favorable at these temperatures:

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + CO_2 \tag{3}$$

and the kinetics of this reaction have been discussed under fluidized-bed conditions (Snow et al., 1988; Tullin and Ljungström, 1989). Chan et al. (1970) investigated the formation of sulfite from $CaCO_3$ and SO_2 in oxygen-free atmospheres:

$$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2 \tag{4}$$

Although the presence of $CaSO_3$ was not detected by XRD in the experiments described herein, it could have formed and oxidized to $CaSO_4$. At 550°C, both the Ca and Mg utilization in CMA decreased and, again, the answer may lie in the TGA data. This temperature was just above the decomposition temperature of CMA to MgO, $CaCO_3$, CO_2 and acetone. Because of the shorter (than in the TGA) furnace residence time, not all of this decomposition may have occurred. Residues of sorbents calcined at this temperature were dark, indicating the presence of carbon, and some of the organics most likely remained within the solid matrix. This could "poison" the activity of the solid surface, precluding reaction with SO_2.

Hence, Mg has both direct and indirect effects on SO_2 removal by CMA. The indirect effect is enhanced Ca utilization at high temperatures due to the dispersion of Ca by the relatively inert MgO sites. At lower furnace temperatures, reactions between SO_2 and MgO to form $MgSO_3$ or $MgSO_4$ are thermodynamically possible but kinetically unfavorable, as mentioned earlier. Considerable evidence of reaction between Mg and SO_2 at these furnace temperatures, and in the post-furnace zone, suggested either the formation of Mg sulfite hydrates or other unknown reactions. For example,

$$MgO + SO_2 + NO \rightarrow MgSO_4 + \frac{1}{2}N_2 \tag{5}$$

is thermodynamically possible below 1,030°C. No kinetic data have been found for this reaction, however.

Also, at the higher temperatures, in atmospheres containing 3% O_2, there was evidence that MA decomposed to a fine aerosol of which some submicron sized particles were trapped in the collection filter. Substantial residues from MA decomposition could be collected only when they were sulfated. This suggested the possible release of MgO fumes during CMA decomposition which, because of their small size, could be efficiently sulfated. The reactions between Mg and SO_2 in the cooler region of the furnace could also occur in the exhaust duct of actual power plants, suggesting the likelihood of continued SO_2 removal by CMA until the final particulate collection devices. This was shown by a simple calculation indicating that utility furnaces experience cooling rates of 200–350°C/s, which are in the same range as those experienced herein.

Sulfation of CaO in Reducing Atmospheres. Because of the reducing atmosphere of the experiments with secondary fuel (acetate) injection, the reaction between CaO and SO_2 could form CaS instead of $CaSO_4$. This is of concern because when CaS passes through fuel-lean zones, established to oxidize CO and any unburned hydrocarbons, CaS could oxidize back to CaO and SO_2. The presence of CO in reducing atmospheres leads to the formation of CaS, as outlined in the following reactions:

$$CaO + SO_2 \rightarrow CaSO_3 \tag{6}$$

$$4CaSO_3 \rightarrow 3CaSO_4 + CaS \tag{7}$$

$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2 \tag{8}$$

Experiments by Ghardashkhani and Lindqvist (1992) for reacting SO_2 and CaO in the presence of CO at temperatures between 600 to 950°C showed complete conversion of CaO to CaS. However, the rate at which this conversion occurred, while relatively fast when considering the time scales in a fluidized bed, was quite slow when compared to the time scale of the present experiments. The rapid initial reactions that form predominantly $CaSO_3$ and $CaSO_4$, Eqs. 6 and 7 above, are followed by surface reduction via CO to CaS (Eq. 8). At temperatures $\leq 700°C$, the dominant products formed were $CaSO_3$ and $CaSO_4$ and the molar ratio of sulfate to sulfide was 3.1 at 750°C. In atmospheres containing 1% CO and 3,000 ppm SO_2 between 600 and 900°C, conversion of sulfate and sulfite to sulfide was reported to begin when the residence time exceeded about 30 s (Ghardashkhani and Lindqvist, 1992).

The introduction of additional air into the high temperature furnace of this work at the end of the heated zone to create a "post-secondary-fuel injection" oxidizing zone changed the measured SO_2 reduction efficiencies somewhat: reduction at 950°C was 98% instead of over 95%, at a residence time of 1 s. Collecting sulfated sorbents on the filter and reinjecting them into the furnace in oxidizing atmospheres with a slight 20 ppm SO_2 background concentration did not release any measurable SO_2. (In fact, the sulfated sorbents further reduced the SO_2 concentration in the background gas, most likely by reaction with unutilized sorbent.) This suggested that the relatively fast residence time of the present experiments precluded the formation of CaS in the presence of CO. Finally, at temperatures below the decomposition of $CaCO_3$ to CaO, the direct sulfation of $CaCO_3$ is possible through Eqs. 3 and 4, presented above.

Reduction of NO_x: Formation of Byproducts. CMA achieved low NO_x reduction (below 50%) at temperatures below about 800°C (Figure 5) most likely because of slow kinetics of pertinent reactions and incomplete evolution of the organic components. Residues from all of the sorbents were darkest from experiments at 550°C, indicating the presence of organically-bound carbon. Residues became progressively lighter as the isothermal zone temperature increased. This suggests that all the organic was available for reaction at the highest furnace temperatures, where NO_x reduction was the greatest at 85%, at and above 1,150°C.

All of the NO_x reduction occurred in the isothermal zone. NO_x reductions measured during rapidly-quenched experiments were identical to those measured during slowly-quenched experiments. This was expected since other observers have reported reaction times of 400 to 750 ms between NO and HC_i radicals (Beér, 1988; Greene et al., 1985), shorter than the residence times provided during the experiments here.

A direct relationship was observed between the fractions of NO, CO and CO_2 in the furnace effluent. CO and CO_2 production were highest when NO_x reduction was highest. Some of the CO_2 evolved from the decomposition of $CaCO_3$ and the direct sulfation of $CaCO_3$, and some was due to oxidation of the acetate. When after-fire air was introduced, CO_2 production increased further and CO production plummeted, suggesting that the oxidation of CO to CO_2 indeed occurred as desired by the additional air.

The after-fire air could also affect the reduction of NO_x if that reduction was associated with formation of other N species including HCN and NH_3. In a modeling study of gas-phase N_2O chemistry, Kilpinen and Hupa (1991) showed that if NH_3 is produced from fuel nitrogen, it would tend to oxidize to NO under fuel-lean conditions (such as those created in after-fire air zones). In this work ammonia was measured to be 20–30 ppm before the oxidizing zone, and it dropped to half that value at the end of the oxidizing zone. If HCN is formed, it would also tend to oxidize to NO under fuel-lean conditions at higher temperatures (such as 930°C), whereas at lower temperatures (730°C) HCN would tend to oxidize to N_2O. When after-fire air was introduced after dual SO_2-NO_x reduction experiments using CMA at a Ca/S molar ratio of 2 during 1-s residence time experiments, the measured NO_x reduction did increase at the lower temperatures (Figure 5b), which may be attributed to increased mixing of the particles in the air stream by disturbing the overall flow with the air jets of the oxidizing zone, as shown in Figure 2. As the carbon burned off in the sorbent particles, it created a reducing atmosphere in the interior of the cenospheres that promoted further reduction of NO. This was more pronounced at lower temperatures where the amount of unburned carbon at the end of the fuel-rich zone (beginning of the oxidizing zone) was larger.

Interaction Between SO_2, NO_x, and Hydrocarbons. To explore the impact of the organic acetate on SO_2 reduction, CMA was pre-calcined at a gas temperature of 750°C in an atmosphere containing 3% O_2 in N_2. The calcined residue was collected and subsequently sulfated at the same gas temperature in an atmosphere containing 1,500 ppm SO_2 and 3% O_2. Low SO_2 reduction—about 10%—was achieved. To introduce oxygenated hydrocarbons analogous to acetate back into the sorbent feed, the collected residue of CaO-MgO cenospheres was mixed with fine particles of sucrose ($C_{12}H_{22}O_{11}$). When the mixture was injected at Ca/S = 2 and a C/S ratio similar to that of uncalcined CMA (C/S = 24 when Ca/S = 2), the SO_2 and NO_x reduction of calcined CMA plus sucrose equaled that of CMA.

The role of the organics in SO_2 reduction is not fully understood at present. Formation of gaseous S compounds such as H_2S is possible. To explore this further, the furnace effluent was passed through an iron oxide catalyst bed at 400°C with additional air injected to oxidize H_2S to SO_2 (Harkness et al., 1968). No significant change in SO_2 reduction was observed during sulfation experiments when the furnace effluent passed through the catalyst bed. Since SO_2 reduction efficiency did not decrease with the addition of after-fire air (Figure 5b), if H_2S and other gaseous S compounds were formed, they oxidized back to SO_2 and subsequently sulfated Ca.

Interactions between NO and SO_2 in the fuel-rich secondary fuel injection region can cause a slight reduction in NO (Chagger et al., 1991; Pfefferle et al., 1989). Chagger et al. (1991) postulated that when HS species were present, the NO_x reduction was due to:

$$HS + NO \rightarrow NS + OH \qquad (9)$$

which is analogous to the main reaction of NO with hydrocarbon fuels under fuel-rich conditions:

$$CH + NO \rightarrow HCN + O \qquad (10)$$

Some carbon in addition to that in $CaCO_3$ remained with the calcined CMA and CA residues and was not oxidized in the oxygen-lean atmosphere. This was evident from EDX as well as the residue colors which were gray or tan at lower temperatures (Steciak et al., 1994a). The carbon may have contributed to NO_x reduction, since carbonaceous solids have been observed to reduce NO (Furusawa et al., 1983; Chen et al., 1986; Teng et al., 1992). Residual carbon disappeared when the post-combustion oxidizing zone was active.

In addition, NO is reduced in the presence of CO when catalyzed over CaO in reducing conditions at 850°C (Hansen et al., 1992):

$$CO + NO \rightarrow \frac{1}{2}N_2 + CO_2 \qquad (11)$$

Hansen et al. (1992) also observed that the catalytic activity of CaO decreased as it became sulfated to $CaSO_4$, which is a poor catalyst. Because N_2O is also readily catalyzed by CaO to N_2, we did not expect significant formation. This was confirmed by unsuccessful attempts to discern the presence of N_2O above 25 ppm by gas chromatography with TCD detection (standards of 25 ppm N_2O in N_2 were easily detected).

The major role of the hydrocarbons may simply be to compete for oxygen and thus reduce NO_x at higher furnace temperatures, and force the formation of $CaSO_3$ throughout the temperature range of the experiments, especially at lower furnace temperatures. To explore this possibility, pre-calcined CMA was injected at Ca/S = 3 at 750°C in atmospheres containing SO_2 and/or NO but no oxygen. 60% reduction in SO_2 resulted. When after-fire air was added, SO_2 reduction soared to 80%. CO_2 was released in all experiments, suggesting additional production of CO_2 from $CaCO_3$ left after incomplete calcination. NO was reduced by about 8% when it was present.

Conclusions

(1) Calcium magnesium acetate was found to be an effective dual SO_2–NO_x reducing agent. SO_2 was reduced by 90% at a gas temperature of 750°C and NO_x by over 70% at gas temperatures at and above 950°C at a Ca/S molar ratio of 2 [Mg/S ratio of 4 and (Ca + Mg)/S ratio of 6] in atmospheres containing 3% O_2, 2,000 ppm SO_2 and 1,000 ppm NO during experiments conducted with a 4-s residence time.

Better dispersion of CMA particles in the background gas was obtained when the residence time was reduced by increasing the flow velocity. This improved SO_2 reduction, but made no appreciable change in NO_x reduction. The presence of CO_2 in the furnace gas did not impede sulfation and made no measurable difference to NO_x reduction.

(2) Calcium magnesium acetate (CMA), calcium acetate (CA) and magnesium acetate (MA) are all water soluble (up to 30 wt. %) and thus allow wet- or dry-injection. Upon calcination in the temperature range of 550–1,200°C, CMA and CA form cenospheres with thin, porous walls.

(3) TGA analysis at low heating rates showed that after the initial evaporation of water below 200°C, MA began to decompose to MgO, CO_2 and acetone (Su, 1990) at temperatures as low as 300°C. CA started forming $CaCO_3$ and acetone (Su, 1990) at 400°C while the final decomposition of $CaCO_3$ to CaO and CO_2 started at 700°C. The decomposition of CMA was largely a superposition of the decomposition histories of CA and MA.

(4) The SO_2 and NO_x reduction capability of CMA was over twice that of CA when the latter was used with Ca/S = 2 under the same experimental conditions. MA was as effective as CMA in reducing SO_2 when injected at Mg/S = 4, but its NO_x reduction capability did not exceed 35%.

The aetiology for the excellent SO_2 and NO_x removal efficiencies of CMA is summarized in the following conclusions.

(5) Mg has both direct and indirect effects on SO_2 removal by CMA. The indirect effect is enhanced Ca utilization at high temperatures due to the dispersion of Ca by relatively inert MgO sites. At lower furnace temperatures, reactions between SO_2 and MgO to form $MgSO_3$ or $MgSO_4$ are thermodynamically possible but kinetically unfavorable. However, considerable evidence of reaction between Mg and SO_2 at these furnace temperatures, and in the post-furnace zone, suggest either the formation of Mg sulfite hydrates or other unknown reactions. For example, the reaction $MgO + SO_2 + NO \rightarrow MgSO_4 + \frac{1}{2}N_2$ is possible below 1,030°C. No kinetic data have been found for this reaction, however. Sulfur was detected in sulfated MA residues by EDX although no Mg compounds other than MgO were identified by XRD.

(6) At 750 and 950°C in atmospheres containing 3% O_2, magnesium acetate decomposed to fine aerosols of which few submicron particles were trapped in the collection filter. These fine particles provided an extensive surface area of sulfation. Residues from MA decomposition could be collected only when they were sulfated.

(7) Decomposition of the organic acetate creates the hydrocarbon radicals that reduce NO_x to N_2. The formation of CO in the fuel-rich environment can assist in the catalytic reduction of NO over CaO. Carbon remaining in the calcined sorbents may also create another catalytic path for NO_x reduction. Reactions between SO_2 and the hydrocarbon fragments can also contribute to NO reduction by the formation of HS radicals that further react to reduce NO. Any N_2O formed during the catalytic reduction of NO may itself be catalytically reduced over CaO. No N_2O to a sensitivity of 25 ppm was detected.

(8) XRD analysis of sulfated CMA residues identified the presence of $CaCO_3$ at temperatures ≤ 900°C. This suggests the importance of the direct sulfation of $CaCO_3$ at lower temperatures where the sulfation of CaO is not kinetically favored.

Future plans include experiments with other carboxylic acid salt sorbents, further experiments with wet-injected sorbents (Steciak et al., 1994b), and experiments at lower initial partial pressures of NO to simulate conditions where CMA would be used in combination with low-NO_x burners.

Acknowledgments

This work was carried out on U.S. Dept. of Energy University grants DE-FG22-89PC89776 and DE-FG22-92PC92535. The authors gratefully acknowledge Dr. Gerard A. Simons for technical comments, Mr. William Fowle for the SEM photographs, Mr. John Palasantzas for preparing the CMA samples with different Ca-to-Mg ratios, Mr. Donald Nieratko for TGA analysis and Mr. Allen Yen for EDX and XRD.

Literature Cited

Arand, J. K., L. J. Muzio, and D. P. Teixeria, "Urea Reduction of NO_x in Fuel Rich Combustion Effluents," US Patent No. 4, 325,924 (1982).

Beér, J. M., "Stationary Combustion: The Environmental Leitmotiv," *Int. Symp. on Combustion*, Combust. Inst., Pittsburgh, p. 1 (1988).

Botsaris, G., personal communication.

Bowman, C. T., "Control of Combustion-Generated Nitrogen Oxide Emissions: Technology Drive by Regulation," *Int. Symp. on Combustion*, Combust. Inst., Pittsburgh, p. 859 (1992).

Bruce, K. R., B. K. Gullet, and L. O. Beach, "Comparative SO_2 Reactivity of CaO Derived from $CaCO_3$ and $Ca(OH)_2$," *AIChE J.*, **35**(1), 37 (1989).

Brunauer, S., *Adsorption of Gases and Vapours: I. Physical Adsorption* Princeton Univ. Press (1945).

Chagger, H. K., P. R. Goddard, P. Murdoch, and A. Williams, "Effect of SO_2 on the Reduction of NO_x by Reburning With Methane," *Fuel*, **70**, 1137 (1991).

Chan, R. K., K. S. Murthi, and D. Harrison, "Thermogravimetric Analysis of Ontario Limestones and Dolomites: II. Reactivity of Sulfur Dioxide with Calcined Samples," *Can. J. of Chemistry*, **48**, 2979 (1970).

Chen, S. L., J. M. McCarthy, W. D. Clark, M. P. Heap, W. R. Seeker, and D. W. Pershing, "Bench and Pilot Scale Process Evaluation of Reburning for In-Furnace NO_x Reduction," *Int. Symp. on Combustion*, Combust. Inst., p. 1159 (1986).

Cole, J. A., J. C. Kramlich, W. R. Seeker, G. D. Silcox, G. H. Newton, D. J. Harrison, and D. W. Pershing, "Fundamental Studies of Sorbent Reactivity in Isothermal Reactors," *Proc.: Joint Symp. on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies*, Electrical Power Res. Inst., Palo Alto, CA, EPRI CS-4966 (1986).

"Control Techniques for Sulfur Oxide Emissions from Stationary Sources," 2nd ed., EPA-450/3-81-004, U.S. EPA, Research Triangle Park, NC (Apr., 1981).

Darmstaedler, E., "Sodium Bicarbonate Injection: A Small-Plant SO_2/NO_x Option," *Power Eng.*, **94**(12), 24 (1990).

Flagan, R. C., and J. H. Seinfeld, *Fundamentals of Air Pollution Engineering*, Prentice Hall, Englewood Cliffs, NJ (1988).

Furusawa, T., D. Kunii, A. Oguma, and N. Yamada, "Rate of Reduction of Nitric Oxide by Char," *Int. Chem. Eng.*, **20**(2), 239 (1983).

Ghardashkhani, S., and O. Lindqvist, "The Influence of Carbon Monoxide on the Reaction Between Sulfur Dioxide and Calcium Oxide," *Thermochimica Acta*, **195**, 113 (1992).

Greene, S. B., S. L. Chen, W. D. Clark, M. P. Heap, D. W. Pershing, and W. R. Seeker, "Bench-Scale Process Evaluation of Reburning and Sorbent Injection for Infurnace NO_x/SO_x Reduction," U.S. EPA, Research Triangle Park, NC, EPA/600/7-85/012 (1985).

Gullett, B. K., K. R. Bruce, W. F. Hansen, and J. E. Hofmann, "Sorbent/Urea Slurry Injection for Simultaneous SO_2/NO_x Removal," *Environ. Prog.*, **11**(2), 155 (1992).

Harkness, A. C., F. E. Murray, and L. Girard, "Catalytic Oxidation of Sulfurous Air Pollutants," *Atmos. Environ.*, **2**, 303 (1968).

Hansen, P. F. B., K. Dam-Johansen, J. E. Johnsson, and T. Hulgaard, "Catalytic Reduction of NO and N_2O on Limestone During Sulfur Capture under Fluidized Bed Combustion Conditions," *Chem. Eng. Sci.*, **47**(9–11), 2419 (1992).

Helfritch, D., S. Bortz, R. Beittel, P. Pergman, and B. Toole-O'Neil, "Combined SO_2 and NO_x Removal by Means of Dry Sorbent Injection," *Environ. Prog.*, **11**(1), 7 (1992).

Kilpinen, P. and M. Hupa, "Homogeneous N_2O Chemistry at Fluidized Bed Combustion Conditions: A Kinetic Modeling Study," *Comb. and Flame*, **85**, 94 (1991).

Kocaefe, D., D. Karman, and F. R. Steward, "Comparison of the Sulfation Rate of Calcium, Magnesium and Zinc Oxides with SO_2 and SO_3," *Can. J. of Chem. Eng.*, **63**, 971 (1985).

Levendis, Y. A., and D. L. Wise, "Method for Simultaneously Removing SO_2 and NO_x Pollutants from the Exhaust of a Combustion System," U.S. Patent 5,312,605 (1994).

Levendis, Y. A., W. Zhu, D. L. Wise, and G. A. Simons, "The Effectiveness of Calcium Magnesium Acetate (CMA) as an SO_x Sorbent in Coal Combustion," *AIChE J.*, **39**(5), 761 (1993).

Lyon, R. K., "Method for the Reduction of the Concentration of NO in Combustion Effluents Using Ammonia," U.S. Patent No. 3,900,554 (1975).

Makansi, J., "Will Combined SO_2/NO_x Processes Find a Niche in the Market," *Power*, **134**(9), 26 (1990).

Myerson, A. L., "Method for Removing the Oxides of Nitrogen as Air Contaminants," U.S. Patent No. 3,867,507 (1975).

Palasantzas, J., "Preliminary Economic Analysis for Production of Calcium Magnesium Acetate From Organic Residues," MS Thesis, Northeastern Univ., Boston (1993).

Palasantzas, I. A., and D. L. Wise, "Preliminary Economic Analysis for Production of Calcium Magnesium Acetate from Organic Residues," *Res. Conserv. and Recy.*, **11**, 225 (1994).

Pfefferle, L. D., and S. W. Churchill, "Effect of Fuel Sulfur on Nitrogen Oxide Formation in a Thermally Stabilized Plug-Flow Burner," *Ind. Eng. Chem. Res.*, **28**, 1004 (1989).

Snow, M. J. H., J. P. Longwell, and A. F. Sarofim, "Direct Sulfation of Calcium Carbonate," *Ind. Eng. Chem. Res.*, **27**, 268 (1988).

Steciak, J., W. G. Zhu, Y. Levendis, and D. Wise, "The Effectiveness of Calcium (Magnesium) Acetate and Calcium Benzoate as NO_x Reduction Agents in Coal Combustion," *Combust. Sci. Technol.*, **102**, 1 (1994a).

Steciak, J., Y. A. Levendis, D. L. Wise, and G. A. Simons, "Reduction of Combustion-Generated SO_2-NO_x by Fine Mists of CMA," *Int. Technical Conf. on Coal Utilization and Fuel Systems*, Coal and Slurry Technol. Assoc. and U.S. DOE Pittsburgh Energy Technology Center (1994b).

Steward, F. R., M. Couturier, and K. Morris, "Firing Coal and Limestone in a Low-NO_x Burner to Reduce SO_2 Emissions," *J. of Inst. of Energy*, **65**, 177 (1992).

Su, F., "Process for Manufacturing Crystalline Calcium Magnesium Acetate," *International Patent*, WO 90/15112, PCT/US90/02766 (1990).

Teng, H., E. M. Suuberg, and J. M. Calo, "Studies of the Reduction of Nitric Oxide by Carbon: The NO-Carbon Gasification Reaction," *Energy and Fuels*, **6**, 398 (1992).

Trantolo, D. I., J. D. Gresser, D. C. Augenstein, and D. L. Wise, "The Feasibility of Residue Biomass Bioconversion to Prepare Calcium Magnesium Acetate Deicing Salt," *Res. Conserv. and Recy.*, **4**, 215(1990).

Tullin, C., and E. Ljungström, "Reaction Between Calcium Carbonate and Sulfur Dioxide," *Energy and Fuels*, **3**, 284 (1989).

Wang, M. R., and K. C. Chang, "Study on Reduction of SO_2 and NO_x Emissions in a Pulsating Combustor Burning Petroleum Coke," *Energy*, **16**(5), 849 (1991).

Wendt, J. O. L., C. V. Sternling, and M. A. Matovich, "Reduction of Sulfur Trioxide and Nitrogen Oxides by Secondary Fuel Injection," *Int. Symp. on Combustion*, Combust. Inst., Pittsburgh, p. 897 (1973).

Wise, D. L., and D. Augenstein, "An Evaluation of the Bioconversion of Woody Biomass to Calcium Acetate Deicing Salt," *Solar Energy*, **41**, 453 (1988).

Wise, D. L., Y. A. Levendis, and M. M. Metghalchi, *CMA: An Emerging Bulk Chemical for Environmental Purposes*, Elsevier, The Netherlands (1991).

Yeh, J. T., W. T. Ma, H. W. Pennline, J. L. Haslbeck, J. I. Joubert, and F. N. Gromicko, "Integrating Testing of the NOXSO Process: Simultaneous Removal of SO_2 and NO_x from Flue Gas," *Chem. Eng. Comm.*, **114**, 65 (1992).

Manuscript received May 9, 1994, and revision received Aug. 22, 1994.