SO_2/NO_X REMOVAL BY $CA(OH)_2$

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Abstract

Previous workers have shown that simultaneous SO_2/NO_x removal can be obtained in a dry scrubbing system with $Ca(OH)_2$ promoted by an additive such as NaOH, and that fly ash and product recycle improve the reactivity of the solids toward SO_2. To test SO_2/NO_x removal with fly ash and product recycle, bench-scale experiments with a packed bed reactor were performed at bag filter conditions. The most reactive solid for NO_x removal was prepared by slurrying $Ca(OH)_2$ with fly ash, $CaSO_3$, and NaOH. The best conditions for NO_x removal were high temperatures (tested up to 125°C) and high concentrations of SO_2 (tested up to 1500 ppm) and O_2 (tested up to 20%). At the best conditions, NO_x removed in 1 hour was 3 - 4 moles per 100 moles $Ca(OH)_2$, compared to 5 - 10 moles SO_2 removed per 100 mols $Ca(OH)_2$. For the greatest SO_2 removal, it was necessary to prepare solids by slurrying $Ca(OH)_2$ with fly ash and NaOH. The best SO_2 removal was obtained at higher relative humidities/lower temperatures. At these conditions, SO_2 removal in 1 hour was 60 - 80 moles SO_2 per 100 moles $Ca(OH)_2$, compared to 0.5 to 1 moles NO_x removed per 100 moles $Ca(OH)_2$. NaOH played an important role in SO_2 and NO_x removal - as an improvement to fly ash dissolution, as a deliquescent, and as a possible catalyst for NO_x removal. When slurried with fly ash and NaOH, $CaSO_3$ substantially improved the solids reactivity toward NO_x, but did not affect SO_2 removal. No optimum temperature for simultaneous SO_2/NO_x removal was found. NO_x removal increased with temperature while SO_2 removal decreased.

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Chapter 1: Project Summary

Introduction

SO_2 and NO_x emissions have been linked to health effects and to acid rain. The major source of SO_2 emissions is coal-fired boilers. While the majority of NO_x emissions are from natural sources, NO_x emissions from power plants are of growing concern. Current NO_x control technology includes selective catalytic reduction with ammonia and combustion modifications. Flue gas desulfurization is presently the most commonly used technology to comply with SO_2 requirements. Dry scrubbing with a spray dryer and bag filter and limestone slurry scrubbing are currently the two most common processes for SO_2 removal.

In a spray dryer, hot flue gas is contacted with an atomized spray of alkali, usually $Ca(OH)_2$. SO_2 absorbs into the droplet and reacts with the alkali particle. The thermal heat of the flue gas evaporates the water, thus forming a solid which is then collected in a bag filter. Since some of the moisture remains in the solid, NO_x removal and additional SO_2 removal takes place in the duct leading to the bag filter and in the bag filter. For NO_x removal, O_2, SO_2, moisture, and an additive, such as NaOH, are necessary. Simultaneous SO_2/NO_x removal was optimum at 100°-110°C (Felsvang et al., 1983).

Recycle of fly ash and product solids from either the spray dryer or bag filter has been shown to yield substantial improvements in SO_2 removal and alkali

utilization. During fly ash recycle, the silica and alumina in fly ash reacts with $Ca(OH)_2$ to form more reactive calcium aluminum silicate hydrates which reprecipitate onto the surface of the fly ash (Jozewicz and Rochelle, 1985). A/S Niro Atomizer investigated the effects of fly ash recycle and found it to improve SO_2 removal in a spray dryer (Felsvang et al., 1981). A spray dryer model based on gas-film mass transfer overpredicted the performance of systems without recycle, but underpredicted systems with recycle (Jozewicz and Rochelle, 1984).

Scope of Research

Previous workers had shown that simultaneous SO_2/NO_x removal can be obtained in a dry scrubbing system with $Ca(OH)_2$ promoted with an additive such as NaOH, and that fly ash and product recycle improved the reactivity of the solids toward SO_2. The scope of this work was to examine SO_2/NO_x removal by $Ca(OH)_2$/fly ash/$CaSO_3$ systems at bag filter conditions. The effects of temperature/relative humidity, additives, and the gas concentration of SO_2, NO_x, and O_2 were examined. The effect of NaOH on fly ash dissolution and on SO_2/NO_x removal was investigated.

Experimental Apparatus

Experiments were conducted in an apparatus designed to simulate bag filter conditions (Ruiz-Alsop and Rochelle, 1986). The pyrex reactor (4 cm in diameter and 12 cm in height) was wrapped with heating tape, and the temperature was controlled within 1°C. Flue gas was synthesized by combining N_2, CO_2, SO_2, and NO from gas cylinders with house air. Water was added to the system by a syringe

pump and evaporated at 120°C in a stainless steel evaporation chamber before being mixed with the gas stream.

Tubing upstream of the reactor was heated to prevent condensation. A PI controller was used to regulate the gas temperature to within 2°C. The reactor was equipped with a bypass to allow for preconditioning of the solids and to allow the gas concentration to stabilize before starting the experiment. After the reactor the gas was cooled and the water condensed out by cooling water. A gas sample of 2.5 - 3.0 ml/min was diluted with 2 l/min of air and then analyzed by a SO_2 analyzer and a $NO/NO_2/NO_x$ analyzer. The SO_2, NO, and NO_x concentrations were continuously recorded and these concentration curves were integrated to determine removal.

Test Conditions

For most experiments, the SO_2 and NO_x concentrations were 500 ppm. The carrier gas flow rate was 4.6 l/min with 7% O_2, 10% CO_2, and the balance N_2. The temperature was varied from 66° to 125°C with the absolute humidity held constant at 14 mol% giving 55% to 6% relative humidities. In the experiments without fly ash, the typical $Ca(OH)_2$ loading was 1 g. In experiments with fly ash, the $Ca(OH)_2$ loading was 0.4 g with 1.6 g each of fly ash and $CaSO_3 \cdot 0.5H_2O$. The reagent was dispersed in 40 g of 100 mesh silica sand to prevent channeling due to $Ca(OH)_2$ agglomeration (Karlsson et al., 1983). Exposure time to the synthetic flue gas was 1 hour.

Sample Preparation

Reagent grade $Ca(OH)_2$ was sieved through a 125 micron screen before being hand-mixed with 40 g of silica sand. Additives were prepared in 5 - 10 ml solutions and mixed with the $Ca(OH)_2$. This was then atmospherically dried overnight at 70 - 80°C. In experiments with fly ash, $Ca(OH)_2$ was slurried with fly ash and $CaSO_3 \cdot 0.5H_2O$ at a weight ratio of 1:4:4 in a pyrex glass beaker. The fly ash used was from a bituminous coal burned at Appalachian Power Company's Clinch River plant and was obtained from Dr. John Chang of the Acurex Corporation. NaOH (10 mol% of $Ca(OH)_2$) was added to the slurry with the amount of water varied to manipulate the concentration of NaOH. The slurrying time was 6 hours and the slurrying temperature was 65°C, unless otherwise specified. After slurrying, the sample was atmospherically dried overnight at 65°C.

Results

During each experiment, the NO, NO_x, and SO_2 concentrations were continuously monitored, and these concentration curves were later integrated to determine removal over the 1 hour period. 'Removal' is defined as moles SO_2 or NO_x removed per 100 moles of $Ca(OH)_2$.

Effects of Temperature/Relative Humidity

NO_x removal increased with increasing temperature while SO_2 removal decreased (see Figures 1.2 - 1.7). In runs up to 125°C, NO_x removal continued to increase. At 66°C, SO_2 removal was from one to two orders of magnitude faster than NO_x removal. At 110°C, SO_2 removal was only 2 - 5 times faster. No optimum temperature window could be found for SO_2/NO_x removal.

Effects of NaOH

NaOH and Na_2SO_3 were effective additives to $Ca(OH)_2$ for SO_2 removal. NaOH enhanced NO_x removal by several fold in some instances, while Na_2SO_3 had no beneficial effect. Both Na_2SO_3 and NaOH improved SO_2 removal by similar amounts, however Na_2SO_3 contains twice as much sodium as NaOH. Some removal can be contributed to NaOH itself. SO_2 removal for a $Ca(OH)_2$:fly ash:$CaSO_3 \cdot 0.5H_2O$ sample at a weight ratio of 1:4:4 was higher than $Ca(OH)_2$ with either the NaOH or Na_2SO_3 as an additive. However for NO_x removal, the $Ca(OH)_2$ with 10% NaOH yielded higher removal.

NaOH concentration in the fly ash slurry played an important role in the reactivity of the solid. Figures 1.1 and 1.2 demonstrate this effect of NaOH concentration. Fly ash dissolution into water was suspected to be the rate limiting step during fly ash slurrying, and NaOH addition was expected to improve fly ash dissolution. A large increase in removal was seen from 0.03 to 0.08M NaOH (moles NaOH per volume water). From 0.08 to 0.25M there was a decrease in reactivity toward both SO_2 and NO_x. At 0.25M the slurry was a paste, and the lack of water and mixing may have limited fly ash dissolution. This sample was hand-mixed, capped, and placed in an oven for 6 hours at 65°C before being dried.

NaOH played an important role in NO_x removal, probably as a deliquescent, as an improvement to fly ash dissolution, and as a possible catalyst. A comparable sample was slurried with NaOH and then filtered so that most of the
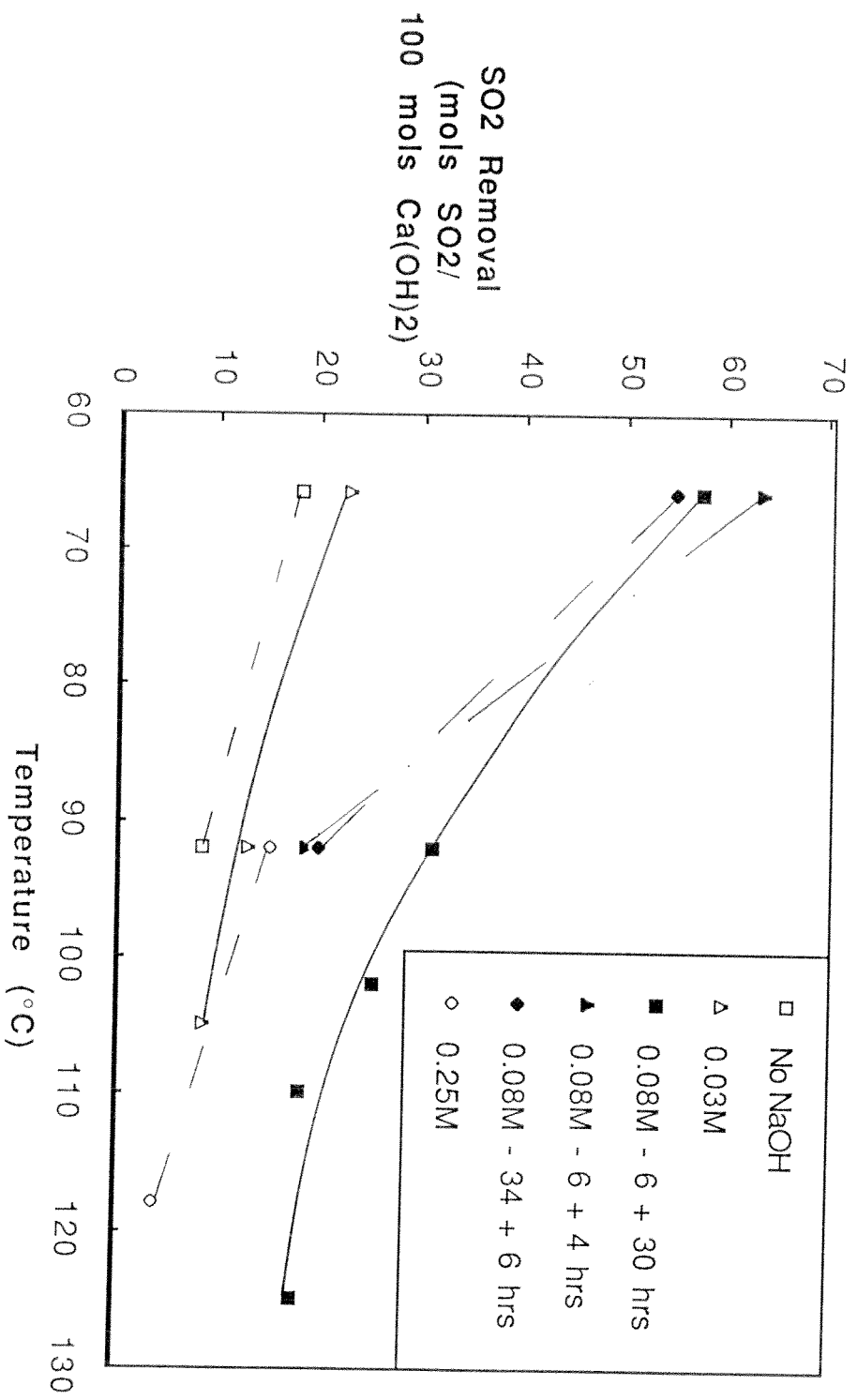
Figure 1.1: Effect of NaOH Concentration on SO_2 Removal

1 $Ca(OH)_2$:4 Fly Ash:4 $CaSO_3$ - 10 mol% NaOH; Removal After 1 Hour; 500 ppm SO_2; 500 ppm NO_x; 14 mol% H_2O; Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2; 83% N_2

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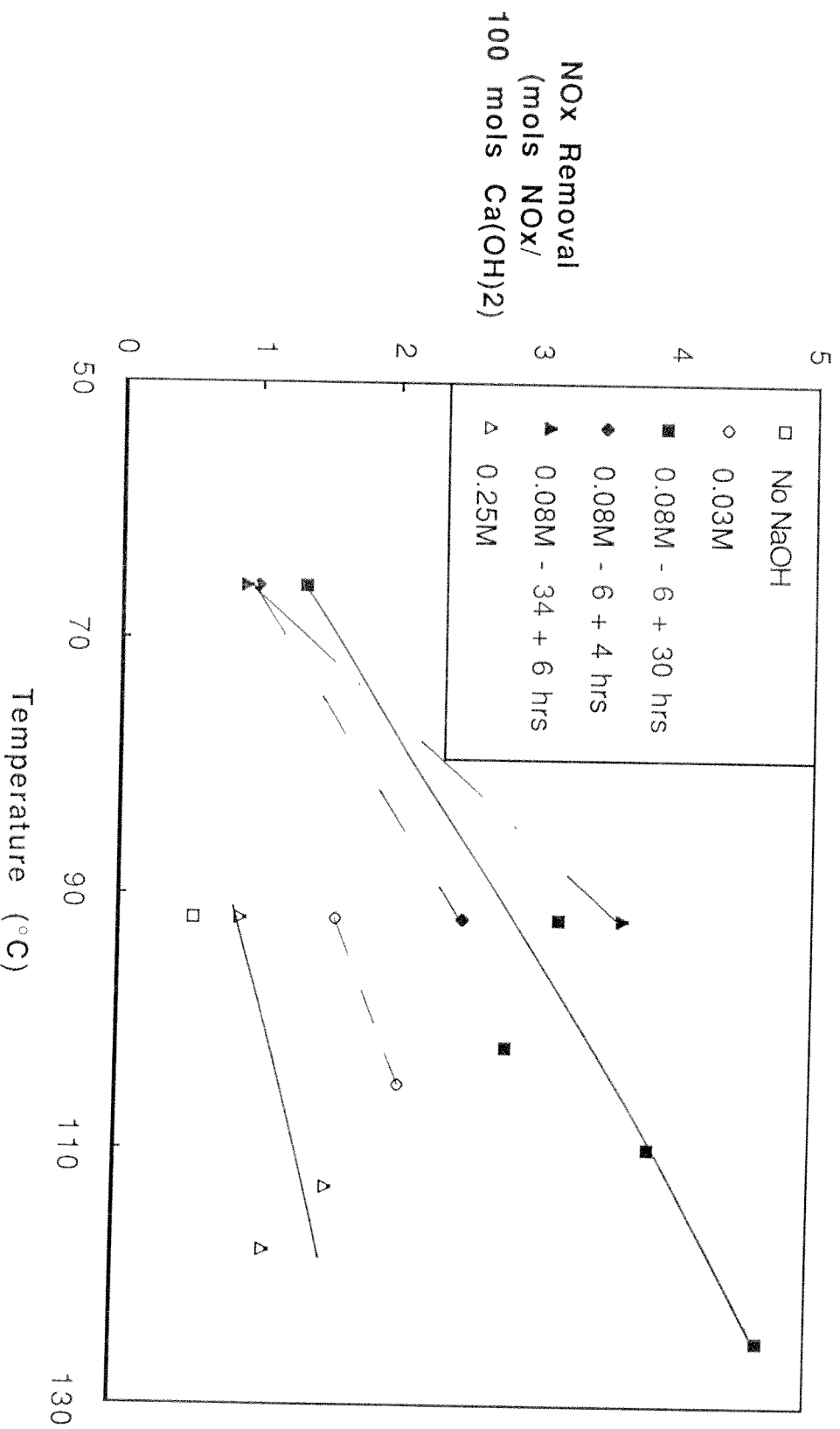
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500 ppm NO$_x$; 14 mol% H$_2$O; Gas Flow: 4.6 l/min - 7% O$_2$, 10% CO$_2$; 83% N$_2$

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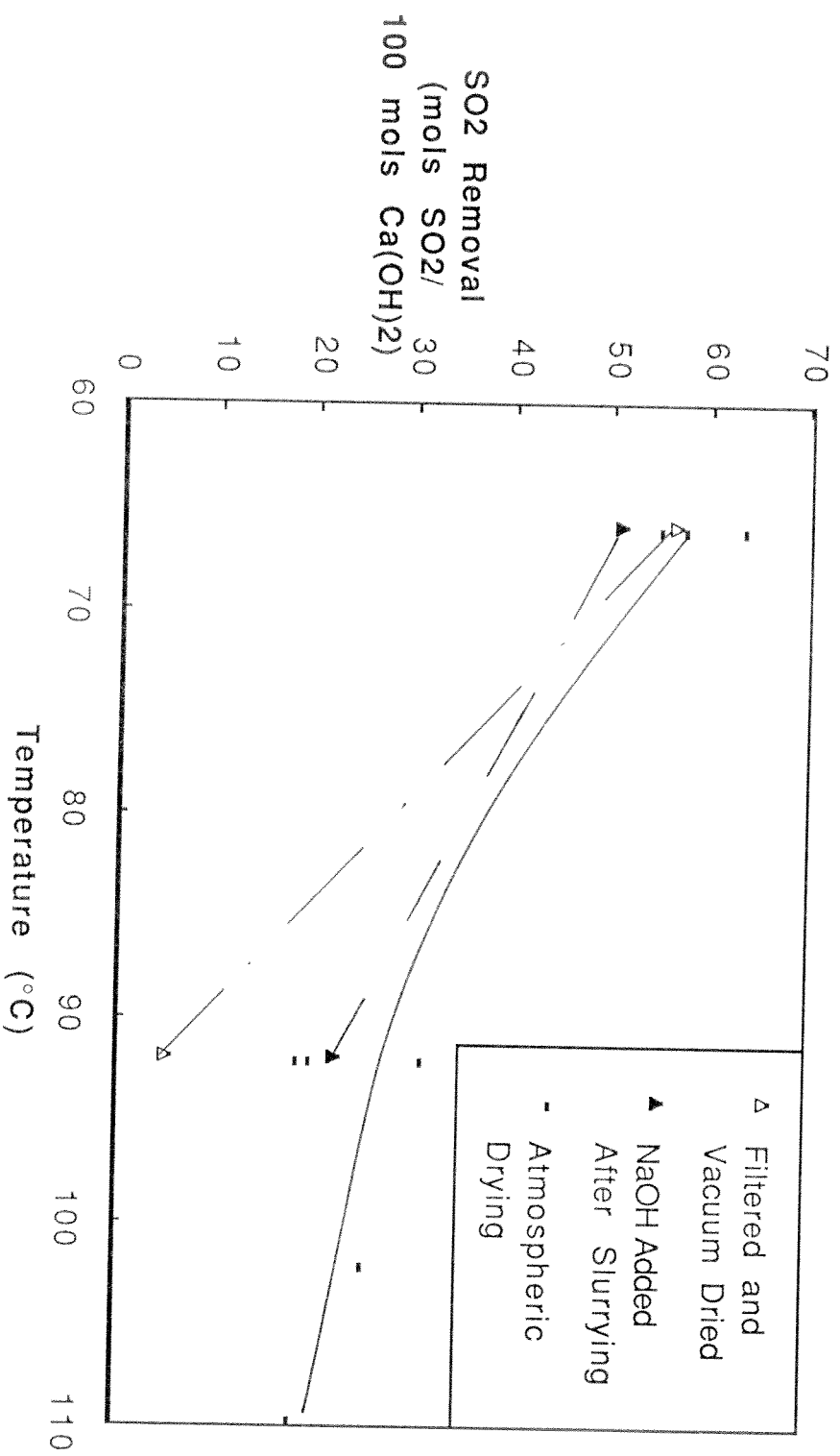
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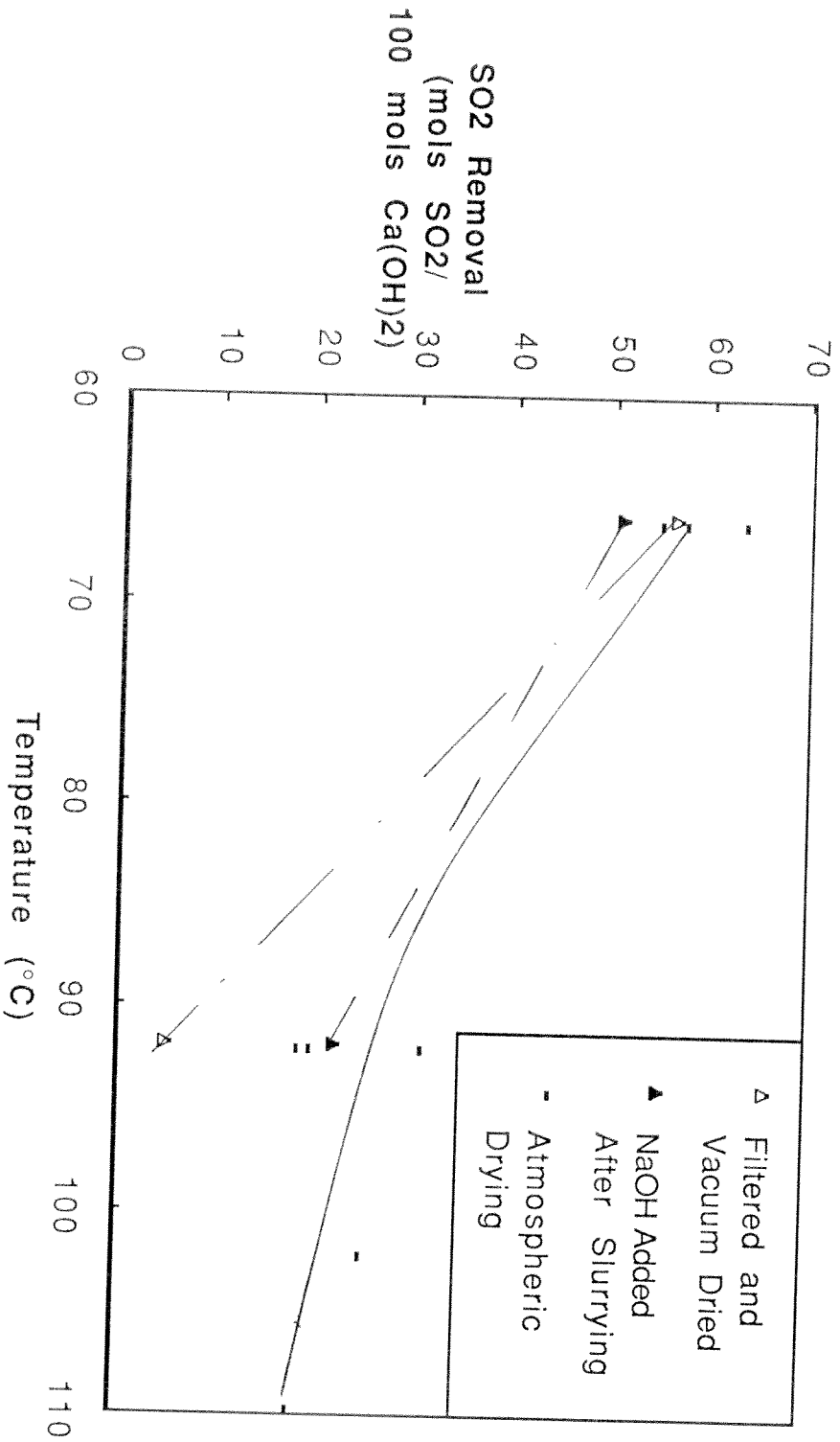
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NaOH was lost. Another sample was slurried without NaOH and, after being dried, NaOH was added. The results of these experiments are given in Figures 1.3 (SO_2) and 1.4 (NO_x). At 66°C SO_2 removal was slightly less for both solids so NaOH did improve fly ash dissolution and also had a deliquescent effect. For the filtered solid, SO_2 removal at 92°C was substantially reduced. The effect of NaOH at higher temperatures/lower relative humidities was quite evident. NO_x removal for both solids was much less. At 92° and 110°C, NO_x removals for $Ca(OH)_2$ and $CaSO_3$ slurried with 0.08M NaOH were 0.3 and 0.2 (moles NO_x removed per 100 moles $Ca(OH)_2$). At 92° and 110°C, NO_x removal for $Ca(OH)_2$ with 10% NaOH was 1.1 and 1.3 (see Figure 1.6).

Effect of CaSO3

Without $CaSO_3$ in the $Ca(OH)_2$ and fly ash slurry, SO_2 removal was unaffected. However, NO_x removal for this $Ca(OH)_2$/fly ash sample was substantially reduced. These results are given in Figures 1.5 (SO_2) and 1.6 (NO_x). $CaSO_3$ improved the reactivity of the slurried solids toward NO_x. However, the $Ca(OH)_2/CaSO_3$ slurry was not reactive toward NO_x, so $CaSO_3$ alone did not enhance NO_x removal.

Effect of Fly Ash

Without fly ash, both SO_2 and NO_x removal for $Ca(OH)_2$:$CaSO_3$ slurried with 0.08M NaOH were much lower than when fly ash is included. Thus fly ash does play an important role in enhancing the $Ca(OH)_2$ reactivity (see Figures 1.5 and 1.6). At 92° and 110°C, NO_x removals for the $Ca(OH)_2/CaSO_3$ sample were 0.3 and
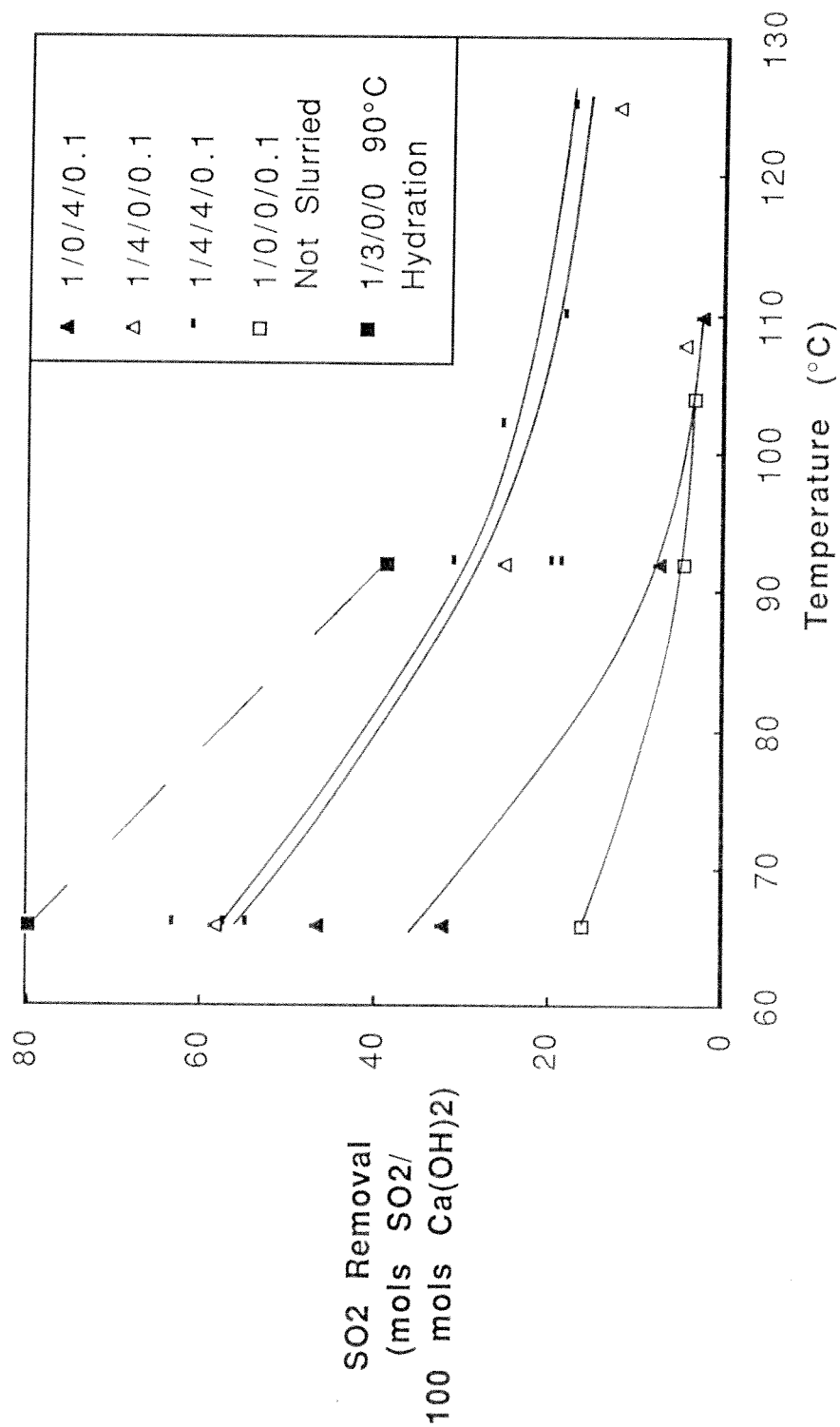
Figure 1.5: Effects of Fly Ash and CaSO₃ on SO₂ Removal

1/4/4/0.1 = 1 Ca(OH)$_2$:4 Fly Ash: 4 CaSO$_3$: 10 mol% NaOH (0.08M); Removal After 1 Hour; 500 ppm SO$_2$; 500 ppm NO$_x$; 14 mol% H$_2$O; Gas Flow: 4.6 l/min - 7% O$_2$, 10% CO$_2$; 83% N$_2$
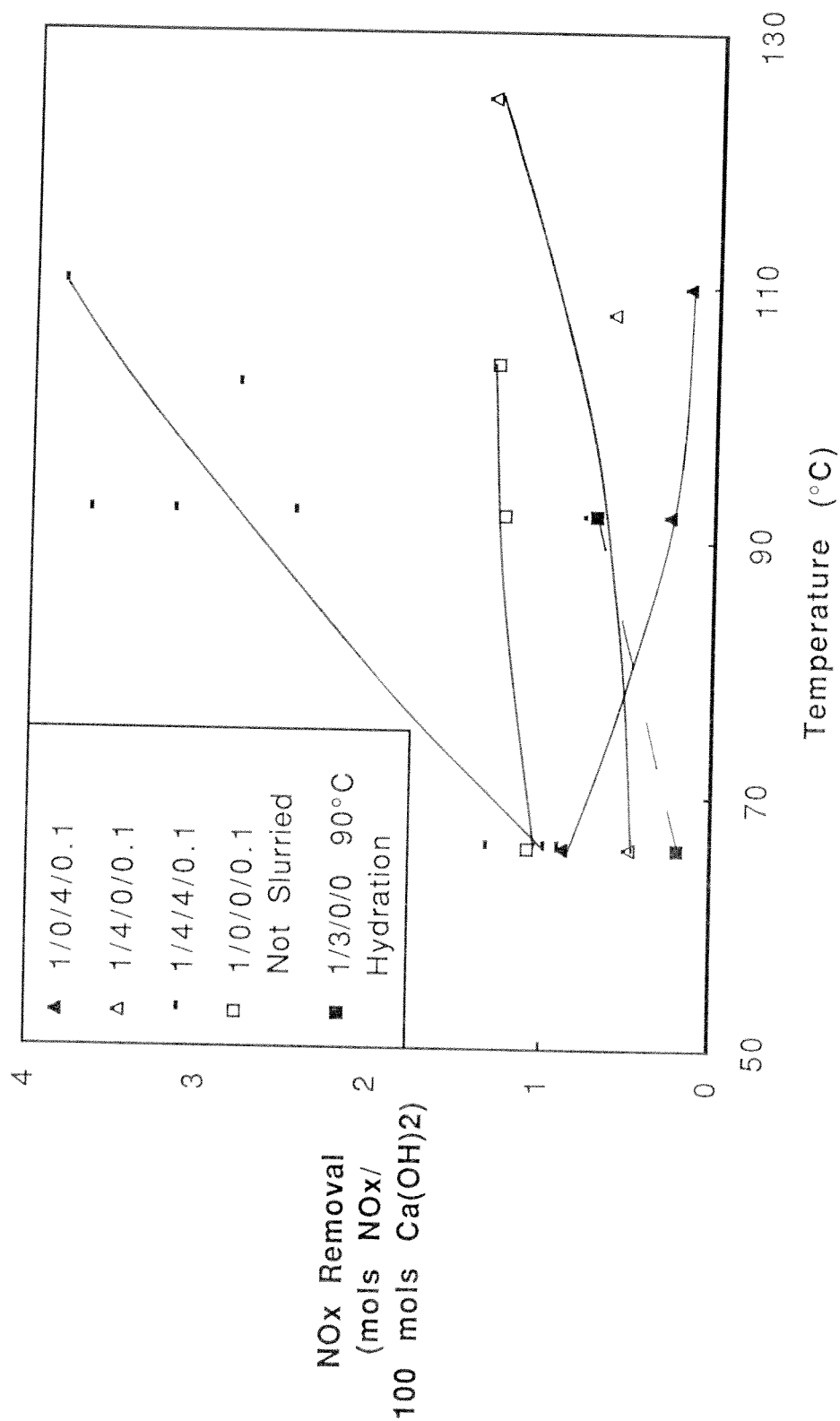
Figure 1.6: Effects of Fly Ash and $CaSO_3$ on NO_x Removal
$1/4/4/0.1 = 1$ $Ca(OH)_2$:4 Fly Ash: 4 $CaSO_3$: 10 mol% NaOH (0.08M); Removal After 1 Hour; 500 ppm SO_2; 500 ppm NO_x; 14 mol% H_2O; Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2; 83% N_2

0.2 which were less than $Ca(OH)_2$ with 10% NaOH, 1.2 and 1.3. The NaOH deliquescent effect which was more important at higher temperatures (See Effects of NaOH) may be less effective since the NaOH precipitated onto all the $Ca(OH)_2$ and $CaSO_3 \cdot 0.5H_2O$. NO_x removal tended to decrease with increasing temperature, which was the opposite of the other samples tested.

At a higher hydration temperature, the solids were substantially more reactive toward SO_2. A $Ca(OH)_2$:fly ash sample at a weight ratio of 1:3 was hydrated at 90°C for 4 hours. The results of these runs are given in Figures 1.5 and 1.6 (NO_x). The SO_2 removal for this sample was greater than that of 1 $Ca(OH)_2$:4 Clinch River fly ash with 10% NaOH slurried at 65°C and for 6 hours, but NO_x removal lower. Because NaOH was included with one of the solids, NO_x removals are difficult to compare.

Effects of NO_x, SO_2, and O_2

NO_x had little effect on SO_2 removal at low NO_x removals. At higher NO_x removals, NO_x had a negative effect on SO_2 removal. For the reactive sample of $Ca(OH)_2$:fly ash:$CaSO_3 \cdot 0.5H_2O$ with 10% NaOH (0.08M), SO_2 removal was substantially better without NO_x present. Table 1.1 illustrates these results. At 66° and 92°C, NO_x removal for both of these runs was fairly high, 1.3 and 3.2.

NO_x removal increased with increasing SO_2 concentration. With no SO_2 present, NO_x removal was higher than at 200 ppm SO_2. Table 1.2 shows these effects. For $Ca(OH)_2$:fly ash:$CaSO_3$ at 0.08M NaOH, NO_x removal without SO_2 present was 1.6 which was actually higher than NO_x removal at 200 ppm SO_2, 1.1.

Table 1.1: Effect of NO_x on SO_2 Removal
SO_2 Removal After 1 Hour; 14 mol% H_2O; 500 ppm SO_2
Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2, 83% N_2

| | SO$_2$ Removal (mols SO$_2$/100 mols Ca(OH)$_2$) | |
Experiment	Without NO$_x$	500 ppm NO$_x$
Ca(OH)$_2$; 66°C	11.3	11.2
Ca(OH)$_2$; 92°C	7.6	8.2
Ca(OH)$_2$ + 10% NaOH; 66°	17.3	16.3
Ca(OH)$_2$:Fly Ash:CaSO$_3$ = 1:4:4 0.08M NaOH (original); 66°C	67.9	57.5
Ca(OH)$_2$:Fly Ash:CaSO$_3$ = 1:4:4 0.08M NaOH (original); 92°C	46.6	31.2

Increasing the SO_2 concentration to 500 ppm, NO_x removal improved to 3.2. At 1500 ppm, NO_x removal improved further to 4.1. The reason for higher NO_x removal with no SO_2 present may be because the SO_2 competes with the NO_x for more reactive pore sites, and only the presence of $CaSO_3$ in the reagent may be necessary for NO_x removal. The $Ca(OH)_2$ run without SO_2 is questionable. For $Ca(OH)_2$ at 66°C, no NO_x removal was obtained with runs using span gas mixtures - 250 ppm NO_x and no SO_2.

Increasing O_2 concentration improved SO_2 and NO_x removal. At low O_2 concentration of 0.5%, little NO_x removal was obtained. These results are illustrated in Table 1.3. With common purity nitrogen - about 0.5% O_2, SO_2 and NO_x removal were only 21.8 and 0.5, respectively. At 7% O_2 both SO_2 and NO_x removal

Table 1.2: Effects of SO_2 on NO_x Removal
NO_x Removal After 1 Hour; 14 mol% H_2O; 500 ppm NO_x
Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2, 83% N_2

1 $Ca(OH)_2$: 4 Fly Ash: 4 $CaSO_3$
0.08M NaOH (original); 92°C

ppm SO_2	NO_x Removal (mols NO_x/100 mols $Ca(OH)_2$)
0	1.6
200	1.1
500	3.2
1500	4.1

1 $Ca(OH)_2$: 4 Fly Ash: 4 $CaSO_3$
0.03M NaOH; 92°C

250	1.1
500	1.6

$Ca(OH)_2$; 66°C

0	1.4
500	0.3

Table 1.3: Effect of O_2 on SO_2/NO_x Removal
Removal After 1 Hour; T = 92°C; 500 ppm SO_2; 500 ppm NO_x
14 mol% H_2O; Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2, 83% N_2
1 $Ca(OH)_2$: 4 Fly Ash: 4 $CaSO_3$; 0.08M NaOH - 10 mol%

% Oxygen	SO_2 Removal	NO_x Removal
0.5	21.8	0.5
7	36.2	3.2
19.9	37.3	1.7
19.9	27.8	5.2

improved to 36.2 and 3.2, respectively. The results at 19.9% O_2 (air and 10% CO_2) are puzzling. The experiment was run twice, with varying results. In both runs either SO_2 or NO_x removal increased while the other decreased.

Conclusions

The most reactive solid for NO_x removal was prepared by slurrying $Ca(OH)_2$ with fly ash, $CaSO_3$, and NaOH. The best conditions for NO_x removal were at high temperatures (tested up to 125°C) and high concentrations of SO_2 (tested up to 1500 ppm) and O_2 (tested up to 20%).

For the highest SO_2 removal, it was necessary to prepare solids by slurrying $Ca(OH)_2$ with fly ash and NaOH. The best conditions for SO_2 removal were at higher relative humidities (lower temperatures) and with no NO_x.

NaOH played an important role in SO_2/NO_x removal - as an improvement to fly ash dissolution, as a deliquescent, and possibly as a catalyst for NO_x removal.

When slurried with fly ash and NaOH, $CaSO_3$ substantially improved the solids reactivity toward NO_x, but did not affect SO_2 removal.

No optimum temperature for simultaneous SO_2/NO_x removal could be found. NO_x removal increased with temperature while SO_2 removal decreased. At 66°C, NO_x removal was from one to two orders of magnitude slower than SO_2 removal. At 110°C, NO_x removal was 2 - 5 times slower than SO_2 removal.

Chapter 2: Introduction

SO$_2$ and NO$_x$ emissions have been linked to health effects and to acid rain. The major source of SO$_2$ emissions is coal-fired boilers. The majority of NO$_x$ emissions are from natural sources, but NO$_x$ emissions from automobiles and power plants are of growing concern (Air Quality Criteria for NO$_x$, 1971). NO$_x$ can be formed by oxidation of either atmospheric nitrogen (thermal NO$_x$) or fuel-bound nitrogen (fuel NO$_x$). While most of the sulfur in coal is oxidized to SO$_2$, the portion of fuel-bound nitrogen which is converted to NO$_x$ may vary (Folsom et al., 1983).

Flue gas desulfurization is presently the most commonly used technology to comply with SO$_2$ requirements. Dry scrubbing with a spray dryer and bag filter and limestone slurry scrubbing are presently the two most popular processes for SO$_2$ removal. Injection of a dry alkaline material such as nahcolite or trona into the ducts leading to the bag filters is a new alternative especially attractive for retrofit applications since capital requirements are low. Coolside desulfurization, humidification of the flue gas followed by injection of a sorbent such as hydrated lime, is able to provide higher SO$_2$ removal because of the higher relative humidity.

Current NO$_x$ control technology includes combustion modifications and selective catalytic reduction (SCR) with ammonia. Combustion modifications such as low excess-air, multistage combustion, low NO$_x$ burners, and flue gas recycling

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reduce NO_x emissions, but are not capable of eliminating all of the NO_x. SCR, which is commonly practiced in Japan, is a simple and reliable process. SCR reduces only NO_x and is fairly expensive. While many problems have been solved, catalyst life is still short (Ando, 1984).

Dry scrubbing with a spray dryer and bag filter using slaked lime is an alternative to limestone slurry scrubbing. A typical spray dryer/bag filter system is given in Figure 1.1. The advantages of dry scrubbing over wet slurry scrubbing are production of a dry solid and lower equipment costs. Economic studies have stated that dry scrubbing is economically competitive for low and medium sulfur coals (Burnett et al., 1981; Drabkin and Robison, 1981). Some recent reports have considered using dry scrubbing systems for high sulfur coals (Jankura et al., 1984; Robards et al., 1985).

In a spray dryer, hot flue gas is contacted with an atomized spray of alkali, usually $Ca(OH)_2$. SO_2 absorbs into the droplet and reacts with the alkali particle. The thermal heat of the flue gas evaporates the water, thus forming a solid which is then collected in a bag filter. Since some of the moisture remains in the solid, NO_x removal and additional SO_2 removal take place in the duct leading to the bag filter and in the bag filter. For significant NO_x removal, O_2, SO_2, moisture, and an additive, such as NaOH, are necessary. About $100°$-$110°C$ was optimum for simultaneous SO_2/NO_x removal (Felsvang et al., 1983; Donnelly et al., 1983).

Recycle of fly ash and product solids from either the spray dryer or bag filter has been shown to yield substantial improvements in SO_2 removal and alkali
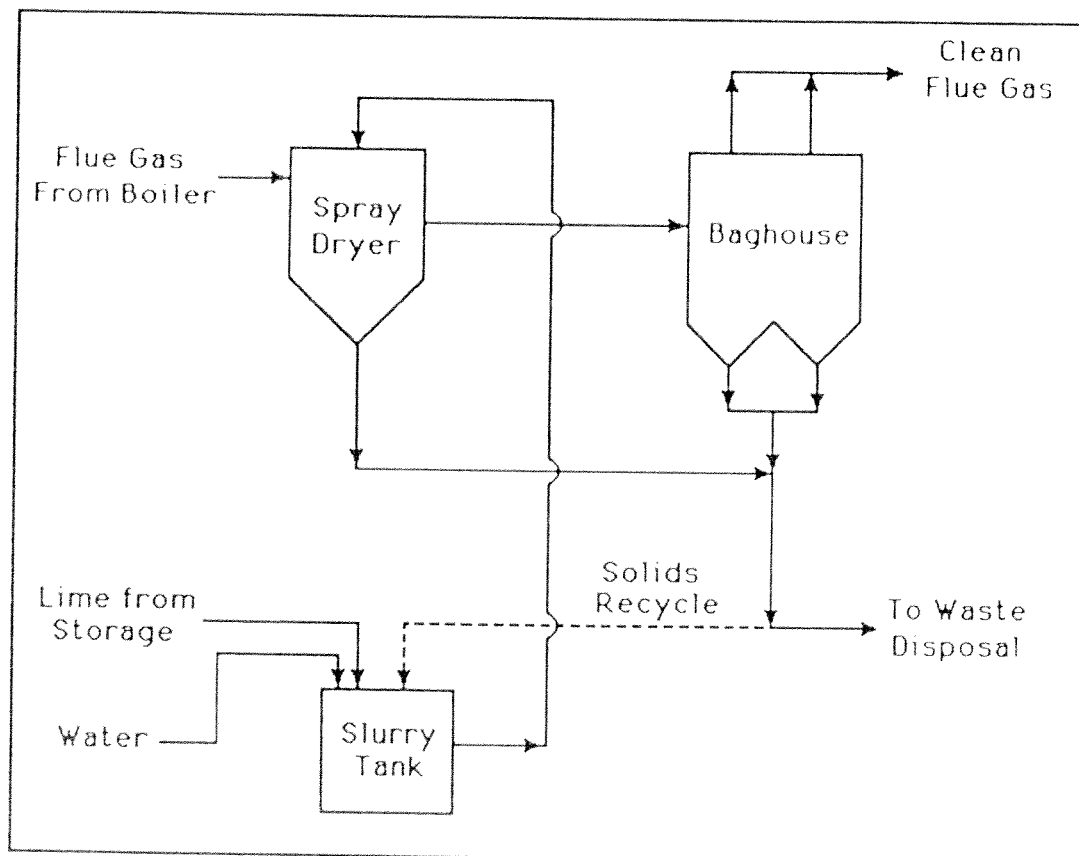
Figure 1.1: Typical Spray Dryer System

utilization (Kelly et al., 1983, Melia et al., 1983, Palazzolo et al., 1983, Parsons et al., 1981). $Ca(OH)_2$ recycle provides additional opportunity for reaction with SO_2. During fly ash recycle, the silica and alumina in fly ash reacts with $Ca(OH)_2$ to form more reactive calcium aluminum silicate hydrates which reprecipitate onto the surface of the fly ash (Jozewicz and Rochelle, 1985).

Previous work at the University of Texas has studied the reaction of $Ca(OH)_2$ and SO_2 (Ruiz-Alsop and Rochelle, 1985; Ruiz-Alsop and Rochelle, 1986) and the effects of fly ash recycle (Jozewicz and Rochelle, 1985). This work was conducted in a sandbed reactor designed to simulate bag filter conditions. The reagent was dispersed in a bed of sand and simulated flue gas was passed through the bed. Bench-scale work in Niro's patent on NO_x removal focused upon the $Ca(OH)_2$ and NO_x reaction with $Ca(OH)_2/CaSO_3/CaSO_4$ with additives.

This study was conducted in a sandbed reactor, similar to previous work, with some improvements and modifications for NO_x. The scope of this work was to examine SO_2/NO_x removal by $Ca(OH)_2/fly$ ash/$CaSO_3$ systems at bag filter conditions. The effects of temperature/relative humidity, additives, and the gas concentration of SO_2, NO_x, and O_2 were examined. The effect of NaOH on fly ash dissolution and on SO_2/NO_x removal was investigated. Early work in SO_2 removal determined the effect of BET surface area, O_2 concentration, and temperature/relative humidity and also investigated various alternative alkalis including portland cement, slaked limes, and pressure hydrated limes.

Chapter 3: Previous Work

NO_x Adsorption/Absorption

Several different materials have been tested for NO_x and SO_2 adsorption/desorption. In a radial fixed bed reactor, Medellin et al., (1978) found alkalized alumina absorbed NO at 100°C. At higher temperatures, NO_x removal decreased. The presence of NO was determined to improve SO_2 adsorption. The NOXSO process is a dry, regenerable process for simultaneous SO_2/NO_x removal (Haslbeck and Neal, 1985). The sorbent is Na_2CO_3 deposited on the surface of a porous alumina substrate. Regeneration is performed at 600°C with hydrogen and carbon dioxide to produce sulfur, hydrogen sulfide, sulfur dioxide, and nitrogen oxides. The NO_x is recycled to the boiler to limit additional NO_x from being produced. The other products are sent to a Claus plant. Removals of 3000 cc SO_2/100g sorbent and 400 cc NO_x/100g sorbent have been obtained. The catalyst has been tested for up to 45 cycles without any decrease in removal.

Rosenberg and Nuzum (1985) tested several metal oxides in a fixed bed reactor for combined SO_2/NO_x removal and found ZnO to be the most favorable. SO_2 removals over 95% and NO_x removals up to 50% were obtained. Zinc sulfate and nitrate were heated to regenerate the ZnO. At 135°F and 70% relative humidity, they found that NO_x improved SO_2 removal with this being less noticeable at higher relative humidities. NO_2 also improved SO_2 removal much more than NO.

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Michigan Technological University (1971) examined NO and NO_2 adsorption by Na_2CO_3. NO_2 removal was improved at higher temperatures and was zero order in NO_2. O_2 was found to enhance NO removal. Little SO_2 removal was obtained. Superior Oil Company (1977) tested nahcolite for SO_2/NO removal. In their pilot plant with a countercurrent moving bed reactor, NO_x removal of 42% (from 160 ppm) and SO_2 removal of 72% (from 675 ppm) were obtained with 72% nahcolite utilization. Stern (1978) performed a bench-scale study of SO_2/NO reaction with nahcolite and trona. The reaction was measured from 300-500°F with SO_2 removal increasing at higher temperatures. NO adsorption was low but more favorable at lower temperatures. Stern was able to model the SO_2/NO reaction by the shrinking core model with diffusion through the Na_2SO_4 product layer as the controlling step.

NO_x Removal by Dry Scrubbing

A/S Niro Atomizer patented a new SO_2/NO_x process which utilizes the same equipment, spray dryer and bag filter, as SO_2 removal (Felsvang et al., 1983; Donnelly et al., 1983). Pilot plant studies showed that the majority of the SO_2 removal occurred in the spray dryer while all of the NO_x removal took place in the bag filter. Bench-scale studies discovered a temperature window between 100° and 110°C for optimum SO_2/NO_x removal. Na_2SO_3 was found to be the preferred additive. For NO_x removal, moisture, O_2, and SO_2 were necessary. In the proposed mechanism, SO_2 removal must take place before NO_x will react with the solids. Increasing the SO_2 concentration was determined to improve NO_x removal.

Reaction of SO_2 with $Ca(OH)_2$

Klingspor et al., (1983) studied the reaction of limestone and slaked limes with SO_2 in a sandbed reactor. They determined that the initial reaction rate was an exponential function of relative humidity. For relative humidities below 20%, SO_2 did not react. Ruiz-Alsop and Rochelle (1986) examined SO_2 removal by $Ca(OH)_2$ in a sandbed reactor. The reaction of SO_2 with $Ca(OH)_2$ is zero order in SO_2, with relative humidity being the most important variable. Deliquescent salt additives, such as sodium salts and chlorides, were found to enhance SO_2 removal. The reaction was simulated by the shrinking core model with an empirical correlation to adjust for changes in the surface area due to reaction with SO_2. At high relative humiditites or with salt addititves, the reaction was kinetically controlled. While at low relative humidities, diffusion through the $CaSO_3$ product layer was the rate determining step.

Coolside desulfurization, humidification of the flue gas followed by dry sorbent injection into the ducts leading to the particulate collection system, is a new technology which could provide SO_2 removal at low capital costs which would be especially attractive for retrofit applications. In a one MW field trial with a 3000-4000 ACFM slipstream diverted through a pilot scale humidifier and electrostatic precipitator, Yoon et al., (1985) reported 80% SO_2 removal with 40% sorbent utilization by injection of hydrated lime with sodium based additives. Laboratory work has shown that Boiler Limestone Injection fly ash could be effective as a sorbent after an activation step or after flue gas humidification.

Fly Ash Recycle

Solids recycle from the spray dryer provides a higher $Ca(OH)_2$ concentration in the slurry feed at the same $Ca(OH)_2$ stoichiometry (moles of $Ca(OH)_2$ fed to the system/moles of SO_2 in feed gas). At 1.5 stoichiometry, recycle tests give 10 to 15% more SO_2 removal than for once-thru tests (Jankura et al., 1984). Increasing the ash content in the feed from 5 to 20% improved SO_2 removal from 80% to 92% at 1.6 stoichiometry. A/S Niro Atomizer investigated the effects of fly ash recycle and found it to improve SO_2 removal in a spray dryer. At 1.4 stoichiometry and 500 ppm SO_2, removal for one pass of lime was 67%. With a 3:1 recycle ratio and with no fly ash present in the recycle, SO_2 removal increased to 76%. With fly ash in the recyle, SO_2 removal improved up to 84% (Felsvang et al., 1981). A spray dryer model based on gas-film mass transfer overpredicted the performance of systems without recycle, but underpredicted systems with recycle (Jozewicz and Rochelle, 1984).

Jozewicz and Rochelle (1985) examined the effects of fly ash slurrying conditions on SO_2 removal in a sandbed reactor. They concluded that higher slurrying temperatures and longer slurrying times yielded more reactive solid. At each slurrying temperature, $Ca(OH)_2$ utilization asymptoted to a maximum value with increasing slurrying time. At a slurrying temperature from 55° to 65°C a step increase in SO_2 removal occurred. Differential scanning calorimetry found an extra compound at 65°C that was not produced at 55°C. Calcium silicate hydrates, which were of high surface area, were believed to be formed. $Ca(OH)_2$ slurried with fly ash and $CaSO_3$ or $CaSO_4$ yielded a product which contained ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot xH_2O$, with x being 30 - 32). At a slurrying temperature of

25°C, addition of $CaSO_3$ or $CaSO_4$ enhanced utilization, with $CaSO_4$ having a more dramatic effect. Experiments with $Ca(OH)_2$ slurried with silicic acid determined that the reaction between $Ca(OH)_2$ and silica in the fly ash was responsible for the improvement of the reactivity of the solids. Digestion of the silica from the fly ash was determined to be the rate controlling step in the $Ca(OH)_2$ and silica reaction. The aluminum oxides helped to form calcium aluminum hydrates and calcium aluminum silicate hydrates which were more reactive than $Ca(OH)_2$, but less reactive than calcium silicate hydrates. The iron oxides were found to have little effect. Yang and Shen (1979) found that even low surface area calcium silicates (less than 10 m^2/g) were more reactive than CaO.

Chapter 4: Experimental

Apparatus

Experiments were conducted in an apparatus (Figure 4.1) designed to simulate bag filter conditions (Karlsson et al., 1983; Klingspor et al., 1983; Klingspor et al., 1984; Ruiz-Alsop and Rochelle, 1985; Jozewicz and Rochelle, 1985; Ruiz-Alsop and Rochelle, 1986). The cylindrical reactor (4 cm in diameter and 12 cm in height) was made of pyrex with a glass frit for support of the solids. Silica sand (100 mesh average) was used to prevent channeling caused by $Ca(OH)_2$ agglomeration (Karlsson et al., 1983). The glass reactor was wrapped with heating tape, and the temperature was regulated by a PID temperature controller (Omega Model CN2000) to within 1°C. Flue gas was synthesized by combining N_2, CO_2, SO_2, and NO from gas cylinders with house air. The flow rates were maintained by mass flow controllers (Brooks Model 5850). Water was added to the system by a syringe pump (Sage Instruments Model 341A) and evaporated at 120°C in a stainless steel evaporation chamber before being mixed with the gas stream. The evaporation chamber was 5 cm in diameter and 14 cm in height and was filled with 5 mm glass beads to increase the contact surface. The evaporator was wrapped with heating tape which was modulated by a voltage controller. The temperature was measured with a Chromel-Alumel thermocouple.

Tubing upstream of the reactor was heated by heating tape to prevent condensation. A PI controller (Omega Series 4200) was used to regulate the gas

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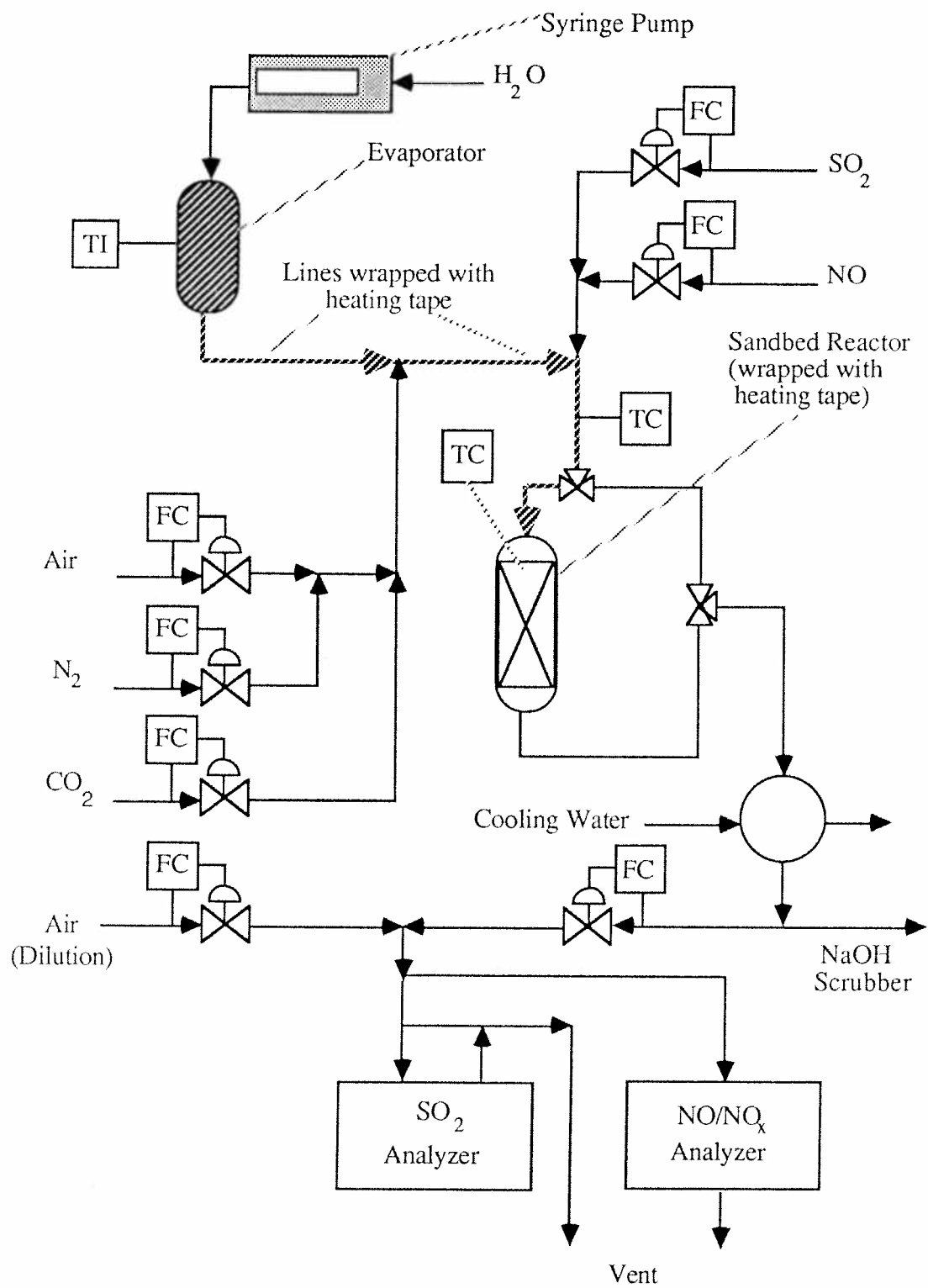
Figure 4.1: Experimental Apparatus

temperature to within 2°C. The reactor was equipped with a bypass to allow for preconditioning of the solids and to allow the gas concentration to stabilize before starting the experiment. After the reactor the gas was cooled and the water condensed out by cooling water. A gas sample of 2.5 - 3.0 ml/min was diluted with 2 l/min of air. Both the sample and dilution stream were maintained with mass flow controllers. This gas mixture was then analyzed by a flame photometric SO_2 analyzer (Columbia Scientific Industries Model SA285E) and a chemiluminescent $NO/NO_2/NO_x$ analyzer (Thermoelectron Model 14B/E).

Procedure

For most experiments, the SO_2 and NO_x concentrations were 500 ppm each. The carrier gas flow rate was 4.6 l/min with 7% O_2, 10% CO_2, and the balance N_2. In the $Ca(OH)_2$ or additives experiments, the typical solids loading was 1 g. In the experiments with fly ash, the loading was 0.4 g of $Ca(OH)_2$ with 1.6 g each of fly ash and $CaSO_3 \cdot 0.5H_2O$. The reagent was dispersed in 40 g of 100 mesh (average) silica sand to prevent channeling due to $Ca(OH)_2$ agglomeration. Exposure time to the synthetic flue gas was 1 hour. The temperature was varied from 66° to 125°C with the absolute humidity held constant. Water was injected at 14 mol%, with the relative humidity at 66°, 92°, and 125°C being 55%, 18%, and 6%. Before each experiment, the solids were preconditioned at 98% relative humidity (2.16 l/min N_2 at 66°C) for 8 minutes, and for 10 more minutes at the relative humidity of the experiment (4.6 l/min at the temperature of the experiment).

Sample Preparation

Reagent grade $Ca(OH)_2$ (Matheson Coleman & Bell Manufacturing Chemist) was sieved through a 125 micron screen before being hand-mixed with 40 g of silica

sand. Additives were prepared in 5 - 10 ml solutions and mixed with the $Ca(OH)_2$. This was then atmospherically dried overnight at 70 - 80°C, before being sieved. For most of the fly ash experiments, $Ca(OH)_2$:fly ash:$CaSO_3 \cdot 0.5H_2O$ was slurried at a weight ratio of 1:4:4. NaOH (10 mol% of $Ca(OH)_2$) was added to the slurry with the amount of water varied to manipulate the concentration of NaOH. The solids to water ratio varied from 1:1 to 1:4. A pyrex glass beaker was used to hold the slurry, and a teflon propeller stirrer at 350 rpm was used to agitate the slurry. A peristaltic pump added water to maintain a fairly constant water level. The slurrying time was 6 hours and the slurrying temperature was 65°C, unless otherwise specified. After slurrying, the sample was atmospherically dried overnight at 65°C. Additional reaction may occur during this drying process. The drying time was typically about 4 hours, but varied with the size of the sample.

Data Analysis

The SO_2, NO, and NO_x concentrations were continuously recorded and these concentration curves were integrated to determine solids conversion. Typical SO_2 and NO_x curves are given in the Appendix - Figures A.1 and A.2. The SO_2 removal for this run was 18.3 moles removed per 100 moles $Ca(OH)_2$, and the NO_x removal was 3.8 moles removed per 100 moles $Ca(OH)_2$.

SO_2/NO_x Mass Balance

The SO_2 concentration from the flame photometric SO_2 analyzer did not agree with the SO_2 concentration calculated from the flow meter controllers. A comparison of the two SO_2 values is given in Table 3.1. The SO_2 concentration from the analyzer was consistently lower than the flow meters, except for run #127 - 225

ppm SO_2. Similarly, the NO_x concentration from the analyzer is compared to that from the flow meter controllers in Table 3.2. The NO_x concentrations from the analyzer and controllers were fairly close and probably within the errors of both systems. Typically, the two NO_x values for most experiments were within 5 - 10%. If all the analyzers and controllers were functioning properly, the maximum error was 4% in the analyzers (at 60% of full range, where most runs were made) and 7% in the dilution system. The maximum error in the flow meter controllers (excluding the dilution system) was only 7%. Inaccuracy in the equipment can not explain these large discrepancies. The analyzers were calibrated about once a week with a known gas concentration, with little drift between calibrations. Two different cylinders of SO_2 span gas were used during this research, with no major differences in calibration. The SO_2 analyzer is sulfur specific and should be free of interferences from O_2, NO_x, and CO_2. The calibration of the flow meter controllers were checked twice and found to be fairly accurate and reproducible.

At 800 ppm NO_x, the amount of O_2 had a major effect on SO_2 reading on the analyzer. Listed below show the effects of changing O_2 concentration.

O_2 (%)	SO_2 Analyzer (ppm)
0.5	640
7	432
21	112

Without NO_x, O_2 had no effect on SO_2 concentration. This supports the possiblity that SO_2 reacts with NO_2 (see Results - NO_2 Removal Compared with NO Removal).

Table 4.1: SO$_2$ Concentration as Determined by
SO$_2$ Analyzer and Flow Meter Controllers
Gas Concentration Prior to Experiment; 92°C; 500 ppm NO$_x$
14 mol% H$_2$O; Gas Flow: 4.6 l/min - 7% O$_2$, 10% CO$_2$, 83% N$_2$

		SO$_2$ Concentration (ppm)		
Run	Experiment	Analyzer	Flow Controllers	% Difference
131	Base Case	584	1000	71
127	225 ppm SO$_2$	263	224	-15
129	No NO$_x$	488	761	56
136	No NO$_x$; N$_2$ only	560	782	40
152	0.5% O$_2$	632	957	51

Table 4.2: NO$_x$ Concentration as Determined by
NO$_x$ Analyzer and Flow Meter Controllers
Gas Concentration Prior to Experiment; 92°C; 500 ppm SO$_2$
14 mol% H$_2$O; Gas Flow: 4.6 l/min - 7% O$_2$, 10% CO$_2$, 83% N$_2$

		NO$_x$ Concentration (ppm)		
Run	Experiment	Analyzer	Flow Controllers	% Difference
124	Base Case	464	500	1
131	Base Case	496	565	-13
128	No SO$_2$	504	522	-12
141	1500 ppm SO$_2$	576	652	-13
152	0.5% O$_2$	560	500	11

Deposits in Lines

For lines which were heat traced, 316 stainless steel was used. Teflon was used for the rest of the lines. The stainless steel lines after NO and SO_2 injection and the stainless steel tee where SO_2 and NO were mixed before blending with the inert gases tended to become scaled with a greenish solid. A sign of buildup was an increase in pressure drop over the system. This 'creeping green' and corrosion by SO_2/NO_x have been documented by several researchers (Hermance et al., 1970; Haslbeck and Neal, 1985). At times green liquid would be seen in the reactor or in the water condenser. To minimize this problem, the problem lines and tees were frequently cleaned with soap water or replaced. The teflon lines did not have any problems. With only SO_2, there was no corrosion problem.

Chapter 5: Results

At the start of this research, an experimental apparatus designed to simulate bag filter conditions was available (Ruiz-Alsop and Rochelle, 1986). Modifications were necessary before SO_2/NO_x experiments could be conducted. Early experiments were performed with only SO_2 while modifications and improvements to the experimental apparatus were added (see Appendix - Modifications to Experimental Apparatus and Procedure). The results have been separated into two sections - SO_2 Removal (with no NO_x) and SO_2/NO_x Removal.

SO_2 Removal

Experiments in SO_2 removal were conducted in a sandbed reactor immersed in a water bath for temperature control, unless otherwise specified. The SO_2 concentration was 500 ppm (no NO_x) with 4.6 l/min of N_2 as the carrier gas. For O_2 experiments, blends of O_2 and N_2 were used. CO_2 was incorporated just before starting the SO_2/NO_x removal experiments. Most experiments were conducted at 66°C giving a relative humidity of 55%. The drying procedure for fly ash and portland cement slurries consisted of filtering the slurry followed by vacuum drying. After each experiment, the SO_2 concentration curve was integrated to determine the moles of SO_2 reacted in 1 hour. The solids were analyzed for $Ca(OH)_2$ and sulfite with acid/base and iodine/thiosulfate titrations. 'Removal' is defined as the moles of SO_2 removed per 100 moles of $Ca(OH)_2$.
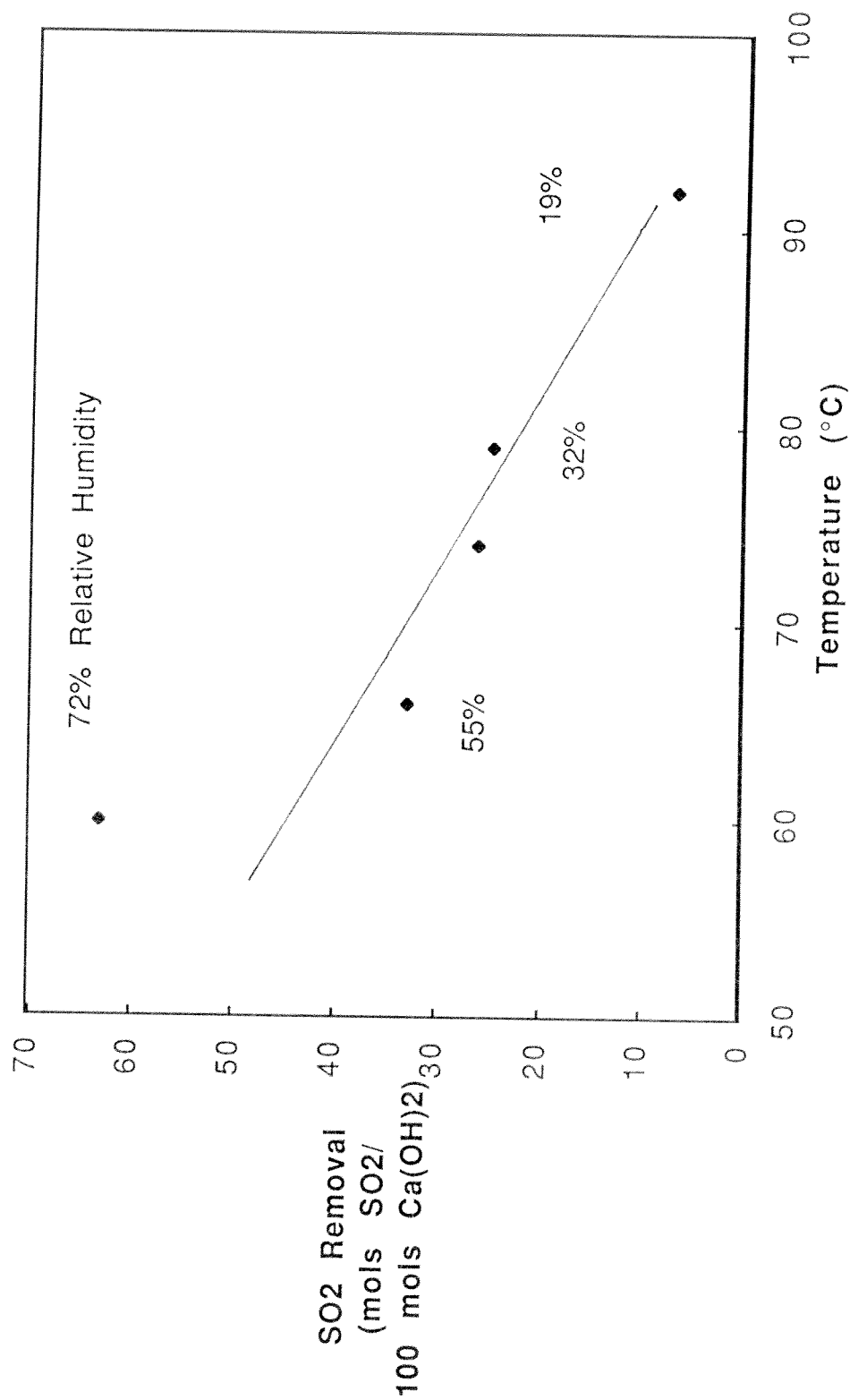
Figure 5.1: Effect of Temperature/Relative Humidity
1 $Ca(OH)_2$:16 Fly Ash:4 $CaSO_3$ - No NaOH; Slurried 6 hrs at 70°C;
SO_2 Removal After 1 Hour; 500 ppm SO_2; 4.6 l/min N_2

Effect of Temperature/Relative Humidity

$Ca(OH)_2$, Clinch River fly ash, and $CaSO_3 \cdot 0.5H_2O$ were slurried at a weight ratio of 1:16:4 for 6 hours and at 65°C. These experiments were conducted at temperatures from 60° to 92°C, with the reactor wrapped with heating tape for temperature control. The absolute humidity was held constant so that relative humidity varied from 72% to 19%. Figure 5.1 gives the results of these experiments. At lower temperatures/higher relative humidities, the removal increased. This result agreed with previous work by Ruiz-Alsop and Rochelle (1986); Acurex (1985); Klingspor et al., (1984). Jozewicz and Rochelle (1985) slurried $Ca(OH)_2$, San Miguel fly ash, and $CaSO_3 \cdot 0.5H_2O$ at a weight ratio of 1:16:4 for 6 hours at 65°C. At 66°C, SO_2 removal was 74 (mols SO2 removed per 100 moles of $Ca(OH)_2$) compared with 33 using Clinch River fly ash.

Alternative Reagents

Several slaked limes, hydrated limes, and portland cements were tested for SO_2 removal. Figure 5.2 gives the correlation of SO_2 removal with the surface area of these limes.

Three types (I,II, and III) of portland cement were tested, with the results given in Table 5.1. The portland cement was hydrated by slurrying in water before being reacted with SO_2. The slurrying conditions were varied from 6 to 50 hours at either room temperature or 65°C. SO_2 removal based on gas phase material balance was consistently lower than that obtained from solids analysis, acid/base and iodometric titrations. Because the portland cement contained non-alkaline
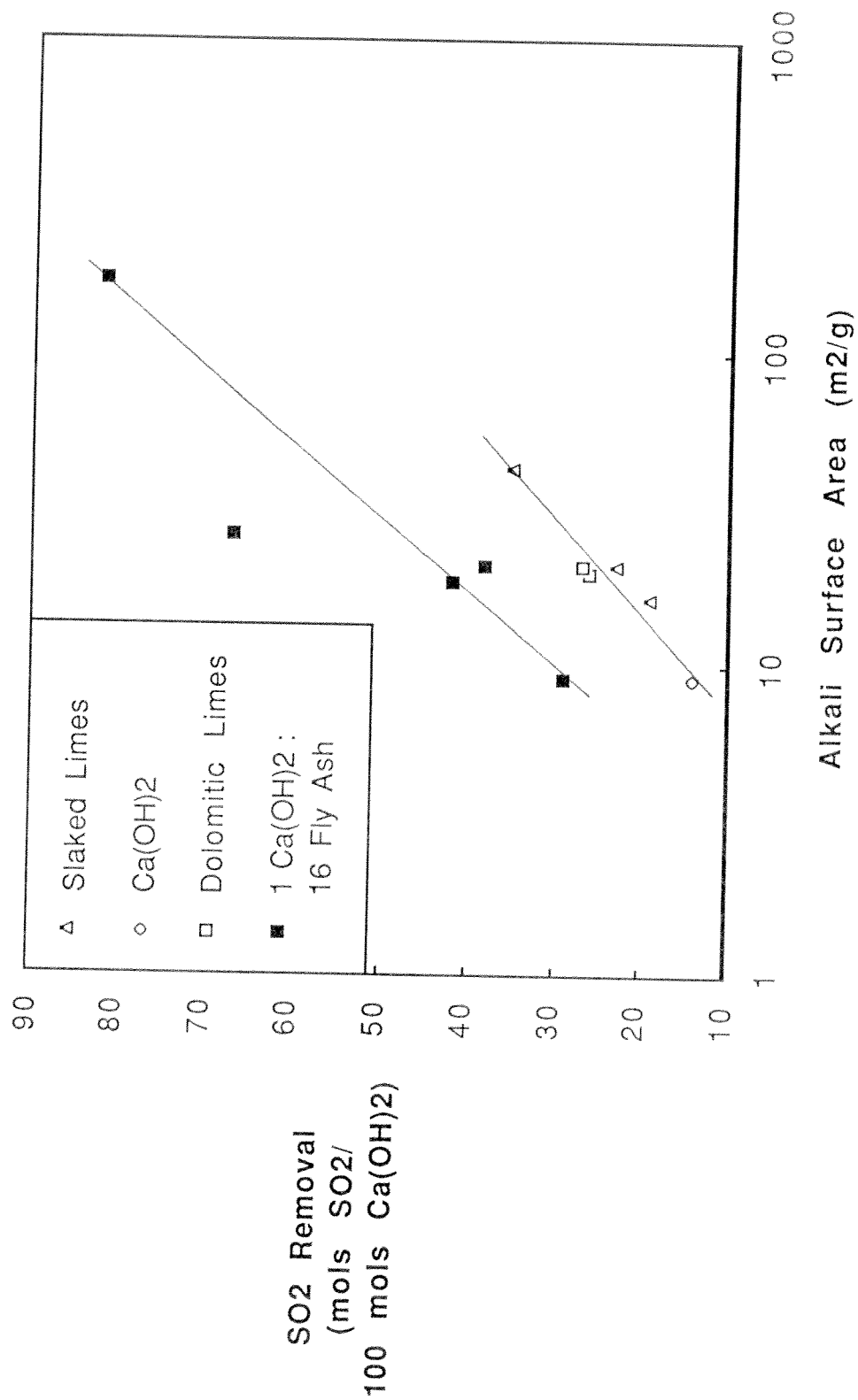
Figure 5.2: Effect of Surface Area
SO$_2$ Removal After 1 Hour; 66°C; 55% RH; 500 ppm SO$_2$; 4.6 l/min N$_2$

Table 5.1: Portland Cement

Samples: Filtered and Vacuum Dried
1 g Reagent ; 66°C; 500 ppm SO_2; 4.6 l/min N_2
Tricalcium Silicate Content: I - 68%, II - 51%, III - 71%

Portland Cement	Slurrying Conditions		SO_2 Removal After 1 Hour (mols SO_2/100 mols$Ca(OH)_2$)	
	Time (hr)	T(°C)	Solids Analysis	Gas Analysis
I	6	26	25	18
I	6	68	35	28
I	16	65	35	18
I	49	25	43	29
I	50	65	43	22
II	6	65	29	14
III	6	66	44	33
III	16	65	44	27

compounds, the initial charge of alkali was based upon the chemical analysis of the cement which was provided by the manufacturer. The chemical analysis of the three types of cement is located in the Appendix. The tricalcium silicate content was 68% for type I, 51% for type II, and 71% for type III. The CaO content of the three cements varied from 63 to 66%. Type III was the most reactive with type II being the least reactive. The reactivity of the cement is a function of the tricalcium silicate content. Generally with increasing slurrying time and temperature, the reactivity of the solid increased since the hydration was greater. At 6 and 16 hours both type I and III had similar removals. According to Bye (1983), a step increase in hydration occurs at 25 - 30 hours. Type I portland cement was slurried for two days at 25° and 65°C. These samples yielded higher removals, but were equivalent. All hydration may have occurred after 48 hours, thus the slurrying temperature had no effect.

Effect of Surface Area

The surface areas of several alkali samples and San Miguel fly ash/$Ca(OH)_2$ samples were measured by nitrogen absorption with an Accusorb Model 2100E Physical Adsorption Analyzer. The fly ash/$Ca(OH)_2$ samples were prepared and tested by Jozewicz and Rochelle (1985). The alkali surface area for the fly ash samples was calculated from the BET surface area by assuming the surface area of the fly ash was constant. Table 5.2 gives the result of these measurements and calculations. The dolomitic limes were tested by Ruiz-Alsop and Rochelle (1986) and were obtained with BET surface area measurements from Dr. John Chang of the Acurex Corporation. Several slaked limes with determined surface areas were obtained and were reacted with SO_2 at similar conditions: 66°C, 55% relative

Table 5.2: Surface Area of Slurried $Ca(OH)_2$:Fly Ash Samples
Fly Ash Samples Prepared and Tested by Jozewicz and Rochelle (1985)
0.5 g $Ca(OH)_2$: 8.15 g San Miguel Fly Ash; 1 Solids : 15 Water
Removal After 1 Hour; 66°C; Relative Humidity = 54%
500 ppm SO_2; 4.6 l/min N_2; 14 mol% H_2O

Slurrying Conditions		SO_2 Removal (mols SO_2 removed	BET Surface	Lime Surface
T (°C)	Time(hr)	100 mols $Ca(OH)_2$)	Area (m^2/g)	Area(m^2/g)
25	6	29	0.85	9.2*
92	2	42	1.4	18.6
25	24	38	1.55	21.1
65	6	67	1.87	26.5
92	6	82	10.5	173.3

* Fly ash surface area was assumed to be constant before and after slurrying. The fly ash surface area was estimated to be 0.33 m^2/g, by assuming the BET surface area, in 25°C and 6 hour slurry, was equal to the sum of the flyash and $Ca(OH)_2$ surface areas.
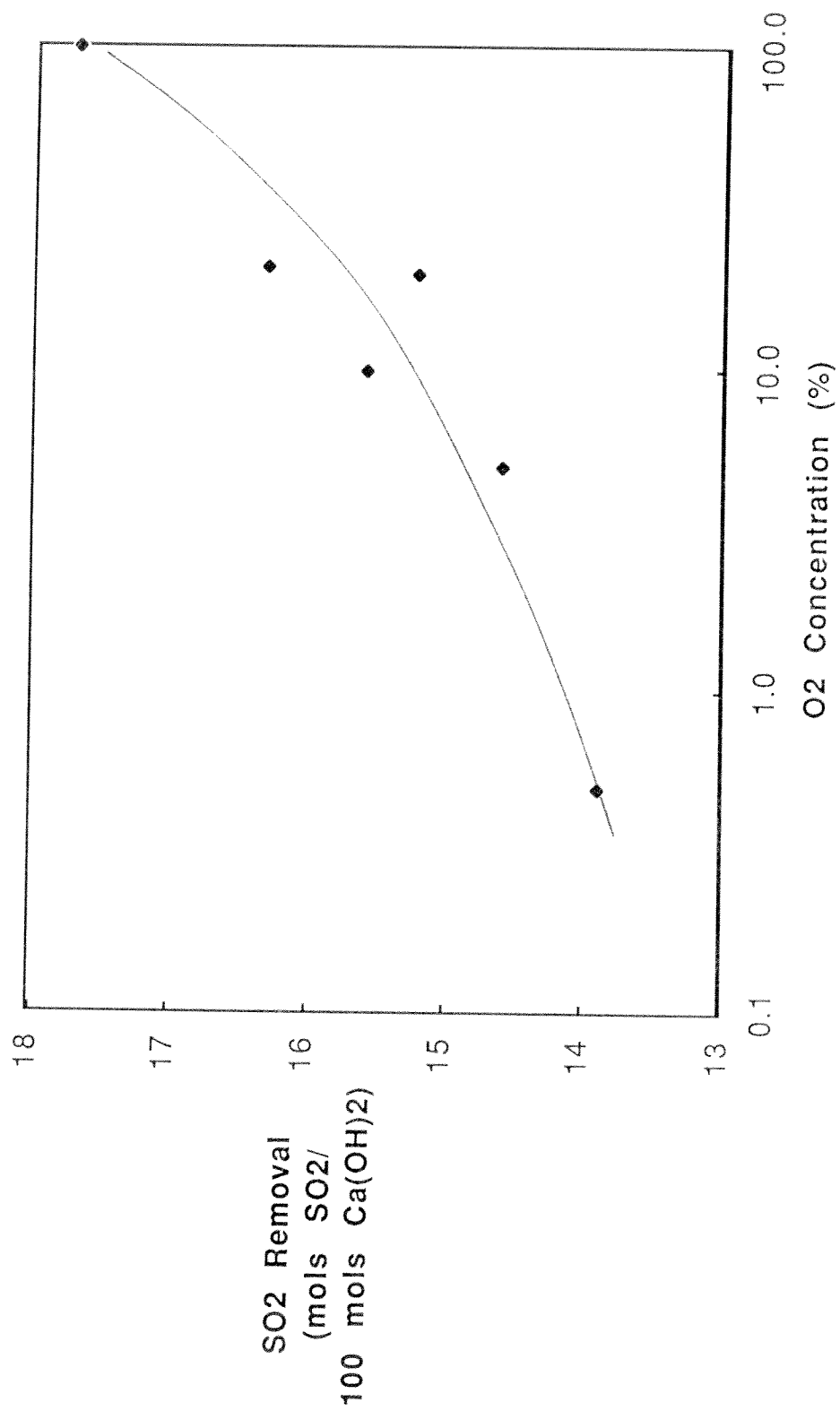
Figure 5.3: Effect of O_2 Concentration
SO_2 Removal After 1 Hour; 1 g $Ca(OH)_2$; 66°C; 55% RH; 500 ppm SO_2
14 mol% H_2O; Gas Flow Flow - 4.6 l/min

humidity, and 500 ppm SO_2. The alkali surface area and removal are plotted in Figure 5.2. For both curves, the removal increased with increasing surface area. While several of the slaked limes and fly ash samples had equivalent alkali surface areas, the fly ash samples were more reactive. Therefore, while reactivity was a function of surface area, it was also dependent upon other factors. The best slaked lime tested had a surface area of 43 m^2/g. Slurrying $Ca(OH)_2$ with 16 parts fly ash at 92°C for 6 hours yielded an alkali product with a surface area of 173 m^2/g of equivalent $Ca(OH)_2$.

Effect of O_2 and CO_2

To simulate flue gas more closely, O_2 and CO_2 were added. Runs were conducted at O_2 concentrations from 0.5 to 100% to examine the effect of O_2. The results of these runs are plotted in Figure 5.3. Removal increased slightly with increasing O_2 concentration. This beneficial effect could be expected since some of the calcium sulfite product would be oxidized to sulfate. With 10% CO_2, no effect could be seen on SO_2 removal. However, in the prehumidification step, CO_2 was not used to insure that there was no reaction with the $Ca(OH)_2$. In the O_2 experiments, an O_2/N_2 mixture was used in prehumidification.

SO_2/NO_x Removal

Upon completing modifications to the experimental apparatus, simultaneous SO_2/NO_x experiments were conducted. The experimental procedure is discussed in greater detail in Chapter 4 - Experimental Apparatus and Procedure, with some minor modifications listed in Appendix - Modifications to Experimental

Apparatus and Procedure. For most experiments, the SO_2 and NO_x concentrations were 500 ppm. The carrier gas flow rate was 4.6 l/min with 7% O_2, 10% CO_2, and the balance N_2. The exposure time to the synthetic flue gas was 1 hour. The temperature was varied from 66° to 125°C giving relative humidities from 55% to 6%. The water concentration was about 14 mol%. Fly ash slurries were atmospherically dried to avoid $Ca(OH)_2$ and NaOH losses in the filtrate. The slurrying conditions were 6 hours and 65°C, unless otherwise specified. Solids analysis was limited to some work with the ion chromatograph. Solids analysis by acid/base and iodometric titrations was not used since most of the fly ash experiments included $CaSO_3$. 'Removal' is defined as moles SO_2 or NO_x removed per 100 moles of $Ca(OH)_2$.

Effect of Additives

Na_2SO_3 and NaOH were tested as additives to $Ca(OH)_2$ for SO_2/NO_x removal. The results of these experiments are plotted in Figures 5.4 (SO_2) and 5.5 (NO_x). Both Na_2SO_3 and NaOH improved SO_2 removal by similar amounts, however Na_2SO_3 contains twice as much sodium as NaOH. Some additional removal can be expected from the NaOH itself. NaOH enhanced NO_x removal by several fold in some instances, while Na_2SO_3 had no beneficial effect. Also plotted is removal for a $Ca(OH)_2$:fly ash:$CaSO_3 \cdot 0.5H_2O$ sample at a weight ratio of 1:4:4. For SO_2 removal this fly ash sample was more reactive than $Ca(OH)_2$ with either the NaOH or Na_2SO_3 as an additive. However for NO_x the $Ca(OH)_2$ with 10% NaOH yielded higher removal. NaOH was an effective additive for NO_x removal.
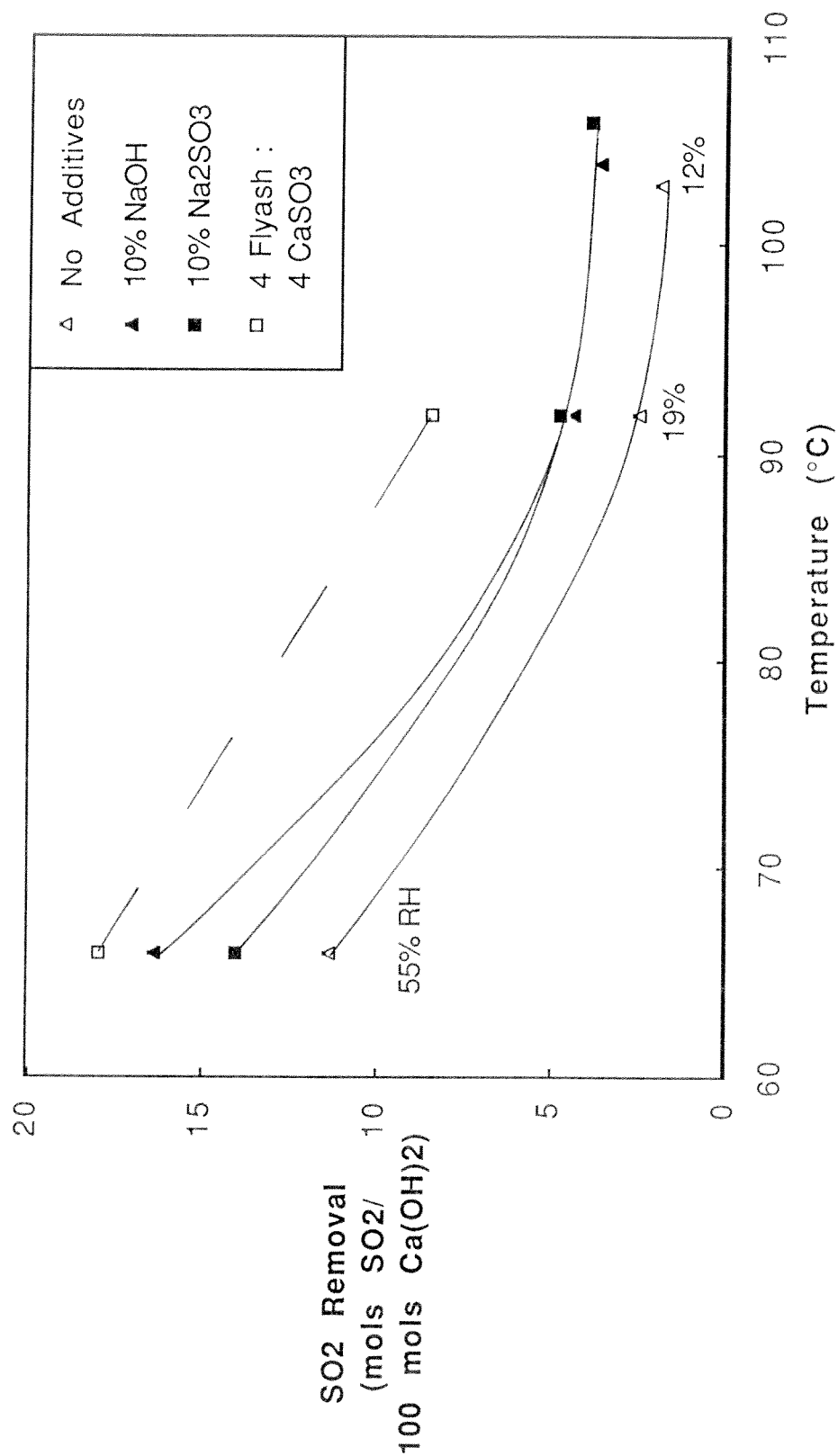
Figure 5.4: Effect of Additives on SO$_2$ Removal
1 g Ca(OH)$_2$ + 10 mol% Additive; Removal After 1 Hour; 500 ppm SO$_2$; 500 ppm NO$_x$;
Gas Flow Flow: 4.6 l/min - 7% O$_2$, 10% CO$_2$; 83% N$_2$

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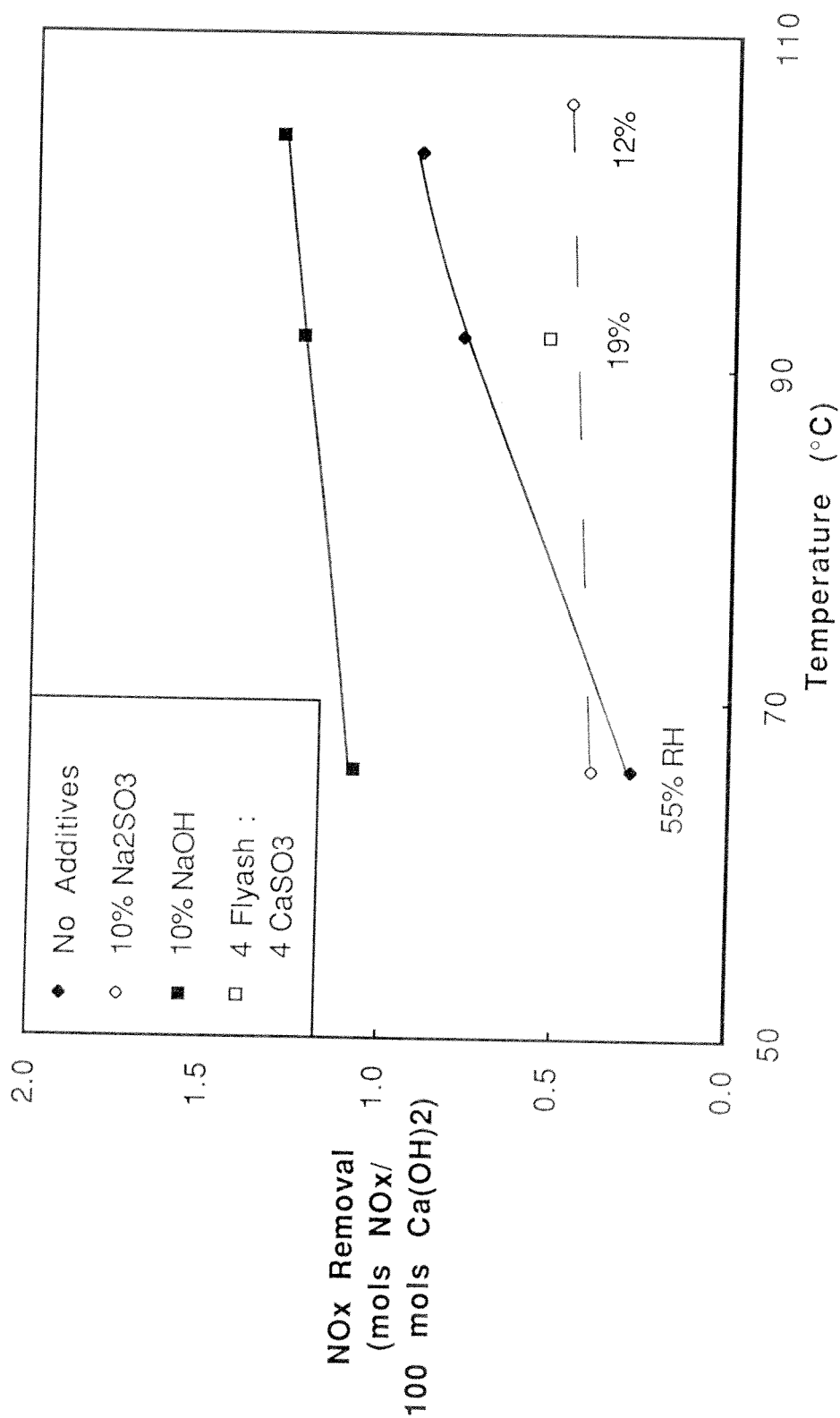
Figure 5.5: Effect of Additives on NO$_x$ Removal
1 g Ca(OH)$_2$ + 10 mol% Additive; Removal After 1 Hour; 500 ppm SO$_2$; 500 ppm NO$_x$; 14 mol% H$_2$O; Gas Flow Flow: 4.6 l/min - 7% O$_2$, 10% CO$_2$; 83% N$_2$

Effect of Temperature/Relative Humidity

The temperature was varied from 66° to 105°C for these additive runs to find an optimum temperature for SO_2/NO_x removal. The absolute humidity was held constant at 14 mol% so that relative humidity varied from 55% to 6%. Figures 5.4 (SO_2) and 5.5 (NO_x) illustrate the results of these experiments. SO_2 removal decreased with increasing temperature while NO_x removal increased. In Figures 5.6 (SO_2) and 5.7 (NO_x), these trends are also evident. In runs up to 125°C, NO_x removal continued to increase. At 66°C, SO_2 removal was from one to two orders of magnitude faster than NO_x removal. At 110°C, SO_2 removal was only 2 - 5 faster. No optimum temperature window could be found for SO_2/NO_x removal. Niro reported that 100° - 110°C was optimum for both SO_2 and NO_x removal (Felsvang et al., 1983).

Effects of NaOH

Fly ash dissolution into water was suspected to be the rate limiting step during fly ash slurrying, and NaOH addition was expected to improve fly ash dissolution. 10 mol% (relative to $Ca(OH)_2$) NaOH was added, with the amount of water varied to examine the effect of NaOH concentration. The slurrying conditions were 65°C and 6 hours. The results of these runs are shown in Figures 5.6 (SO_2) and 5.7 (NO_x). In both plots, a large increase in removal was seen from 0.03 to 0.08M NaOH (moles NaOH per liter of water). An effort was made to duplicate this result at 0.08M NaOH. Two similar samples were prepared, differing only in slurrying time and drying time from the original. The original was slurried for 6 hours, and the drying time in the atmospheric oven was 30 hours. The first solid was
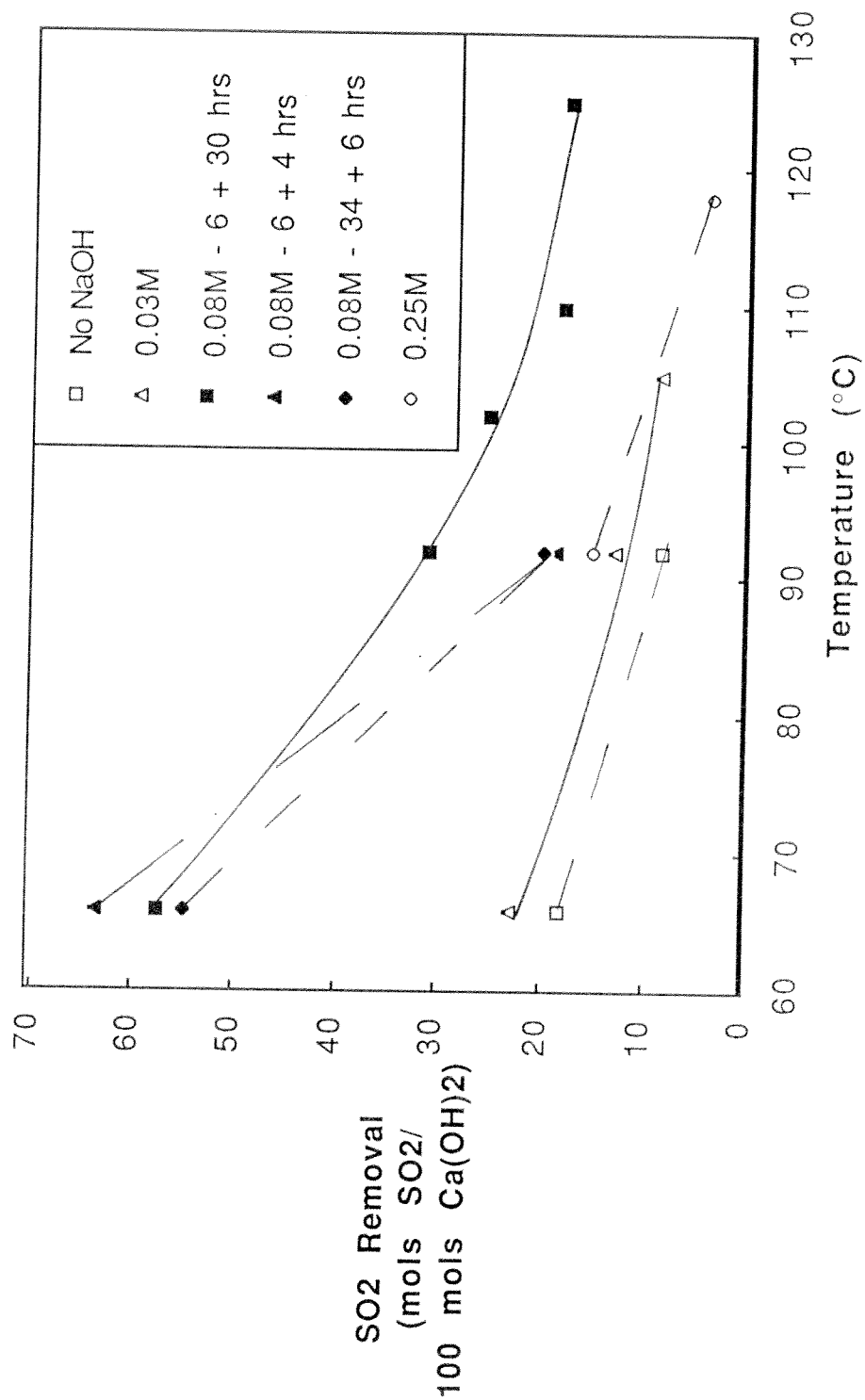
Figure 5.6: Effect of NaOH Concentration on SO_2 Removal
1 $Ca(OH)_2$:4 Fly Ash:4 $CaSO_3$ - 10 mol% NaOH; Removal After 1 Hour; 500 ppm SO_2; 500 ppm NO_x; 14 mol% H_2O; Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2; 83% N_2
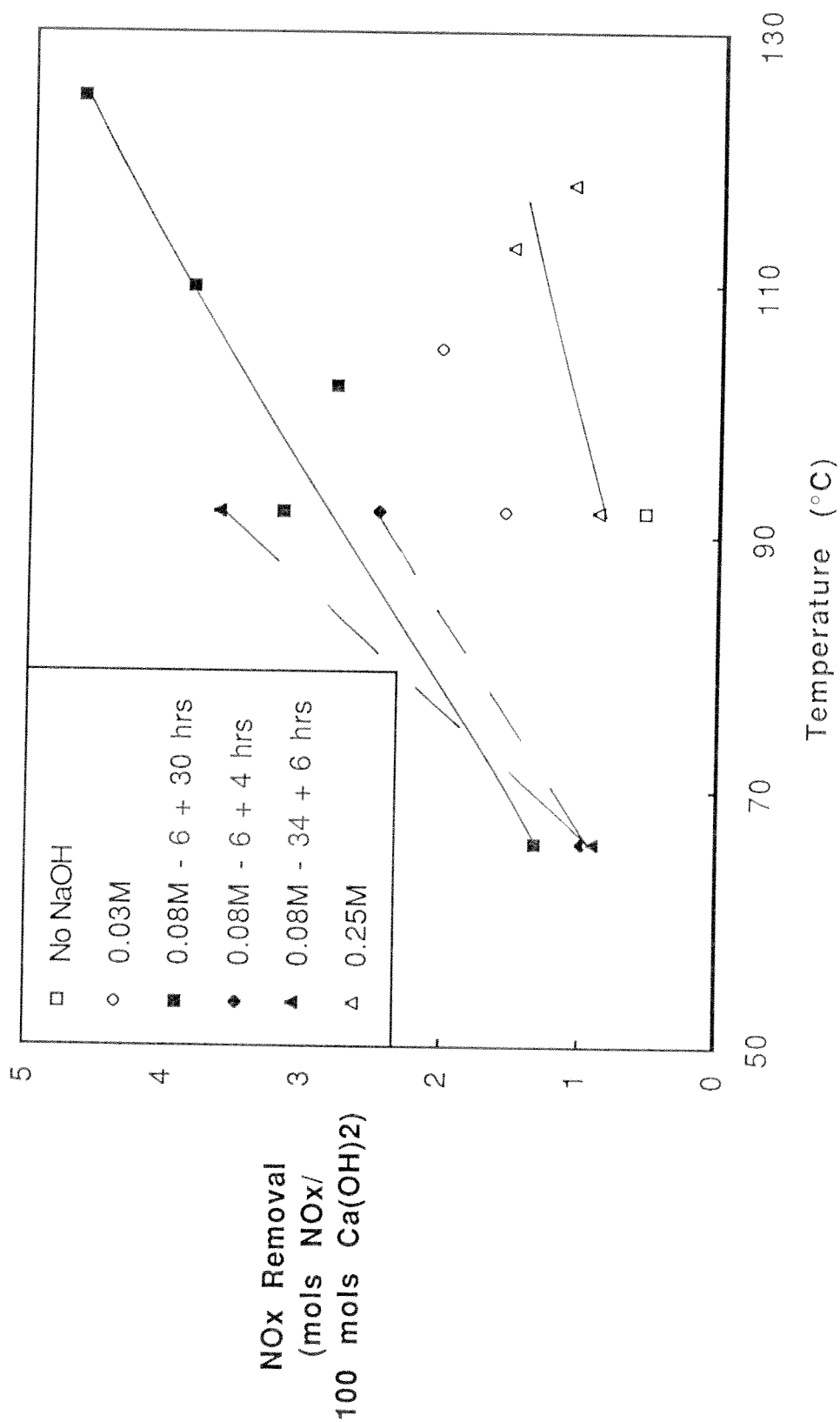
Figure 5.7: Effect of NaOH Concentration on NO_x Removal
1 $Ca(OH)_2$:4 Fly Ash:4 $CaSO_3$ - 10 mol% NaOH; Removal After 1 Hour; 500 ppm SO_2; 500 ppm NO_x; 14 mol% H_2O; Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2; 83% N_2

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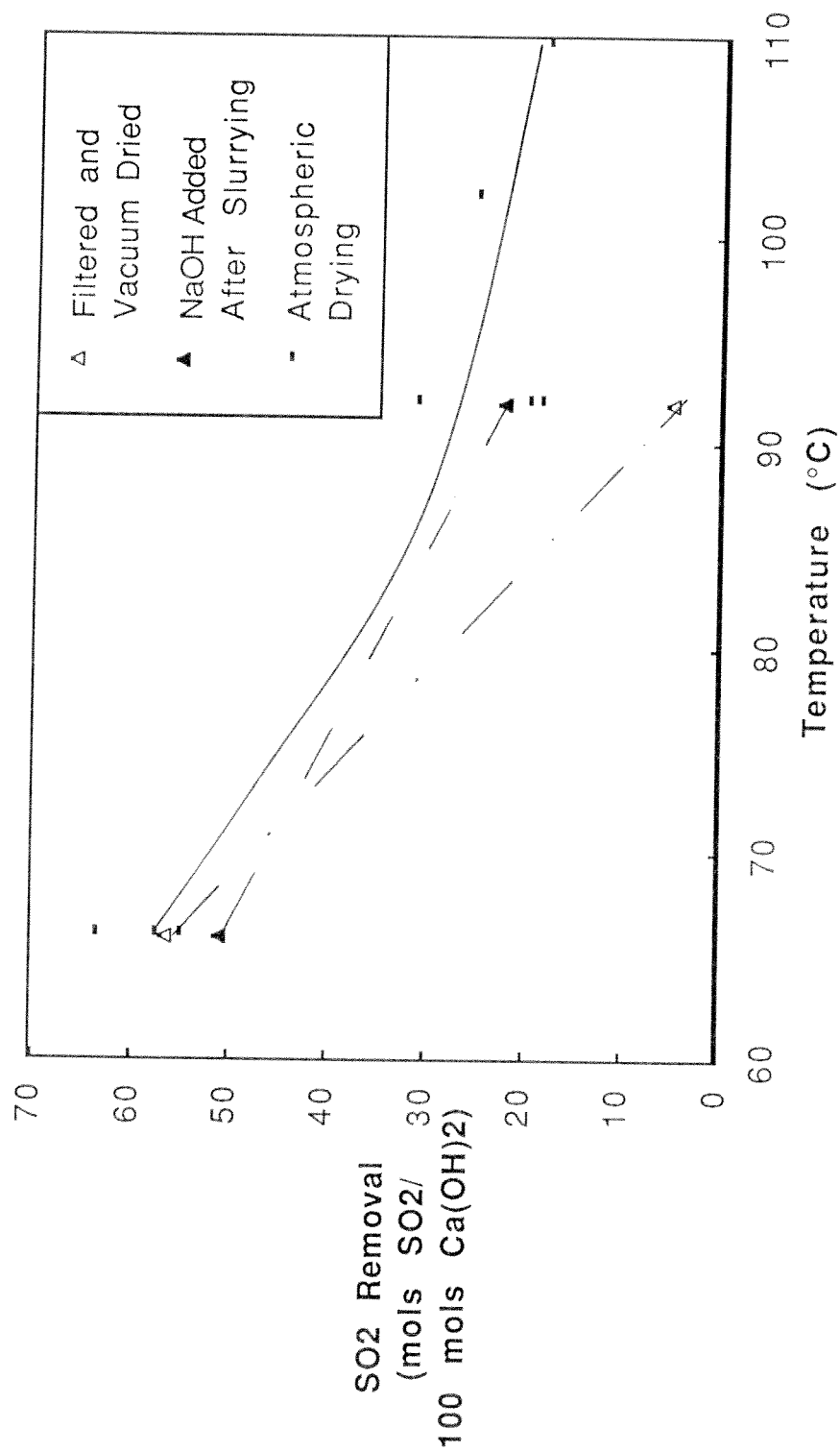
Figure 5.8: NaOH: Effect on Fly Ash Dissolution and Effect as an Additive - SO_2 Removal - After 1 Hour; 1 $Ca(OH)_2$:4 Fly Ash:4 $CaSO_3$ - 10 mol% NaOH (0.08M); 500 ppm SO_2; 500 ppm NO_x; 14 mol% H_2O; Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2; 83% N_2

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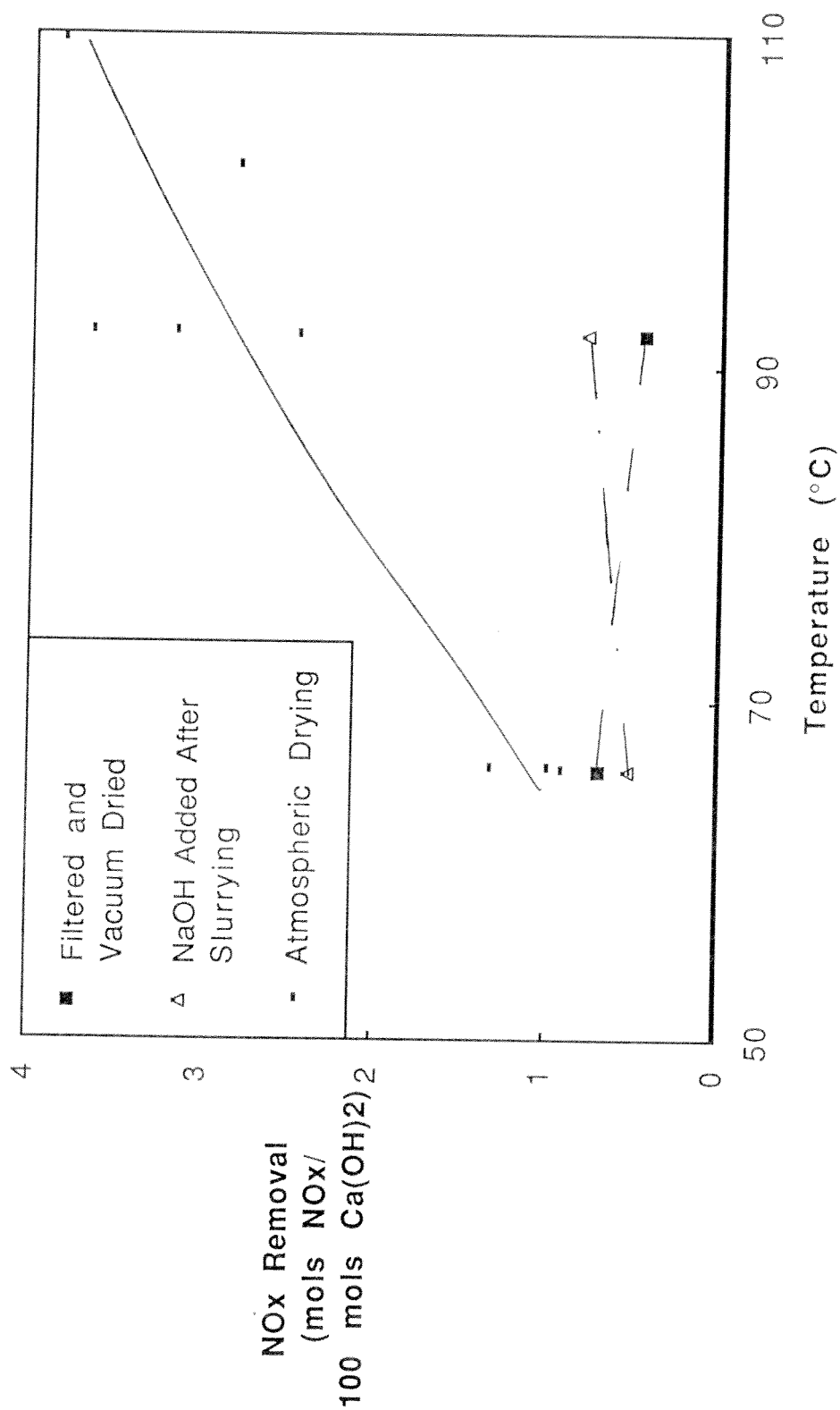
Figure 5.9: NaOH: Effect on Fly Ash Dissolution and Effect as an Additive - NO_x Removal - After 1 Hour; 1 $Ca(OH)_2$:4 Fly Ash:4 $CaSO_3$ - 10 mol% NaOH (0.08M); 500 ppm SO_2; 500 ppm NO_x; 14 mol% H_2O; Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2; 83% N_2

slurried for 6 hours with 4 hours of drying time. The second sample was slurried for 30 hours with 4 hours of drying time. While both 'duplicates' were less reactive than the original, they were still more reactive than 0.03M NaOH. From 0.08 to 0.25M there was a decrease in reactivity toward both SO_2 and NO_x. At 0.25M the slurry was a paste, and the lack of water and mixing may have limited fly ash dissolution. This sample was hand-mixed, capped, and placed in an oven for 6 hours at 65°C before being dried. NaOH concentration is important factor in the reactivity of the slurried solid.

To determine the additional removal from the effect of NaOH on fly ash dissolution and from the deliquescent effect of NaOH, a comparable sample was slurried with NaOH and then vacuum filtered and dried so that most of the NaOH was lost. Another sample was slurried without NaOH and, after being dried, 10 mol% NaOH was added. The results of these experiments are given in Figures 5.8 (SO_2) and 5.9 (NO_x). At 66°C SO_2 removal was slightly less for both solids; so NaOH did improve fly ash dissolution and also had a deliquescent effect. For the filtered solid, SO_2 removal at 92°C was substantially reduced. The effect of NaOH at higher temperatures/lower relative humidities was quite evident. NO_x removal for both solids was much less. At 92° and 110°C, NO_x removals for $Ca(OH)_2$ and $CaSO_3$ slurried with 0.08M NaOH were 0.3 and 0.2 (moles NO_x removed per 100 moles $Ca(OH)_2$). At 92° and 110°C, NO_x removal for $Ca(OH)_2$ with 10% NaOH was 1.2 and 1.3 (see Figure 5.11). NaOH plays an important role in NO_x removal, probably as a deliquescent, as an improvement to fly ash dissolution, and as a possible catalyst.

Effect of CaSO$_3$

Ca(OH)$_2$ and fly ash were slurried at a weight ratio of 1:4 with 10 mol% NaOH (0.08M) to examine the effect of CaSO$_3$·0.5H$_2$O. These results are given in Figures 5.10 (SO$_2$) and 5.11 (NO$_x$). Without CaSO$_3$ in the Ca(OH)$_2$ and fly ash slurry, SO$_2$ removal remained unchanged. However, NO$_x$ removal for this Ca(OH)$_2$/fly ash sample was substantially reduced. CaSO$_3$ improved the reactivity of the slurried solids toward NO$_x$. However, the Ca(OH)$_2$/CaSO$_3$ slurry was not reactive toward NO$_x$, so CaSO$_3$ alone did not enhance NO$_x$ removal. The absence of CaSO$_3$ had little effect on the solids reactivity toward SO$_2$. Jozewicz and Rochelle (1985) found that Ca(OH)$_2$:fly ash:CaSO$_3$ slurried at a weight ratio of 1:16:4 was slightly more reactive to SO$_2$ than Ca(OH)$_2$:fly ash at a weight ratio of 1:20.

Effects of Fly Ash

Ca(OH)$_2$ and CaSO$_3$·0.5H$_2$O at a weight ratio of 1:4 were slurried with 10% NaOH (0.08M) for 6 hours and at 65°C to examine the effect of fly ash. The results of these experiments are shown in Figures 5.10 (SO$_2$) and 5.11 (NO$_x$). Without fly ash both SO$_2$ and NO$_x$ removal were low. Thus fly ash does play an important role in enhancing the Ca(OH)$_2$ reactivity. The removal for Ca(OH)$_2$ with 10% NaOH is also plotted. At 92° and 110°C, NO$_x$ removal for the Ca(OH)$_2$/CaSO$_3$ sample was even less than Ca(OH)$_2$ with 10% NaOH (See Effects of NaOH). The NaOH deliquescent effect which was more important at higher temperatures may be less effective since the NaOH precipitated onto all the Ca(OH)$_2$ and CaSO$_3$·0.5H$_2$O. NO$_x$ removal tended to decrease with increasing temperature, which was the opposite of the other samples tested.
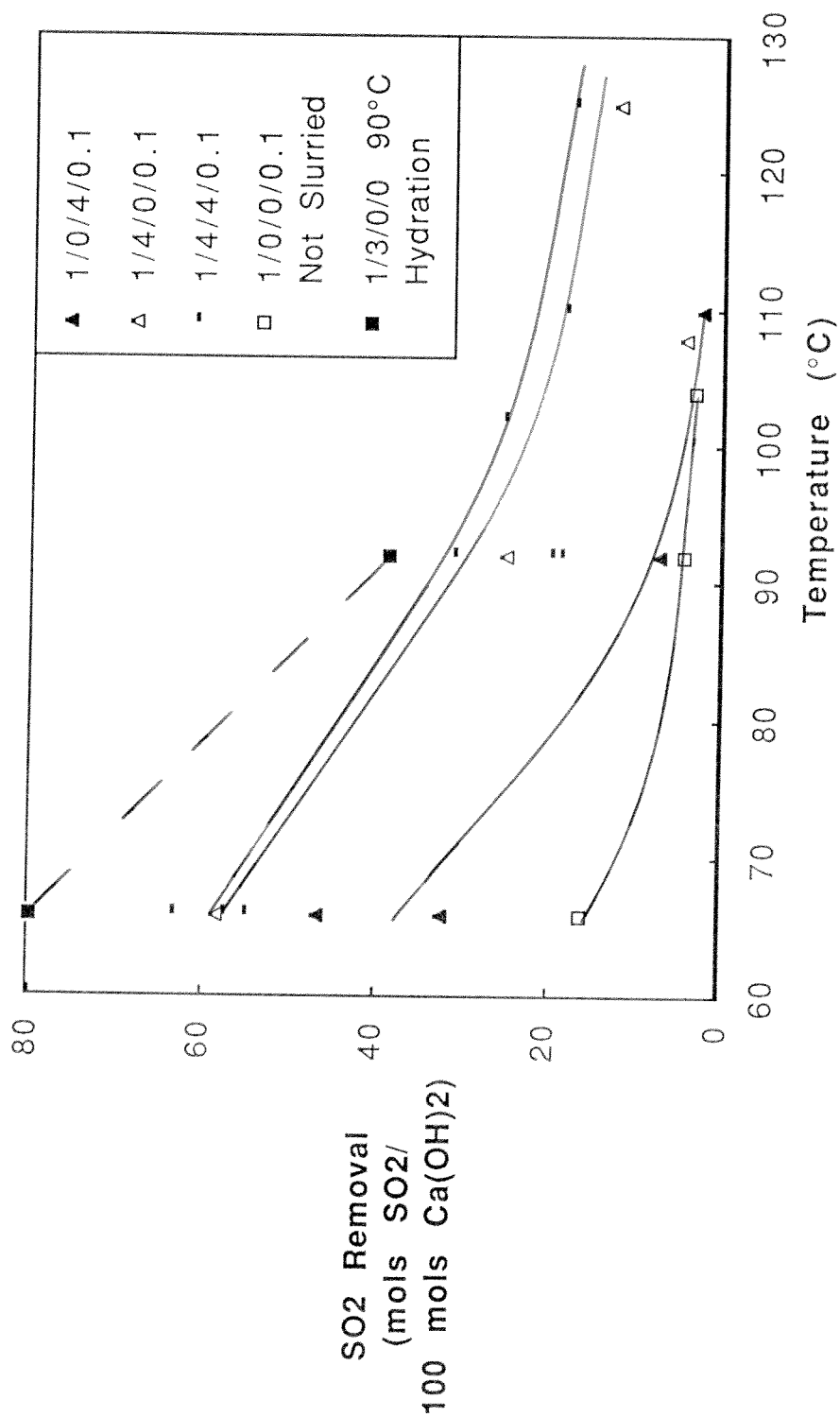
Figure 5.10: Effects of Fly Ash and CaSO$_3$ on SO$_2$ Removal
1/4/4/0.1 = 1 Ca(OH)$_2$:4 Fly Ash: 4 CaSO$_3$: 10 mol% NaOH (0.08M); Removal After 1 Hour; 500 ppm SO$_2$; 500 ppm NO$_x$; 14 mol% H$_2$O; Gas Flow: 4.6 l/min - 7% O$_2$, 10% CO$_2$; 83% N$_2$
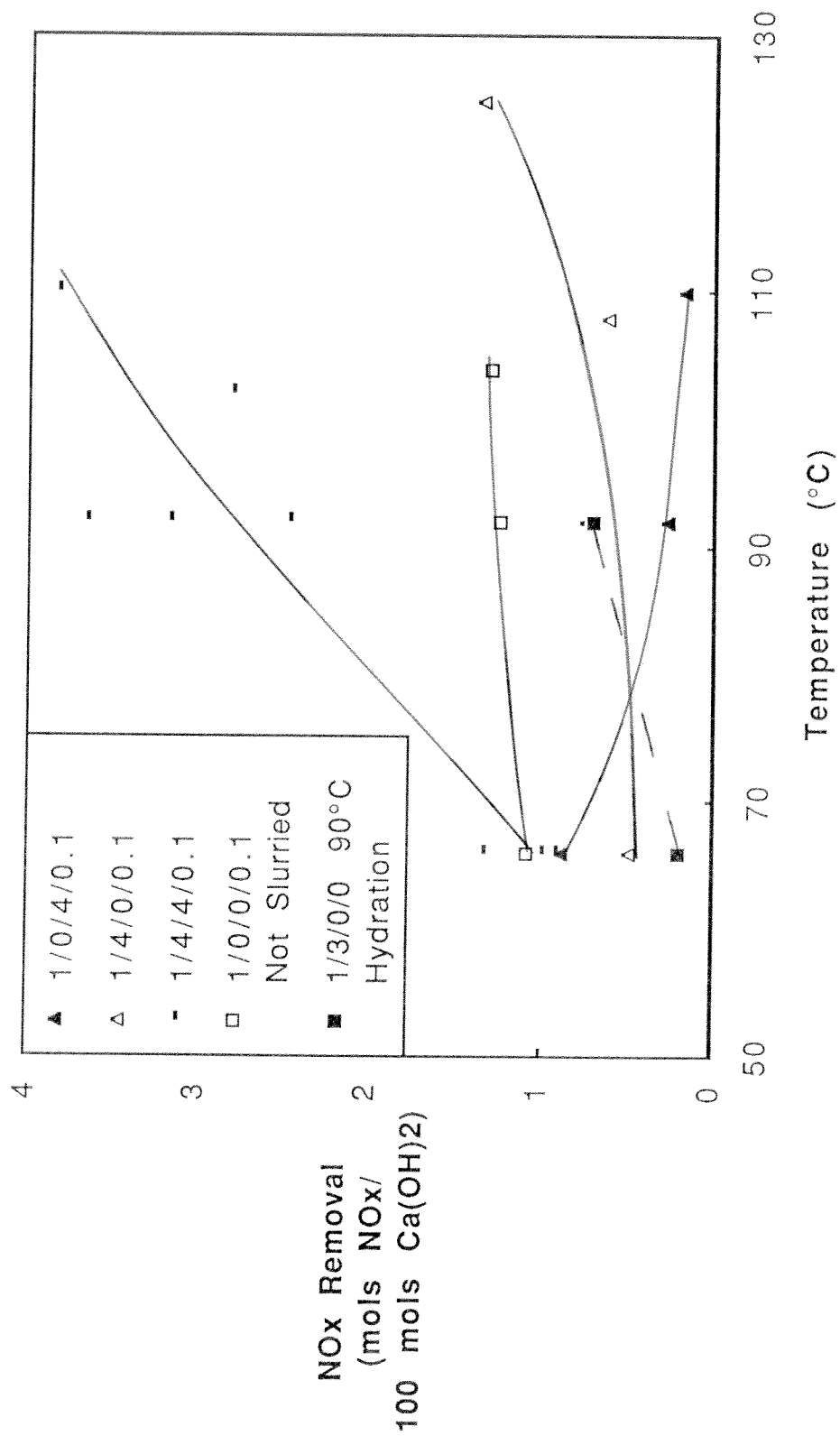
Figure 5.11: Effects of Fly Ash and CaSO₃ on NOₓ Removal
$1/4/4/0.1 = 1$ Ca(OH)₂:4 Fly Ash: 4 CaSO₃: 10 mol% NaOH (0.08M); Removal After 1 Hour; 500 ppm SO₂; 500 ppm NOₓ; 14 mol% H₂O; Gas Flow: 4.6 l/min - 7% O₂, 10% CO₂; 83% N₂

A $Ca(OH)_2$:Clinch River fly ash sample which had been tested to be very reactive to SO_2 was obtained from Dr. Wojciech Jozewicz of the Acurex Corporation. The $Ca(OH)_2$:fly ash sample at a weight ratio of 1:3 was hydrated at 90°C for 4 hours. The results of these runs are given in Figures 5.10 (SO_2) and 5.11 (NO_x). The Clinch River fly ash used in this study at the University of Texas was from the same batch as the Clinch River fly ash used at Acurex. The SO_2 removal for this sample which was hydrated at 90°C was improved over 1 $Ca(OH)_2$:4 Clinch River fly ash with 10% NaOH slurried at 65°C and for 6 hours. NO_x removal for the Acurex sample was 0.2 and 0.7 less than NO_x removal for $Ca(OH)_2$:Clinch River fly ash with 10% NaOH slurried at 65°C. Because NaOH was included with one of the solids, NO_x removals are difficult to compare. However, at higher hydration temperature, the solids were substantially more reactive toward SO_2.

Effect of NO_x on SO_2 Removal

Several experiments were conducted at 0 and 500 ppm NO_x to examine the effect of NO_x on SO_2 removal. Table 5.3 gives the results of these runs. In the three of the runs, there was little effect on SO_2 removal. For the reactive sample of $Ca(OH)_2$:fly ash:$CaSO_3 \cdot 0.5H_2O$ with 0.08M NaOH, SO_2 removal was substantially better without NO_x present. At 66 and 92°C, SO_2 removal without NO_x was 68 and 47, compared with 58 and 31 with NO_x. NO_x removal for both of these runs was fairly high, 1.3 and 3.1. It is possible that diffusion through the nitrite product layer could become the rate limiting step. NO_x had little effect on SO_2 removal at low NO_x removal. For more reactive solids with higher NO_x removals, NO_x had a negative effect on SO_2 removal.

Table 5.3: Effect of NO_x on SO_2 Removal
SO_2 Removal After 1 Hour; 14 mol% H_2O; 500 ppm SO_2
Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2, 83% N_2

	SO_2 Removal (mols SO_2/100 mols $Ca(OH)_2$)	
Experiment	Without NO_x	500 ppm NO_x
$Ca(OH)_2$; 66°C	11.3	11.2
$Ca(OH)_2$; 92°C	7.6	8.2
$Ca(OH)_2$ + 10% NaOH; 66°	17.3	16.3
$Ca(OH)_2$:Fly Ash:$CaSO_3$ = 1:4:4 0.08M NaOH (original); 66°C	67.9	57.5
$Ca(OH)_2$:Fly Ash:$CaSO_3$ = 1:4:4 0.08M NaOH (original); 92°C	46.6	31.2

Table 5.4: Effects of SO_2 on NO_x Removal
NO_x Removal After 1 Hour; 14 mol% H_2O; 500 ppm NO_x
Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2, 83% N_2

1 $Ca(OH)_2$: 4 Fly Ash: 4 $CaSO_3$
0.08M NaOH (original); 92°C

ppm SO_2	NO_x Removal (mols NO_x/100 mols $Ca(OH)_2$)
0	1.6
200	1.1
500	3.2
1500	4.1

1 $Ca(OH)_2$: 4 Fly Ash: 4 $CaSO_3$
0.03M NaOH; 92°C

250	1.1
500	1.6

$Ca(OH)_2$; 66°C

0	1.4
500	0.3

Effect of SO_2 Concentration on NO_x Removal

Three different solids were used to test the effect of SO_2 concentration on NO_x removal. The SO_2 concentration was varied from 0 to 1500 ppm. A summary of these experiments is given in Table 5.4. For 1 $Ca(OH)_2$:4 fly ash:4 $CaSO_3$ at 0.08M NaOH, NO_x removal without SO_2 present was 1.6, which was actually higher than NO_x removal at 200 ppm SO_2, 1.1. Increasing the SO_2 concentration to 500 ppm, NO_x removal improved to 3.2. At 1500 ppm, NO_x removal improved further to 4.1. The reason for higher NO_x removal with no SO_2 present may be because the SO_2 competes with the NO_x for more reactive pore sites, and only the presence of $CaSO_3$ may be necessary for NO_x removal. The $Ca(OH)_2$ run without SO_2 is questionable. For $Ca(OH)_2$ at 66°C, no NO_x removal was obtained with runs using span gas mixtures (250 ppm NO_x and no SO_2). NO_x removal increased with increasing SO_2 concentration. NO_x removal was obtained without SO_2 present, but $CaSO_3$ was present in the reagent. Felsvang et al., (1983) found that SO_2 was necessary for NO_x removal, and that NO_x removal increased with increasing SO_2 concentrations.

Effect of O_2 Concentration on SO_2/NO_x Removal

Experiments were performed from 0.5 to 19.9% O_2 to investigate the effects of O_2 concentration. The results of these runs are given in Table 5.5. With common purity nitrogen - about 0.5% O_2, SO_2 and NO_x removal were only 21.8 and 0.5, respectively. At 7% O_2, SO_2 and NO_x removal improved to 36.2 and 3.2, respectively. The results at 19.9% O_2 (air and 10% CO_2) are puzzling. The experiment was run twice, with varying results. In both runs either SO_2 or NO_x

Table 5.5: Effect of O_2 on SO_2/NO_x Removal
Removal After 1 Hour; T = 92°C; 500 ppm SO_2; 500 ppm NO_x
14 mol% H_2O; Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2, 83% N_2
1 $Ca(OH)_2$: 4 Fly Ash: 4 $CaSO_3$; 0.08M NaOH - 10 mol%

% Oxygen	SO_2 Removal	NO_x Removal
0.5	21.8	0.5
7	36.2	3.2
19.9	37.3	1.7
19.9	27.8	5.2

removal increased while the other decreased. Felsvang et al., (1983) had determined that about 1% O_2 was necessary for NO_x removal. This oxygen effect was duplicated, with SO_2 and NO_x removal improving with increased O_2 concentration.

X-ray Diffraction

$Ca(OH)_2$ was reacted with NO_x (no SO_2) overnight at 7% O_2 to determine the reaction product. The sand was separated from the reagent, and the remaining solid was examined by X-ray powder diffraction. Only $Ca(OH)_2$ and $CaCO_3$ were detected. In hopes of extracting the nitrite/nitrate from the sample, the solid was dissolved in water and filtered. After evaporating the water, the remaining solid was used for X-ray. Only $Ca(NO)_2 \cdot 2H_2O$ and $CaCO_3$ were present in detectable amounts. Since the reacted $Ca(OH)_2$ had $CaCO_3$ present, unreacted reagent grade $Ca(OH)_2$ was also examined. The $Ca(OH)_2$ was determined to have some $CaCO_3$, probably from reaction with air. Using a carbon analyzer (Oceanography International Model 525) the amount of $CaCO_3$ in the reagent grade $Ca(OH)_2$ was estimated to be about 8%.

Table 5.6: Comparison of NO_x Removal As Determined by Ion Chromatograph and NO_x Analyzer
Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2, 83% N_2
14 mol% H_2O; 500 ppm SO_2, 500 ppm NO_x

| Experiment | NO$_x$ Removal After 1 Hour (mols NO$_x$/ 100 mols Ca(OH)$_2$) | | |
	IC	NO$_x$ Analyzer	% Nitrate (IC)
1 Ca(OH)$_2$: 4 Fly Ash: 4 CaSO$_3$ 0.03M NaOH; 105°C	1.07	1.02	63
Slaked Lime; 103°C	0.33	0.37	26
1 Ca(OH)$_2$: 4 Fly Ash: 4 CaSO$_3$ 0.08M NaOH; 92°C	1.28	4.18	57
1 Ca(OH)$_2$: 4 Fly Ash: 4 CaSO$_3$ 0.08M NaOH; 66°C	0.41	1.32	33
Ca(OH)$_2$; 103°C	0.09	0.91	25

Ion Chromatograph (IC) Analysis of Solids

The ion chromatograph (IC) was used to determine the amount of nitrite/nitrate produced. Because $CaSO_3$ was added to the fly ash experiments, the scope of the IC work was toward nitrite and nitrate analysis only. The NO_x removals from the IC are compared to the values obtained from the NO_x analyzer in Table 5.6. For two of the experiments, there was good agreement between the IC and NO_x analyzer. However, the other three show great discrepancies. A possible reason is that some of the nitrite/nitrate was not being extracted into solution. Also, two peaks, which were not identified, were formed due to exposure to simulated flue gas. Preliminary work showed that there is a sulfamic acid peak at the same time as one of the unknown peaks. Also included in Table 5.6 is the per cent nitrate compared to

nitrite. The amount of nitrate was scattered without any correlation. The concentration of O_2 in the flue gas was 7% for each run. The extraction step with water did provide opportunity for nitrite oxidation. In preparing the sample for X-ray, water was used to extract the nitrite from the $Ca(OH)_2$. X-ray powder diffraction of the $Ca(OH)_2$ reacted with NO_x indicated that only calcium nitrite was present in detectable quantities. Calibration solutions of nitrite/nitrate showed no oxidation in the IC or in solution.

NO_2 Removal Compared With NO Removal

During each experiment, the NO and NO_x concentrations were continuously monitored; however, the sampling technique used did not allow for accurate measurement of NO or NO_2 removal. After the reactor, the gas was passed through a water condenser. A sample of the gas was continuously taken and diluted with 2 l/min of air before being analyzed. During this period (about 2-3 minutes) NO/NO_2 concentrations could equilibrate or NO could oxidize. For most experiments, the NO and NO_x curves ran fairly parallel to each other, with no changes after being switched from bypass to reactor. Several runs did show a large amount of NO being oxidized in the reactor. For the 1 $Ca(OH)_2$:3 fly ash hydrated at 90°C, NO_x removal after 30 minutes was 12.9, but the NO_x concentration actually returned above the baseline - as if NO_x was being desorbed or calcium nitrite was reacting with SO_2. The 'net' NO_x removal for this run was 1.2. The NO and NO_x concentration curves for this run are shown in Figure 5.12. When this experiment was re-run, the SO_2 removal was 80, and the NO and NO_x concentrations were less erratic, but NO_x removal was less than 0.2. When the experiment was redone, this phenomenon was not reproducible, even though the SO_2 removal was.

60
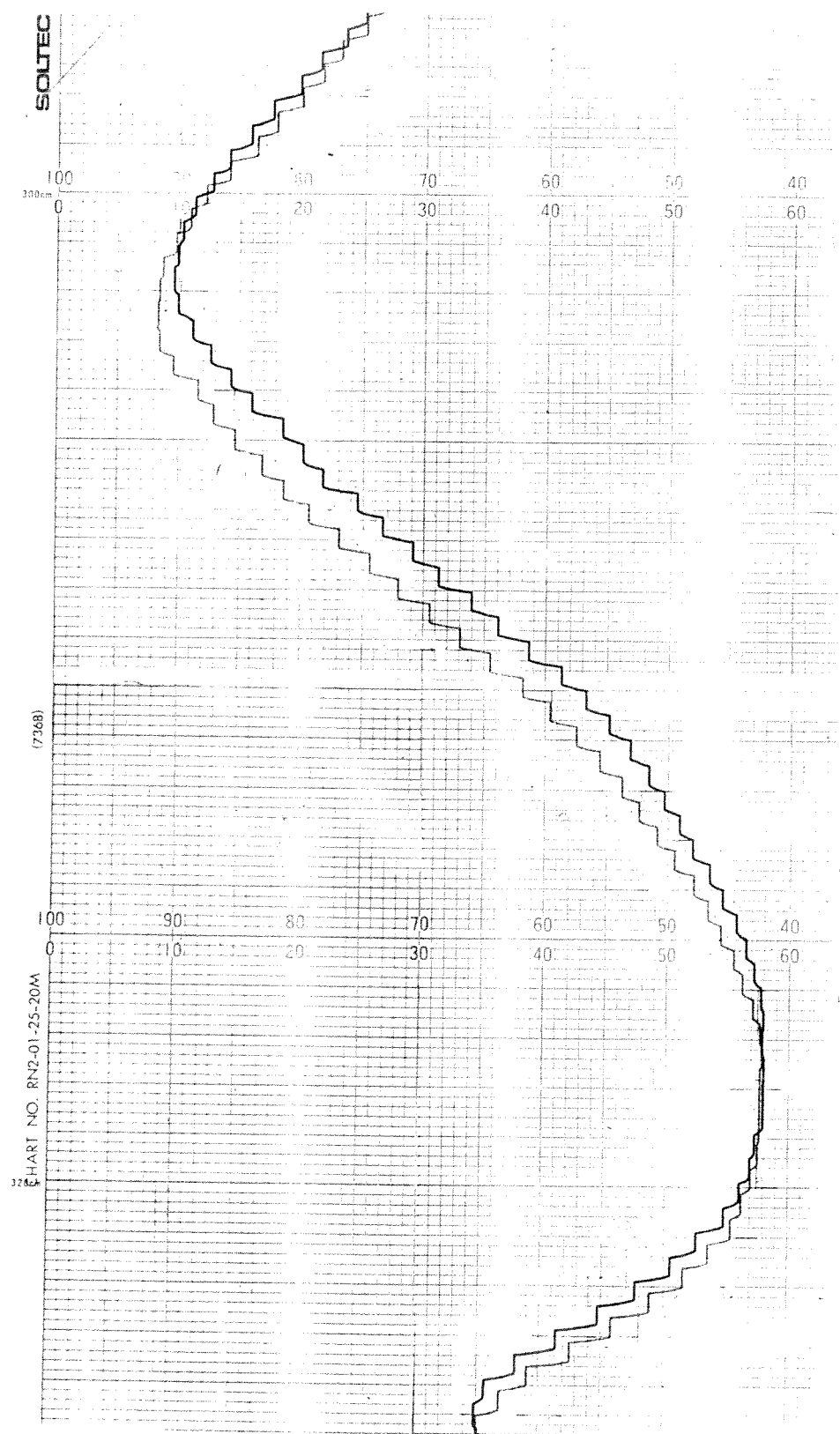
Figure 5.12: NO/NO$_x$ Concentration Curve for Acurex Fly Ash Sample - 1 Ca(OH)$_2$: 3 Fly Ash Hydrated at 90°C

Table 5.7: Effect of SO_2 on NO_2 Concentration
Gas Concentration Prior to Experiment; 92°C
14 mol% H_2O; Gas Flow: 4.6 l/min - 7% O_2, 10% CO_2, 83% N_2

Run	SO2 Analyzer (ppm)	% NO2	Analyzer (ppm) NO	NO2	Flow Controllers NOx (ppm)
128	0	26	344	120	522
127	263	14	384	64	522
131	592	10	448	48	565
141	1472	4	552	24	652

NO/NO₂ Concentration

Table 5.7 illustrates the effect of SO_2 on the inlet NO/NO_2 concentration. These runs were all conducted at 7% O_2. The NO, NO_2, and SO_2 concentrations are prior to the experiment. With increasing SO_2 concentration, NO_2 concentration decreased. It is possible that SO_2 reacts with the NO_2 to form NO and SO_3. This would explain the SO_2 material balance problem (see Chapter 4: Experimental - SO_2/NO_x Mass Balance), if the SO_3 were removed in the water condenser. Oxygen concentration did not affect NO/NO_2 ratio as much as SO_2. At 7% O_2, the NO_2 concentration was about 5 - 10% of the total NO_x concentration. At 0.5%, the NO_2 concentration dropped to 1 - 3%. With no SO_2 present and 21% O_2, the NO_2 concentration was, in some instances, over 50%. At 66°C, the NO/NO_2 ratio remained fairly constant at 0 and 55% relative humidities. While there was a fluctuation of several ppm in NO and NO_2 concentration, the ratio of NO/NO_2 was about the same.

NO oxidation decreases with increasing temperature (Burdick, 1921). However, the temperature of the preheat section had little effect on the NO/NO_2 ratio. Therefore, most of the oxidation occurs after the reactor, in the water condenser and in the dilution system. Originally an ice bath was used in conjuction with the water condenser, but was removed to reduce NO oxidation. An immediate drop in NO_2 concentration from 20 to 5% was seen. During calibration with NO span gas, about 2 - 5% oxidation was observed in the dilution system. Calibration was performed by injecting span gas after the reactor. A sample of 2.5 - 3.0 ml was taken and diluted with air, before analysis.

Chapter 5: Conclusions and Recommendations

Conclusions

The most reactive solid for NO_x removal was $Ca(OH)_2$ slurried with fly ash, $CaSO_3$, and $NaOH$. The best conditions for NO_x removal were at high temperatures (tested up to 125°C) and high concentrations of SO_2 (tested up to 1500 ppm) and O_2 (tested up to 20%).

For optimum SO_2 removal, it was necessary to slurry $Ca(OH)_2$ with fly ash and $NaOH$. The best conditions for SO_2 removal were at higher relative humidities (lower temperatures) and with no NO_x.

$NaOH$ played an important role in SO_2 and NO_x removal - as an improvement to fly ash dissolution, as a deliquescent, and as a possible catalyst for NO_x removal.

When slurried with fly ash and $NaOH$, $CaSO_3$ substantially improved the solids reactivity toward NO_x, but did not affect SO_2 removal.

No optimum temperature for simultaneous SO_2/NO_x removal could be found. NO_x removal increased with temperature while SO_2 removal decreased. At 66°C, NO_x removal was from one to two orders of magnitude slower than SO_2 removal. At 110°C, NO_x removal was 2 - 5 times slower than SO_2 removal.

O_2 improved both SO_2 and NO_x removal. With 0.5% O_2, NO_x removal was substantially lower than at 7%. O_2 was necessary for NO_x removal.

NO_x removal increased with increasing SO_2 concentration. SO_2 may not be necessary to obtain some NO_x removal, and only the presence of $CaSO_3$ in the reagent may be necessary to obtain NO_x removal.

SO_2 removal was relatively unaffected by NO_x. At high NO_x removals, NO_x had a negative effect.

There was a direct correlation between surface area and reactivity toward SO_2. Fly ash samples were more reactive than slaked limes with equivalent alkali surface areas. Therefore, reactivity was also a function of other variables.

Recommendations

Higher slurrying temperatures and longer slurrying times should be examined. Preliminary work with a sample hydrated at 90°C proved to be much more reactive toward SO_2. NaOH addition may not be necessary at higher slurrying temperatures. Different fly ash and $CaSO_3$ loadings should be attempted. $CaSO_4$, $Ca(NO_2)_2$, and $Ca(NO_3)_2$ should also be incorporated to examine a more realistic solids recycle.

Additional ion chromatograph (IC) work is needed for precise analysis of solids. Preliminary work with the IC disagreed with NO_x removal from the chemiluminescent analyzer. Complete extraction of the nitrites/nitrates could be

insured by possible adding HCl or by dissolving the sample in a very large volume of water. The several peaks which were not identified should be investigated further. These peaks are definitely formed due to exposure to the flue gas and possibly one of the peaks could be sulfamic acid.

NO_x removal continued to increase at higher temperatures up to 125°C. NO_x removal at temperatures above 125°C should be investigated.

Appendix

66

Modifications to Experimental Apparatus and Procedure

Date	Run Implemented	Modification
1/30/85	Run #6	O_2 incorporated into system.
8/31/85	Run #48	Heating tape used instead of water bath.
10/16/85	Run #59	New flow meter controllers used instead of rotameters and regulating valves.
10/17/85	Run #60	New flame photometric analyzer used for SO_2 analysis. Dilution system used in conjuction with old analysis.
11/1/85	Run #69	CO_2 and NO included in flue gas.
11/11/85	Run #77	Pulsed fluorescent SO_2 analyzer removed.
11/22/85	Run #87	New $NO/NO_2/NO_x$ chemilumenescent analyzer in place. SO_2/NO_x experiments begin.
12/3/85	Run #94	Fly ash samples are atmosperically oven dried instead of filtered and vacuum dried.
1/10/86	Run #106	Move to new Chemical Engineering building. Air used for O_2 source. System 'slightly' modified - tubing, etc. Entire apparatus under hood. New glass syringe is used to replace broken one.
2/22/86	Run #117	Regenerate catalyst of $NO/NO_2/NO_x$ analyzer with H_2.
2/27/86	Run #119	Ice bath removed to reduce NO oxidation after reactor.
3/6/86	Run #125	New PID temperature controller. Old PI controller now on preheat section.
3/12/86	Run #127	Sample stream lines are shortened to reduce lag time.
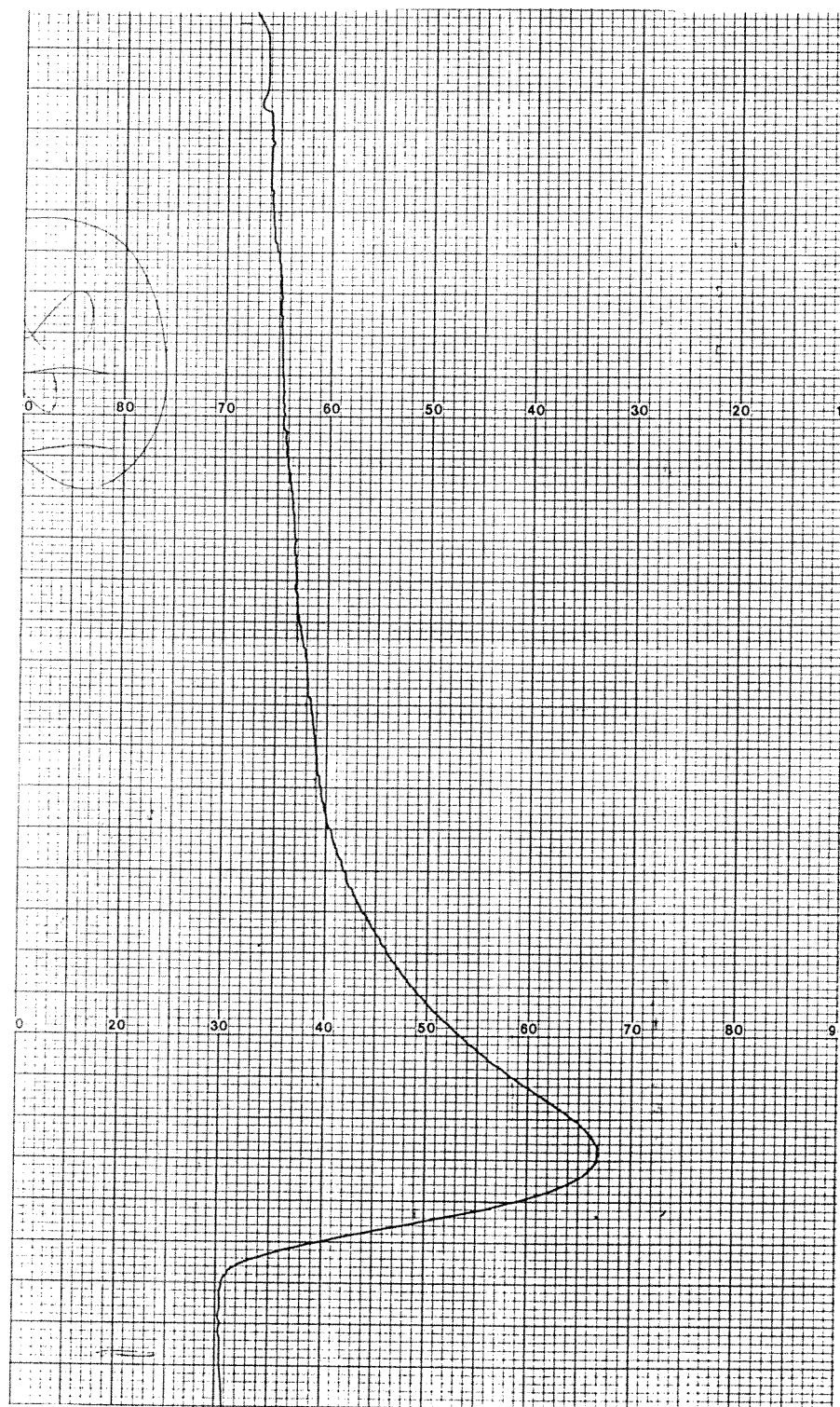
Figure A.1: Typical SO_2 Concentration Curve (Run #145)
SO_2 Removal - 18.3 moles SO_2 per 100 moles $Ca(OH)_2$
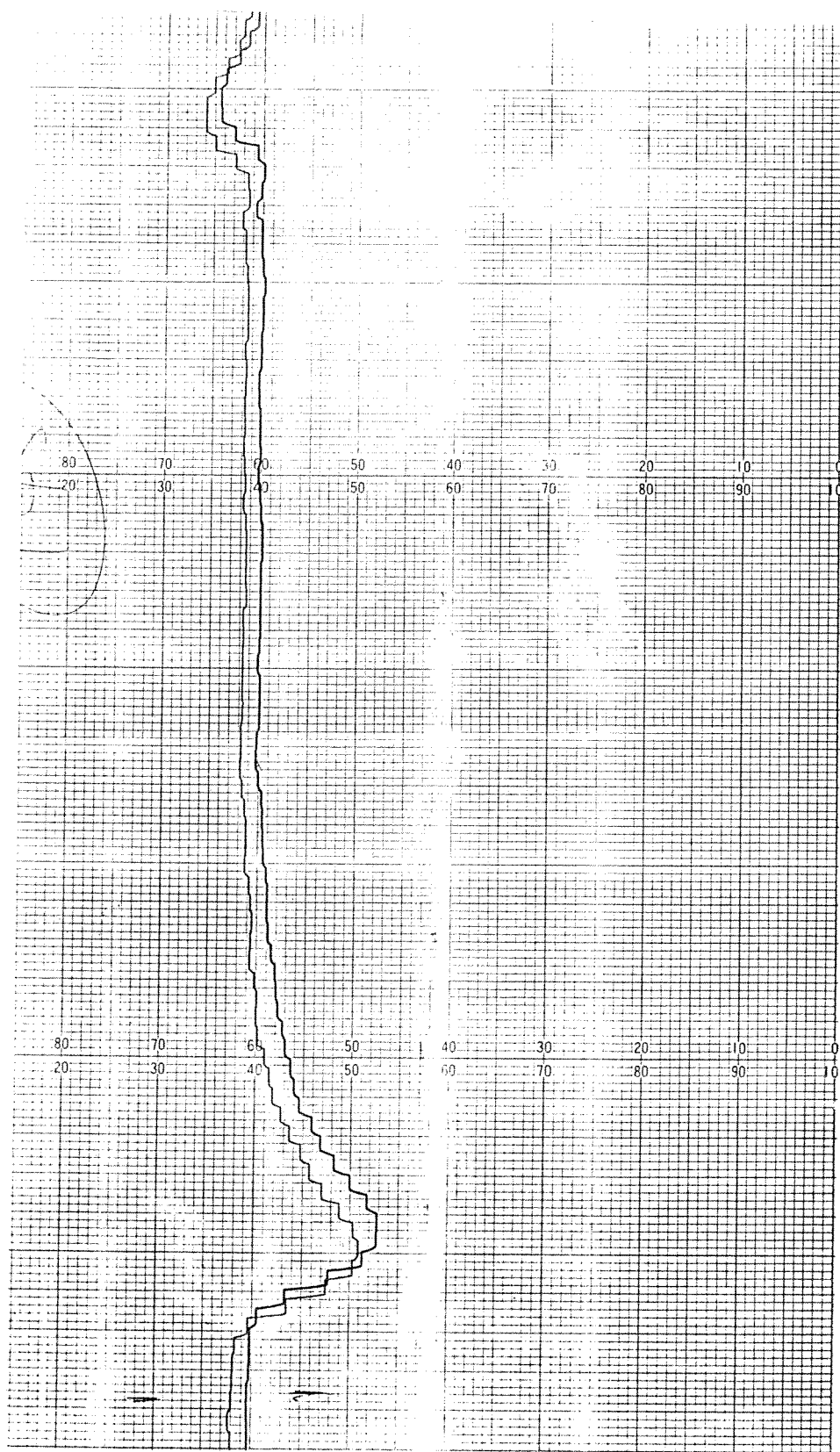
Figure A.2: Typical NO_x Concentration Curve (Run #145)
NO_x Removal - 3.8 moles NO_x per 100 moles $Ca(OH)_2$

Chemicals Used

The reagent grade $Ca(OH)_2$ was obtained from Matheson Coleman & Bell Manufacturing Chemist. The maximum impuriities were 1.213 wt% with the main impurities being magnesium and alkali salts. X-ray powder diffraction detected some $CaCO_3$ in the reagent grade $Ca(OH)_2$, and carbon analysis (Oceanography International Model 525) showed about 8% $CaCO_3$ was present, apparently from reaction with CO_2 in the air. The particle size distribution was measured with a Coulter Counter model T_{AII} and is located in Figure A.3. The BET surface area was determined to be 9.2 m^2/g by nitrogen absorption with an Accusorb Model 2100E Physical Adsorption Analyzer. The fly ash used was bituminous coal burned at Appalachian Power Company's Clinch River Plant and was provided by Dr. John Chang of the Acurex Corporation. The analysis of the fly ash is located in Table A.1. The $CaSO_3 \cdot 0.5H_2O$ was synthesized by reacting $CaCl_2$ and Na_2SO_3 in solution. Iodine titration of the $CaSO_3 \cdot 0.5H_2O$ showed about 5% calcium sulfate.

Various alternative solids were tested, and these were obtained from varous sources. The portland cement was obtained from Capitol Aggregates in Austin, TX. The analyses of the three types of portland cement are located in Table A.2. A high-Ca pressure hydrated lime from the Western Lime & Cement Co. was provided by Dr. John Chang of Acurex. Chemical analyses and BET surface area measurements of this lime are given in Tables A.3. A solution of slaked lime was obtained from Bryan Jankura of Babcock & Wilcox. After being dried and sieved, the particle size distribution was measured using the Coulter Counter and a Hiac-Royco particle
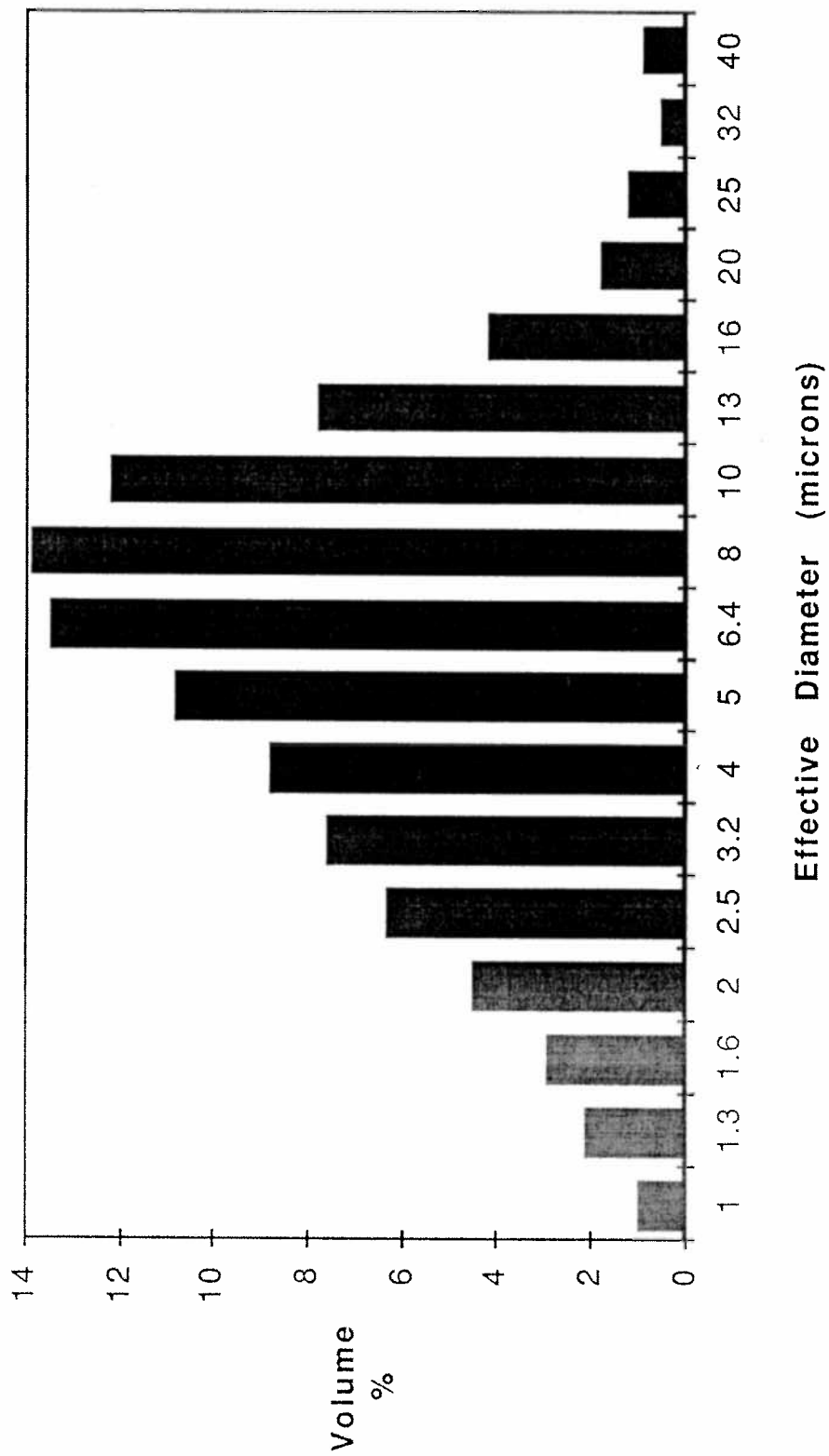
Figure A.3: Particle Size Distribution for Reagent Grade $Ca(OH)_2$ as Determined by Coulter Counter model T_{AII}

AMERICAN ELECTRIC POWER SERVICE CORPORATION
ASH UTILIZATION & RESEARCH SECTION

REPORT OF FLY ASH TESTS

Company: __Appalachian Power Company__ Location: __Units 1-3__
Plant: __Clinch River Plant__ Sample Date: __1-7-85__
Project: _____

CHEMICAL ANALYSIS

	Test Results	Specification* ASTM C 618 Class "F"	Corps of Engineers
Silica	54.2		
Aluminum Oxide	25.6	.	
Iron Oxide	7.8		
Combined 1, 2 & 3	87.6	Min 70%	Min 70%
Titanium Dioxide	1.5		
Calcium Oxide	1.8		
Magnesium Oxide	1.4		.
Sodium Oxide	0.4		
Potassium Oxide	2.9		
Sulfur Trioxide	0.6	Max 5%	Max 5%
Phosphorus Pentoxide	0.2		
Other Constituents	1.5		
TOTAL, %	99.9	.	.
pH @ 26°C, 1% Slurry	11.8		.
Available Alkalies, %	0.74	Max 1.5%	Max 1.5%
Sp. Cond., @ 21°C, Umho of 1% Slurry	1350		

PHYSICAL TESTS

	Test Results	ASTM C 618 Class "F"	Corps of Engineers
Moisture Content, %		Max 3%	Max 3%
Net Ignition Loss/Gain, -/+%		Max 6%	Max 6%
Retained on No. 325,Wet-Sieved, %		Max 34%	Max 34%
Specific Gravity			
Soundness Autoclave Expansion With Portland Cement, %		Max 0.8%	Max 0.8%
Pozzolanic Activity Index Water Requirement, % Control		Max 105%	Max 105%
With Cement at 28 Days, % Control		Min 75%	Min 75%
With Lime at 7 Days, Psi.		Min 800 psi	Min 900 psi

*For fly ash as a replacement for cement
  in Portland Cement Concrete

** Sample fails ASTM C-618 or Corps of Engineers Specifications

Table A.1: Chemical Analysis of Clinch River Fly Ash

P.O. BOX 33240, SAN ANTONIO, TEXAS 78265-3240; AREA CODE 512, 655-3010

TEST CERTIFICATE

CAPITOL CEMENT

Reported to: Mr. Paul Chu
U.T.-Austin

Date Produced: April, 1985

PORTLAND CEMENT - TYPE III

	Percent
Chemical Composition:	
Calcium Oxide (CaO)	65.62
Magnesium Oxide (MgO)	1.31
Silicon Dioxide (SiO2)	19.55
Aluminum Oxide (Al2O3)	5.17
Ferric Oxide (Fe2O3)	1.95
Sulfur Trioxide (SO3)	3.57
Loss on Ignition (L.O.I.)	1.48
Insoluble Residue (I.R.)	0.23
Total Alkalies as Na2O	0.53
Tricalcium Silicate (C3S)	70.86
Tricalcium Aluminate (C3A)	10.40
Specific Surface (Fineness):	
Blaine (Sq. Cm./Gm.)	4917
Wagner (Sq. Cm./Gm.)	2775
Screen (% Less Than 325)	98.6

Soundness:
Autoclave Expansion ---------------------- -.02

Time Setting:
Initial 1 Hrs. 35 Mins. (Gillmore)
Final 3 Hrs. 10 Mins. (Gillmore)
Set 0 Hrs. 50 Mins. (Vicat)

Compressive Strength:
A.S.T.M. C-109

1 Day	3600	Lbs./Sq. In.
3 Days	4610	Lbs./Sq. In.
7 Days	5460	Lbs./Sq. In.
28 Days	6165	Lbs./Sq. In.

Air Entrainment:
Percent by Volume 10.2

Quality Control Manager

Table A.2: Chemical Analysis of Portland Cement Type III

P.O. BOX 33240, SAN ANTONIO, TEXAS 78265-3240; AREA CODE 512, 655-3010

CA

CAPITOL CEMENT

TEST CERTIFICATE

Reported to: Mr. Paul Chu
U.T.-Austin

Date Produced: May, 1985

PORTLAND CEMENT - TYPE II

	Percent
Chemical Composition:	
Calcium Oxide (CaO) --------------------	63.01
Magnesium Oxide (MgO) -------------------	1.48
Silicon Dioxide (SiO2) ------------------	21.14
Aluminum Oxide (Al2O3) ------------------	4.56
Ferric Oxide (Fe2O3) --------------------	4.58
Sulfur Trioxide (SO3) -------------------	2.59
Loss on Ignition (L.O.I.) ---------------	1.54
Insoluble Residue (I.R.) ----------------	0.31
Total Alkalies as Na2O ------------------	0.54
Tricalcium Silicate (C3S) ---------------	51.28
Tricalcium Aluminate (C3A) --------------	4.33
Specific Surface (Fineness):	
Blaine (Sq. Cm./Gm.) --------------------	3545
Wagner (Sq. Cm./Gm.) --------------------	1991
Screen (% Less Than 325) ----------------	92.1

Soundness:
  Autoclave Expansion -------------------- -.04

Time Setting:
  Initial ___3___ Hrs. ___25___ Mins. (Gillmore)
  Final ___5___ Hrs. ___00___ Mins. (Gillmore)
  Set ___2___ Hrs. ___05___ Mins. (Vicat)

Compressive Strength:
  A.S.T.M. C-109
          1 Day   ------   Lbs./Sq. In.
          3 Days   2505   Lbs./Sq. In.
          7 Days   3375   Lbs./Sq. In.
         28 Days   5770   Lbs./Sq. In.

Air Entrainment:
  Percent by Volume 11.8

(signature) Thomas L. Vick
Quality Control Manager

Table A.2: Chemical Analysis of Portland Cement Type II

TEST CERTIFICATE

CAPITOL CEMENT

Reported to: Mr. Paul Chu

U.T.-Austin

Date Produced: May, 1985

PORTLAND CEMENT - TYPE   I

                                                                    Percent

Chemical Composition:

Calcium Oxide (CaO) ---------------------- 65.50

Magnesium Oxide (MgO) -------------------- 1.30

Silicon Dioxide (SiO$_2$) ------------------- 19.91

Aluminum Oxide (Al$_2$O$_3$) ------------------ 5.32

Ferric Oxide (Fe$_2$O$_3$) -------------------- 2.09

Sulfur Trioxide (SO$_3$) ------------------- 2.96

Loss on Ignition (L.O.I.) --------------- 1.51

Insoluble Residue (I.R.) ---------------- 0.24

Total Alkalies as Na$_2$O ------------------ 0.57

Tricalcium Silicate (C$_3$S) -------------- 68.16

Tricalcium Aluminate (C$_3$A) ------------- 10.56

Specific Surface (Fineness):

Blaine (Sq. Cm./Gm.) --------------------- 3640

Wagner (Sq. Cm./Gm.) --------------------- 1901

Screen (% Less Than 325) ---------------- 92.0

Soundness:

Autoclave Expansion --------------------- .03%

Time Setting:

Initial   2   Hrs.   35   Mins. (Gillmore)

Final   4   Hrs.   35   Mins. (Gillmore)

Set   1   Hrs.   40   Mins. (Vicat)

Compressive Strength:

A.S.T.M. C-109

1 Day   - - - -   Lbs./Sq. In.

3 Days   3715   Lbs./Sq. In.

7 Days   4375   Lbs./Sq. In.

28 Days   5820   Lbs./Sq. In.

Air Entrainment:

Percent by Volume   11.3

Quality Control Manager

STATE OF TEXAS

Table A.2: Chemical Analysis of Portland Cement Type I

PROJECT 5055 / 5250-2   DATE 11/5/84

Western Lime + Cement Co. (HCPH)

CHEMICAL ANALYSES

Wt %

SAMPLE NUMBER

	C495-17 -1 (1714)	C495-17 -2 (1715)	C495-17 -3 (1716)	C495-17 -4 (1717)		
Li_2O	<0.01	<0.01	<0.01	<0.01		
Na_2O	0.03	0.04	0.04	0.05		
K_2O	<0.01	0.02	0.02	0.02		
MgO	1.3	1.2	1.1	1.5		
CaO	95.1	96.3	95.7	97.3		
Fe_2O_3	0.22	0.21	0.22	0.22		
Al_2O_3	<0.2	<0.2	<0.2	<0.2		
SiO_2	0.22	0.22	0.22	0.22		
TiO_2	<0.3	<0.3	<0.3	<0.3		
P_2O_5	<0.05	<0.05	<0.05	<0.05		
SO_3	0.25	0.21	0.24	0.31		
LOI	25.0	25.8	25.6	25.2		
$BET, m^2/g$	17.6	16.8	15.4	16.9		

Remarks:

Except for BET, analyses on ignited sorbents

$MMD, \mu m$	3.7	4.4	} Micromeritics' analysis of	
$\rho, g/cm^3$	2.21	2.23	} as-received samples	

Table A.3: Chemical Analysis of High-Ca Pressure Hydrated Lime
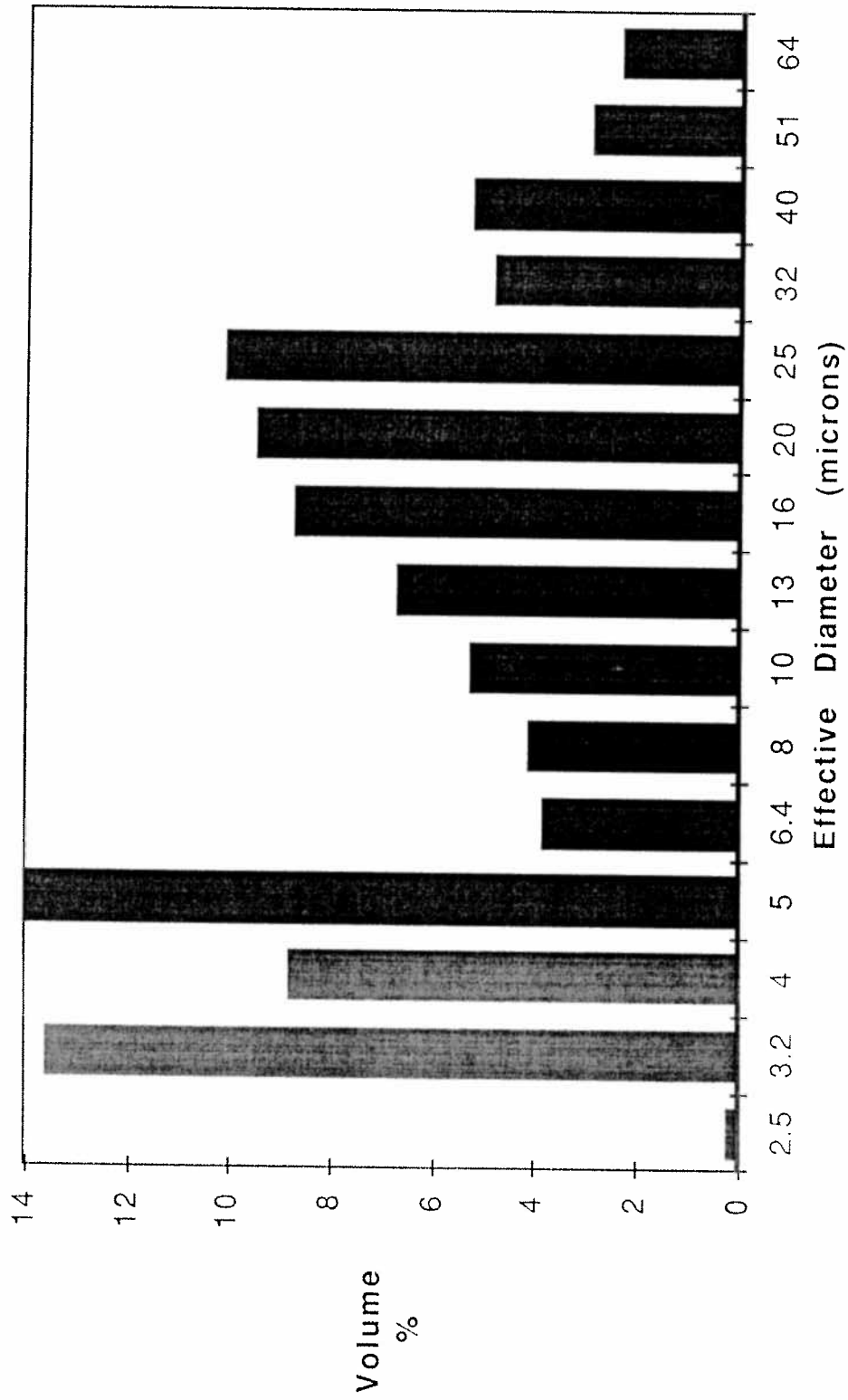
Figure A.4: Particle Size Distribution for B&W Slaked Lime as Determined by Coulter Counter model T$_{AII}$

Table A.4: Particle Size Distribution for B&W Slaked Lime
Determined by Hiac-Royco Particle Counter Model 4100A
Lime Solution: Filtered, Vacuum Dried, the Sieved

Size of Particle (Microns)	(%)
2 - 5	46.0
5 - 10	38.3
10 - 15	10.1
15 - 20	3.0
20 - 40	1.7
> 40	0.9

counter (Model 4100A). The two distributions are given in Figure A.4 and Table A.4. Various other alkali samples were obtained from Dr. Chang and Dr. Wojciech Jozewicz of Acurex and Professor Ingemar Bjerle of the University of Lund.

Acid/Base and Iodometric Titrations

Acid/base and iodometric titrations were used to analyze the reacted solids for $CaSO_3$ and $Ca(OH)_2$ (Ruiz-Alsop and Rochelle, 1986). The analysis procedure consisted of dissolving the sample with about 20 - 30 ml of distilled water, adding excess iodine until the solution turned brown, adding excess HCl to about pH 2-3, back-titrating with NaOH to pH 6, and titrating with sodium thiosulfate to the starch end point. Titrations with known amounts of $CaSO_3$ and $Ca(OH)_2$ were within 2% error.

Ion Chromatograph Procedure

Preliminary work with the ion chromatograph (Dionex 2000i/SP) was used to determine the amount of nitrites/nitrates produced. Approximately 200 ml of distilled water was added to the sample. After hand stirring, the solution was covered with parafilm and allowed to stand overnight. 10 ml of this solution was pipetted and diluted with enough distilled water to correspond with the range of the IC. At least two injections were made for each sample. At the beginning and end of the day, calibration solutions of nitrite/nitrate were run to produce a calibration curve and check for drift. Several of the samples were ground with a mortar and pestle to improve dissolution, but these samples actually contained more error.

Before the Dionex 2000i/SP was purchased, a Dionex Model 14 was used for sulfate analysis during early runs with only SO_2 - O_2 experiments and several limes. The reacted sample was divided into two - one for acid/base and iodometric titrations and the other for IC analysis. Each sample was weighed with the assumption that there was an equal proportion of hydroxide and sulfite. About 25 ml of distilled water was added to the solid, and 0.8 ml of H_2O_2 was added to oxidize all the sulfite. After allowing the solution to sit for 20-30 minutes, a known excess of HCl was added, and then back-titrated with NaOH to pH 6. Additional HCl was added to pH 2-3 to help dissolve any sulfate in solution. After stirring for 20-30 minutes, the solution was filtered, and washed repeatedly to insure complete sulfate dissolution. The filtrate was placed in a volumetric flask (normally 2000 ml), and distilled water was added to fill the flask. Several samples of this solution were injected into the IC to insure reproducibility. There was a lot of drift with this IC, so a calibration solution was injected before and after each different experiment. The amount of

$Ca(OH)_2$ was determined from the acid/base titration, and the amount of sulfite was calculated from the IC results. Tests with known amount of sulfite and hydroxide were accurate within 5%.

Detailed Experimental Procedure

In the $Ca(OH)_2$ and $Ca(OH)_2$ with additive experiments the loading was 1 g of reagent grade $Ca(OH)_2$ plus any additive. For fly ash experiments, the loading was 0.4 g of $Ca(OH)_2$ with 1-16 parts fly ash and $CaSO_3$. The reagent was sieved through a 125 micron sieve. Some of the fly ash was retained on the sieve, but this was incorporated in the experiment. After being dispersed in 40 g of 100 mesh (average) silica sand, this mixture was loaded into the reactor. A standard tapered clamp, stopcock grease, and rubber bands were used to help seal the reactor and help prevent leaks. The reactor was then wrapped with heating tape. A thermocouple was inserted into the temperature well. For best results, a temperature 15-20°C lower than the desired temperature was tried first to prevent the temperature from overshooting to much.

Air (for economic reasons) was bypassed around the reactor at 4.6 l/min. The preheat section was heated by dialing in the desired temperature. The evaporator temperature was about 110°-120°C. Water was injected into the evaporator by a syringe pump as soon as the evaporator temperature reaches 100°C. Cooling water was necessary for water knock-out. If the back pressure was too high, the syringe pump will stick because the air lines are probably scaled and should be cleaned/replaced immediately. When the temperatures reach steady-state, the flow was adjusted to 2.16 l/min of common purity nitrogen. At position 2 of the syringe

pump, this corresponded to about 98% relative humidity at 66°C. The nitrogen flow could be adjusted to manipulate the relative humidity.

Before starting the prehumidification, enough water (20 ml) for the entire procedure should be in the syringe pump. At this point, prehumidification of the bed was ready. The nitrogen flow was switched from bypass to the reactor by turning both three-way valves simultaneously. Prehumidification was for 8 minutes at 66°C (98% relative humidity). After this the flow was adjusted to 4.6 l/min and the desired experimental temperature was programmed for the reactor and preheat section. If this was 66°C, then solids were conditioned for 10 more minutes at 55% RH (4.6 l/min at 66°C). For any other temperature, this step was continued until the desired temperature in the reactor was obtained. This step lasted from 15 - 20 minutes depending upon the experimental temperature. During prehumidification, the sample stream flow should be checked to see if the flow rate was constant. If not, the resistance should be increased on the vent stream by tightening the regulating valve.

After switching to bypass and returning to air, SO_2 and NO_x were metered into the system. For faster results, the system was 'flooded' with SO_2 and NO_x before dialing in the desired flow rates. As these concentrations began to reach steady-state, the desired concentrations of O_2 (from air), CO_2, and N_2 were programmed in. When the SO_2 and NO_x concentrations stabilized, the experiment was about ready to start. The syringe pump should have at least 35 ml of water. If not, load up, and wait 10 - 15 min. You're now ready to roll! Reactor, preheat, and evaporator temperatures and the water in the syringe pump (this was a major source of error) should be monitored.

After the run has ended, the gas was placed in bypass and the SO_2 and NO_x concentrations were measured after the experiment to determine the amount of drift. The beginning and final concentrations were normally averaged. If the removal occurred only in the first few minutes, then the beginning concentration was used. The reagent and sand were kept for further analysis (IC, wet titration, etc). All heating elements, cooling water, and cylinder gases were turned off. About 2 l/min air was left on to help flush out any SO_2 and NO_x in the lines.

Summary of Experiments

SO$_2$ Removal

Experimental Conditions: Removal after 1 hour; 500 ppm SO$_2$; 14 mol% water

Ca(OH)$_2$/Alternative Limes Experiments

Experimental : 1 g reagent, T = 66°C, 4.6 l/min of N$_2$

Run	Description of Experiment	Removal (mols SO$_2$/100 mols Ca(OH)$_2$)		
		Integration	Analysis	IC
1	Miracle Lime T - 64.4°C	26.2	20.5	---
2	Ca Based Reagent	2.8	3.1	---
3	Owens Lake Trona	28.4	---	---
4	Miracle Lime	18.9	16.1	---
14	High Ca; pressure hydrated	19.2	18.8	9.1
21	Reagent Ca(OH)$_2$	13.9	14.0	13.1
23	Reagent Ca(OH)$_2$	14.5	---	---
26	B&W slaked lime	23.1	30.5	31.3
28	B&W 'Special Brew'	23.9	33.2	---
29	B&W 'Special Brew'	23.3	31.2	---
132	I. Bjerle slaked lime	35.1	---	---

Oxygen Experiments

Experimental: 1 g reagent + mol% additive, T = 66°C, Gas flow - 4.6 l/min

Run	Description of Experiment	(%) O$_2$	Removal (mols SO$_2$/100 mols Ca(OH)$_2$)		
			Integration	Analysis	IC
10	Ca(OH)$_2$ + 10 mol% NaCl	100	23.7	32.7	---
11	Ca(OH)$_2$ + 5 mol% NaCl	100	17.8	25.8	---
12	Ca(OH)$_2$ + 10 mol% NaCl	100	23.2	---	---
13	Ca(OH)$_2$ + 5 mol% NaCl	100	20.6	27.6	---
14	High Ca; pressure hydrated	0.5	19.2	18.8	9.1
15	High Ca; pressure hydrated	100	27.6	25.0	8.4
16	Reagent Ca(OH)$_2$	100	17.7	---	---
17	Reagent Ca(OH)$_2$	20	15.2	14.3	13.5
18	Reagent Ca(OH)$_2$	10	15.6	15.6	16.1
19	Reagent Ca(OH)$_2$	21	16.3	15.7	21.8
20	Reagent Ca(OH)$_2$	5	19.4	14.6	14.4
21	Reagent Ca(OH)$_2$	0.5	13.9	14.0	13.1
25	B&W slaked lime	100	23.8	34.6	28.2
26	B&W slaked lime	0.5	23.1	30.5	31.3

Flyash/Portland Cement Experiments

Samples slurried at a solids:water of 1:15. Sample filtered and vacuum dried.

    SM - San Miguel Flyash
    CR - Clinch River Flyash
    CH - Reagent grade Ca(OH)$_2$
    I - Type I Portland Cement
    II - Type II Portland Cement
    III - Type III Portland Cement

Experimental: 500 ppm SO$_2$, 4.6 l/min of N$_2$, T = 66°C unless otherwise specified

Run	Description of Expt	Temp(°C)	Time(hr)	Integration	Analysis
27	1 B&W lime : 8 SM	65	6	23.3	42
30	1 CH : 4 CR	66	6	17.3	17.5
31	1 I : 4 SM	70	2	27.8	17.1
33	1 CH : 4 CR Solids:Water - 1:1	65	2	20.3	28.2
34	1 CH : 4 CR	70	2	6.9	15.2
35	1 CH : 16 CR	68	2	26.6	23.0
37	I	68	6	28.2	33.9
38	II	65	6	10.6	30.9
40	I	65	16	17.6	34.7
41	II	65	6	17.2	26.8
42	III	65	16	27.4	44.4
43	III	66	6	32.6	44.0
44	I	25	49	29.0	43.1
45	I	26	6	17.7	27.2
46	I	65	50	22.0	43.0

(Removal in mols SO$_2$/100 mols Ca(OH)$_2$)

62 - 68 all used: CH:CR:CaSO$_3$ = 1:16:4 - Slurrying conditions - 70°C, 6 hrs.

Run	T (°C)	SO$_2$ Removal by Integration
62	66	33
63	74	26
64	92	7
65	60	63
66	79	25
68	66	33

(mols SO$_2$/100 mols Ca(OH)$_2$)

SO_2/NO_x Removal

Experimental: 500 ppm SO_2, 500 ppm NO_x, 14 mol% H_2O; Gas flow = 4.6 l/min, 7% O_2, 10% CO_2, 83% N_2 ; Removal after 1 hr

$Ca(OH)_2$ and Additives Experiments
Sample: 1 g reagent plus 10 mol% additive

Run	Description of Experiment	T(°C)	Removal (mols/100 mols $Ca(OH)_2$) SO_2	NO_x
87	Reagent $Ca(OH)_2$	66	11.2	0.28
88	Reagent $Ca(OH)_2$	92	2.7	0.78
143	Reagent $Ca(OH)_2$	103	1.9	0.91
114	Reagent $Ca(OH)_2$ - No SO_2	66	--	1.4
115	Reagent $Ca(OH)_2$ - No SO_2 Span gas/Air - 1/1	66	--	0.0
116	Reagent $Ca(OH)_2$ - No SO_2 Span gas/N_2 -1/1	66	--	0.0
132	I. Bjerle slaked lime	66	35.1	--
135	I. Bjerle slaked lime	92	5.7	0.04
140	I. Bjerle slaked lime	92	3.5	0.37
90	$Ca(OH)_2$ + 10 mol% NaOH	66	16.3	1.08
91	$Ca(OH)_2$ + 10 mol% NaOH	92	4.5	1.28
92	$Ca(OH)_2$ + 10 mol% NaOH	92	4.3	1.20
93	$Ca(OH)_2$ + 10 mol% NaOH	104	3.6	1.30
97	$Ca(OH)_2$ + 10 mol% Na_2SO_3	66	14.0	0.4
98	$Ca(OH)_2$ + 10 mol% Na_2SO_3	92	4.7	?
99	$Ca(OH)_2$ + 10 mol% Na_2SO_3	106	3.9	0.48
102	5 g $Ca(OH)_2$ + 10 mol% Na_2SO_3	92	4.3	1.26

? - Concentration curve erratic; unable to integrate curve

SO$_2$/NO$_x$ Removal (continued)

Ca(OH)$_2$/Fly Ash/CaSO$_3$ Experiments:

Sample Prep: Slurrying Conditions - 65°C for 6 hours. Sample was oven dried at 65°C. NaOH addition - 10 mol% of Ca(OH)$_2$. Solids:water - varied from 1:1 to 1:15 - dependent upon NaOH concentration.

Experimental: 0.4 g Ca(OH)$_2$ plus fly ash, CaSO$_3$, and 10 mol% NaOH (if added).

Run	Description of Experiment	T(°C)	Removal (mols/100 mols Ca(OH)$_2$) SO$_2$	NO$_x$
94	1/4/4*	66	17.9	?
103	Same solid as 94	92	8.4	0.54
120	"	92	20.5	0.8
95	1/4/4 - 0.03M**	66	23.0	?
96	Same solid as 95	92	5.5	?
100	"	92	13.0	1.58
101	"	105	8.8	2.04
104	" - 200 ppm SO$_2$	92	9.8	1.06
123	1/4/4 - 0.08M	66	57.5	1.32
124	Same solid as 122	92	31.2	4.18
130	"	102	25.4	2.81
139	"	125	17.7	4.66
144	"	113	12.3	3.08
145	"	110	18.3	3.84
151	"	92	36.2	3.18
127	" - 225 ppm SO$_2$	92	14.7	1.06
128	" - No SO$_2$	92	--	1.61
129	" - No NO$_x$	92	46.6	--
141	" - 1500 ppm SO$_2$	92	28.7	4.08
148	" - Air + 10% CO$_2$	92	37.3	1.73
149	" - Air + 10% CO$_2$	92	27.8	5.18
152	" - N$_2$ + 10% CO$_2$	92	21.8	0.45
173	" - No NO$_x$	66	67.9	--

* 1/4/4 - 1 Ca(OH)$_2$: 4 Clinch River Fly ash: 4 CaSO$_3$•0.5H$_2$0
** 0.03M - 0.03 mols NaOH/liter of water
? - Concentration curve erratic; unable to integrate curve

Ca(OH)₂/Fly Ash/CaSO₃ Experiments (continued)

Run	Description of Experiment	Temp(°C)	Removal (mols/100 mols Ca(OH)$_2$) SO$_2$	NO$_x$
131	1/4/4 - 0.25M*	92	15.2	0.88
142	Same solid as 131	113	?	1.54
146	"	118	4.0	1.10
150	1/0/4 - 0.08M	92	7.4	0.27
153	Same solid as 150	66	46.5	0.63
155	"	66	32.0	1.13
157	"	110	2.8	0.18
154	1/4/4 - 0.08M Reproduce original sample 'Slurry time' - 10 hrs.	92	18.6	2.47
156	Same solid as 154	66	63.4	0.98
158	1/4/4 - 0.08M Reproduce original sample 'Slurry time' - 40 hrs.	66	54.8	0.90
159	Same solid as 158	92	19.9	3.65
160	1/4/0 - 0.08M	92	23.4	0.74
161	Same solid as 160	66	59.1	?
162	"	66	57.6	1.88
165	"	66	25.2	0.47
A new 1/4/0 - 0.08M sample for 171, 172, and 174				
171	1/4/0 - 0.08M	125	12.6	1.36
172	Same solid as 171	108	4.4	0.62
174	"	66	67.0	0.49

* 1/4/4 - 1 Ca(OH)$_2$: 4 Clinch River Fly ash: 4 CaSO$_3$·0.5H$_2$0
** 0.25M - 0.25 mols NaOH/liter of water
? - Concentration curve erratic; unable to integrate curve

Ca(OH)$_2$/Fly Ash/CaSO$_3$ Experiments (continued)

Run	Description of Experiment	Temp(°C)	Removal (mols/100 mols Ca(OH)$_2$) SO$_2$	NO$_x$
163	1/3/0 - hydrated, 90°C, 4+ hrs. Prepared - 5/16/86 Acurex Corp. - Wojciech Jozewicz	66	80.8	12.9@
166	Same solid as 163	92	38.9	0.71
175	"	66	79.9	?
164	1 CaO: 1 diatomaceous earth (MN-53) Hydrated - 90°C, 8 hrs. Prepared - 5/18/86 Acurex Corp. - Wojciech Jozewicz	66	67.9	0.65
167	1/4/4 - 0.08M NaOH added after slurrying	92	22.4	0.79
168	Same solid as 167	66	50.8	0.52
169	1/4/4 - 0.08M Vacuum filtered and dried	66	56.3	0.69
170	Same solid as 169	92	5.0	0.46

* 1/4/4 - 1 Ca(OH)$_2$: 4 Clinch River Fly ash: 4 CaSO$_3$·0.5H$_2$0
** 0.25M - 0.25 mols NaOH/liter of water
? - Concentration curve erratic; unable to integrate curve
@ Removal for 30 minutes; total 'net' removal - 1.4%

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