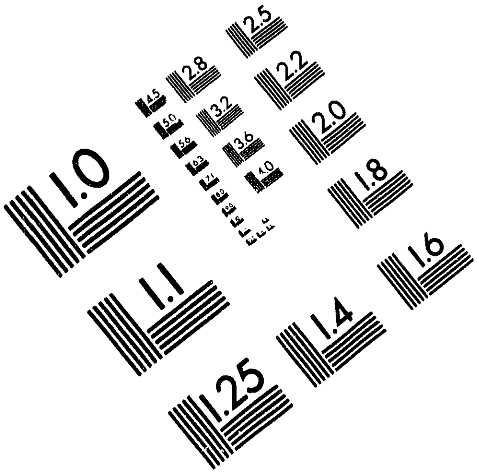

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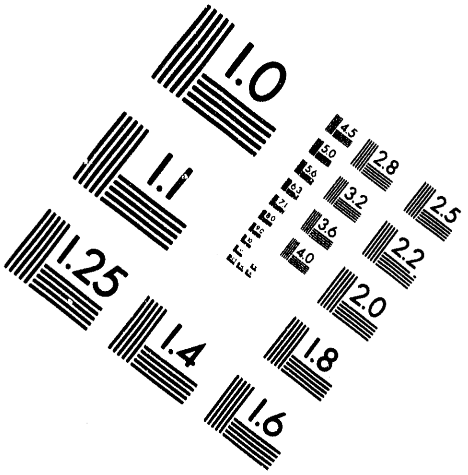

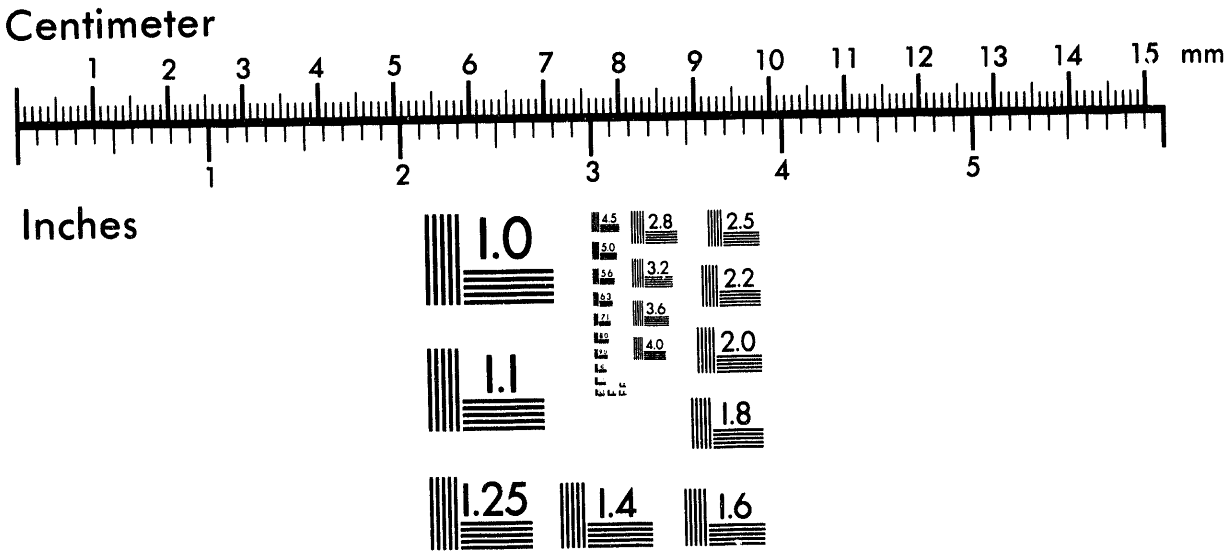

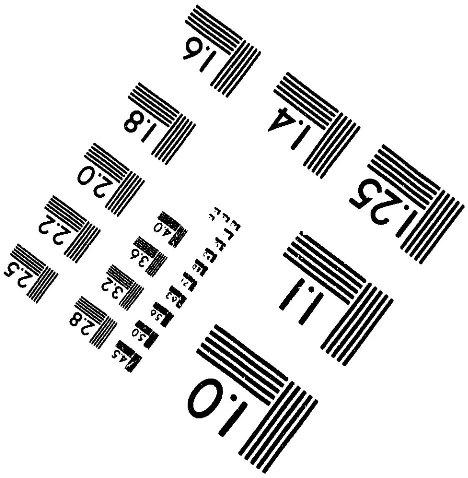

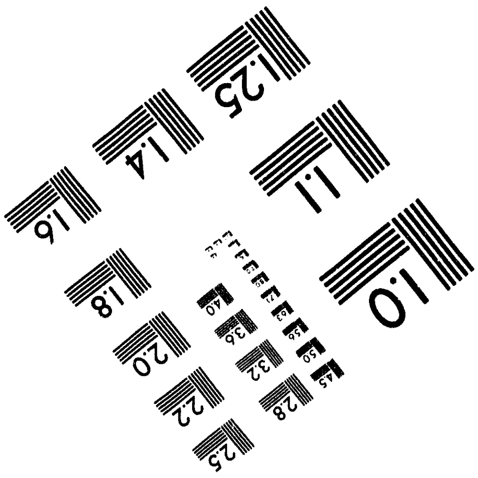

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Project Number: OCRC/90-1.5

Project Title: Sorbent Utilization Studies Using a Mini-Pilot Spray Dryer

Name of Grantee:

Address:
Civil & Environmental Engineering Department
University of Cincinnati
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Project Manager: Tim C. Keener

Period of Performance: September 1, 1992 - August 31, 1993

FINAL REPORT

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Other Investigators:
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MASTER

Table of Contents

Executive Summary

This report summarize the test results and model developments of the mini-pilot scale spray dryer at the University of Cincinnati for high sulfur coal applications for the project period from September 1, 1992 through August 31, 1993. The main body of the report consists of four parts: 1. additives to change process chemistry for SO_2 absorption by $Ca(OH)_2$ slurry; 2. recycle tests and hydration of fly ash with $Ca(OH)_2$ to increase reactivity; 3. limestone as an alternative sorbent and additive effects; 4. physical and chemical model developments for some of the additive effects and spray dryer mathematical model applications.

The results of sorbent enhancement with various additives is summarized in this section. Hydrogen peroxide which can oxidize sulfite ions into sulfate ions has a significant effect on enhancing sorbent utilization and increasing SO_2 removal efficiencies. Sugar which can increase the dissolution rate of $Ca(OH)_2$ has some positive effects on sorbent utilization with a small amount of addition, but the effect decreases with increased sugar concentration. Benzoic acid and formic acid which have buffering effects have little effect on the $Ca(OH)_2$ sorbent utilization in the spray dryer system.

In the recycle tests, a 9.1% recycled spray dryer $Ca(OH)_2$ product resulted in almost no. change in the overall SO_2 removal. However, when the recycled product were raised to 33%, the SO_2 removal was decreased by about 10%. Fly ashes have been slurried with quicklime at elevated temperatures to enhance spray dryer performance. Bench scale experimental results indicate that this hydration process greatly increased the total surface area of the solids. Mini-pilot scale tests in the spray dryer reveal that the heating step significantly increases calcium utilization and SO_2 removal of these fly ash/quicklime sorbents.

Limestone type and size have certain effects on spray dryer SO_2 removal, but the test results indicated that using limestone in the spray dryer for desulfurization is not very encouraging, and no effective additives were found for limestone application. The reasons are postulated as the following: The Ca/S ratio of a $CaCO_3$ slurry is almost half as much as that of CaO ($Ca(OH)_2$) if the same concentration (by weight) is fed into the spray dryer, and this leads to high slurry solids concentrations and heavy spray nozzle loadings. The low solubility and

dissolution rate of $CaCO_3$ and short liquid phase residence time (the high slurry concentration will make the residence time shorter) of the sprayed droplets are considered as combining to reduce the effectiveness of limestone for SO_2 removal.

In the theoretical study, the enhancement of sorbent utilization due to hygroscopicity of additives has been investigated, and a relationship between saturation ratio and droplets containing dissolved material has been given. This relationship explains the hygroscopicity phenomena. The modified SPRAYMOD model has been used for the estimation of spray dryer desulfurization performance, and the results seem to over-predict the baseline test results.

A modification factor for the Ca/S molar ratio calculation has been formulated. This modification was initiated from the difference between calculated Ca/S value and experimental observations.

Introduction

This report summarize last year's test results and model developments of the mini-pilot scale spray dryer at the University of Cincinnati for high sulfur coal applications. The main body of the report consists of four parts: 1. additives to change process chemistry for SO_2 absorption by $Ca(OH)_2$ slurry; 2. recycle tests and hydration of fly ash with $Ca(OH)_2$ to increase reactivity; 3. limestone as an alternative sorbent and additive effects; 4. physical and chemical model developments for some of the additive effects and spray dryer mathematical model applications.

Using $Ca(OH)_2$ slurry in the spray dryer absorber for SO_2 removal has shown to be both economic and technologically reliable for treating flue gases of low to medium sulfur coal, but as the concentration of SO_2 in the flue gases increases, the SO_2 removal efficiency will go down. For the flue gases of high sulfur coal, $Ca(OH)_2$ slurry alone in the spray dryer could not achieve SO_2 removal efficiency higher enough to meet the EPA regulations. However, the $Ca(OH)_2$ slurry treated by additive recipes have shown some positive aspects of using spray dryer to clean high sulfur coal flue gases.

Additives such as delinquent salts (NaOH, NaCl, and $NaHCO_3$) have been shown to improve SO_2 uptake, and these additive tests have indicated that SO_2 uptake may be increased by as much as 60% over baseline conditions [1]. These delinquent salt additives are known to retain the moisture on the droplet surface of $Ca(OH)_2$ slurry, and thus prolong the most effective liquid phase reaction for SO_2 removal.

It is very important to integrate and manipulate the process chemistry in the spray drying desulfurization.

Some additives can change the SO_2 absorption process chemistry, and thus enhance the SO_2 removal. By examining the chemical processes in the SO_2 reaction with $Ca(OH)_2$, other additives such as H_2O_2, sugar, and some organic acids which can change the chemical reaction processes are suggested and tested, and some promising results have been obtained.

Most spray drying system today recycle a portion of their waste solids back into the feed slurry. Recycle has been shown to increase sorbent utilization by allowing partially reacted sorbent to react further with the SO_2 in the flue gases. In addition, recycle of fly ash together with $Ca(OH)_2$ has been shown to be more beneficial towards SO_2 removal than recycle of $Ca(OH)_2$ alone [2]. The reason for the above phenomenon was postulated to be the pozzolanic reaction between the recycled fly ash and the calcium hydroxide in the feed slurry to form hydrated calcium silicates and/or calcium aluminates [3].

A recycle test has been conducted. Two types of Ohio coal fly ashes have been extensively studied, and improvement of utilization in spray dryer flue gas desulfurization has been demonstrated.

Limestone represents an area where significant cost savings can be realized. The spray dryer tests were designed to provide some results for understanding the magnitude of the limestone performance in the spray dryer system and the additive effects. Since the dissolution rate of limestone is the overall rate control step for the SO_2 absorption, unless an effective dissolution rate increasing additive is found the other additives will not be very helpful.

The additive effects on increasing SO_2 absorption by $Ca(OH)_2$ slurry were investigated, and the chemical and physical properties of these tested additives were studied. Some models have been formed to explain the additive phenomena. The mathematical model developed by Damle, S.A. [4] and modified by Partridge, P.G. Jr. [5] was used as the model prediction of spray dryer performance, and the results are compared to the experimental data.

Additives that change the process chemistry for SO_2 absorption by $Ca(OH)_2$ Slurry

Oxidation of S(IV) to S(VI): Since the diffusion of H^+ from droplet surface into droplet core might become the limiting step, the pH decrease of the droplet surface can lead to the halt of $SO_2(aq)$ dissolution into ion forms and this is illustrated in Figure 1 [6]. If there is a way to oxidize the $SO_2(aq)$, HSO_3^- and SO_3^{2-} to $SO_3(aq)$, HSO_4^- and SO_4^{2-} respectively (SO_2, HSO_3^- and SO_3^{2-} known as S(IV), and SO_3, HSO_4^- and SO_4^{2-} known as S(VI)), then due to the high dissolution rate of $SO_4(aq)$ and H_2SO_4 at low pH, the $SO_2(aq)$ concentration will nearly not be affected by the liquid side equilibrium and pH, therefore; the limiting step will be pushed to the gas phase diffusion.

S(VI) form is also known as a crystallization inhibitor, on the contrary; S(IV) form can be crystallized easily. If the S(IV) can be oxidized to S(VI), this implies less crystallization and more available sorbent surface area for dissolution since the crystal of the S(IV) form will deposit onto the surface of the sorbent and block its contact with the liquid. Yet in the wet scrubbing process where gypsum scaling (due to the S(VI) forms) needs to be controlled, the natural sulfite oxidation rate (oxidation by oxygen in flue gases) is inhibited through the use of thiosulfate to the point where gypsum scaling does not occur [7].

We know that in the process of $SO_2(g)$ diffusion into the droplet certain amount of oxygen will simultaneously diffuse into the droplet, but in the absence of catalysts the reactions between dissolved O_2 and S(IV) are negligible. Certain dissolved metal ions can act as the catalysts in the oxidation reaction [6], and the metal ions such as Fe^{2+}, Mg^{2+}, K^+, Cs^+ etc. could be the catalysts. H_2O_2 (hydrogen peroxide) is found to be a more powerful oxidizing agent. The conversion rates of S(IV) to S(VI) in the presence of H_2O_2, together with those in the presence of dissolved oxygen where the Fe(III), Mn^{2+}, NO_2 and HNO_3 denote the catalysts in the oxidation reaction, are shown in Figure 2 [6]. Considering that H_2O_2 have significantly higher Henry's Law constant and conversion rate than O_2, the oxidation of S(IV) into S(VI) can be more effective if H_2O_2 is used. The Henry's Law constants are listed below:

Gas	H, $Matm^{-1}$ (298 °K)
O_2	1.3×10^{-3}
O_3	9.4×10^{-3}
SO_2	1.24
H_2O_2	7.1×10^4

The H_2O_2 used in the additive test was from Fisher Scientific, 30% liquid form. It was added directly into the slurry. The test results of H_2O_2 as an oxidizing additive is shown in Figure 3. Indeed, the H_2O_2, as an additive, has a significant effect in enhancing sorbent utilization and SO_2 removal. At 20°F approach to saturation temperature, the SO_2 removal efficiency under the H_2O_2 additive is about 20% higher than that in the baseline. The additive concentration is from 1 ml/liter to 5 ml/liter, and the increase in additive concentration leads to the increase in SO_2 removal efficiency.

Dissolution Rate Enhancement: The dissolution rate of $Ca(OH)_2$ in the spray dryer system could become the limiting step due to the short residence time of the droplets and high ion concentration in the droplets. Sugar was tested as an additive for enhancing the dissolution rate of $Ca(OH)_2$ [8], and this is shown in Figure 4. The test results for sugar as

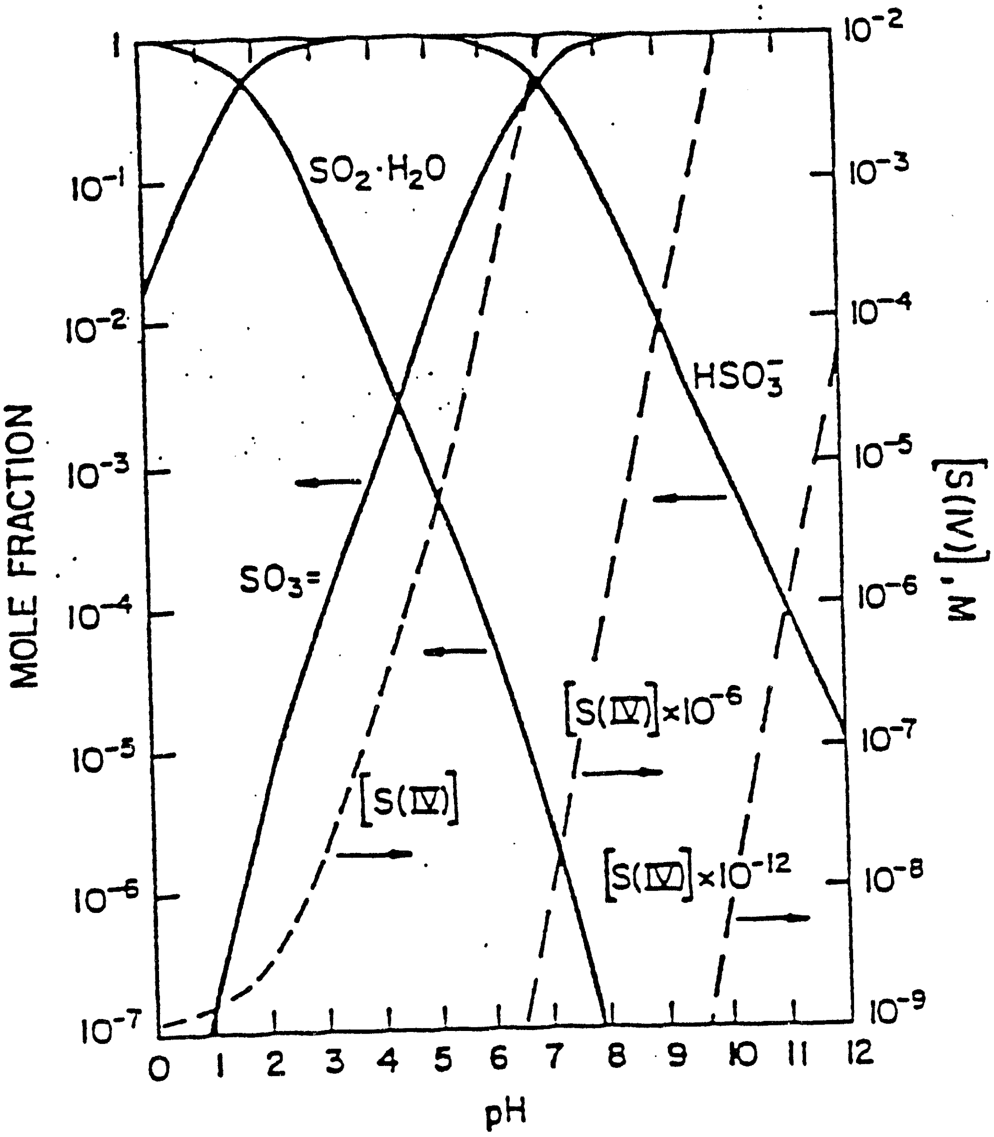

Figure 1. Mole Fractions and concentrations of the three dissolved S(IV) species, $SO_2 \cdot H_2O$ [$SO_2(aq)$], HSO_3^-, and SO_3^{2-}, as a function of pH at T=298°K, and p_{SO2} = 10^{-9} atm (1ppb). From Seinfeld, H.J., "Atmospheric Chemistry and Physics of Air Pollution" p.206, John Wiley & Sons, Inc., (1986).

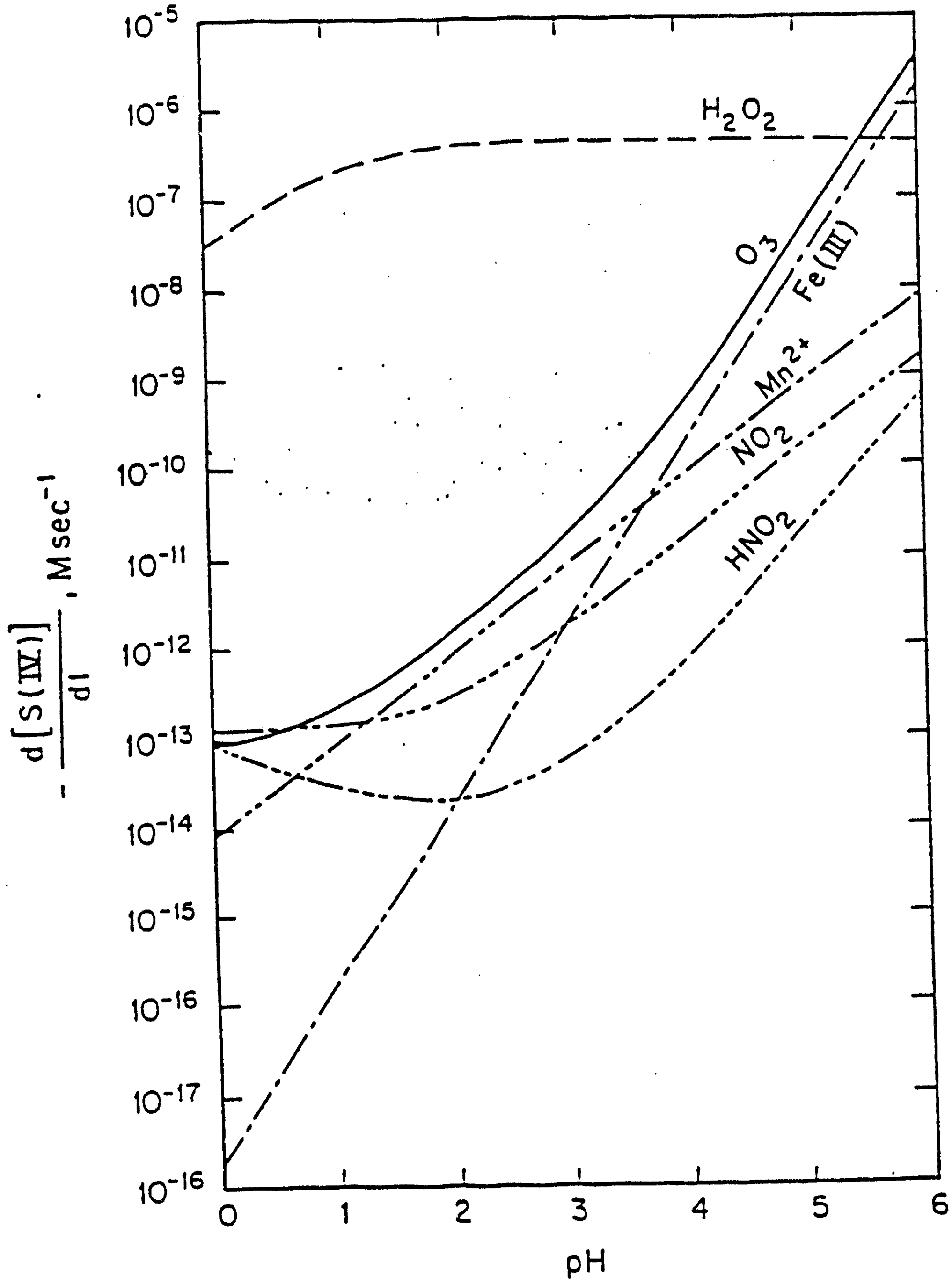

Figure 2. Comparison of aqueous-phase SO_2 oxidation paths. The rate of conversion of S(IV) to S(VI) as a function of pH. Conditions assumed are: $[SO_2(g)]=5$ ppb; $[HNO_2(g)]=2$ ppb; $[H_2O_2(g)]=1$ ppb; $[NO_2(g)]=1$ ppb; $[O_3(g)]=50$ ppb; $[Fe^{3+}(aq)]=3 \times 10^{-7}$ M; $[Mn^{2+}(aq)]=3 \times 10^{-8}$ M. From Seinfeld, H.J., "Atmospheric Chemistry and Physics of Air Pollution" p.228, John Wiley & Sons, Inc., (1986).

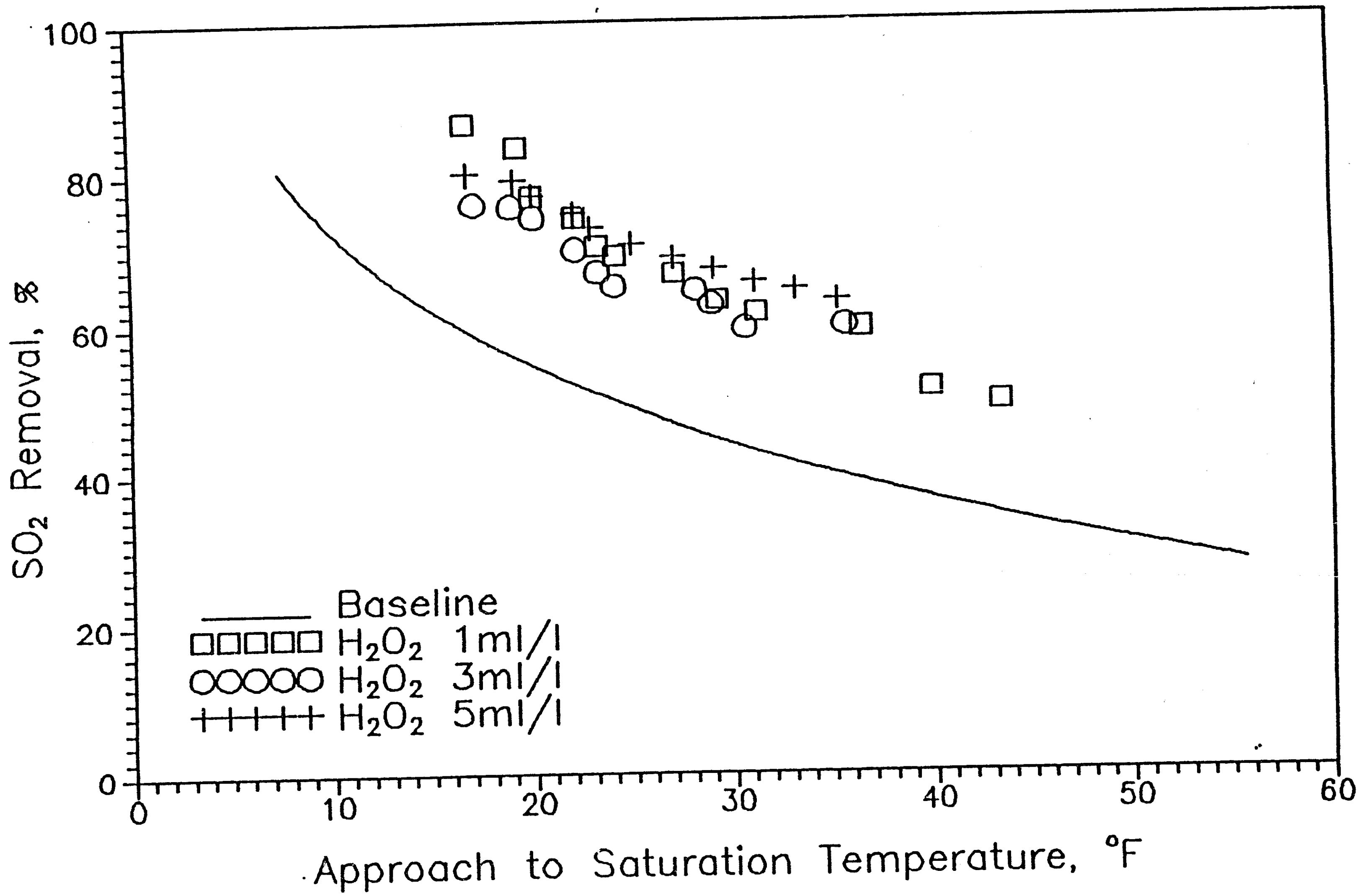

Figure 3. SO_2 Removal by $Ca(OH)_2$ with H_2O_2 Additive

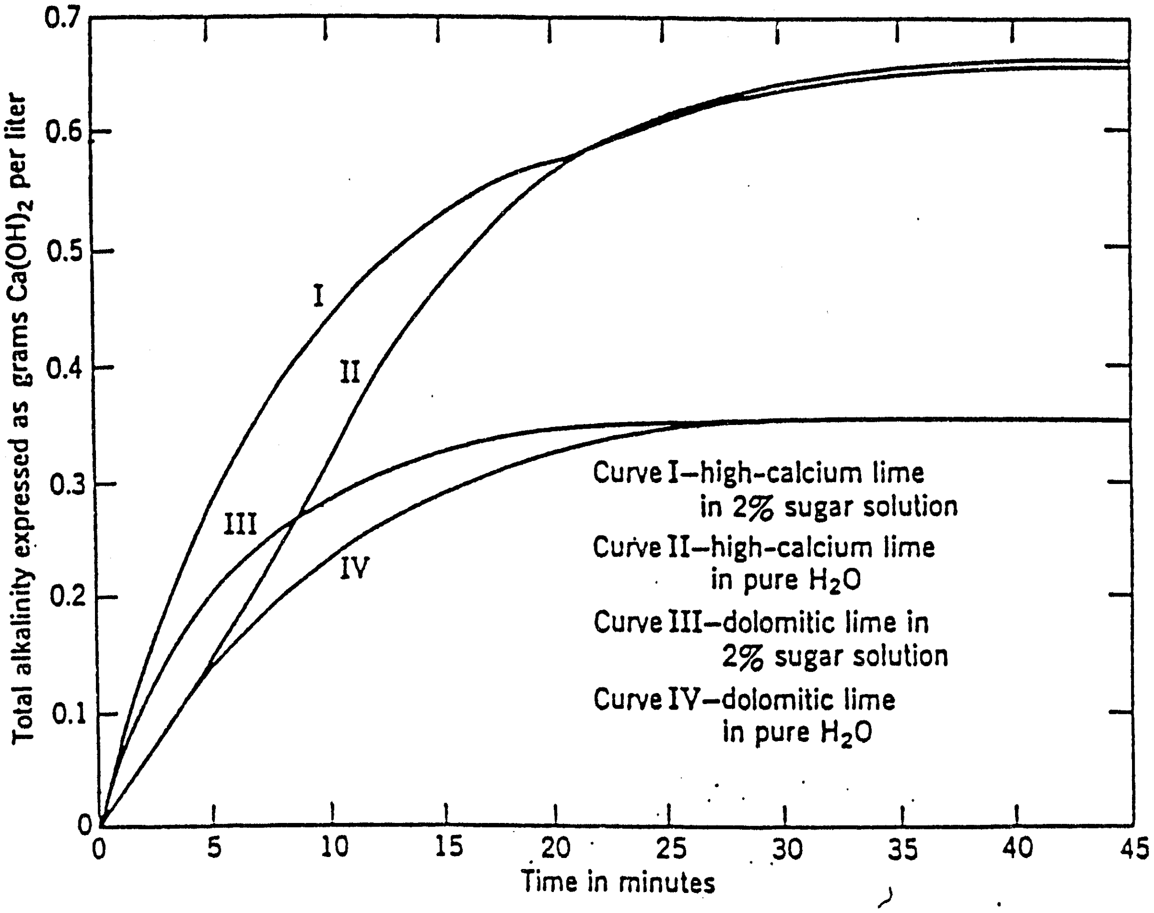

Figure 4. Rate of dissolution of limes, with and without sugar.
From Soynton, S.R., "Chemistry and Technology of Lime and Limestone", p.189, Interscience Publishers, a Division of John Wiley & Sons, Inc., (1967)

an additive are shown in Figure 5, and we can see that with small amount of sugar added the removal efficiency is increased over the baseline, but further increase of sugar (from 100mg/l to 500mg/l) leads to the decrease of the SO_2 removal efficiency. The removal efficiency improvement is about 10% at 20°F approach to saturation temperature.

Buffer: The pH at the surface of the droplets in spray dryer can drop well below 5 as SO_2 is absorbed, and this low pH value will inhibit further absorption of SO_2. The organic acid can be effected as a buffer for preventing the pH from falling too low. In the experiment, benzoic acid and formic acid were used as the organic acid buffer, and the test results are shown in Figure 6 and Figure 7. Little improvements on SO_2 removal were observed compared to baseline results. The benzoic acid used is in crystal form, and the addition is from 100mg/l to 500mg/l. The formic acid used is in liquid form (88% concentration), the addition is from 1ml/l to 5ml/l. The test results devaluated the organic acid buffer function which is considered effective in wet scrubber system. This probably is due the fact that $Ca(OH)_2$ particles can dissolute faster than the $CaCO_3$ particles, and the pH in the droplets will not go down to as low as 5 before the $Ca(OH)_2$ dissolution increases the pH. Since the organic acid buffers will not work until the pH falls low, the buffers will not have much value if the pH in the droplets maintains far above 5.

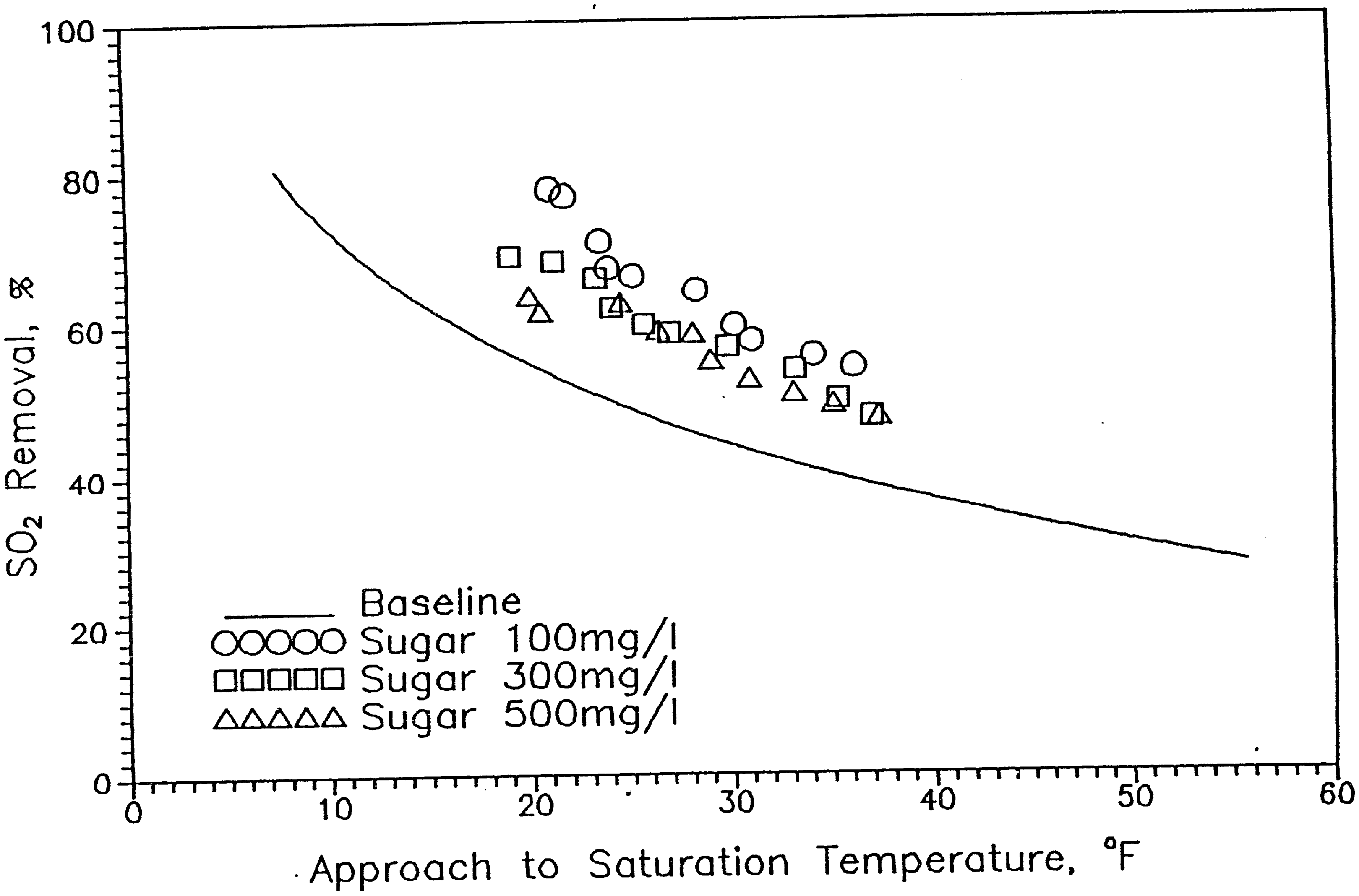

Figure 4. SO_2 Removal by $Ca(OH)_2$ with Sugar Additive

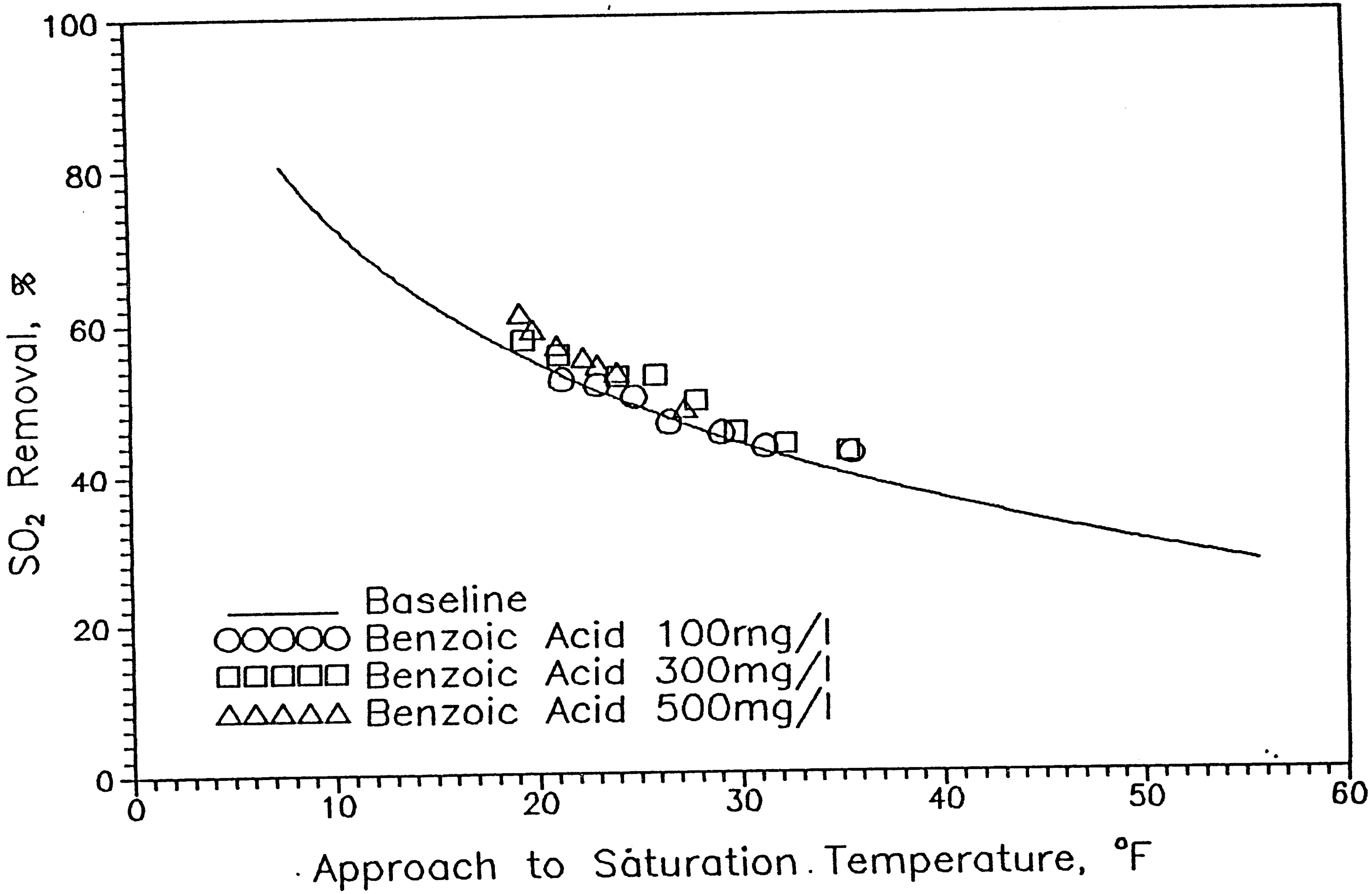

Figure 6. SO_2 Removal by $Ca(OH)_2$ with Benzoic Acid

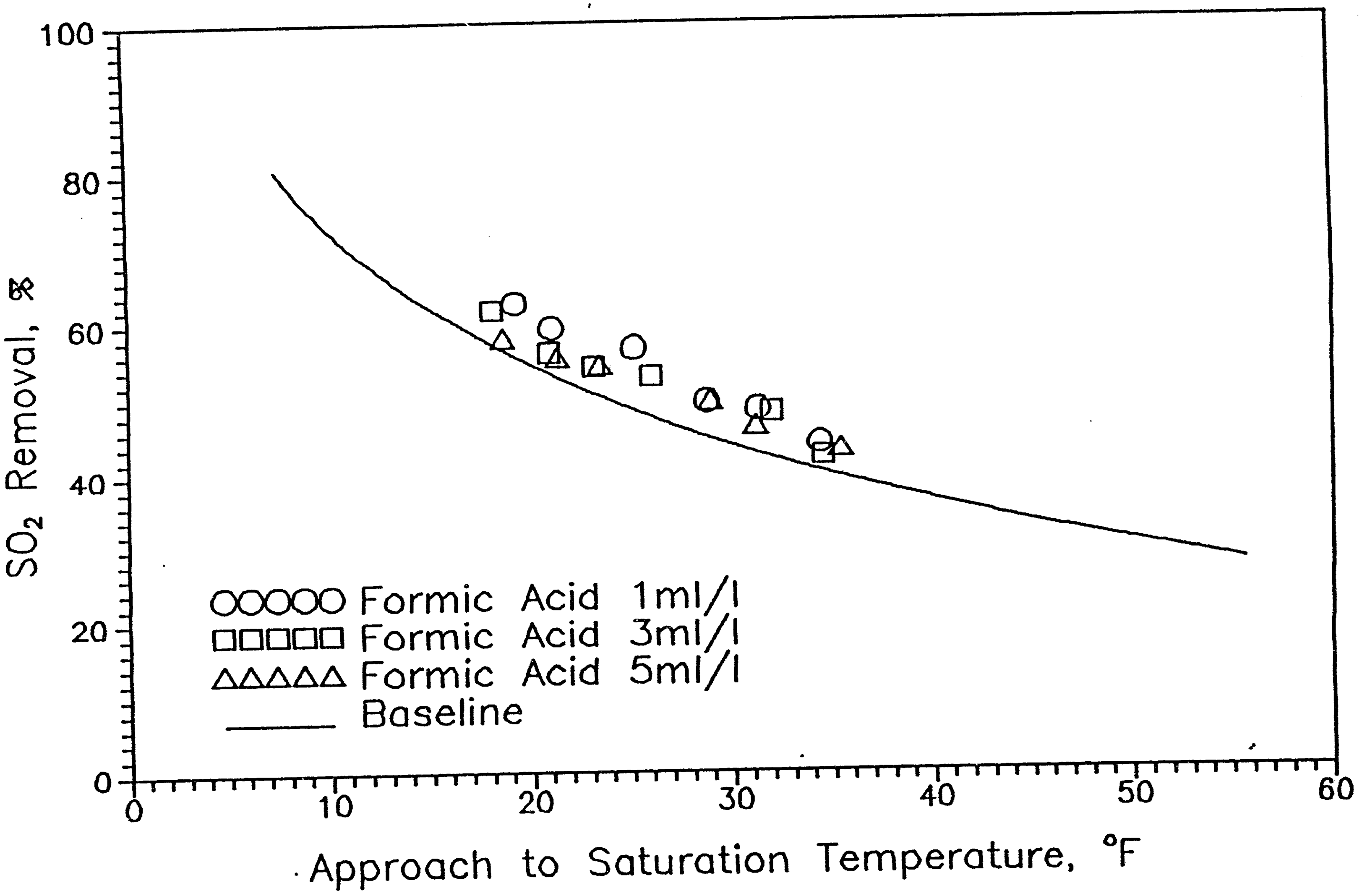

Figure 7. SO_2 Removal by $Ca(OH)_2$ with Formic Acid

Recycle Tests and Hydration of Fly Ash with $Ca(OH)_2$ to Increase Reactivity

Recycle of the Spray Dryer $Ca(OH)_2$ Reaction Product: Since there is certain amount of unreacted $Ca(OH)_2$ in the spray dryer product, most spray drying systems today recycle a portion of their waste solids back into the feed slurry. Recycle has been shown to increase sorbent utilization by allowing partially reacted sorbent to react further with the flue gas. In addition, recycle of fly ash together with $Ca(OH)_2$ has been shown to be more beneficial towards SO_2 removal than recycle of $Ca(OH)_2$ alone [2].

The recycle test results are shown in Figure 8 where the recycled spray dryer products are from a $Ca(OH)_2$ sorbent test. As can be seen, the SO_2 removal efficiency did not change for the 9.1% (by weight based on the CaO and recycled products, corresponding to Product/CaO = 10%) recycled products. The SO_2 removal decreased as the recycled products were increased to 23.1% (Product/CaO = 30%), and further SO_2 removal decrease was observed after the recycled products were raised to 33.3% (Product/CaO = 50%). Although with the increase of the recycled products the SO_2 removal efficiency was decreased, the decrease seems not so substantial as anticipated. This could be due to the fact that the utilization of $Ca(OH)_2$ in the baseline test is relatively low, and there is large amount of unused $Ca(OH)_2$ in the spray dryer products.

Recycle of Fly Ashes [8]: Although the SO_2 removing potential of fly ash/lime sorbents has been established in bench scale sandbed reactors [9][10][11][12] and in dry sorbent injection [13][14], their usefulness in spray drying applications has not been thoroughly studied. Jozewicz et al. [13] attempted to spray dry these solids in a pilot scale unit and found significant wet solids deposits on the wall at approaches to saturation lower than 75°C.

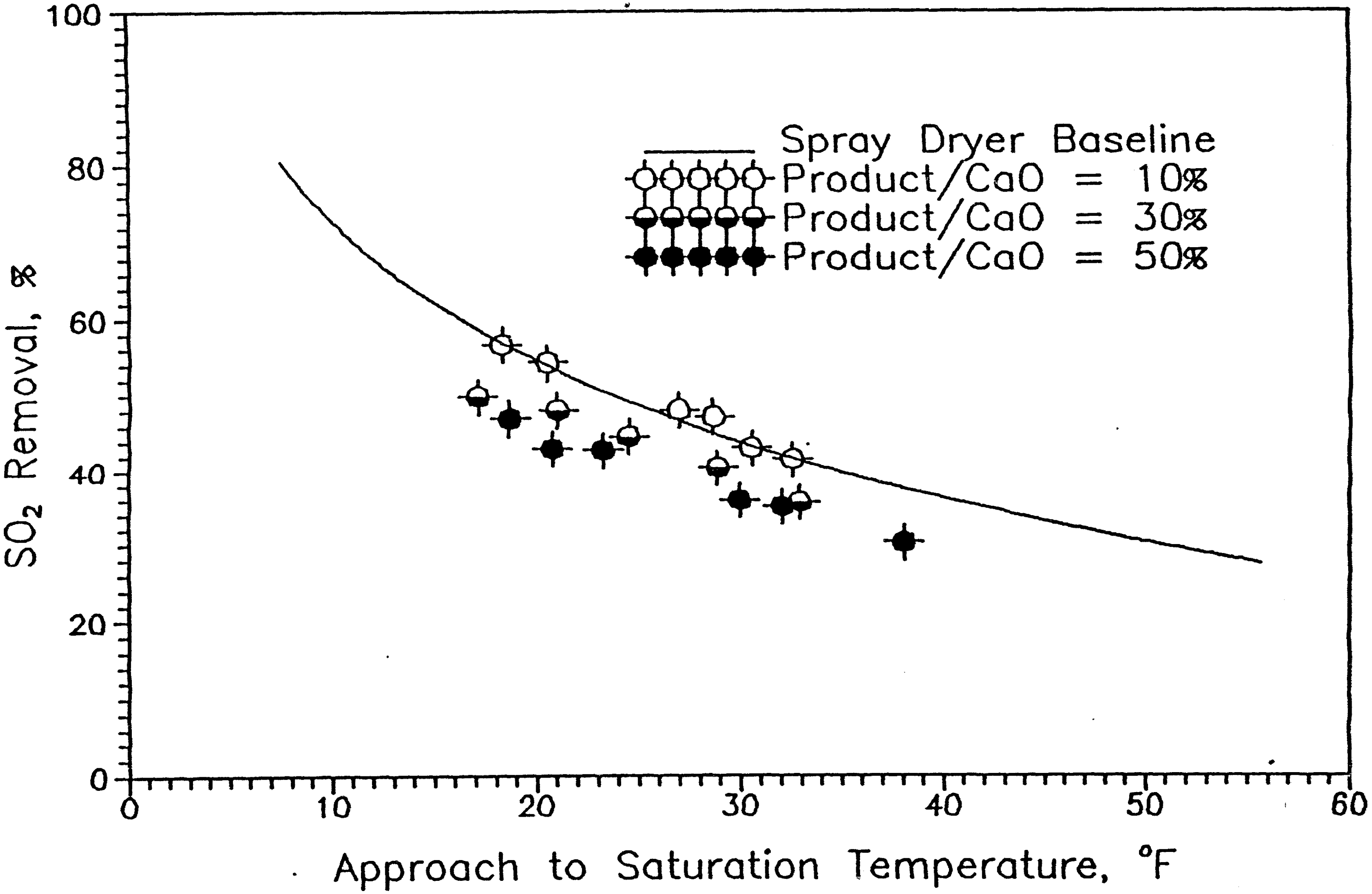

Figure 8. Recycle with $Ca(OH)_2$ Reaction Product

Petersen et al. [15] attempted the same in a bench scale spray dryer and did not experience a wall deposits problem. They did not, however, see any significant improvement in calcium utilization or SO_2 removal over $Ca(OH)_2$ alone. Nakamura et al. [16] attempted a bench scale spray drying study with heated slurries of fly ash, $Ca(OH)_2$, and gypsum, and reported removals of up to 30% over $Ca(OH)_2$ alone. This study examines the surface area development and strength development in mixtures of fly ash and hydrated lime and attempts to determine the benefit of using fly ash as a spray dryer additive.

The fly ashes used were obtained from the #7 and #8 boilers of Cincinnati Gas and Electric Company's Miami Fort (MF) Station. The MF7 ash was from a 2.1% sulfur coal and the MF8 ash was from a 0.7% sulfur coal. An analysis of the ashes can be found in Table I. The surface areas of the MF7 and MF8 ashes were measured to be 0.5 m^2/g and 1.2 m^2/g, respectively. Reagent grade $Ca(OH)_2$ from Fisher Scientific with a surface area of 13.9 m^2/g was used in forming fly ash/lime sorbents for surface area determination. Commercial grade quicklime from Dravo Lime Company was used to prepare sorbents that were tested in the spray dryer.

Bench scale sorbent samples consisted mostly of 4 parts fly ash to 1 part hydrated lime. The water:solids ratio was kept at 15:1. The samples were heated in a Fisher Scientific water bath at 80°C or 95°C for varying periods of time. After heating, the samples were filtered and a portion of the solids vacuum desiccated over night. The solids were then measured for surface area with a Quantachrome Monosorb single point BET machine.

Table 1. Mineral Analysis of Ashes on a % Ignited Basis
(Courtesy of Standard Laboratories, Inc., South Charleston, W.V., U.S.A.)

Fly Ash	MF7	MF8
SiO_2	49.77	56.51
Al_2O_3	23.76	28.53
Fe_2O_3	17.86	4.62
K_2O	2.21	2.39
TiO_2	1.65	2.08
CaO	1.59	1.49

Figure 9 displays the surface areas obtained from slurrying the MF7 and MF8 ashes with $Ca(OH)_2$ at a 4:1 ash/lime ratio at 95°C for varying amounts of time. The surface areas of both sorbents increased markedly with time, most likely due to the formation of high surface area hydrated calcium silicates and aluminates. The MF8 ash sorbents; however, developed on average higher surface areas than the MF7 ash sorbents. The reason for this seemingly greater pozzolanic activity in MF8 ash sorbents is probably that MF8 ash has more available silica and alumina than the MF7 ash. From Table I, one can see that the total percentages of silica and alumina are 85.04 in the MF8 ash and 73.53 in the MF7 ash.

Figure 10 displays the surface area results from heating 4:1 MF8/$Ca(OH)_2$ sorbentsat two different temperatures, 80°C and 95°C. The surface areas developed at 95°C were

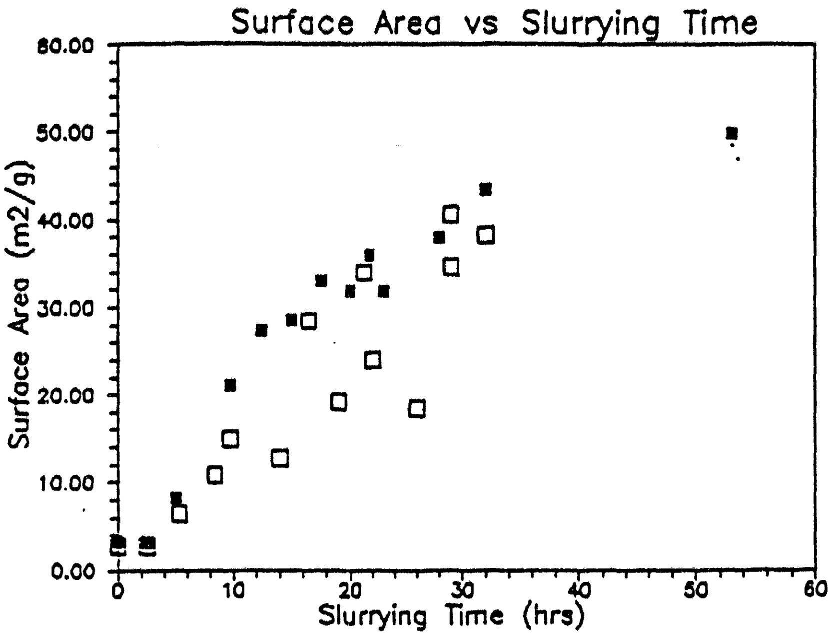

Figure 9. Surface Area Development in MF7 Sorbents (□) and MF8 Sorbents (■).

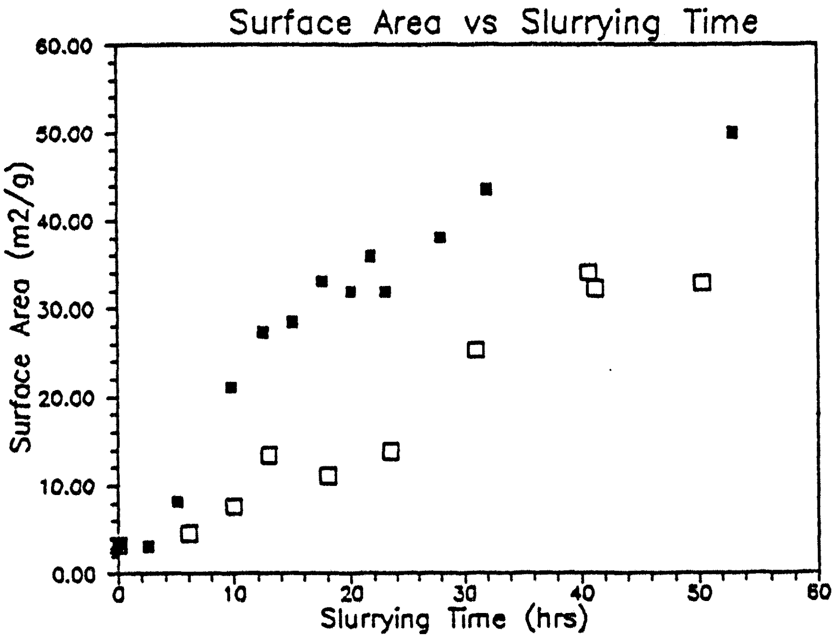

Figure 10. Surface Area Development in MF8 Sorbents heated at 80°C (□) and 95°C (■).

significantly greater than those developed at 80°C. Hence, the rate of the pozzolanic reaction increases with increasing temperature. The SEM photographs of the surface area developments are demonstrated in Appendix I.

Sorbents to be spray dried were made with varying ratios of fly ash and quicklime, but mostly 4:1 and 1:1. The solids loading of the slurries was kept at 10 %, which was the maximum that the two fluid atomizer could handle without clogging. In addition, the fly ashes were sieved through a 250 μm sieve to prevent large carbon black particles in the fly ashes from plugging the atomizer. Samples were heated in an insulated 150 L stainless steel drum by allowing steam to flow through the outer jacket. A steam solenoid and temperature controller kept the slurry temperature constant at 95°C.

The results of the spray dryer tests with the fly ash sorbents are in Figures 3,4, and 5. Figure 11 compares the spray dryer performance of the MF7 and MF8 ash sorbents. The average inlet SO_2 concentration was 2500 ppm. Both sorbents consisted of 4 parts ash to 1 part quicklime, and were hydrated at 95°C for 15h prior to testing. The MF8 sorbent proved to be more effective at removing SO_2 probably due to the reason given above.

Figure 12 displays the effect that the heating of a 4:1 MF8/quicklime slurry for 15h at 95°C has upon SO_2 removal in the spray dryer. The removal increased 20% at 11°C (20°F) approach to saturation, which translates into an increase in calcium utilization from 45% to 95%.

Figure 13 compares the SO_2 removal of a 12.8% $Ca(OH)_2$ solution (10% CaO prior to hydration) to three heated slurries each with a different amount of MF8 ash substituted for

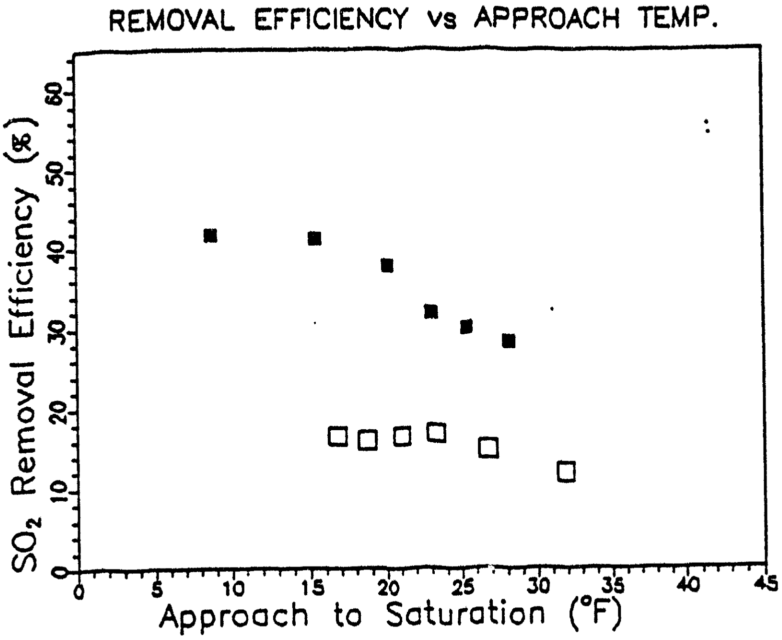

Figure 11. SO_2 Removal in Spray Dryer from MF7 Sorbent (□) and MF8 Sorbent (■).

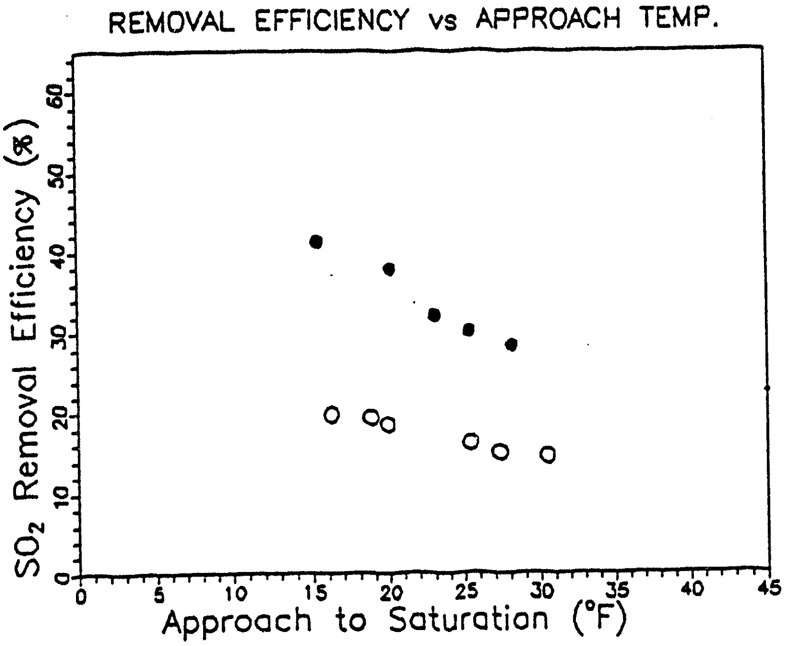

Figure 12. SO_2 Removal in Spray Dryer from Heated MF8 Sorbent (●) and Unheated MF8 Sorbent (○).

CaO. The objective of this set of experiments was to determine if the increase in calcium utilization noted above would lead to the existence of a fly ash/$Ca(OH)_2$ slurry that removed more SO_2 than the pure $Ca(OH)_2$ slurry. The fly ash loadings of the slurries were 20%, 50%, and 80%, and the heating time was once again 15h. None of the slurries removed as much SO_2 as the pure CaO slurry, although the 80% and 50% fly ash slurries were within 10% at 11°C (20°F) approach. Table II summarizes the SO_2 removal efficiencies and calcium utilizations of each slurry. The Ca utilization in the 0% and 20% fly ash slurries was only 30%, but rose dramatically as more fly ash was substituted. The 50% fly ash slurry had a Ca utilization of 45%, and the 80% fly ash slurry had a 95% Ca utilization. However, the presence of a large percentage of inert material in the fly ash plus the limit of 10% solids loading in the slurries imposed by the two fluid atomizer prevented the testing of a 4:1 fly ash/CaO slurry with heavier solids loading.

Additional sulfur uptake tests with MF7 and MF8 slurries were performed after the spray dryer tests to help verify the results obtained in bench scale and mini-pilot scale tests. Both ashes were slurried with $Ca(OH)_2$ at a 4:1 ratio. The solids loading was 10% in each case. Samples were heated at 100°C for 2 hours, cooled to room temperature, and then sparged with 2800 ppm SO_2 for 0 min, 5 min, or 30 min. After sparging the samples were filtered, dried overnight in a heated vacuum desiccator, and measured for sulfur content in a Leco sulfur analyzer.

Table 2. Removal Efficiency and Ca Utilization at 11°C Approach of Various Heated MF8/$Ca(OH)_2$ Slurries with Different Fly Ash/Quicklime Mass Ratios.

Fly Ash/CaO	Removal Efficiency (%)	Ca/S Ratio	Ca Utilization (%)
0:1	52	1.75	30
1:4	49.5	1.65	30
1:1	44	1.0	45
4:1	38	0.4	95

The results of the bench scale SO_2 sparging tests are located in Figure 14. The MF8 sorbent proved to be more reactive than the MF7 sorbent when reacted with SO_2 in solution for 5 minutes or 30 minutes. The unreacted MF8 sorbent contained approximately 0.3% more sulfur than the unreacted MF7 sorbent. However, the amount of additional sulfur picked up by the MF8 sorbent during the reaction was significantly greater. The MF8 sorbent had 0.9% more sulfur than the MF7 sorbent when reacted for 5 minutes and 2.8% more sulfur when reacted for 30 minutes. These results verify the greater reactivity of MF8 sorbents observed in the spray dryer and also show that this increase in reactivity is also present when the SO_2 reaction occurs in solution.

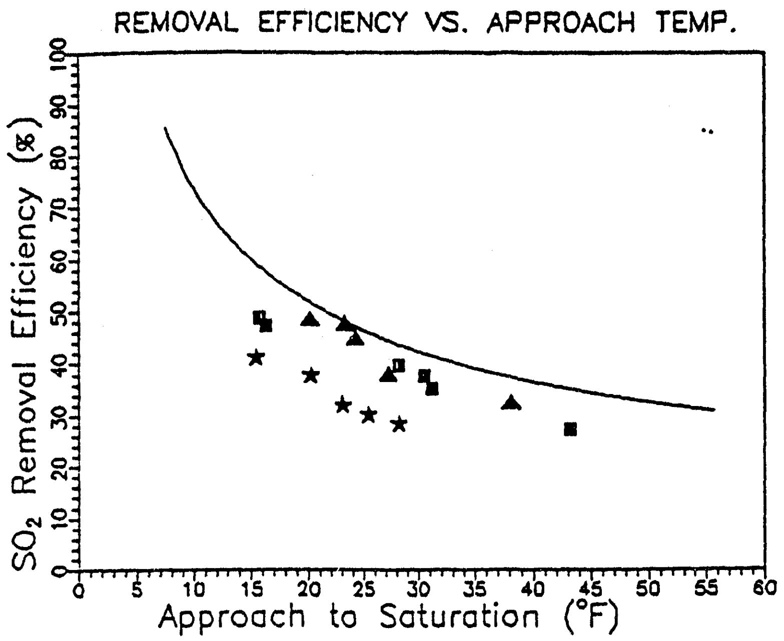

Figure 13. SO_2 Removal in Spray Dryer from Baseline CaO Slurry (-), 1:4 MF8/CaO Sorbent (▲), 1:1 MF8/CaO Sorbent (■), and 4:1 MF8/CaO Sorbent (★).

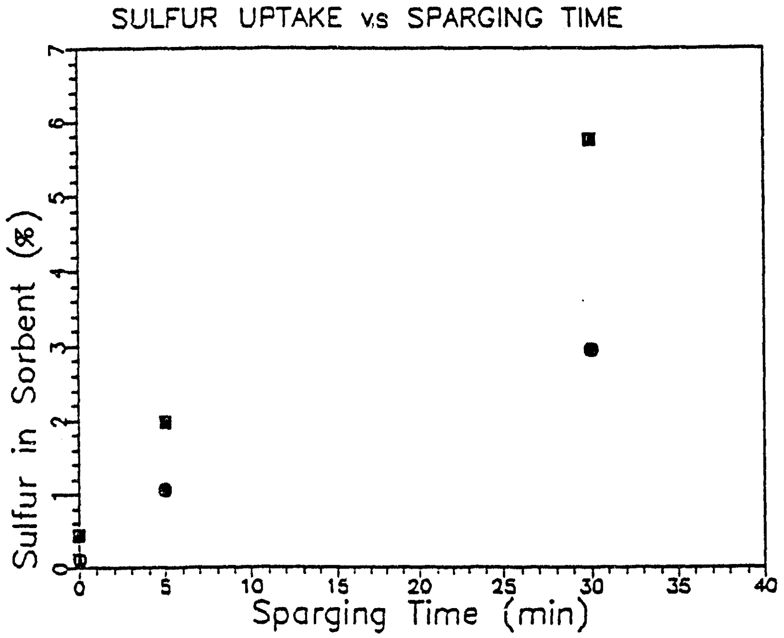

Figure 14. Sulfur Capture in Solution from Heated MF7 Sorbent (●) and heated MF8 Sorbent (■).

Limestone as an Alternative Sorbent and Additive Effects

Limestone Baseline Test: In wet limestone flue gas desulfurization (FGD) systems, the performance of the system depends on three limestone properties [17]; 1. reactivity, 2. hardness, and 3. composition. Reactivity is a measure of how rapidly a limestone dissolves under typical FGD chemistry conditions. In theory, a very highly reactive limestone requires less excess reagent in the scrubbing slurry to maintain a constant SO_2 removal efficiency (or achieves higher removals at a constant utilization). Hardness is a measure of the energy required to grind a limestone to FGD reagent size. With respect to composition, a high inert fraction (or a low calcium carbonate content) means there is less reactive carbonate available per gram of reagent. A limestone with a high dolomitic fraction will adversely impact scrubber performance since the reactive carbonate fraction of the feed reagent is lower. A limestone with a high soluble magnesium content can have either a positive or negative impact on performance, depending on system chemistry. This knowledge was used in the selection of the sorbent for the limestone/spray dryer tests.

A high calcium limestone (source: the Dravo Lime Company) and a lower calcium limestone were used for these tests. The typical analysis are given in Table 3 and Table 4 respectively.

One problem in the use of limestone as a sorbent in the spray dryer system is since the Ca/S ratio is inversely proportional to the molecule weight of the sorbent and the molecule weight of limestone (100g/mole) is almost twice as large as that of quicklime (56g/mole), If the same concentration (by weight) of limestone and quicklime is fed into the spray dryer, the Ca/S ratio of limestone is almost half as much as that of quicklime. Suppose there are two spray dryers and one with quicklime another with limestone as sorbents, the spray dryer with limestone must operate at almost twice as much solid load as the one with quicklime if the same Ca/S ratio is to be maintained.

The limestone of Dravo Lime Company was ground and sieved to two sizes. One is less than (<) 45um, and the another <38um. The limestone of National Lime & Stone Company were delivered in powder form which is less than 31um. A series of spray dryer tests were performed with the slurries at a solid concentration of 10% by weight and the simulated inlet flue gas SO_2 concentration of 2500 ppm. The spray dryer desulfurization results of <45um Dravo stone and <31um National stone are given in Figure 15, and the desulfurization results for Dravo's <45um and <38um stone are given in Figure 16. As shown in the Figure 15, the limestone form Dravo Lime Company has a higher reactivity, and the SO_2 removal efficiency of the <45um limestone is almost the same as that of the <31um limestone from National Lime & Stone Company. From Figure 16, the <38um limestone has slightly higher SO_2 removal than the <45um limestone at low approach to saturation temperature. But as the approach to saturation temperature increases, the difference in SO_2 removal is diminished.

The limestone particle size is a very important factor in wet FGD system performance (usually the size used is less than 45um), and large limestone particle external surface area could result in fast dissolution. Since the liquid-phase chemistry is similar for the coarse and fine-ground reagents, this indicates that the difference in performance is a result of difference in the available solid-phase alkalinity. The difference in available solid-phase alkalinity between fine- and coarse-ground limestones can be attributed to difference in the specific surface area (m^2/g) of the solid particles in the slurry. As the particles in the

Table 3

DRAVO LIME COMPANY
LIMESTONE
TYPICAL ANALYSIS

: **BLACK RIVER PLANT**

Chemical Analysis	1/2 x 0 ROMF
$CaCO_3$	94.5
$MgCO_3$	3.6
SiO_2	1.1
R_2O_3	0.48
Fe_2O_3	0.15
Al_2O_3	0.33
Sulfur (Total)	0.05

Physical Analysis

Screen Size	% Passing
3/4	99.0
1/2	96.6
3/8	83.4
No. 4	26.3
No. 8	15.8
No. 16	12.1

Types of Carriers Available: dump truck, barge

Foregoing Approved Data Reported by Keith Bingham
Effective 4/20/88

Table 4

National
Lime & Stone Company
Since 1903

Typical Analysis for Bucyrus Microfine

Chemical

Insolubles (including SiO_3)	2.5 %
Iron Oxide (Fe_2O_3)	0.2 %
Calcium Carbonate ($CaCO_3$)	80 %
Magnesium Carbonate ($MgCO_3$)	17 %
Sulfur (SO_3)	0.25%

Physical

Mesh	% Passing
100	99.9+
200	99.9
325	99.9

Average weight per cubic foot is 60 to 70 pounds.

Available in 50# bags only.

Shipping is spore (Bucyrus), Ohio.

The analysis set forth above is generally typical of the product described. NATIONAL LIME AND STONE MAKES NO WARRANTY OF FITNESS FOR ANY PARTICULAR PURPOSE, THE DETERMINATION OF SUITABILITY BEING THE SOLE RESPONSIBILITY OF THE PURCHASER AND USER. IN THE EVENT OF BREACH OF ANY WARRANTY OF ANY TYPE, THE SOLE REMEDY OF THE PURCHASER AND USER SHALL BE REPLACEMENT OF THE PRODUCT PURCHASED. SELLER SHALL HAVE NO LIABILITY FOR DAMAGES INCLUDING INCIDENTAL OR CONSEQUENTIAL DAMAGES.

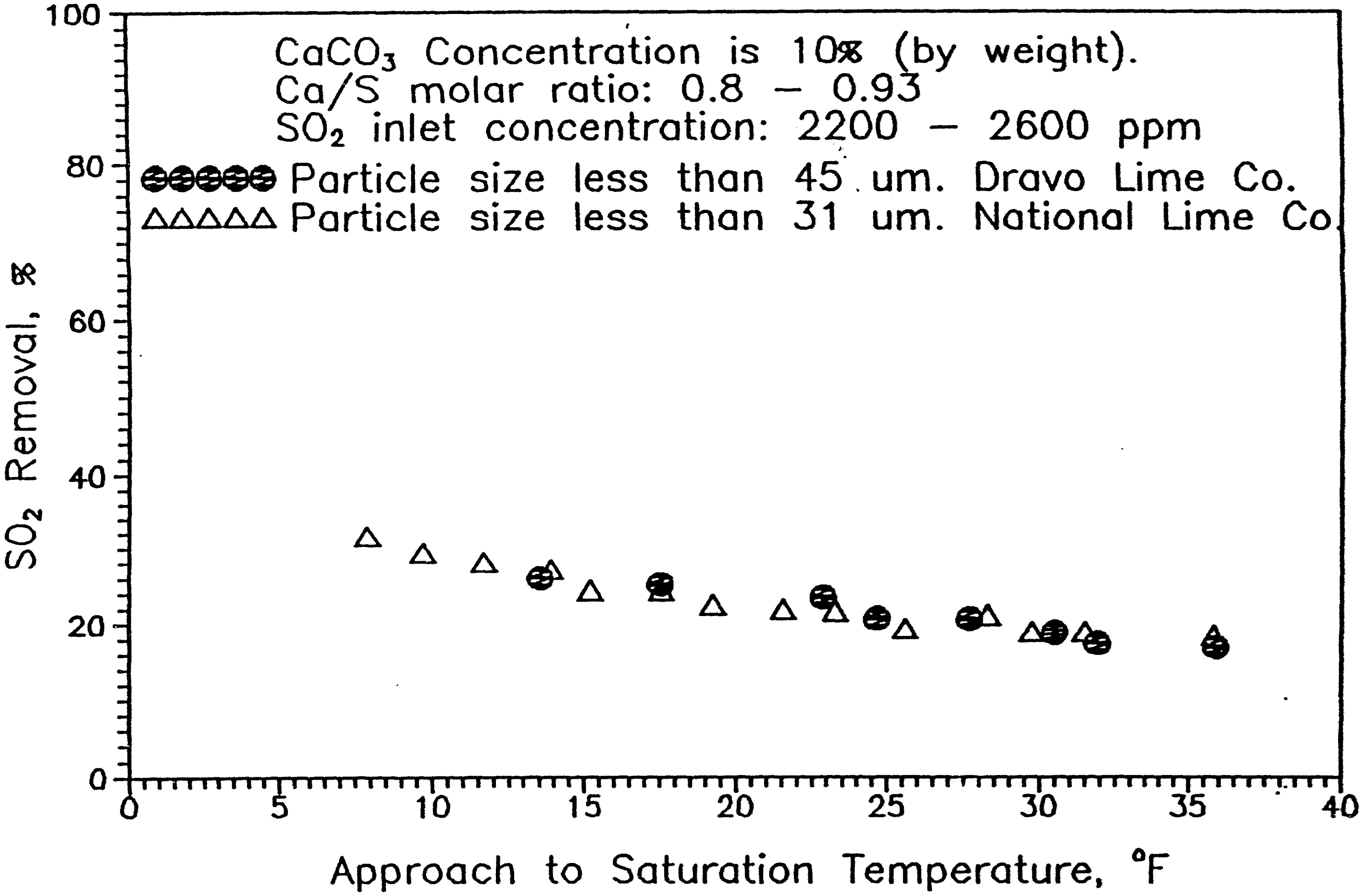

Figure 15. SO_2 Removal by <45um Dravo Co. and <31um National Co. Limestone

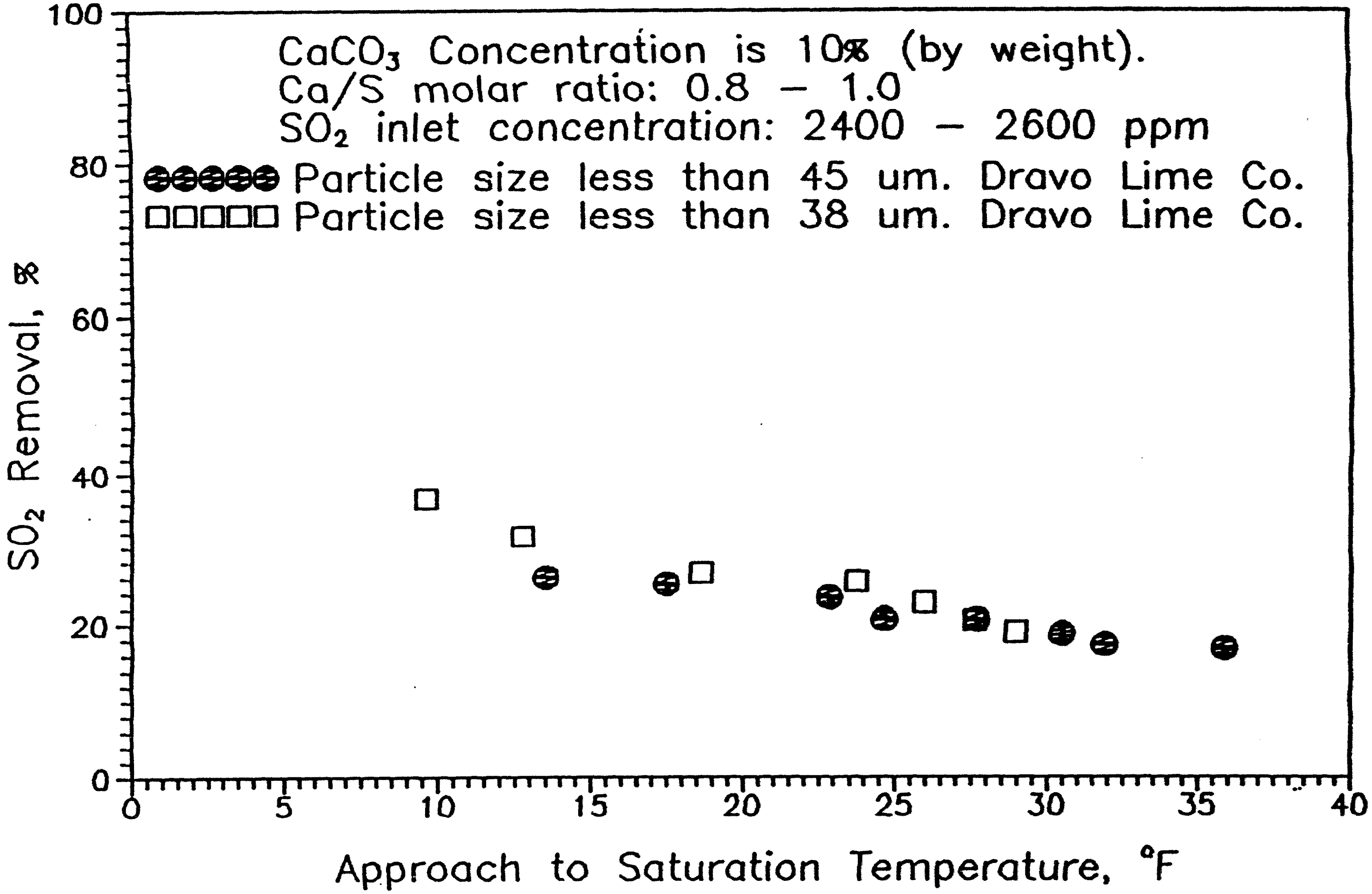

Figure 16. SO$_2$ Removal by <45um and <38um Dravo Limestone

reagent feed stream become smaller, the surface-area-to-mass ratio of the limestone particles also increases. Therefore, there is more reactive limestone surface area per gram of solids available to react with the absorbed SO_2 compared to a coarse-ground limestone. In the spray dryer system, a finer grind can also provide greater limestone particle surface area and therefore better performances. But since the SO_2 removal efficiency is largely determined by liquid alkalinities, and the liquid phase residence time is very short, the SO_2 removal improvement depends on how much dissolution rate increase can be offered by merely reduced the limestone particle size.

Limestone with Additives: Because of the reduction of limestone particle size, the increase of the total particle surface area in a slurry droplet enhances the total dissoluted $CaCO_3$ in a certain time interval whereas the dissolution rate of limestone is slightly changed by the increase of surface area, as demonstrated in the following formula [18].

$$\ln(DR) = a + b_1(TP) + b_2(pH) + b_3\ln(STIR) + b_4\ln(TSA) + b_5\ln(Mg)$$

where,
a = intercept constant
DR = the dissolution rate of calcium or magnesium (mg/g.min)
TP = the inverse of temperature (1/°K)
pH = the solution pH
STIR = the stirring rate in the reactor (rpm)
TSA = the total surface area of the test material (cm^2/g)
Mg = the magnesium concentration in the reactor feed solution (mg/l)

The constant b_1 and b_2 are in negative values, and b_4 is in positive value while the signs of a, b_3 and b_5 values depend upon the specific limestones.

Literature review made by Meserole etc. [18] indicated that six different rate forms exist describing $CaCO_3$ dissolution kinetics. At low pH (<4), the rate is reported to be directly proportional to the hydrogen ion concentration and is thought to be diffusion controlled. At pH values between 4.5 and 7.0, the dissolution rate is directly proportional to pH, and is thought to proceed via adsorption phenomena. At higher pH levels, the rate of dissolution has been correlated with the difference between the square root of solubility product constant and the square root of the product of calcium and carbonate concentrations.

Magnesium has been shown to reduce the limestone dissolution rate. This was explained by the adsorption of magnesium ions onto the crystal surface, thereby inhibiting dissolution in much the same way as phosphate ions. The presence of sulfate ions has been shown to enhance the dissolution rate as have been strontium. barium, and benzoic acid.

From a FGD process point of view, pH is one of the most important variables that can affect the dissolution of limestone, but pH is also one of the most important variables that affect the mass transfer of SO_2 into the droplets. Since $SO_{2(g)} \rightarrow SO_{2(aq)}$, $SO_{2(aq)} + H_2O \rightarrow H_2SO_3$, and $H_2SO_3 \rightarrow H^+ + HSO_3^-$, at low pH (high H^+ concentration), these equilibriums are difficult to move toward RHS (right hand side). Based on these facts, the additives were chosen to possess such properties that either they can oxidize H_2SO_3 into H_2SO_4 because H_2SO_4 can dissolute completely at low pH, or they have buffer effects since buffer solution can keep the pH from falling too low. In the additive tests, the limestone sorbent used is <45um limestone from Dravo Lime Company. H_2O_2 was chosen as the oxidizing additive, and the test results are shown in Figure 17 where the SO_2 removal efficiency has been slightly increased by the H_2O_2 additive. Formic acid and benzoic acid were used as the buffer acids, and the test results are shown in Figure 18 and Figure 19 respectively. It can be seen from the figures that these two organic acids buffers have no effects on the SO_2 removal by limestone.

The poor effects of additives on limestone utilization are related to two combined facts. One is the short liquid phase residence time of the sprayed droplets, and another is the low solubility and dissolution rate of limestone particles. As the droplets get into the hot flue gas, the water will be evaporated within less than about two seconds. In this short period, SO_2 will diffuse into the droplets, neutralize the meager OH^- ions, and reduce the pH of the solution. Then SO_2 stops diffusing into the droplets because of the low pH of the solution. When the SO_2 is waiting for the limestone particles to slowly dissolute into the liquid phase to deliver the needed alkalinity, the fast evaporation dries up the liquid. The application of limestone in the spray dryer system largely depends on how to improve the limestone dissolution rate.

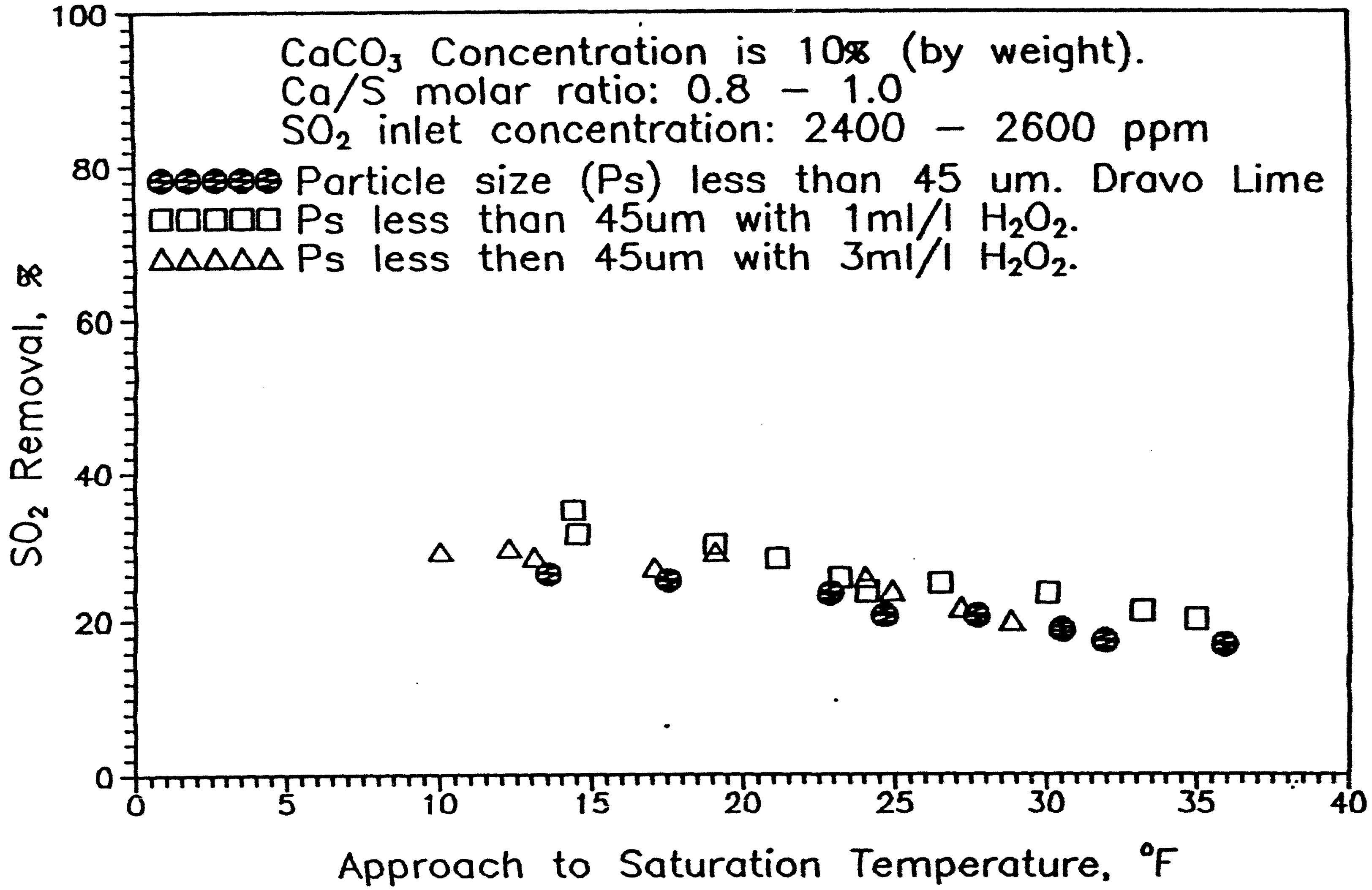

Figure 17. SO_2 Removal by <45um Dravo Limestone with H_2O_2 Additive

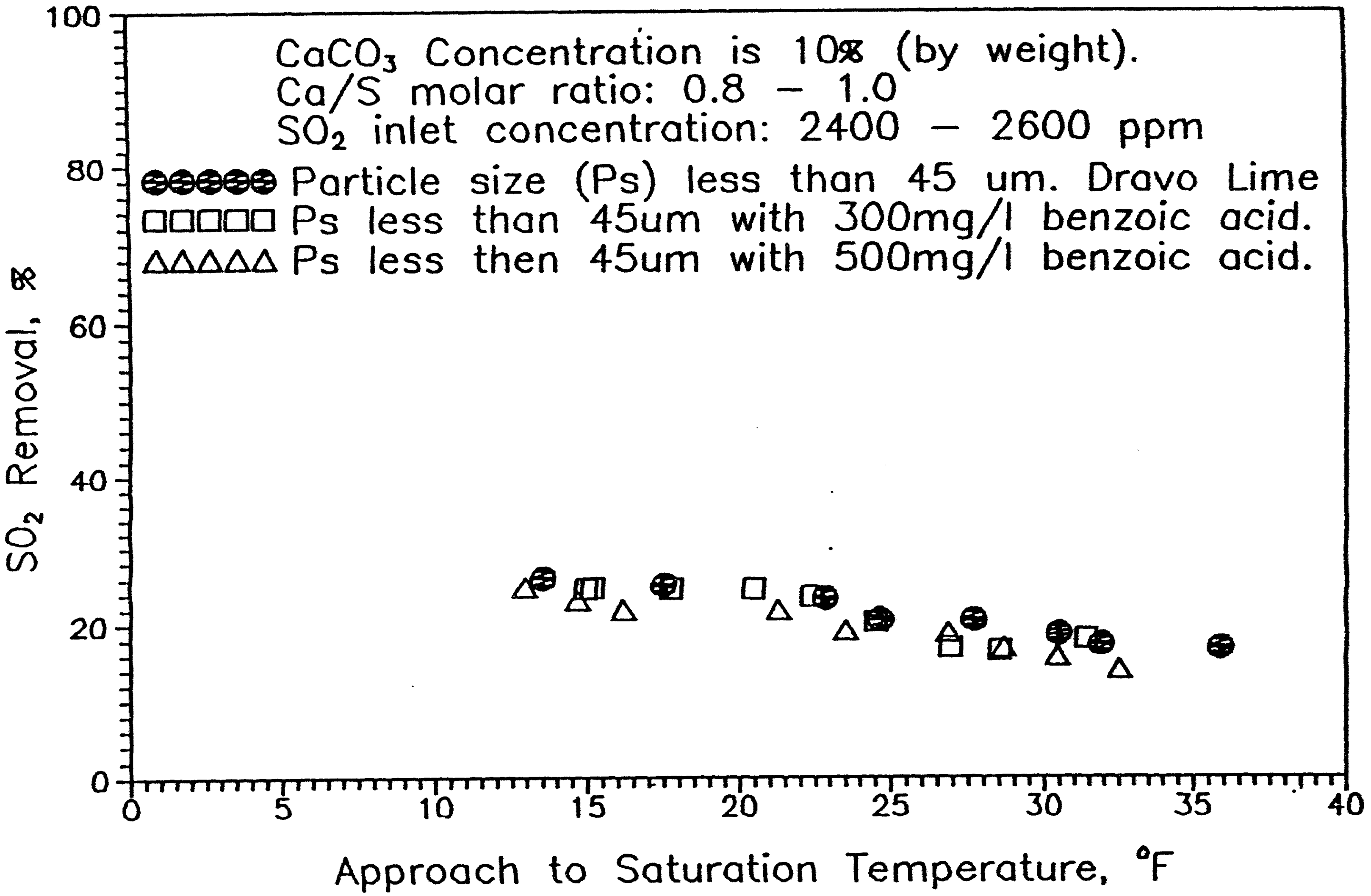

Figure 18. SO_2 Removal by <45um Dravo Limestone with Benzoic Acid Additive

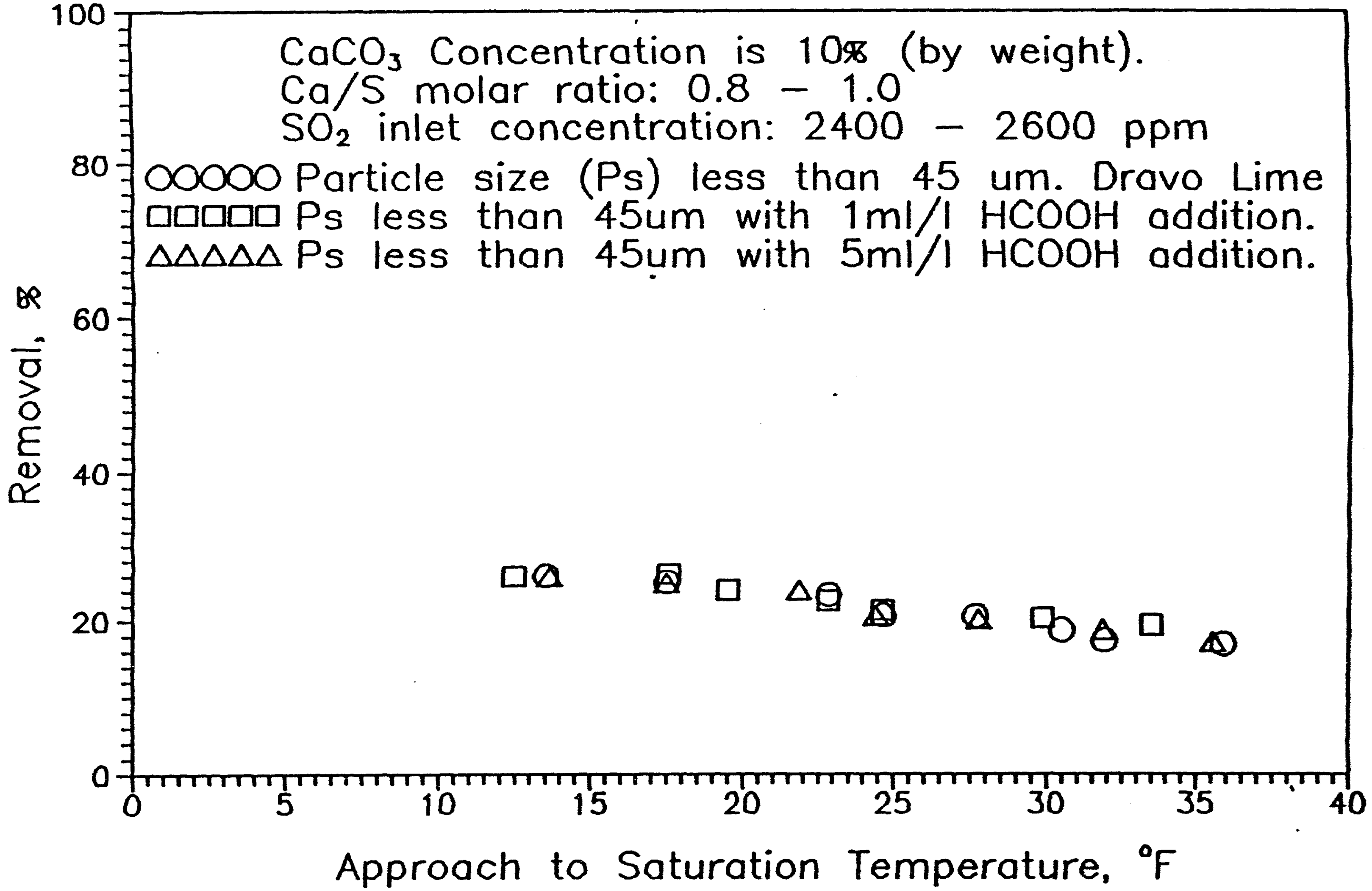

Figure 19. SO_2 Removal by <45um Dravo Limestone with Formic Acid Additive

Physical and Chemical Model developments for Some of the Additives and Spray Dryer Mathematical Model Applications

The Mechanism of Hygroscopicity

The enhancement of sorbent utilization due to the hygroscopicity of additives can be explained as following. Since the insoluble solids in slurries and pastes (referred to as suspensions) have negligible vapor-pressure lowering effects, the total drying time of the lime slurry droplets containing insoluble and dissolved solids can be evaluated as the drying time as if the liquid contained only dissolved species. Since nearly all the sodium salts have high solubilities and vapor-pressure lowering effects (see Table 5 and Figure 20, from Perry's Chemical Engineer's Handbook, 1984 [19]), therefore the dissolved sodium salts can increase the residence time of the liquid phase in droplets. Since most of the reactions take place more effectively in the liquid phase, the prolonged residence time has a significant effect on SO_2 removal.

Table 5. Solubilities of Ca^{2+} and Na^+ related Substances (g in 100g H_2O)

Substances	Temperature				
	20°C	30°C	40°C	60°C	80°C
$CaCl_2 \cdot 6H_2O$	74.5	102	-	-	-
$CaCl_2 \cdot 2H_2O$	-	-	-	136.8	147.0
$Ca(OH)_2$	0.165	0.153	0.141	0.116	0.094
$CaSO_4 \cdot 2H_2O$	-	0.2090	0.2097	0.2047	-
$NaHCO_3$	9.6	11.1	12.7	16.4	-
$NaCl$	36.0	36.3	36.6	37.3	38.4
$NaOH \cdot 1H_2O$	109	119	129	174	-
Na_2SO_4	-	-	48.8	45.3	43.7

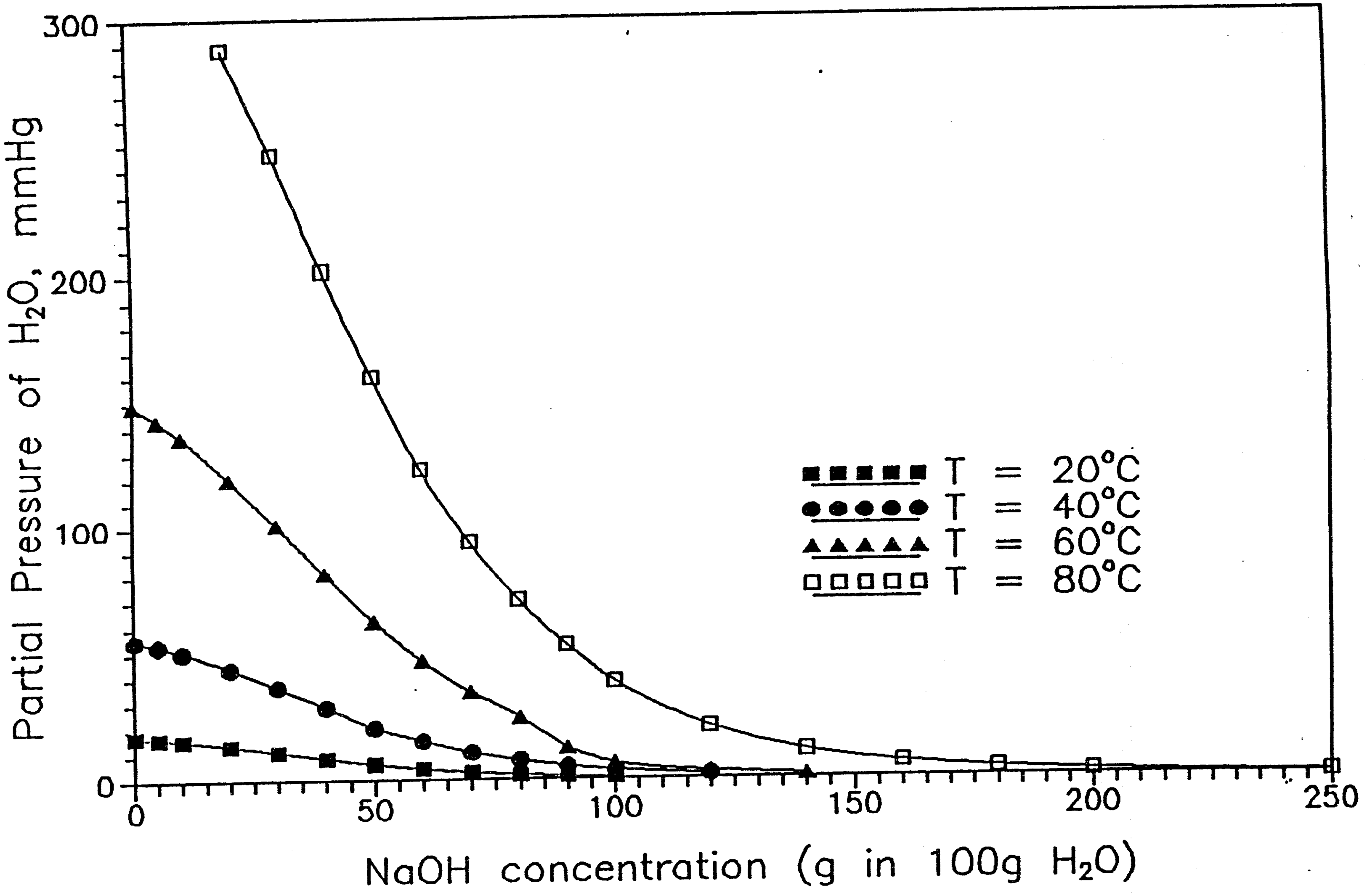

Figure 20. Water Vapor Partial Pressure Over Plane NaOH Solution

When water evaporates from the droplets in the spray dryer, the salt concentration in a droplet will increase with decreasing droplet size if the salt is highly soluble because the mass of the salt remains constant and it is only the water that evaporates. Thus, a given mass of dissolved salt serves to reduce the vapor pressure at the droplet surface to a greater degree as droplet size decreases. In competition with this trend is the Kelvin effect that causes an increase in vapor pressure as droplet size decreases. The relationship between saturation ratio and droplet (containing dissolved material) size is given by Hinds [20]:

$$\frac{p}{p_s} = \frac{1}{1 + \dfrac{6imM_w}{M_s \rho \pi d_p^3}} \cdot \exp\left(\frac{4\gamma M_w}{\rho R T d_p}\right) \tag{1}$$

Where,

P = the partial pressure of water vapor at the droplet surface.

P_s = the saturation pressure at the plane surface of pure water.

M_s = molecular weight of dissolved salt.

m = the weight of dissolved salt in the droplet.

i = # of ions each molecule of salt forms when it dissolves, 2 for NaOH.

ρ = density of water (or solvent).

M_w = molecular weight of water.

γ = surface tension of water.

d_p = droplet diameter.

R = ideal gas law constant.

T = temperature of the droplet.

In the spray dryer the Kelvin effect may be small because of the relatively large droplet size, but from the above formula we can see how the additive salts affect the partial water vapor pressure at the droplet surface. If keeping other variable to be constant, the salts change the partial pressure through im/M_s term. In other words, in order to get a greater reduction of the water vapor pressure on a droplet surface, higher concentration of the dissolved salts in the droplet, more ions each dissolved salt molecule forms, and less molecular weight of the salts are required. A comparison of the im/M_s term for different substances is shown in table 6.

Table 6. Comparison of the im/M_s term for different substances

Substance	NaOH	$NaHCO_3$	NaCl	$CaCl_2$	Na_2SO_4
i	2	3	2	3	3
M_s	40	84	58.5	111	142
im/M_s	0.05m	0.036m	0.034m	0.027m	0.021m

From the table, it is obvious that if m (the mass of the dissolved salts) is kept constant for all the substances, NaOH has the more potential for retaining the moisture...

Figure 21 gives pressure ratio vs droplet size under the influence of additives. The pressure ratio is the ratio of the water vapor pressure on the droplet surface to the water vapor pressure on a plane surface of pure water. The calculation was made from equation (1). The saturated concentration of $Ca(OH)_2$ is 1280 mg/l which is at the temperature of 50°C. Obviously, NaOH has the most significant vapor pressure lowering effect.

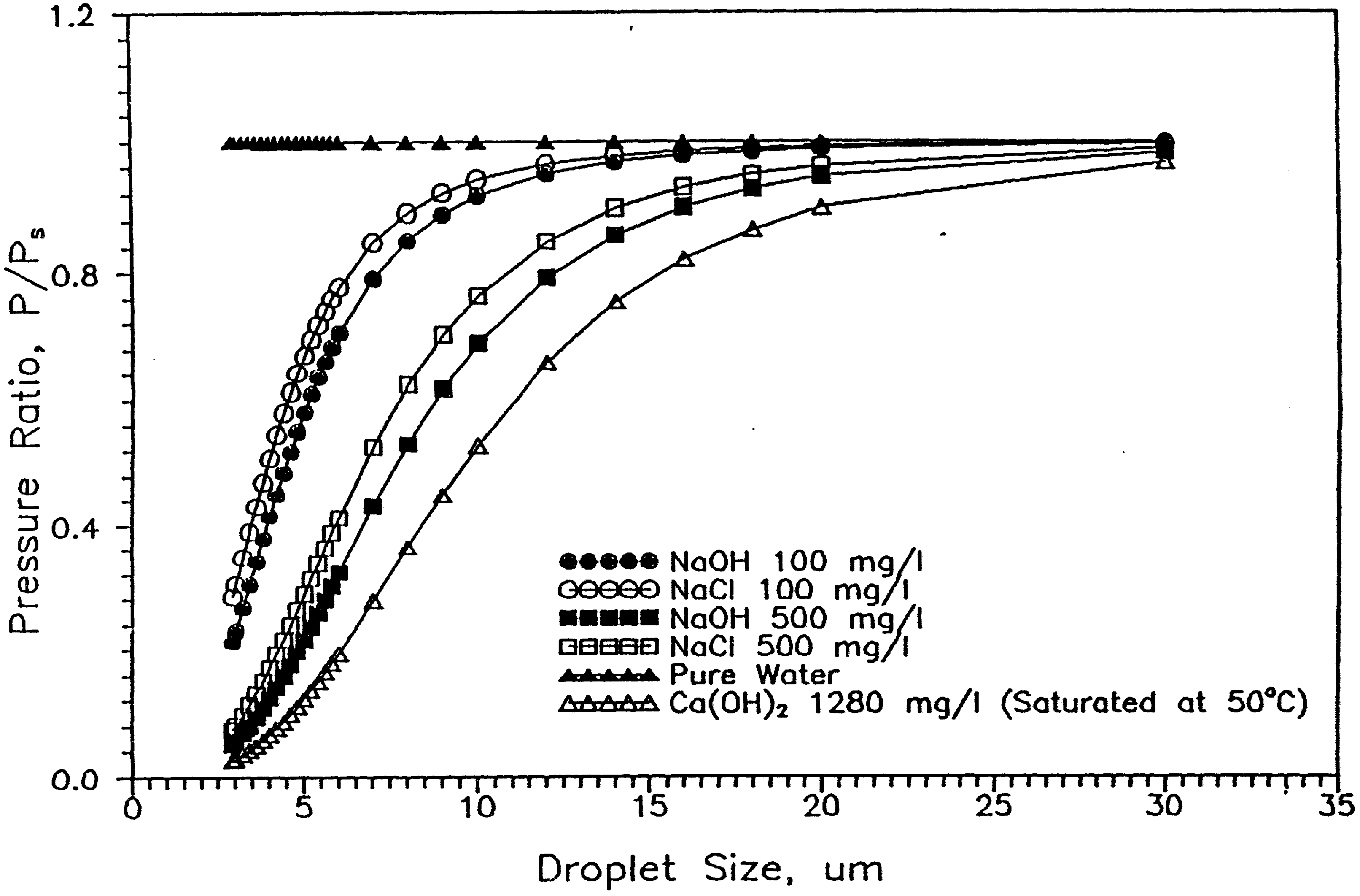

Figure 21. Water Vapor Pressure Ratio of Droplet Surface to Plane Pure Water Surface vs Droplet Size

Mathematical Model Applications

The modified spray dryer mathematical model was used as a model prediction for the spray dryer performance. This model was initially developed by Damle, S.A.[4] and later modified by Partridge, P.G. Jr. [5].

The initial Model (named as SPRAYMOD) was observed to be less sensitive to the effects of slurry concentration and SO_2 concentration than the observed data [5]. SPRAYMOD tended to underpredict at low slurry concentrations and overpredict at high slurry concentrations. SPRAYMOD neglected the liquid phase mass transfer resistance and calculated the SO_2 removal during the evaporation/reaction process considering only the individual resistance that was dominate.

By considering the approach in the SPRAYMOD in error, the modified model only borrowed the material and energy balance calculations from the program SPRAYMOD. The modified model (named as SPRAYMOD-M) aimed at developing a comprehensive model for the constant rate period using a mechanistic approach which combines the individual resistances that affect the SO_2 absorption rate into a single relationship. Both the gas phase mass transfer and liquid phase mass transfer coefficients were included as well as a relationship to predict the resistance to lime dissolution. The model was based on film theory and treated the atomized slurry droplet as a sphere of discrete sorbent particles with the fluid phase uniformly distributed around the individual sorbent particles. This approach was said to allow predictions of the mass transfer coefficients and the enhancement due to increasing solid concentration as evaporation proceeds. Efficiency predictions using the new model had been compared with the pilot -plant data taken the pilot spray dryer/baghouse facility using a slipstream of the University of Tennessee's stoker fired boilers.

Based on the available SPRAYMOD-M model from the University of Tennessee, a model calculation was made, and the results were compared to the experimental data. As shown in Figure 22, in the model prediction of SO_2 removal efficiency vs Ca/S molar ratio the model results overpredicted the SO_2 removal from our experiments, but underpredicted the SO_2 removal from the EPRI's High Sulfur Test Center. Figure 23 gives the model prediction of SO_2 removal vs approach to saturation temperature and the experimental data as a comparison. It can be seen from Figure 23 that the model underpredicted the SO_2 removal for baseline under 14°F approach to saturation temperature, but it overpredicted the SO_2 removal for baseline above 14°F approach to saturation temperature. The SO_2 removal of the model prediction is always below the removal with the $Ca(OH)_2$ and additives combination.

Table 7 gives a list of the parameters and standard operating conditions which are typical in our mini-pilot plant. The stoichiometric Ca/S molar ratio was varied from 0 to 3.0, and the approach to saturation temperature from 5°C (9°F) to 30°C (54°F). When either of them was changed, the other was kept constant in the standard condition listed in Table 7.

Table 7. SPRAYMOD-M Operating Parameters and Standard Conditions

List of Parameters	SI Units	Eng. Units
Inlet Gas Conditions		
Inlet Gas Temperature	149°C	300°F
% Water in Inlet Gas	1%	1%
Inlet SO_2 Concentration	2500 ppm	2500 ppm
Molecular Weight of Dry Inlet Gas	28.9	28.9
Operating Parameters		
Approach to Saturation Temperature	11°C	20°F
Stoichiometric Ca/S Molar Ratio	1.5	1.5
Mass Fraction of Sorbent in Fresh Solids	1.0	1.0
Recycle Solids Ratio by Mass	0.0	0.0
Mass Fraction of Sorbent in Recycle	0.0	0.0
Residence Time of Gas Phase	10 sec.	10 sec.
Flow System in Spray Dryer	Plug	Plug
Sorbent Properties		
Inlet Droplet Diameter	100 um	100 um
Inlet Droplet Temperature	15.6°C	60°F
Form of Sorbent	Slurry	Slurry
Sorbent Particle Diameter	3.5 um	3.5 um
Molecular Weight of Sorbent	74	74
Density of Solid Sorbent	2.24 g/cm^3	140 lb/ft^3
Critical Moisture Content	29.2%	29.2%
Equilibrium Moisture Content	6%	6%
Dry Sorbent Reaction Rate Coefficient	0.0	0.0
Assumed Spray Dryer Efficiency	50%	50%
Program Parameters		
Maximum Allowable Time Step	0.1 sec	0.1 sec
Time Between Printouts	0.5 sec	0.5 sec
Time Step Control Parameter	0.01 sec	0.01 sec

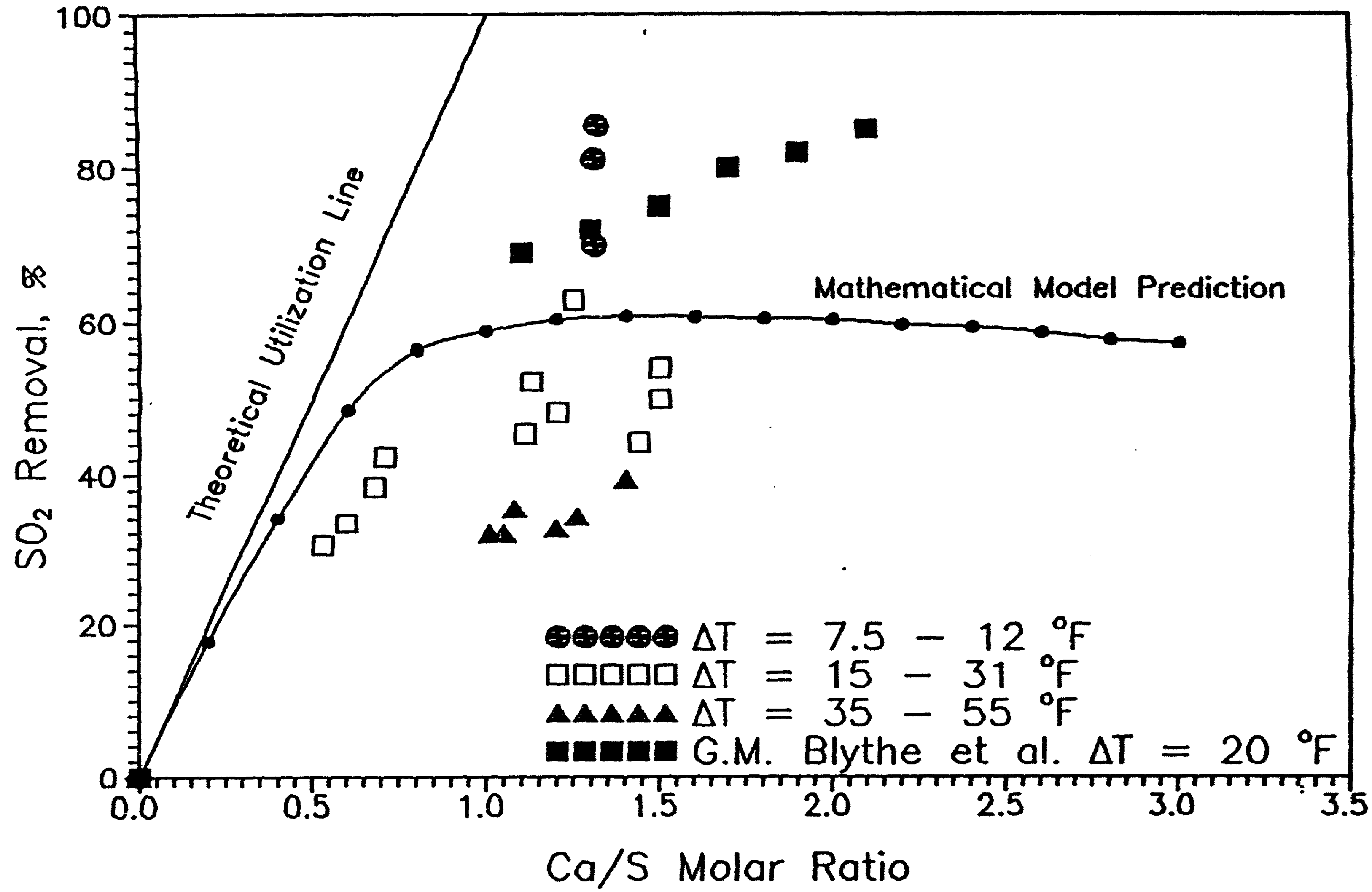

Figure 22. SO_2 Removal vs Ca/S Molar Ratio for Baseline $Ca(OH)_2$

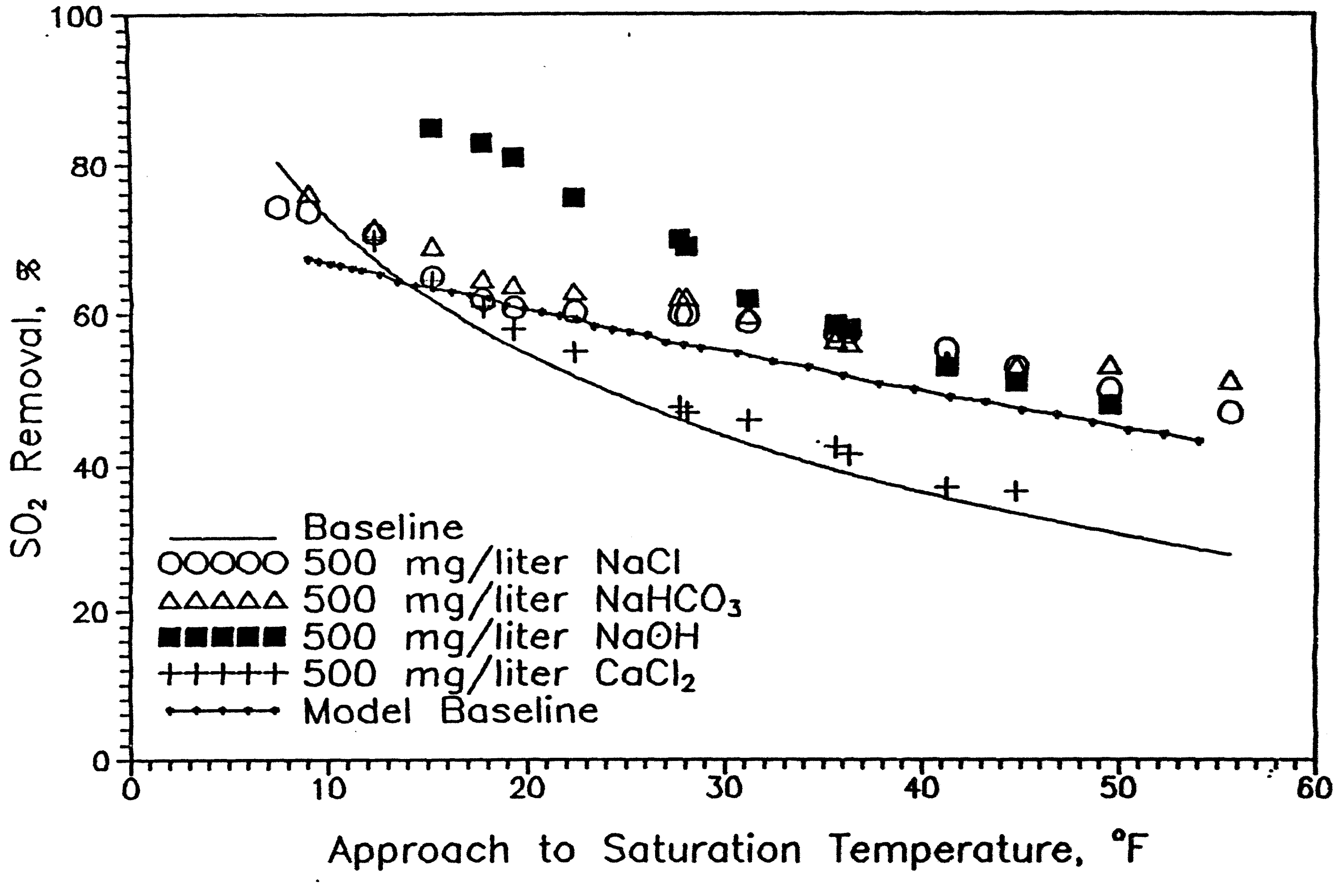

Figure 23. SO_2 Removal vs Approach to Saturation Temperature

Modification to the Ca/S Molar Ratio Calculation

Due to the water content in the spray dryer reaction product especially the product on the wall of the spray dryer, the original Ca/S molar ratio calculation formula tends to under-calculate the Ca/S ratio. The Ca/S molar ratio calculation was modified by a modification factor which considers the water content in the product. The modification factor is shown in equation 2.

$$\alpha = \frac{1}{\frac{1}{p} - \frac{c}{1-c} \cdot \frac{x}{1-x} \cdot \left[(1-w)\frac{M_h}{M_c} + w\frac{M_s}{M_c} + \frac{1}{p} - 1\right]} \qquad (2)$$

Where,

p = Purity of lime (percent of CaO).

x = Product water content (percent unbound moisture in the product).

w = percent CaO which is converted to $CaSO_3$.

M_h = Molecular weight of $Ca(OH)_2$.

M_s = Molecular weight of $CaSO_3$.

M_c = Molecular weight of CaO.

The product deposited on the spray dryer wall holds a lot of moisture which consists of the major error in the original formula calculation for Ca/S ratio. This new modification factor times the original calculated Ca/S ratio should give a close estimate of the true Ca/S molar ratio.

Conclusion

Hydrogen peroxide which can oxidize SO_3 forms into SO_4 forms has significant effect on enhancing sorbent utilization and increasing SO_2 removal efficiencies. Sugar which can increase the dissolution rate of $Ca(OH)_2$ has some positive effects on sorbent utilization with small amount addition, but with the sugar concentration increased the utilization will decrease. Benzoic acid and formic acid which have buffer effects have little effects on the $Ca(OH)_2$ sorbent utilization in the spray dryer system.

In the recycle test, a 9.1% recycled spray dryer $Ca(OH)_2$ products almost has no adverse effects on the overall system SO_2 removal. However, when the recycled product were raised to 33%, the SO_2 removal was decreased by about 10%. Fly ashes have been slurried with quicklime at elevated temperatures to enhance spray dryer performance. Bench scale experimental results indicate that this hydration process greatly increased the total surface area of the solids. Mini-pilot scale tests in the spray dryer reveal that the heating step significantly increases calcium utilization and SO_2 removal of these fly ash/quicklime sorbents.

Limestone type and size have certain effects on the spray dryer SO_2 removal, but the test results indicated that using limestone in the spray dryer for desulfurization is not very encouraging, and no very effective additives were found for limestone applications. The reasons are postulated as the following: The Ca/S of $CaCO_3$ is almost half as much as that of CaO if the same concentration (by weight) is fed into the spray dryer, and this leads to high slurry concentration and heavy spray nozzle loading. The low solubility and dissolution rate of $CaCO_3$ and short liquid phase residence time (the high slurry concentration will make the residence time shorter) of the sprayed droplets are considered combining to reduce the effectiveness of limestone for SO_2 removal.

In the theoretical study, the enhancement of sorbent utilization due to hygroscopicity of additives has been investigated, and a relationship between saturation ratio and droplets containing dissolved material has been given. This relationship explains the hygroscopicity phenomena. The modified SPRAYMOD model has been used for the estimation of spray dryer desulfurization performance, and the results seem to overpredict the baseline test results.

A modification factor for the Ca/S molar ratio calculation has been formulated. This modification was initiated from the difference between calculated Ca/S value and experimental observation.

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