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REACTIVITY OF FLY ASHES IN A SPRAY DRYER FGD PROCESS

Final Report

By
Wayne T. Davis
Gregory D. Reed

May 1, 1983

Work Performed Under Contract No. AC18-81FC10492

University of Tennessee
Knoxville, Tennessee

TECHNICAL INFORMATION CENTER
UNITED STATES DEPARTMENT OF ENERGY

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FINAL REPORT

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EXECUTIVE SUMMARY

Introduction

During the period 1981-1982, an investigation was conducted at The University of Tennessee on behalf of the Department of Energy to investigate the ability of various fly ashes to retain sulfur dioxide in a pilot plant spray dryer/fabric filter flue gas desulfurization system. This knowledge would provide design engineers with the necessary data to determine whether the fly ash from a particular utility could be used as an effective supplement or substitute for slaked lime in a spray dryer system. The study commenced with the collection of 22 fly ashes including lignite, subbituminous, and bituminous eastern and western ashes.

The ashes were contacted with the flue gas entering the pilot plant by two different techniques. In the first, the ashes were slurried in water and injected into the spray dryer through a spinning disk atomizer. In the second, the ashes were injected as a dry additive into the flue gas upstream of the spray dryer.

Analyses were conducted to determine the ability of each ash to retain sulfur dioxide in the system followed by statistical correlations of the sulfur retention with the physical/chemical properties of each ash.

Conclusions

The major conclusions of the study are summarized in the following paragraphs. More detailed discussions of the results may be found in Chapter III.

Sulfur dioxide removal efficiencies of 0-33% were achieved across the spray dryer/fabric filter system when the fly ashes were slurried in water at 1.45 pounds of fly ash per gallon of water and injected into the spray dryer by atomization. This efficiency range corresponded to a sulfur retention of 0.11 up to 4.61 grams of sulfur per 100 grams of fly ash injected. The total sulfur retained (TSR) by the fly ashes, which included the sulfur content of the as received fly ashes plus the retention across the pilot plant system varied from 0.54 up to 6.3 g/100g of fly ash.

It was further demonstrated on one fly ash that the retention of sulfur could be significantly enhanced by a dry ball milling of the fly ash prior to its being slurried with water. The ball milling resulted in a 17% increase in the surface area of the ash, a 62% increase in the alkalinity of the filtrate of the slurry, and an increase in sulfur retention in the system of 156 percent. The SO_2 removal efficiency was increased from 16 to 46% which corresponded to an increase in sulfur retention from 1.81 up to 4.61 g/100g of fly ash.

Statistical correlations were conducted on the sulfur retention across the spray dryer/fabric filter system (SRS) and the total sulfur retention (TSR) to determine the physical/ chemical characteristics of the ashes which might be suitable parameters to use to provide a quantitative prediction of sulfur retention. It was found that the total alkaline metal oxide content of the fly ashes (as determined by ASTM mineral analyses) was not a

reliable predictor of sulfur retention for either SRS or TSR. A combined model which incorporated the independent parameters of surface area, and slurry alkalinity as measured by the hydroxide (OH), carbonate (CO_3) and bicarbonate (HCO_3) provided significant correlations with sulfur retention. For the sulfur retention across the system (SRS) the above four parameter model (surface area, OH, CO_3, and HCO_3) yielded correlation coefficients (R^2) of 0.56, 0.93, 0.28, and 0.93 for correlations using all fly ashes, only lignite fly ashes, only subbituminous fly ashes, and only bituminous fly ashes, respectively. While further study is needed, the analyses suggest that the retention of sulfur in the system is dependent on both physical (surface area) and chemical (slurry alkalinity) characteristics of the fly ashes.

Similar correlations were conducted on the total sulfur retention (TSR) in which it was found that a five parameter model including the above four plus total alkaline metal oxides provided correlations (R^2) of 0.58, .94, .57, and .95 for all fly ashes, lignite, subbituminous, and bituminous, respectively. The predictive equations are summarized in Chapter III.

Tests in which the fly ashes were injected as a dry additive into the flue gas upstream of the spray dryer showed significantly less tendency to retain sulfur than when the fly ashes were slurried and atomized into the spray dryer. The maximum retention in the system was only 1.37 sulfur/100g ash. However, in most of the cases the retention was considered to be negligible.

The effect of the approach to the saturation temperature (ΔT) in the spray dryer on sulfur retention by fly ash slurried in water was demonstrated to be significant. For the fly ash tested, the SO_2 removal efficiency increased from 22 up to 48% when ΔT was lowered from 40°F down to 15°F.

A final series of tests were conducted in which four different fly ashes were individually co-slurried with $Ca(OH)_2$ to determine whether the positive benefits cited above could be used to enhance the removal of a lime-based system. The effects of the fly ashes were found to be masked by the $Ca(OH)_2$. Further study is needed to determine whether there is a technique whereby the potential sulfur retention could be utilized in fly ash/lime slurries.

CHAPTER I

Background

Introduction

Since 1978 there has been an increased emphasis placed on the application of dry scrubbing for the control of sulfur dioxide (SO_2) emissions from flue gases, commonly referred to as dry flue gas desulfurization (FGD) One system which has been applied is a spray dryer followed by a particulate control device, typically a fabric filter collector or an electrostatic precipitator. In these systems a reactive, calcium or sodium-based slurry is atomized by nozzles or spinning disk atomizers and introduced into a spray dryer or drying chamber where the SO_2 is reacted forming a dried product. The dried product is then collected in the spray dryer hopper and/or the particulate collector. The product that is transported to the particulate collector has been found to undergo further reaction. In the case of the fabric filter, the filter serves as a support for the product as a thin fixed bed of potentially reactive product.

Numerous studies have been conducted to quantify the relationship between the stoichiometric ratio of the injected calcium and sodium-based slurries and the sulfur dioxide removal efficiency across the dry FGD systems.[1-5] Parameters studied have included residence time, the approach to the adiabatic saturation, SO_2 inlet concentration, the ratio of recycled product, and flue gas temperature, each of which has been shown to affect the

performance as measured by the efficiency at a given stoichiometric ratio.

One parameter which has been documented as affecting the performance which has not yet been adequately quantified is the fly ash present in the flue gas. The fly ash in the flue gas enters the spray dryer, is collected in the same manner as the dried product and, for recycle systems, is partially recycled into the spray dryer along with the product.

The following paragraphs are intended to briefly summarize the present understanding of the reaction of fly ash with the flue-gas sulfur and the reported effects of the fly ash in dry FGD systems.

Sorbent Potential of Fly Ash

The reactivity of fly ash with sulfur dioxide in a spray dryer has been found to be a complex function of the combustion history of the fly ash entering a FGD system. Meyer[6] has suggested that the sulfur retained in fly ash is linked to its metal oxide content by the following reaction scheme:

$$MO(S) + SO_2(g) + \tfrac{1}{2}(O_2)(g) \rightarrow MSO_4(S)$$

where MO is the metal oxide species. The steps involved were proposed to be 1) adsorption of SO_2 onto the oxide surface and reaction to form the sulfite (M_2SO_3) and (2) further oxidation to the sulfate (MSO_4). The reaction rate was proposed to be a function of temperature, gas concentration, metal oxide particle size, and surface properties.

Natusch[7] and Keyser[8] found the levels of potassium, sodium, iron, and sulfur to be higher in the surface layers of fly ash than in the core of the ash particles. It was hypothesized that this surface enrichment was due to the volatilization and adsorption (or condensation) that occured on the ash as it cooled and exited the high temperature combustion zone. Hulett et. al.[9] Ensor et.al.[10] and Ray et.al.[11] have also reported that the surface concentrations of sulfur increased in conjunction with decreasing particle size suggesting a surface area-related phenomenon in addition to the chemical reaction between condensing species.

Rothenberg[12] investigated the specific surface area (SSA) exhibited by fly ashes using nitrogen as an adsorbate and calculated by the method developed by Brunnauer, Emmet, and Teller (BET Method). Ashes collected from Stoker-fired power plants showed greater SSA compared to pulverized coal power plants. Also a Montana subbituminous and a Texas lignite ash resulting from a fixed bed combustor exhibited values of SSA of 3.7 to 10.5 m^2/g for subbituminous and 12.8 to 20.4 m^2/g for lignite. Sulfur retention was reported to be greater for the subbituminous ash due primarily to the fact that 1) calcium content was 2.75 times greater and 2) the fixed bed combustor operated at temperatures substantially less than the fusion temperature of fly ash. This reduced operating temperature produced ash with considerable pore volume, as shown by scanning electron microscope, thus permitting physical and/or chemical sorption of the sulfur on the calcium.

Davis et.al[13] conducted a statistical analysis of the sulfur retention of 165 fly ashes based on the ASTM mineral analysis of the ashes. In the analysis, the total sulfur retained was correlated against the total alkaline metal oxides content (reported as CaO) determined by the following equation:

$$TAMO = \left[\frac{g\ CaO/100g}{56.1g/g\text{-}mole} + \frac{g\ Na_2O/100g}{62.0g/g\text{-}mole} + \frac{g\ MgO/100g}{40.3g/g\text{-}mole} + \frac{g\ K_2O/100g}{94.2g/g\text{-}mole} \right] \times \frac{56.1gCaO}{g\text{-}mole} \qquad \text{Eq. 1}$$

where

TAMO = grams of total alkaline metal oxides per 100 grams of ash (as CaO)

The ashes were all reported to have been obtained from pulverized coal-fired boilers from either a mechanical collector or an electrostatic precipitator. Figure I-1 shows the relationship between sulfur retention and TAMO.

A first order linear correlation showed the sulfur to be related to TAMO by the following equation with a correlation coefficient, R^2, of 0.617:

$$g\ S/100g\ Ash = .0623\ (TAMO) - .189$$

When the mechanical collector data were eliminated from the analysis (see Figure I-2), the correlation coefficient, R^2, was increased to 0.924 with the following empirical equation:

$$g\ S/100g\ Ash = .0909\ (TAMO) - .197$$

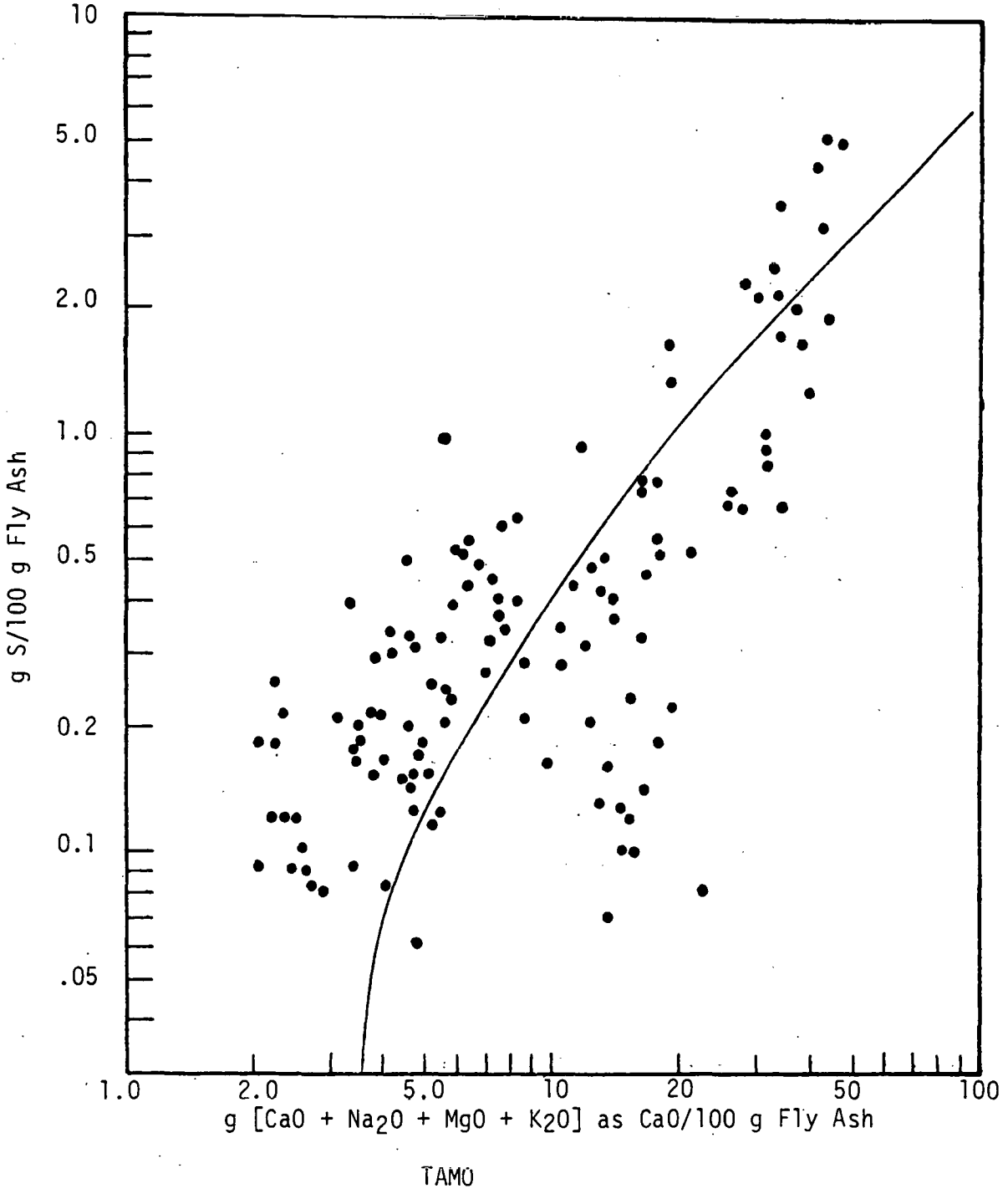

Figure I - 1. Grams Sulfur Retained vs. Weighted Grams Alkaline Metal Oxides as CaO per 100 Grams Fly Ash (All Data).

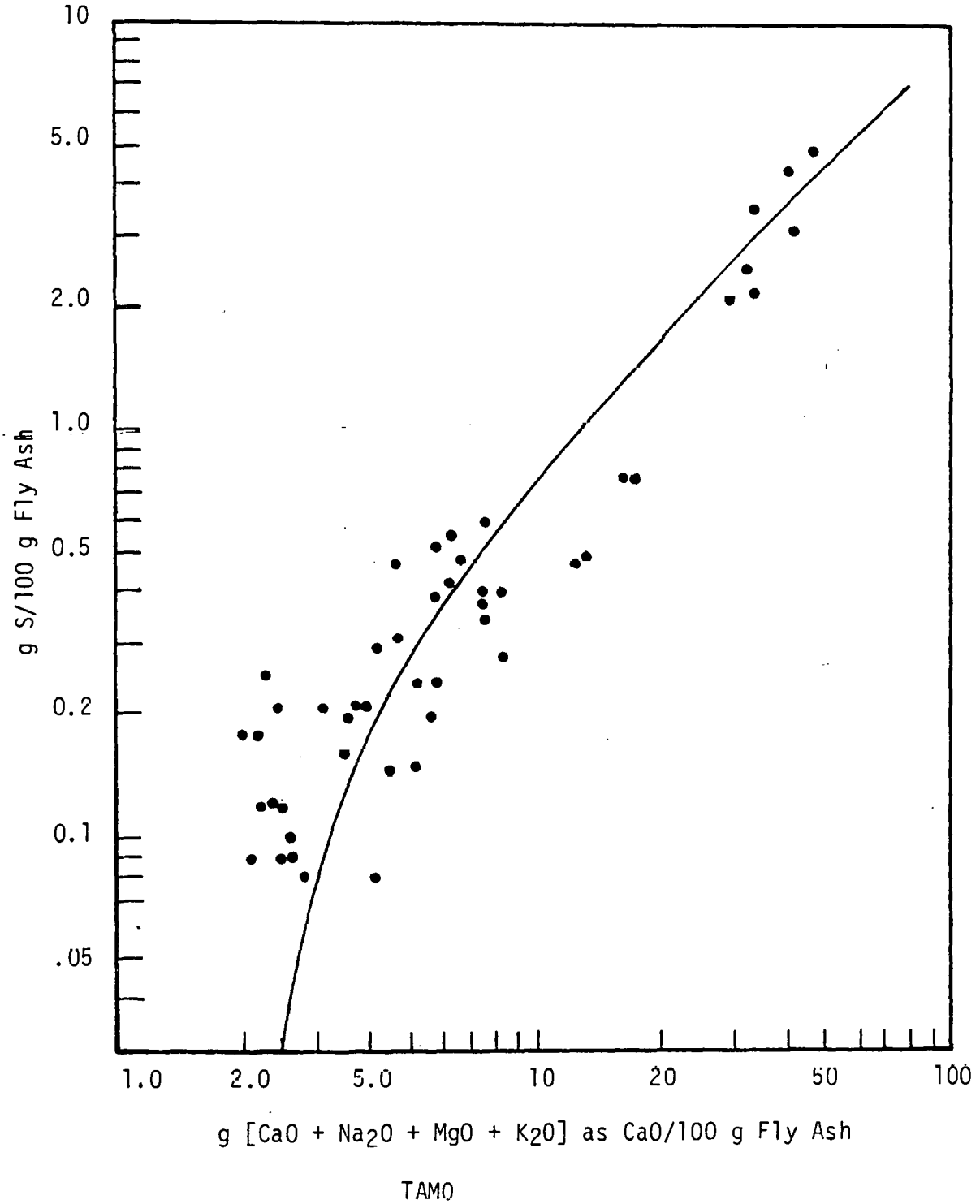

Figure I - 2. Sulfur Retained vs. Alkaline Metal Oxide Content for Pulverized Coal - Fired Boilers (No Mechanical Collector Ashes).

These latter data produced greater sulfur retention at a given TAMO, possibly due to the decreased particle size of the fly ashes, when the mechanical data were eliminated. The data shown in Figures I-1 and I-2 suggest that ashes may have greater potential for sulfur retention than is typically observed. For example, from Figure I-2 at a TAMO of 10g/100g ash, the sulfur retained was approximately 0.7 g S/100 g ash. On a molar basis, 0.022 moles of sulfur was retained per 0.178 moles as CaO. Since the typical reaction of sulfur with CaO has been reported to be a 1:1 molar reaction, it can be hypothesized that only 10-15% of the alkaline metals reacted with sulfur.

Downs et.al.[1] reported that alkaline flyashes have been known to contribute significantly to the absorption of SO_2 in wet scrubbers with some scrubbers relying principally upon the fly ash alkalinity for a source of reactant. Further it was reported that fly ash was observed to have a significant effect on the SO_2 removal efficiency of a 1500 ACFM dry scrubber.[1] It was hypothesized that the principal mechanism enhancing fly ash reactivity in the dry scrubber was the wetting of the fly ash by absorption/condensation of water vapor from the humid flue gas in the dry scrubber. In the study, six different coals were tested by burning the coals in a combustor followed by scrubbing the flue gases in a dry scrubber using only water. Each of the six ashes were analyzed for ash composition from which the available alkalinity was determined as:

$$AA = \frac{\text{moles } (Na_2O + K_2O + MgO + CaO - SO_3) \text{ entering scrubber}}{\text{moles of } SO_2 \text{ entering scrubber}}$$

While AA was reported as available, it should be noted that the actual chemical availability of the alkaline elements for reaction with SO_2 is uncertain. A second analysis of reactive alkalinity (RA) was measured by titrating the fly ashes with a strong acid according to the equation

$$RA = \frac{\text{Milliequivalents of acid titrated per gram ash}}{2000} \times \frac{\text{lbs ash to dry scrubber/hr}}{\text{lb-moles } SO_2 \text{ to dry scrubber/hr}}$$

Defined in the above manner, AA and RA had the same units as stoichiometric ratio. A comparison of AA and RA is shown in Table I-1[1] from which it was concluded that while RA and AA were not similar except at very low pH (less than pH=3) the ashes all showed that RA and AA were in the same relative order. In other words, fly ashes with increased AA had increased RA. Figure I-3[1] shows the relationship between SO_2 removal efficiency, approach to saturation, and available alkalinity for four ashes from which it is apparent that the efficiency increased as the AA increased. Further, the effect of a closer approach to the adiabatic saturation temperature was also evident showing a significant improvement in efficiency at closer approaches. It was also reported that the utilization of the available alkalinity decreased with increasing available alkalinity as shown in Figure I-4[1]. This effect is similar to that found when $Ca(OH)_2$ based slurry was utilized in the dry scrubber where it was observed that utilization decreased with increasing stoichiometric ratio[1-5].

Table I-1. Comparison of Reactive Alkalinity (RA) Versus Available Alkalinity (AA) for Six Fly Ashes.

	Reactive Alkalinity of Fly Ashes*					
pH/RA	NDLV	MSUB	PEBC	GNDL	JBBC	LRBC
7	0.24	0.13	---	0.10	0.065	0.13
5	0.46	0.15	0.0015	0.13	0.086	0.19
4	0.95	0.19	0.0047	0.18	0.10	0.23
3	2.33	0.42	0.0097	0.55	0.13	0.38
2	3.12	0.69	0.024	0.69	0.37	1.24
Available alkalinity	2.1	0.69	0.040	0.30	0.27	0.80
Initial pH	10.5	11.4	5.4	11.0	10.6	10.9

*NDLV = North Dakota lignite (Velva)
MSUB = Montana Subbituminous (Sarpy Creek)
PEBC = Pennsylvania bituminuous (Pittsburgh)
GNDL = North Dakota lignite (Glenharold)
LRBC = Wyoming Subbituminous (Laramie River)
JBBC = Wyoming bituminous (Jim Bridger)

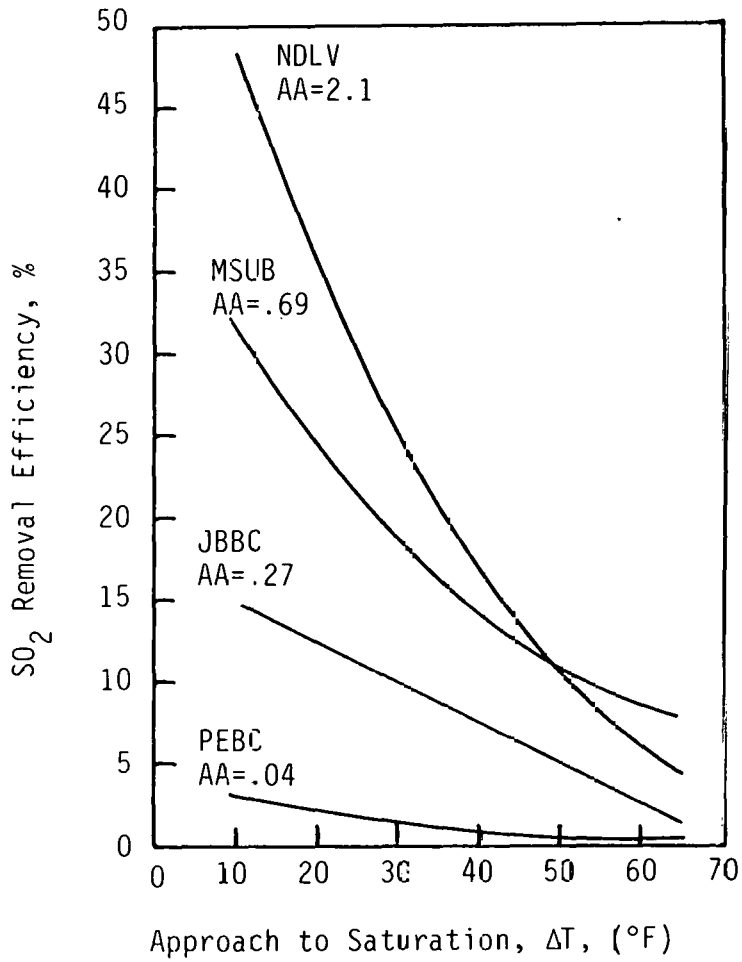

Figure I-3. SO_2 Removal Efficiency of Four Fly Ashes as a Function of Approach to Saturation.[1]

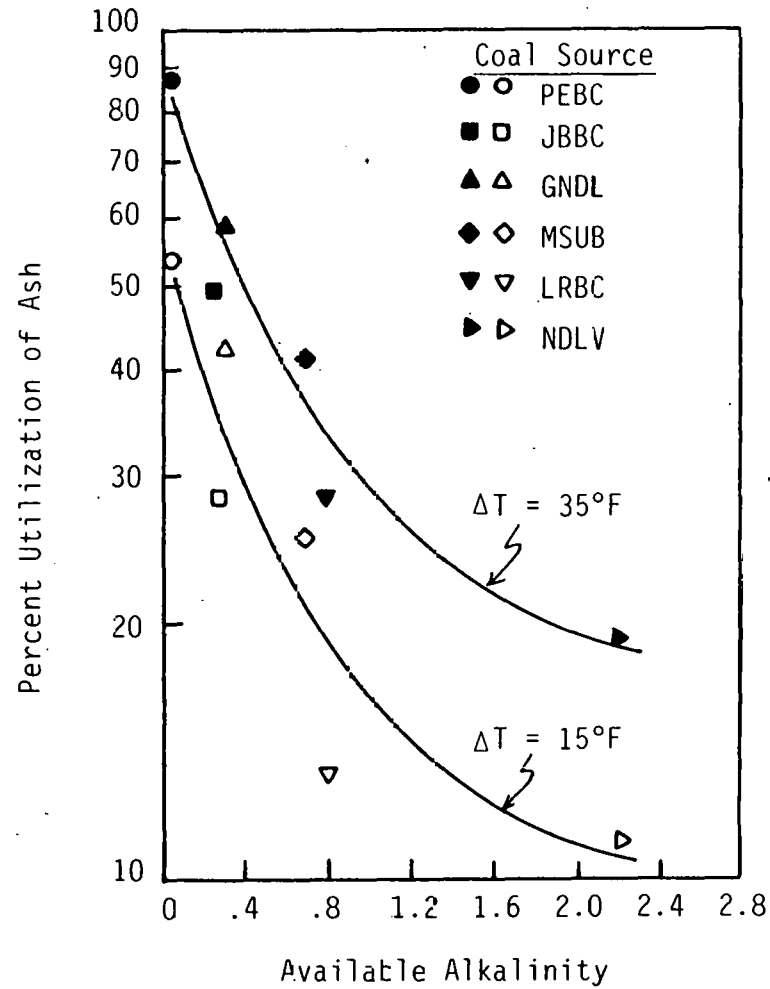

Figure I-4. Utilization of Ash as a Function of Available Alkalinity at a Constant Approach to Saturation.[1]

No results were reported on the relationship between reactive alkalinity (RA) and SO_2 removal. However it was reported that there was potential difficulty in relating RA to SO_2 removal due to the fact that the RA measurement is a liquid measurement dependent on the pH, while in the dry scrubber the pH cannot be increased or controlled.

In a separate study, on a 20MW dry scrubber at the Jim Bridger Station of Pacific Power and Light, Hurst et.al.[2] showed that a slurry of fly ash and water obtained from the Laramie River station of Basin Electric produced a 63% SO_2 removal efficiency when atomized into the scrubber at an inlet temperature of 280-290°F and an approach to the adiabatic saturation temperature of 20°F. The slurry concentration, was not reported preventing a determination of the available alkalinity, AA. In a separate test, the fly ash in the flue gas from the Jim Bridger Station yielded 15% SO_2 removal at the same temperature conditions of the Laramie River ash test. It was not reported whether or not the 63% removal of the slurry in the Laramie River ash test included the 15% contributed by the Jim Bridger ash already present in the flue gas.

In summary, it has been documented that the fly ash present in the flue gas has potential reactivity as a dry reactant or as a reactant slurried with water. Reactivity has been shown to be a function of many parameters including the concentration of alkaline metal oxides, and the approach to saturation. However, predictive equations have not yet been formulated to allow quantitative prediction of the effects.

CHAPTER II

Description of Test Facilty and Test Procedures

Approach

The purpose of this research effort, as stated earlier was to identify the potential reactivity of various types of fly ash and thus determine their capability for SO_2 removal. The ashes tested originated from three different rank coals: bituminous, subbituminous, and lignite. Each ash was slurried in H_2O, mixed, and evaluated in both a pilot plant spray dryer/fabric filter collector and in a bench scale laboratory complete mix reactor to determine reactivity.

Description of the Test Facility

The dry scrubber testing reported in this effort was conducted on a nominal 1000 acfm spray dryer/fabric filter collector FGD pilot plant which operated on a slipstream from the flue gas of a stoker-fired boiler located at the University of Tennessee Steam Plant, Knoxville, Tennessee. A schematic of the pilot plant is shown in Figure II-1. The slipstream was extracted downstream from the mechanical cyclones of any one of three boilers at a temperature of approximately 450°F and a fly ash loading of less than 0.5 grains/acf (~0.1 kg/m^3).

The flue gas temperature was controlled by a dilution air damper located upstream of the spray dryer. The SO_2 concentration upstream of the spray dryer was controlled by supplemental injection of gaseous SO_2 from liquid SO_2 storage tanks.

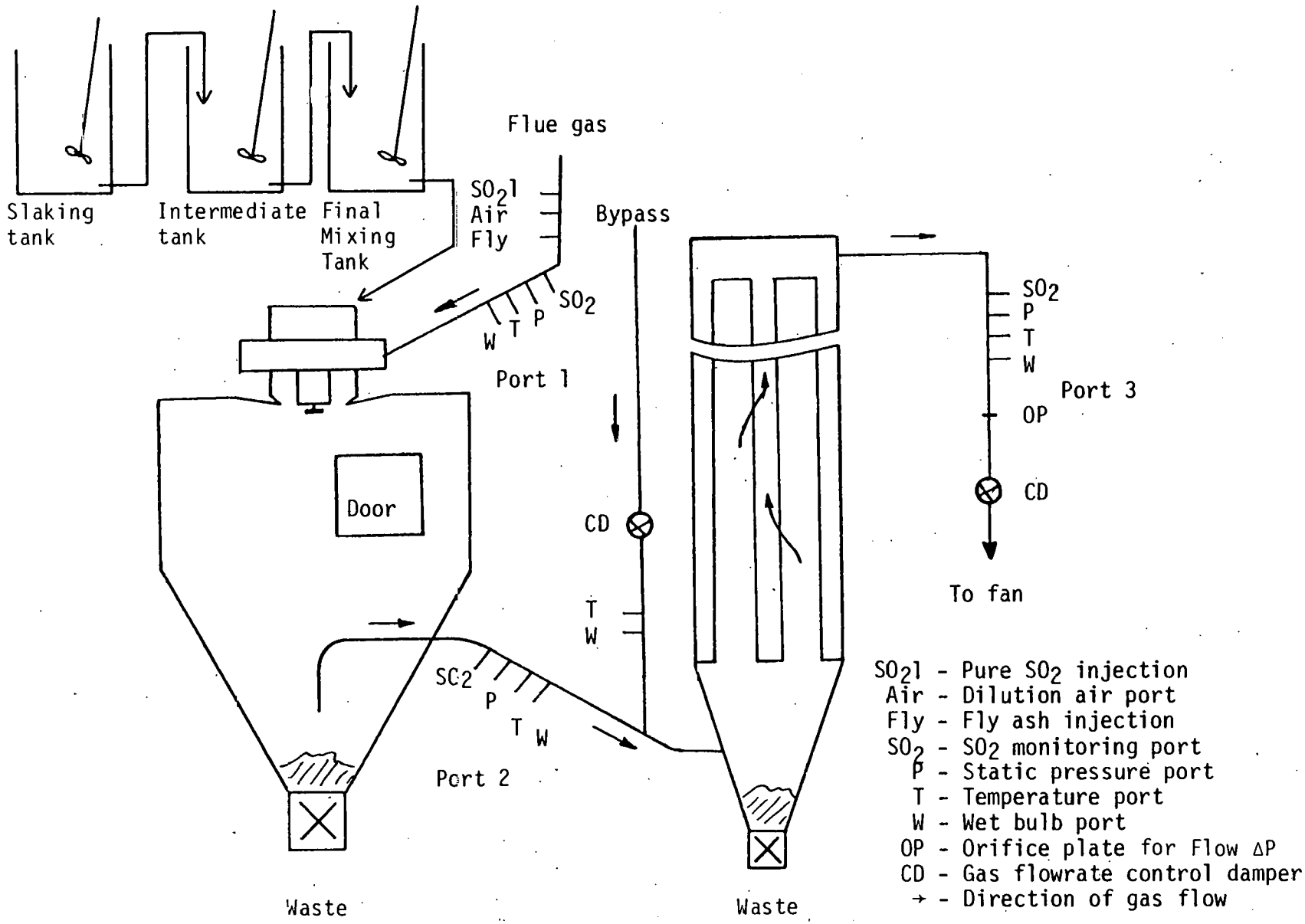

Figure II - 1. Schematic of FGD Pilot Plant

The dry scrubbing pilot plant consisted of 1) a spray dryer which was seven feet in diameter which housed a Stork-Bowen centrifugal spinning disk atomizer capable of speeds of 11,000-19,000 rpm, and 2) a particulate collector consisting of a low energy shaker-cleaned fabric filter collector which housed 4 fiberglass filter bags which were 32 feet long by 11.5 inches in diameter (air/cloth ratio = 2.6/1 CFM/ft^2). Figure II-2 shows a photograph of the system.

Flue gas was extracted from the boiler using a suction fan located downstream from the fabric filter collector. The flue gas entered the spray dryer concentrically around the spinning disk atomizer through a set of vanes which imparted an angular downward swirling motion. In the spray dryer the flue gas was mixed and reacted with the atomized water, fly ash/water, or fly ash/lime/water slurry. The flue gas then exited the spray dryer and entered the fabric filter collector where the fly ash and spray-dried product-laden flue gas was filtered. Rotary valves located on the hoppers of the spray dryer and baghouse were utilized to periodically remove the collected solids.

Description of the Test Procedures

The procedures for each spray dryer test consisted of 1) estabishing the appropriate flue gas conditions of flowrate, inlet SO_2 concentration, and flue gas temperature; 2) preparation of the slurry to be atomized in the spray dryer; and 3) calibration of the SO_2 monitors. The only one of these which needs to be described in detail is the preparation of the slurry.

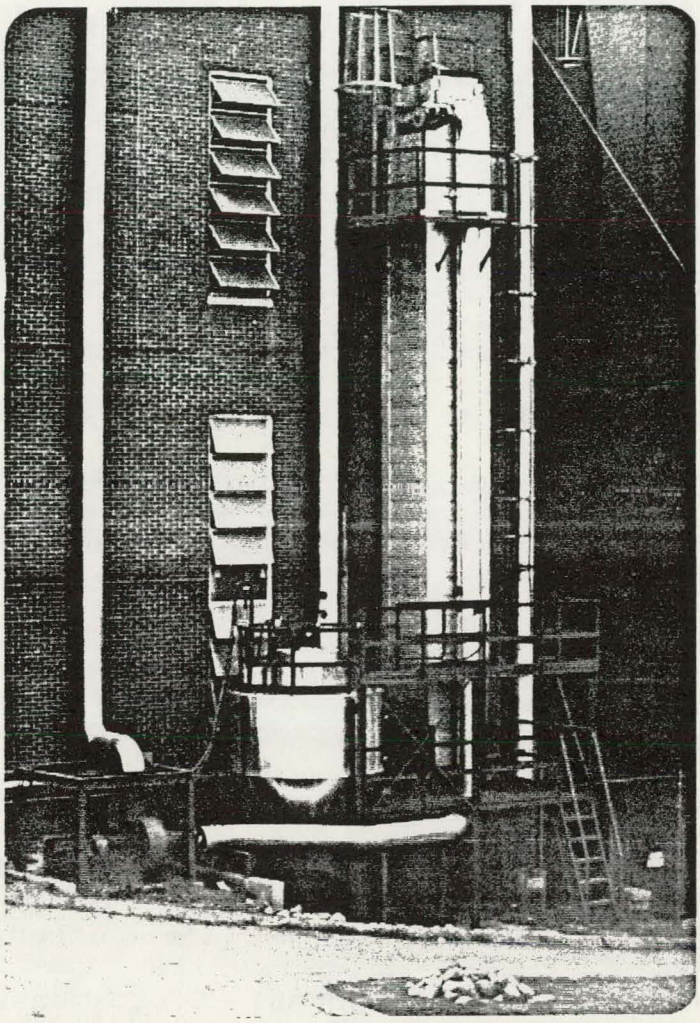

Figure II-2. Spray dryer/fabric filter pilot facility.

Three different types of slurries were tested in the study: fly ash, calcium hydroxide [$Ca(OH)_2$], and fly ash plus $Ca(OH)_2$. The fly ash slurries were prepared by mixing a predetermined mass of fly ash in water (at 140°F) for a mixing time of greater than thirty minutes. The test conditions for the fly ash slurries were as follows:

1. Inlet temperature range (300 ± 10°F)
2. Inlet SO_2 concentration (600 - 800 ppm)
3. Flue gas volumetric flow rate (1,000 acfm)
4. Slurry preparation temperature (130 - 140°F)
5. Slurry concentration (1.45 lbs fly ash/gallon H_2O)
6. Temperature at the spray dryer outlet (20°F above the dew point)
7. Atomizer disc speed (17,000 rpm) equivalent to 75-85 micrometer mean drop diameter).

Calcium hydroxide slurries were prepared by on-site slaking of quick pebble lime (CaO) at a 3.5/1 mass ratio of H_2O to lime, followed by dilution to an intermediate concentration. The slurry was then titrated using 3 Normal HCl to measure the available lime followed by 1) dilution to the final desired concentration and 2) a final titration.

The typical test consisted of sequentially monitoring SO_2, temperature, and moisture content at the inlet and outlet of the spray dryer (Ports 1 and 2) and the outlet of the fabric filter (Port 3) for approximately 40-50 minutes.

A more detailed description of the parameters measured and the analytical instrumentation used to measure each of the above

parameters is included in Appendix A, Table A-1. Also Appendix A includes summaries of the data collected on the spray dryer system for the various tests reported in this study.

The SO_2 removal efficiency was determined by correcting the SO_2 concentrations at the inlet and outlet of the spray dryer and the fabric filter to a dry basis (required since water is injected between the inlet and outlet of the spray dryer) according to the following equations:

$$SO_2 \text{ Efficiency} = \frac{\dfrac{SO_2(1)}{1-BW(1)} - \dfrac{SO_2(2)}{1-BW(2)}}{\dfrac{SO_2(1)}{1-BW(1)}}$$

where (1) and (2) designated the inlet and outlet SO_2 concentrations on a wet basis, respectively.

Description of Laboratory Chemical Kinetic Studies

A bench scale complete mix slurry reactor was used to collect dissolution and equilibrium kinetic data on selected fly ash samples to determine the availability of reactants for reaction with SO_2 in the spray dryer system. In addition, equilibrium values were determined for all 22 fly ash samples received. Parameters monitored and evaluated included 1) pH, 2) alkalinity (bicarbonate, carbonate, and hydroxide), 3) calcium, 4) total divalent cations, 5) sodium, 6) residence time, 7) slurry concentrations, and 8) slurry temperature. These variables were

measured for correlation with actual spray dryer performance. Testing was also conducted on selected fly ash samples which were ball-milled.

Other Analyses Conducted

In addition to the pilot testing and laboratory chemical kinetics testing described above, analyses were also conducted on the fly ashes as received to determine the physical/chemical characteristics of the ashes prior to being slurried. The analyses are summarized below in Table II-1 which also includes the analytical instrumentation used to measure the parameter.

Table II-1. Physical/Chemical Parameters Measured on as Received Fly Ashes.

Physical/Chemical Property	Analytical Technique/Instrument
Particle Size Distribution	Coulter Counter Model TAII
Particle density	Micromeritics Model 1302 Pycnometer
Sulfur Content	Fisher Total Sulfur Analyzer
Surface Area	Micromeritics Surface Area Analyzer
ASTM Ash Mineral analyses for CaO, Na_2O, MgO, K_2O	ANSI/ASTM D 3682-78: Atomic Absorption Spectroscopy (Perkin Elmer Model 403)

CHAPTER III

RESULTS AND DISCUSSION

Physical Description of Fly Ashes

In an effort to obtain samples for study, approximately fifty different electric utilities and/or power plants were contacted with a request to provide a 200 pound sample of the ash collected from their plants. Table III-1 includes 1) a summary of the power plants/utilities that responded with samples of ash, 2) the rank of the coal used to produce the ash, and 3) the source of the coal. There were five lignite, eight sub-bituminous, and nine bituminous ashes for a total of twenty-two.

Table III-2 provides a summary of the physical properties of each of the fly ashes including the mass mean diameter (MMD), the geometric standard deviation (σg), the particle density (ρp), and the specific surface area (SA). The MMD ranged from 7.4-18.0 micrometers with an average of 11.8 micrometers. The geometric standard deviations ranged from 1.7-2.8 with an average of 2.1. The particle density ranged from 1.5 to 3.2 g/cm^3 (1500-3200 kg/m^3) with an average value of 2.5 g/cm^3.

The surface area of the fly ashes typically ranged from 0.21-3.39 m^2/g of ash with an average of 1.59 m^2/g. One exception to the above was fly ash 49 (obtained from a stoker-fired boiler) which had a surface area of 12.52 m^2/g. This was attributed to the high carbon content of the ash which was typically 30-40%. The surface areas, measured utilizing a Micromeritics surface area analyzer which utilized the B.E.T.

Table III-1. Origin of the Fly Ashes.

Flyash I.D.	Company: Plant	Source
Lignite		
27	Texas Ut. Gen. Co.: Big Brown	Freestone County
38C	Basin Electric Power: Coop. Unit 1	Consolidated Coal Co., Stanton, ND
41	Milton R. Young Station: Center Unit 1	Bankol-Nconan Mine, Center, ND
42	United Power Assoc./Coop Power Assoc.	Falkirk Mine, Underwood, ND
44	Otter Tail Power: Hoot Lake Unit 2	Knife River Coal Min. Co., Beula, ND
Subbituminous		
13[a]	Minn. Pow and Lt.: Clay Boswell Station	Big Sky Mine - Colstrip Montana
14	Neb. Pub. Pow: Gerald Gentleman Station	Black Thunder Mine, Campbell Co., WY
18A	Pacific Power and Light: Wyodak	Wyodak Resources - Wyodak Mine
37	SWPS: Harrington Station	Black Thunder Mine, Gillette, WY
38B	Laramie River Station	Cordero Mine, Wyoming
43	Black Hills Power and Light Company	Wyodak Mine - Wyoming
45[a]	Minn. Pow. and Lt.: Clay Boswell Station	Big Sky Mine, Colstrip, MT
46	San. Ant. Pub. Serv.: Monifer Resources	Cordero Mine, Wyoming
Bituminous		
6	Belews Creek Steam Station	Low sulfur eastern coal
10	Bowen Steam Plant	Eastern Kentucky
18B	Hunter Steam Plant	Wilberg Mine - Emery County, Utah
23B	Cherokee #4	Colorado western slope
24	Pub. Serv. Indiana: Gallagher Station II	Amax Aryshire
34	New Madrid Power Plant #2	Southern Illinois
36	Ohio Edison Gorge	Ohio strip mine
49	University of Tennessee Steam Plant	Eastern Kentucky
50	Duke Power: Marshall Steam Plant	Low sulfur eastern coal

[a]These fly ashes were obtained from the same source, however, their production resulted from different combustion conditions.

Table III-2. Summary of Fly Ash Physical Characteristics.

Fly Ash I.D. No.	MMD (microns)	Geometric Deviation	Particle Density, (g/cm^3)	Specific Surface[a] Area, (m^2/g)
Lignite				
27	9.5	2.5	2.4	0.74
38C	15.6	2.6	3.2	0.76
41	12.0	1.8	2.7	3.27
42	9.4	1.9	2.6	0.29
44	11.0	1.9	2.7	2.37
Subbituminous				
13	9.4	1.9	1.5	0.21
14	9.5	1.8	2.7	2.09
18A	15.0	1.9	2.5	0.73
37	7.4	2.5	2.7	1.15
38B	11.5	2.2	2.6	1.66
43	18.0	2.4	2.5	1.03
45	10.0	2.0	2.5	3.39
46	8.5	1.8	2.5	1.48
Bituminous				
6	12.0	2.3	2.7	1.31
10	14.8	2.2	2.1	2.14
18B	7.8	1.9	2.3	2.14
23B	14.9	2.8	2.2	2.85
24	12.3	2.2	2.7	2.88
34	9.2	1.7	2.5	1.23
36	15.3	2.0	2.6	0.22
49	12.9	1.9	2.1	12.52
50	14.0	2.1	2.2	1.47

[a]B.E.T. adsorption techniques

low-temperature nitrogen adsorption technique, were generally greater than those calculated from the particle size distributions assuming perfect spheres. The average surface area was 1.59 m^2/g using the B.E.T. procedure and 0.98 m^2/g using the particle size data. The B.E.T. measured values of surface area reported in Table III-2 were used in all statistical evaluations in this report.

Chemical Description of Fly Ashes as Received

Table III-3 is a summary of the chemical characteristics of each fly ash determined by conducting ASTM mineral analyses on the ashes. The concentrations of each constituent in percent by weight for all fly ashes tested were as follows:

S:	0.3 - 4.1%
CaO:	4.0 - 25.0%
Na_2O:	7.0 - 35.9%
MgO:	0.4 - 4.6%
K_2O:	0.8 - 5.6%

The total alkaline metal oxide content (TAMO) was also reported for each ash. This value was determined by weighting each constituent by its molecular weight according to equation I-1 and reporting the result as CaO. The TAMO had values of 8.9 - 45.6% by weight. The lowest value was associated with the stoker-fired ash which had a very high surface area due to its high unburned carbon content (typically 30-40%).

Table III-3. Summary of Fly Ash Chemical Characteristics.

Fly Ash I.D. No.	%S	%CaO	%Na_2O	%MgO	%K_2O	TAMO[a]
Lignite						
27	0.66	14.99	11.19	2.40	1.70	28.33
38C	0.00	13.95	35.88	5.58	3.69	56.47
41	4.06	18.01	16.68	3.98	1.52	32.47
42	1.02	18.96	10.97	3.79	1.90	33.57
44	0.75	23.80	17.71	4.57	1.14	45.56
Subbituminous						
13	0.49	13.96	10.96	2.79	1.79	28.06
14	0.73	22.91	10.96	3.49	1.29	38.22
18A	0.70	18.96	10.78	3.79	1.50	33.73
37	0.78	24.95	10.98	3.59	1.00	39.19
38B	0.72	21.81	13.48	2.97	1.29	37.70
43	0.66	6.97	10.76	1.00	2.49	18.50
45	0.68	11.63	10.66	2.71	1.45	24.68
46	0.75	28.90	14.94	3.98	1.39	47.47
Bituminous						
6	0.43	7.79	10.71	0.97	2.53	19.61
10	0.32	5.44	9.42	0.91	2.36	16.03
18B	0.45	9.72	10.89	2.14	1.94	22.83
23B	1.87	7.88	10.25	1.18	1.68	16.54
24	1.22	8.60	9.94	1.91	0.76	17.67
34	1.04	6.76	11.79	0.97	2.90	18.78
36	0.36	0.98	12.69	0.39	5.56	15.75
49	2.19	4.02	6.97	0.94	1.94	8.89
50	0.41	5.75	12.47	1.44	2.78	20.01

[a]total alkaline metal oxides reported in g/100g as CaO (see Chapter 1, Equation 1).

Chemical Description of Fly Ashes in a Slurry

Equilibrium data were collected on all 22 fly ashes (plus one fly ash which was ball-milled) at two slurry conditions: 1) 10% fly ash by weight at 70°C, and 2) 15% fly ash by weight at 60°C. The first condition was based on an initial estimate of the proposed pilot plant test conditions, while the second condition represented the condition at which the pilot plant tests were actually conducted. The spray dryer data were correlated against the data for the second condition since these represented the same slurry conditions.

Prior to conducting the equilibrium studies on all of the fly ashes, two of the fly ashes (ashes 38C and 44) had extensive chemical kinetic studies conducted on them in order to determine an indication of the behavior of the ashes in a slurry as well as to determine the time required to reach equilibrium. In these laboratory studies, aliquots were removed from the slurry as a function of time and the filtrates were analyzed for pH, Na, Ca, OH, CO_3, total alkalinity, and total divalent cations. Figures III-1 through III-6 illustrate the complexity of the dissolution kinetics. The conditions of these tests are summarized below:

Figure III-1: Fly Ash 44, 19°C, w/o milling

Figure III-2: Fly Ash 44, 74°C, w/o milling

Figure III-3: Fly Ash 38C, 28°C, w/o milling

Figure III-4: Fly Ash 38C, 76°C, w/o milling

Figure III-5: Fly Ash 38C, 25°C, with milling

Figure III-6: Fly Ash 38C, 76°C, with milling

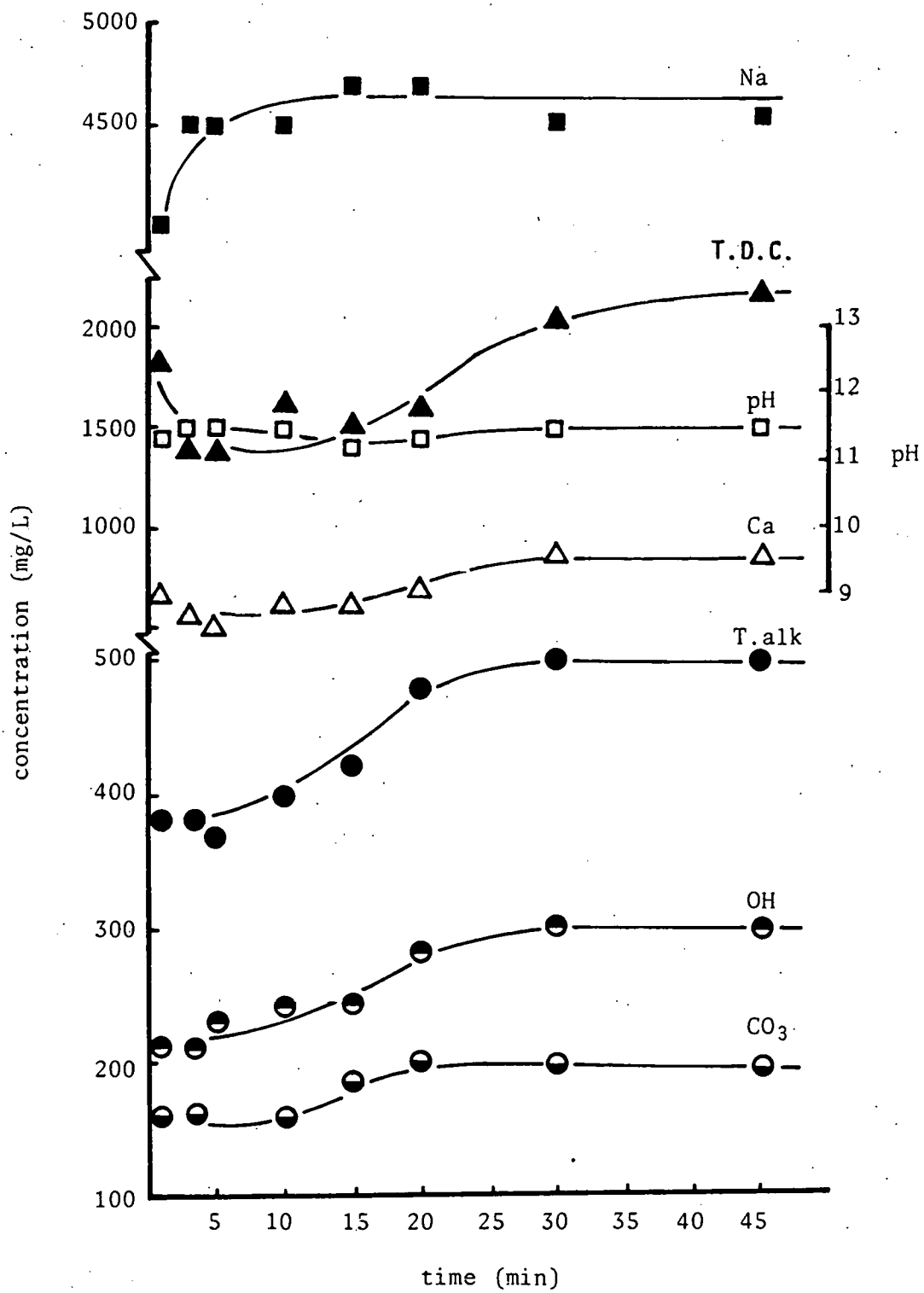

Figure III-1. Dissolution Kinetics of Hoot Lake Fly Ash in Distilled Water at 19° C.

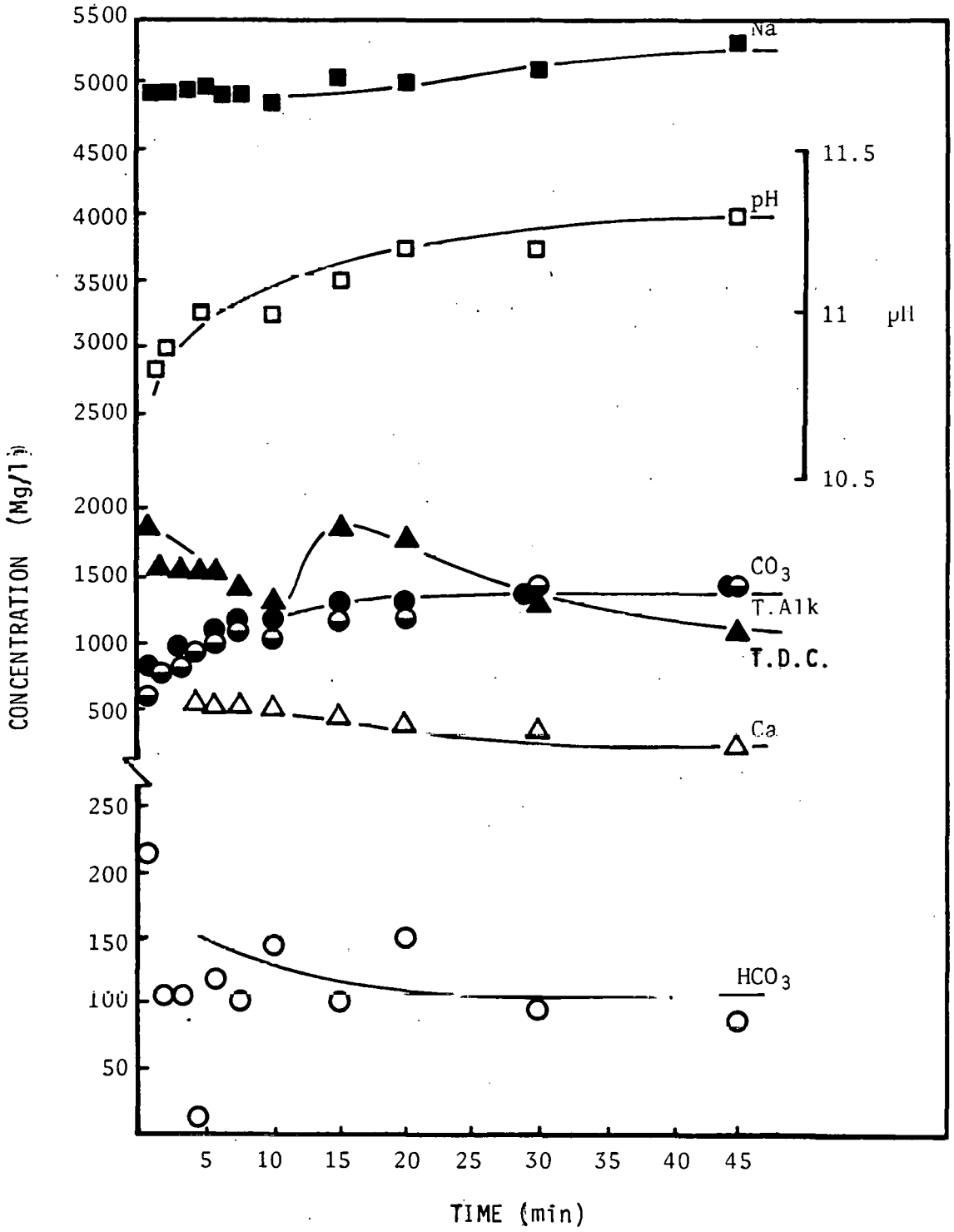

Figure III-2. Dissolution Kinetics of Hoot Lake Fly Ash in Distilled Water at 74° C.

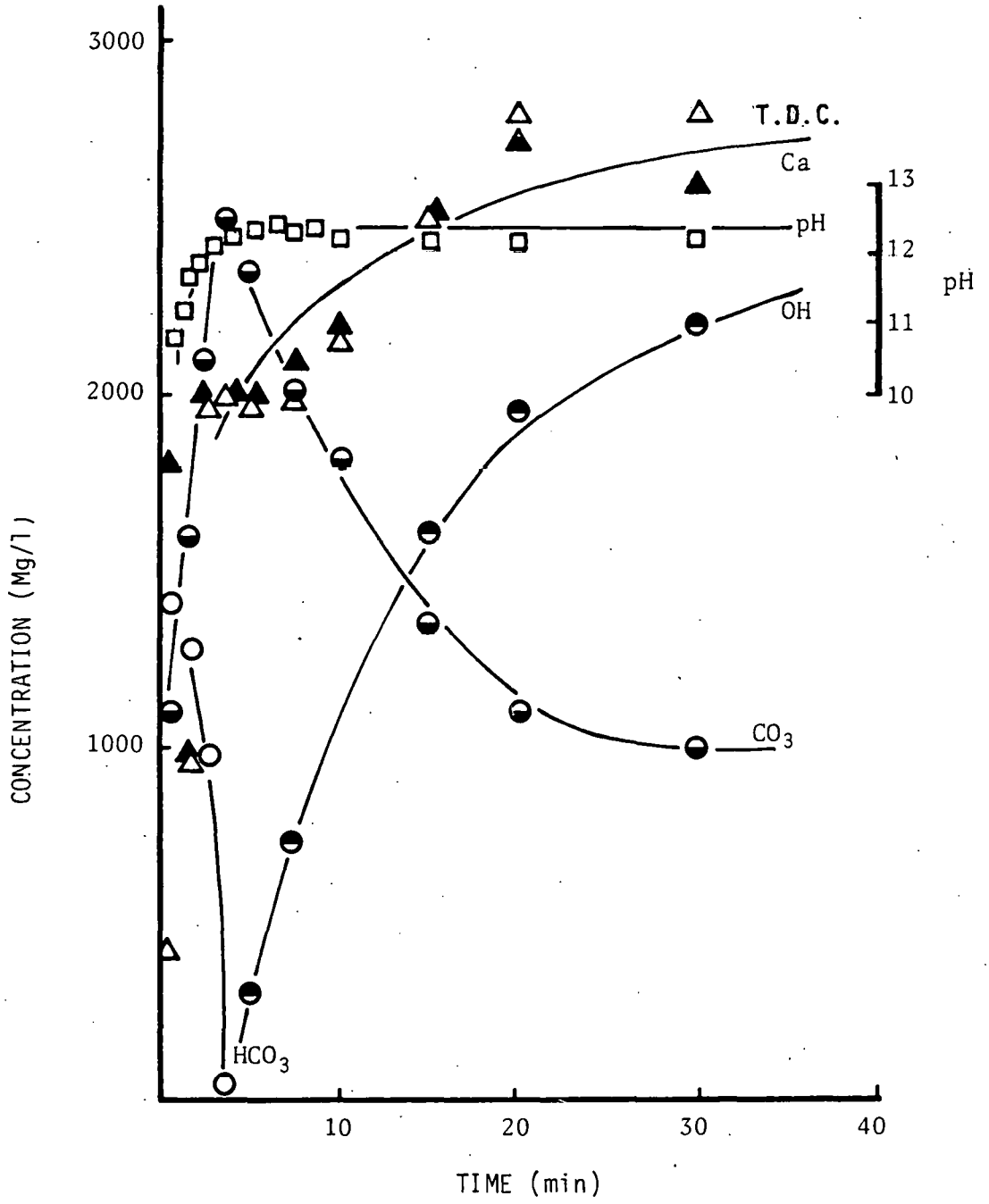

Figure III-3. Dissolution Kinetics of Leland Olds Fly Ash in Distilled Water at 28° C.

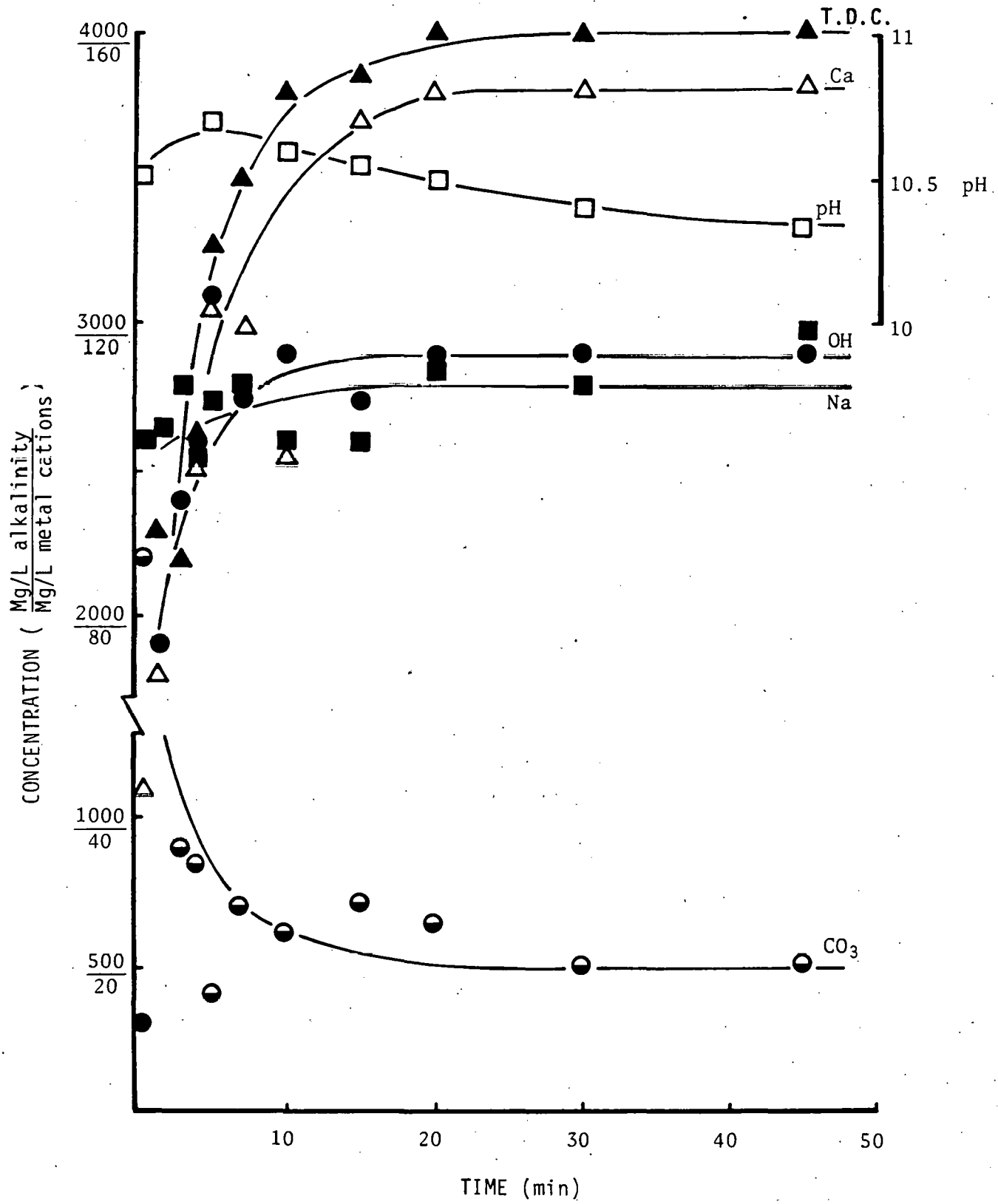

Figure III-4. Dissolution Kinetics of Leland Olds Fly Ash in Distilled Water at 76°C.

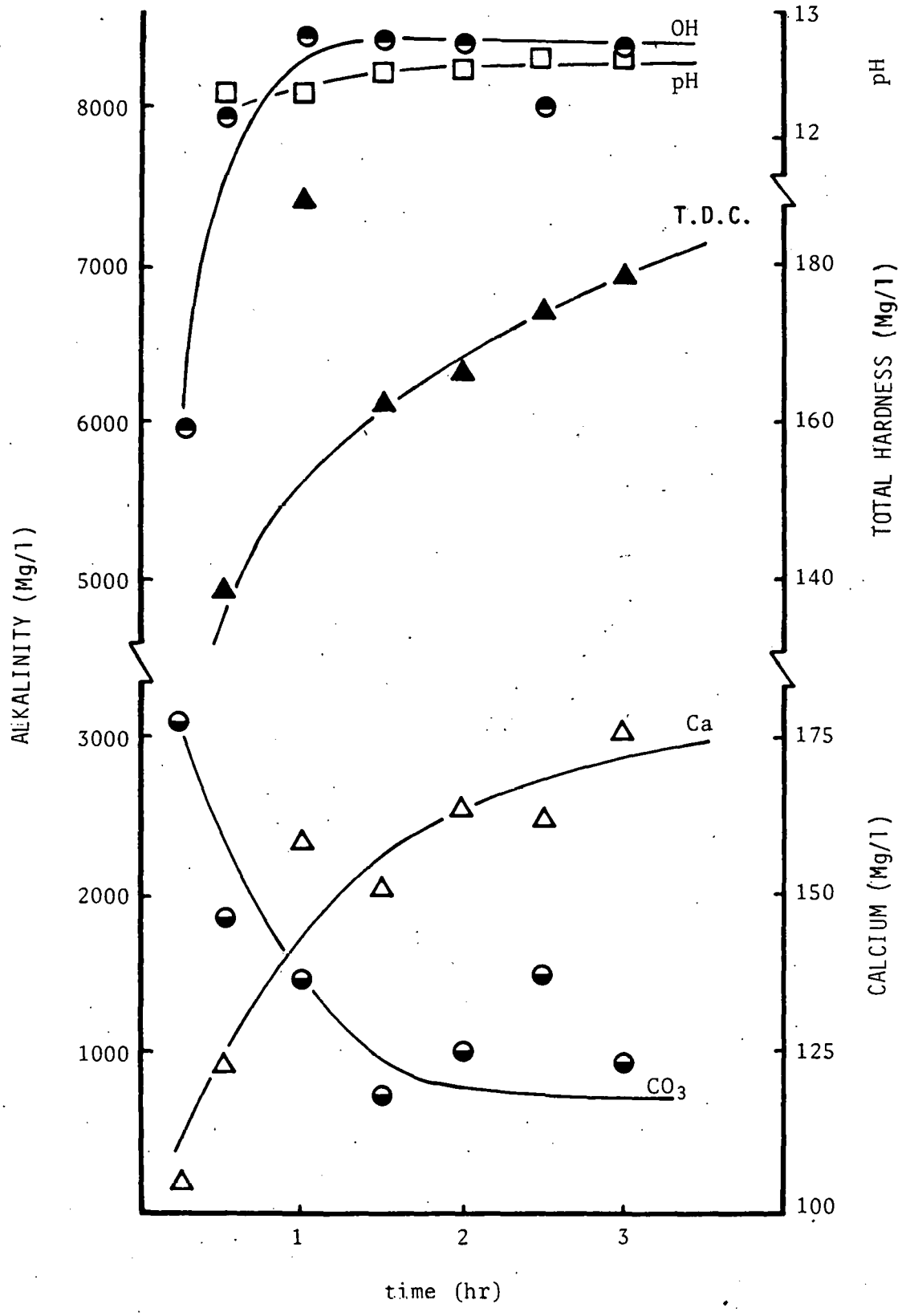

Figure III-5. Dissolution Kinetics of Leland Olds Fly Ash (after ball milling) in Distilled Water at 25° C.

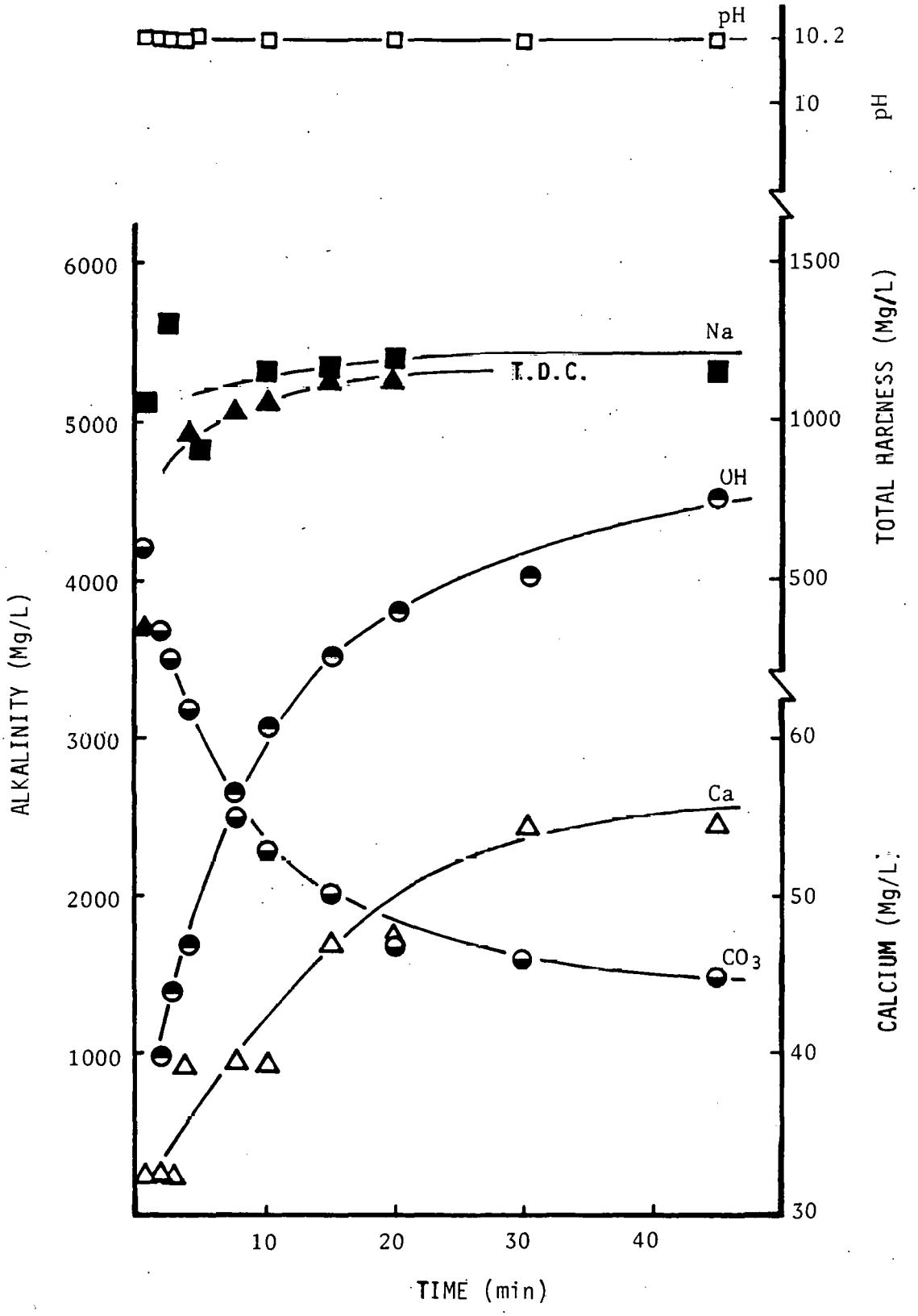

Figure III-6. Dissolution Kinetics of Leland Olds Fly Ash (after ball milling) in Distilled Water at 76°C.

An examination of the data in the figures indicates that the initial dissolution was very rapid followed by a more gradual approach to a final equilibrium. The gradual approach to equilibrium was attributed to changes in pH which resulted in some shifting of the species in solution.

It is also apparent that the kinetics of the ashes are very complex. Table III-4 summarizes the final equilibrium concentration of pH, OH, CO_3, Ca, total divalent cations (TDC) and Na for the above six tests. There were no consistent trends observed as the temperature was increased from 19-29°C up to 74-76° due to the complexity of the interaction between the various chemical species and the pH.

It was possible, however, to obtain one important parameter which was the mixing time required to reach equilibrium. The value of this parameter was needed in order to determine the desired detention time in the mixing tanks of the spray dryer/ fabric filter system prior to injection of the slurry. A summary of the time required to reach 95% of the equilibrium values is given in Table III-5. These data were based on the final equilibrium values given in Table III-4 and were read from Figures III-1 through III-6. In general, the time required to reach 95% of the final equilibrium value was less than thirty minutes.

This concentration was further supported by a more detailed analysis of the mass transfer coefficients for three chemical components: hydroxide alkalinity (OH), calcium (Ca), and total divalent cations. The mass transfer coefficient, k, was based on the following equation form:

Table III-4. Fly Ash Concentrations at Equilibrium.

	pH	OH	CO_3	Ca	TDC	Na
Hoot Lake, 19°C w/o milling	11.5	300	200	757	852	4650
Hoot Lake, 74°C w/o milling	11.3	ND	1380	349	422	5300
Leland Olds, 28°C w/o milling	12.1	2200	1000	112	109	----
Leland Olds, 76°C w/o milling	10.4	2925	500	154	160	3000
Leland Olds, 25°C w/milling	12.4	7650	1900	176	180	9300
Leland Olds, 76°C w/milling	10.3	4500	1500	55	514	5400

pH = no units

OH, CO_3 = mg/l as $CaCO_3$

Ca, TDC = mg/l as Ca

Na = mg/l as Na

Table III-5. Time to Reach 95% of Equilibrium (min).

	pH	OH	CO_3	Ca	TDC	Na
Hoot Lake, 19°C* w/o milling	<0.25	20	17	28	29	2.5
Hoot Lake, 74°C w/o milling	<0.25	ND	29	36	42	
Leland Olds, 28°C w/o milling	<0.50	33	30	17	17	
Leland Olds, 76°C w/o milling	<0.25	16	28	10	10	19
Leland Olds, 25°C w/milling	<<0.25	65	65	120	120	15
Leland Olds, 76°C w/milling	<0.10	35	32	26	13	0.5

Table III-6. Mass Transfer Coefficients k, min^{-1}.

	OH	Ca	TDC
Hoot Lake, 19°C* w/o milling	ND	ND	ND
Hoot Lake, 74°C w/o milling	ND	0.57	0.55
Leland Olds, 28°C w/o milling	0.08	0.26	0.27
Leland Olds, 76°C w/o milling	0.41	0.43	0.48
Leland Olds, 25°C w/milling	1.65	1.23	1.43
Leland Olds, 76°C w/milling	0.12	0.27	0.28

*initial dissolution very rapid followed by a slow increase to equilibrium.

ND - Not determined

$$C = C_E - (C_E - C_O)e^{-kt}$$

where

C = the concentration at time t

C_E = the equilibrium concentration

C_O = the concentration at t = 0

t = time

which is a form of the basic mass transfer equation:

$$\frac{dC}{dt} = k\ (C_F - C)$$

The mass transfer coefficients are summarized in Table III-6. While the coefficients were not studied as a function of the fly ash particle size (surface area) or degree of mixing, they are representative of the overall rate of approach to equilibrium as measured and can be used to provide a reasonable estimate of the final equilibrium time under just enough mixing to keep the slurry completely suspended.

Based on the results of the above in depth studies on two of the fly ashes, all fly ashes were tested as described at the beginning of the section to determine the equilibrium values for the chemical components in the filtrate of each ash. The values of filtrate pH, total alkalinity, Ca, Na, and total divalent cations are summarized in Table III-7 for each fly ash for the 15% fly ash slurry at 60°C. The data for the 10% fly ash slurry at 70°C is included in Appendix B, although it was not used in any of the correlations shown later.

Table III-7. Summary of Fly Ash Slurry Filtrate Analyses[a].

I.D. No.	pH	Alkalinity[b], mg/l as $CaCO_3$	Ca, mg/l	Na, mg/l	TDC mg/l as Ca
Lignite					
27	10.3	1700	415	300	547
38C	10.8	1600	274	4200	368
41	10.7	1100	321	8000	396
42	11.4	3700	887	62	981
44	10.9	1300	340	8200	396
44M[c]	10.9	2100	302	8500	472
Subbituminous					
13	11.2	3800	962	48	1094
14	11.0	2500	132	200	210
18A	10.6	1200	130	54	160
37	11.3	1800	85	200	170
38B	11.2	1500	123	54	245
43	10.9	2100	179	75	274
45	10.7	1600	302	58	396
46	10.9	1600	128	100	170
Bituminous					
6	5.2	200	472	40	547
10	6.7	500	265	26	
18B	11.2	3400	849	88	1000
23B	11.3	1800	264	51	340
24	11.4	2900	1151	91	1208
34	4.4	0	604	300	717
36	10.5	1400	245	49	283
49	3.6	0	175	150	
50	4.8	0	321	52	358

[a]The slurry parameters shown in this table were obtained by analysis of the filtered supernatant of the 15% fly ash slurries at 60°C.

[b]Alkalinity is an indirect estimate of the soluble cations by measurement of the hydroxide (OH), carbonate (CO_3), and bicarbonate (HCO_3) species.

[c]This ash was obtained by grinding fly ash number 44 in a ball mill.

Based on prior data which suggested that reactions on the surface of the fly ash might also be important relative to the retention of sulfur, a second series of analyses was conducted which consisted of determining the alkalinity of the fly ash slurry rather than that of just the filtrate. A summary of both the filtrate and slurry titrations is shown in Table III-8 for the 15% fly ash slurries at 60°C. The results of this analysis revealed that some ashes have considerably more alkalinity available on the surface than in the filtrate. This is easily seen by the graphical presentations of the data in Figures III-7 through III-10. The dashed line represents equality between filtrate and slurry titrations. Although the individual samples had species shifting from one form to another, the slurry total alkalinity was always greater than the filtrate total alkalinity (sometimes significantly greater, Figure III-10). Because of this trend, slurry titration values were judged more likely to reflect reactivity than filtrate titrations and were used in all correlations between the sulfur retention and the chemical components.

Results of Fly Ash Slurry Testing at the FGD Facility

Each of the above 22 fly ashes was tested in the spray dryer/ fabric filter pilot plant as described in Chapter II. The results of the tests in which each fly ash was slurried at 1.45 lbs/gallon of water and atomized into the flue gas in the spray dryer are summarized in Table III-9. For comparative

Table III-8. Summary of Filtrate and Slurry Alkalinity Species.

	Filtrate				Slurry			
I.D. No.	OH	CO_3	HCO_3	TOTAL	OH	CO_3	HCO_3	TOTAL
Lignite								
27	1300	400	0	1700	0	2141	428	2569
38C	600	1000	0	1600	1713	3854	0	5567
41	900	200	0	1100	0	8135	7065	15200
42	3300	400	0	3700	0	8564	1285	9849
44	900	400	0	1300	0	16701	8350	25051
44M	1900	200	0	2100				
Subbituminous								
13	3000	800	0	3800	4496	3425	0	7921
14	1300	1200	0	2500	6637	3854	0	10491
18A	1000	200	0	1200	3426	0	0	3426
37	800	1000	0	1800	5352	13702	0	19054
38B	700	800	0	1500	642	5139	0	5781
43	1700	400	0	2100	3426	8564	0	11990
45	800	800	0	1600	0	3854	1070	4924
46	800	800	0	1600	0	5566	2569	8135
Bituminious								
6	0	0	200	200	0	0	0	0
10	0	0	500	500	0	0	8564	8564
18B	2200	1200	0	3400	1285	5995	0	7280
23B	1000	800	0	1800	2783	0	0	2783
24	2700	200	0	2900	1285	3426	0	4711
34	0	0	0	0	0	0	0	0
36	1400	0	0	1400	2141	0	0	2141
49	0	0	0	0	0	0	0	0
50	0	0	0	0	0	0	0	0
30A	0	0	0	0	0	0	0	0

*all values are mg/l as CaCO3

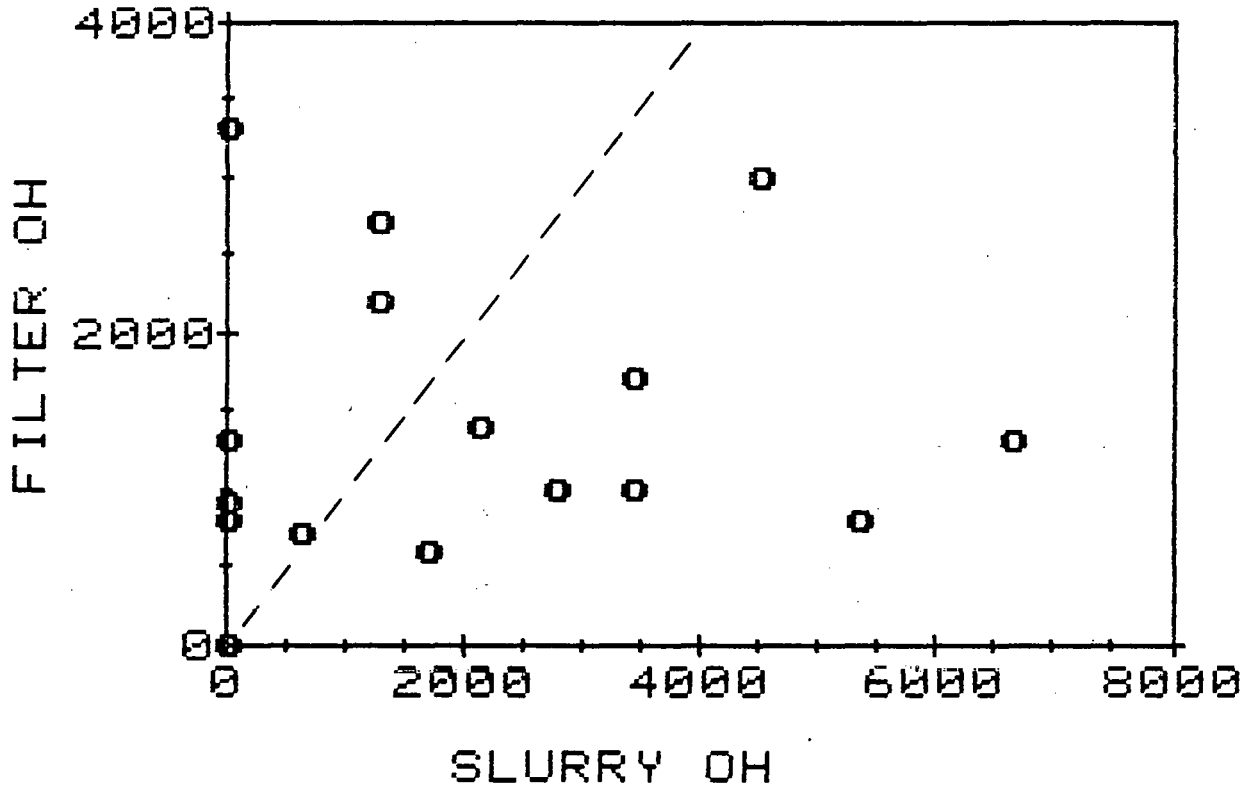

Figure III - 7. A Comparison of Filtrate versus Slurry OH Alkalinity (Mg/l as $CaCO_3$).

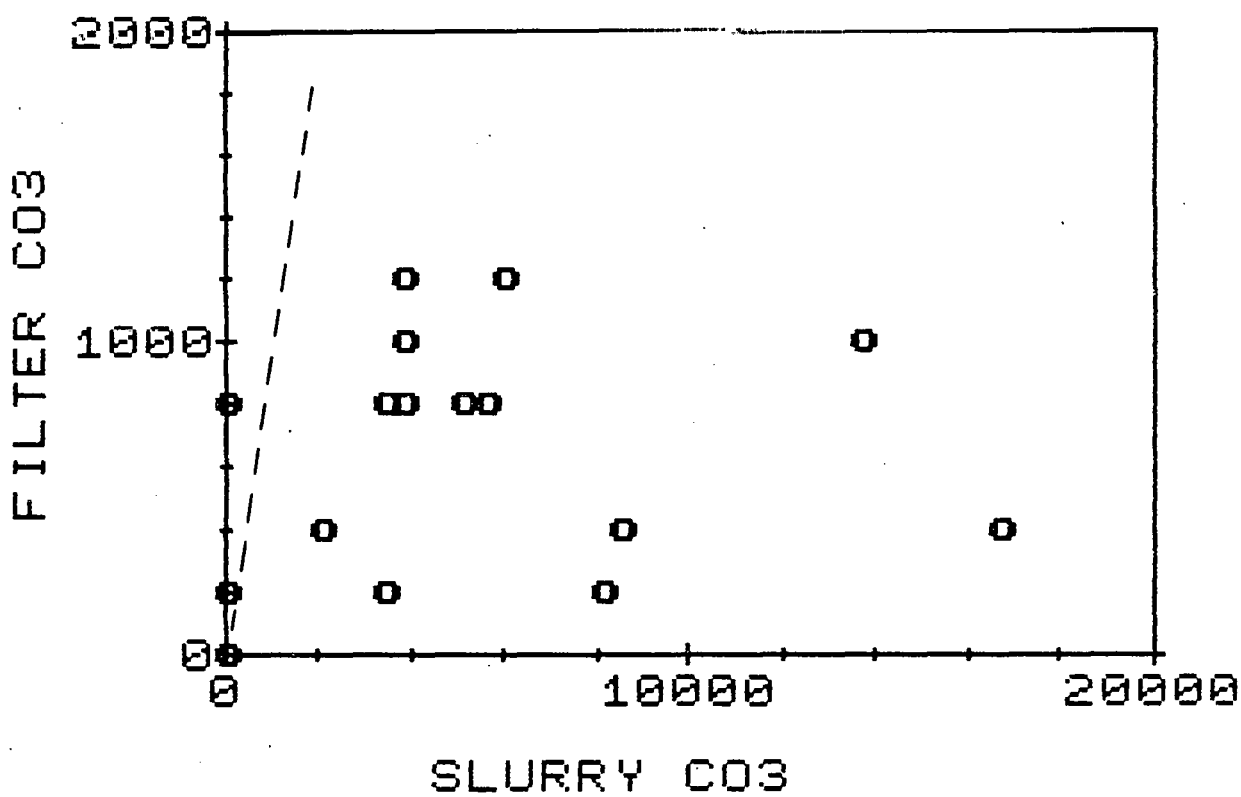

Figure III - 8. A Comparison of Filtrate versus Slurry CO_3 Alkalinity (Mg/l as $CaCO_3$).

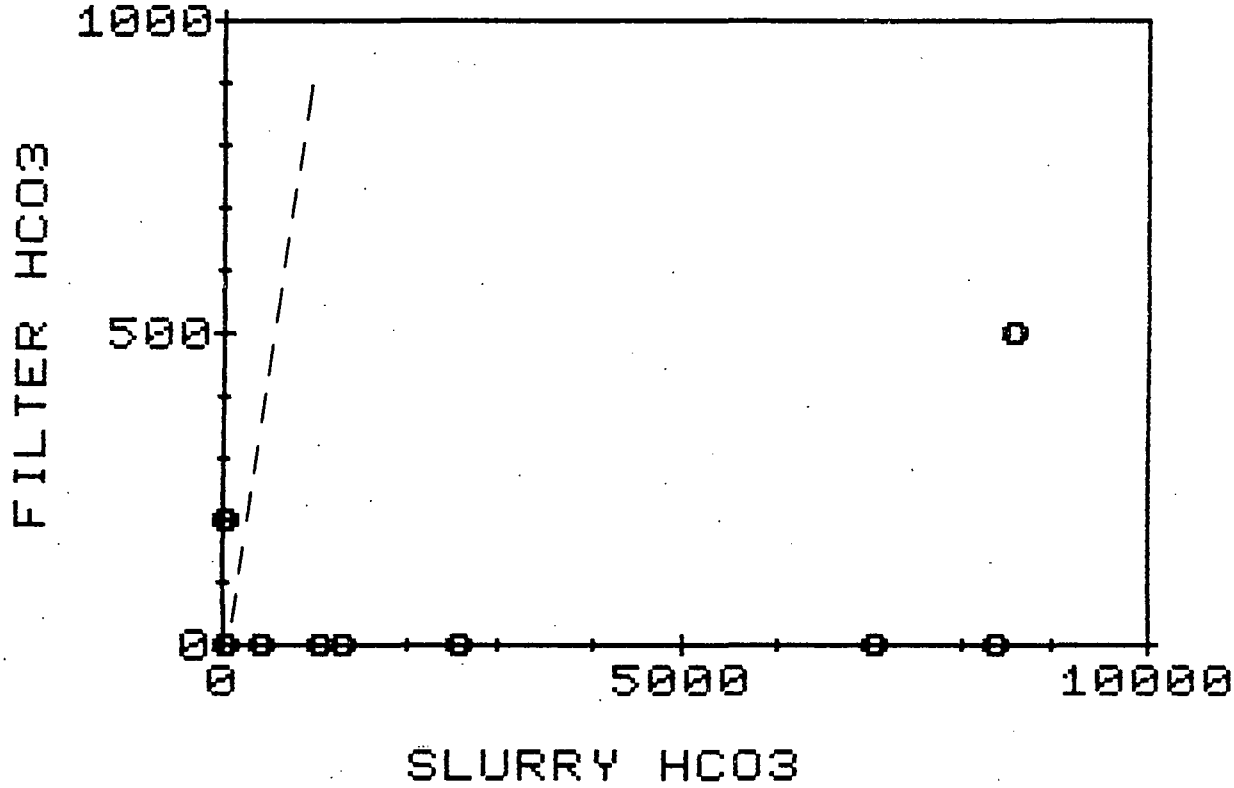

Figure III - 9. A Comparison of Filtrate versus Slurry HCO_3 Alkalinity (Mg/l as $CaCO_3$)

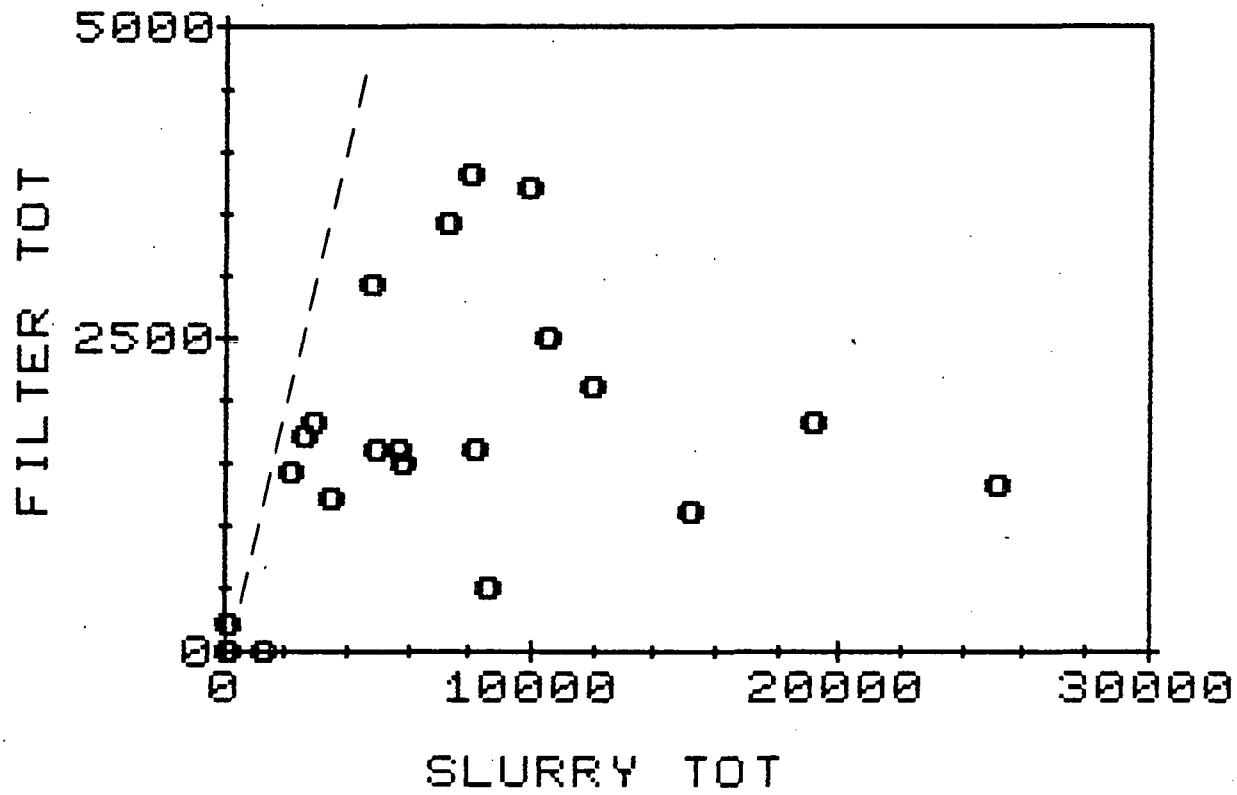

Figure III - 10. A Comparison of Filtrate versus Slurry Total Alkalinity (Mg/l as $CaCO_3$)

Table III-9. Sulfur Retention by Fly Ash.

Fly Ash I.D. No.	SRB (g/100g Fly Ash)	SRS (g/100g Fly Ash)	TSR (g/100g Fly Ash)	SO_2 Removal, % Spray Dryer	SO_2 Removal, % Total (System)
Lignite					
27	0.66	0.35	1.01	1	5
38C	0.00	1.33	1.33	11	15
41	4.06	2.23	6.29	17	21
42	1.03	0.88	1.91	8	9
44	0.75	1.81	2.56	15	16
44M	0.75	4.61	5.36	15	46
Subbituminous					
13	0.49	1.44	1.93	5	17
14	0.73	3.35	4.08	33	30
18A	0.70	2.46	3.16	20	21
37	0.78	2.76	3.54	25	26
38B	0.72	2.87	3.59	17	26
43	0.66	2.89	3.55	21	26
45	0.68	2.48	3.16	11	24
46	0.75	1.21	1.96	12	13
Bituminous					
6	0.43	0.11	0.54	0	1
10	0.32	0.53	0.85	10	7
18B	0.45	2.95	3.40	24	23
23B	1.87	0.15	2.02	2	2
24	1.22	1.05	2.27	5	6
34	1.04	0.49	1.53	5	6
36	0.36	0.00	0.36	0	0
49	2.19	3.12	5.31	11	29
50	0.41	0.25	0.66	0	1

SRB = Sulfur Retained in Boiler (fly ash as received)
SRS = Sulfur Retained by Spray Dryer/Fabric Filter
TSR = Total Sulfur Retained (SRB + SRS)

purposes the table includes sulfur retained by the boiler (SRB) which was the original sulfur retained in the fly ashes as received, the sulfur retained by the spray dryer/fabric filter system (SRS), the total sulfur retention (TSR = SRB + SRS), the SO_2 removal efficiency across the spray dryer, and the SO_2 removal efficiency across the spray dryer/fabric filter system (EFFSYS). Values reported for SRS and EFFSYS were two percent lower than actually measured to account for the removal across the system which occurred when water containing no fly ash was injected. In this manner, the reported values represent the effects due to just the fly ashes.

The SO_2 removal efficiency across the spray dryer/fabric filter system varied from 0-33% at the conditions studied. This corresponded to a sulfur retention (SRS) of 0.11 up to 4.61 grams of sulfur per 100 grams of fly ash. It is of interest to note that in some cases (i.e. fly ashes 18B, 18A, 37, 38B, 43, and 45) the sulfur removal across the spray dryer/fabric filter (SRS) was substantially greater than the removal in the boiler (SRB). In other cases (fly ashes 27, 41, 42, 23B, 24, and 34) the SRB was substantially greater than SRS. The explanation of these widely differing behaviors is not readily obvious.

Fly ash 44 (a North Dakota lignite) was ball-milled dry and re-tested to determine if this procedure would improve the sulfur retention. This test is reported as Fly ash 44M in Table III-9 and was found to provide a significant improvement. The retention

increased from 1.81 to 4.61 grams of sulfur per 100 grams of fly ash (16% to 46% SO_2 removal efficiency) indicating that the dry ball milling provided additional physical or chemical retention of sulfur.

Analysis of the Effects of Fly Ash Properties on SO_2 Removal

In an effort to explain the wide variations in fly ash behavior shown in Table III-9, statistical analyses were conducted in which sulfur retention was correlated against a variety of parameters involving fly ash physical/chemical characteristics. Literature surveyed in Chapter I suggested that sulfur retention in a spray dryer might be related to the total alkaline metal oxide concentration in the fly ash[1] when corrected for the sulfur already removed in the boiler. Figure III-11 shows the relationship between the SO_2 removal in the spray dryer/fabric filter system (in gram-moles/sec) versus the total alkaline metal oxide content of each ash (corrected for the sulfur already retained in the as-received ashes). Also shown on the graph is a theoretical curve which indicates a one to one molar reaction between SO_2 and the metal oxides (when reported as CaO). It is evident that 1) there is substantially less SO_2 removed than is theoretically possible based on the assumption that the alkaline methods are available for reaction, and 2) there is little correlation between SO_2 removal and the alkaline metal oxides content (corrected for sulfur).

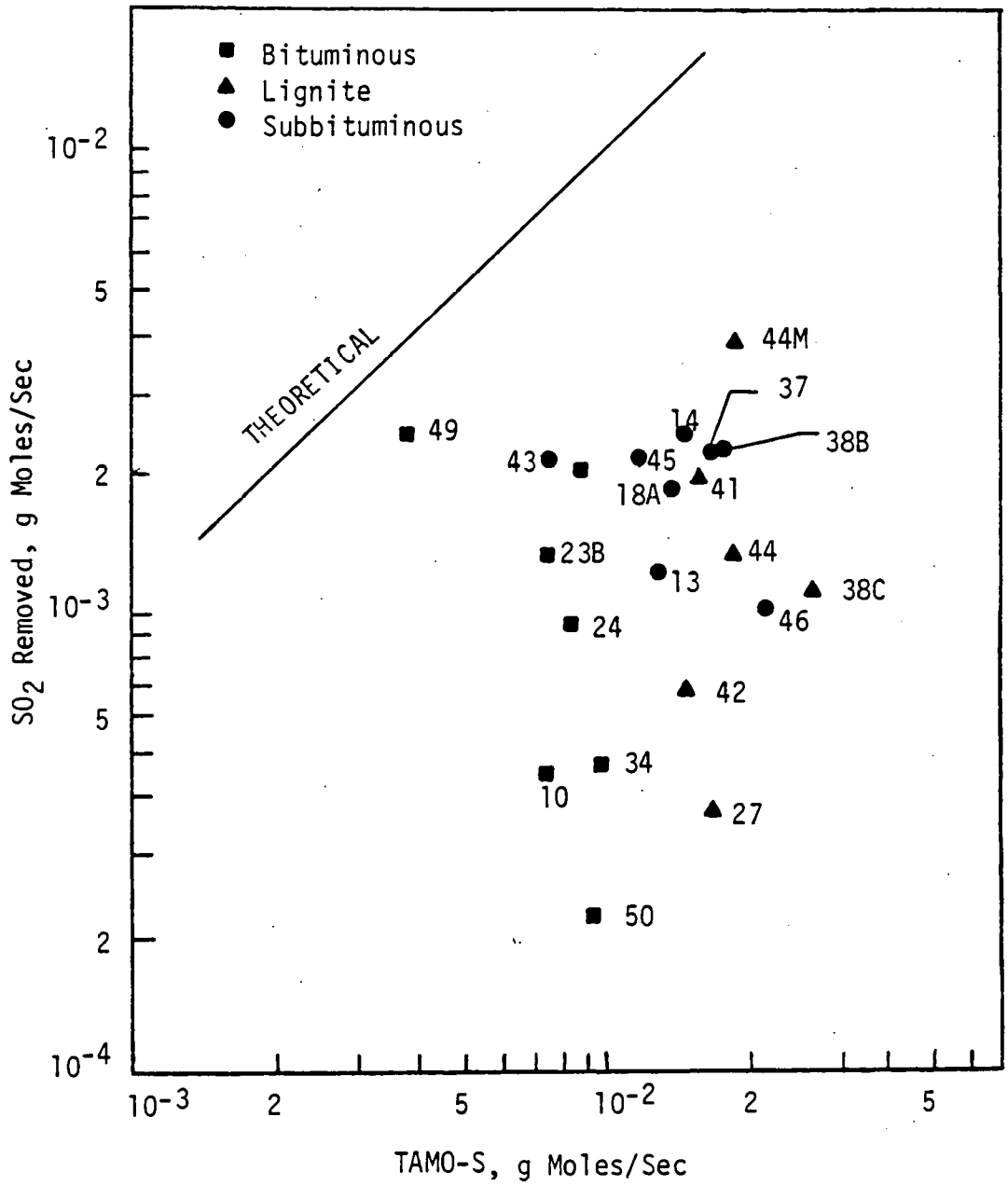

Figure III - 11. SO_2 Removed as a Function of Total Available Alkaline Metal Oxides (TAMO-S) Injected.

A possible limiting factor in the reaction of SO_2 with alkaline metal oxides is the inability of these compounds within the ash to dissolve into the slurry. This limitation may be due to either pH or blinding effects. Barnes[14] has cited a similar problem which developed as a result of new control strategies for sulfuric acid produced by the oxidation of pyrite, FeS_2, in acid mine waters. One approach under investigation for elimination of excess acidity involved the use of limestone. A difficulty encountered in neutralizing the iron-rich waters with limestone was the precipitation of insoluble ferric hydroxide on reacting surfaces. This blinding effect prevented further reaction of the limestone with the acid, and the neutralization reaction was quenched after a short time. Similarly, the elemental sulfur retained by the fly ash after combustion in various sulfite and sulfate forms may provide an impermeable barrier to further reaction with SO_2. If this is true, destruction of such a barrier should increase the reaction potential of the ash. Barnes[14] suggested that the problem of blinding might be minimized by grinding and stirring during reaction.

In the case of the fly ashes being studied herein, grinding could potentially reduce the blinding effect as well as expose additional metal oxides and surface area. Fly ash 44 discussed above showed a 250% increase in sulfur retention when it was ball milled while the slurry alkalinity and surface area of the fly ash were increased by 62 and 17%, respectively.

The importance of fly ash surface area was demonstrated by the lignite and bituminous fly ashes in particular. The specific surface area measured in square meters per gram was expressed in terms of square meters per second of fly ash injected and correlated with SO_2 removal in g-moles per second. The resulting correlation coefficients were, $R^2 = 0.76$, for the lignite ashes and $R^2 = 0.73$ for the bituminous ashes. It was also shown, in one instance, that a fly ash, number 49, with considerable surface area (12.5 m^2/g) but negligible alkaline metal content had an SO_2 removal efficiency of 30 percent. This large amount of surface area was due primarily to the incomplete combustion within the stoker-fired boiler; thus producing an ash with a high carbon content. Consequently, physical adsorption of the SO_2 in the internal pores was considered to be the mechanism responsible for this removal.

An additional analysis was conducted on the data to determine if there was a relationship between the sulfur retained in the fly ashes in the boiler and the total metal oxide content as suggested by Fiedler (15) and Davis et. al. (13). Figure III-12 shows a comparison of sulfur retained in the fly ash as received versus total alkaline metal oxides (TAMO) in grams/100 grams. These data are superimposed on the data presented by Fiedler (15). In general the present data tended to produce more scatter and exhibited less sulfur retention than previously reported.

A graphical comparison was also made between the total sulfur retained (sulfur in the fly ash received plus the sulfur

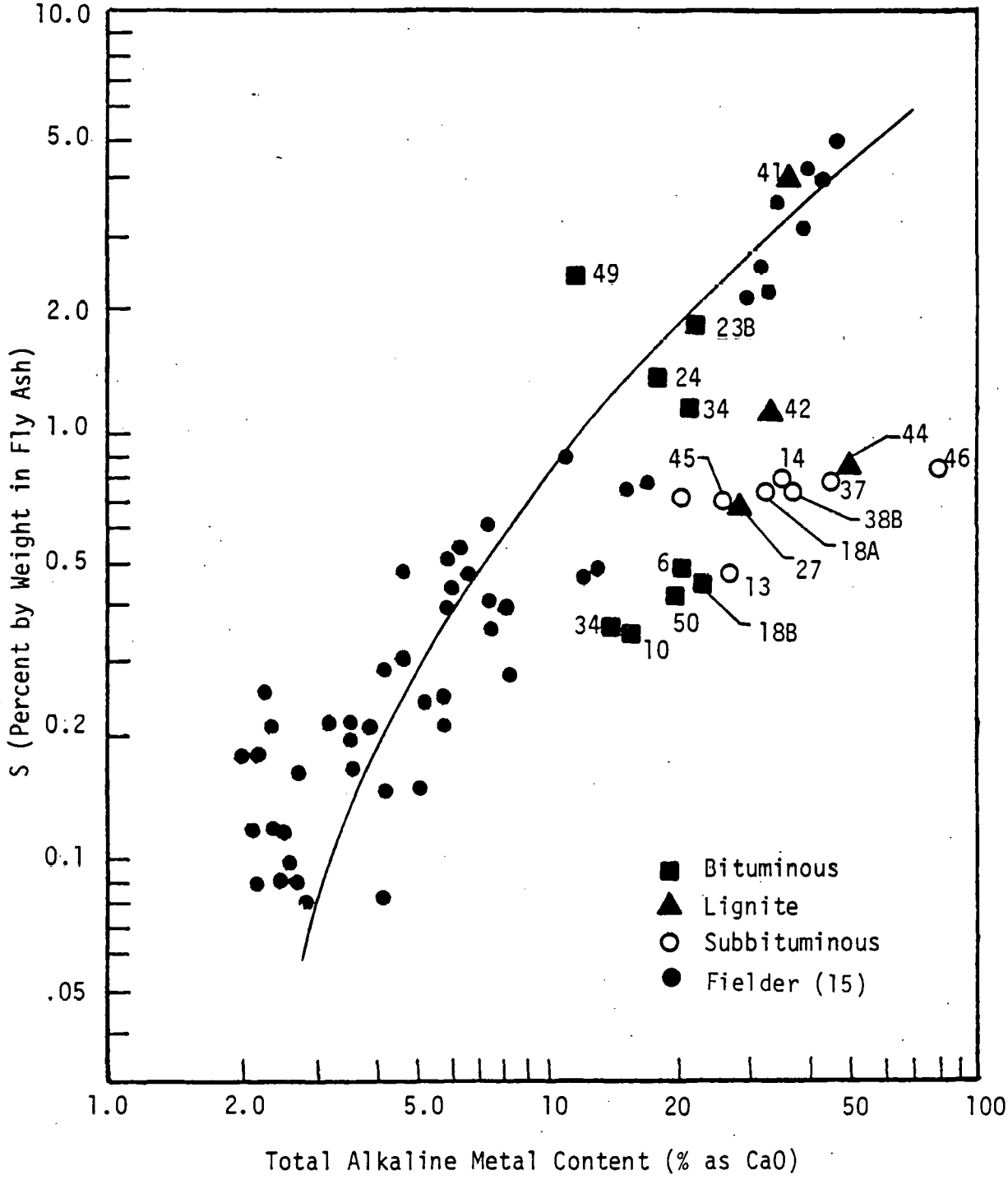

Figure III - 12. Sulfur Retention versus Total Alkaline Metal Content (Reported as CaO).

retained in the spray dryer/fabric filter) and the total alkaline metal oxide content (TAMO) expressed in g-moles/100g of fly ash. This comparison, shown in Figure III-13, is similar to that of Figure III-11 in that there is no obvious relationship between the parameters and there is significantly less sulfur retained than that which would be predicted assuming that the TAMO was available for reaction.

The above preliminary analyses suggested that the retention of sulfur cannot be explained adequately by an evaluation of individual parameters such as surface area, TAMO or slurry alkalinity but is more likely due to a more complex process involving both physical adsorption and chemical reactions where slurry alkalinity is governed by the surface area and possibly limited by pH effects on solubility.

To substantiate this theory, both surface area and slurry alkalinity were used as independent variables in a model to predict system sulfur retention. The resulting statistics showed correlation coefficients of 0.99 for the lignite, 0.78 for the subbituminous, and 0.93 for the bituminous fly ashes. It is evident from the level of significance that both surface area and slurry alkalinity are critical to the models. The contribution of the intercept to the models exhibited minimal significance, consequently, the final equations were forced through a zero intercept as shown below with R^2 values of 0.56, 0.93, 0.28, and 0.93, respectively:

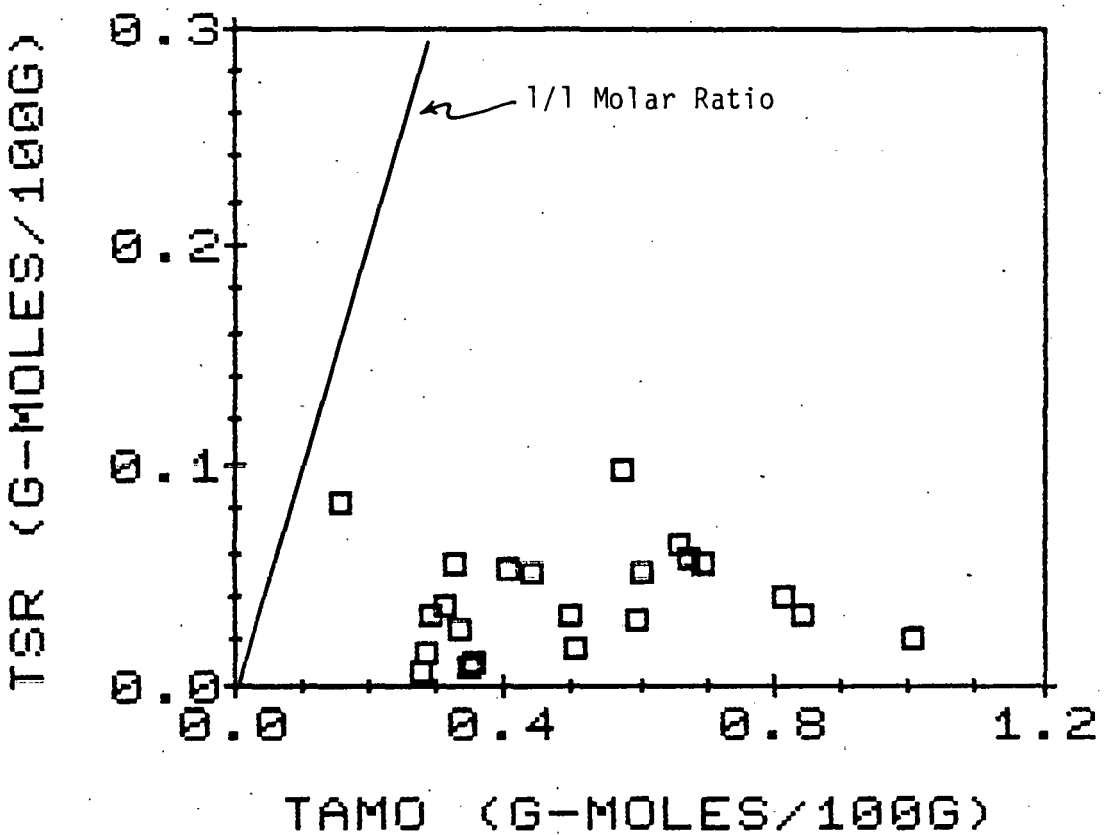

Figure III - 13. A Comparison of the Total Sulfur Retention versus the Total Alkaline Metal Oxide Content of the Fly Ashes.

$$SRS = 0.00278\ SA + 47.58\ OH + 23.37\ CO_3 - 6.39\ HCO_3$$

$$SRS(L) = 0.00688\ SA + 53.85\ OH + 12.53\ CO_3 - 18.45\ HCO_3$$

$$SRS(SB) = 0.00881\ SA + 43.56\ OH + 11.52\ CO_3 - 44.96\ HCO_3$$

$$SRS(B) = 0.00240\ SA - 28.08\ OH + 65.00\ CO_3 + 0.0366\ HCO_3$$

where:

SRS = combined data for sulfur retention across the spray dryer and baghouse (g/100g ash)

SRS(L) = lignite data only (g/100g ash)

SRS(B) = subbituminous data only (g/100g ash)

SRS(SB) = bituminous data only (g/100g ash)

SA = surface area of the fly ash (m^2/100g ash)

OH = slurry hydroxide alkalinity (g-moles/100g ash)

CO_3 = slurry carbonate alkalinity (g-moles/100g ash)

HCO_3 = slurry bicaronate alkalinity (g-moles/100g ash)

A graphical presentation of these models is shown in Figures III-14 through III-17.

It was further hypothesized that the total alkaline metal oxides (TAMO) in the fly ash should have an effect on the sulfur retention in the boiler. This effect in conjunction with the spray dryer plus bag house effect would allow a prediction of the total sulfur removal. To test this theory, a combination of the total alkaline metal oxides, surface area, and slurry alkalinity were used as independent variables with total sulfur retention (TSR) as the dependent variable. The resulting statistics showed correlation coefficients of 0.82 for lignite, 0.77 for subbituminous, and 0.96 for bituminous. The combined model had a R^2 of 0.59.

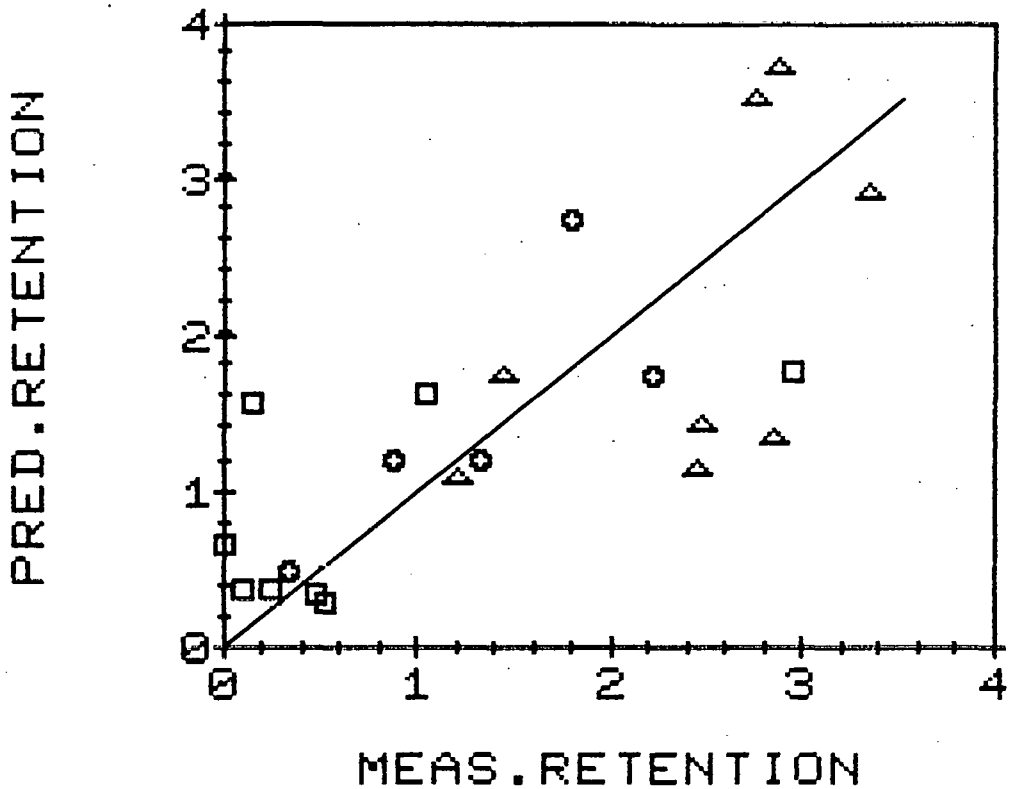

Figure III - 14. A Comparison of Predicted versus Measured Sulfur Retention across the System (g s/100 g ash) for all Ashes. (SRS)

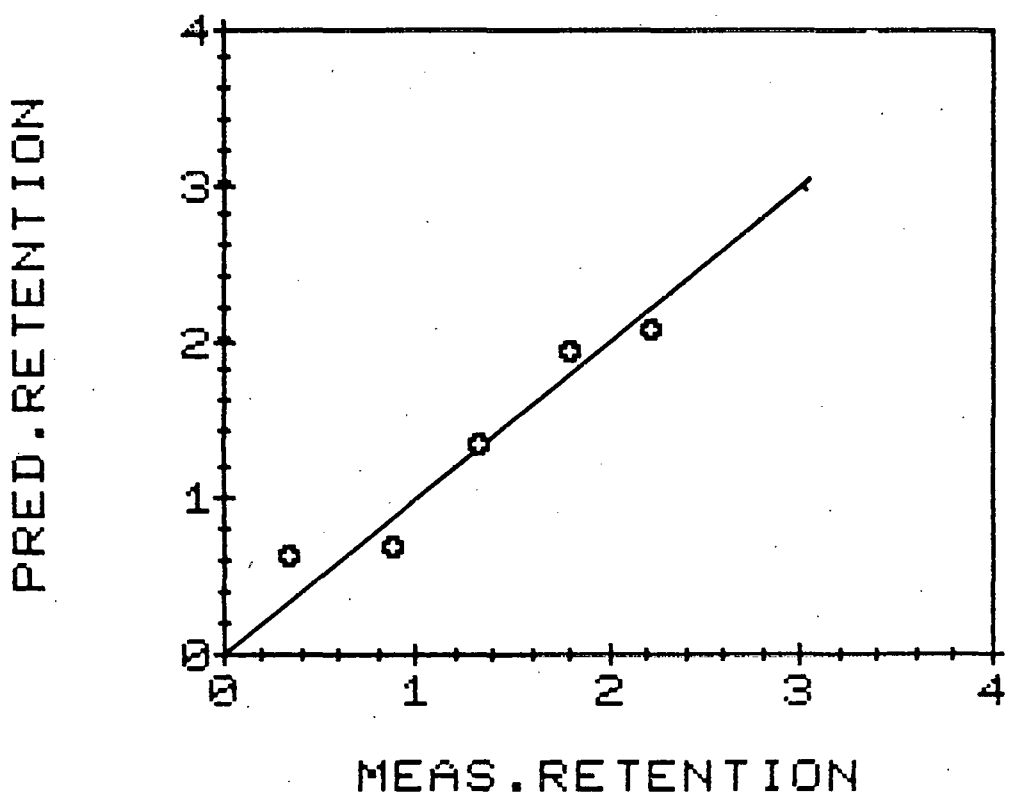

Figure III - 15. A Comparison of Predicted versus Measured Sulfur Retention across the System (g S/100 g ash) for the Lignite Ashes. (SRS (L)).

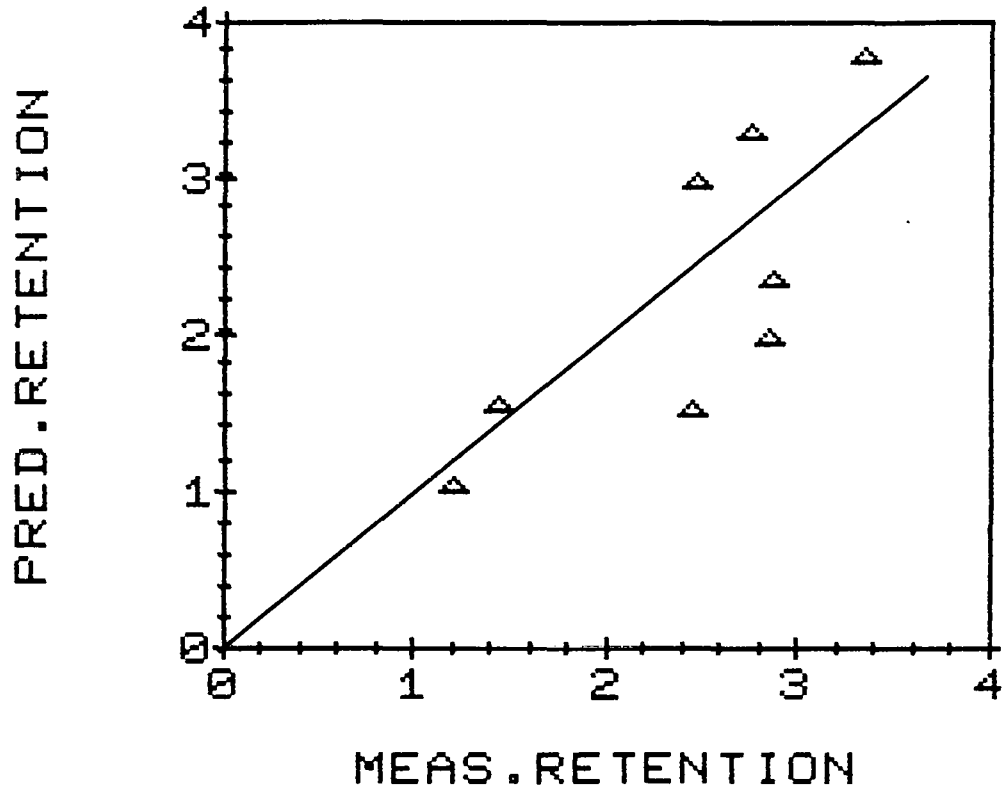

Figure III - 16. A Comparison of Predicted versus Measured Sulfur Retention Across the System (g S/100 g ash) for the Subbituminous Ashes. (SRS (SB))

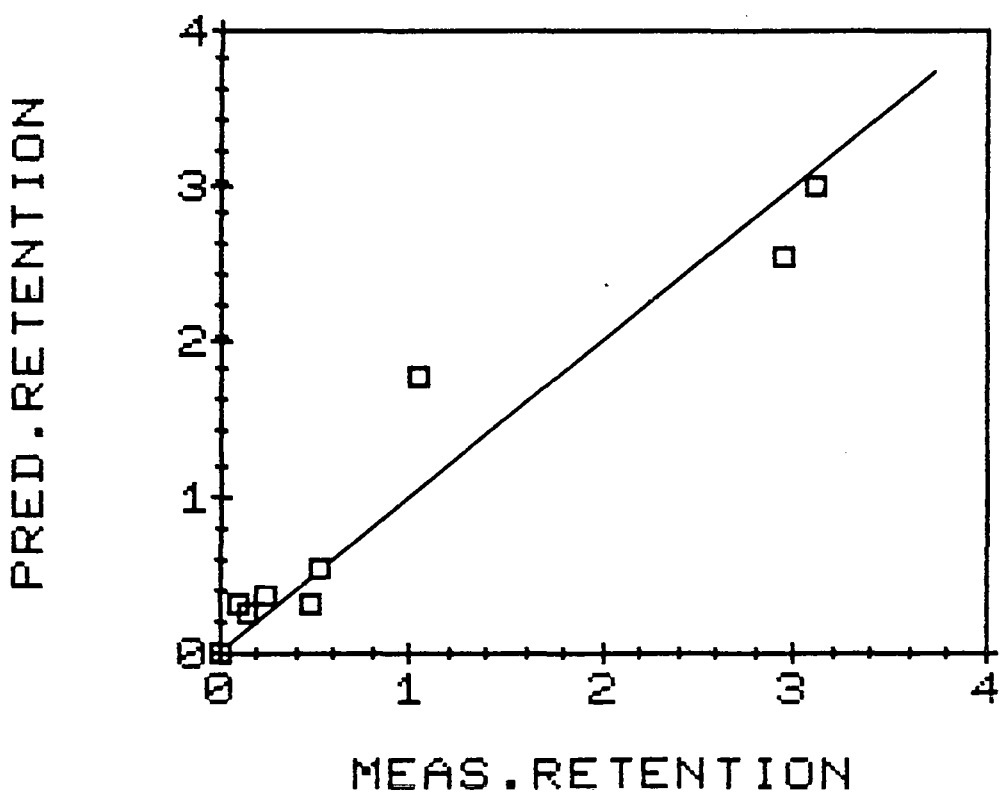

Figure III - 17. A Comparison of Predicted versus Measured Sulfur Retention Across the System (g S/100 g ash) for the Bituminous Ashes. (SRS (B))

The intercept data from these models was inconsistent due to the clustering of each individual coal classification. To be consistent with the previous model, the total sulfur retention model was also forced through a zero intercept. The final equations are shown below with R^2 values of 0.58, 0.94, 0.57, and 0.95, respectively.

$$TSR = 0.00459\ SA + 0.0209\ TAMO + 45.65\ OH + 19.92\ CO_3 + 5.23\ HCO_3$$

$$TSR(L) = 0.0631\ SA - 0.124\ TAMO + 146.15\ CO_3 - 428.4\ HCO_3$$

$$TSR(SB) = 0.00772\ SA + 0.0538\ TAMO + 13.26\ OH + 8.46\ CO_3 - 139.4\ HCO_3$$

$$TSR(B) = 0.00412\ SA + 0.0182\ TAMO + 18.00\ OH + 51.02\ CO_3 - 7.35\ HCO_3$$

where:

TSR = combined data for the total sulfur retention (g/100g ash)

TSR(L) = lignite data only (g/100g ash)

TSR(SB) = subbituminous data only (g/100 ash)

TSR(B) = bituminous data only (g/100g ash)

SA = surface area of the fly ash (m^2/100g ash)

TAMO = total alkaline metal oxides in the fly ash (g as CaO/100g ash)

OH = slurry hydroxide alkalinity (g-moles/100g ash)

CO_3 = slurry carbonate alkalinity (g-moles/100g ash)

HCO_3 = slurry bicarbonate alkalinity (g-moles/100g ash)

A graphical presentation of these models is shown in Figures III-18 through III-21.

The correlation coefficients for these modeling equations are reasonably good, however, to advocate modeling total sulfur

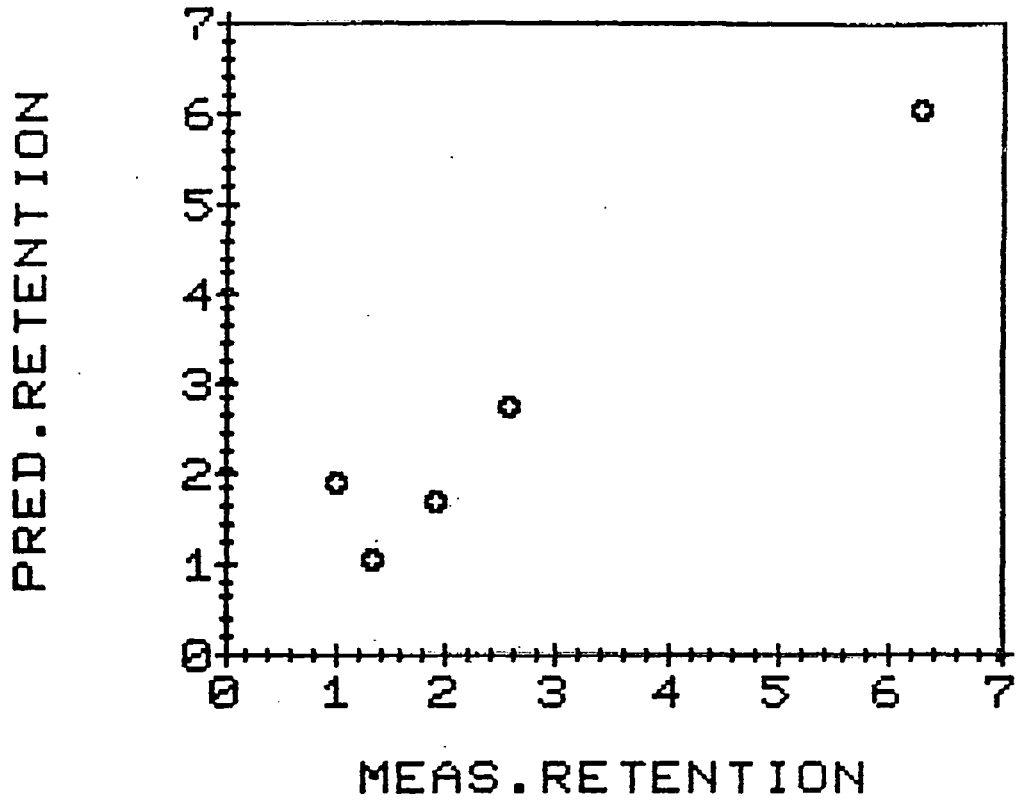

Figure III - 18 A Comparison of Predicted versus Measured Total Sulfur Retention (g S/100 g ash) for the Lignite Ahses. (TSR (L))

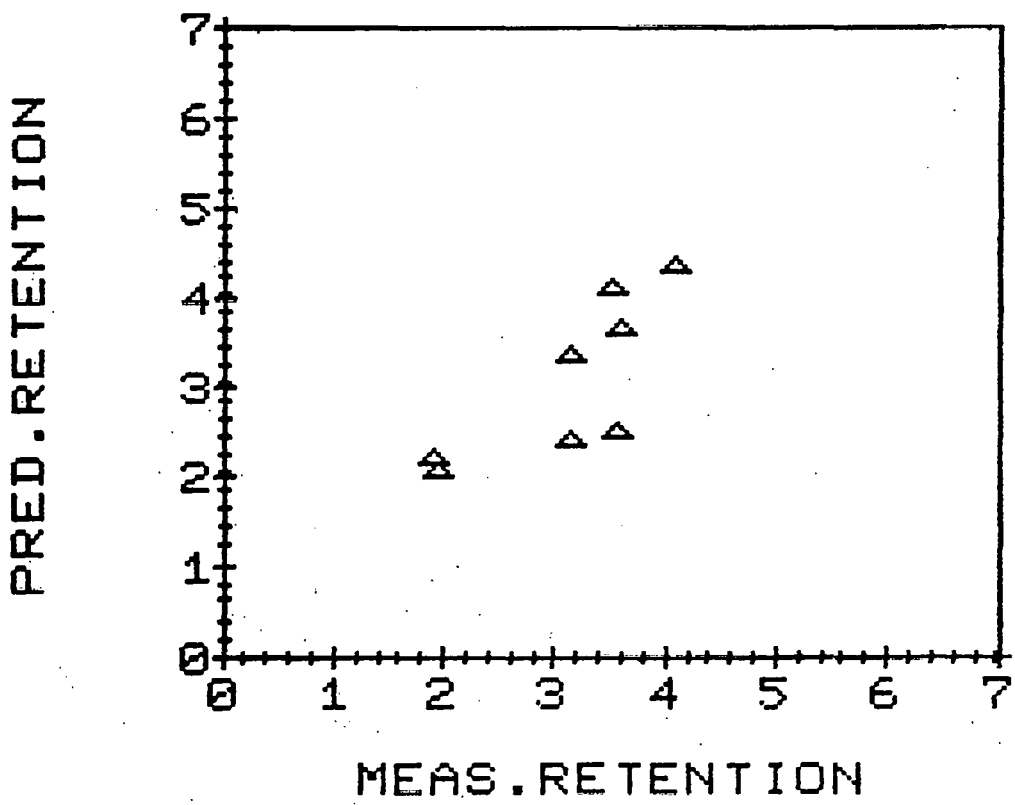

Figure III-19. A Comparison of Predicted versus Measured Total Sulfur Retention (g S/100 g ash) for the Subbituminous Ashes (TSR(SB)).

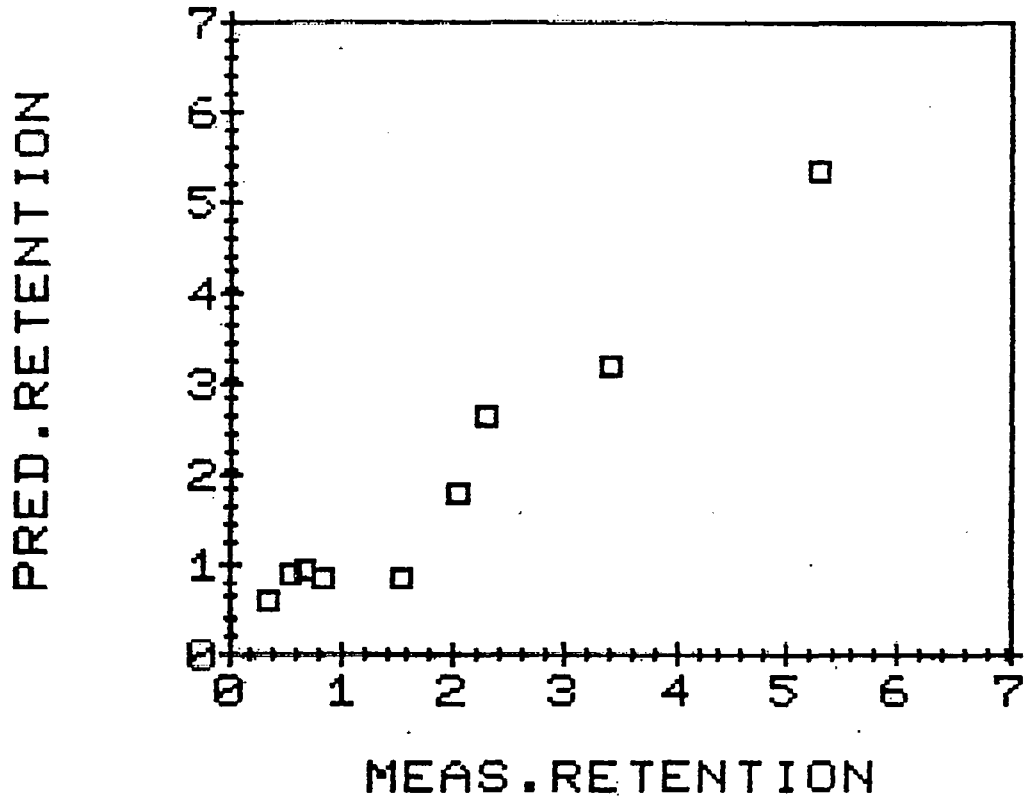

Figure III-20. A Comparison of Predicted versus Measured Total Sulfur Retention (g S/ 100 g ash) for the Bituminous Ashes (TSR(B)).

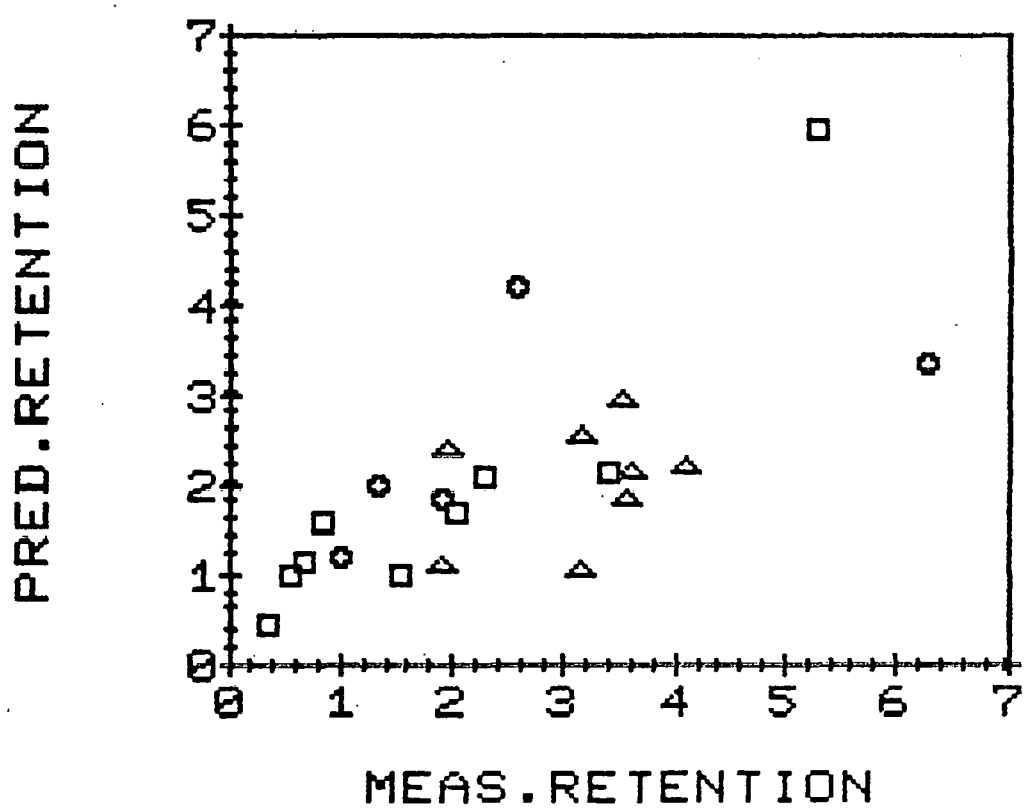

Figure III-21. A Comparison of Predicted versus Measured Total Sulfur Retention (g S/100 g ash) for all Ashes (TSR).

retention dependent on fly ash rank incorporates several risks. For example, the reduction in sample size for each of the 3 rank specific models provides a greater chance for error. Also, the variability in slurry alkalinity within the bituminous rank ashes indicates a weakness in the scheme of using coal classification. Hence, improperly ranked ashes may yield an inaccurate estimate of total sulfur retention. It is recommended that the complete fly ash models based on 23 ashes be used to minimize these risks.

Results of Dry Injection of Fly Ash

Sufficient quantities of fly ash were available on eleven of the twenty-two fly ashes to conduct a series of tests in which the fly ashes were injected as a dry addition into the flue gas upstream of the spray dryer. In this manner, an evaluation was conducted of the ability of the fly ashes to remove sulfur dioxide as it passes through the spray dryer/fabric filter system. The operating conditions of these tests were the same as for the fly ash slurry tests described in the previous section. The outlet temperature of the spray dryer was controlled at a 20°F approach to the wet bulb temperature by atomization of water through the spinning disk. The nominal fly ash injection rate was 0.42 lb/min (3.0 grains/ACF) which is typical of the fly ash loading from a coal-fired boiler.

The results of these tests are shown in Table III-10 which summarizes (1) the sulfur dioxide removed efficiency across the spray dryer and the system, and (2) the sulfur retained in the

TABLE III-10. Summary of Dry Injection Data

ID	Fly Ash Injection Rate (lb/min.)	SO_2 Removal (%) Spray Dryer	SO_2 Removal (%) System	SRS (g S/100g ash)
50	0.49	neg*	neg	neg
37	0.46	11.8	neg	neg
38-C	0.55	4.3	3.7	.35
46	0.40	4.9	11.	1.37
27	0.46	2.9	2.0	.21
13	0.42	2.2	4.2	.45
13	0.42	2.2	1.3	.15
13	0.42	10.6	6	.64
44	0.23	5.0	neg	neg
49	0.33	5.0	neg	neg
24	0.55	4.4	8.7	.69
23B	0.51	neg	neg	neg
10	0.51	12	11.9	1.16

neg = negligible

system (SRS) in grams of sulfur per 100 grams of ash. The maximum sulfur retention was 1.37/100g which was considerably less than the maximum amount obtained when the fly ashes were slurried (4.61 g/100g). Also it is evident that many of the fly ashes had a negligible ability to retain sulfur when utilized in this mode. No further statistical treatment was conducted on the data due to the relatively small number of ashes which showed removal. A comparison of the sulfur retained in the system (SRS) by dry injection versus SRS by slurry injection was made, however, there was no apparent relationship.

The Effect of Approach to Saturation on Reactivity

One of the parameters that was held constant during the testing of all 22 fly ashes was the approach to the flue gas dew point, ΔT, which was maintained at a 20°F approach to saturation. Since previous testing of spray dryers utilizing lime have shown sensitivity to this parameter a series of tests was conducted in which fly ash 44 (Hoot Lake) was slurried in the same manner as described above (1.45 lbs/gallon) but the approach to saturation was varied from 15 up to 40°F. These data are summarized in Appendix A and are shown graphically in Figure III-22. As shown in the figure, the SO_2 removal efficiency increased from approximately 20% up to 46% when the ΔT was lowered from 40 down to 15°F. A series of tests with water (no fly ash added) ranged from 6-9% efficiency. The data clearly show that the approach to saturation has a significant influence on the SO_2 removal efficiency of the spray dryer/fabric filter collector.

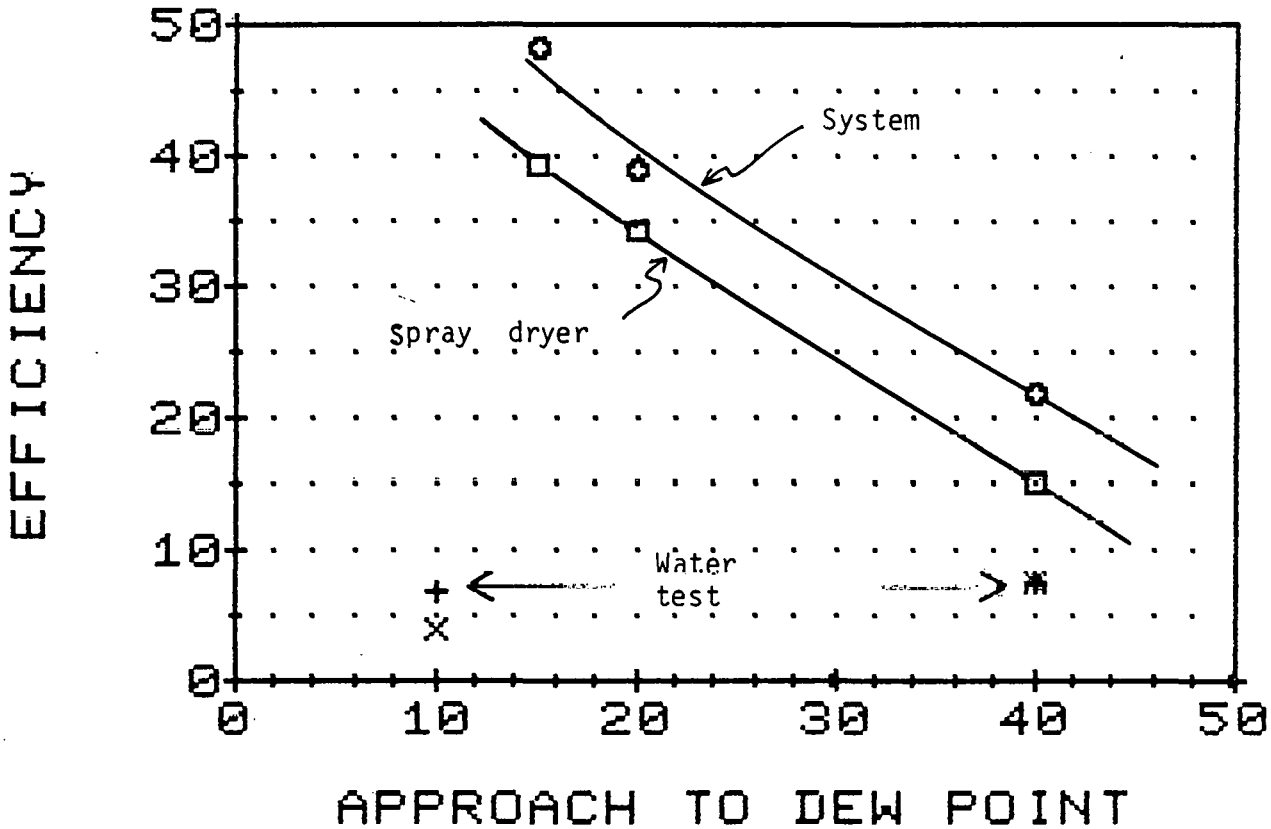

Figure III - 22. Efficiency (%) versus Approach to Dew Point (^{o}F) for the Spray Dryer and the System for Fly Ash #44.

Results of Testing Fly Ash in Lime Slurry

All of the fly ashes tested showed some degree of reactivity with SO_2 when slurried in H_2O and injected into the spray dryer as shown above. A series of tests was conducted to determine the combined benefit of the fly ash when co-slurried with $Ca(OH)_2$ and injected into the spray dryer/fabric filter FGD system. For the purpose of comparison, a series of tests were conducted to establish the SO_2 removal efficiency versus stoichiometric ratio of $Ca(OH)_2$ for the operating conditions of the study. Once this baseline was established, three different fly ashes were co-slurried with lime, and injected into the system, the results of which were compared to the baseline. The tests were conducted by pre-mixing the fly ash in one mixing tank, slaking and pre-mixing the $Ca(OH)_2$ in a second tank, followed by a final mixing of the two slurries into a final tank to arrive at the final desired concentration of fly ash (lb/gallon) and lime concentration (lbs of CaO/gallon of slurry).

The following conditions summarize the baseline test conditions:

SO_2 in = 740 - 1200 ppm

Temperature ≅ 300°F (275 - 310°F)

Flow Rate* = 886 AFCM ± 10 ACFM

Residence Time ≅ 15 second (spray dryer only)

Approach to dew point = 20° F ± 1°F

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*Measured at outlet of system at 130-155° depending on the approach to saturation.

The spinning disk atomizer was operated at 17000 rpm which yielded a predicted drop diameter of nominally 75-85 μm at a 1.0 stoichiometric ratio. The drop diameter reported herein was the mean diameter predicted by the equation developed by Masters[16].

Figures III-23 and III-24 show the baseline data obtained for the lime slurry (no fly ash added) indicating the relationship between SO_2 removal efficiency and stoichiometric ratio for the spray dryer and the spray dryer/fabric filter system, respectively.

The system (spray dryer plus fabric filter) provided substantially better performance than the spray dryer alone as shown in Figures III-24 and III-23, respectively. In excess of 90% efficiency was obtained at a stoichiometric ratio of approximately 1.0 for the system. Using only the spray dryer (typical of applications using an electrostatic preciptiator as a final collection device), 90% efficiency required in excess of a 1.5 stoichiometric ratio and was not achieved consistently.

It should also be noted that the performance of the system is also depdendent on the SO_2 concentration. In a separate study[17] of tests conducted on the system reported herein it was shown that the stoichiometric ratio required to achieve 90% SO_2 removal efficiency across the system increased significantly as the SO_2 concentration was increased, going from 1.0 at 442 ppm, to 1.6 at 1400 ppm, to 2.2 at 2000 ppm for a 25°F approach to the dew point.

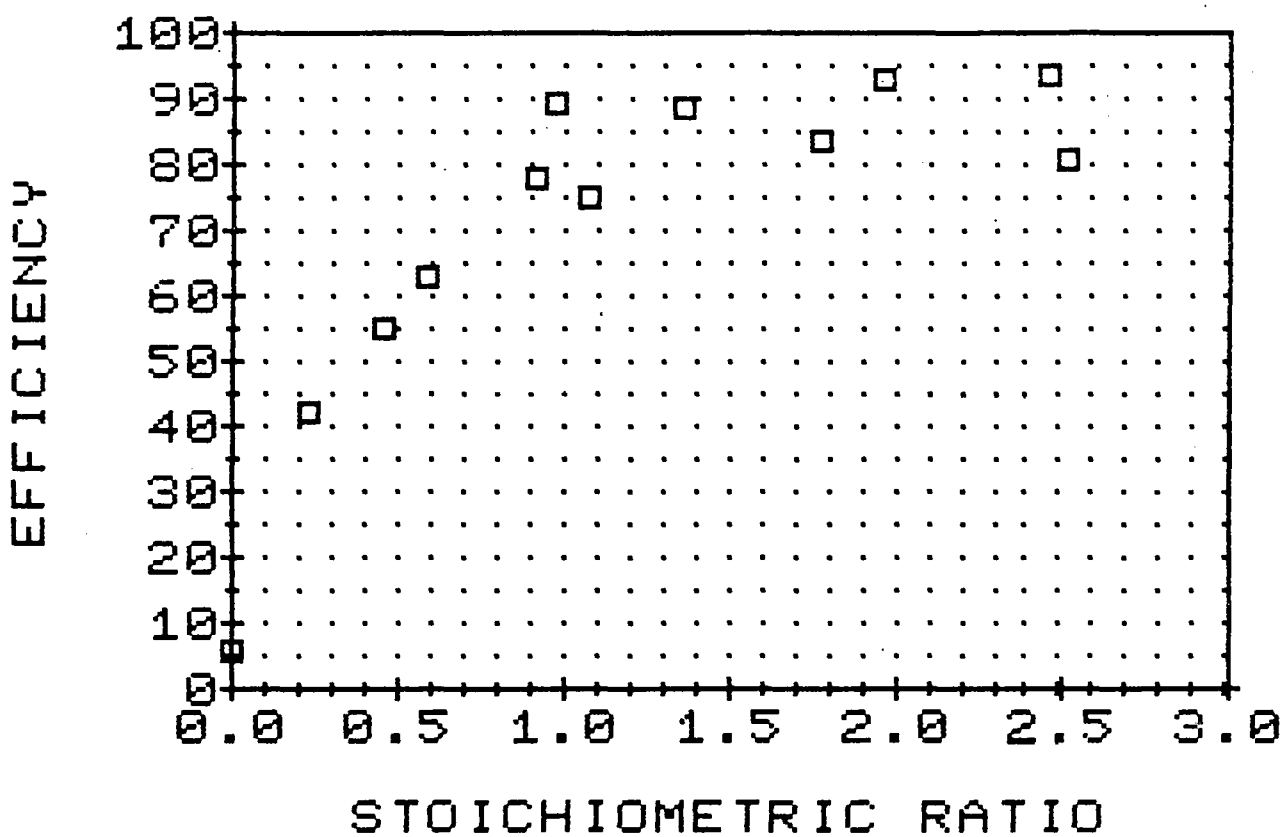

Figure III - 23. SO_2 Removal Efficiency (%) versus Stoichiometric Ratio for the Spray Dryer.

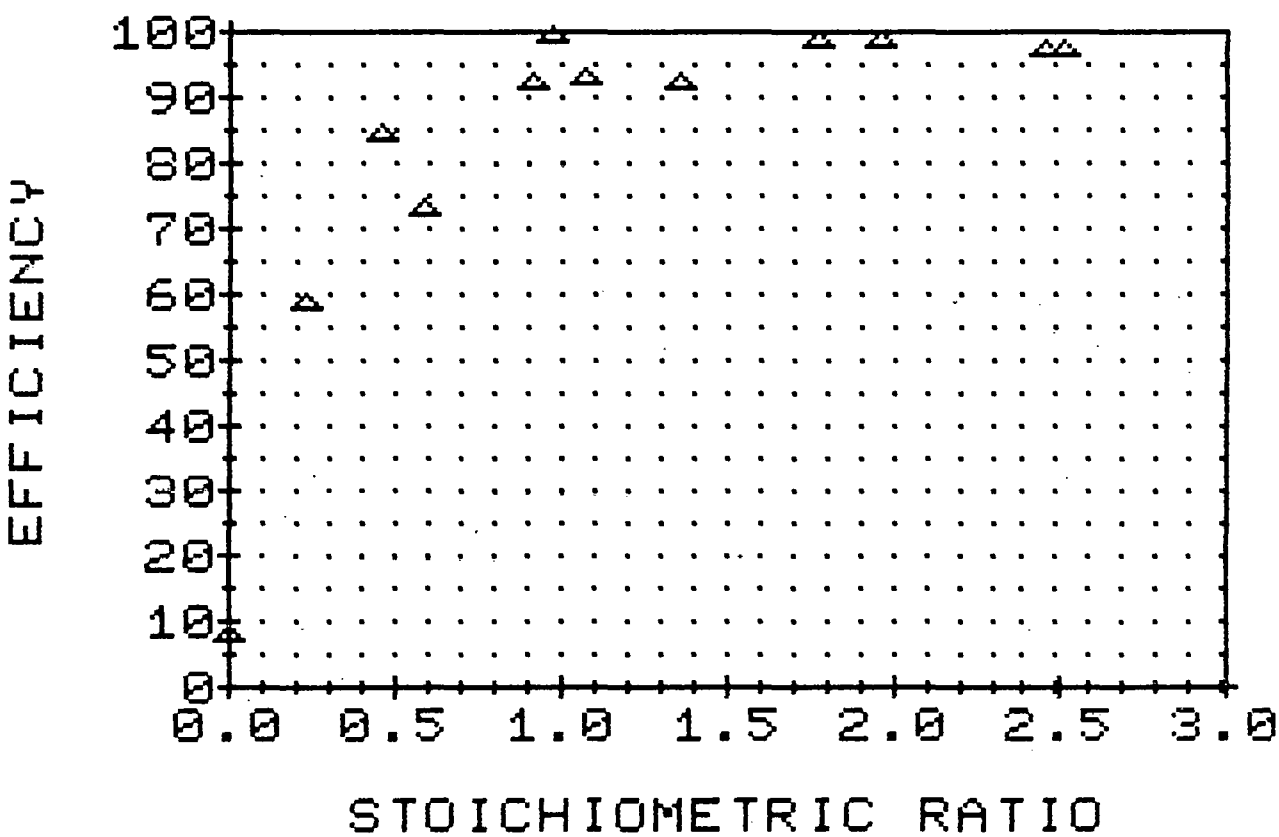

Figure III - 24. SO_2 Removal Efficiency (%) versus Stoichiometric Ratio for the System (Spray Dryer + Fabric Filter).

In an effort to evaluate the effect of the addition of fly ash to the lime slurry, three different fly ashes were added to the $Ca(OH)_2$ slurry at concentrations of 1.45 lbs/gallon of slurry.

Prior to mixing each fly ash slurry into the final "$Ca(OH)_2$ + fly ash" mixing tank, the fly ash slurries were titrated to determine the available CaO. The following values were found:

Fly ash 45: 0.0075 - 0.014 lb/gal as CaO

Fly ash 42: 0.012 - 0.029 lb/gal as CaO

Fly ash 43: 0.0078 - .028 lb/gal as CaO

These values were based on a concentration of 1.45 lbs/gal of ash in the final mix tank. In comparison, the available CaO of the $Ca(OH)_2$ was approximately 0.30 lb CaO/gallon of slurry at a stoichiometric ratio of 1.0. Therefore it can be concluded that the fly ashes contributed only 0.01 to 0.1 equivalent stoichiometric ratios to the overall available lime. The SO_2 removal efficiency versus stoichiometric ratio data obtained from the "$Ca(OH)_2$ + fly ash" tests are shown in Figures III-25 and III-26 for the spray dryer and the spray dryer/fabric filter system, respectively. These tests were conducted at 700-900 ppm of SO_2 with other conditions being the same as those of the baseline lime tests. The baseline $Ca(OH)_2$ data are also shown in these figures to provide a comparison to the "$Ca(OH)_2$ + fly ash" tests.

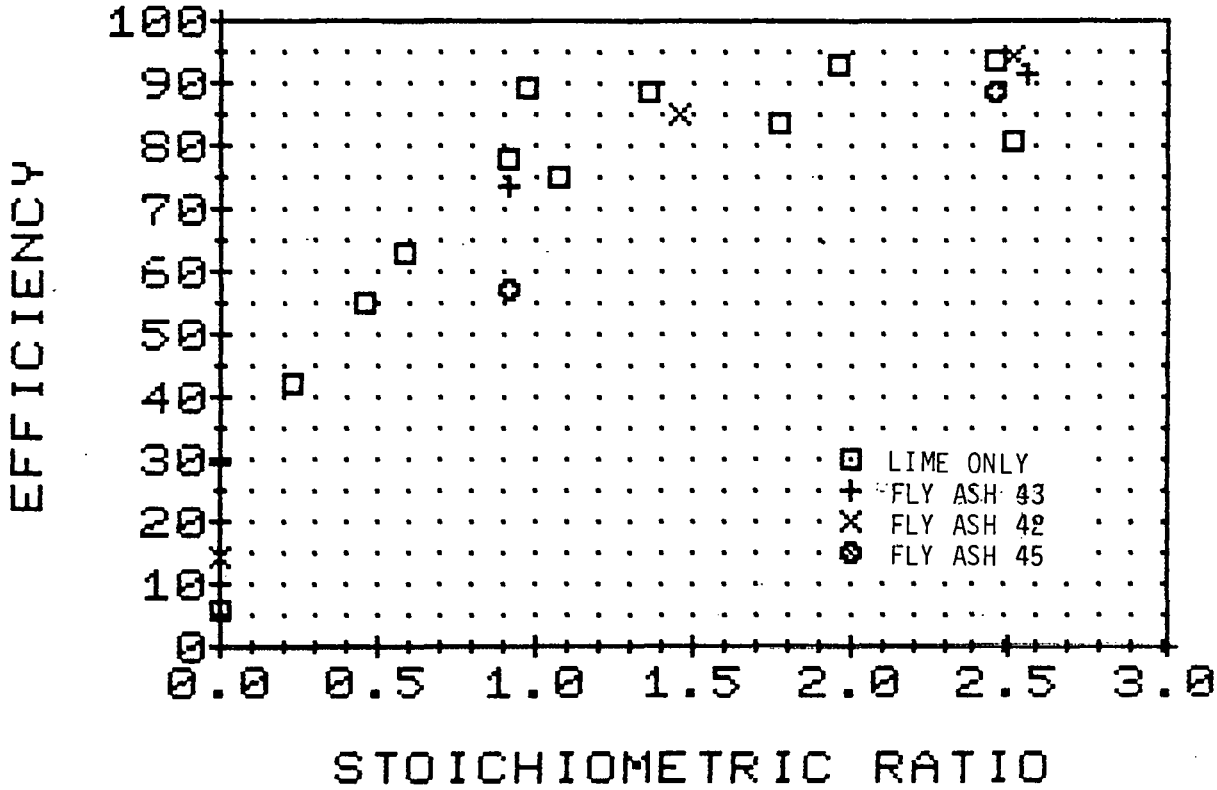

Figure III - 25. SO_2 Removal Efficiency (%) Across the Spray Dryer versus Stoichiometric Ratio with Fly Ash as an Slurry Additive.

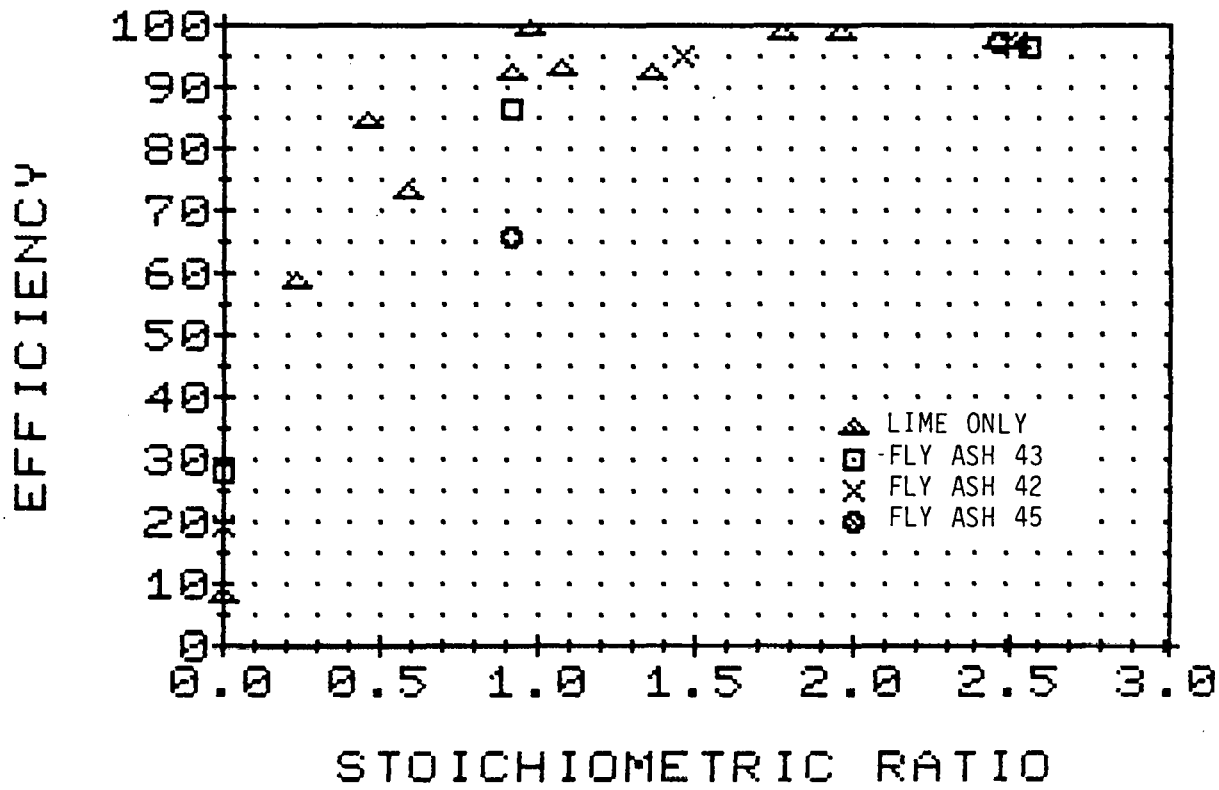

Figure III - 26. SO_2 Removal Efficiency (%) Across the System versus Stoichiometric Ratio with Fly Ash as an Slurry Additive.

In general, the addition of the fly ashes to the $Ca(OH)_2$ slurries provided no net improvement in the SO_2 removal efficiency at a given stoichiometric ratio either in the spray dryer or across the entire system. These results were unexpected in light of the positive benefits observed when those same fly ashes were added to water and injected. Additional study is needed to ascertain why the lime slurry masked the effects of the fly ashes and to determine if there is an alternate procedure which might be utilized to enhance the ability of fly ashes to react when placed in lime slurries. In a separate study[17] conducted on the system described herein, it was shown that spray dryer product (which also had very low available CaO when titrated) produced a significant improvement in performance when mixed with a $Ca(OH)_2$ slurry. The product, however, had approximately 20 m^2/g of surface area compared to the 0.29 - 3.0 m^2/g of the fly ashes in this study suggesting that surface area may be a significant factor required to enhance the reactivity of the $Ca(OH)_2$.

References

1. Downs, W., W. J. Sanders, and C. E. Miller. "Control of SO_2 Emissions by Dry Scrubbing." American Power Conference, Chicago, Illinois, paper PGTP80-22, April, 1980.

2. Hurst, T. B., and G. T. Bielawski. "Dry Scrubber Demonstration Plant - Operating Results." GPA Symposium on Flue Gas Desulfurization, Houston, Texas, October, 1980.

3. Stevens, N. J. "Dry Scrubbing Pilot Test Results." EPA Symposium on Flue Gas Desulfurization, Houston, Texas, October, 1980.

4. Parsons, E. L., O. T. Kragh, T. G. Brna, and R. L. Ostop. "SO_2 Removal by Dry FGD." EPA Symposium on Flue Gas Desulfurization, Houston, Texas, October, 1980.

5. Karlsson, H. T., J. Klingspor, M. Linné, and I. Bjerle." Activated Wet-Dry Scrubbing of SO_2." JAPCA, Vol. 33, No. 1, pp. 23-28, 1983.

6. Meyer, B. and C. Carlson. "Mechanism of SO_2 Adsorption of Metal Oxides, Carbonates, and Hydroxides." In Proc. 2nd Intl. Clean Air Conf., Academic Press, 1971.

7. Natusch, D., et al. "Toxic Trace Elements: Preferable Concentration in Respirable Particles." Science, Vol. 183, pp. 202-204, 1974.

8. Keyser, T., et al. "Characterizing the Surfaces of Environmental Particles." Environmental Science and Technology, 12:7, July, 1978.

9. Hulett, L. D. and A. J. Weinberger. "Some Etching Studies of the Microstructure and Composition of Large Aluminosilicate Particles in Fly Ash from Coal Burning Power Plants." Oak Ridge National Laboratory, Oak Ridge, TN, 1979.

10. Ensor, D. S., et al. Elemental Analysis of Fly Ash from Combustion of a Low Sulfur Coal. Presented at 68th annual meeting of APCA, Boston, MA, June, 1975.

11. Ray, S. S. and F. G. Parker. Characterization of Ash from Coal-Fired Power Plants. EPA Contract No. 600/7-77-010, January, 1977.

12. Rothenberg, S. J. "Coal Combustion Fly Ash Characterization: Adsorption of Nitrogen and Water." Atmospheric Environment, Vol. 14, pp. 445-456, 1979.

References (continued)

13. Davis, W. T. and M. A. Fiedler. "The Retention of Sulfur in Fly Ash from Coal-Fired Boilers." APCA Journal, Vol. 32, No. 4, April, 1982, pp. 395-397.

14. Barnes, H. L. and S. B. Romberger. "Chemical Aspects of Acid Mine Drainage." JWPCF, 40:1, March, 1968.

15. Fiedler, M. A. Sulfur Retention in Fly Ash, thesis, The University of Tennessee, August, 1980.

16. Masters, K. Spray Drying Handbook, 3rd Ed., John Wiley & Sons, New York, p. 180, eq. 6-12, 1979.

17. Davis, W. T. and G. D. Reed. "Parametric Testing of a Spray Dryer/Fabric Filter FGD System." Final Report submitted to the Energy Demonstration and Technology Division, Tennessee Valley Authority, Chattanooga, TN, Dec. 15, 1982.

APPENDIX A

SPRAY DRYER TEST DATA

TABLE A-1. Parameters Defined on the Data Summaries

INPUT DATA

Test No.	= 8 digit number; first 6 digits are the date (i.e., 102982); last two digits represent the test number (i.e. 01, 02, 03 . . .)
RPM	= Atomizer speed (revolutions/minute): frequency inverter
SO2ONE	= SO_2 concentration (wet basis) at SD inlet (ppm) -Port 1: Lear Siegler SM800
SO2TWO	= SO_2 concentration (wet basis) at SD outlet (ppm) - Port 2: Lear Siegler SM800
SO2THR	= SO_2 concentration (wet basis) at Baghouse outlet (ppm) - Port 3: Lear Siegler SM800
TEMP1	= Flue gas temperature at Port 1 (°F): Thermocouple
TEMP2	= Flue gas temperature at Port 2 (°F): Thermocouple
TEMP3	= Flue gas temperature at Port 3 (°F): Thermocouple
SLCONC	= Slurry concentration (in lbs/gallon of available CaO): Iteration of Slurry with 3N HCL.
DPORIF	= Flow orifice pressure drop (inches of H_2O): Photohelic gauge
SP1	= Static pressure below atmospheric pressure (inches H_2O) - Port 1: Magnehelic gauge
SP2	= Static pressure below atmospheric pressure (inches H_2O) - Port 2: Magnehelic gauge
SP3	= Static pressure below atmospheric pressure (inches H_2O) - Port 3: Magnehelic gauge

NOTE: 5.4" recorded value is really -5.4" H_2O pressure relative to atmospheric pressure since system is under suction.

TABLE A -1. Continued

GPM	=	Slurry feed rate (gallons/minute): Volumetric Displacement in final feed tank.
PBAR	=	Atmospheric or Barometric pressure (inches Hg): Barometer
TW1	=	Wet-Bulb temperature at Port 1 (°F): Wet bulb thermometer
TW2	=	Wet-bulb temperature at Port 2 (°F): Wet bulb thermometer
TW3	=	Wet-bulb temperature at Port 3 (°F): Wet bulb thermometer
TAMB	=	Ambient temperature (°F): Thermometer

CORRECTED DATA/RESULTS

ACFM3	=	Flue gas flow rate at Port 3 at actual stack conditions of temperature, pressure, and moisture
SCFM1C	=	Flue gas flow rate at spray dryer inlet including air in-leakage (at standard temperature and pressure-wet basis)
TEMP1C	=	Flue gas temperature at spray dryer inlet (°F)
SO2ONEC	=	So_2 concentration at spray dryer inlet corrected for air in-leakage (ppm-wet basis)
EFFSD	=	SO_2 removal efficiency of the spray dryer (%)
EFFSYS	=	SO_2 removal efficiency of the system (%)
SR	=	Stoichiometric ratio (moles CaO/mole SO_2 at inlet)
DVS	=	Mean Drop diameter (um) - Masters[16], p. 180, e.q. 6-12.
BW1	=	Moisture fraction by volume - spray dryer inlet
BW2	=	Moisture fraction by volume - spray dryer outlet
BW3	=	Moisture fraction by volume - fabrication outlet

Note: BWI = .10 (10% by volume)

DELTAT (ΔT) = TEMP2 - TW2 = approach to saturation (°F)

TABLE A-2. Data for Fly Ash in H_2O

TEST NO.	FLY ASH ID	RPM	SO2 OME	SO2 TWO	SO2 THR	TEMP 1	TEMP 2	TEMP 3	DPORIF	SP 1	SP 2	SP 3	GPM	PBAR	TW 1	TW 2	TW 3
Lignite																	
111381	27	17000	630	550	530	307	137	141	.41	4.4	9.8	12.3	.30	29.43	119	117	116
111181	38C	17000	675	530	510	302	137	162	.36	3.9	7.5	9.9	.25	29.40	119	117	116
111881	41	17000	725	530	510	303	137	159	.44	4.2	7.3	9.8	.25	29.33	120	118	117
100581	42	17000	625	510	510	312	138	132	.42	3.5	5.9	6.5	.23	29.39	120	116	112
100581	44	17000	658	500	500	298	138	139	.42	3.5	5.0	6.2	.21	29.39	120	116	112
Subbituminous																	
100781	13	17000	592	500	440	310	136	151	.38	3.5	5.0	6.5	.24	29.01	120	116	112
111081	14	17000	665	390	410	310	139	138	.41	4.0	5.6	9.0	.21	29.40	120	118	117
111081	18A	17000	680	480	470	307	137	140	.40	4.1	7.0	9.2	.21	29.40	119	117	116
121081	37	17000	680	450	445	303	139	136	.42	5.3	7.2	7.3	.23	29.33	119	117	116
110681	38B	17000	655	480	430	304	137	133	.44	4.1	5.8	9.3	.22	29.42	119	115	114
100581	43	17000	633	440	417	310	138	130	.42	3.5	5.0	6.2	.21	29.39	120	116	112
100681	45	17000	678	530	455	310	138	132	.41	3.7	5.5	6.2	.24	29.13	120	118	114
100581	46	17000	630	490	490	315	138	131	.42	3.5	5.0	6.5	.24	29.39	120	116	113
Bituminous																	
121081	6	17000	670	610	590	304	138	144	.43	5.2	7.2	7.3	.22	29.33	120	118	117
100781	10	17000	578	460	480	311	136	138	.38	5.5	5.0	6.5	.24	29.01	120	117	114
100681	18B	17000	735	475	480	316	138	132	.41	3.5	5.9	6.5	.20	29.13	119	117	116
111181	23B	17000	635	550	550	314	137	138	.40	4.2	7.2	9.7	.24	29.40	119	117	116
110481	24	17000	1015	850	850	310	135	146	.39	3.9	6.4	7.0	.25	29.16	120	117	114
111381	34	17000	670	510	560	305	136	143	.41	4.4	9.5	12.2	.27	29.43	119	117	116
111181	36	17000	670	590	600	302	135	152	.39	4.3	8.9	11.5	.26	29.40	119	117	116
121181	49	17000	640	505	400	292	138	145	.43	6.0	8.1	8.2	.22	29.13	120	118	117
100181	50	17000	1000	880	870	315	138	135	.41	3.8	5.5	6.5	.24	28.96	120	119	119

Table A-3. Data for Approach to Saturation (Fly Ash Only)

TEST NO.	RPM	SO2ONE	SO2TWO	SO2THR	TEMP1	TEMP2	TEMP3	SLCONC	DPORIF	SP1	SP2	SP3	GPM	PBAR	TW1	TW2	TW3
07228201	17000	597	466	453	315	123	126	-	0.40	4.0	6.0	6.0	0.273	29.3	119	113	112
07228203	17000	622	469	463	303	154	135	-	0.40	4.0	6.0	6.0	0.225	29.3	118	114	111
07228204	17000	640	340	320	315	134	135	-	0.39	4.0	5.9	6.1	0.193	29.3	118	114	110
07228205	17000	590	290	250	307	129	130	-	0.40	3.9	5.8	6.2	0.358	29.3	118	114	110
07228206	17000	635	440	410	312	154	145	-	0.40	4.0	5.2	5.9	0.142	29.3	118	114	110

TEST NO.	TAMB	ACFM3	SCFM1C	TEMP1C	SO2ONEC	EFFSD	EFFSYS	SR	DVS	BW1	BW2	BW3	DELTAT	FLYASHID	C*ONCASH
07228201	74	876	738	280	511	3.6	6.7	0	82.8	0.050	0.095	0.091	10	-	-
07228203	82	883	735	276	533	7.5	9.0	0	79.0	0.049	0.088	0.085	40	-	-
07228204	82	873	737	383	547	34.2	38.9	0	76.2	0.047	0.094	0.082	20	44	1.45
07228205	85	879	740	275	504	39.1	48.2	0	88.4	0.049	0.096	0.084	15	44	1.45
07228206	85	890	733	279	543	14.9	21.5	0	70.8	0.047	0.087	0.078	40	44	1.45

*Concentration of fly ash (lbs/gallon). The equivalent lime (as CaO) in the slurry was .014 lb/gal.

Table A-4. Data for Baseline $Ca(OH)_2$

TEST NO.	RPM	SO2ONE	SO2TWO	SO2THR	TEMP1	TEMP2	TEMP3	SLCONC	DPORIF	SP1	SP2	SP3	GPM	PBAR	TW1	TW2
10188201	17000	1055	923	927	320	135	146	0.000	0.40	3.1	4.2	6.8	0.21	29.33	120	116
10118202	17000	1194	644	472	312	134	130	0.127	0.40	3.2	4.5	6.2	0.226	29.26	118	114
10198203	17000	1120	467	177	312	134	132	0.262	0.40	3.5	4.5	6.3	0.21	29.26	118	114
10118204	17000	1065	225	80	313	133	133	0.450	0.40	4.0	5.0	6.2	0.23	29.02	119	113
10118205	17000	1005	155	20±10	309	133	137	0.700	0.40	3.7	4.9	6.0	0.269	29.02	119	113
10118206	17000	1040	70	20±10	309	133	150	0.820	0.40	3.5	4.5	5.5	0.26	29.02	119	113
10198204	17000	1072	110	14	313	134	136	0.500	0.40	3.5	4.5	6.4	0.22	29.32	118	114
07128202	17000	984	200	60	313	137	140	0.367	0.40	3.0	5.0	6.0	.262	29.30	119	117
07128201*	17000	950	150	25	313	137	138	0.840	0.40	3.0	5.0	6.0	0.26	29.3	119	117
07098205	17000	847	80	60	310	134	140	0.375	0.40	3.0	4.8	5.1	.288	29.33	119	114
07098204	17000	830	250	190	310	134	134	0.189	0.40	3.0	4.8	5.0	0.24	29.33	119	114
07098203	17000	740	40	20	308	133	132	0.694	0.40	2.9	4.9	5.1	0.245	29.33	118	113

Table A-4. Continued

TEST NO.	TW3	TAMB	ACFM3	SCFM1C	TEMP1C	SO2ONEC	EFFSD	EFFSYS	SR	DVS	BW1	BW2	BW3	DELTAT
10188201	108	62	891	735	313	1027	5.3	7.6	0.000	77.7	0.052	0.099	0.730	20
10118202	108	65	880	738	306	1163	41.7	57.9	0.230	79.3	0.048	0.094	0.078	20
10198203	108	65	881	737	306	1091	54.9	83.7	0.470	78.2	0.048	0.094	0.078	20
10118204	106	67	886	740	307	1037	77.3	92.1	0.927	80.2	0.052	0.093	0.073	20
10118205	106	67	889	740	303	979	83.5	97.9	1.780	83.7	0.054	0.095	0.072	20
10118206	106	66	898	736	303	1013	92.8	97.9	1.970	83.2	0.053	0.092	0.067	20
10198204	108	61	884	736	306	1044	88.9	98.6	0.985	79.4	0.047	0.094	0.076	20
07128202	113	83	887	731	279	840	74.6	92.5	1.080	82.6	0.050	0.102	0.089	20
07128201*	114	79	885	731	279	811	80.3	96.8	2.520	83.2	0.050	0.102	0.093	20
07098205	106	75	885	747	276	725	88.4	91.5	1.370	84.5	0.051	0.094	0.069	20
07098204	106	76	881	749	276	710	62.8	72.4	0.586	80.6	0.051	0.094	0.071	20
07098203	106	76	879	748	274	633	93.3	96.7	2.470	81.8	0.049	0.091	0.072	20

*Excessive SR, atomizer may have been clogging.

Table A-5. Data for Fly Ash + $Ca(OH)_2$

TEST NO.	RPM	SO2ONE	SO2TWD	SO2THR	TEMP1	TEMP2	TEMP3	SLCONC	DPORIF	SP1	SP2	SP3	GPM	PBAR	TW1	TW2	TW3
07148201	17000	1030	225	117	307	133	144	0.336	0.40	3.0	4.8	5.3	0.263	29.3	120	113	107
07168202	17000	850	40	20	302	135	135	0.695	0.40	3.1	5.0	5.1	0.284	29.3	119	115	112
07168201	1700	870	110	40	307	135	135	0.398	0.40	3.1	5.0	5.1	0.292	29.3	119	115	112
07158202	17000	993	689	655	308	137	145	-	0.40	2.5	4.1	4.5	0.246	29.3	119	116	114
07158201	17000	1052	605	618	310	135	144	-	0.40	3.0	5.0	5.0	0.278	29.3	118	115	113
07138201	17000	990	70	30	310	136	162	0.806	0.040	3.0	5.0	5.0	0.287	29.3	120	115	114
07138202	17000	1060	100	30	316	136	145	0.830	0.40	3.0	5.0	5.0	0.286	29.3	121	116	113
07128201	17000	903	317	253	305	137	133	0.297	0.40	3.0	5.0	5.0	0.246	29.3	120	117	115

TEST NO.	TAMB	ACFM3	ACFM1C	SCMF1C	SO2ONEC	EFFSD	EEFSYS	SR	DVS	BW1	BW2	BW3	DELTAT	FLYASHID	C* ONCASH	C** ONCCAO
17148201	90	889	746	276	882	73.3	86.4	0.920	82.6	.056	.091	.071	20	43	1.45	.024
07168202	85	882	738	271	727	94.2	97.1	2.520	84.7	.054	.097	.087	20	42	1.45	.012
07168201	86	882	737	275	744	84.4	94.4	1.460	84.9	.052	.097	.088	20	42	1.45	.015
07158202	86	889	729	276	849	14.0	19.0	0.000	80.8	.050	.099	.090	21	42	1.45	.029
07158201	83	888	729	277	899	28.6	27.8	0.000	83.2	.048	.097	.088	20	43	1.45	.028
07138201	85	902	725	277	847	91.2	96.3	2.570	83.9	.055	.096	.084	21	43	1.45	.0078
07138202	80	889	735	282	907	88.4	96.5	2.460	85.1	.057	.099	.087	20	45	1.45	.0075
07128201	86	880	735	273	772	56.5	65.4	0.922	82.0	.057	.103	.098	20	45	1.45	.014

*Concentration of fly ash (lbs/gallon)
**Concentration of equivalent CaO in fly ash (titrated value)

Table A-6. Data for Dry Fly Ash Injection

TEST NO.	RPM	SO2ONE	SO2TWO	SO2THR	TEMP1	TEMP2	TEMP3	DPORIF	SP1	SP2	SP3	GPM	PBAR	TW1	TW2	TW3
83032504	17000	887	727	794	312	128	126	.40	4.2	5.1	6.0	.22	29.12	115	108	104
83032503	17000	805	748	723	300	128	124	.41	4.2	5.2	6.1	.21	29.12	115	108	104
83032502	17000	905	809	764	302	128	123	.41	4.2	5.2	6.1	.22	29.12	115	108	104
83032501	17000	890	789	687	308	128	124	.40	4.1	5.1	6.1	.196	29.12	115	108	104
83032304	-	828	716	-	300	128	119	.41	4.2	5.2	6.2	.205	29.39	111	108	104
83032303	17000	822	735	677	320	129	124	.40	4.3	5.2	6.1	.216	29.15	111	109	104
83032202	17000	850	770	716	299	128	119	.41	4.1	5.1	5.8	.20	29.02	112	108	105
83032202	17000	797	659	647	296	128	119	.41	4.1	5.1	5.8	.20	29.02	112	108	105
83032301	17000	698	658	652	300	129	124	.40	4.1	5.1	6.0	.20	29.15	111	109	104
83032201	17000	850	782	748	297	128	121	.41	4.2	5.2	5.8	.20	29.02	112	108	105
83033101	17000	808	728	657	305	128	121	.39	3.7	4.8	5.8	.197	28.88	112	108	105
83033102	17000	799	749	679	305	128	126	.40	3.9	4.9	5.8	.222	28.88	112	108	105
83032801	17000	800	710	706	307	130	125	.40	4.0	5.1	5.9	.226	28.92	117	110	105
83033103	17000	817	718	718	301	128	119	.39	3.7	4.8	5.8	.192	28.88	112	108	105
83033104	17000	766	679	602	297	129	120	.42	3.9	5.0	6.1	.20	28.88	112	108	105
83032902	17000	811	735	567	299	127	118	.40	3.9	5.2	7.0	.21	29.21	118	107	107
83033105	17000	751	699	655	303	128	122	.40	3.9	4.9	6.0	.213	28.88	112	108	105
83032901	17000	935	769	714	312	127	124	.36	3.9	6.9	7.9	.216	29.21	118	109	107

Table A-6. Continued

TEST NO.	TAMB	ACFM3	SCFM1C	TEMP1C	SO2ONEC	EFFSD	EFFSYS	SR	DVS	BW1	BW2	BW3	DELTAT	FLYASH ID	INJ RATE*
83032504	42	813	682	312	887	14.4	7.4	0	78.6	.038	.08	.07	20	37	.46
83032503	46	821	694	300	805	3.3	7.4	0	77.8	.042	.08	.071	20	50	.49
83032502	50	821	694	302	905	6.9	12.9	0	78.6	.042	.08	.071	20	38C	.55
83032501	54	811	683	308	890	7.5	20.2	0	76.5	.04	.08	.071	20	46	.40
83032304	46	818	687	300	828	8.8	-	0	77.3	.03	.08	.073	20	27	.46
83032303	46	817	687	299	868	5.5	11.2	0	77.3	.03	.08	.073	20	27	.46
83032302	38	811	672	320	822	4.8	13.4	0	78.3	.023	.082	.071	20	13	.42
83032202	45	819	686	299	850	4.8	11.9	0	76.9	.033	.08	.075	20	13	.42
83032202	48	819	687	296	797	13.2	15.2	0	76.9	.034	.08	.075	20	13	.42
83032301	36	811	677	300	698	0.4	2.4	0	76.9	.03	.082	.071	20	-	-
83032201	38	820	686	297	850	3.4	8.1	0	76.9	.034	.08	.075	20	-	-
83033101	56	802	666	305	808	5.2	14.9	0	76.6	.032	.08	.075	20	-	-
83032801	54	816	672	305	799	1.3	11.2	0	78.8	.032	.08	.073	20	-	-
83033103	46	815	684	307	800	7.6	9.3	0	79.2	.048	.085	.074	20	44	.23
83033104	57	801	667	301	817	7.6	8.2	0	76.1	.033	.08	.076	20	49	.33
83033104	60	832	693	297	766	7.0	17.9	0	76.9	.035	.08	.075	21	24	.55
83032902	43	807	690	299	811	7.0	28.0	0	77.8	.053	.077	.081	20	14	.48
83033105	57	813	674	303	751	2.5	8.8	0	78.0	.033	.08	.075	20	23B	.51
83032901	43	770	648	312	935	14.6	21.1	0	78.3	.048	.083	.079	18	10	.51

*Fly Ash injection rate (lb/min).

APPENDIX B

CHEMICAL KINETICS DATA

Table B-1

Summary of Fly Ash Slurry Equilibrium Data

(1) = 10% slurry, 70°C
(2) = 15% slurry, 60°C (mg/1)

ASH #		pH	Ca as Ca	T.D.C as Ca	Na as Na	Alkalinity as $CaCO_3$ OH	CO_3	HCO_3
Lignite								
27	(1)	10.5	443	601	180	240	160	0
	(2)	10.3	415	547	300	1300	400	0
38C	(1)	10.5	462	601	4000	410	220	0
	(2)	10.8	274	368	4200	600	1000	0
41	(1)	10.5	350	504	6000	250	340	0
	(2)	10.7	321	396	8000	900	200	0
42	(1)	10.5	762	795	45	930	140	0
	(2)	11.4	886	981	62	3300	400	0
44	(1)	10.4	482	601	5050	600	200	0
	(2)	10.9	340	396	8200	900	400	0
44	(1)	ND	ND	ND	ND	ND	ND	ND
MB	(2)	10.9	302	472	8500	1900	200	0
Subbituminous								
13	(1)	11.3	886	989	50	1820	160	0
	(2)	11.2	962	1094	48	3000	800	0
14	(1)	10.8	140	178	145	640	120	0
	(2)	11.0	132	210	200	1300	1200	0
18A	(1)	10.5	135	213	45	230	240	0
	(2)	10.6	130	160	54	1000	200	0
37	(1)	10.7	241	330	155	420	160	0
	(2)	11.3	85	170	200	800	1000	0
38B	(1)	10.7	101	213	40	400	200	0
	(2)	11.2	123	245	54	700	800	0

Table B-1 (continued)

ASH #		pH	Ca as Ca	T.D.C as Ca	Na as Na	Alkalinity as $CaCO_3$ OH	CO_3	HCO_3
Subbituminous continued								
43	(1)	10.8	109	378	55	370	300	0
	(2)	10.9	179	274	75	1700	400	0
45	(1)	10.9	241	368	50	350	80	0
	(2)	10.7	302	396	58	800	800	0
46	(1)	10.1	48	175	60	280	240	0
	(2)	10.9	128	170	100	800	800	0
Bituminous								
6	(1)	6.3	358	446	30	0	0	30
	(2)	5.2	472	547	40	0	0	200
10	(1)	6.1	342	601	25	0	0	80
	(2)	6.7	265	-	26	0	0	500
18B	(1)	11.1	855	1028	85	590	120	0
	(2)	11.2	849	1000	88	2200	1200	0
23B	(1)	9.5	443	562	80	920	160	0
	(2)	11.3	264	340	51	1000	800	0
24	(1)	11.1	1282	1513	95	1620	360	0
	(2)	11.4	1151	1208	91	2700	200	0
30A	(1)	4.3	629	814	225	0	0	20
	(2)	4.1	604	679	450	0	0	0
34	(1)	5.5	800	1086	180	0	0	20
	(2)	4.4	604	717	300	0	0	0
36	(1)	10.7	319	-	65	300	200	0
	(2)	10.5	245	283	49	1400	0	0
49	(1)	3.4	190	ND	115	0	0	0
	(2)	3.6	175	ND	150	0	0	0
50	(1)	5.4	210	248	40	0	0	30
	(2)	4.8	321	358	52	0	0	400
Tap Water		7.8	38	57	26	0	0	0