To the Graduate Council:

I am submitting herewith a thesis written by Mark A. Fiedler entitled "Sulfur Retention in Fly Ash." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

Wayne T. Davis, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:

Vice Chancellor
Graduate Studies and Research

SULFUR RETENTION IN FLY ASH

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Mark A. Fiedler

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ABSTRACT

The results of the acquisition and analysis of a large body of data on the properties of fly ash from coal fired power plants support the conclusion that sulfur retention by fly ash is mainly controlled by the alkaline metal oxide content of that ash. Investigation of the chemical and physical nature of sulfur retention indicates that although physical adsorption may play a role in retaining a portion of the sulfur, the ultimate amount of sulfur retained is controlled by the percentage of the ash that is available to combine chemically with the sulfur. Nearly all sulfur retained will be in the sulfate form, even though it possibly did not initially condense as a sulfate.

Of the relationships studied relating sulfur retention to alkaline metal oxide content, the best correlations were found using the total alkaline metal oxide values, with the true molar or weighted total providing the best fit. The importance of how the coal was burned, the temperature history of a particle and the method of ash collection were demonstrated to have a very significant impact on reducing data scatter. The particle size and ash surface area data did not show a significant relationship with sulfur retention.

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I. INTRODUCTION

As the 1980's begin, the people of the United States find themselves trying to increase domestic energy supplies to compensate for declining petroleum production at home and rapidly increasing prices abroad. In the near term, only a few methods are available that offer proven ability to generate large amounts of electrical energy. With the future of nuclear power somewhat in doubt and with most significant hydroelectric sites already occupied, fossil fuel conversion by coal-burning power plants can be expected to increase dramatically. Fortunately, the United States has the vast coal reserves needed to support a much higher level of consumption.

The recognized environmental problems associated with the mining, transport, and combustion of coal range from the possibility of climatic change to concern over the noise and dirt of passing trains. One of the widest acknowledged problems of coal burning is the emission of sulfur dioxide, SO_2. Long recognized as a corrosive, toxic gas formed when the sulfur in coal oxidizes, most control measures prior to 1970 attempted to dilute SO_2 emissions to the point where they were not an immediate health hazard near a source. Once diluted to below the threshold of human detection, SO_2 was not considered to be a problem, with natural removal mechanisms cleaning the air sufficiently to prevent a build-up. However, an overwhelming amount of evidence has been compiled linking SO_2 emissions with various health problems, damage to plants, buildings, and acidification of alpine lakes. In response to these problems,

legislation at the state and federal levels has mandated SO_2 control measures for most new coal burning facilities.

The Federal New Source Performance Standards promulgated in 1978 limit emissions of SO_2 to 1.2 lb./10^6 BTU and a 90% reduction at all times (70% removal for very low sulfur coals) (1). This is a nationwide, minimum standard and SO_2 may be restricted even more by state or local air quality laws. The challenge of increasing our coal burning capacity has thus become even greater. Not only must designers and engineers strive to build the most efficient power plants, they must also cope with increasingly stringent environmental regulations.

Present technology presents very few choices for reliable, proven methods of SO_2 control that are acceptable to the utility industry. At this time, only coal washing (mechanical separation of sulfur compounds prior to coal combustion) and flue gas desulphurization (FGD) processes are considered to be sufficiently developed for reliable, long term use. Since coal washing alone can not achieve the required removal efficiency, virtually all new coal-fired boilers must be equipped with an FGD system of some type.

Selecting and designing an FGD system for a new plant presents the engineers with numerous unknowns. One of the most difficult determinations is to decide exactly how much SO_2 will need to be removed from the flue gas stream. Power plant systems must be designed for nearly 100% availability over a wide range of conditions. Thus, the FGD system must be able to provide the necessary SO_2 reduction at all times. However,

the utility companies, through the competitive bidding process, do not wish to buy any more equipment than is absolutely necessary. Federal regulations allow credit to be taken for any SO_2 removal that occurs before, during, or after the combustion process. All sulfur present in the coal does not necessarily exit the boilers as SO_2. Some sulfur will be captured and retained in the ash. Since the FGD system may have to be designed and purchased five to eight years before commercial operation of the plant, a simple sampling of the flue gas stream is not feasible. A method needs to be developed for estimating sulfur removal by coal ash during and immediately after the combustion process. This study examines some of the factors that influence sulfur retention in coal ash. The results should be of use in determining the ultimate emissions of SO_2 that must be controlled.

II. SULFUR REMOVAL MECHANISMS

A. CHEMICAL REACTIONS

A review of much of the current literature concerned with coal combustion and sulfur shows little agreement regarding the fate of sulfur and sulfur compounds during the combustion process. Through the relatively routine analysis of coal it has been well established that the sulfur in coal exists in varying proportions of organic and inorganic compounds. The organic sulfur is chemically bound in the coal and is derived from once-living materials. The inorganic sulfur, typically 40% or less of the total is in the pyritic form, FeS_2, with small amounts of sulfate, $SO_4^{=}$ present (2,3). As the coal is rapidly heated and burned in a boiler, the sulfur compounds are nearly all converted to SO_2 with SO believed to exist as an important intermediate product. It is assumed that SO is produced by some mechanism early in the reaction zone, followed by:

$$SO + O_2 \rightarrow SO_2 + O \qquad (1)$$

and

$$SO + OH \rightarrow SO_2 + H \qquad (2)$$

These are thought to be the major SO_2 forming reactions in the presence of hydrocarbon fuel. Sulfur trioxide, SO_3 can then be evolved either directly with oxygen or with a third body, M, which acts as an energy absorber. The simplified reactions are:

$$SO_2 + O \rightarrow SO_3 \qquad (3)$$

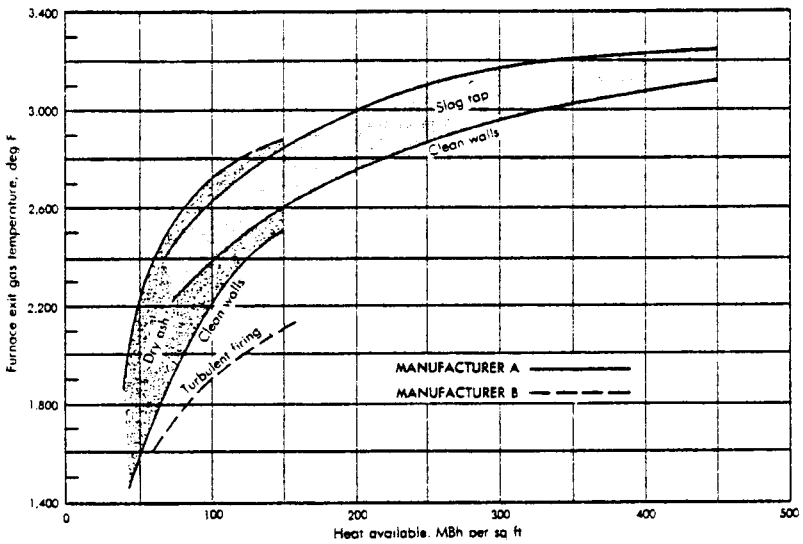
or

$$SO_2 + O + M \rightarrow SO_3 + M \qquad (4)$$

Wark and Warner (4) state that although the ideal gas equilibrium favors SO_3 at low temperatures and SO_2 at high temperatures, it has been found that the opposite occurs. The SO_3 level in the flame zone is higher than predicted and much lower than the equilibrium value in the cooled flue gas. Thermal decomposition of SO_3 to SO_2 by the reversal of equation 4 is believed to be responsible.

The almost limitless possibilities for reactions to be mediated by the various trace elements present during and after combustion of coal have forced researchers to generalize their theories for mechanisms of sulfur retention by the solid waste (fly ash and bottom ash). In general, higher boiler temperatures favor increased SO_2 production with measurable amounts of SO_3 only occuring below about 2500°F (5). Since most utility boilers achieve flame temperatures near 2500°F, liberating virtually all coal sulfur, most researchers believe the sulfur that is retained with the ash originated as SO_2 and has either been captured directly by some physical and/or chemical means or has been oxidized to SO_3 and then captured. Figure II-1 shows typical temperature profiles for a pulverized coal, (PC) boiler. A report prepared for EPA (5) determined on a thermochemical equilibrium basis the distribution of gas phase and condensed phase sulfur species based on coal mineral analysis, flame temperature, and air/fuel ratio.

Although the possibilities exist for hundreds of distinct compounds and amorphous combinations of metals, silicates, and sulfur, the predominant reactions, as listed in simplified form, are combinations with alkaline metal oxides that result in sulfate or sulfite end products (6, 7).



Furnace exit gas temperature with pulverized coal firing

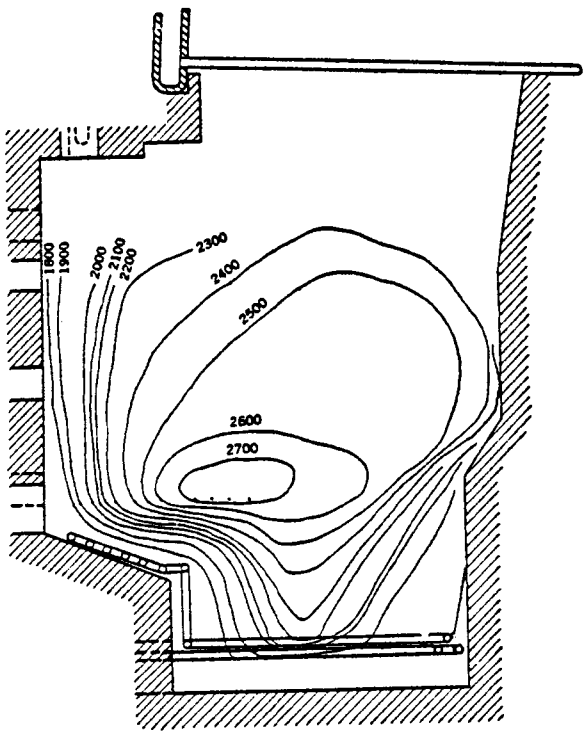


Chart showing lines of constant temperature in an early pulverized-fuel furnace equipped with a bottom water-screen.

Figure II-1. P.C. Furnace Temperatures

Sources: (a) C. Sheilds, "Boilers," (McGraw-Hill, New York, New York) 1961.

(b) "Combustion Engineering," edited by O. de Lorenzi (Combustion Engineering, New York, New York) 1955.

$$CaO + SO_2 \rightarrow CaSO_3 \quad (5)$$

$$CaSO_3 + \tfrac{1}{2}O_2 \rightarrow CaSO_4 \quad (6)$$

$$CaO + SO_3 \rightarrow CaSO_4 \quad (7)$$

$$Na_2O + SO_2 \rightarrow Na_2SO_3 \quad (8)$$

$$Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 \quad (9)$$

$$Na_2O + SO_3 \rightarrow Na_2SO_4 \quad (10)$$

$$MgO + SO_2 \rightarrow MgSO_3 \quad (11)$$

$$MgSO_3 + \tfrac{1}{2}O_2 \rightarrow MgSO_4 \quad (12)$$

$$MgO + SO_3 \rightarrow MgSO_4 \quad (13)$$

$$K_2O + SO_2 \rightarrow K_2SO_3 \quad (14)$$

$$K_2SO_3 + \tfrac{1}{2}O_2 \rightarrow K_2SO_4 \quad (15)$$

$$K_2O + SO_3 \rightarrow K_2SO_4 \quad (16)$$

Other chemically bound sulfur probably exists, such as FeS, Fe_2S_3, and Al_2S_3 (8), but they are difficult to distinguish from sulfur believed trapped in a matrix of silica, alumina, iron, and other mineral compounds (9, 10). The reactions given above are greatly simplified, contain many possible intermediate steps, and are dependent on the conditions at each area of the flame and post flame zones of the boiler. An alternate sulfur collection and reaction mechanism will be discussed later in this section.

A computer program originally developed by NASA was utilized in Reference 5 to evaluate four coal types over a range of temperatures and air/fuel ratios. The program can consider up to 200 chemical species, which it then evaluates for each set of temperature, pressure, and oxygen

concentration conditions. The analysis of the four coals are given in Appendix Table A-1. The summarized results are included in Appendix Tables A-2 to A-6. Examination of this computer data shows the predicted sensitivity of these compounds to various conditions. Of particular note are the changes in sulfur retention as condensed compounds such as $CaSO_4$ over a range of temperatures at the same theoretical air (% TA) value. Table A-6 summarizes the results and predicts ranges of 0 to 100% sulfur retention for three out of four coals over a relatively narrow temperature range. Such dramatic sulfur retention rates have not been observed. However, the trends indicated were substantiated by field testing. "The conclusions were that, for boilers tested, a greater sulfur retention tendency was exhibited at higher excess oxygen and a tendency for less sulfur retention at higher loads" (higher flame temperature). The same trends in sulfur retention were predicted for high and low alkalinity coals. Field observations confirmed the predictions of the greatest sulfur retention being associated with the highest alkalinity levels. The report also stated that although the bulk stoichiometry in a pulverized coal flame may be fuel rich, the rate of fuel combustion is not sufficiently rapid to make the region surrounding a coal particle fuel rich. "This, along with the equilibrium constraints are the reasons that large amounts of SO_2 are formed even in sub-stoichiometric flames" (5).

The difficulty of determining actual conditions at any point in a boiler clouds the history of a given particle. In situ measurements are nearly impossible. Any particle removed from the combustion zone will probably continue to react much as it would have if it had followed the flue gas through the heat removal zones and into the dust collector. Studies by

Fisher (11) and Keyser (12) have concluded that sulfuric acid condensation on particle surfaces is a first step, followed by relatively slow leaching of metal oxides to the surface and formation of sulfate crystals. Kaakinen (13), who did not specifically look at sulfur, found increasing enrichment of all volatile trace elements as the particles cooled and proceeded downstream from the boiler. Hulett, et al. (14) found both higher sulfur concentrations on the surface of fly ash particles and a higher amount of sulfur on small particles, due to the increased relative surface area of the finest particles. The work of Ensor (15) supports this conclusion. Natusch (16) found a surface concentration 7.7 times the bulk concentration of sulfur. Natusch has also suggested (17) that the surface predominance of sulfur can best be explained if the sulfur is present as an element. All of this work suggests that mechanisms other than chemical reaction to condensed species are important in the retention of sulfur by fly ash.

B. ADSORPTION

Adsorption is the term applied to the taking up of a gas, vapor, or liquid by a solid surface. Technically, adsorption refers only to the surface attachment of adsorbed material. If the interior of the solid participates in the process it is known as sorption. Distinction is also made between physical adsorption, where the molecules are held in contact by van der Waals forces, and chemisorption, where bonds are formed from the exchange of electrons. An attempt to distinguish physical from chemisorption has been made by assuming the heat of physical adsorption is generally less than 10 Kcal/mole and the heat of chemisorption is above 20 Kcal/mole (18).

Since adsorption is a surface area-related phenomenon, it would be logical to support a sulfur retention by adsorption theory by examining the sulfur retention qualities of various sized fly ash particles. Much of the size classification work that has been done has resulted from studies of the health effects of various sizes of particles in combustion effluents and in the atmosphere. The work cited earlier by Fisher, Natusch, Hulett, and others all agree that the surfaces of fly ash particles are enriched with sulfur and/or sulfur compounds. Natusch (15) has also found surface enrichment of potassium and sodium but not calcium. Thus, these two metals may participate in a chemisorption of sulfur as alkali-iron sulfates disproportionate to their bulk concentrations. He also states that the surface-associated elements, (including sulfur) are considerably more soluble than the same elements in the bulk matrix. Thus, etching studies that monitor the ions released as a particle is etched will show an even greater surface predominance of sulfur. Hulett (10) has suggested that some sulfur may diffuse out of the bulk material during solidification. Natusch believes that "certain elements or their compounds are volatilized in the high-temperature coal combustion zone and then either condense or adsorb onto entrained particles" (17). Following this surface adsorption model, it becomes evident that the quantity of sulfur retained will depend on the surface area of a particle. Since a given mass of small particles will have more surface area than the same mass of large particles, the sulfur retention per unit weight will be greater in the small particles.

Smith et al. (19) has followed up on the work of Natusch and while in basic agreement has extended the model by showing that surface enrichment of volatilized elements is not a function of particle size for particles less than a few microns in diameter. They suggest that the smallest particles consist of elements not likely to be volatilized during combustion and are more homogeneous than the larger particles. Their mechanism of formation involves the bursting of large particles from gas evolution to form large numbers of very tiny particles. "The submicron particles would then result from a combination of processes involving both coagulation of the smaller particles concurrent with the condensation of volatilized elements" (19). This theory suggests a surface adsorption mechanism that results in internal sulfur deposits, possibly only forming sulfates at a later time. A recent paper by Carpenter (20) and another by Horney (21) support this explosion or popcorn effect, where many small particles are produced by the inflation and explosion of gas-filled spheres. Henry (22) agrees with the earlier work of Hulett that nearly all retained sulfur is in the form of water soluble sulfates. How and when it obtained that form is not apparent. As an added note of confusion, Reference 21 contains a graph that shows increasing percentages of CaO and MgO in the ash result in smaller particles and another that shows increasing particle size with increasing Na_2O content. These graphs are included in the appendix as Figures B-1 and 2. It should be noted that data were not included, nor was it stated that there was data. An attempt will be made to use the available data set to verify these mineral analysis vs. size relationships.

The rentention of sulfur by fly ash, if it is a purely chemical phenomenon, should be directly related to the alkaline metal content of the ash. If it is controlled by a largely surface area-dependent mechanism, it should be closely related to particle size. Analysis of the following data, acquired by literature review and by sample collection and analysis is designed to help resolve this question.

III. DATA ACQUISITION

A. DATA SOURCES

To compile as much data as possible that would be useful in relating sulfur retention by fly ash to the chemical constituents and particle size of that ash, a search of EPA publications, EPRI sponsored projects and various independent research programs produced over 150 useful data points. To qualify, the data had to be based on actual power plant-produced coal ash. Laboratory ashing of coal samples was not acceptable. Most power plant ash was identified by source (fly ash or bottom ash), point of collection, and type of coal burner. Where both fly ash and bottom ash data were available, the chemical constituents and sulfur retention were combined in the same ratio as the relative production of each type of ash. Since most utility boilers utilize pulverized coal firing, a process that generates 80% or more of the solid waste as fly ash and less than 20% as bottom ash (23), the total quantity of sulfur retained in the bottom ash was not likely to be significant. The water-quenching mechanism used to cool and remove the bottom ash also makes any data acquired somewhat less reliable. Before a bottom ash sample can be collected and analyzed, it has been in contact with an unknown quantity of water. Thus, many soluble sulfate species are likely to be removed to some degree. Also, since bottom ash consists of the largest, heaviest size fraction of ash particles (generally an order of magnitude of more larger than the fly ash particles), much less surface area is available for adsorption of sulfur compounds.

Published data on sulfur analysis of bottom ash was confirmed by the writer's analysis of bottom ash samples. It was concluded that the small proportion of bottom ash, which contained very little sulfur, had little statistical effect on the data. For the purpose of this study, when bottom ash data was not available for a plant, it was assumed that the fly ash data was representative of the total ash.

In addition to the review and compilation of available ash analysis data, two additional investigations were conducted. The co-operation of Tennessee Valley Authority Personnel at the Bull Run Steam Plant was obtained. With their help, 22 daily fly ash and bottom ash samples were collected over a one month period (five days/week). The Bull Run Plant is a base-loaded facility that maintains 850 to 900 Mw output. Since the samples were collected with a small cyclone-type sample collection device, the daily particle size distribution should not have varied greatly. It was hoped that samples from such relatively constant conditions might show a change in sulfur retention related to the alkaline metal content of the ash.

An attempt was also made to determine the amount of adsorbed, chemically uncombined sulfur present on the ash samples, using the Bull Run samples and additional fly ash samples obtained from the University of Kentucky (23) from 20 different utility boilers.

B. EXPERIMENTAL PROCEDURE

Sulfur analysis of all fly ash samples was conducted using a Fisher Model 470 sulfur analyzer. A description of the sulfur analyzer is included in Appendix C on Page 73. Subsequent chemical analyses of selected

Bull Run samples for Ca, Mg, Si, Al, Fe, Na, and K were performed using atomic absorption spectrophotometry. The samples obtained from the University of Kentucky had been previously analyzed for all constituents.

Since the tube furnace of the Fisher Model 470 sulfur analyzer is approximately 500 mm long and maximum temperature exists only near the center, it was possible to make use of this temperature gradient to test ash samples at a lower temperature, as well as the maximum temperature. Selection of a lower temperature value was based on staying below the thermal decomposition temperature (24) of the various sulfate species believed to exist, but still achieving a high enough temperature to drive off uncombined sulfur oxides. At 550°C, the sulfate and most sulfite species of Al, Ca, K, Li, Mg, Mn, Na, and Pb will not decompose. However, ammonium, ammonium-iron, barium, and iron sulfates and sulfites will be lost. It was decided that 550°C would be a reasonable test temperature that might evolve measurable quantities of sulfur. Careful positioning of the sample boat achieved a sample temperature of 550°C, $\pm$50°C.

In preparation for the two-temperature studies, a temperature profile was prepared for the tube furnace and is included in Appendix C. The temperatures were recorded using a thermocouple inserted in an ash sample, placing the sample boat at various distances along the entrance area of the furnace. Since the temperature gradient was quite large, the variation across a sample was approximately $\pm$50°C.

Since many of the analyzer operational parameters are adjustable, such as how fast it reacts to SO_2 and how rapidly it approaches the

titration end point, several trial runs were conducted to optimize sample testing. It was found that the sample temperature would stabilize at any of the low temperature positions in three to four minutes. However, SO_2 would be given off at a decreasing rate for up to 20 minutes. The analyzer was adjusted to approach the end point sufficiently slow to be able to measure about 85% of the SO_2 given off at 550°C. A sample of several successive data points at one position is included in the data. One additional sample of several data points is also included that shows the sulfur evolved at several positions (and temperatures) for the same sample.

All data acquired by literature review and sample collection has been put into a standard format and is listed in Table III-1. The data sources are listed at the end of Table III-1 on Page 22. Figure III-1 on Page 23 is included to show the daily variation of coal and ash sulfur content at the Bull Run Steam Plant for the period when samples No. 155 to 165 were collected. Tables III-2 and III-3 on Page 24 and 25, are a summary of the two-temperature sulfur data obtained with the Fisher analyzer. Table III-4 on Page 26 is a sample of the additional test data used to adjust the sulfur analyzer time and temperature settings.

Particle surface area and size distribution information was included in several of the references. Particle size distribution measurements of the University of Kentucky and Bull Run ash samples were made using a Colter Counter. Tables III-5 and III-6 on Pages 27 and 28 summarize the surface area and particle size data.

Table III-1. Ash Mineral Analysis Data Summary

Data Point[a]	%S	%CaO	%Na_2O	%MgO	%K_2O	Σ Alk.	Weighted Σ Alk. as CaO
1*	0.49	1.10	0.38	1.25	3.28	6.01	4.58
2*	0.56	2.87	0.59	0.87	2.40	6.73	6.36
3*	0.15	2.17	0.36	0.92	2.45	5.90	4.86
4*	0.40	5.39	0.32	0.65	1.84	8.20	7.44
5*	0.20	1.56	0.22	0.92	1.62	3.92	3.59
6*	0.15	1.66	0.37	1.35	3.13	6.51	5.13
7	0.06	1.54	0.29	1.37	2.90	6.10	4.78
8*	0.31	1.33	0.46	1.21	3.02	6.02	4.74
9	0.15	1.05	0.36	1.00	2.53	4.92	3.86
10*	0.29	1.03	0.36	1.14	2.90	5.43	4.17
11	0.18	1.00	0.29	0.93	2.40	4.62	3.58
12*	0.21	1.06	0.34	0.90	2.56	4.86	3.77
13*	0.21	1.45	0.30	0.87	2.16	4.78	3.85
14*	0.39	3.19	0.38	0.92	2.32	6.81	5.83
15*	0.53	3.11	0.45	0.92	2.32	6.80	5.84
16	0.99	2.33	0.56	0.85	2.92	6.66	5.50
17*	0.34	3.62	0.97	1.28	2.79	8.66	7.64
18	0.13	2.95	0.57	0.93	2.30	6.75	5.85
19*	0.42	3.28	0.40	0.98	2.62	7.28	6.17
20*	0.37	4.37	0.47	1.04	2.79	8.67	7.51
21	0.16	0.94	0.36	1.11	2.82	5.23	4.01
22	0.62	5.99	0.32	0.86	2.20	9.37	8.43
23*	0.91	8.81	0.64	1.03	2.18	12.66	11.82
24	0.20	9.0	0.79	2.54	0.86	13.24	12.76
25	0.32	10.8	1.12	4.4	0.78	17.10	16.58
26	0.52	11.5	1.18	4.9	0.96	18.54	17.90
27	0.55	10.9	1.57	4.9	1.11	18.48	17.91
28	0.74	9.8	1.97	4.0	1.20	16.97	16.61
29*	0.24	1.9	0.38	1.1	4.4	7.78	5.89
30*	0.20	2.2	0.53	1.2	3.1	7.03	5.74

Table III-1 (Continued)

Data Point[a]	%S	%CaO	%Na_2O	%MgO	%K_2O	Σ Alk.	Weighted Σ Alk. as CaO
31	0.12	1.5	0.35	1.6	3.8	7.25	5.54
32*	0.48	3.1	0.66	1.2	2.9	7.86	6.70
33*	0.24	2.1	0.48	1.1	2.8	6.48	5.31
34*	0.48	9.6	0.30	2.2	0.8	12.90	12.37
35*	0.76	14.5	0.46	2.9	1.6	19.46	18.56
36	0.52	15.6	3.20	1.2	0.7	20.7	21.33
37	0.12	12.8	0.29	1.8	0.7	15.59	15.16
38*	0.76	9.6	0.34	6.8	0.5	20.39	16.27
39	0.16	9.1	1.85	1.9	0.6	13.45	13.58
40	1.68	13.0	2.02	2.8	1.4	19.22	18.95
41	1.28	13.7	1.85	3.0	1.4	19.95	19.60
42*	2.28	17.3	9.70	3.7	0.6	31.30	33.86
43*	0.4	2.6	2.27	1.1	2.8	8.77	8.21
44*	0.52	8.6	0.29	3.6	1.8	14.29	13.15
45*	0.28	5.2	1.38	0.9	1.1	8.58	8.46
46*	0.6	4.7	0.47	1.0	2.7	8.87	7.75
47	0.08	0.4	0.22	0.8	2.7	4.12	2.94
48	0.3	1.2	0.32	1.3	3.6	6.42	4.83
49	0.32	1.5	0.33	0.8	2.7	5.33	4.19
50	0.32	1.4	0.43	1.5	3.9	7.23	5.52
51*	4.4	23.3	8.52	5.9	1.0	38.72	40.43
52*	3.16	32.2	1.58	8.9	0.2	42.88	42.18
53	0.32	4.3	0.55	1.2	1.7	7.75	7.06
54	0.46	11.8	1.67	1.9	0.8	16.17	16.15
55	0.2	1.8	0.29	1.0	2.7	5.79	4.61
56*	0.08	1.6	0.29	1.0	2.4	5.29	4.23
57	0.20	4.6	0.45	2.1	3.1	10.25	8.81
58*	0.16	1.2	0.24	0.8	2.2	4.44	3.48
59	0.24	11.5	4.67	1.6	0.8	18.57	19.61
60*	0.12	0.3	0.26	0.3	2.7	3.56	2.46
61*	0.08	0.8	0.36	1.1	0.9	3.16	2.84
62	0.16	7.0	0.67	1.7	1.2	10.57	10.07
63	0.68	22.7	1.13	4.0	0.7	28.53	28.10
64	1.0	21.7	1.2	7.3	1.8	32.0	30.70
65	0.08	16.7	0.6	6.1	1.6	25.0	23.74

Table III-1 (Continued)

Data Point[a]	%S	%CaO	%Na_2O	%MgO	%K_2O	Σ Alk.	Weighted Σ Alk. as CaO
66	1.1	16.8			0.65		
67	0.8	16.8			0.66		
68	0.33	8.4			0.44		
69	0.32	8.3			0.43		
70	2.6	39.2			0.28		
71	2.0	35			0.25		
72	2.0	35			0.24		
73	2.5	37.8			0.23		
74	1.2	13.3			0.14		
75	1.28	24.1	7.0	6.2	1.1	38.4	39.51
76*	4.96	30.3	8.4	6.4	0.7	45.8	47.53
77	5.08	28.7	5.9	7.7	0.4	42.7	43.54
78	1.64	23.8	6.4	6.4	0.7	37.3	38.35
79	0.84	21.1	4.7	5.1	1.3	32.2	32.58
80	2.0	24.7	3.6	7.3	1.3	36.9	36.62
81*	3.48	23.9	2.1	8.4	0.3	34.7	34.20
82	0.28	7.5	1.2	1.2	0.9	10.8	10.67
83	0.68	26.4	0.4	8.6	1.0	36.4	35.00
84*	2.52	27.6	1.5	4.1	0.4	33.6	33.41
85	2.32	20.3	2.1	5.5	0.2	28.1	28.02
86	1.76	27.2	1.8	5.6	0.4	35.0	34.72
87	0.36	10.0	0.8	3.0	1.0	14.8	14.26
88*	2.12	23.3	0.6	6.9	0.4	31.2	30.34
89	0.92	24.3	2.0	5.9	0.4	32.6	32.35
90	0.4	9.3	1.9	1.7	1.3	14.2	14.07
91a	0.23	0.86	0.19	0.88	2.95	4.88	
91b	0.21	0.74	0.27	0.85	2.80	4.66	
91c	0.20	0.85	0.21	0.93	3.19	5.13	
91d	0.21	0.64	0.24	0.88	2.80	4.56	
91e	0.21	0.62	0.24	0.83	2.78	4.47	
91f	0.51	0.69	0.23	0.86	2.57	4.35	
91g	0.16	0.58	0.28	0.85	2.79	4.5	
91h	0.17	0.56	0.28	0.76	2.57	4.17	
91i	0.19	0.74	0.21	0.91	2.37	4.23	
91j	0.16	0.69	0.26	0.80	2.49	4.24	

Table III-1 (Continued)

Data[a] Point	%S	%CaO	%Na_2O	%MgO	%K_2O	Σ Alk.	Weighted Σ Alk. as CaO
91k	0.15	0.68	0.20	0.88	2.51	4.27	
91l	0.15	0.48	0.20	0.81	2.53	4.02	
91m	0.20	0.58	0.27	0.87	2.83	4.55	
91n	0.24	0.55	0.22	0.83	2.73	4.33	
91o	0.19	0.40	0.26	0.85	2.97	4.48	
91p	0.15	0.61	0.24	0.84	2.94	4.66	
91q	0.12	0.66	0.29	0.85	3.11	4.91	
91r	0.16	0.70	0.21	0.91	3.37	5.19	
91s	0.30	0.64	0.22	0.90	3.24	5.00	
91 avg.*	0.206	0.651	0.238	0.857	2.282	4.56	3.03
91 σ	0.084	0.119	0.031	0.041	0.263	0.334	
92	0.68	21.50	0.09	5.40	0.30	27.29	26.50
93	0.73	23.50	0.24	3.30	0.89	27.93	27.20
94	0.13	11.10	0.25	1.88	0.89	14.12	13.58
95	0.07	11.60	0.34	1.60	0.77	14.31	13.89
96	0.13	12.70	0.32	1.80	0.90	15.72	15.21
97	0.10	12.20	0.53	1.70	1.10	15.53	15.02
98	0.42	8.60	1.30	2.50	0.72	13.12	12.93
99	0.31	8.30	1.07	2.23	0.70	12.30	12.08
100	0.32	6.36	1.27	1.93	1.13	11.19	10.39
101	0.10	10.40	3.10	0.90	0.80	15.20	15.79
102	0.14	12.30	2.10	0.99	1.00	16.39	16.55
103	0.18	13.60	2.40	0.93	1.00	17.93	18.20
104	0.23	11.41	0.38	2.59	2.36	16.74	15.53
105	0.44	7.33	1.47	1.73	0.68	11.21	11.20
106	1.92	31.00	1.84	12.75	0.20	45.79	44.68
107	0.28	0.87	0.48	0.88	2.75	4.98	3.86
108	0.23	2.48	0.49	1.09	3.12	7.18	5.88
109	0.28	4.60	0.32	0.98	2.30	8.20	7.20
110	0.52	2.20	0.23	0.86	2.80	6.09	4.87
111	0.38	0.26	0.51	0.93	2.80	4.50	3.36
112	0.26	3.72	0.35	1.66	2.36	8.09	6.99
113	0.15	0.77	0.33	1.57	3.88	6.55	4.81
114	0.17	1.04	0.38	1.29	3.34	6.05	4.59
115	0.12	1.40	0.40	1.20	3.10	6.10	4.76

Table III-1 (Continued)

Data[a] Point	%S	%CaO	%Na_2O	%MgO	%K_2O	Σ Alk.	Weighted Σ Alk. as CaO
116	0.09	0.87	0.16	0.93	2.60	4.56	3.39
117	0.14	0.68	0.51	1.30	3.80	6.29	4.68
118	0.45	2.50	1.55	1.15	2.80	8.00	7.19
119	0.18	1.10	0.42	1.30	3.70	6.52	4.92
120	0.61	6.45		0.78			
121	0.89	7.40		0.78			
122	0.76	7.10		0.82			
123	0.57	5.80		0.98			
124	0.63	5.45		1.02			
125	0.64	5.00		1.02			
126	0.62	5.38		1.05			
127	0.61	5.38		1.09			
128	0.21	0.86		1.50			
129	0.20	1.20		1.50			
130	0.11	0.94		2.00			
131	0.24	0.86		1.32			
132	0.18	0.94		1.32			
133	0.15	1.12		1.26			
134	0.20	1.12		1.26			
135	0.20	1.14		1.38			
136	0.20	1.15		1.32			
137	0.24	1.15		1.26			
138	0.24	1.15		1.24			
139	0.22	0.81		1.24			
140	0.27	1.08		1.30			
141	0.79	6.80		0.92			
142	0.86	8.80		1.24			
143	0.63	8.80		1.02			
144	0.60	8.80		1.02			
145	0.71	8.45		0.85			
146	0.25	2.36		1.02			
147	0.16	1.14		1.02			
148	0.21	2.13		1.05			
149	0.22	1.90		1.05			
150	0.24	3.94		0.88			

Table III-1 (Continued)

Data Point[a]	%S	%CaO	%Na_2O	%MgO	%K_2O	Σ Alk.	Weighted Σ Alk. as CaO
151	0.08	3.39	1.45	1.09			
152	0.92	11.16	7.11	0.61			
153	1.45	26.59	1.38	8.42			
154	0.29	4.49			0.31		
155	0.87	5.11			1.66		
156*	0.18	0.49	0.17	0.43	1.84	2.93	2.15
157*	0.10	0.43	0.28	0.64	2.23	3.58	2.64
158*	0.12	0.56	0.18	0.58	1.86	3.18	2.37
159*	0.09	0.56	0.20	0.69	2.09	3.54	2.63
160*	0.09	0.43	0.19	0.64	2.25	3.51	2.53
161*	0.12	0.39	0.17	0.60	1.98	3.14	2.28
162*	0.09	0.30	0.17	0.58	1.86	2.91	2.10
163*	0.21	0.39	0.22	0.67	1.89	3.17	2.35
164*	0.17	0.22	0.19	0.53	1.89	2.83	2.02
165*	0.25	0.30	0.19	0.62	2.00	3.11	2.24

NOTE: (a) *Indicates P.C. fired, ESP collected ash data point.

SOURCES:

Data Points		Data Points	
1 - 23	Reference 23	92 - 119	Reference 30
24 - 28	Reference 25	120 - 150	Reference 31
29 - 63	Reference 26	151 - 153	Reference 32
64 - 74	Reference 27	154 - 155	Reference 19
75 - 90	Reference 28	156 - 165	Bull Run Steam Plant Samples
91 - All	Reference 29		

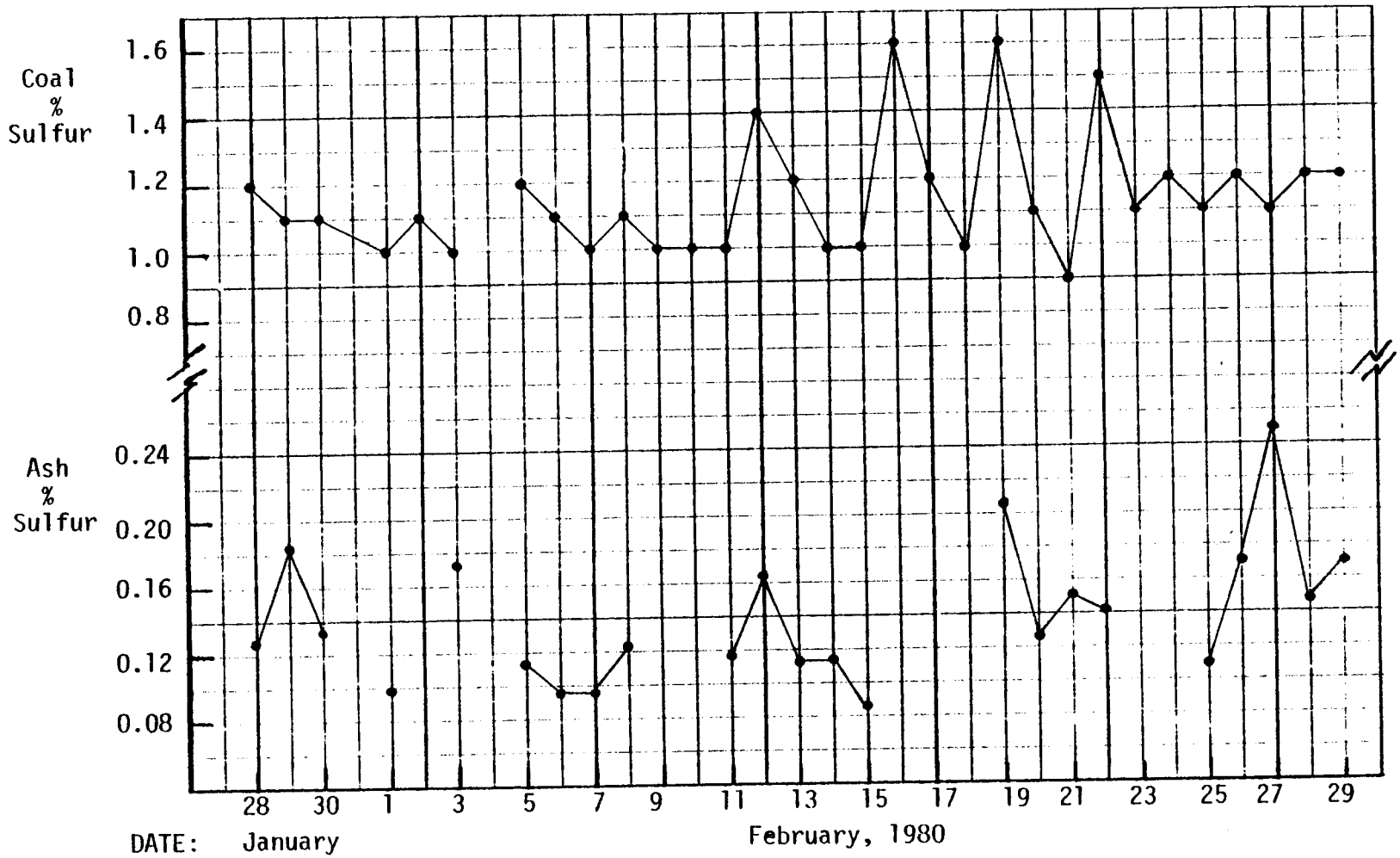


Figure III-1 Bull Run Steam Plant, Dialy Ash and Coal Sulfur Content.

Table III-2. Two-Temperature Sulfur Data, University of Kentucky Samples

Data Point [a]	%S @ 550°C	%S @ 1350°C	Σ %S	% Variation [b]	%S Adsorbed
1	0.014	0.470	0.484	-1.2	2.3
2	0.014	0.638	0.652	+16	2.2
3	0.003	0.146	0.149	-0.6	2.0
4	0.014	0.474	0.488	+22	2.9
5	0.027	0.231	0.258	+29	10
6	0.036	0.152	0.188	+25	19
7	0.016	0.059	0.075	+25	21
8	0.014	0.098	0.112	-25	13
9	0.081	0.256	0.337	+8.0	24
10	0.088	0.193	0.281	-3.1	31
11	0.065	0.099	0.164	-8.9	40
12	0.025	0.217	0.242	+15	10
13	0.015	0.172	0.187	-11	8
14	0.011	0.317	0.328	-16	3.4
15	0.022	0.453	0.475	-10	4.6
17	0.011	0.348	0.359	+5.5	3.0
19	0.087	0.320	0.407	-3.1	21
20	0.030	0.395	0.425	+15	7.1
21	0.014	0.103	0.117	-27	12
23	0.015	0.968	0.983	+8.0	1.5

Average Variation = $\pm$13.72% σ = 8.96%

Average Adsorption = 11.90% σ = 5.17%

NOTES: (a) Data point numbering identical to Table III-1.

(b) Percent variation from data received from University of Kentucky.

Table III-3. Two-Temperature Sulfur Data, Bull Run Samples

Data[a] Point	%S @ 550°C	%S @ 1350°C	Σ %S	%S Adsorbed
156	0.092	0.062	0.154	60
157	0.022	0.083	0.105	21
158	0.019	0.118	0.137	14
159	0.045	0.065	0.110	41
160	0.037	0.055	0.092	40
161	0.058	0.078	0.136	43
162	0.038	0.045	0.083	46
163	0.099	0.091	0.190	52
164	0.068	0.111	0.179	38
165	0.130	0.133	0.263	49

Average Σ %S = 0.145% σ = 0.0518%

Average %S adsorbed = 39.4% σ = 15.26%

NOTES: (a) Data point numbering identical to Table III-1.

Table III-4. Additional Tests

A. Sample No. 23, Owensboro Municipal Utilities, 0.983% sulfur. Sample placed at 165 mm into tube furnace (550°C).

Cycle No.	Time (mn)	%S
1	9	0.0168
2	5	0.0014
3	4	0.0010
4	4	0.0005
		Σ = 0.0197

B. Sample No. 23, 0.983% sulfur. Sample placed at several points of increasing temperature along the tube furnace.

Location No.	Distance, mm	Temperature, °C	%S
1	140	350	0.0036
2	165	550	0.0158
3	178	650	0.0826
4	190	750 (Est.)	0.1972
			Σ = 0.2992

Table III-5. Particle Surface Area and Size Data Summary

Data Point[a]	Area, $cm^2/g.$	MMD[b]	Data Point	Area, $cm^2/g.$	MMD
1	5271.5	10	132	3618	
2	3060.1	17	133	3018	
3	3166.6	12	134	3431	
4	1935.6	45	135	4497	
5	1622.4	30	136	4400	
6	3470.2	35	137	3845	
7	2172.9 (m)	80	138	5015	
8	6450.1	9	139	3806	
9	2114.0 (m)	22	140	4191	
10	6427.7	6	141	4383	
11	3331.0 (m)	14	142	4170	
12	4585.4	17	143	3498	
13	2148.6	21	144	3207	
15	3309.1	16	145	3783	
17	5092.4	8	146	2732	
19	3599.8	11	147	2581	
20	2750.4	18	148	2850	
21	2952.3	17	149	2706	
23	3593.4	8	150	2794	
120	2530				
121	3399		156		25
122	2955		157		17
123	3297		158		17
124	2766		159		19
125	3020		160		15
126	3438		161		18
127	3190		162		22
128	4255		163		19
129	4267		164		29
131	4803		165		21

(a) Data point numbering identical to Table III-1.

(b) MMD = Mass median diameter, microns (10^{-6} meters).

(m) = Mechanical collector.

Table III-6. Particle Size Data Summary

Data Point[a]	MMD[b]	Data Point	MMD
24	40	49	16 (m)
25	11.5	50	4
26	8.2	51	6
27	7.2	52	12
28	7.2	53	11
29	26	54	15
30	15	55	12
31	7 (m)	56	13
32	13	57	19 (m)
33	13	58	4
34	24	59	13
35	50	60	8
36	10	61	13
37	20 (m)	62	80
38	11	63	7
39	35	91p	9.0
40	10	91q	10.2
41	10	91r	6.5
42	12	91s	5.5
43	14		
44	3		
45	38		
46	16		
47	14		
48	6		

(a) Data point numbering identical to Table III-1.

(b) MMD = Mass median diameter, microns (10^{-6} meters).

(m) = Mechanical collector.

IV. DATA ANALYSIS AND DISCUSSION

A. SULFUR RETENTION BY ALKALINE ASH CONSTITUENTS

As stated earlier, the prime objective of this study was to examine factors that influence the retention of sulfur in fly ash. If the results of this work are to be of use to designers of FGD systems, information normally available to designers must be utilized. Other studies have attempted to relate sulfur retention to oxygen, temperature, and boiler load (5), and to particle size (17, 19). The particle size vs. sulfur retention phenomenon will be examined relative to the available data. However, other than gross differences between boiler types (ie. P.C. vs. stoker fired), information to evaluate the variables above is generally not available during design of a plant. This study follows the direction taken by Myers (27) in attempting to relate ash mineral analysis to sulfur retention. Coal and ash analysis information is always a part of the design package for a plant.

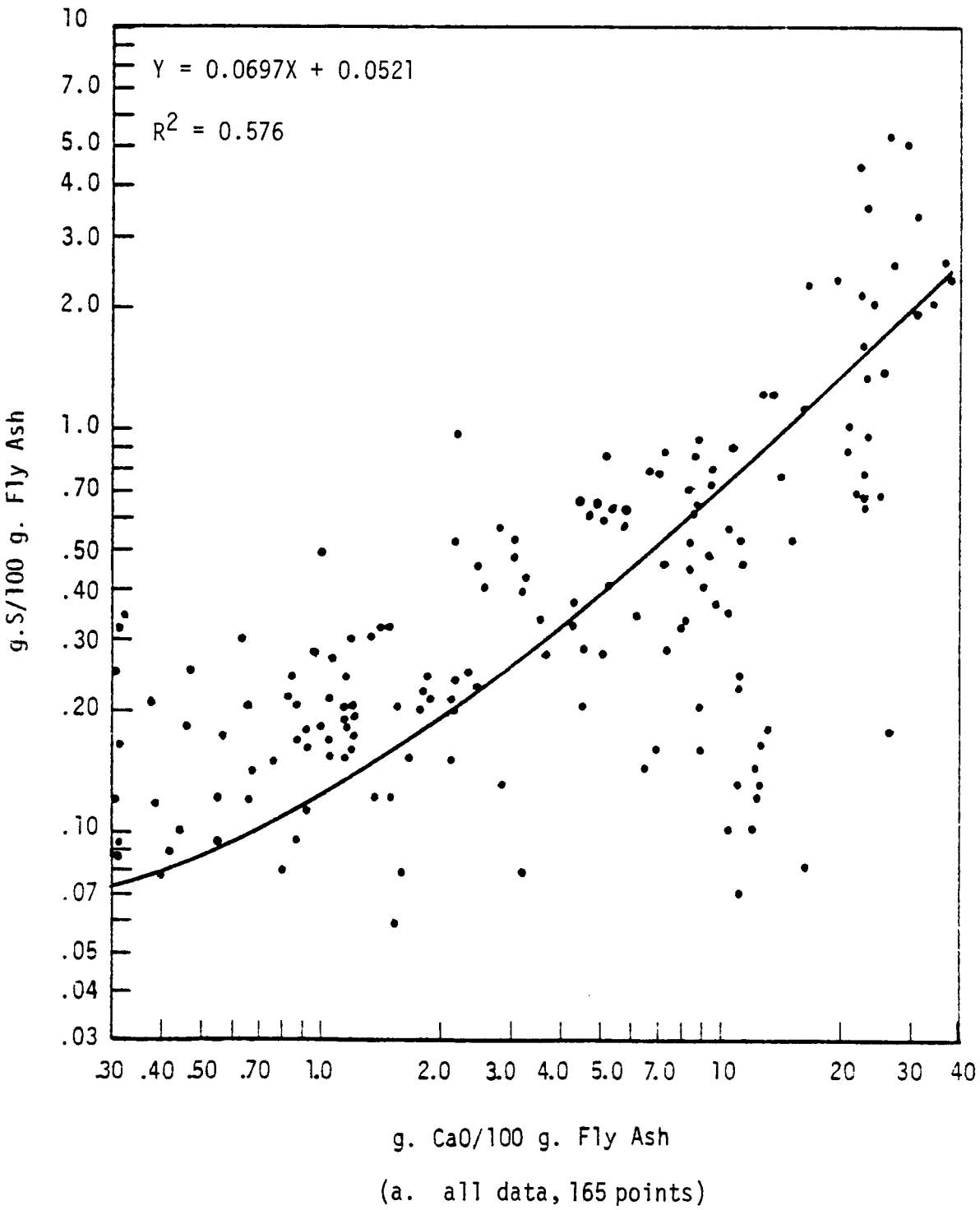
All data have been tabulated on a percentage basis (or grams per 100 grams of ash). Using typical coal analysis data the production of sulfur and ash can be predicted. If the amount of sulfur retained with the ash can be estimated as a percent of the total ash, the net quantity of sulfur emitted can be calculated.

A number of possibilities exist to relate the sulfur retention of fly ash to one or more constituents of the ash. The reactions discussed in Section II of alkaline metal oxides with sulfur served as a guide to select several relationships for examination graphically and statistically. The grams of sulfur retained per 100 grams of fly ash is plotted against grams of CaO, Na_2O, MgO, K_2O, and the arithmetic sum of

the weights of these oxides per 100 grams of fly ash in Figures IV-1 to IV-5, respectively. In each case all available data were used and a least squares fit line was calculated. Both linear and logarithmic methods were used in attempting to fit the data to equations. Generally, the regression coefficient (R^2), indicated a better fit was obtained with the linear equations.

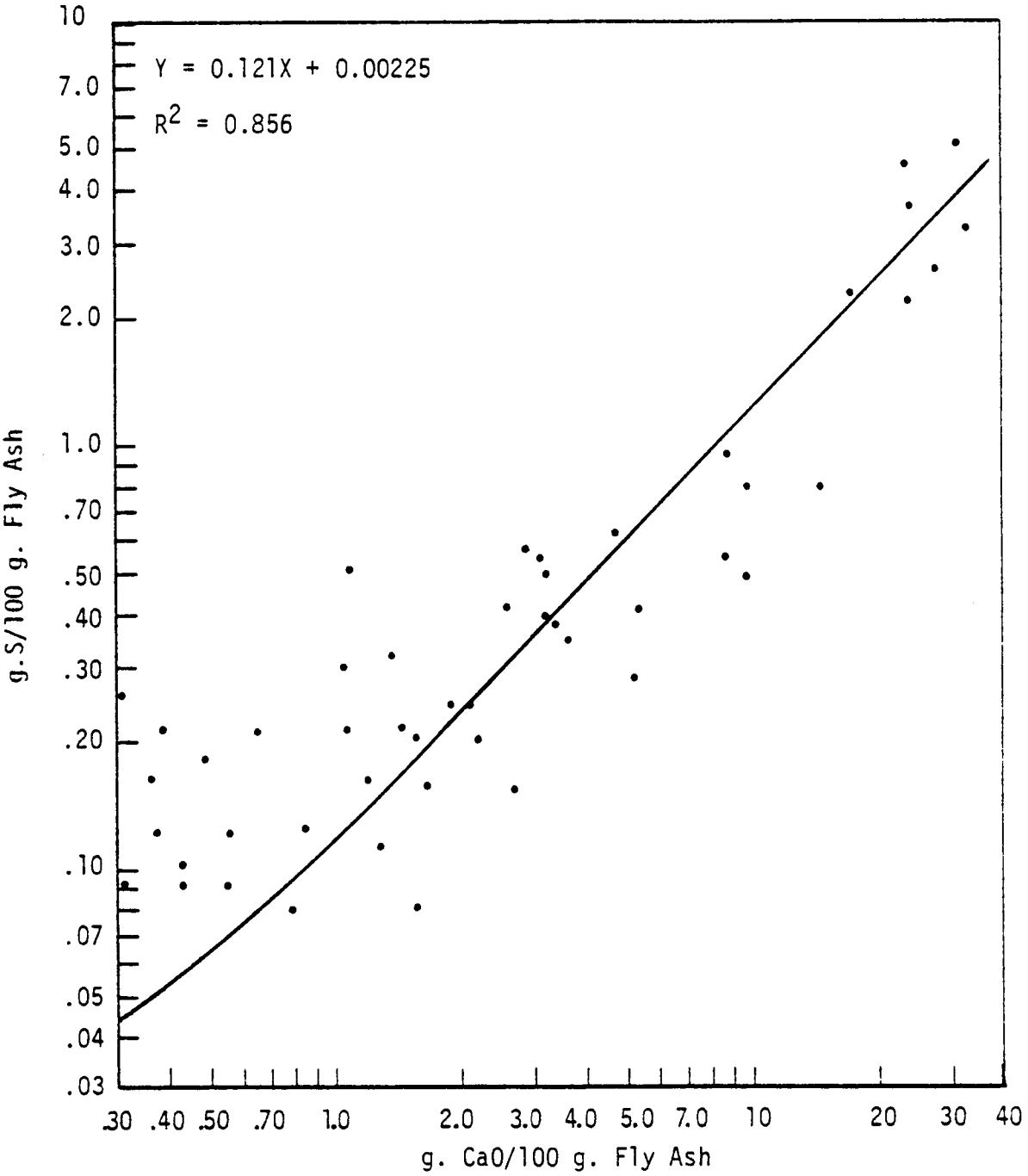
Examination of the data plots and the regression coefficients revealed a large degree of scatter in the amount of sulfur retained for any given value of an ash constituent. Three approaches were tried to narrow the degree of spread in the data. Acknowledging that the work of Natusch, Hulett, Keyser, and others all indicated a surface concentration of sulfur, the data was re-examined to note methods of ash collection that might have resulted in a non-representative sample. Mechanical collectors (cyclones) have fractional efficiency characteristics that segregate out the larger ash particles. Particles below a few microns in a diameter are not well represented in such samples. After eliminating data points for mechanical collector ashes, an improvement was noted in the regression coefficients for some data sets.

Referring again to the chemical equilibrium and adsorption theories presented earlier, it would be a logical step to eliminate from the data sets particles that did not have a similar history of temperature, oxygen conditions, etc. Since most utility boilers utilize pulverized coal firing, only ash collected from P.C. furnaces was considered. Elimination of all but known P.C. fired, electrostatic precipitator (ESP)



(a. all data, 165 points)

Figure IV-1. Grams Sulfur Retained Vs. Grams CaO Per 100 Grams Fly Ash.



(b. only P.C. fired, ESP collected ash data, 49 points)

Figure IV-1 (Continued).

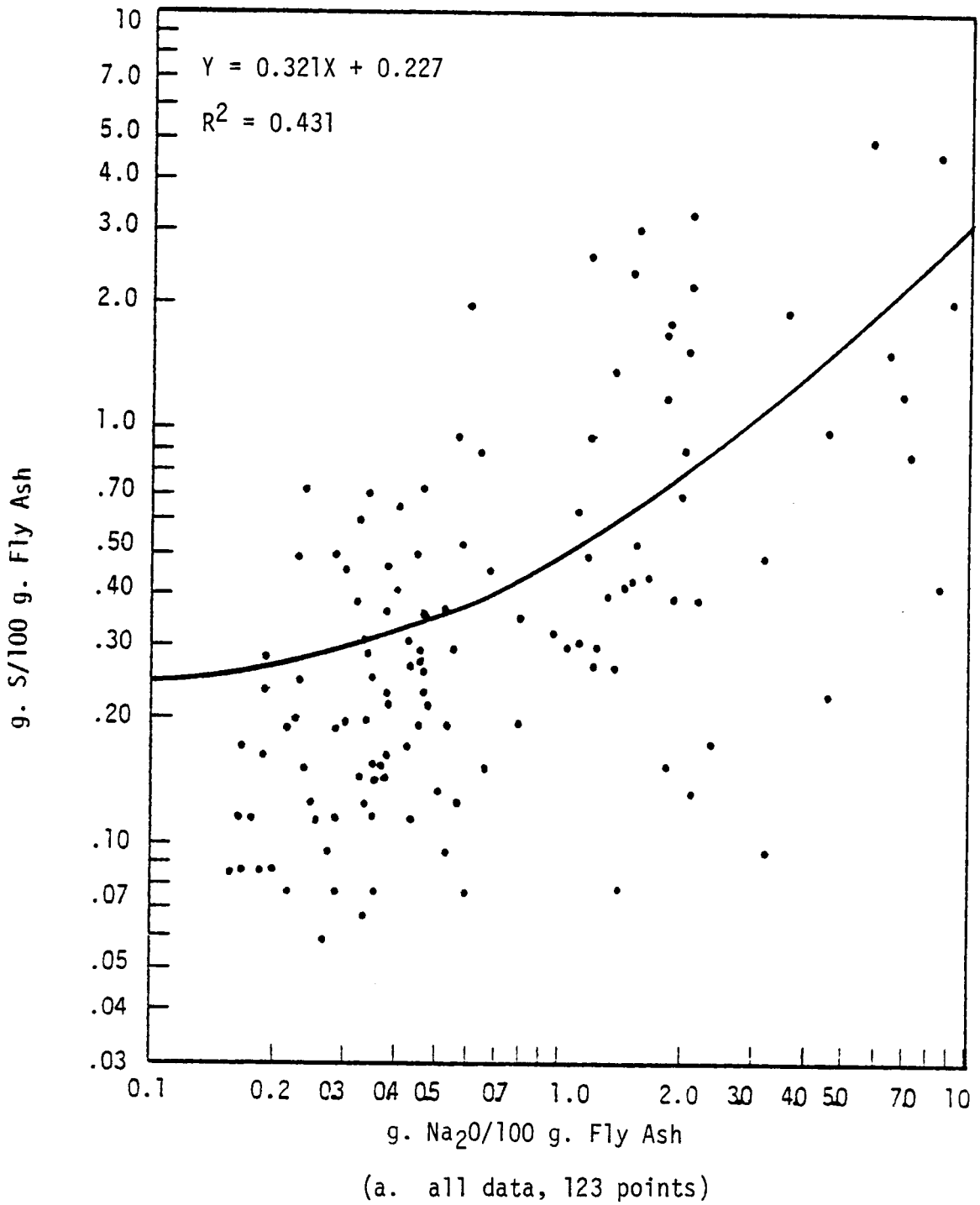
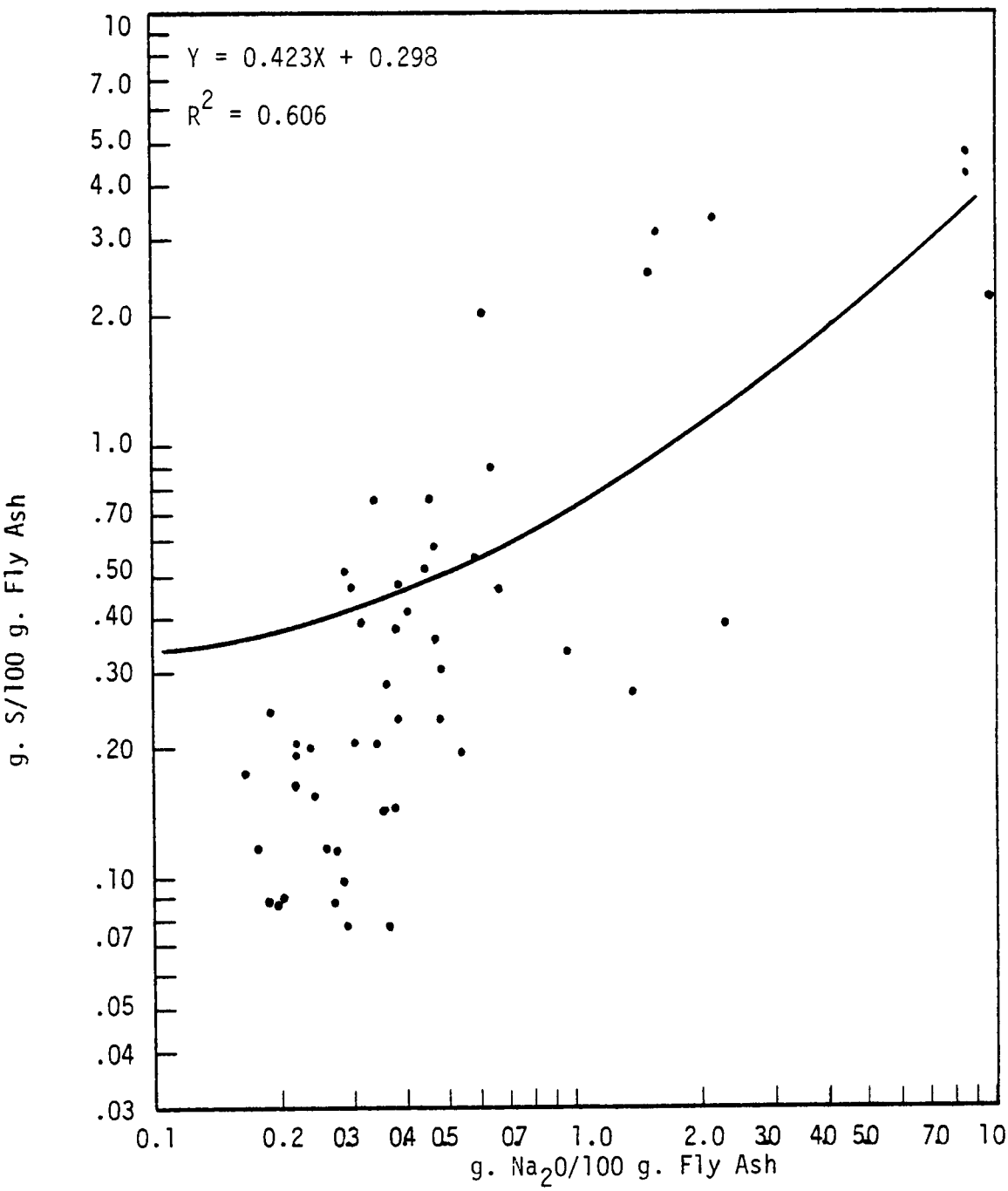


Figure IV-2. Grams Sulfur Retained Vs. Grams Na_2O Per 100 Grams Fly Ash.



(b. only P.C. fired, ESP collected ash data, 49 points)

Figure IV-2 (Continued).

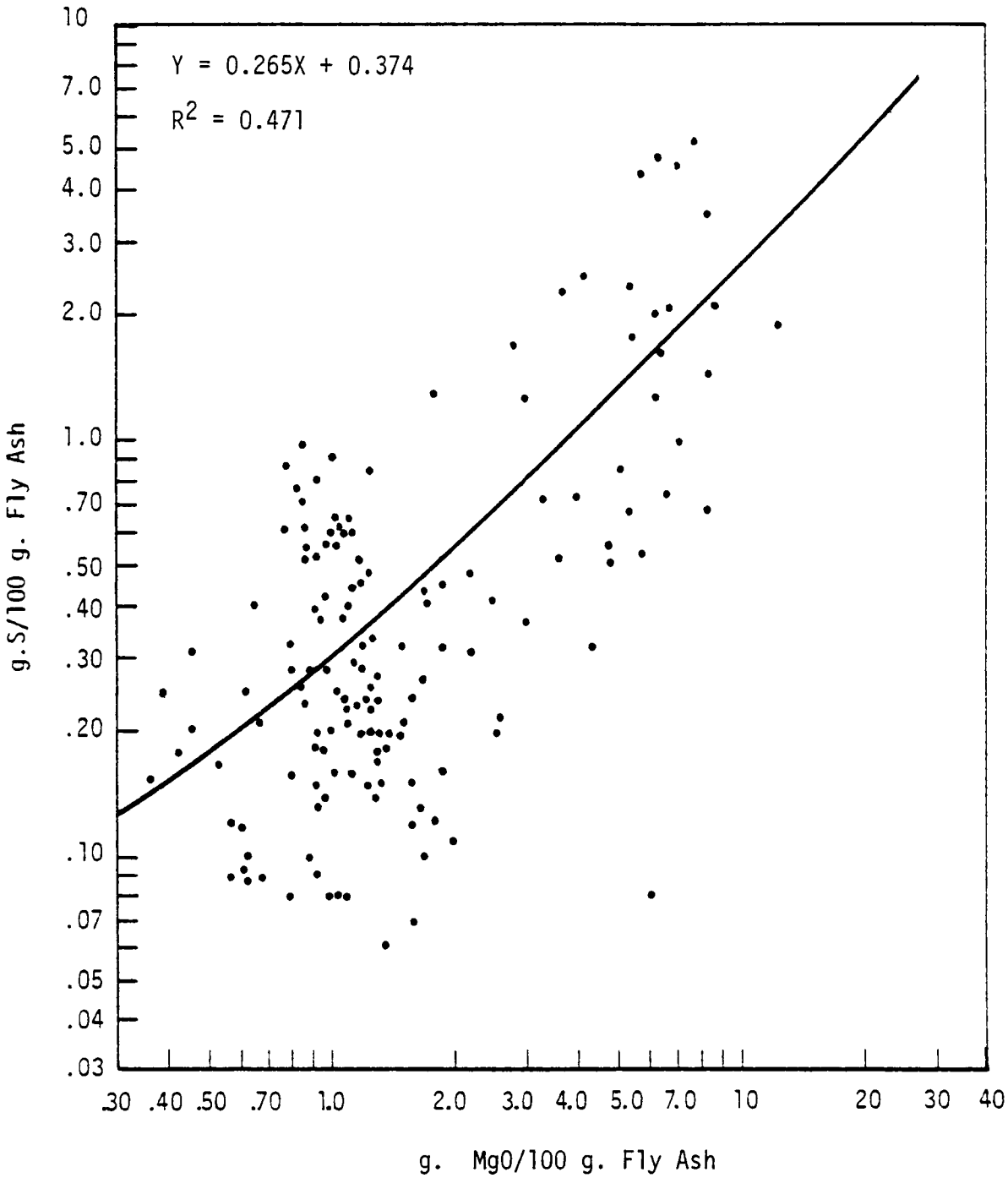


Figure IV-3. Grams Sulfur Retained Vs. Grams MgO Per 100 Grams Fly Ash, All Data (153 points).

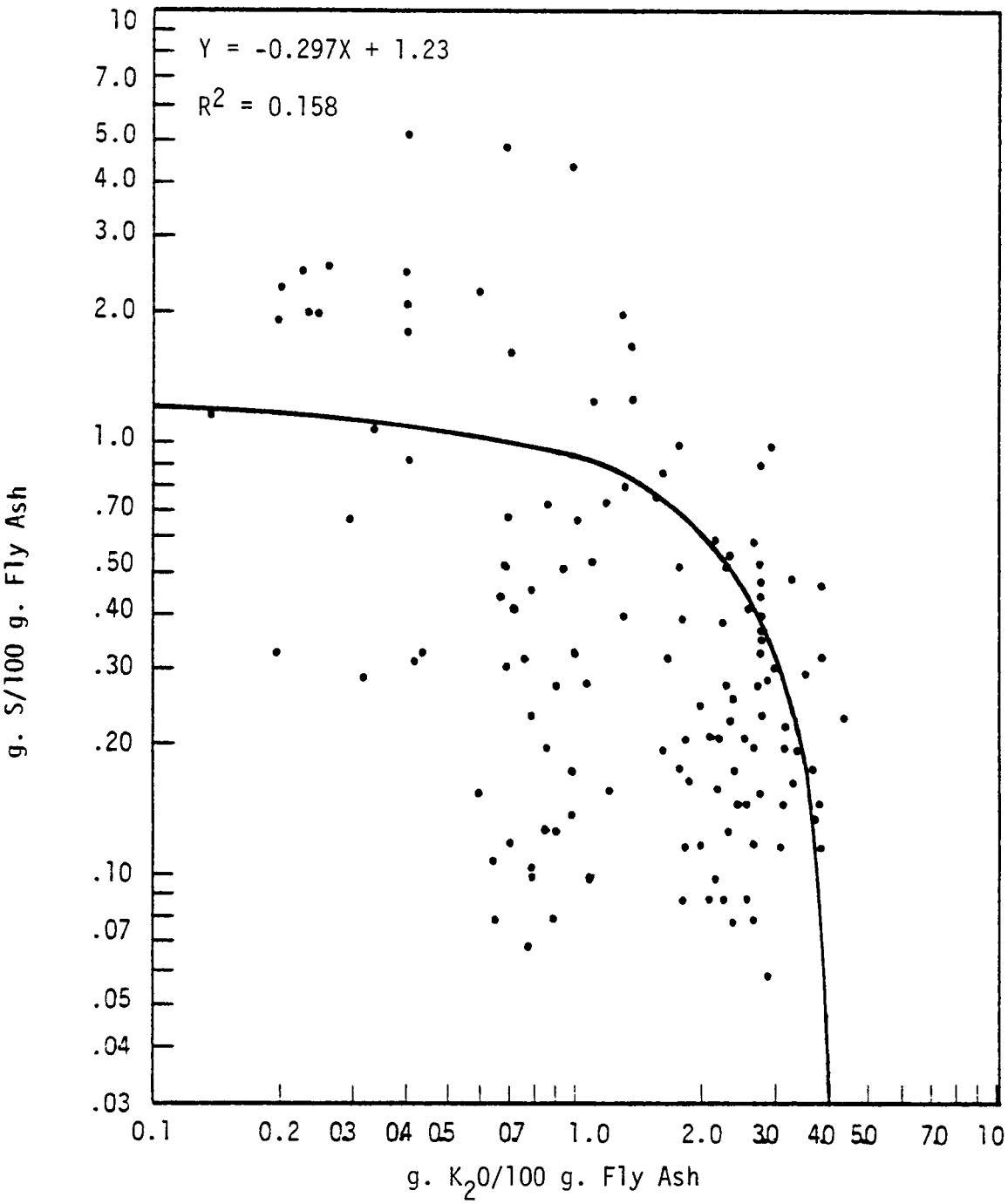


Figure IV-4. Grams Sulfur Retained Vs. Grams K_2O Per 100 Grams Fly Ash, All Data (129 points).

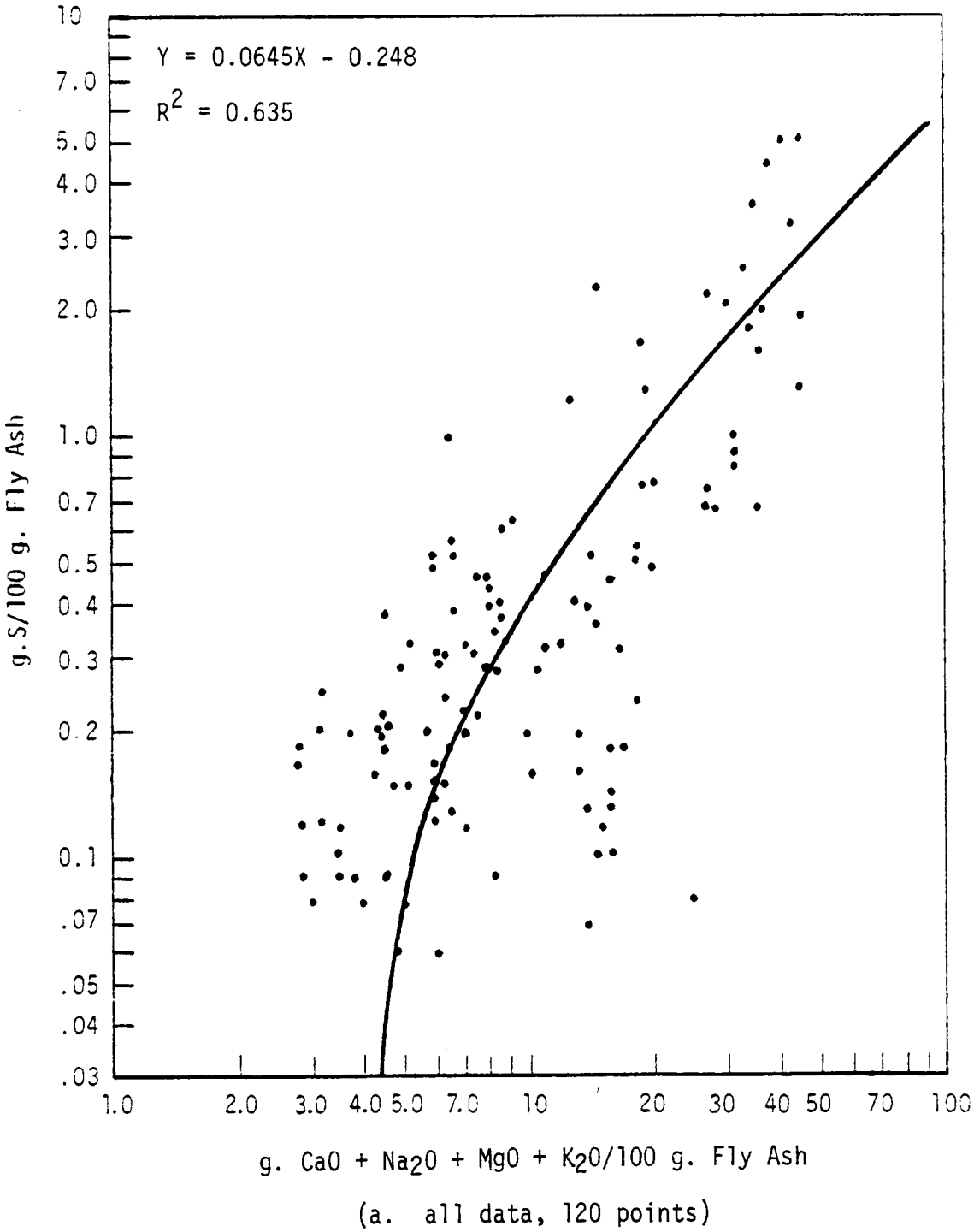
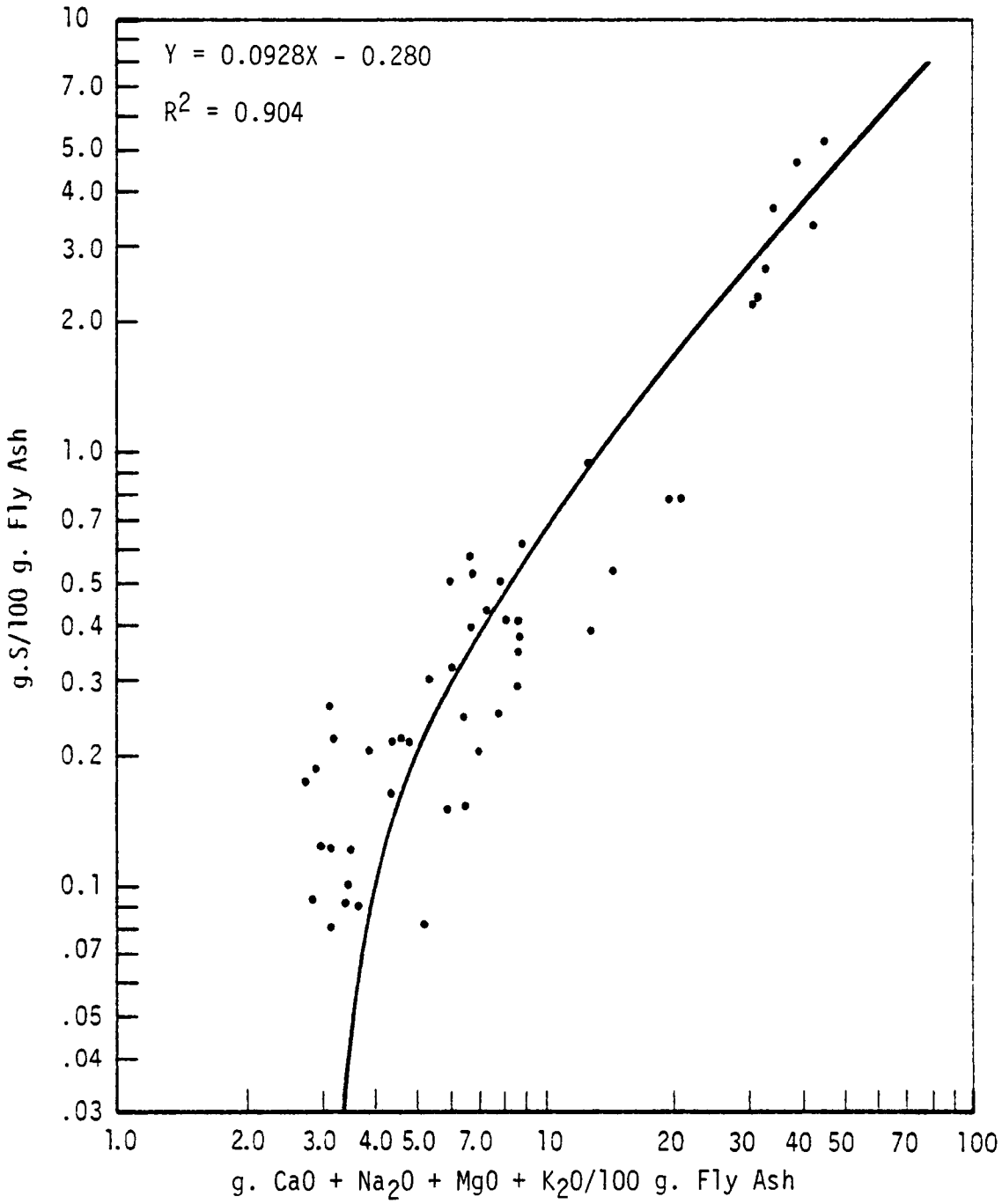


Figure IV-5. Grams Sulfur Retained Vs. Grams Alkaline Metal Oxides Per 100 Grams Fly Ash.



(b. only P.C. fired, ESP collected ash data, 49 points)

Figure IV-5. (Continued).

collected ash data produced a significant improvement in several of the regression coefficients. For example, in Figure IV-1a., S retained vs. CaO for all data points, R^2 = 0.576. For the same data without mechanical collectors, R^2 = 0.629 (graph not shown). In Figure IV-1b., showing only data points from P.C. fired, ESP collected ash, R^2 = 0.856. A similar improvement in the regression coefficients can be noted between Figures IV-2 a. and b., (S vs. Na_2O) and between Figures IV-5 a. and b. (S vs. sum alkaline metal oxides). A summary of regression coefficients is given in Table IV-1.

Acknowledging the fact that the alkaline metal oxide compounds react with sulfur on a molar basis, there is some inaccuracy in simply adding their weights together as shown in Figure IV-5. To try to improve on this overly simplistic approach, a weighting scheme was developed to add the metal oxides together on a molar basis, expressing the results as CaO.

$$\frac{\text{g. CaO/100 g.}}{54.08\ \text{g./mole}} + \frac{\text{g. } Na_2O\text{/100 g.}}{61.98\ \text{g./mole}} + \frac{\text{g. MgO/100 g.}}{40.31\ \text{g./mole}} + \frac{\text{g. } K_2O\text{/100 g.}}{94.20\ \text{g./mole}} = \text{Moles alkaline metal oxides/100 g.} \quad (17)$$

$$\text{Moles alkaline metal oxides/100 g.} \times 54.08\ \text{g./mole CaO} = \text{Weighted } \Sigma \text{ Alk. as CaO} \quad (18)$$

This approach is similar to one of the regression equations in Reference 5. Figure IV-6a. is a plot of sulfur vs. the weighted sum of alkaline metal oxides for all data. Figure IV-6b. is a plot of the same relationship, for only P.C. fired, ESP collected ash. Note that the regression coefficient is 0.924 for the first order linear equation.

Table IV-1 Summary of Regression Equation Coefficients and Correlation Coefficients.

S Retained Vs.	No. Points	Coefficient Term[a] 0	1	2	R^2
CaO	165	.0521	.0697		.576
	153	.0825	.0722		.629
	49	.00225	.121		.856
	49	.100	.00729	1.72×10^{-3}	.866
Na_2O	124	.227	.321		.431
	103	.225	.307		.417
	49	.298	.423		.606
	49	-.176	1.49	-.118	.774
MgO	153	.374	.265		.471
	132	.0477	.260		.458
	49	-.106	.436		.709
K_2O	129	1.23	-.297		.158
	108	1.11	-.253		.135
	49	.913	-.0265		.017
Σ Alk.	120	-.248	.0645		.635
	107	-.212	.0662		.659
	49	-.280	.0928		.904
Weighted Σ Alk. As CaO	120	-.189	.0623		.617
	107	-.139	.0644		.672
	49	-.197	.0909		.924
	49	.127	.00177	1.72×10^{-3}	.958
CaO + Na_2O	122	-.0386	.0710		.576
	101	-.619	.0741		.626
	49	-.0343	.110		.915
	49	.163	.00310	2.33×10^{-3}	.945

NOTES: (a) Coefficient terms of form: $Y = (0) + (1)X + (2)X^2$

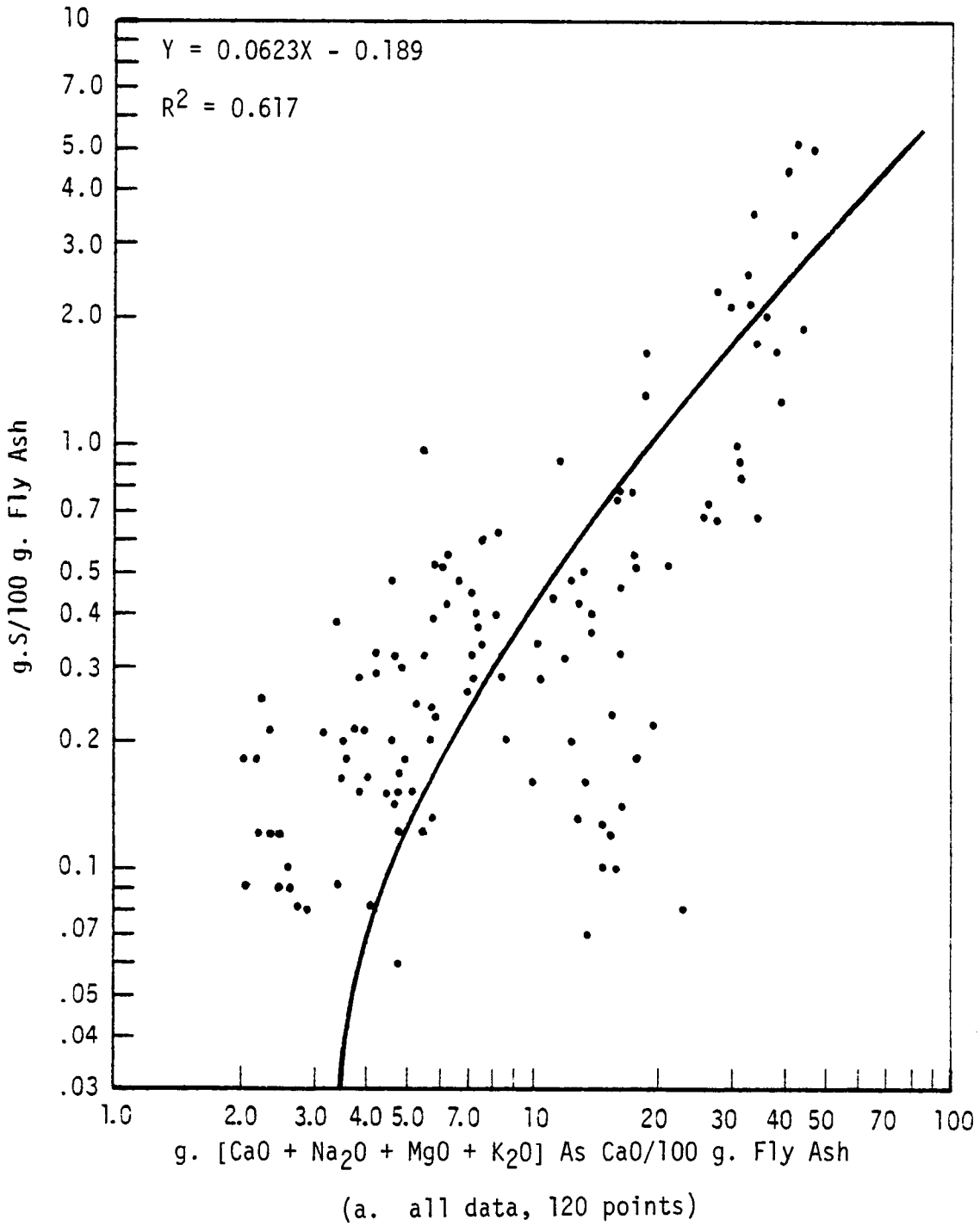
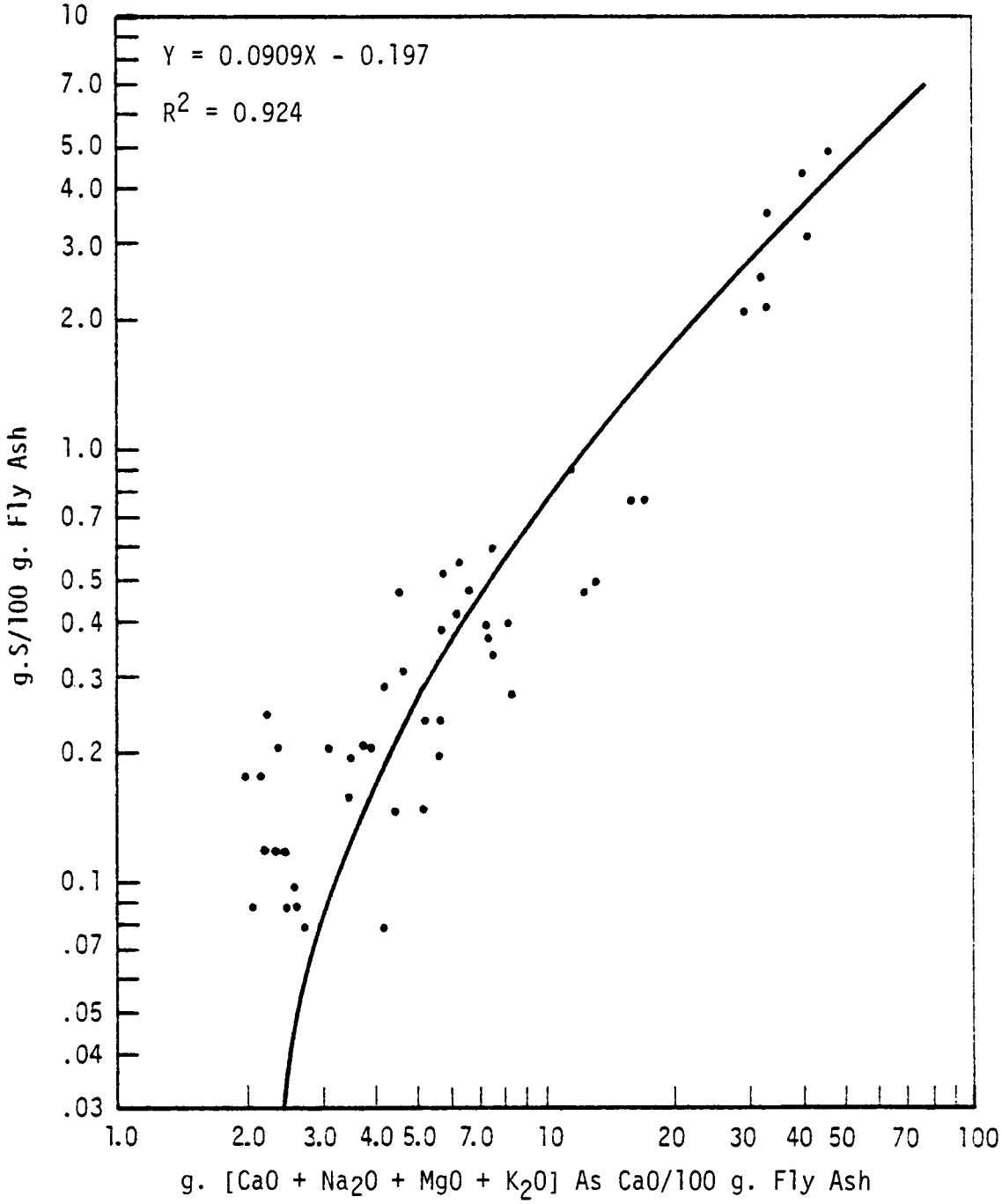


Figure IV-6. Grams Sulfur Retained Vs. Weighted Grams Alkaline Metal Oxides Expressed As CaO Per 100 Grams Fly Ash.



(b. Only P.C. fired, ESP collected ash data, 49 points)

Figure IV-6 (Continued).

The data set was sufficient to test one other equation from Reference 5. A plot of sulfur vs. CaO plus Na_2O is shown in Figure IV-7a for all data points, and the same plot for only P.C. fired, ESP collected ash is shown in Figure IV-7b. An excellent regression coefficient was again obtained. All equations and regression coefficients are summarized in Table IV-1.

Statistical analysis of the reduced data set was carried out using The General Electric Statistical Analysis System II (33). Routines run included PLOT (a data plotting routine), POLFIT (least squares polynominal fitting), CORR, XREG, SREG, and MREG (correlation and multiple regression routines). The XREG routine was used to test the significance of relating the variables to each other, with %S as the dependent variable and %CaO, %Na_2O, %MgO, and %K_2O as the independent variables. The intercept and no-intercept linear models were used, with the no-intercept model producing a slightly better fit (multiple correlation coefficient = 0.976 vs. 0.967). A summary of multiple regression statistics is given in Table IV-2. Physically, it is more logical to use the intercept model (no alkaline ash implies no sulfur retention). However, most of the data points and design situations are far enough removed from the orgin to allow either model to be used successfully.

The data in Table IV-2 indicates that there exists a nearly 100% probability that sulfur retention is linked to CaO and Na_2O. The no-intercept model indicates a low probability (44%) of K_2O participating in the data relationship with the MgO probability of significance at 84.6%. Clearly this helps to justify the earlier contention that CaO and Na_2O

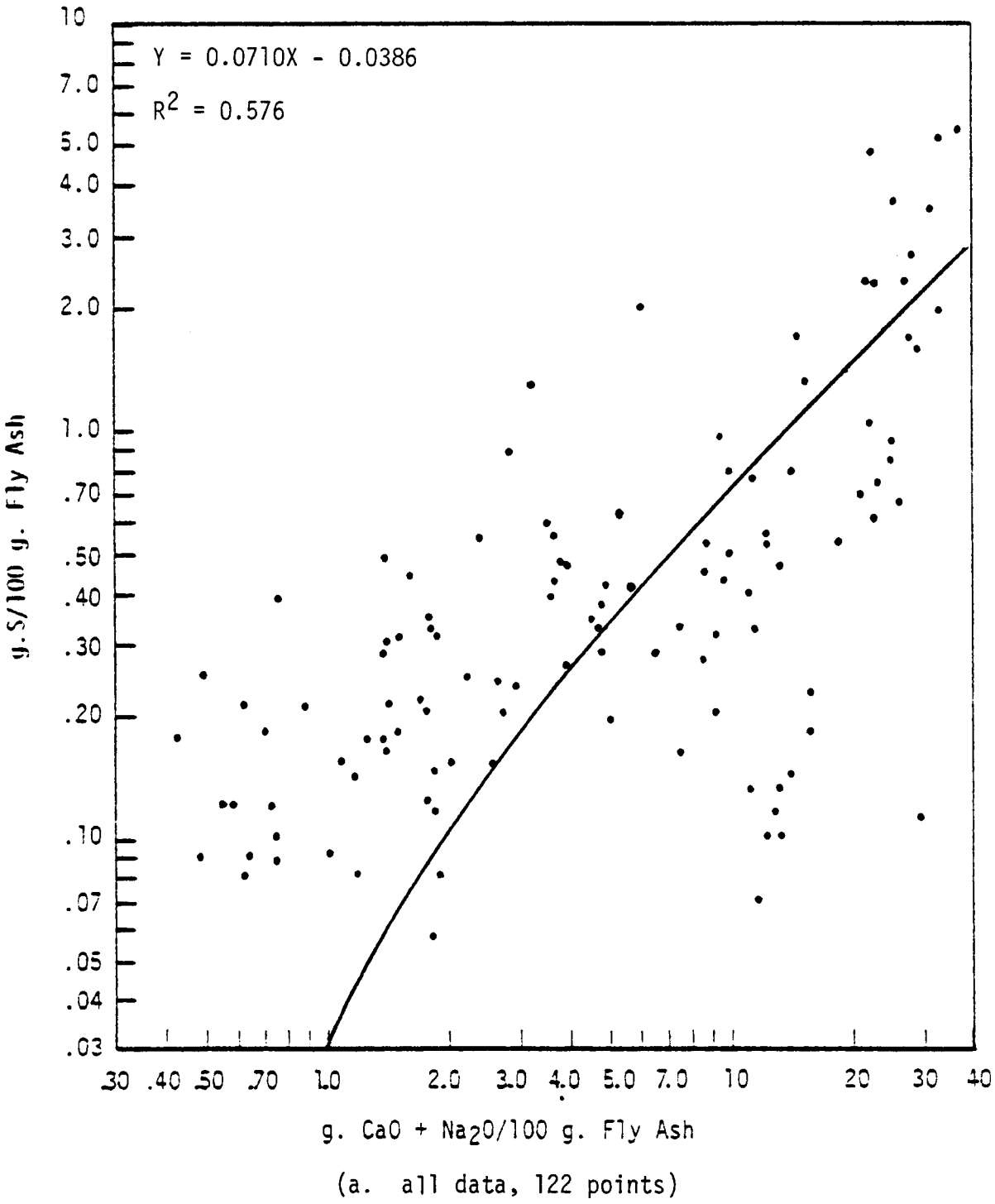
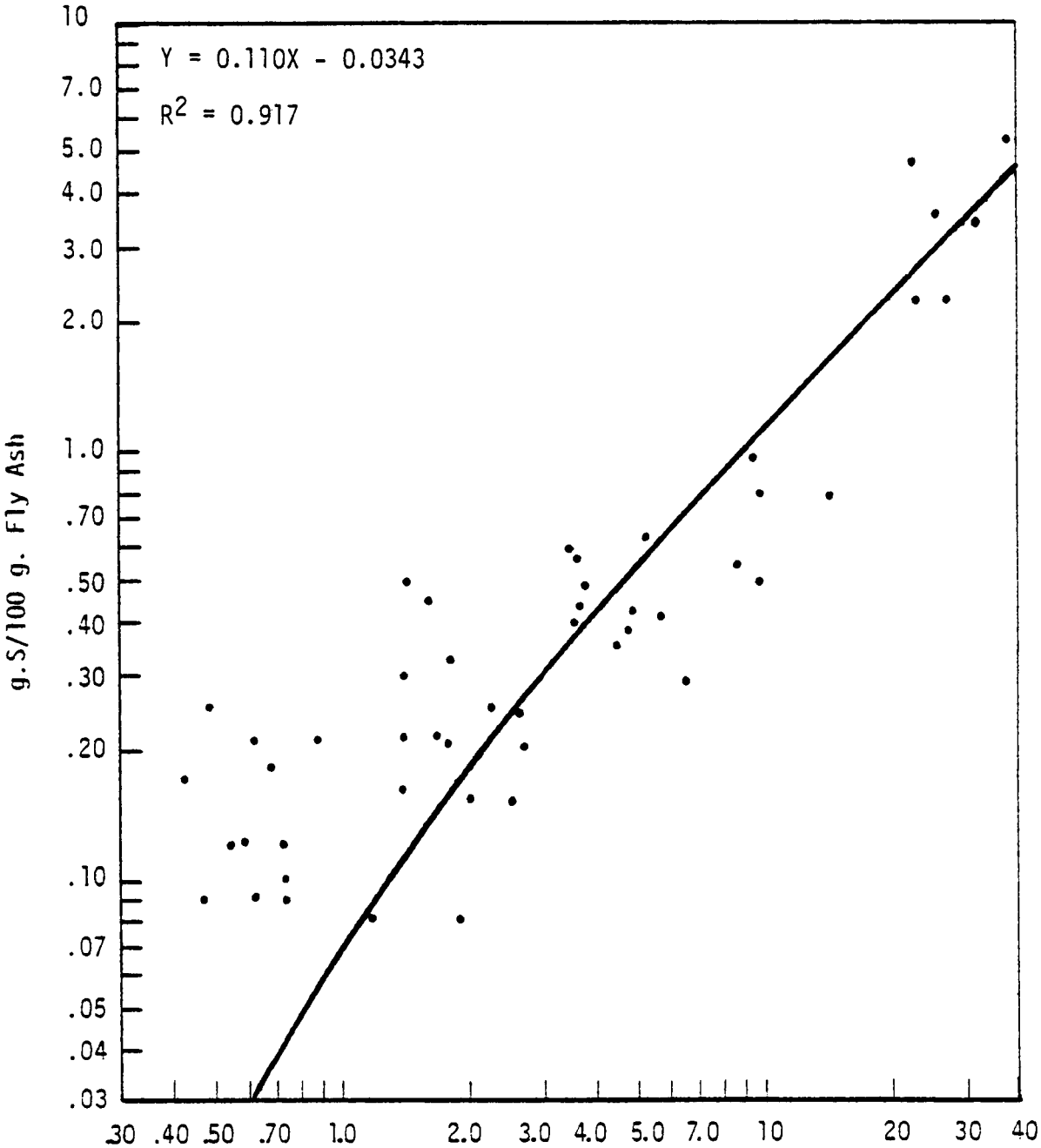


Figure IV-7. Grams Sulfur Retained Vs. Grams CaO + Na_2O Per 100 Grams Fly Ash.



(b. only P.C. fired, ESP collected ash data, 49 points).

Figure IV-7 (Continued).

Table IV-2. Multiple Regression Summary

INTERCEPT MODEL

Independent Variable	Regression Coefficient (a)		Standard Error (b)	T Value (c)	Significance Level (d)
Intercept	-.349	(0)	.186	-1.87	93.2%
%CaO	.0793	(C_1)	.0134	5.91	100%
%Na_2O	.192	(C_2)	.0267	7.17	100%
%MgO	.0947	(C_3)	.0475	1.99	94.8%
%K_2O	.111	(C_4)	.0697	1.59	88.1%

Analysis of Variance

Degrees of freedom, regression = 4, error = 44.
F - ratio = 160.73 (a 100% value).
Multiple correlation coefficient = 0.967
Index of determination = 0.936

NO-INTERCEPT MODEL

Independent Variable	Regression Coefficient (a)	Standard Error	T Value (b)	Significance Level (c)
%CaO	.0748	.0136	5.52	100%
%Na_2O	.190	.0275	6.94	100%
%MgO	.0673	.0465	1.45	84.6%
%K_2O	-.0132	.0224	-.587	44.0%

Analysis of Variance

Degrees of freedom, regression = 4, error = 45.
F - ratio = 220.82 (a 100% value).
Multiple correlation coefficient = 0.976
Index of determination = 0.952.

NOTES: (a) Coefficient terms of form:
$Y = (0) + (C_1)X_1 + (C_2)X_2 + (C_3)X_3 + (C_4)X_4$
X_1 = %CaO, X_2 = %Na_2O, X_3 = %MgO, X_4 = %K_2O.

(b) = Square root of the estimated variance of the regression coefficient.

(c) T-value = Regression Coefficient ÷ Standard Error

(d) Significance level = 1 - α, with α = the probability of rejecting the existence of a relation when, in fact, one exists.

are the dominant sulfur retention compounds. The XREG routine was repeated using only CaO and Na_2O as independent variables, producing a slightly improved correlation. Basically, the multiple regression analysis of the ash mineral data proves that there exists a nearly 100% probability that sulfur retention is controlled by the alkaline metal oxide content of the ash.

B. PARTICLE SIZE RELATIONSHIPS

An attempt was made to further correlate sulfur retention with other known ash characteristics. Data was available regarding particle size and/or surface area for many of the samples. Additional work was performed to obtain size distributions for the Bull Run samples and the samples obtained from the University of Kentucky. Various relationships were explored with little success. At best, a few trends were indicated.

Adsorption data obtained with the Fisher analyzer at two temperatures was plotted against particle size and area. Figure IV-8 illustrates the lack of any apparent correlation between ash surface area and either total sulfur or adsorbed sulfur. The dashed lines indicate linear least squares fit lines. However, the correlation coefficients are so low that the lines are nearly meaningless, except possibly to indicate a trend of slightly increasing sulfur retention with surface area.

Sulfur retention was plotted against mass median diameter (MMD) for all available data. A trend of decreasing sulfur retention with increasing particle size was indicated, as shown in Figure IV-9. The scatter of data was very large, with no improvement being found by limiting the data set to P.C. fired, ESP collected ash. As can be observed from the graph, the sulfur retention for the same size particles varied by more

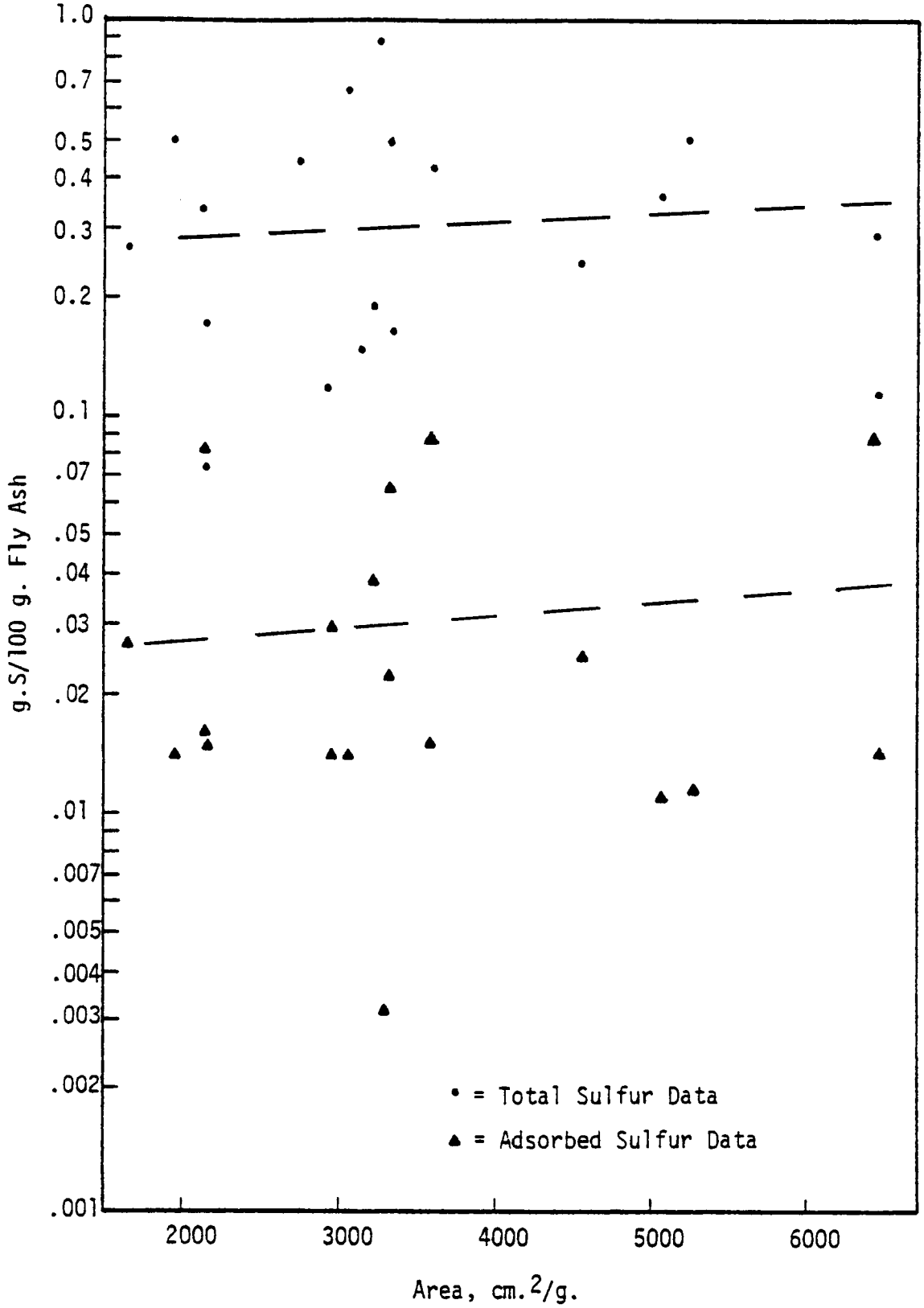


Figure IV-8. Grams Sulfur Retained Per 100 Grams Fly Ash Vs. Ash Surface Area.

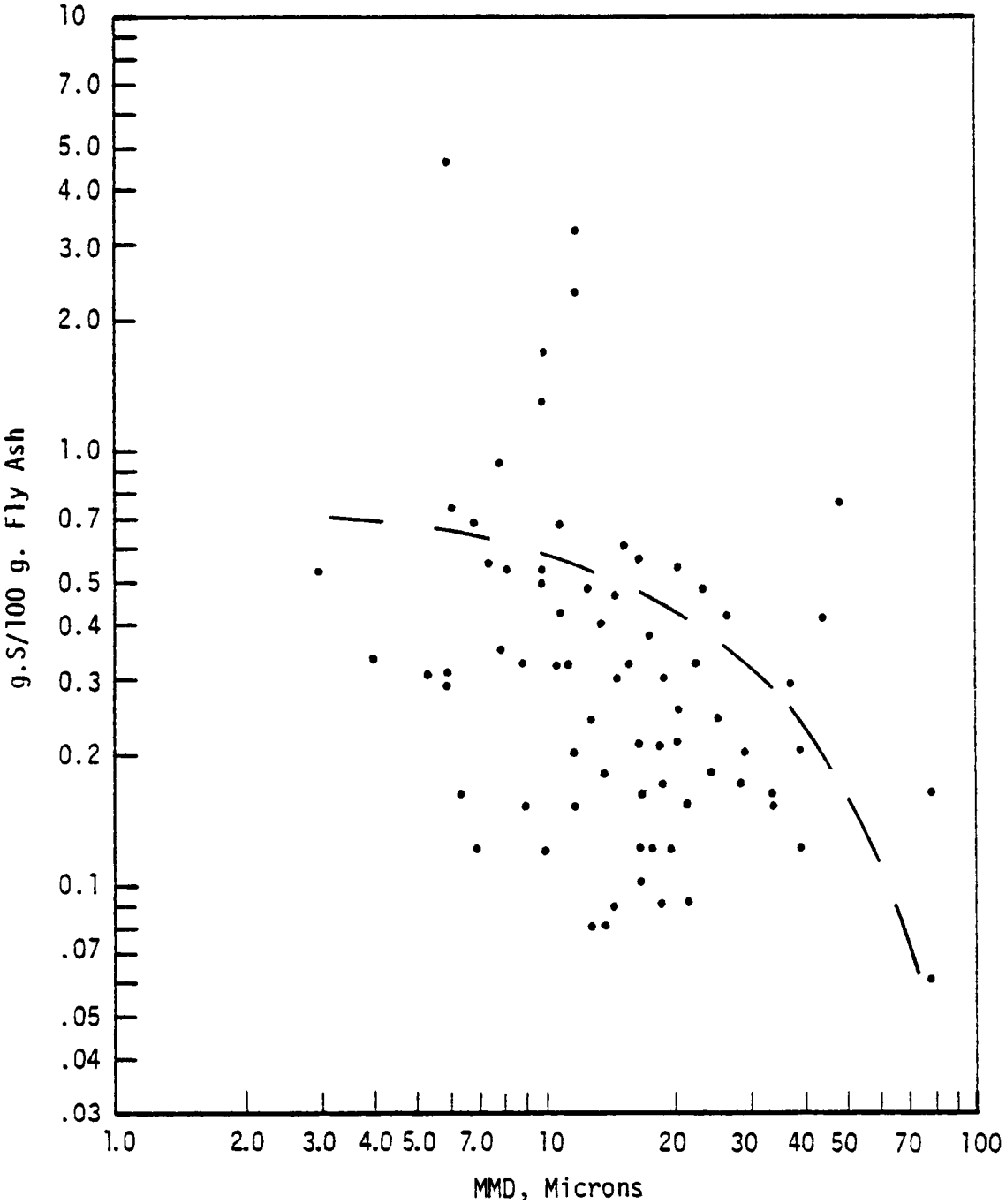


Figure IV-9. Grams Sulfur Retained Per 100 Grams Fly Ash Vs. Mass Median Diameter.

than an order of magnitude over most of the range plotted.

The information cited earlier from Horney (21) indicated a relationship between particle size and ash mineral content. To test this theory as a possible link between the definite increase of sulfur retention with alkaline metal oxide content and a possible decrease in sulfur retention with increasing particle size, CaO and Na_2O were plotted against MMD. Figures IV-10 and IV-11 show the tremendous scatter of data around what again amounts to only trend lines. The very low value of the regression coefficients allow little confidence to be placed in these relationships.

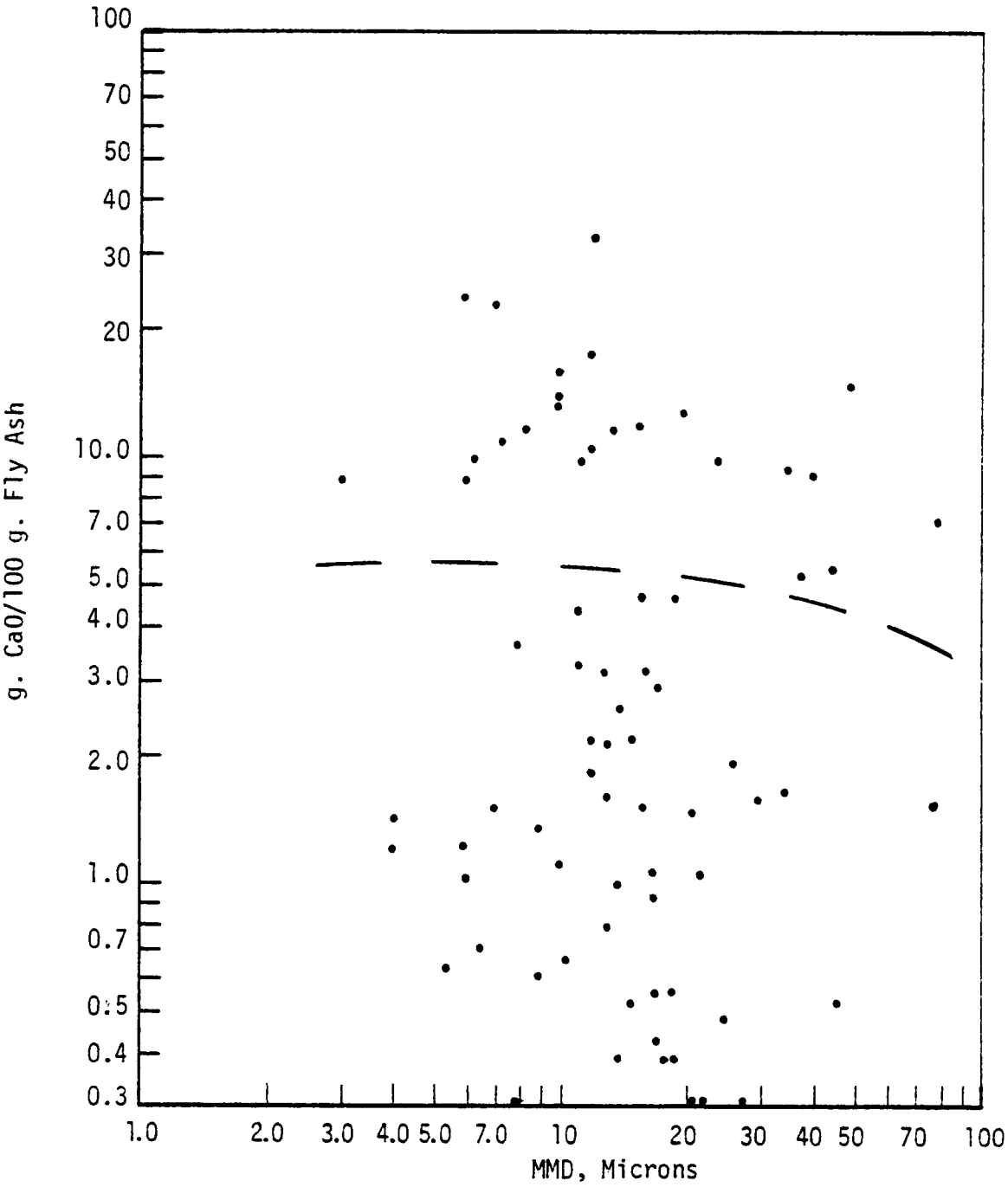


Figure IV-10. Grams CaO Per 100 Grams Fly Ash Vs. Mass Median Diameter.

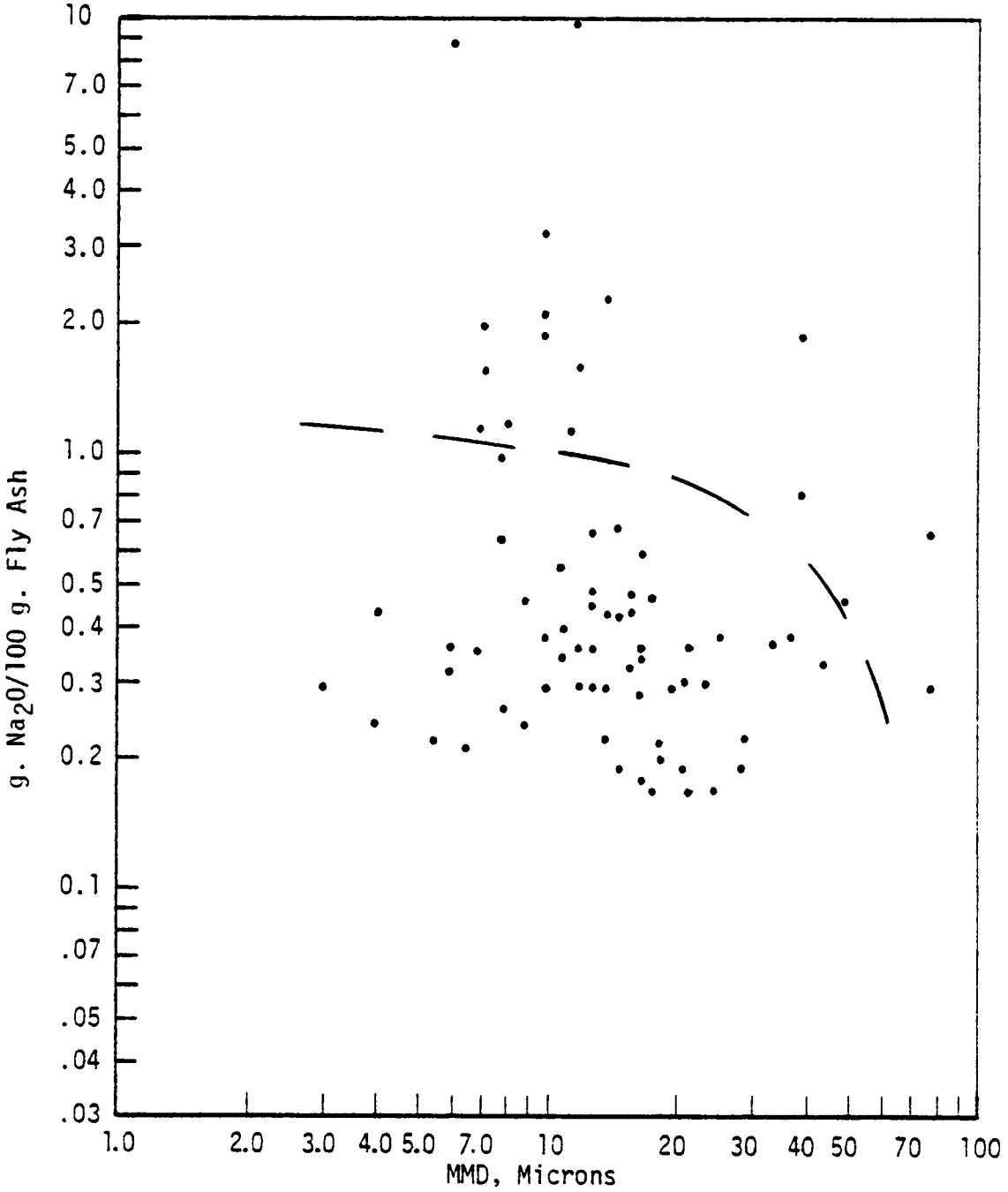


Figure IV-11. Grams Na_2O Per 100 Grams Fly Ash Vs. Mass Median Diameter.

V. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The graphical and statistical analysis of up to 165 data points indicate that sulfur retention is linked to the alkaline metal oxide content of fly ash. The best comparison of data can be made by selecting only those fly ash samples burned in the same type of combustion system. It is important that the ash samples collected be truly representative of the total fly ash generated. The changes in size distribution that occur in mechanically collected ash result in larger particles and less condensed sulfur being present. The removal of mechanical collector data from the data set generally results in improved regression coefficients.

The alkaline metal oxide components of fly ash investigated included CaO, Na_2O, MgO, and K_2O. The sulfur retained by fly ash had little correlation with the K_2O content of the ash. Although a slight negative trend was indicated, the magnitude of the data scatter was very large. The MgO content of the ash did appear to contribute to sulfur retention but the correlation did not improve significantly with the reduced data set (P.C., ESP ash only). The CaO and Na_2O content of the ash seem to be the controlling factors in sulfur retention. Either one considered alone will produce a reasonable correlation. However, the combination of these two metal oxides produces a dramatic improvement in data correlation. The addition of all alkaline metal oxides on a true molar basis produces an excellent correlation. The use of multiple linear regression yields the best fit to the data set with the following equation (multiple correlation coefficient = 0.976):

$$Y = .0748X_1 + .190X_2 + .0673X_3 - .0132X_4 \quad (19)$$

Y = %S retained

X_1 = %CaO

X_2 = $\%Na_2O$

X_3 = %MgO

X_4 = $\%K_2O$

The sulfur content of an ash sample does tend to increase with decreasing particle size. However, this is a general trend and sulfur content can vary greatly for a given particle size. There is evidence that for a specific ash, most of the sulfur is concentrated in the smaller particles.

The results of this study should be of use in designing FGD systems by helping engineers to better estimate the potential SO_2 removal capability of the ash being generated. The design of a new system may be calculated on a more realistic basis by taking credit for sulfur retained in the ash. If a scrubber is contemplated to utilize the residual alkalinity of the collected ash, the results of this study may be of use in calculating the amount of alkalinity remaining.

B. RECOMMENDATIONS FOR FURTHER RESEARCH

There are several areas where further study of sulfur retention in fly ash should be pursued.

1. Investigate additional ash samples from utility boilers with particular care to assure representative sample acquisition. Medium to high alkalinity coals should receive additional attention.

2. Study the effects of boiler load, humidity, and oxygen conditions at several operating plants. If a real-time data acquisition scheme could be developed it would be a great asset.
3. Staged combustion systems, generally developed to lower NO_x emissions, should be investigated using high alkalinity coals and/or sorbent addition to evaluate sulfur retention capabilities.
4. Alteration of flue gas moisture and temperature conditions with water or steam injection should be evaluated for enhanced sulfur retention.
5. Since most sulfur is apparently associated with the smaller particles, size classification of fly ash prior to utilizing residual alkalinity in a scrubbing system may improve alkaline availability. This should be evaluated.

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LIST OF REFERENCES

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APPENDICES

APPENDIX A

Table A-1 Coal Compositions

Coal	Weight Percent, Dry													
	C	H	N	O	S	Ash	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O
Montana Lignite	69.78	6.51	0.96	8.70	1.05	13.00	4.34	4.15	0.13	1.50	1.50	0.33	0.08	0.96
Augmented Lignite	66.41	4.45	1.31	17.12	1.00	9.70	3.72	1.68	0.12	0.73	1.98	0.78	0.04	0.09
Pittsburgh #8	59.27	4.58	1.10	20.99	0.98	13.07	3.45	1.47	0.10	0.61	5.39	0.68	0.08	0.07
	77.45	5.19	1.51	6.71	1.84	7.28	3.59	1.81	0.08	1.42	0.15	0.05	0.11	0.02

Table A-2 Sulfur Distribution, Montana Coal

Species	Weight % of Total Sulfur																							
	50% TA Temperature, 10^2 °F								75% TA Temperature, 10^2 °F								100% TA Temperature, 10^2 °F							
	33	29	25	21	17	13	9	5	33	29	25	21	17	13	9	5	33	29	25	21	17	13	9	5
COS	3.6	5.9	2.8	1.3	1.1	0.6	0.1		0.1	0.0	4.9	3.6	1.1	0.8	0.1									
CaS(S)		8.7	60.8	80.9	80.9	80.9	80.9	48.0				59.0	80.9	80.9	80.9	48.8							6.6	12.2
$CaSO_4$(S)																						45.6	43.6	36.9
FeS(S)						6.9	8.1								7.9									
H_2S	36.3	65.0	34.8	17.7	18.0	11.6	8.4	2.6	0.7	5.0	37.0	35.1	17.8	18.3	8.6	1.8						0.6	0.5	1.5
K_2SO_4(S)							2.5	2.5							2.5	2.5					1.9	2.5	2.5	2.5
Na_2SO_4(S)								46.9								46.9						46.9	46.9	46.9
Na_2SO_4(L)																				32.0	46.7			
Na_2SO_4																			0.1	0.7				
S	4.9	1.0							0.4	0.3	0.1													
SH	16.8	9.2	1.1	0.1					0.7	1.4	2.3	0.3												
SO	18.0	4.1	0.2						11.1	8.7	4.1	0.1					0.6	0.1						
SO_2	20.0	5.9	0.3						87.0	87.3	51.7	2.0					99.4	99.9	99.9	67.4	51.4	4.5		
SO_3																								
S_2O	0.2	0.1																						
SIS	0.3																							

Table A-2 (Continued)

Species	Weight % of Total Sulfur															
	125% TA Temperature, 10^2 °F								150% TA Temperature, 10^2 °F							
	33	29	25	21	17	13	9	5	33	29	25	21	17	13	9	5
COS																
CaS(S)																
$CaSO_4$(S)				22.7	51.0	50.6	50.6	50.6				25.5	51.0	50.6	50.6	50.6
FeS(S)																
H_2S																
K_2SO_4(S)					2.2	2.5	2.5	2.5					2.2	2.5	2.5	2.5
Na_2SO_4(S)						46.9	46.9	46.9						46.9	46.9	46.9
Na_2SO_4(L)				43.8	46.8							43.5	46.8			
Na_2SO_4			1.3	0.8							1.4	1.0				
S																
SH																
SO	0.2															
SO_2	99.8	99.8	98.3	32.3					99.9	99.8	98.1	29.6				
SO_3	0.1	0.2	0.4	0.4					0.1	0.2	0.5	0.4				
S_2O																
SIS																

Note: Only non-zero entries are shown.

(s) = solid

Table A-3 Sulfur Distribution, Lignite

	Weight % of Total Sulfur																							
	50% TA Temperature, 10^2 °F								75% TA Temperature, 10^2 °F								100% TA Temperature, 10^2 °F							
Species	33	29	25	21	17	13	9	5	33	29	25	21	17	13	9	5	33	29	25	21	17	13	9	5
COS	4.0	6.6	3.1	1.2	0.3				0.1	0.7	5.2	3.7	0.8	0.1										
CaS(S)		20.9	68.5	87.5	96.4	99.4	96.6	89.9				60.2	90.6	98.2	96.6	90.3							12.0	17.2
$CaSO_4$(S)																					8.7	85.3	79.0	73.4
H_2S	28.0	50.6	26.8	11.3	3.3	0.5	0.2	1.5	0.4	3.2	27.9	25.7	8.6	1.7	0.2	1.0						1.0	0.1	0.8
K_2SO_4(S)							3.2	3.2							3.2	3.2					3.0	3.2	3.2	3.2
Na_2SO_4(S)								5.4								5.4						5.4	5.4	5.4
Na_2SO_4(L)																				0.3	5.3			
Na_2SO_4																				0.6				
S	5.0	1.1							0.4	0.3	0.1													
SH	14.9	8.2	1.0	0.1					0.5	1.1	2.0	0.2												
SO	21.0	4.8	0.2						10.1	8.2	4.4	0.1					0.6	0.1						
SO_2	26.8	7.8	0.4						88.5	86.6	60.3	2.1					99.5	99.9	100.0	99.1	83.0	5.0		
SO_3																								
S_2O	0.2										0.2													
SiS	0.3																							

Table A-3 (Continued)

Species	Weight % of Total Sulfur															
	125% TA Temperature, 10^2 °F								150% TA Temperature, 10^2 °F							
	33	29	25	21	17	13	9	5	33	29	25	21	17	13	9	5
COS																
CaS(S)																
$CaSO_4$(S)				67.1	91.7	91.4	91.4	91.4				69.6	91.7	91.4	91.4	91.4
H_2S																
K_2SO_4(S)					3.0	3.2	3.2	3.2					3.0	3.2	3.2	3.2
Na_2SO_4(S)						5.4	5.4	5.4						5.4	5.4	5.4
Na_2SO_4(L)				2.9	5.3							2.6	5.3			
Na_2SO_4				0.8								0.9				
S																
SH																
SO	0.2															
SO_2	99.8	99.8	99.6	29.0					99.9	99.8	99.5	26.6				
SO_3	0.1	0.2	0.4	0.3					0.1	0.2	0.5	0.4				
S_2O																
SiS																

Note: Only non-zero entries are shown.

(s) = solid

Table A-4 Sulfur Distribution, Augmented Lignite

Species	Weight % of Total Sulfur																							
	50% TA Temperature, 10^2 °F								75% TA Temperature, 10^2 °F								100% TA Temperature, 10^2 °F							
	33	29	25	21	17	13	9	5	33	29	25	21	17	13	9	5	33	29	25	21	17	13	9	5
COS	3.3	6.9	3.3	1.2	0.3				0.1	0.7	4.7	3.4	0.8	0.1								0.1		
CaS(S)		6.1	63.4	85.3	95.7	99.3	98.1	100.0				66.5	89.9	98.1	98.1	92.6						17.4	37.7	42.8
$CaSO_4$(S)																						66.9	55.7	50.0
H_2S	25.8	58.7	31.4	13.4	4.1	0.7	0.2		0.5	3.4	28.8	27.5	9.3	1.8	0.2	1.2					0.1	3.3	0.4	1.0
K_2SO_4(S)							1.7								1.7	1.8					1.2	1.8	1.8	1.8
Na_2SO_4(S)																4.5						4.5	4.5	4.5
Na_2SO_4(L)																					4.3			
Na_2SO_4																								
S	4.3	1.1							0.3	0.3	0.1													
SH	13.3	9.3	1.1	0.1					0.5	1.1	1.9	0.2												
SO	21.3	6.1	0.2						9.9	7.9	4.2	0.1					0.6	0.2	0.1					
SO_2	31.7	11.7	0.6						88.7	86.7	60.0	2.2					99.4	99.9	99.9	100.0	94.5	6.1		
SO_3																								
S_2O	0.2	0.2									0.2													
SiS	0.2																							

Table A-4 (Continued)

Species	Weight % of Total Sulfur															
	125% TA Temperature, 10^2 °F								150% TA Temperature, 10^2 °F							
	33	29	25	21	17	13	9	5	33	29	25	21	17	13	9	5
COS																
CaS(S)																
$CaSO_4$(S)				69.9	94.0	93.8	93.8	93.8				72.4	94.1	93.8	93.8	93.8
H_2S																
K_2SO_4(S)					1.5	1.8	1.8	1.8					1.5	1.8	1.8	1.8
Na_2SO_4(S)						4.5	4.5	4.5						4.5	4.5	4.5
Na_2SO_4(L)				2.0	4.4							1.7	4.4			
Na_2SO_4				0.7								0.8				
S																
SH																
SO	0.2															
SO_2	99.8	99.8	99.6	27.0					99.9	99.8	99.5	24.7				
SO_3	0.1	0.2	0.4	0.3					0.1	0.2	0.5	0.4				
S_2O																
SiS																

Note: Only non-zero entries are shown.

(s) = solid

Table A-5 Sulfur Distribution, Pittsburgh #8

Species	Weight % of Total Sulfur																							
	50% TA Temperature, 10^2 °F								75% TA Temperature, 10^2 °F								100% TA Temperature, 10^2 °F							
	33	29	25	21	17	13	9	5	33	29	25	21	17	13	9	5	33	29	25	21	17	13	9	5
COS	4.7	8.0	7.2	5.7	5.0	4.5	0.7		0.2	0.9	5.8	11.0	5.7	3.7	1.1									
CaS(S)		4.7	4.7	4.7	4.7	4.7	4.7	4.7				4.7	4.7	4.7	4.7	4.7								
$CaSO_4$(S)																					4.7	4.7	4.7	4.7
FeS(S)				31.9	32.0	32.0	32.0						31.9	31.9	31.9									
FeS(L)			19.7																					
FeS_2(S)								63.9								63.9								4.6
$Fe_2(SO_4)_3$(S)																								
H_2S	35.5	65.9	65.2	57.4	58.3	58.9	59.8	28.6	0.6	4.0	31.7	77.8	57.6	59.6	59.4	28.6							1.6	0.2
H_2SO_4																								
K_2SO_4(S)							2.2	2.2							2.2	2.2					2.1	2.2	2.2	2.2
K_2SO_4(L)																								
$MgSO_4$(S)																								2.1
Na_2SO_4(S)							0.7	0.7							0.7	0.7						0.7	0.7	0.7
Na_2SO_4(L)																					0.6			
Na_2SO_4																								
S	5.9	1.3	0.1						0.4	0.3	0.2													
SH	18.2	10.4	2.3	0.3					0.6	1.3	2.2	0.7												
SO	18.3	4.3	0.3						11.1	8.8	4.4	0.3					0.6	0.1						
SO_2	17.3	5.1	0.5						87.2	84.6	55.4	5.4					99.5	99.9	100.0	100.0	92.6	92.5	90.9	85.6
SO_3																								
S_2O	0.3	0.2								0.1	0.1	0.1												

Table A-5 (Continued)

Species	Weight % of Total Sulfur															
	125% TA Temperature, 10^2 °F								150% TA Temperature, 10^2 °F							
	33	29	25	21	17	13	9	5	33	29	25	21	17	13	9	5
COS																
CaS(S)																
$CaSO_4$(S)				4.7	4.7	4.7	4.7	4.7				4.7	4.7	4.7	4.7	4.7
FeS(S)																
FeS(L)																
FeS_2(S)																
$Fe_2(SO_4)_3$(S)							47.9	47.9							47.9	47.9
H_2S																
H_2SO_4							0.3	36.7							0.3	35.8
K_2SO_4(S)					2.2	2.2	2.2	2.2					2.2	2.2	2.2	2.2
K_2SO_4(L)				0.9								0.8				
$MgSO_4$(S)						2.1	2.1	2.1						2.1	2.1	2.1
Na_2SO_4(S)						0.7	0.7	0.7						0.7	0.7	0.7
Na_2SO_4(L)					0.7								0.7			
Na_2SO_4				0.3								0.3				
S																
SH																
SO	0.2								0.1							
SO_2	99.8	99.8	99.6	93.1	87.9	61.3	2.4		99.8	99.8	99.5	92.8	86.7	55.9	1.9	
SO_3	0.1	0.2	0.4	1.1	4.6	29.1	39.8	5.8	0.1	0.2	0.5	1.4	5.8	34.5	40.1	6.7
S_2O																

Note: Only non-zero entries are shown.

(s) = solid

Table A-6 Sulfur Retention By Condensed Species
Weight % of Total Sulfur

Coal	% TA	Temperature, °F 3300	2900	2500	2100	1700	1300	900	500
Montana	50	0	8.7	60.8	80.9	80.9	87.8	91.5	97.4
	75	0	0	0	59.0	80.9	80.9	91.2	98.2
	100	0	0	0	32.0	48.6	95.0	99.5	98.6
	125	0	0	0	66.5	100.0	100.0	100.0	100.0
	150	0	0	0	68.9	100.0	100.0	100.0	100.0
Lignite	50	0	20.9	68.5	87.5	96.4	99.4	99.8	98.5
	75	0	0	0	68.2	90.6	98.2	99.8	99.0
	100	0	0	0	0.3	17.0	94.0	99.7	99.2
	125	0	0	0	69.9	100.0	100.0	100.0	100.0
	150	0	0	0	72.1	100.0	100.0	100.0	100.0
Augmented Lignite	50	0	6.1	63.4	85.3	95.7	99.3	99.8	100.0
	75	0	0	0	66.5	89.9	98.1	99.8	98.8
	100	0	0	0	0	5.5	90.5	99.7	99.1
	125	0	0	0	72.0	100.0	100.0	100.0	100.0
	150	0	0	0	74.2	100.0	100.0	100.0	100.0
Pittsburgh #8	50	0	4.7	24.3	36.6	36.6	36.6	39.5	71.4
	75	0	0	0	4.7	36.6	36.6	39.5	71.4
	100	0	0	0	0	7.4	7.5	7.5	14.2
	125	0	0	0	5.6	7.5	9.6	57.5	57.5
	150	0	0	0	5.5	7.5	9.6	57.5	57.5

APPENDIX B

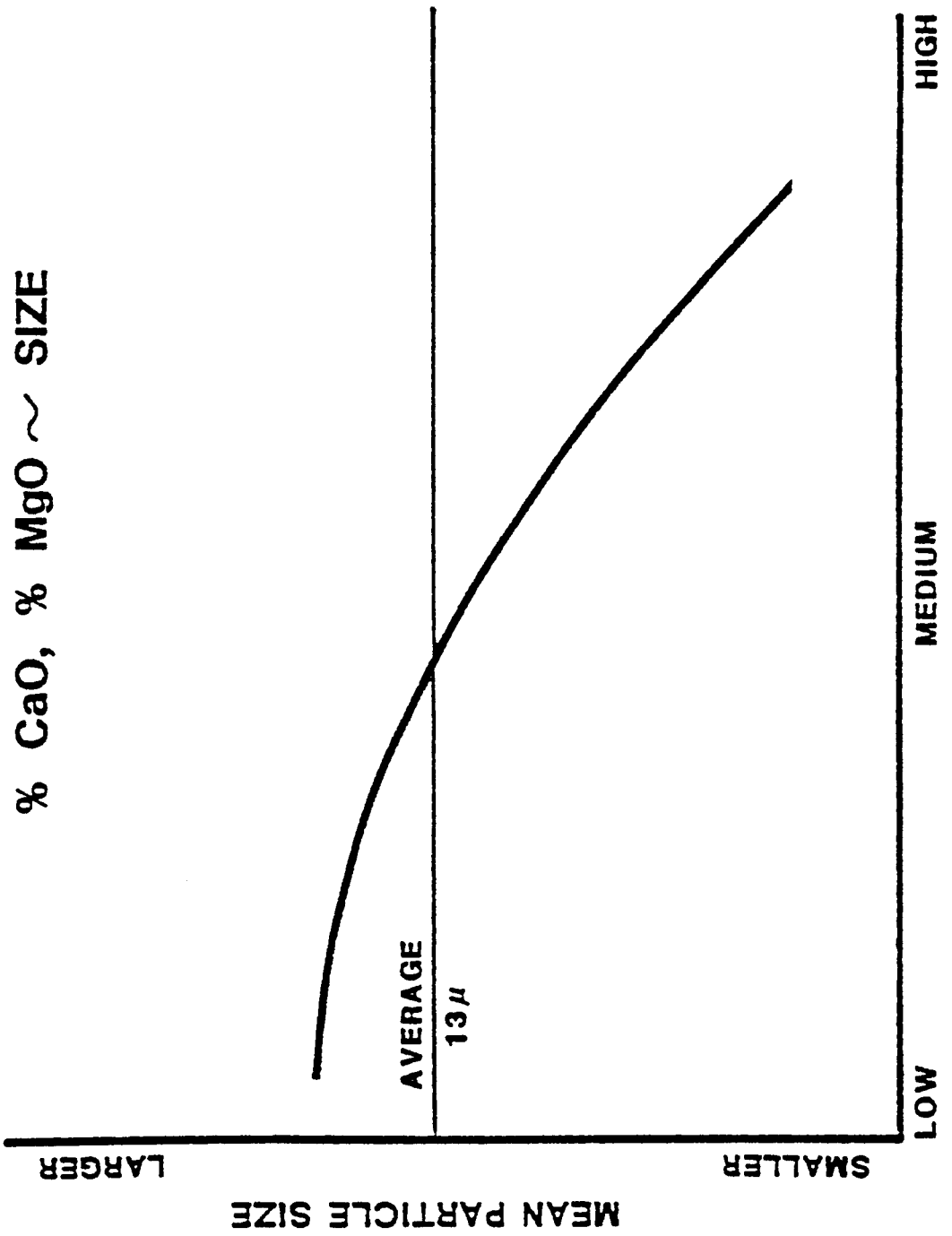


FIGURE B-1. Mean Particle Size Vs. %CaO + %MgO

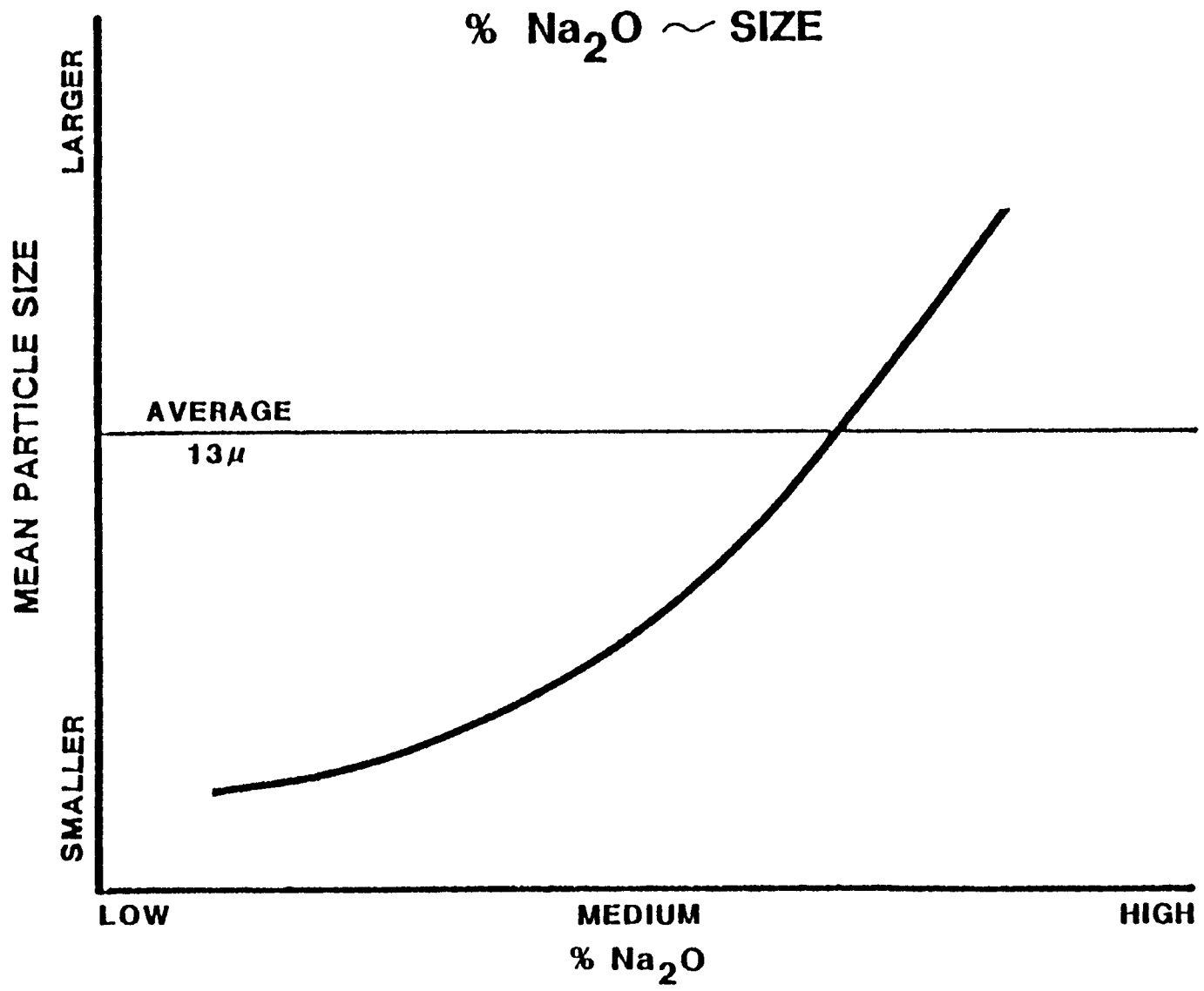


FIGURE B-2. Mean Particle Size Vs. %Na_2O

APPENDIX C

The Fisher Model 470 sulfur analyzer uses an amperometric titration procedure to measure the SO_2 content of gas given off when a sample is combusted in an attached 1350°C tube furnace. Figure C-1 is a block diagram of the analyzer. Following the diagram from left to right, the sample is placed in a ceramic boat and inserted into the high temperature zone of the furnace. As the combustible materials are burned in the oxygen atmosphere they are carried to the titration cell. The SO_2 is selectively scrubbed from the gas stream, polarizing the cell and reducing the conductivity of the solution of iodine, water, pyridine, and methanol. The titrate demand circuitry senses the change and activates the digital burette to dispense additional iodine solution at a preprogrammed, adjustable rate to depolarize the cell and re-establish the cell current. The end-point is reached when no further SO_2 remains to be reduced and the cell current exactly matches the starting value. The microprocessor then uses titrant volume and the previously entered titrant factor and sample weight to calculate either the percent or parts per million sulfur content of the fuel. The operation is completely automatic once the sample weight is entered and the sample inserted in the tube furnace. Coal and oil samples can be run in approximately two minutes. Ash samples, because of the lower levels of sulfur being measured require 5 to 10 minutes.

The following analysis procedure was used for the two-temperature tests. Other tests that determined only total sulfur followed the same procedure, but without steps 5 and 6.

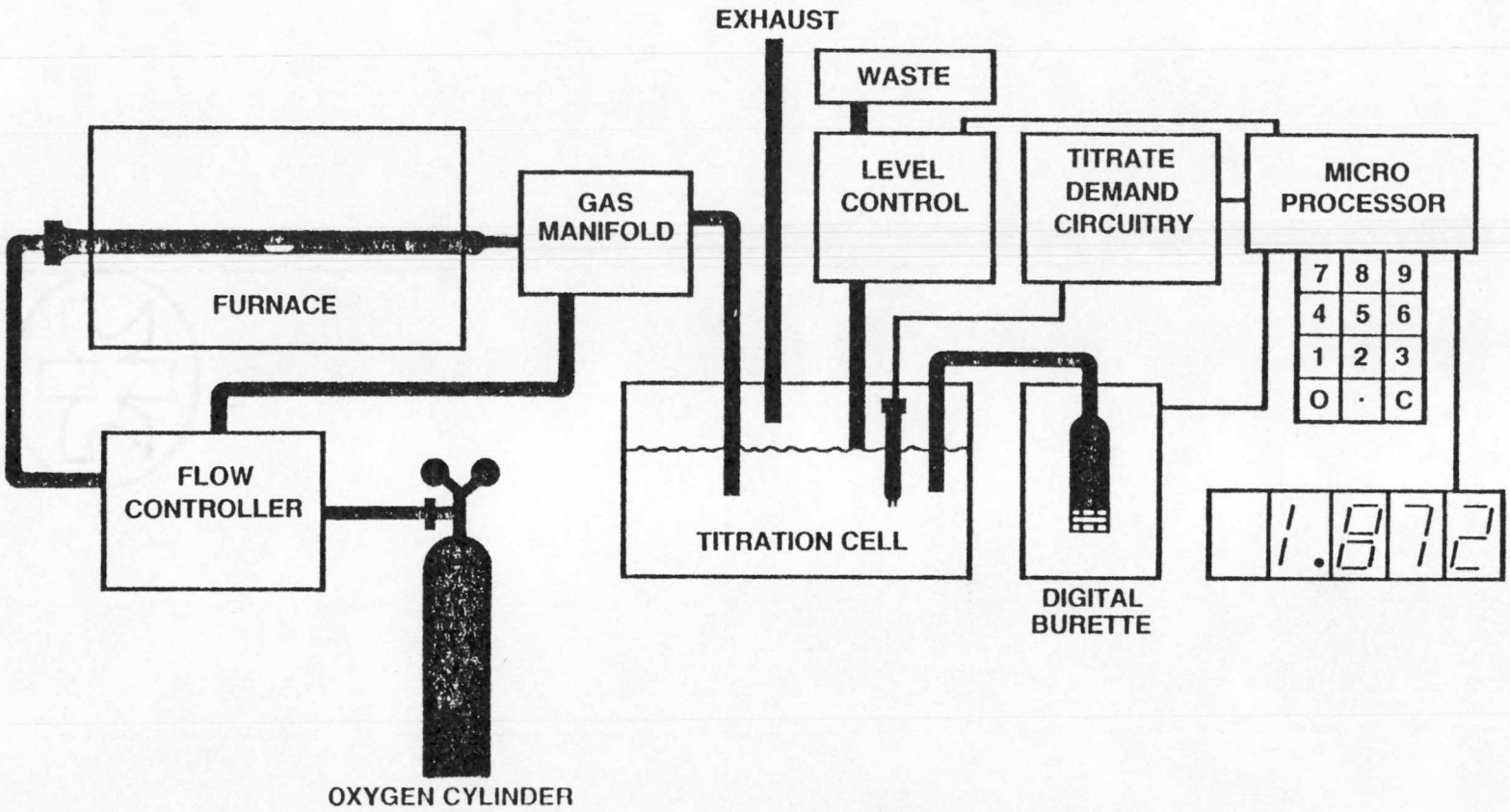


FIGURE C-1. Sulfur Analyzer Block Diagram

1. Dessicate samples 48 hours at room temperature.
2. After proper startup and cell conditioning, establish titrant factor using NBS standard coal sample. Average at least five trials.
3. Weight sample in tared sample boat (usually 100 to 300 mg) and enter weight in analyzer. For two-temperature runs, place sample in end of boat.
4. Place sample boat in the end of the tube furnace. Push start button.
5. Carefully position the ash sample 165 mm into the tube. Insert stopper.
6. When the % sulfur value appears, record immediately and push start button again as soon as the analyzer resets. It will retain the same sample weight.
7. Insert sample to full depth of furnace. Replace stopper.
8. When % sulfur value appears, remove the sample boat and record the value.
9. Return to Step No. 3 for next sample.

The temperature profile of the sulfur analyzer tube furnace (used to determine the sample boat positions) is included as Figure C-2.

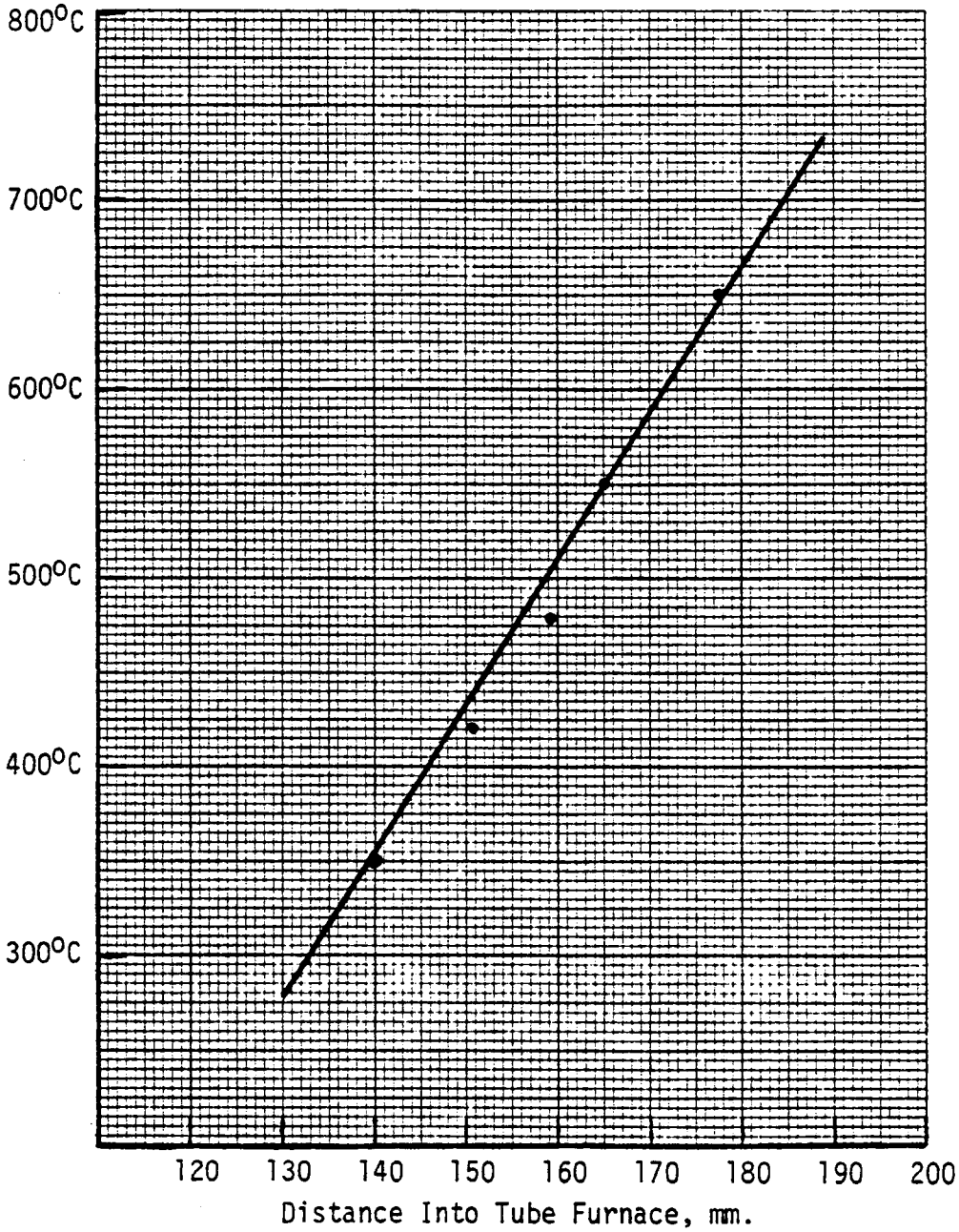


Figure C-2. Position Vs. Temperature Profile Of Fisher Model 470 Sulfur Analyzer Tube Furnace.

VITA

Mark A. Fiedler was born in Lockport, New York on October 4, 1950. He attended elementary school in Newfane, New York and graduated from Newfane Central High School in June, 1968. The following September he entered S.U.N.Y. at Binghamton (Harpur College). After two years he transferred to S.U.N.Y. College at Buffalo where he received a Bachelor of Science degree (Magna Cum Laude) in Industrial Arts Education, June, 1972. He returned to school on a part-time basis in January, 1974 at S.U.N.Y. at Buffalo to take Civil Engineering courses. After moving to Knoxville he entered the graduate school of the University of Tennessee, Knoxville, in September, 1978, as an evening school student. He received the Master of Science degree in Environmental Engineering in August, 1980.

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