

**BOILER DESIGN AND OPERATING
VARIABLES AFFECTING
UNCONTROLLED SULFUR EMISSIONS
FROM PULVERIZED-COAL-FIRED
STEAM GENERATORS**

by

Carlo Castaldini and Meredith Angwin

**Acurex Corporation/Aerotherm Division
485 Clyde Avenue
Mountain View, California 94042**

**Contract No. 68-02-2611
Project No. 6**

EPA Project Officer: Kenneth R. Durkee

Prepared for

**ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711**

December 1977

This report is issued by the Environmental Protection Agency to report technical data of interest to a limited number of readers. Copies are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations - in limited quantities - from the Library Services Office (MD-35), Research Triangle Park, North Carolina 27711; or, for a fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

This report was furnished to the Environmental Protection Agency by Acurex Corporation/Aerotherm Division, 485 Clyde Avenue, Mountain View, California 94042, in fulfillment of Contract No. 68-02-2611, Project No. 6. The contents of this report are reproduced herein as received from Acurex Corporation. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of the Environmental Protection Agency. Mention of company or product names is not to be considered as an endorsement by the Environmental Protection Agency.

Publication No. EPA-450/3-77-047

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1 INTRODUCTION	1
2 COAL SULFUR CONTENT AND CHEMICAL REACTIONS	3
2.1 Coal Sulfur	3
2.2 Chemistry of Sulfur Emissions	4
2.3 Sulfur Input and Output Streams in a Typical Pulverized Coal-Fired Steam Generator	5
3 EFFECT OF BOILER DESIGN AND PROCESS VARIABLES ON SULFUR EMISSIONS	9
3.1 Boiler Firing Type	25
3.2 Coal Type	28
3.2.1 SO ₂ and SO ₃ Gaseous Emissions	28
3.2.2 Sulfate Emissions	29
3.2.3 Alkali Constituents in Coal Ash	36
3.3 Percent Sulfur in the Coal	39
3.4 Burner Stoichiometry	39
3.5 Boiler Firing Rate	42
3.6 Boiler Size	42
4 GASEOUS SULFUR EMISSION ACROSS PARTICULATE COLLECTION DEVICES	57
5 CONCLUSIONS AND RECOMMENDATIONS	61
5.1 Conclusions and Recommendations	61
5.2 Recommendations for Further Investigations	62
REFERENCES	65
APPENDIX A — MATHEMATICAL RELATIONSHIPS USED	67
APPENDIX B — COMPARISON OF SO ₂ EMISSION FACTORS	69
APPENDIX C — INSTRUMENTATION AND SAMPLING TECHNIQUES	71
APPENDIX D — TABLE OF CONVERSION UNITS	77

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Sulfur input and output streams	6
2	Average SO ₂ conversion versus boiler firing type . . .	26
3	Ratio of SO ₃ gaseous emissions to SO ₂ and SO ₃ emissions	27
4	Minimum sulfur retention required to ash to meet SO _x standard of 1.2 lb SO _x /10 ⁶ Btu (516 ng/J)	30
5	Predicted versus actual sulfur emission (S.E.) for pc-fired plants	37
6	Percent SO ₂ conversion as a function of ash sodium content for lignite coals	38
7	Effect of sulfur content on SO ₂ emissions	40
8	Effect of burner stoichiometry on the percentage conversion of bituminous coal sulfur to SO ₂	41
9	Effect of burner stoichiometry on the percentage conversion of subbituminous coal sulfur to SO ₂	43
10	Effect of burner stoichiometry on SO ₃ emissions from bituminous coal-fired boilers	44
11	Effect of burner percent stoichiometry on SO ₃ emissions from bituminous coal-fired boilers	45
12	Effect of firing rate on SO ₂ emissions for bituminous coal-fired boilers	46
13	Effect of firing rate on SO ₂ emissions for lignite and subbituminous coal-fired boilers	47
14	Effect of boiler size on SO ₂ emission rate	48
15(a)	Effect of boiler size on SO ₂ emissions	50
15(b)	Effect of boiler size for bituminous coals	51
15(c)	Effect of boiler size for subbituminous coals	52
15(d)	Effect of boiler size for lignite coals	53
16	Effect of sulfur content on SO ₂ emissions	54
17	Effect of boiler size on SO ₂ emissions	56

SECTION 1

INTRODUCTION

In 1971 EPA promulgated new source performance standards (NSPS) for coal-fired boilers greater than 250 MBtu/hr. These standards set a limit of 516 ng/J (1.2 lb/MBtu) on the emissions of SO₂ from new, modified, or reconstructed facilities in this category. That standard is now under review by EPA to determine whether the best demonstrated technology currently available (taking the cost of the controls into account) justifies revision of the standard to a lower limit. The results presented in this report provide general background information for use by the Emission Standards and Engineering Division in their review of the NSPS for SO₂ emissions. Specifically they show which boiler design and operating variables affect SO₂ emissions and to what extent. Thus, trends on the conversion of sulfur in the coal to SO₂, SO₃, and particulate sulfate are reported. The results are based on uncontrolled sulfur emissions data from eight field test reports of coal-fired steam generators. These eight reports contain data from 21 boiler/coal type combinations.

SECTION 2

COAL SULFUR CONTENT AND CHEMICAL REACTIONS

This section presents general background information on the sulfur content of coals and the chemical reactions occurring in pulverized coal combustion flames. Some of the factors affecting sulfur emissions are briefly mentioned. A more detailed description of their effects is given in Section 3.

2.1 COAL SULFUR

Coal contains sulfur in three forms: "organic sulfur" is bound into the chemical structure of the coal; "pyritic sulfur" is contained in coal as discrete particles of sulfide minerals such as iron pyrite (FeS_2); and "sulfate sulfur" is an oxidation product which is usually found in fresh coal only in concentration below 0.05 percent (Reference 1). Sulfate emissions from pulverized coal-fired boilers originate from the reaction of SO_3 with metals found in the ash, rather than being the direct discharge of non-combustible constituents of the fuel.

Organic sulfur and pyritic sulfur are both capable of being oxidized to SO_2 and SO_3 during combustion. Under extremely low oxygen combustion conditions, pyritic sulfur may not be oxidized, but instead FeS and S may be deposited on the boiler walls. However, under normal operating conditions, both forms of sulfur will be oxidized to SO_2 or SO_3 (Reference 2).

Pyritic sulfur can be separated from coal before combustion through a combination of fine grinding and flotation (specific gravity separation). This form of coal precleaning depends on the fact that pyritic sulfur is usually found in discrete particles within the coal; in addition, it has a specific gravity of about 5.0, while coal's specific gravity is approximately

1.7. There are two drawbacks to this technique of coal cleaning: (1) some energy bearing material in the coal is inevitably lost during the separation process, and (2) only the pyritic sulfur is capable of being removed in this fashion. The efficiency of this kind of coal cleaning for various forms of coal is fully discussed in Reference 1.

Coals exhibit much variation in sulfur content, percent of pyritic sulfur and heating values. For example, the total sulfur content of midwest regional bituminous coal averages 5.25 percent (3.58 percent pyritic), while western regional subbituminous and lignitic coals have an average total sulfur content of 0.68 percent (0.23 percent pyritic) (Reference 1). Eastern coal can have a heating value as high as 14,000 Btu/lb, while lignite can have an average heating value of 8,500 Btu/lb. Because coals differ so greatly in their heating values, emissions of sulfur oxides from coal combustion is most usefully expressed as a weight of pollutant per unit of heat energy (ng/J or lbs/MBtu).

2.2 CHEMISTRY OF SULFUR EMISSIONS

Most sulfur emitted from utility boilers is emitted as the gaseous sulfur oxides, SO_2 and SO_3 . The proportion of SO_2 to SO_3 is controlled by several factors: the temperature in the combustion area, the percentage of excess air, and the availability of certain catalysts. In general, more SO_2 is formed at characteristic flame temperatures than SO_3 . At lower temperatures, however, the tendency would be to form more SO_3 . This tendency is offset by the short residence times of the combustion gases in conventional boilers. Therefore, SO_3 is only a small percentage of the sulfur oxides emitted from the stack. The SO_3 percentage should theoretically rise with the percentage of excess air in the combustion chamber, but there is not enough data to confirm this (see Section 3.1.4). Studies on sulfur emissions from oil-fired boilers have shown that the SO_2 to SO_3 transformation can be catalyzed by certain metal oxides, such as vanadium and iron oxides. Catalytic reaction of SO_2 to SO_3 by iron, silicon, and aluminum oxides in pulverized coal boilers has received considerable interest as a potential SO_2 control technique* (Reference 3).

*The presumption is that the boiler is already equipped with a particle control device which would collect the sulfites and, hence, indirectly help to control SO_2 .

Most sulfur is emitted from coal-fired boilers in the form of gaseous oxides, as described above. However, a certain percent of the sulfur is emitted with the flyash as sulfates. Sulfuric acid and metal alkali sulfates are often found as a coating on particles of flyash. The percentage of sulfur in the flyash particles tends to increase as the particle size decreases. In chemically analyzed airborne flyash, the sulfur content increased from 8.3 to 48.8 weight percent as the particle diameter decreased from greater than 11 μm to about 1 μm (Reference 4). The partition of emitted sulfur between SO_2 gas and particulate sulfate will be discussed more fully in the data analysis section of this report (see Section 3.1.2.2).

2.3 SULFUR INPUT AND OUTPUT STREAMS IN A TYPICAL PULVERIZED COAL-FIRED STEAM GENERATOR

Figure 1 shows a typical pulverized coal-fired steam generator. The burners are located on one wall (rear wall-fired) in a 4 x 4 matrix arrangement.

Location No. 2 represents the only sulfur input stream being fed into the boiler with the coal. The quantity of input sulfur is known, therefore, if a coal analysis has been performed. Location No. 3 represents the bottom ash exit stream. The sulfur content and the quantity of ash depends on many factors, and these are discussed in Section 3 of this report. Location No. 4 represents the economizer or superheater hopper ash exit stream. Similarly to the bottom hopper, ash quantity and sulfur content here depend on many factors. Location No. 6 represents the dust collector exit stream. The dust collector may be a set of mechanical cyclones, an electrostatic precipitator or a scrubber device. Finally, Location 7 represents the stack emission exit stream which accounts for all airborne sulfur emissions emitted to the atmosphere (with the exception of potential fugitive emissions from the ash piles associated with any of the hoppers). It should be noted that some ash remains in the boiler in the form of slag deposits on the furnace water walls and superheater tube surfaces. It is assumed that intermittent soot blowing will dislodge most of these deposits. Some fraction of this dislodged matter is collected in the dust collector, but a portion is also released to the atmosphere.

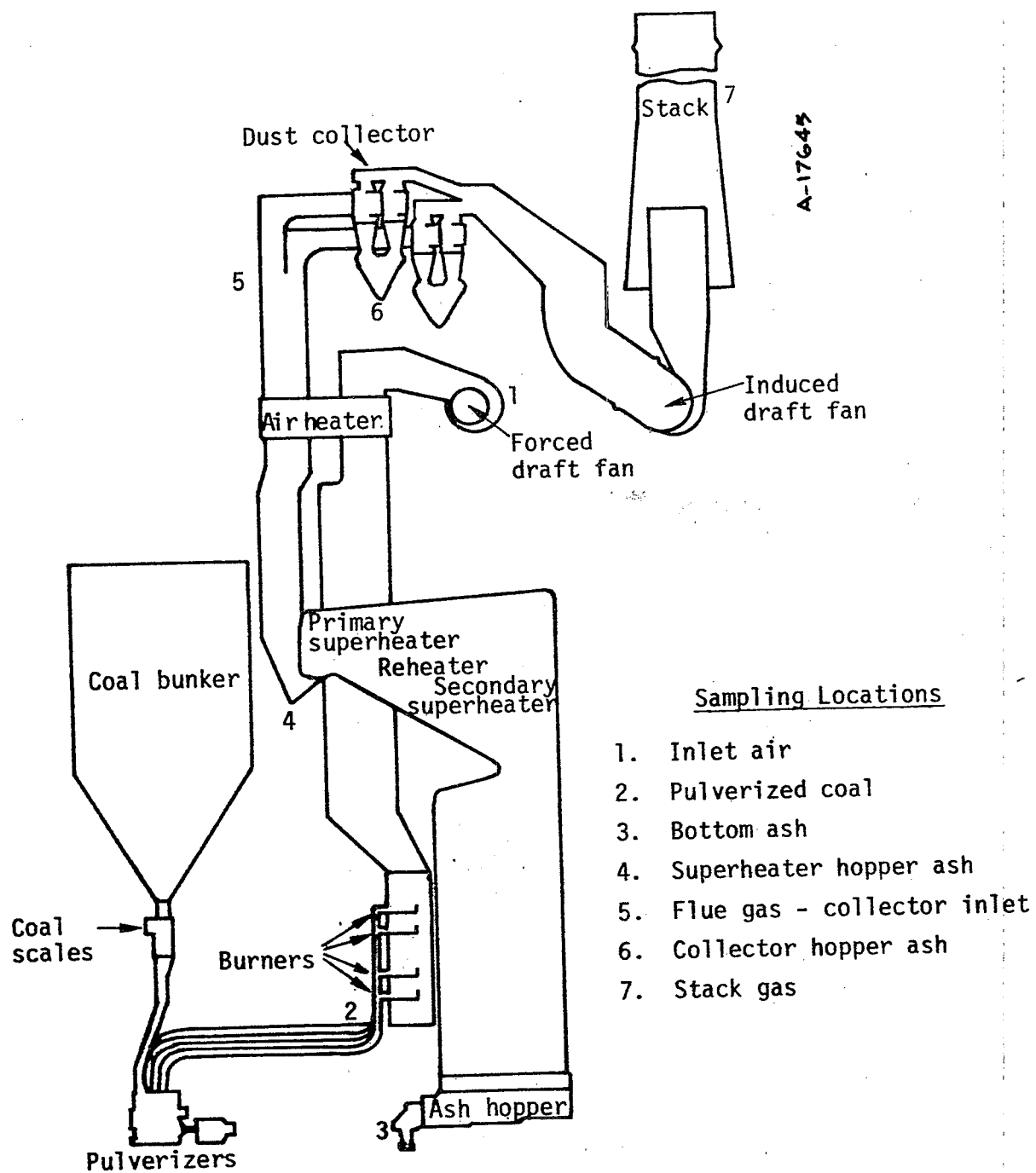


Figure 1. Sulfur input and output streams (Reference 8).

The sulfur emissions data reported in this study are uncontrolled levels which were measured in the ducts leaving the boiler, ahead of any particulate collection devices. A separate analysis of the potential effect of particulate collection devices on SO₂ emissions was also made and is presented in Section 4.

SECTION 3

EFFECT OF BOILER DESIGN AND PROCESS VARIABLES ON SULFUR EMISSIONS

Very little research has been conducted on the effect of boiler design and process variables on SO_2 emissions. While other pollutants, such as nitrogen oxides, have been known to be affected by boiler design and process variables, it has generally been accepted that SO_2 emissions are almost entirely dependent on the sulfur content of the coal.

The following subsections will show that nearly complete ("quantitative") conversion of coal sulfur to SO_2 emissions occurs with most eastern bituminous coals. In the case of western subbituminous and lignitic coals, however, the conversion of fuel sulfur to SO_2 is frequently about 80 percent and sometimes as low as 60 percent (Reference 5).

The following boiler design and process variables have been considered in this study:

- Boiler firing type
 - Front wall (FW)
 - Horizontally opposed (HO)
 - Cyclone (CY)
 - Tangential (T)
 - Vertical (V)
- Boiler size
 - (MW-J/hr)
- Coal type
 - Bituminous
 - Subbituminous
 - Lignite
- Percent sulfur in the coal

- Firing rate or percent of maximum continuous rating (MCR)
- Burner stoichiometry (percent excess air)
- Ash characteristics of the coal

These represent a total of seven independent variables. To eliminate the obvious impact that the sulfur content of the coal has on the emissions, the data were normalized on sulfur content and were plotted as percentage conversion of the input sulfur to the boiler.

Table 1 shows all the firing/coal type combinations for which sulfur emission data were obtained. A total of 21 combinations of firing type and coal have been identified. These 21 combinations represent a total of 183 individual test runs.

TABLE 1. SO₂ DATA SETS AVAILABLE BY FIRING TYPE AND COAL

	Front Wall	Horizontally Opposed	Tangential	Cyclone	Vertical	Total
Bituminous	4	2	4		1	11
Subbituminous			5			5
Lignite	1	1	1	2		5
Total	5	3	8	2	1	21

Tables 2(a) and 2(b) list gaseous sulfur emissions from these test runs (Table 2(a) presents the emissions in ng/J whereas Table 2(b) gives them in lb/MBtu). These data are grouped by boiler firing type. These results are discussed below, with a separate subsection devoted to each boiler type and operating vehicle. Appendix A shows the mathematical relationships used to convert emission rates and emission factors to percent sulfur conversions. Appendix B presents a comparison of SO₂ emission factors obtained in this study with emission factors published in U.S. E/A AP-42 (Reference 13). Appendix C lists the instrumentation and sampling techniques used to collect gaseous sulfur oxide data presented in this report. A discussion of possible sources of errors is also presented. Finally, Appendix D presents a list of conversion units.

TABLE 2(a). GASEOUS SULFUR EMISSION DATA

Boiler			Coal		Boiler Variables			Gaseous Emissions				Remarks	Reference
Firing Type	Furnace Type	Size Mw	Type	Source	Sulfur Percent	Load % MCR ^b	Percent Stoch	SO ₂ ng/J	SO ₃ ng/J	SO ₃ /(SO ₂ +SO ₃) Percent	Percent Conversion		
Front wall	Dry bottom Unit "g"	137	Bituminous	Kentucky Kentucky West Virginia West Virginia Mixed	2.3	70	135	1257	1.2	0.10	88	The 229% sulfur conversion to SO ₂ is obviously incorrect. This value and test No. 5 have been deleted from the calculated average - percent sulfur in the coal is given on an ash-free basis. Average coal ash content = 9.0%.	6
					2.6	93	127	1858	27.9	1.5	118		
					1.3	93	134	1738	4.7	0.27	229		
					1.3	70	135	780	5.8	0.74	103		
					1.4-3.3	100	137	2310	4.8	0.21	164		
					3.8	96	115	3844	NA	NA	123		
					3.8	96	117	3721			119		
					2.1	100	111	1941			123		
					2.7	100	113	2744			133		
					1.0	46	121	833			115		
	Dry bottom Widows Creek #5	125	NA	NA	1.0	46	122	956			132	Samples drawn before preheater - only baseline tests listed - low NO _x firing tests not included	7
					2.2	70	115	1175			64		
					1.1	80	116	1556			193		
					1.5	80	114	2237			199		
					4.2	38	163	1010			31		
					4.1	38	170	1091			35		
					0.9	60	128	1158			176		
					1.0	60	150	1112			152		
					4.3	40	157	3100			91		
					3.2	40	185	3611			145		
	Dry bottom Widows Creek #5	125	a	Alabama	2.6	96	143	1285	NA	NA	71.9	SO ₂ emissions are at the outlet of dust collector given in ppm - emissions in ng/J calculated using given fuel carbon and sulfur content and assumed hydrogen and oxygen.	8
					3.85	99	132	2204			79.8		
					3.95	98	136	1829			62.15		
	Wet bottom Mercer #1	270	a		1.20	78	Exc. O ₂ 4.4	759	9	1.17	102	Percent sulfur in the coal is an averaged value from three fuel analyses.	9
					1.20	78	4.4	821	10	1.20	110		
					1.20	100	4.4	736	11	1.47	99		
	Dry bottom Wm. J. Neal	20	Lignite	Velva Mine Consolidation Coal Company	0.57	100	Exc. O ₂ NA	331	NA	-	74	0.9% Na in ash 0.8% Na in ash 0.9% Na in ash	10
					0.70	100	4.0	490	NA	-	89		
					0.66	100	Exc. O ₂ NA	426	NA	-	82		

^aAssumed to be a bituminous coal based on fuel and regional coal properties

^bPercent of maximum continuous rating

TABLE 2(a). Continued

Boiler			Coal			Boiler Variables		Gaseous Emissions				Remarks	Reference
Firing	Furnace	Size in	Type	Source	Sulfur Percent	Load % HR	Percent Stoich	SO ₂ ng/d	SO ₃ ng/d	SO ₂ /(SO ₂ +SO ₃) Percent	Percent Conversion		
Vertical	Dry bottom Unit "A"	162	Bituminous	Pennsylvania	3.0	100	140	1756	95	5.13	106	Percent sulfur given on ash-free basis. Coal contains 19.8% ash. Correction made to calculate percent conversion.	6
					2.9	100	142	1364	23	1.66	78		
					2.9	100	141	1192	123	9.35	74		
					2.9	75	141	1946	80.7	3.98	115		
					2.8	75	149	1501	35.4	2.3	94		
Horizontally Opposed	Wet bottom Unit "D"	220	Bituminous	Illinois	2.3	100	146	1610	16.6	1.02	118	Percent sulfur given on ash-free basis. Coal contains 8% ash. Correction made to calculate percent conversion.	6
					2.8	100	148	1738	15.6	0.90	104		
					3.1	75	142	1864	7.4	0.40	100		
					2.7	75	135	1590	8.3	0.50	98.7		
					2.1	100	124	1233	5.4	0.44	98.4		
Cyclone	E. G. Gaston #2	270	a	NA	1.47	NA	4.2 Exc. O ₂	726	128	14.9	96.5	No information on type of coal burned. From coal analysis it is assumed that a bituminous coal was used.	9
					1.31			552	127	18.7	71.3		
					1.73			883	130	12.8	89.7		
	Dry bottom Leland Olds #8	215	Lignite	Glenharold	0.63	93	NA	400	<1 ppm	-0	78	8.8% Na in the ash 8.0% Na in the ash 7.7% Na in the ash 6.0% Na in the ash 7.0% Na in the ash 6.2% Na in the ash 7.8% Na in the ash 5.1% Na in the ash	10
					0.65	93		443			84		
					0.61	84		438			89		
					0.85	56		610			89		
					0.84	55		550			80		
					0.75	92	4.8 Exc. O ₂	490			79		
	Wet bottom Milton R. Young	235	Lignite	North Dakota	0.74	100		477			81	0.7% Na in the ash 0.8% Na in the ash 0.4% Na in the ash 0.4% Na in the ash 0.7% Na in the ash	10
					1.09	100		619			70		
					0.90	106	NA	735	<1 ppm	-0	100		
					0.93	92		692			91		
					1.11	106		868			86		
	Station #3	250	Lignite	North Dakota	0.97	106		756			82	16.23% CaO in the ash 3.24% Na ₂ O in the ash	11
					1.10	106		722			73		
	Station #3	250	Lignite	North Dakota	1.30	100	NA	965			97		

^aAssumed to be a bituminous coal based on fuel analysis and regional coal properties.

TABLE 2(a). Continued

Boiler			Coal			Boiler Variables		Gaseous Emissions				Remarks	Reference
Firing	Furnace	Size MM	Type	Source	Sulfur Percent	Load % MCR	Percent Stoich	SO ₂ ng/J	SO ₃ ng/J	SO ₃ /(SO ₂ +SO ₃) Percent	Percent Conversion		
Tangential	Twin furnace NavaJo #2	800	Sub- bituminous	Black Mesa	.55	NA	6.1	218	5	2.2	58	Sulfur content of the coal is an average value taken from analyses of five coal samples.	9
							Exc. O ₂	263	6	2.2	68		
							3.0	230			60		
							5.2						
							Exc. O ₂	261			58		
							3.0	210			47		
							Exc. O ₂						
							6.0	259			68		
							Exc. O ₂						
							3.0						
	Single furnace Comanche #1	350	Sub- bituminous	Wyoming	.61	95	3.38	215	15	6.5	52	Samples drawn from upstream of dust collector. Bottom ash accounts for 10-15 percent of total ash. Flyash accounts for 80-85 percent. Exxon assumed that the unaccounted sulfur remains in the ash and on the furnace walls slag.	9
							Exc. O ₂	228	16	6.5	55		
							3.0	235	15	6.0	57		
							Exc. O ₂						
							3.81	246	16	6.1	59		
							Exc. O ₂						
							3.0	225	-	-	51		
							Exc. O ₂	219	9	4.0	52		
							-						
							.61						
	Dry bottom Hoot Lake	50	Beulah Lignite	North Dakota	1.09	80	NA	400	<1 ppm	-0	48	8.2% Na ₂ O in ash 9.0% 1.7% 1.6% 4.8% 5.3% 5.6% 5.8% 5.4% 5.5% 7.8% 3.8% 7.5% 3.8% Na ₂ O in ash — 4.5% SO ₃ in dust collector, 8.7% in ESP	10
							1.03	430			52		
							1.15	757			84		
							82						
							1.10	787			92		
							84	804			97		
							1.36						
							102	714			58		
							84	666			43		
							1.52						
					1.31	84	84	679			68		
							1.25						
							84	800			65		
							1.54						
							84	808			76		
							1.33						
							84	576			59		
							1.32						
							104	589			69		
							1.10						
					0.92	112	112	490			66		
							0.97	554			71		

TABLE 2(a). Continued

T-401a

Boiler			Coal		Boiler Variables			Gaseous Emissions			Remarks	Reference		
Firing	Furnace	Size mm	Type	Source	Sulfur Percent	Load % MCR	Percent Stoich	SO ₂ ng/J	SO ₃ ng/J	SO ₂ /(SO ₂ +SO ₃) Percent			Percent Conversion	
Tangential (Continued)	Dry bottom Hoot Lake	50	Baulah Lignite	North Dakota	1.06	110	NA		546	<1 ppm	-0	64	5.1% Na ₂ O in ash	10
					1.11	100		649			64	1.1%		
					1.21	100		731			75	1.0%		
					1.14	100		778			76	0.9%		
					1.03	100		748			91	0.9%		
					1.14	84		576			61	6.1%		
					1.03	84		546			66	6.1%		
					1.12	84		524			59	6.1%		
					1.52	96		1053	<1 ppm	-0	83	3.1%		
					1.33	106		1101			99	5.8%		
					1.38	108		1277			100	3.0%		
					1.68	110		1247			89	3.5%		
					1.68	108		1311			94	2.1%		
					1.71	110		1221			86	2% Na ₂ O in ash		
Berry #4	350		Bituminous	Alabama	2.41	93	113	1371	NA		81	Samples drawn from air heater inlet duct. Low NO _x tests not included.	12	
					2.41	94	104	1213			72			
					2.41	94	108	1423			84			
					2.41	94	104	1371			81			
					2.63	100	111	1849			106			
					2.63	100	109	2107			121			
					2.63	100	107	2204			126			
					2.63	100	103	2161			124			
					2.63	100	109	2075			119			
					2.63	100	109	1951			112			
					2.63	100	105	2128			122			
					2.63	100	111	2085			119			
					4/5 Bituminous 1/5 Petro coke									

TABLE 2(a). Continued

Firing	Boiler		Coal		Boiler Variables		Gaseous Emissions				Remarks	Reference
	Furnace	Size M	Type	Source	Sulfur Percent	Load % MCR	Percent Stoich	SO ₂ ng/J	SO ₃ ng/J	SO ₃ /(SO ₂ +SO ₃) Percent	Percent Conversion	
Tangential (Continued)	Berry #4	350	4/5 Bituminous 1/5 Petro. coke	Midwestern	3.07	83	115.3	2696	-	-	138	12
	Berry #2	125	Bituminous	Alabama	2.1 2.2 1.8 2.9 3.2 4.2 3.2 3.0 2.3 3.0 3.1 1.4 1.7 2.3 2.3 3.0 2.7 2.3 2.4 3.1 3.0 1.9 2.8 2.9 1.5 3.1 2.5	53 53 53 53 53 53 53 55 53 75 75 100	131 117 151 128 127 113 155 124 109 111 107 125 117 108 121 116 119 115 107 119 112 107 120 116 119 144	1617 1623 1156 1629 2560 2570 1817 1780 1713 1139 1833 1150 1016 1022 826 1414 1493 1323 952 1567 1863 1884 1351 1727 1739 1784 1830 1497	- -	104 100 87 75 100 77 74 81 77 67 83 50 98 82 49 84 67 67 56 87 80 85 94 82 85 158 78 81	Samples drawn from air heater inlet duct. Low NO _x tests not included	12

T-401a

TABLE 2(a). Continued

Boiler			Coal		Boiler Variables			Gaseous Emissions				Remarks	Reference
Firing Type	Furnace	Size PM	Type	Source	Sulfur Percent	Load % ICR	Percent Stoich	SO ₂ ng/J	SO ₃ ng/J	SO ₂ /(SO ₂ +SO ₃) Percent	Percent Conversion		
Tangential (Continued)	Dry bottom Unit "C"	~100	Bituminous	Ohio	1.85	100	128	1445	8.9	0.60	105	Coal is mixed with 1% by weight lime. Lime seems to have no effect on SO ₂ emissions since sulfur conversions are nearly 100 percent.	6
				Ohio	1.85	75	122	1258	15	1.18	92		
				Ohio	1.68	100	131	1143	8	0.70	91.5		
				West Virginia	0.88	100	127	526	9	1.70	89		
				West Virginia	0.97	75	127	677	5.6	0.80	103		
	Station 1 Unit #4	330	Sub-bituminous	Wyoming	0.72	88	NA	378	NA	-	58	13% CaO, 0.15% H ₂ O in the coal ash. Bottom ash is slurried continuously with water from a settling pond.	11
				Wyoming	0.49	96-100	NA	347	NA	-	100		
	Station 2	350	Sub-bituminous	Montana Rosebud Seam	1.0	100	118	799.7	-	-	79	Samples taken in left duct leaving the economizer	14
					0.8	100	119	792.6	-	-	100		
					0.7	90	131	708.4	-	-	99		
					0.8	75	133	770.4	-	-	96		
					0.8	60	127	932.8	-	-	116		
Tangential	Columbia #1	550	Sub-bituminous "C"		0.9	60	136	985	-	-	108		
					0.6	60	141	864	-	-	147		
					0.7	100	116	818	-	-	115		
					1.0	100	121	860	-	-	86		
					0.8	90	127	809	-	-	100		
					0.7	60	117	926.4	-	-	135		
					0.7	60	145	791.8	-	-	115		
					0.8	100	114	839.8	-	-	103		
					0.7	100	120	747	-	-	107		
					0.8	90	129	891.1	-	-	110		
					0.7	75	132	718.5	-	-	97		
					0.6	60	123	875.4	-	-	146		
					0.6	60	134	1074.4	-	-	180		
					0.6	60	145	800.0	-	-	134		

TABLE 2(a). Continued

Firing Type	Boiler		Coal		Boiler Variables			Gaseous Emissions			Remarks	Reference
	Furnace	Size MW	Type	Source	Sulfur Percent	Load % MCR	Percent Stoch	SO ₂ ng/J	SO ₃ ng/J	SO ₃ /(SO ₂ +SO ₃) Percent	Percent Conversion	
Tangential	Huntington Canyon #2	425	Bituminous high volatile "B"	Deer Creek Mine	0.7	100	125	266.3	-	-	53	Samples taken in left duct leaving economizer. During some of the testing the Deer Creek Mine coal was mixed with coal from Peabody Coal Company's Wilberg and from American Coal Company's Church mines. All three coals have very similar properties.
					0.5	100	130	273.2	-	-	78	
					0.5	100	138	259.1	-	-	67	
					0.5	85	127	300.1	-	-	83	
					0.5	61	123	256.2	-	-	73	
					0.5	61	131	250.5	-	-	72	
					0.5	61	150	222.8	-	-	63	
					0.5	100	117	252.5	-	-	70	
					0.5	100	126	163.4	-	-	44	
					0.4	100	138	187.3	-	-	64	
					0.5	60	126	160.9	-	-	45	
					0.5	60	148	228.0	-	-	65	
					0.5	100	113	177.7	-	-	48	
					0.5	100	118	255.2	-	-	70	
					0.8	100	133	245.2	-	-	41	
					0.5	85	121	281.1	-	-	80	
					0.5	60	124	306.1	-	-	86	
					0.5	60	128	309.0	-	-	88	
					0.5	60	147	328.2	-	-	94	

1-401a

TABLE 2(b). Continued

Firing Type	Boiler		Coal		Boiler Variables			Gaseous Emissions			Remarks	Reference
	Furnace Type	Size ft ²	Type	Source	Sulfur Percent	Load % HCR ^b	Percent Stotch	SO ₂ lb/Hrtu	SO ₂ /(SO ₂ +SO ₃) Percent	% Percent Conversion		
Front wall	Dry bottom Unit "B"	137	Bituminous	Kentucky	2.3	70	135	2.92	0.003	88	The 229% sulfur conversion to SO ₂ is obviously incorrect. This value and Test No. 5 have been deleted from the calculated average - percent sulfur in the coal is given on an ash-free basis. Average coal ash content = 9.0%.	6
				West Virginia	2.6	93	127	4.32	0.065	118		
				West Virginia	1.3	93	134	4.04	0.011	229	Samples drawn before preheater - only base line tests listed - low NO _x firing tests not included.	7
				Mixed	1.3	70	135	1.81	0.013	103		
					1.4-3.3	100	137	5.37	0.011	164		
	Dry bottom Widows Creek #5	125	NA	NA	3.8	96	115	8.94	NA	123		
					3.8	96	117	8.65		119		
					2.1	100	111	4.51		123		
					2.7	100	113	6.38		133		
					1.0	46	121	1.94		115		
					1.0	46	122	2.22		132		
					2.2	70	115	2.73		64		
					1.1	80	116	3.62		193		
					1.5	80	114	5.20		199		
					4.2	38	163	2.35		31		
					4.1	38	170	2.54		35		
					0.9	60	128	2.69		176		
					1.0	60	150	2.59		152		
					4.3	40	157	7.21		91		
					3.2	40	185	8.40		145		
	Dry bottom Widows Creek #5	125	a	Alabama	2.6	96	143	2.99	NA	71.9	SO ₂ emissions are at the outlet of dust collector given in ppm - emissions in ng/l calculated using given fuel carbon and sulfur content and assumed hydrogen and oxygen.	8
					3.95	99	132	5.13		79.8		
					3.95	98	136	4.25		62.15		
	Net bottom Mercer #1	270	a		1.20	78	Exc. O ₂ 4.4	1.77	0.021	102	Percent sulfur in the coal is an averaged value from three fuel analyses.	9
					1.20	78	4.4	1.91	0.023	110		
					1.20	100	4.4	1.71	0.025	99		
					1.20	100	4.4	1.85	0.028	107		
	Dry bottom Wm. J. Neal	20	Lignite	Velva Mine Consolidation Coal Company	0.57	100	NA	0.77	NA	74	0.9% Na in ash 0.8% Na in ash 0.9% Na in ash	10
					0.70	100	4.0	1.14		89		
					0.66	100	Exc. O ₂ NA	0.99		82		

^aAssumed to be a bituminous coal based on fuel and regional coal properties
^bPercent of maximum continuous rating

TABLE 2(b). Continued

Boiler			Coal		Boiler Variables		Gaseous Emissions				Remarks	Reference
Firing	Furnace	Size MW	Type	Source	Sulfur Percent	Load % MCR	Percent Stoich	SO ₂ lb/Mbtu	SO ₃ lb/Mbtu	SO ₃ /(SO ₂ +SO ₃) Percent	Percent Conversion	
Vertical	Dry bottom Unit "A"	162	Bituminous	Pennsylvania	3.0	100	140	4.08	0.221	5.13	106	Percent sulfur given on ash-free basis. Coal contains 19.8% ash. Correction made to calculate percent conversion.
					2.9	100	142	3.17	0.053	1.66	78	
					2.9	100	141	2.77	0.286	9.35	74	
					2.9	75	141	4.53	0.187	3.98	115	
					2.8	75	149	3.49	0.082	2.3	94	
Horizontally Opposed	Wet bottom Unit "D"	~20	Bituminous	Illinois	2.3	100	146	3.74	0.036	1.02	118	Percent sulfur given on ash-free basis. Coal contains 8% ash. Correction made to calculate percent conversion.
					2.8	100	148	4.04	0.035	0.90	104	
					3.1	75	142	4.33	0.017	0.40	100	
					2.7	75	135	3.69	0.019	0.50	98.7	
					2.1	100	124	2.87	0.012	0.44	98.4	
Cyclone	E. G. Gaston #2	270	a	MA	1.47	NA	4.2 Exc. O ₂	1.69	0.297	14.9	96.5	No information on type of coal burned. From coal analysis it is assumed that a bituminous coal was used.
					1.31			1.28	0.295	18.7	71.3	
					1.73			2.05	0.302	12.8	89.7	
					0.63	93	NA	0.93	<1 ppm	-0	78	
					0.65	93		1.03			84	
	Dry bottom Leland Olds #8	215	Lignite	Glenharold	0.61	84		1.02			89	8.8% Na in the ash 8.0% Na in the ash 7.7% Na in the ash 6.0% Na in the ash 7.0% Na in the ash 6.2% Na in the ash 7.8% Na in the ash 5.1% Na in the ash 0.7% Na in the ash 0.8% Na in the ash 0.4% Na in the ash 0.4% Na in the ash 0.7% Na in the ash
					0.85	56		1.42			89	
					0.84	55		1.28			80	
					0.75	92	4.8 Exc. O ₂	1.14			79	
					0.74	100		1.11			81	
Cyclone	Wet bottom Milton R. Young	235	Lignite	North Dakota	1.09	100		1.44			70	16.23% C ₂ O in the ash 3.24% H ₂ O in the ash
					0.90	106	NA	1.71	<1 ppm	-0	100	
					0.93	92		1.61			91	
					1.11	106		2.02			86	
					0.97	106		1.76			82	
Cyclone	Station #3	250	Lignite	North Dakota	1.10	106		1.68			73	
					1.30	100	NA	2.24			97	

^a Assumed to be a bituminous coal based on fuel analysis and regional coal properties.

TABLE 2(b). Continued

295-1

Boiler			Coal		Boiler Variables		Gaseous Emissions				Reference	
Firing	Furnace	Size mm	Type	Source	Sulfur Percent	Load % MCR	Percent Stoich	SO ₂ lb/Hbtu	SO ₃ lb/Hbtu	SO ₂ /(SO ₂ +SO ₃) Percent		Percent Conversion
Tangential	Twin furnace Navajo #2	800	Sub- bituminous	Black Mesa	.55	NA	6.1 Exc. O ₂	0.507	0.011	2.2	58	Sulfur content of the coal is an average value taken from analyses of five coal samples.
							3.0 Exc. O ₂	0.611	0.014	2.2	68	
							5.2 Exc. O ₂	0.535			60	
							3.0 Exc. O ₂	0.607			58	
							6.0 Exc. O ₂	0.488			47	
							3.0 Exc. O ₂	0.602			68	
							3.38 Exc. O ₂	0.500	0.035	6.5	52	
	Single furnace Comanche #1	350	Sub- bituminous	Wyoming	.61	95	3.0 Exc. O ₂	0.530	0.037	6.5	55	Samples drawn from upstream of dust collector. Bottom ash accounts for 10-15 percent of total ash. Flyash accounts for 80-85 percent. Excess assumed that the unaccounted sulfur remains in the ash and on the furnace walls slag.
							3.81 Exc. O ₂	0.546	0.035	6.0	57	
							3.0 Exc. O ₂	0.572	0.037	6.1	59	
							3.0 Exc. O ₂	0.523	-	-	51	
							3.0 Exc. O ₂	0.509	0.021	4.0	52	
							NA	0.93	<1 ppm	-0	48	
							80	1.00			52	
Dry bottom Hoot Lake	50	Baulah Lignite	North Dakota	1.03	80	82	1.15	1.76			84	8.2% Na ₂ O in ash 3.8% Na ₂ O in ash - 4.5% SO ₃ in dust collector, 8.7% in ESP
						84	1.10	1.83			92	
						102	1.36	1.87			97	
						84	1.52	1.66			58	
						84	1.31	1.55			43	
						84	1.25	1.58			68	
						84	1.54	1.86			65	
						84	1.33	1.88			76	
						104	1.32	1.34			59	
						104	1.10	1.37			69	
						112	0.92	1.14			66	
0.97	1.29			71								

TABLE 2(b). Continued

Boiler			Coal		Boiler Variables			Gaseous Emissions			Remarks	Reference
Firing	Furnace	Size in	Type	Source	Sulfur Percent	Load % MCR	Percent Stoich	SO ₂ lb/Mbtu	SO ₃ lb/Mbtu	SO ₂ /(SO ₂ +SO ₃) Percent	Percent Conversion	
Tangential (Continued)	Dry bottom Hoot Lake	50	Beulah Lignite	North Dakota	1.06	110	NA	1.27	<1 ppm	-0	64	5.1% Na ₂ O in ash
					1.11	100		1.51			64	1.1%
					1.21	100		1.70			75	1.0%
					1.14	100		1.81			76	0.9%
					1.03	100		1.74			91	0.9%
					1.14	84		1.34			61	6.1%
					1.03	84		1.27			66	6.1%
					1.12	84		1.22			59	6.1%
					1.52	96		2.45	<1 ppm	-0	83	3.1%
					1.33	106		2.56			99	5.8%
					1.38	108		2.97			100	3.0%
					1.68	110		2.90			89	3.5%
					1.68	108		3.05			94	2.1%
					1.71	110		2.84			86	2% Na ₂ O in ash
Berry #4	350	Bituminous 1/5 Petro coke	Bituminous	Alabama	2.41	93	113	3.19	NA		81	Samples drawn from air heater inlet duct. Low NO _x tests not included.
					2.41	94	104	2.82			72	
					2.41	94	108	3.31			84	
					2.41	94	104	3.19			81	
					2.63	100	111	4.30	NA		106	
					2.63	100	109	4.90			121	
					2.63	100	107	5.13			126	
					2.63	100	103	5.03			124	
					2.63	100	109	4.83			119	
					2.63	100	109	4.54			112	
					2.63	100	105	4.95			122	
					2.63	100	111	4.85			119	

TABLE 2(b). Continued

Firing	Boiler		Coal		Boiler Variables		Gaseous Emissions				Remarks	Reference
	Furnace	Size in	Type	Source	Sulfur Percent	Load % MCR	Percent Stoich	SO ₂ lb/Hr	SO ₃ lb/Hr	SO ₂ /(SO ₂ +SO ₃) Percent	Percent Conversion	
Tangential (Continued)	Berry #4	350	4/5 Bituminous 1/5 Petro. coke	Midwestern	3.07	83	115.3	6.27	NA	-	138	12
	Berry #2	125	Bituminous	Alabama	2.1 2.2 1.8 2.9 3.2 4.2 3.2 3.0 3.0 2.3 3.0 1.4 1.7 2.3 2.3 3.0 2.7 2.3 2.4 3.1 3.0 1.9 2.8 2.9 1.5 3.1 2.5	53 53 53 53 53 53 53 55 53 75 100	131 117 151 128 127 113 155 124 154 109 111 118 107 125 117 108 121 116 119 115 107 119 112 107 120 116 119 144	3.76 3.77 2.69 3.79 5.95 5.98 4.23 4.14 3.98 2.65 4.26 2.67 2.36 2.38 1.92 3.29 3.47 3.08 2.21 3.64 4.33 4.39 3.14 4.02 4.04 4.15 4.26 3.48	- -	104 100 87 75 100 77 74 81 77 67 83 50 98 82 49 84 67 67 56 87 80 85 94 82 85 158 78 81	Samples drawn from air heater inlet duct. Low NO _x tests not included	12

TABLE 2(b). Continued

Boiler			Coal		Boiler Variables		Gaseous Emissions				Remarks	Reference
Firing Type	Furnace	Size MW	Type	Source	Sulfur Percent	Load % MCR	Percent Stoich	SO ₂ lb/MBtu	SO ₃ lb/MBtu	SO ₃ /(SO ₂ +SO ₃) Percent	Percent Conversion	
Tangential (Continued)	Dry bottom Unit "C"	≈100	Bituminous	Ohio	1.85	100	128	3.36	0.021	0.60	105	Coal is mixed with 1% by weight lime. Lime seems to have had no effect on SO ₂ emissions since sulfur conversions are nearly 100 percent.
				Ohio	1.85	75	122	2.93	0.035	1.18	92	
				Ohio	1.68	100	131	2.66	0.018	0.70	91.5	
				West Virginia	0.88	100	127	1.22	0.021	1.70	89	
				West Virginia	0.97	75	127	1.57	0.013	0.80	103	
Tangential	Station 1 Unit #4	330	Sub-bituminous	Wyoming	0.72	88	NA	0.88	-	-	58	13% CaO. 0.15% Na ₂ O in the coal ash. Bottom ash is slurried continuously with water from a settling pond.
	Station 2	350	Sub-bituminous	Wyoming	0.49	96-100	NA	0.81	-	-	100	
	Columbia #1	550	Sub-bituminous "rc"	Montana Rosebud Seam	1.0	100	118	1.86	-	-	79	
					0.8	100	119	1.84	-	-	100	
					0.7	90	131	1.65	-	-	99	
					0.8	75	133	1.79	-	-	96	
					0.8	60	127	2.17	-	-	116	
					0.9	60	136	2.29	-	-	108	
					0.6	60	141	2.01	-	-	147	
					0.7	100	116	1.90	-	-	115	
					1.0	100	121	2.00	-	-	86	
					0.8	90	127	1.88	-	-	100	
					0.7	60	117	2.15	-	-	135	
					0.7	60	145	1.84	-	-	115	
					0.8	100	114	1.95	-	-	103	
					0.7	100	120	1.74	-	-	107	
					0.8	90	129	2.07	-	-	110	
					0.7	75	132	1.67	-	-	97	
					0.6	60	123	2.04	-	-	146	
					0.6	60	134	2.50	-	-	180	
					0.6	60	145	1.86	-	-	134	

TABLE 2(b). Concluded

Boiler			Coal		Boiler Variables		Gaseous Emissions			Remarks	Reference		
Firing Type	Furnace	Size #4	Type	Source	Sulfur Percent	Load % MCR	Percent Storch	SO ₂ lb/H ₂ TU	SO ₂ lb/H ₂ TU			SO ₂ /(SO ₂ +SO ₃) Percent	Percent Conversion
Tangential	Huntington Canyon #2	425	Bituminous high volatile "B"	Peabody Coal Co. Deer Creek Mine	0.7	100	125	0.62	-	-	53	Samples taken in left duct leaving economizer. During some of the testing the Deer Creek Mine coal was mixed with coal from Peabody Coal Company's Wilberg and from American Coal Company's Church mines. All three coals have very similar properties.	14
					0.5	100	130	0.64	-	-	78		
					0.5	100	138	0.60	-	-	67		
					0.5	85	127	0.70	-	-	83		
					0.5	61	123	0.60	-	-	73		
					0.5	61	131	0.58	-	-	72		
					0.5	61	150	0.52	-	-	63		
					0.5	100	117	0.59	-	-	70		
					0.5	100	126	0.38	-	-	44		
					0.4	100	138	0.44	-	-	64		
					0.5	60	126	0.37	-	-	45		
					0.5	60	148	0.53	-	-	65		
					0.5	100	113	0.41	-	-	48		
					0.5	100	118	0.59	-	-	70		
0.8	100	133	0.57	-	-	41							
0.5	85	121	0.65	-	-	80							
0.5	60	124	0.71	-	-	86							
0.5	60	128	0.72	-	-	88							
0.5	60	147	0.76	-	-	94							

3.1 BOILER FIRING TYPE

Figure 2 shows the average percent conversion of coal sulfur to SO_2 . Each point on the graph represents the SO_2 emission averaged from all test runs performed on each boiler. Vertical dotted lines separate the emissions data by the five boiler firing types investigated.

The data scatter is quite large indicating essentially no correlation between boiler firing type and percent SO_2 conversion. Sulfur conversion to SO_2 from tangential-fired boilers ranged from 54 to 114 percent, cyclone fired from 86 to 97 percent, horizontally opposed from 81 to 86 percent, and from wall-fired from 72 to 122 percent. The conversion of the sulfur in the coal, burned in the only vertical fired boiler, was 93 percent.*

Figure 3 presents the ratio of gaseous SO_3 to total gaseous SO_x (SO_2 and SO_3) emissions in percentage. Again, the data are averages of several test runs in each boiler. This ratio would give an indication of the conversion to SO_2 if most of the sulfur in the coal was emitted in either SO_2 or SO_3 . Then Figure 3 would show a high percentage of SO_3 in the flue gas where the SO_2 conversion was reduced. Several of the limited number of data points on Figures 2 and 3 do not confirm this hypothesis because the sum of SO_2 and SO_3 emission represents substantially less than 100-percent conversion (e.g., the lignite-fired boilers emitted virtually no SO_3 , for the SO_3 to SO_x ($\text{SO}_2 + \text{SO}_3$) ratios are about 0.01 percent, but yet these same boilers converted only 70 to 86 percent of the input sulfur to SO_2). Unfortunately the data are insufficient and too scattered to identify any trends.

The available data, although limited, strongly suggest that the firing type of a boiler has little effect on the conversion of coal sulfur to SO_2 and SO_3 . A closer look at Figure 2 indicates that the coal type may have an effect on sulfur conversion to SO_2 . For example, the highest conversions occur with bituminous coal, the lowest with subbituminous, and nearly all the lignite results are at intermediate values. These variations, which are discussed in more detail in the next subsection, may obscure any effect of boiler firing type.

*Measurement uncertainties are probably the cause of data showing conversions greater than 100 percent.

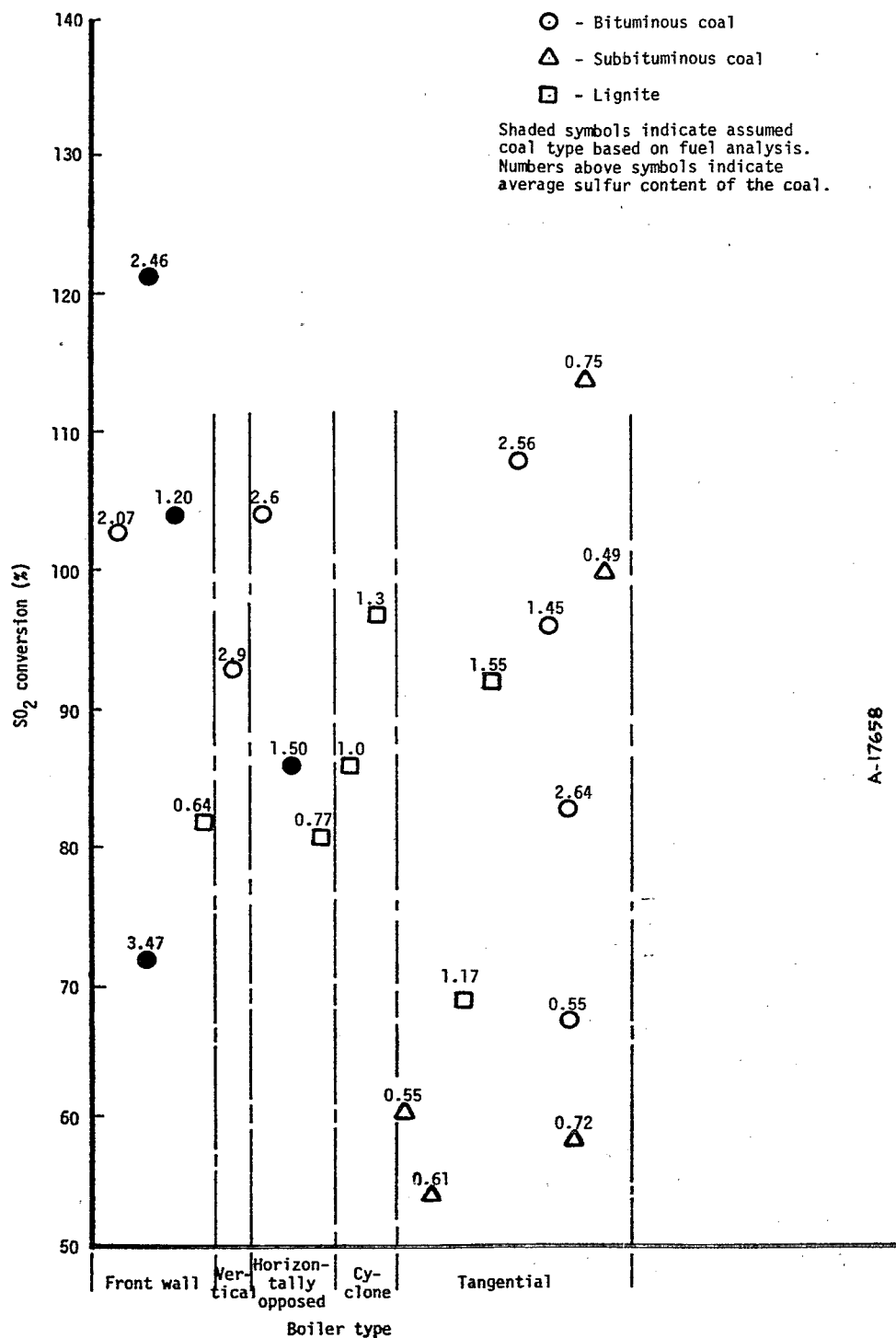


Figure 2. Average SO₂ conversion versus boiler firing type.

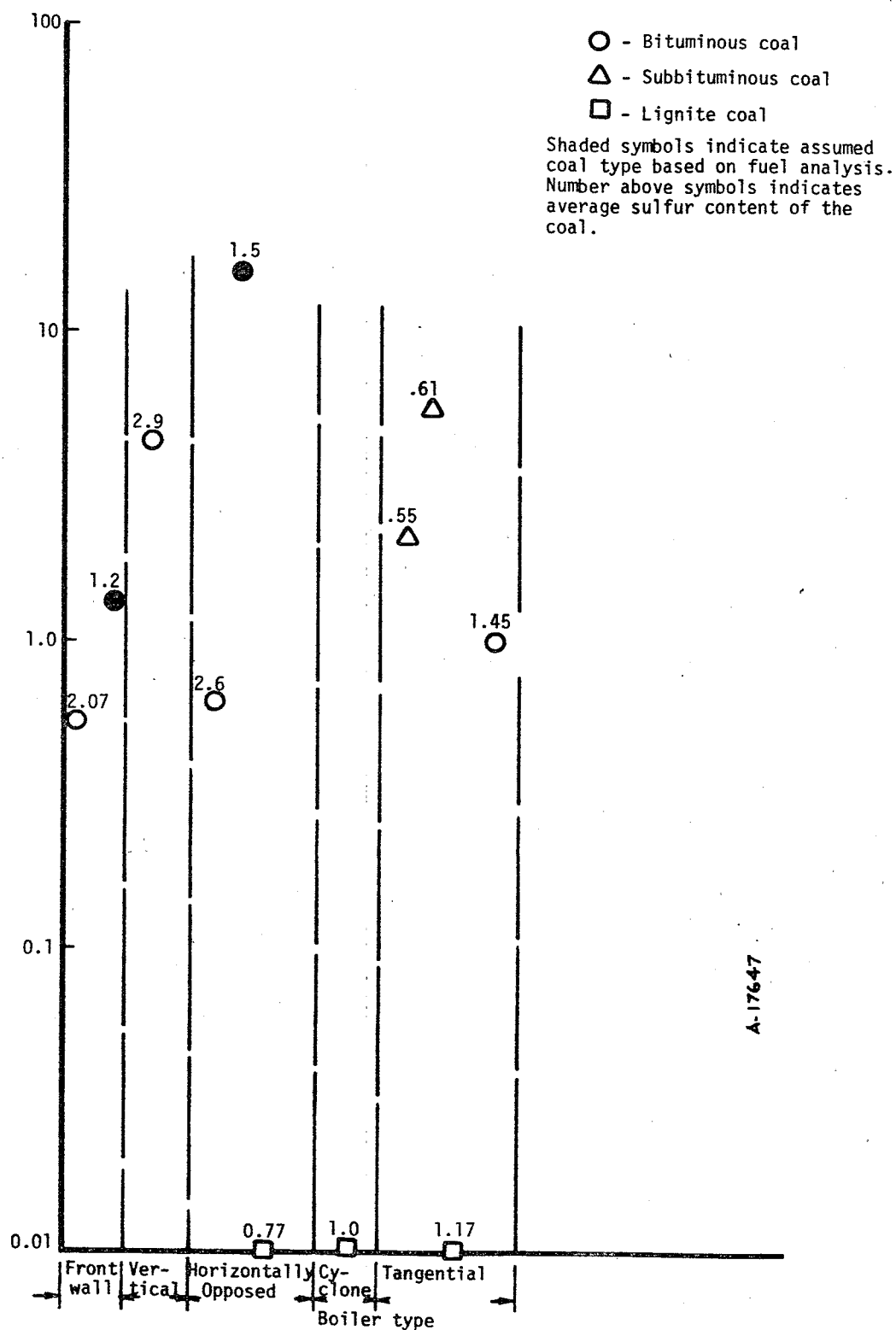


Figure 3. Ratio of SO_3 gaseous emissions to SO_2 and SO_3 emissions.

3.2 COAL TYPE

The type of coals used for the tests listed in Table 2 were bituminous, subbituminous and lignitic. Four coals were not specified by type but were assumed to be all bituminous, based on their chemical analyses. The heating value, ash content, and ash chemical compositions of these coals differ significantly from one another. Eastern bituminous coals are generally high in sulfur content and heating value and lower in fuel moisture content. Western subbituminous coals and lignitic coals are low in sulfur content and heating value while their moisture content is much higher than in bituminous coals. Ash content in eastern bituminous coals is higher than in western subbituminous coals. However, ash content per Btu is higher for subbituminous coals than for bituminous coals. The potential impact of these variables on sulfur conversion to SO_2 is discussed in this subsection.

3.2.1 SO_2 and SO_3 Gaseous Emissions

As noted above, in the discussion of Figure 2, the type of coal burned has a definite effect on SO_2 emissions. If the 67- and 72-percent SO_2 conversion for the bituminous tangentially-fired and front wall-fired boilers are disregarded (bituminous coal was assumed for the data from the latter boiler based on the fuel analysis), the sulfur conversion for bituminous coal ranged from 86 to 108 percent. That is to say, practically all the sulfur in the coal gets converted to SO_2 . Subbituminous coal was burned only on tangentially-fired boilers. The conversion varied from 54 to 114 percent. It is believed that ash properties differed substantially among these coals, causing the conversions to vary over this wide range. An explanation of the effect of coal ash properties on sulfur emissions is presented in the following section. SO_2 conversion for lignitic coals ranged from 69 to 97 percent.

Conversion of sulfur to SO_3 also varied with coal type. Western subbituminous and lignitic coals are known to convert SO_2 to SO_3 in significant quantities due to catalytic oxidation of SO_2 to SO_3 by some oxides. But the free SO_3 radical quickly reacts with alkaline metals present in the ashes of these coals to form sulfates which remain in the boiler bottom or flyashes. It appears that for lignite the catalytic transformation of SO_2 to SO_3 is more than offset by the reaction of the SO_3 radical with alkaline metals

resulting in the very low conversions of coal sulfur to SO_3 . For subbituminous coals the sulfate production does not completely eliminate the gaseous SO_3 in the flue gas. Sulfur conversion to SO_3 in subbituminous coal-fired boilers was approximately the same as in bituminous coal-fired boilers.

3.2.2 Sulfate Emissions

The concentration of sulfur in the particulate emissions can be a very important factor in determining how much sulfur is converted to SO_2 . With coals that could almost be burned without an SO_2 control device and still meet the NSPS, this conversion becomes important; it can mean the difference between having to install a scrubber or not (under the current NSPS).

Sulfur retention in bottom ash and flyash can account for a considerable percentage of the sulfur input depending on the coal type and the ash properties of the coal. For example, western subbituminous and lignitic coals can retain a larger amount of sulfur in the boiler ash in the form of sulfates than can eastern bituminous coals. The sulfates will be partly retained in the bottom ash, partly in the flyash, and the rest in the slag on the water walls. The percentages of sulfur in each of these exit streams depend mostly on the ash properties of the coal (i.e., the alkaline characteristics of the coal) and partly on the burner type and burner configuration of the boilers (i.e., cyclone versus front wall) (Reference 5).

Sulfates are formed by the reaction of alkaline metals in the ash (such as Na and Ca) with the free SO_3 radical. The free SO_3 radical can be formed by the catalytic oxidation of SO_2 by iron, silicon, and aluminum oxides in pulverized coal boilers (Reference 3). Figure 4 shows the sulfur content of the ash (as SO_3) in percent by weight necessary for a 9-percent ash coal to meet the federal standards of 516 ng/J (1.2 lb/MBtu). It is assumed that 2 percent by mole SO_3 appears in the flue gas. The graph shows that a coal with a heating value of 27,912 J/g (12,000 Btu/lb typical of eastern bituminous coals) and a sulfur content of 1.3 percent would need a 17.0-percent sulfur retention in the ash in order to meet the federal regulations without a control device. The heavy horizontal lines indicate the maximum sulfur retention in the ash for both nonwestern and western coals.

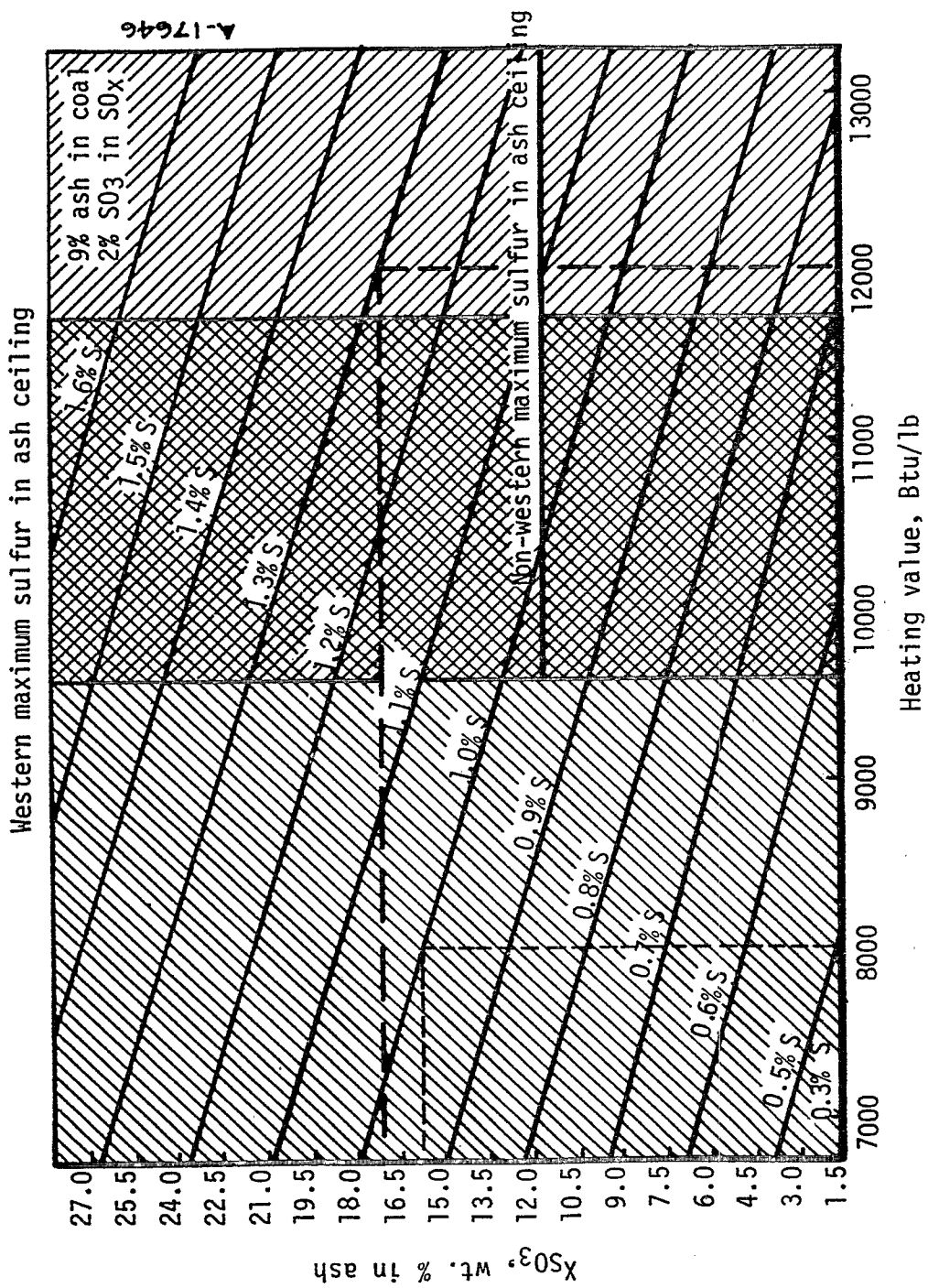


Figure 4. Minimum sulfur retention required to ash to meet SO_x standard of 1.2 lb SO_x/10⁶ Btu (516 ng/J) (Reference 15).

These data are based on average ranges of SO_3 in the ash for a large number of U.S. coals.* Table 3 lists these ranges, which are obtained from coal analyses listed in Table 4. From Table 3 it can be seen that the maximum SO_3 content in the ash for eastern coals is approximately 10 percent. Therefore, in the case of the 27,912 J/g (12,000 Btu/lb) eastern coal, the required 17.0-percent sulfur retention will probably not be obtained. These data do not reflect exact sulfur retention in the ash of pulverized coal-fired boilers, but they give an indication of the ability of a coal to meet the federal emission levels without SO_2 controls. Similar graphs can be obtained for coals with ash contents other than 9 percent by using the following expression (Reference 15).

$$X_{\text{SO}_3} = \frac{250}{X_{\text{ash}}} \left(X_s - \frac{0.6 \text{ Btu} \times 10^{-4}}{1 - Y_{\text{SO}_3}} \right)$$

X_{SO_3} = sulfur content of ash (as SO_3) in percent/weight

X_{ash} = ash content of the coal

Btu = the heating value of the coal in Btu/lb

X_s = sulfur content of coal in percent/weight

Y_{SO_3} = the mole fraction of SO_3 to SO_2 in the flue gas

Tables 5(a) and 5(b) list all flyash and bottom ash sulfur emission data obtained during the study. (Table 5(a) presents the data in SI units whereas Table 5(b) gives the same data in engineering units). Flyash sulfur contents (as SO_3) ranged between 0.033 to 60 ng/J (0 to 0.1395 lb/MBtu). These emissions represent a conversion of coal sulfur to sulfates in the flyash of 0+ to 4.4 percent. The lowest flyash sulfur content was measured on the cyclone-fired unit, while the highest flyash sulfate concentrations were measured on the two tangential boilers firing a bituminous and sub-bituminous coal. The bituminous coal-fired boiler retained this high quantity of SO_3 in the flyash probably because of the lime additive to the coal. Subbituminous coals characteristically retain SO_3 in the ash due to their high alkaline metal content in the coal ash.

* Values of SO_3 in the ash can be determined by the method ASTM D1757-62.

TABLE 3. SULFUR RANGE IN COAL ASH (Reported as SO_3 from Table 4) (Reference 15)

Region	Average Range % SO_3 in Ash	Average Range ^a % S in Ash	Minimum ^a % SO_3	Maximum ^a % SO_3
Western states	3.6 - 20.6	1.4 - 8.2	0.2	27.4
Interior province	1.1 - 3.1	0.4 - 1.2	0.2	10.3
Eastern province	1.6 - 2.1	0.6 - 0.8	0.2	9.6

^a% S = 0.4 x % SO_3

TABLE 4. TYPICAL ASH COMPOSITION (WT. -%)^{a,b} (Reference 15)

State		% of Moisture Free Coal Ash	% of Moisture Free Coal Sulfur	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	CaO	MgO	Na ₂ O	K ₂ O	SO ₃
NORTHERN GREAT PLAINS PROVINCE													
Colorado	Min.	3.0	0.4	34.8	15.2	3.2	1.0	0.01	0.4	0.4	0.1	0.1	0.2
	Ave.	10.0	0.7	59.4	26.8	6.1	1.3	0.5	6.2	1.1	0.7	0.3	5.2
	Max.	19.7	1.1	71.8	34.2	11.9	1.7	2.8	12.8	2.9	3.0	0.8	15.1
Montana	Min.	4.2	0.4	21.9	13.8	2.9	0.6	0.02	1.8	1.4	0.1	0.3	2.4
	Ave.	12.6	0.6	35.4	21.5	5.3	0.8	0.4	13.4	4.6	2.8	0.7	13.3
	Max.	19.3	0.9	53.6	31.9	8.0	1.2	0.76	31.4	10.4	8.1	1.8	26.2
New Mexico	Min.	2.9	0.6	28.9	14.3	3.6	0.9	0.02	1.7	0.8	0.1	0.1	0.5
	Ave.	10.5	1.3	49.2	21.8	13.8	1.1	0.06	6.4	2.0	0.7	0.6	4.7
	Max.	16.3	3.2	61.9	30.0	27.3	1.3	0.12	14.0	4.2	2.2	1.1	17.3
North Dakota	Min.	7.5	0.5	15.0	8.0	4.1	0.6	0.04	14.5	3.3	0.5	0.1	16.6
	Ave.	11.8	1.0	26.3	12.1	6.9	0.7	0.2	21.1	6.4	4.4	0.3	20.6
	Max.	16.9	1.5	40.4	16.8	10.1	0.9	0.42	36.0	10.8	8.2	0.6	27.4
Utah	Min.	5.7	0.4	39.4	9.1	3.7	0.6	0.03	3.5	0.3	0.4	0.1	1.8
	Ave.	7.7	0.8	51.4	15.1	7.4	1.0	0.6	11.8	3.3	1.7	0.6	6.0
	Max.	9.6	2.2	63.2	20.3	19.3	1.3	1.4	21.9	7.6	4.3	1.4	8.6
Wyoming	Min.	6.4	0.6	24.5	14.2	9.0	0.9	0.21	9.4	4.4	0.1	0.5	14.4
	Ave.	10.4	1.2	31.5	16.9	9.6	1.3	0.36	20.1	4.5	0.1	0.5	15.2
	Max.	14.4	1.8	38.6	19.6	10.3	1.8	0.51	30.8	4.7	0.2	0.6	16.1
COAST PROVINCE													
Washington	Min.	6.1	0.4	37.2	29.7	2.8	1.2	0.18	1.7	0.9	0.2	0.6	1.0
	Ave.	10.6	0.5	45.9	33.5	5.6	2.3	1.7	3.1	1.5	0.7	1.1	3.6
	Max.	22.4	0.5	54.1	38.2	9.2	4.7	2.6	7.6	2.6	1.5	1.7	10.5
INTERIOR PROVINCE													
Arkansas	Min.	4.0	2.5	24.4	12.1	20.3	0.6	0.82	7.4	4.4	0.8	1.2	10.0
	Ave.	8.3	2.5	24.8	19.7	23.4	0.9	1.1	13.1	4.9	1.5		
	Max.	12.5	2.5	25.2	27.4	26.5	1.3	1.3	18.8	5.4	2.1	1.3	10.3
Illinois	Min.	7.7	2.4	36.0	15.4	16.3	0.6	0.03	1.7	0.4	0.1	1.7	0.8
	Ave.	10.0	3.3	45.5	19.1	23.3	0.9	0.16	5.2	0.9	0.4	2.0	1.7
	Max.	17.1	4.8	54.5	23.2	35.4	1.5	0.44	10.4	1.3	0.6	2.6	2.8
Indiana	Min.	6.1	0.7	30.7	16.1	7.0	0.8	0.02	1.7	0.5	0.2	1.3	0.2
	Ave.	9.3	2.9	46.9	22.8	20.7	1.1	0.14	3.4	0.9	0.5	2.4	1.1
	Max.	14.0	4.5	55.2	31.6	40.7	1.3	0.59	8.4	1.5	1.1	3.3	3.1
Iowa	Min.	10.8	5.0	29.0	12.1	32.5	0.8	0.02	4.3	0.9	0.2	1.2	2.4
	Ave.	13.4		34.3	13.9	33.4			9.7	1.3	0.5		3.1
	Max.	16.0	5.3	39.6	15.8	34.3	0.9	0.56	15.0	1.6	0.8	1.2	3.7
Kansas	Min.	9.2	3.3	35.9	14.2	25.0	0.6	0.05	1.8	0.3	0.2	0.4	1.4
	Ave.	10.5	4.0	38.2	16.3	32.7			6.7	0.5	0.3	1.0	2.7
	Max.	11.7	4.7	40.5	18.5	40.5	0.7	0.27	11.7	0.8	0.4	1.6	4.0
Missouri	Min.	10.1	4.2	37.9	14.5	25.8	0.6	0.02	1.7	0.4	0.1	1.3	1.1
	Ave.	11.7	4.6	42.2	15.8	31.1	0.7	0.10	4.9	0.7	0.15	2.1	2.5
	Max.	12.8	5.2	45.4	16.8	41.0	0.8	0.14	7.0	0.8	0.2	3.0	3.5
EASTERN PROVINCE													
Alabama	Min.	4.5	0.8	23.9	18.4	5.3	0.6	0.06	1.7	0.6	0.2	0.9	0.6
	Ave.	9.1	1.6	43.7	26.4	19.9	1.1	0.23	3.0	1.3	0.27	2.4	2.1
	Max.	17.0	3.8	54.0	33.3	45.0	1.8	0.57	12.4	2.4	0.5	4.0	4.7
Kentucky	Min.	2.2	0.6	31.6	18.8	4.1	0.8	0.04	0.9	0.3	0.2	0.9	0.2
	Ave.	8.5	2.1	48.7	26.2	16.5	1.3	0.15	2.25	1.0	0.37	2.3	1.6
	Max.	15.6	3.5	57.9	34.5	30.4	2.3	0.48	5.7	2.1	3.0	4.1	6.6
Ohio	Min.	4.6	1.2	30.2	18.8	8.6	0.6	0.04	0.4	0.2	0.1	0.4	0.2
	Ave.	11.5	3.6	43.3	22.8	27.9	1.0	0.20	2.0	0.7	0.2	1.5	1.2
	Max.	17.2	6.9	56.1	30.2	45.2	2.2	0.91	4.8	1.7	0.4	2.7	3.6
Pennsylvania	Min.	5.7	0.7	26.9	18.2	5.1	0.7	0.06	1.2	0.2	0.1	0.6	0.2
	Ave.	9.6	1.9	43.5	26.3	22.9	1.1	0.47	2.52	0.6	0.2	1.7	1.4
	Max.	13.4	6.3	57.7	32.7	52.5	1.7	2.9	9.1	1.4	0.5	3.6	3.6
Tennessee	Min.	4.8	0.6	33.6	18.6	6.1	0.9	0.13	1.7	0.7	0.2	1.0	0.8
	Ave.	10.4	2.0	47.7	26.3	15.9	1.2	0.79	1.9	1.2	0.3	2.7	1.6
	Max.	17.2	4.1	56.5	32.7	41.6	1.7	1.8	2.8	1.6	0.5	3.3	3.0
West Virginia	Min.	3.2	0.5	25.8	14.1	2.1	0.5	0.02	0.4	0.2	0.1	0.2	0.3
	Ave.	9.0	1.8	46.1	28.5	16.9	1.3	0.33	2.7	0.81	0.49	1.7	2.0
	Max.	27.9	6.0	64.5	41.6	48.2	2.3	3.0	12.7	3.8	2.1	3.5	9.6

^aModified from data in reference b.^bAnon. Major Ash Constituents in U.S. Coals. Bureau of Mines Report of Investigations. 7240. 1969. pp. 4-9.

TABLE 5(a). SULFATE EMISSIONS

Boiler Type & Name	Size MM	Coal		Flyash		Bottom Ash		Remarks
		Type	Source	Sulfur (as SO ₃) (ng/J)	Percent Conversion	Sulfur (ng/J) as SO ₃	Percent Conversion	
Unit "B" Dry bottom-Front wall	137	Bit.	Kentucky & West Virginia	4.85	0.34	17.7	1.24	Furnace retained 15% of total ash
Widows Creek No. 15 Dry bottom-Front wall	125	(Bit.)	Alabama	12.17	0.50	4.81	0.18	
Unit "A" Dry bottom-Vertical	162	Bit.	Pennsylvania	8.5	0.50	NA	NA	Furnace retained 40% of total ash
Unit "D" Wet bottom- Horizontally opposed	150	Bit.	Illinois	3.4	0.26	0.77	0.056	
Leland Olds No. 8 Dry bottom- Horizontally opposed	215	Lign.	Glenharold	3.68	0.72	NA	NA	2.3% SO ₃ in mechanical dust collector, 6% SO ₃ in pilot ESP, 7.07% average Na in the ash
Station 3 Cyclone	250	Lign.	North Dakota	0.033	-0	2.14	0.02	Bottom ash and econo- mizer ash are sluiced intermittently
Unit "C" Dry bottom-Tangential	~100	Bit.	Ohio & West Virginia	60	4.15	NA	NA	Coal is mixed with 1% lime
Station "2" Tangential	350	Subbit.	Wyoming	16	4.4	7.2	2.0	1.32% Na ₂ O in the ash

TABLE 5(b). Concluded

Boiler Type & Name	Size MW	Coal		Flyash		Bottom Ash		Remarks
		Type	Source	Sulfur (as SO ₃) (lb/MBtu)	Percent Conversion	Sulfur (lb/MBtu) as SO ₃	Percent Conversion	
Unit "B" Dry bottom-Front wall	137	Bit.	Kentucky & West Virginia	0.0113	0.34	0.0412	1.24	Furnace retained 15% of total ash
Widows Creek No. 5 Dry bottom-Front wall	125	(Bit.)	Alabama	0.0283	0.50	0.0112	0.18	
Unit "A" Dry bottom-Vertical	162	Bit.	Pennsylvania	0.0198	0.50	NA	NA	Furnace retained 40% of total ash
Unit "D" Wet bottom- Horizontally opposed	150	Bit.	Illinois	0.0079	0.26	0.0018	0.056	
Leland Olds No. 8 Dry bottom- Horizontally opposed	215	Lign.	Glenharold	0.0086	0.72	NA	NA	2.3% SO ₃ in mechanical dust collector, 6% SO ₃ in pilot ESP, 7.07% average Na in the ash
Station 3 Cyclone	250	Lign.	North Dakota	7.67×10^{-5}	~0	0.0049	0.02	Bottom ash and econo- mizer ash are sluiced intermittently
Unit "C" Dry bottom-Tangential	~100	Bit.	Ohio & West Virginia	0.1395	4.15	NA	NA	Coal is mixed with 1% lime
Station "2" Tangential	350	Subbit.	Wyoming	0.0372	4.4	0.0167	2.0	1.32% Na ₂ O in the ash

T-3976

Sulfur retention in the bottom ash was highest for subbituminous, tangential-fired boiler. It is interesting to note that the bottom ash in the horizontally opposed wet bottom boiler had very little sulfur content. This is contrary to the speculation that the sulfur in the coal would come in contact with the furnace bottom ash and form molten iron sulfate, thus reducing the concentration of SO_2 in the flue gas. The bottom ash in the cyclone-fired boiler contained very little sulfur (0.02-percent conversion) even though lignite was burned. Therefore the cyclone-fired boiler converted little of the lignite sulfur to sulfates. In fact, sulfur input was nearly all converted to SO_2 in the two cyclone boilers.

3.2.3 Alkali Constituents in Coal Ash

As previously discussed, the retention of sulfur in flyash, bottom ash or water wall slag is due to the presence of alkali constituents such as sodium, magnesium, potassium and calcium in reactive form. A high percentage of alkali ash constituents is found in western subbituminous and lignite coals. Gronhovd, et al., (Reference 10) analyzed the sulfur retention properties of lignite ash. In their study, they suggested that the percent input sulfur in the coal emitted as SO_2 (S.E.) could be expressed as (Reference 10):

$$\text{S.E.} = 12.7 \frac{\text{CaO}}{\text{Al}_2\text{O}_3} - 48.1 \frac{\text{Na}_2\text{O}}{\text{SiO}_2} + 110.1$$

Where CaO , Al_2O_3 , Na_2O , and SiO_2 are expressed as percent of moisture-free lignite. With this correlation a 71-percent variance in the data can be explained (see Figure 5).

Sodium has been known to be the most effective of these alkali ash constituents in reducing SO_2 emissions. Figure 6 shows SO_2 percent conversion for all the boilers firing lignite coals as a function of percent sodium in the ash. Even though the data are somewhat scattered, a general trend of SO_2 reduction for increased sodium content can be seen. For instance, the tangential-fired boiler decreased its SO_2 emissions from 800 ppm to 590 ppm when the sodium weight percent in the ash was increased from 0.9 to 6.1 percent. However, the high sodium content coals contribute to increased ash fouling rate of the water walls and convective tubes in the boiler.

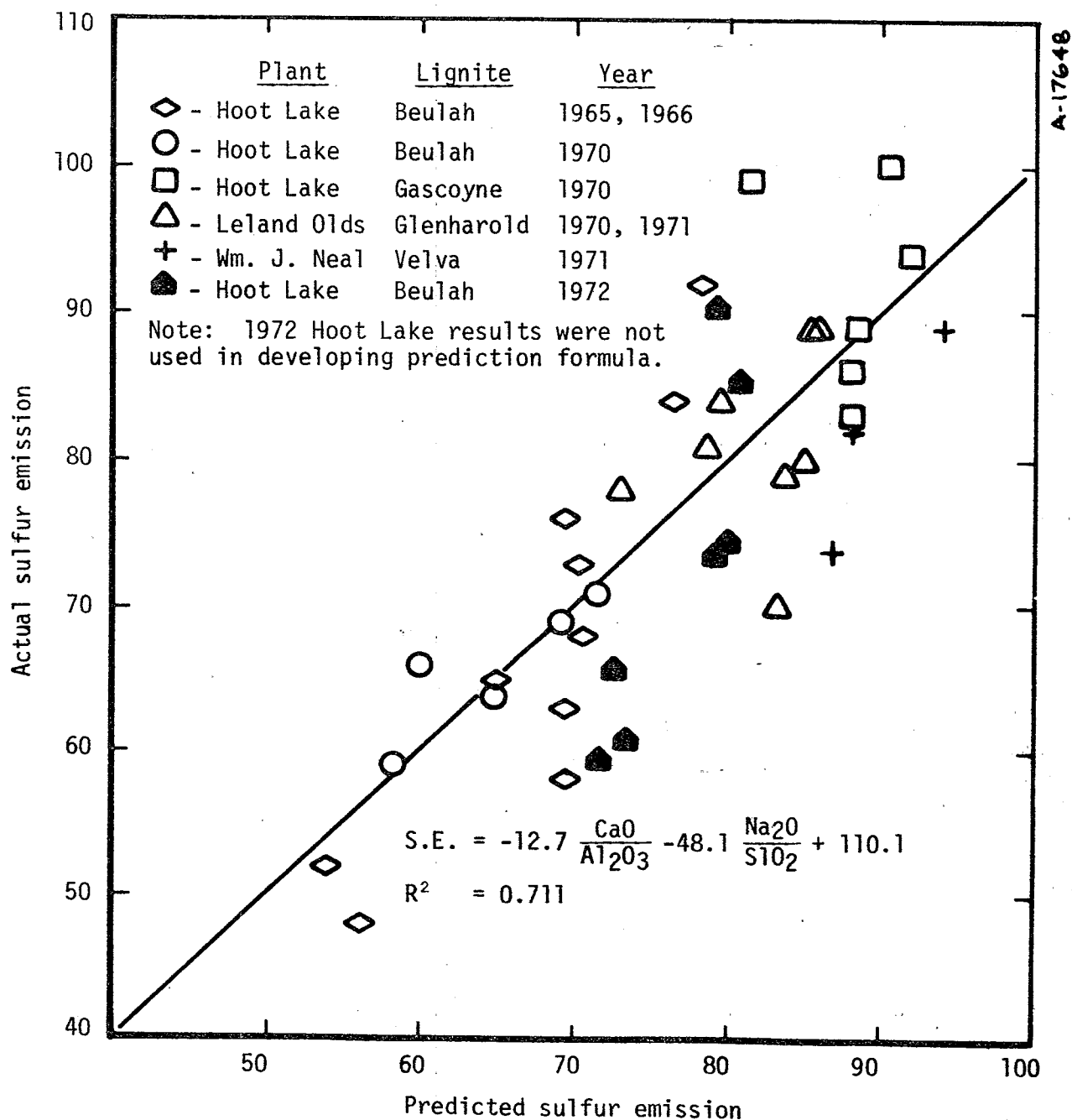


Figure 5. Predicted versus actual sulfur emission (S.E.) for pc-fired plants (Reference 10).

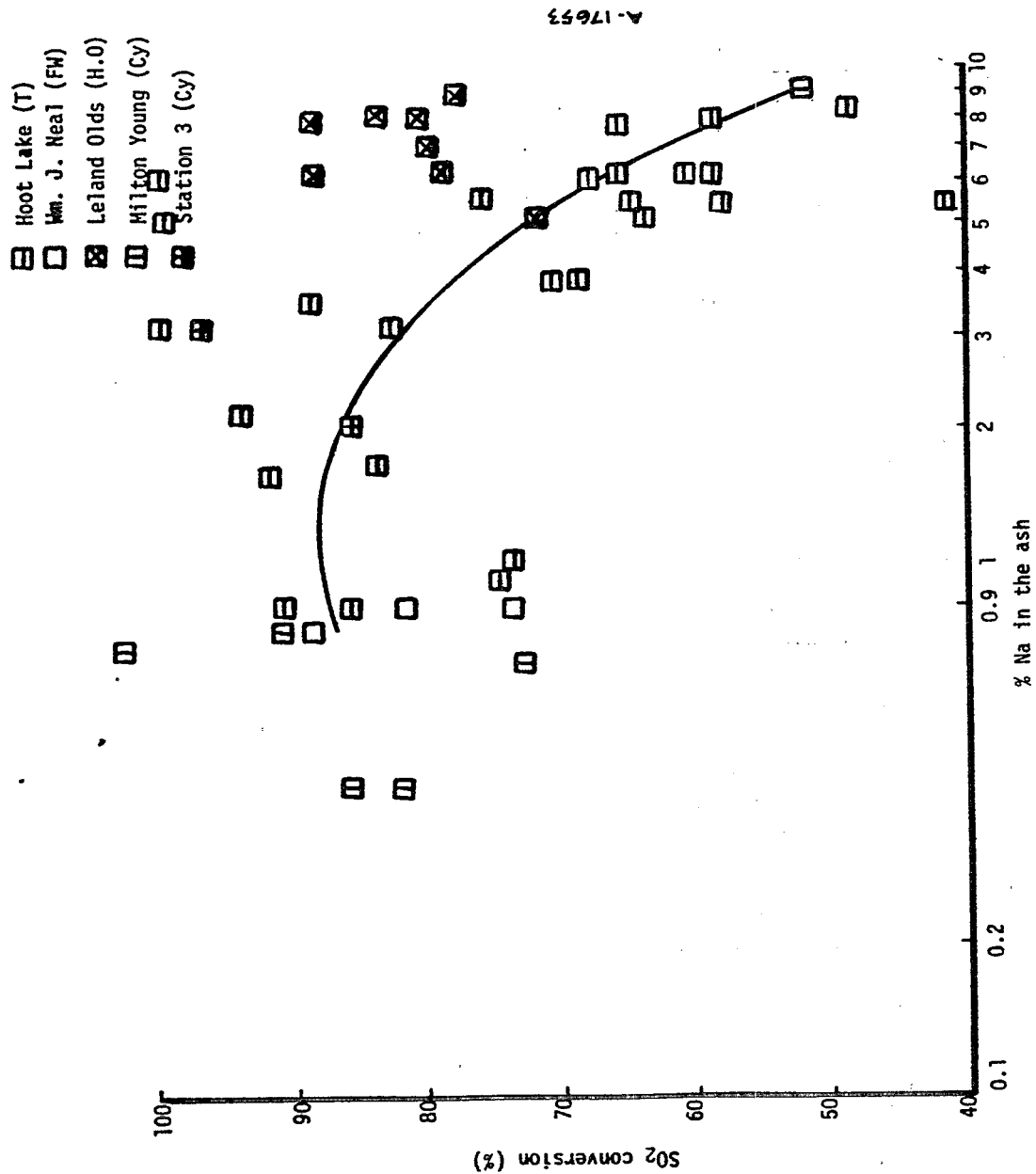


Figure 6. Percent SO₂ conversion as a function of ash sodium content
for lignite coals.

3.3 PERCENT SULFUR IN THE COAL

SO₂ emissions obviously increase with increased sulfur content of the coal. But Figure 7 shows that the percent conversion of fuel sulfur to SO₂ (dashed line) also increases from approximately 50 to 100 percent when sulfur content increases from 0.5 to 1.5 percent. Beyond 1.5 percent sulfur in the coal the conversion remains constant at approximately 100 percent. The reason for this increase in percentage conversion appears to be due mostly to the change in coal characteristics as the sulfur is increased. The low sulfur content coals represent subbituminous and lignitic coals, while the higher sulfur content coals represent bituminous coals. Together with a reduction in sulfur content, ash properties also change, causing the reduction in percent conversion to SO₂.

The three solid lines indicate the allowable percent conversion of the fuel sulfur in order to maintain SO₂ emissions at the 516 ng/J (1.2 lb/MBtu) level promulgated by the NSPS without any scrubbing device. For example, a boiler firing bituminous coal with a typical heating value of 30,238 J/g (13,000 Btu/lb) and a sulfur content of 2.0 percent would have to retain at least 60 percent of the sulfur to comply with the NSPS without an added control (see short dashed line). All subbituminous coal-fired boilers investigated fell below their curve indicating that no SO₂ control would be necessary to meet the federal standards. Emissions from lignite-fired boilers were slightly above the allowable limit. SO₂ emissions from bituminous-fired boilers were far above the federal standards, indicating that SO₂ control devices would be necessary to meet the 516 ng/J level. It should be noted that the three solid lines represent typical coals with typical heating values. The heating values chosen to calculate these curves are not necessarily the heating values of the coals used in the reported field tests, but represent a good approximation for each generic coal type.

3.4 BURNER STOICHIOMETRY

One of the mechanisms by which SO₃ can be formed is the SO₂-atomic oxygen reaction. Based on this theory, an increase in SO₃ production should be observed when the percent burner stoichiometry (excess air) is increased. This increase in SO₃ production would shift the SO₂-SO₃ equilibrium composition toward SO₃, thus reducing SO₂ emissions. Figure 8 shows the percentage conversion of sulfur to SO₂ as a function of burner stoichiometry for the

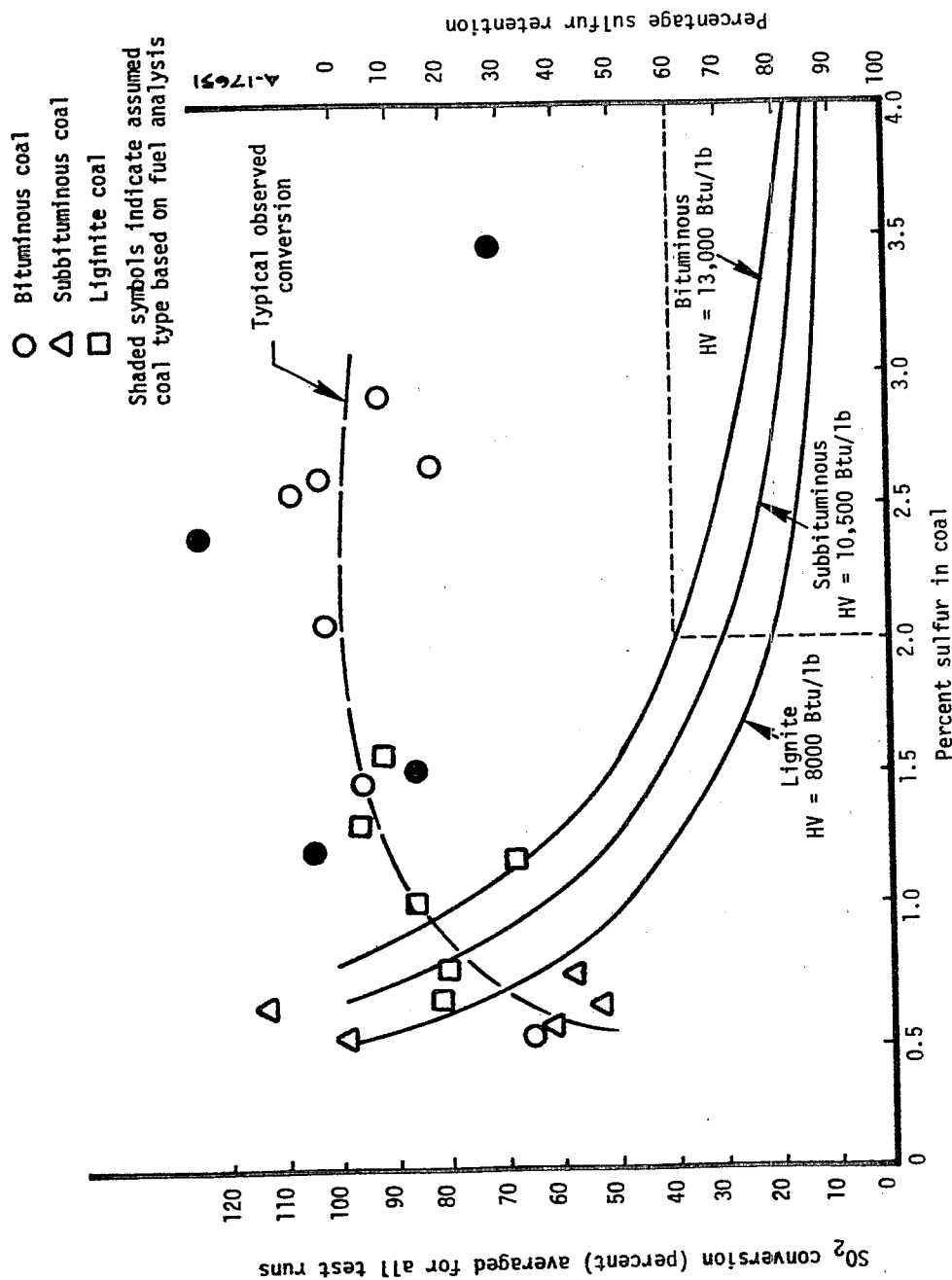


Figure 7. Effect of sulfur content on SO_2 emissions.

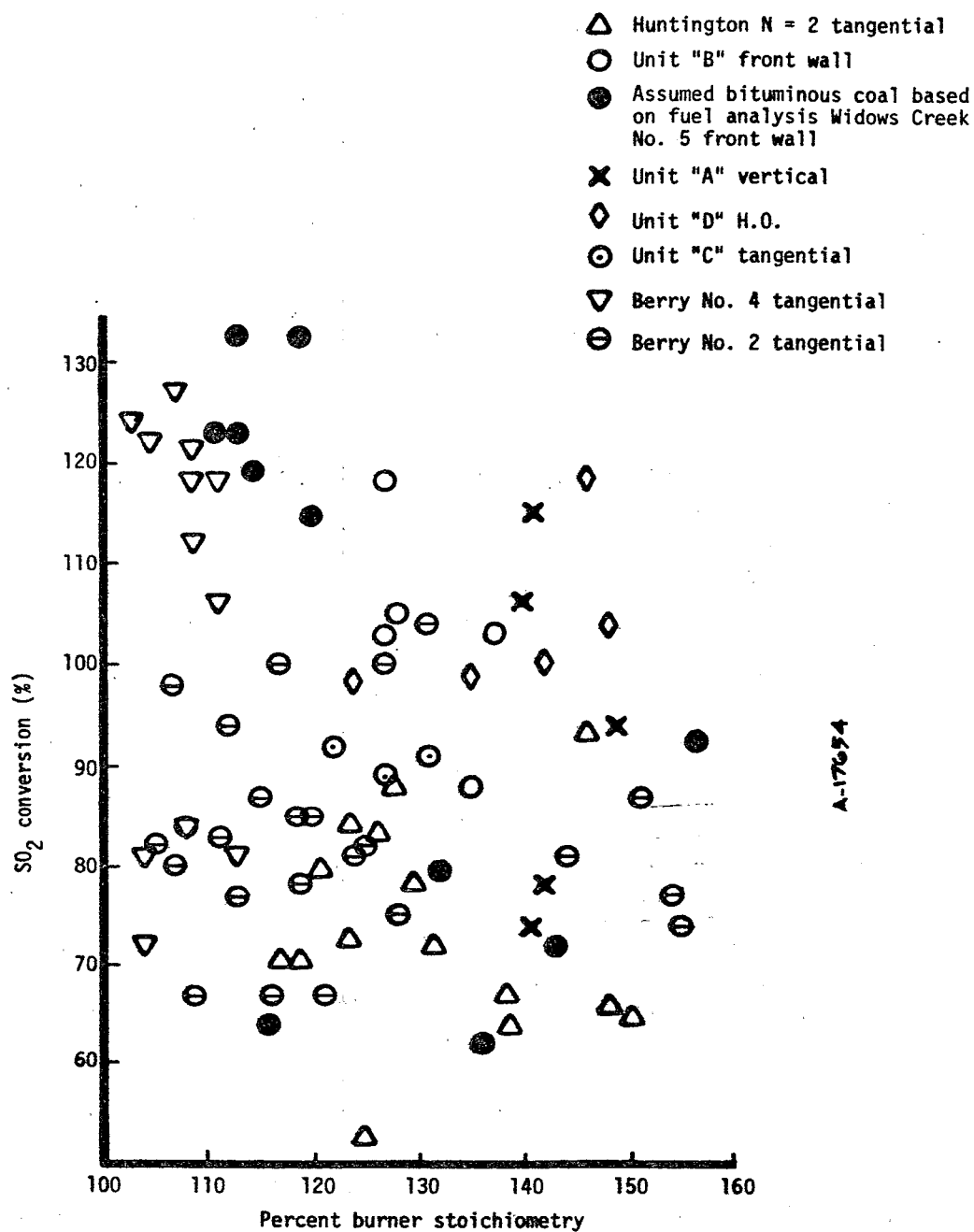


Figure 8. Effect of burner stoichiometry on the percentage conversion of bituminous coal sulfur to SO₂.

bituminous coal and Figure 9 for all the subbituminous coal data. No trends of SO_2 reduction with increased furnace excess air can be seen. The data are scattered to such a degree that no clear trend can be seen whatsoever, even within each boiler test run series.

Figure 10 and 11 show the percent conversion of coal sulfur to SO_3 for three boilers. An increase in the percentage SO_3 emissions can be seen for Unit "D" boiler, although the increase is rather speculative since it is based on only few data points. Figure 11 shows SO_3 conversion for a vertically-fired boiler. The percent SO_3 to total sulfur oxides was higher than for Units "B," "C," and "D," ranging from 1.6 to 9.2. However, SO_3 seems to be insensitive to changes in burner stoichiometry. Additional data are necessary to draw any conclusions on the higher SO_3 percentages in vertically-fired units than other boiler firing types.

3.5 BOILER FIRING RATE

The equilibrium mixture of SO_2 and SO_3 is both a function of temperature and pressure. Lowering the temperature shifts the equilibrium toward SO_3 production. Thus, it would be expected that as the boiler firing rate is reduced, and lower gas temperatures occur in the firebox, an increase in SO_3 emissions would take place with a consequent decrease in SO_2 emissions. Figures 12 and 13 show that this may not be the case. Again, there is considerable scatter of both the individual data and the effects of firing rate changes on different boilers. Although the available data are insufficient to justify any conclusion about conversions as a function of firing rates for individual boiler types or coals, it is clear that there is no general trend for all boilers and coals.

3.6 BOILER SIZE

Another boiler parameter that could affect sulfur conversion is unit capacity. To assess this possibility, emission rates (Mg/hr) of SO_2 were plotted as a function of boiler size with sulfur content of the coal indicated for each point (Figure 14). As expected SO_2 emissions increase with both boiler size and sulfur content of the coal. For comparison the emission limit stipulated by the current NSPS is also shown. All points below this standard represent low sulfur western and lignitic coals.

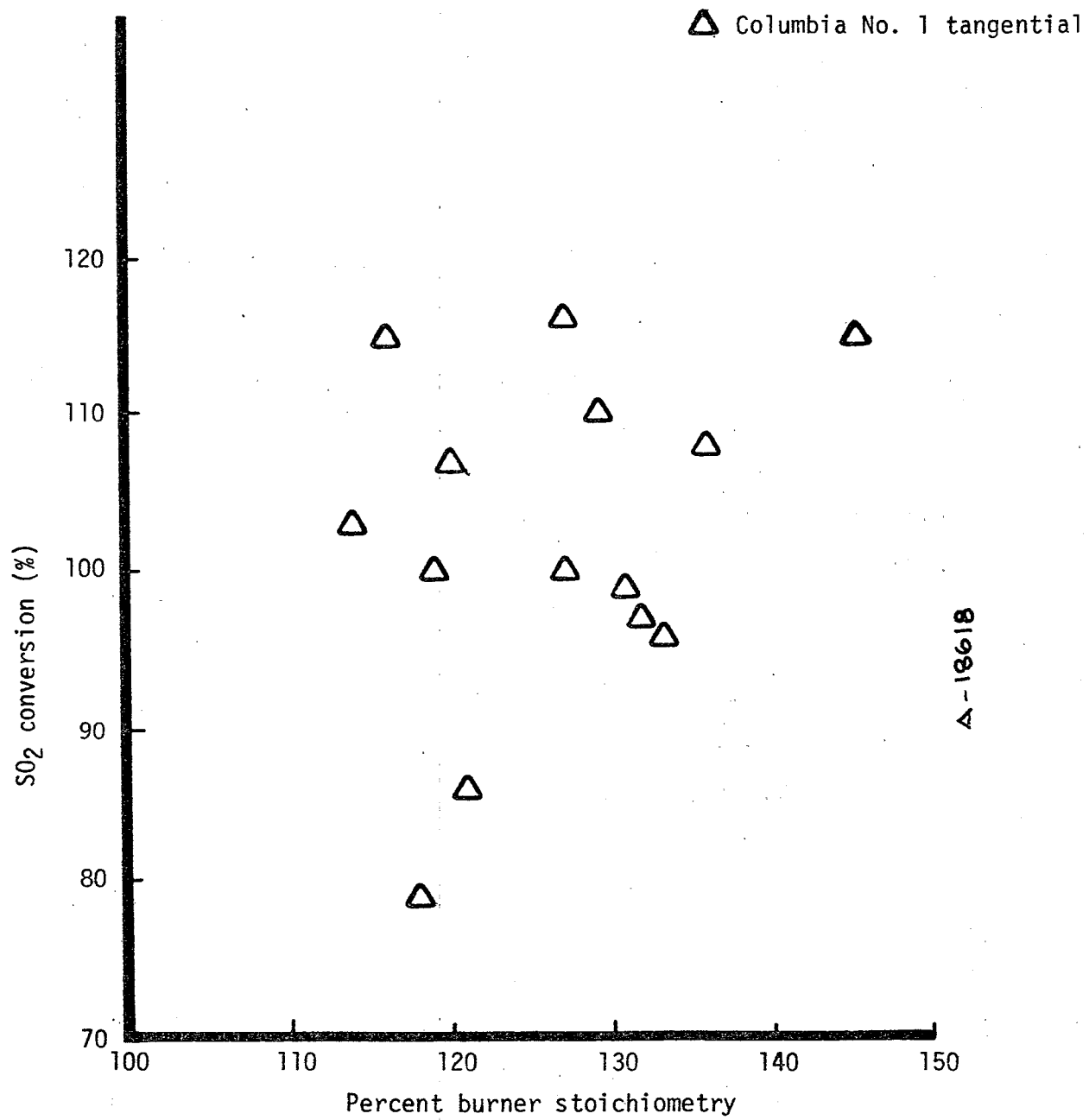


Figure 9. Effect of burner stoichiometry on the percentage conversion of subbituminous coal sulfur to SO₂.

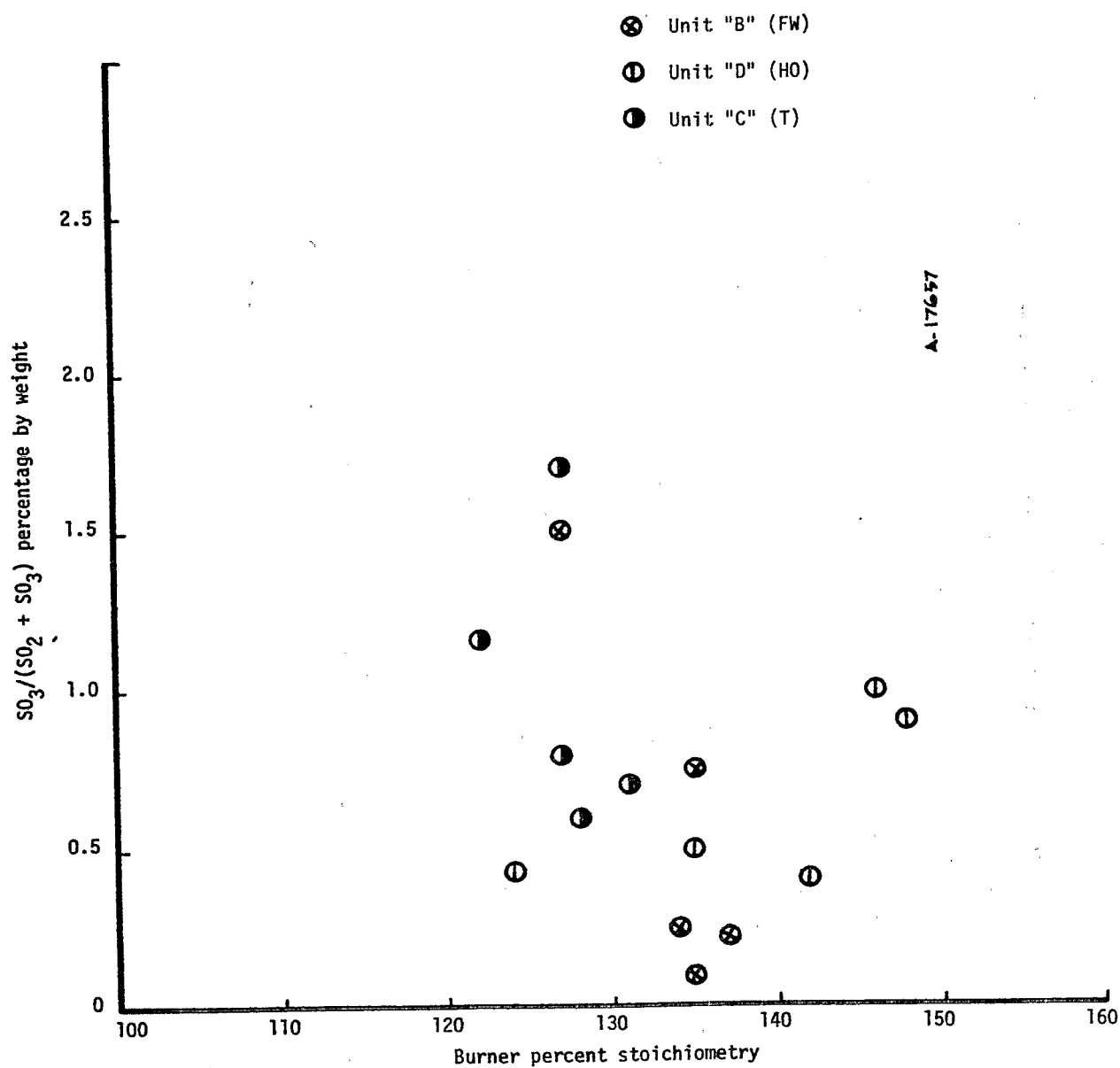


Figure 10. Effect of burner stoichiometry on SO_3 emissions from bituminous coal-fired boilers.

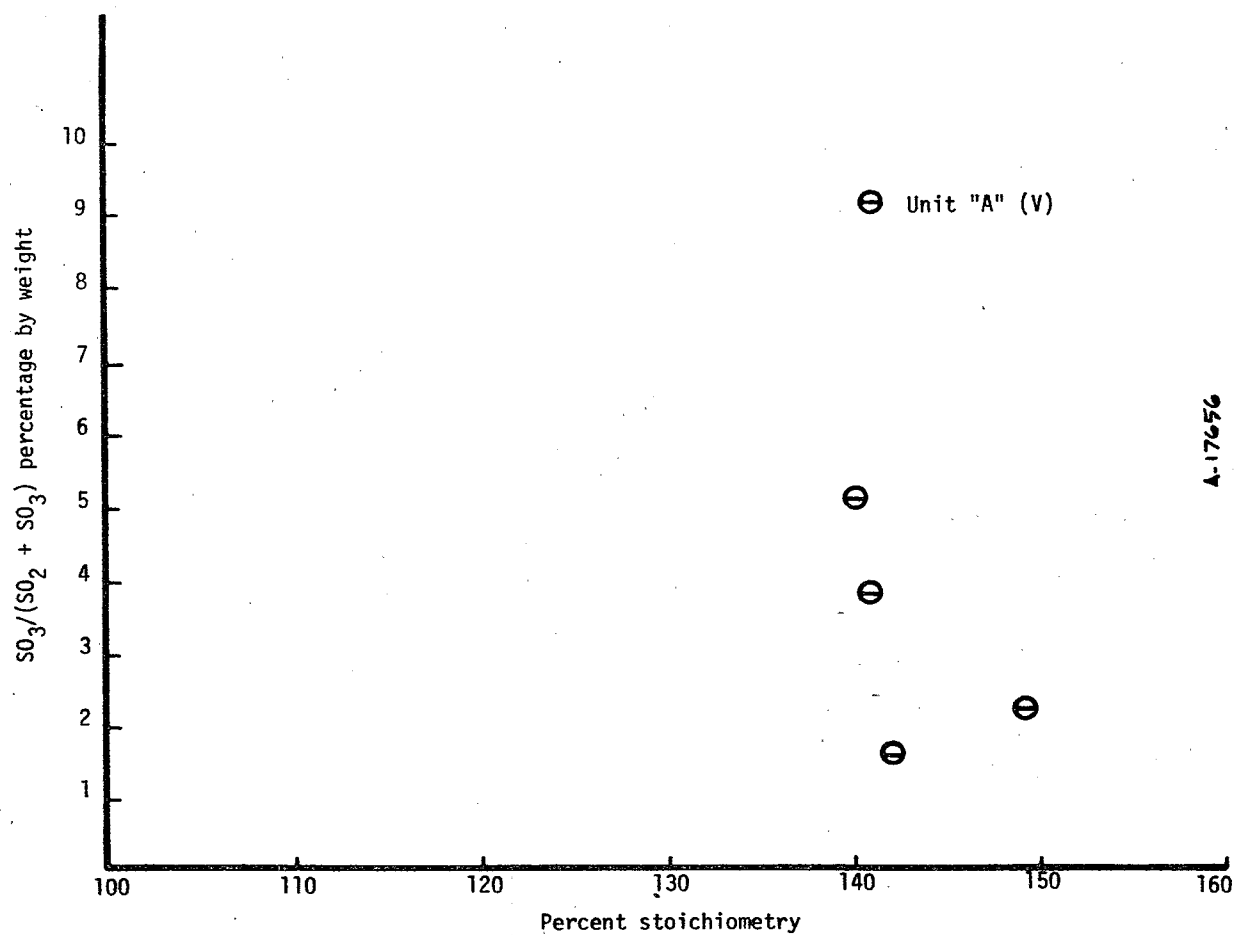


Figure 11. Effect of burner percent stoichiometry on SO_3 emissions from bituminous coal-fired boilers.

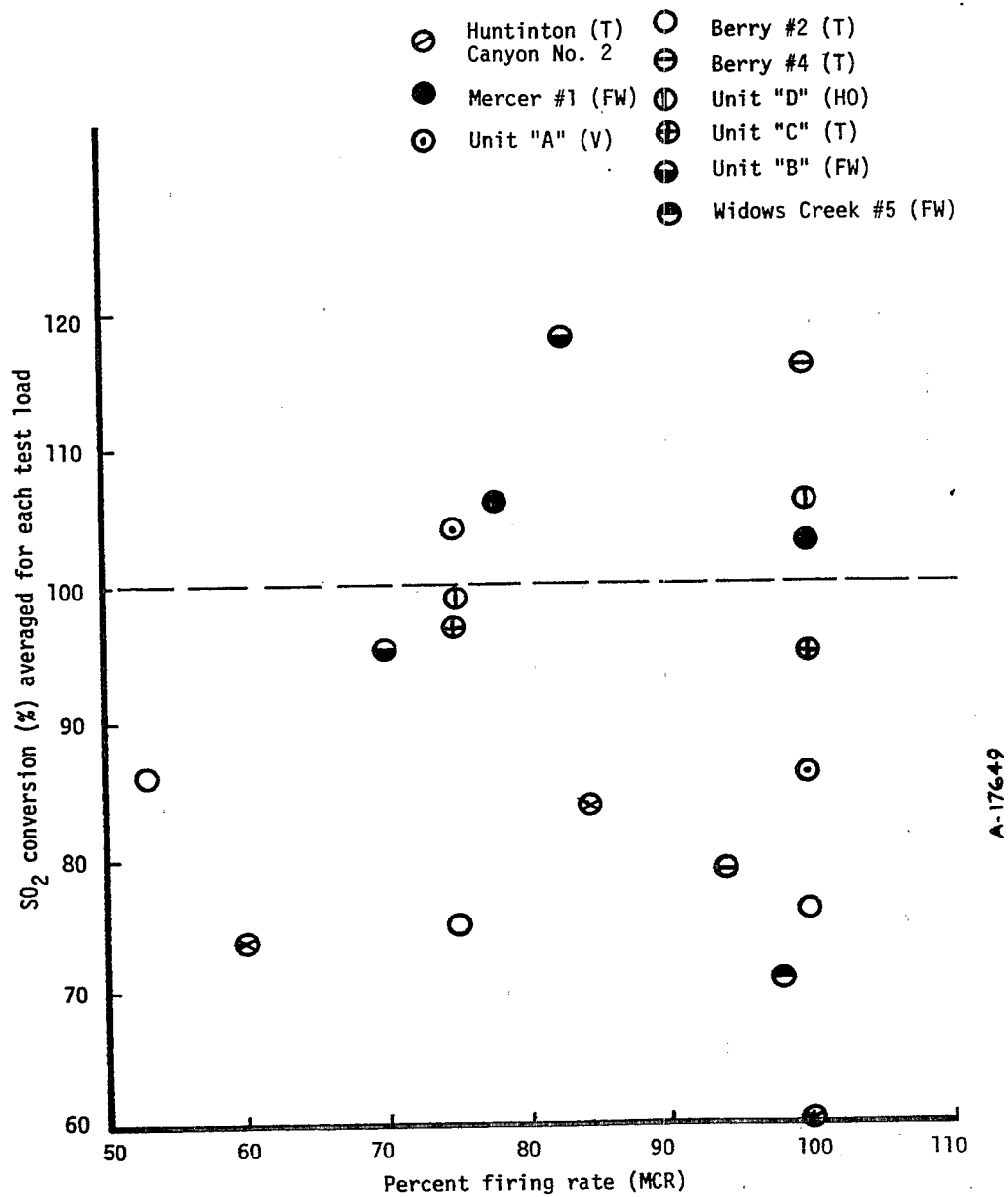


Figure 12. Effect of firing rate on SO₂ emissions for bituminous coal-fired boilers.

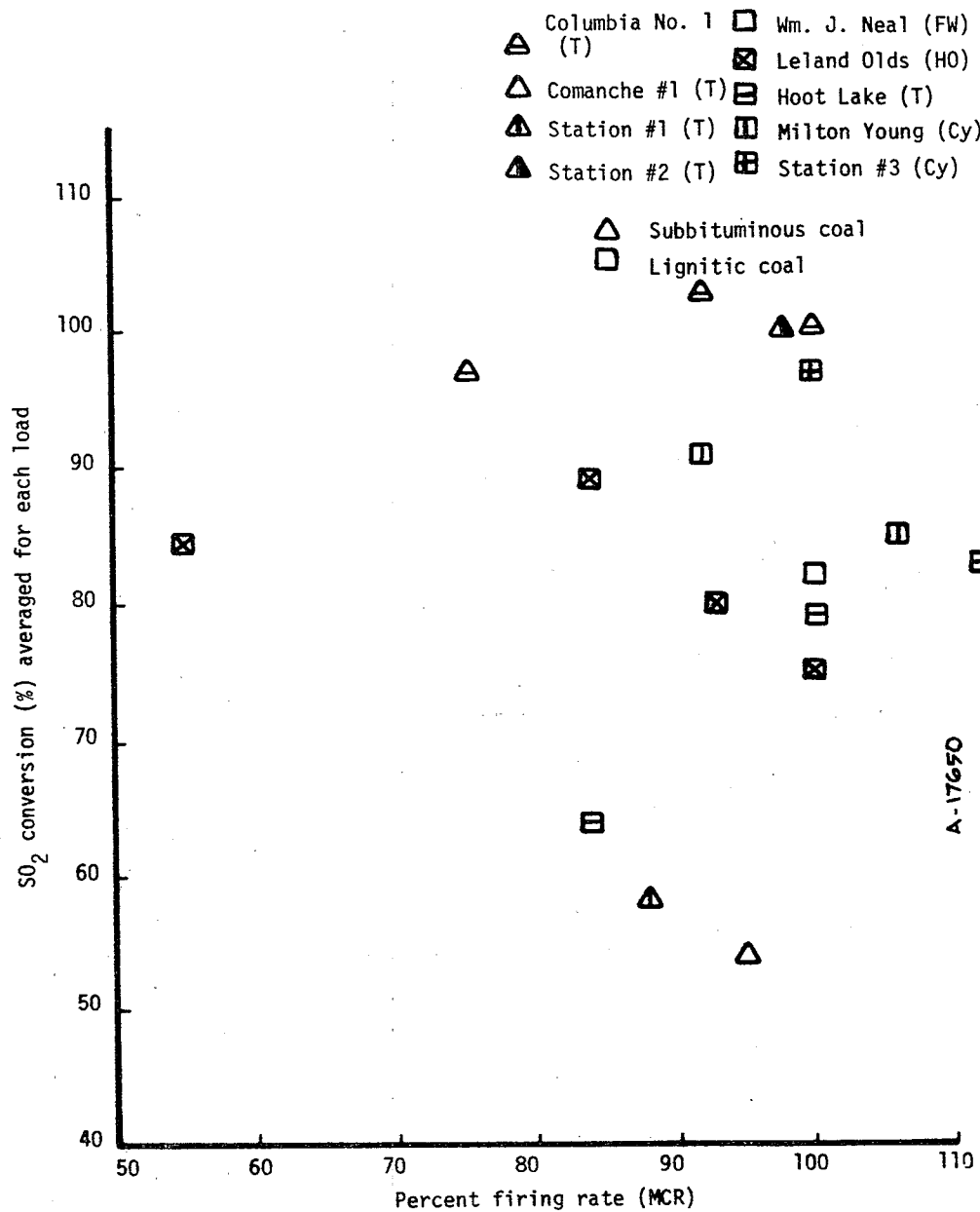


Figure 13. Effect of firing rate on SO₂ emissions for lignite and subbituminous coal-fired boilers.

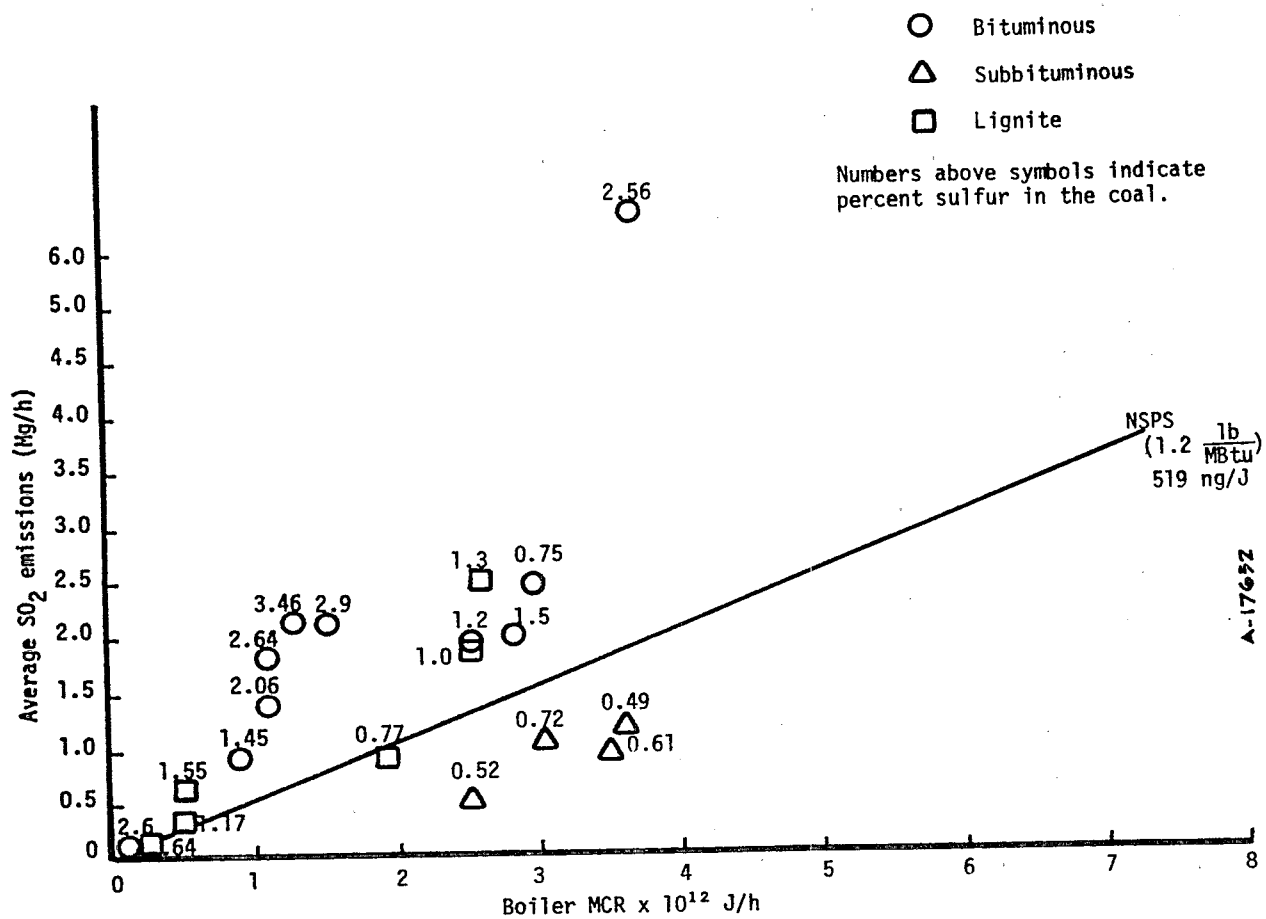


Figure 14. Effect of boiler size on SO₂ emission rate.

To determine whether sulfur conversion does, in fact, depend on boiler size, one needs to analyze the sulfur emission rate per unit energy produced (MW-hr). If such a dependence exists, it is probably the indirect consequence of differences in boiler efficiency (for a given fuel). To check this possibility, mass emission rates per energy output (kg/MW-hr) were plotted as a function of boiler size (see Figure 15(a)). The results show considerable scatter with no apparent correlation to boiler size. The major cause of this scatter is, of course, the variation in coal type, sulfur and moisture content, and heating value among the data points. Coal type and sulfur content have already been shown to affect sulfur emissions. Variations in coal moisture content and heating value effect emissions when measured in mass per energy output because of their effects on boiler efficiency. One can try to separate out the effects of coal type and sulfur content by (1) plotting the data for each coal on a different graph (Figures 15(b) to 15(d)) and (2) comparing emissions from different sized boilers when each fires coal of approximately the same sulfur content as the others. The following selected examples show that there is no unique relationship between emissions (per energy output) and boiler size, even for a given coal type and sulfur content.

- Bituminous: coals with $S = 2.60 \pm 0.04$ percent were fired in a 20-, 125-, and 350-MW boiler. Emissions per energy output increased with size from about 6.2 to 18.4 kg/MW-hr. However, a 1.45-percent S coal fired in a 125-MW boiler emitted at essentially the same rate as did a 270-MW boiler burning a 1.5-percent S coal and another 270-MW unit using a 1.2-percent S coal.
- Subbituminous: an 0.52-percent S coal in a 425-MW boiler emitted less than a 350-MW unit firing 0.49-percent S, but about the same as one would expect the other two units (330 MW and 350 MW) to emit if they were firing 0.5-percent S coal (instead of 0.61 and 0.72-percent S)
- Lignite: a 20 MW-boiler emitted more burning 0.64-percent S coal than did a 215-MW boiler burning 0.77-percent S coal, but a 50-MW unit burning 1.17-percent S coal emitted substantially less than did a 250-MW boiler on 1.3-percent S coal

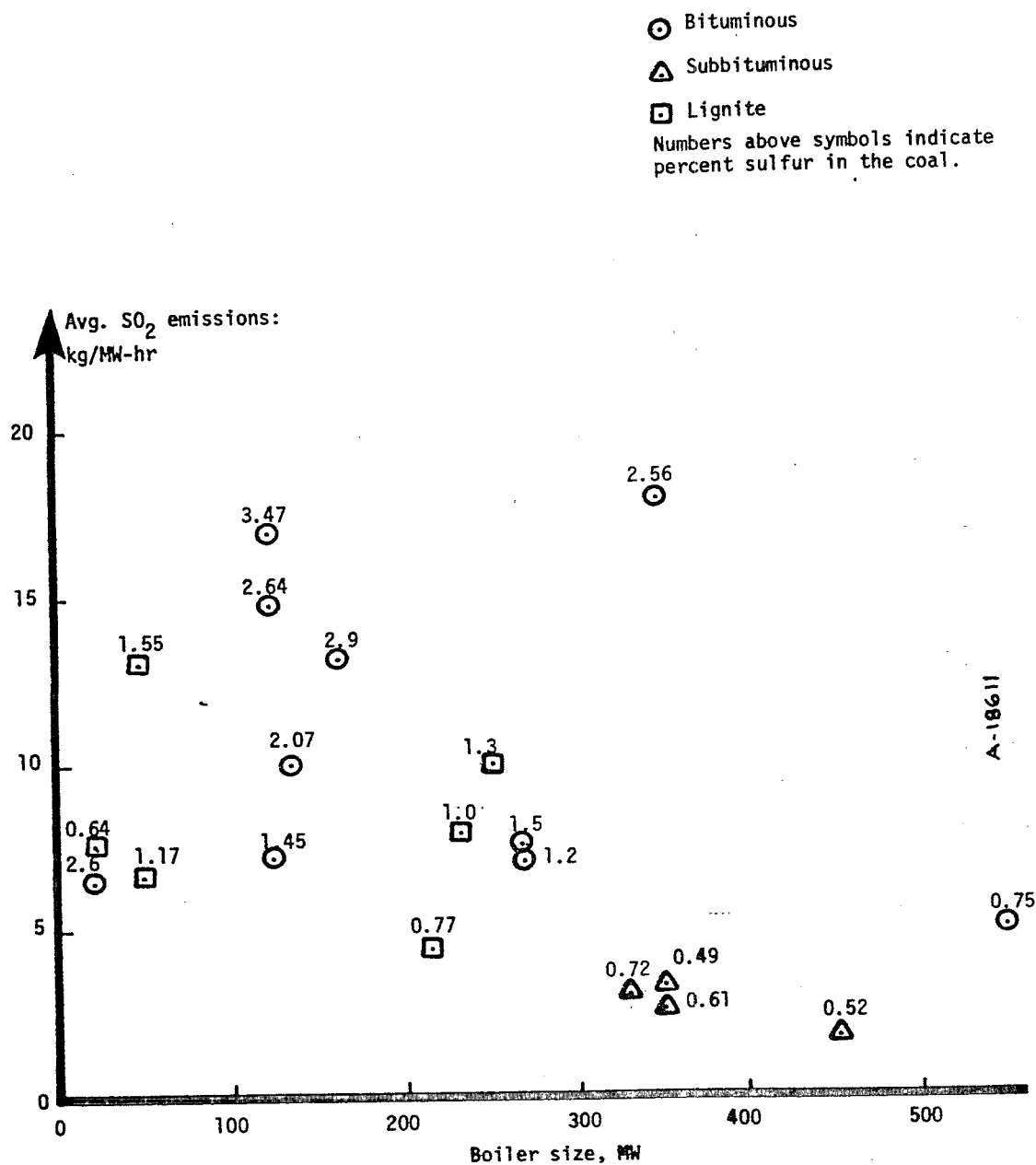


Figure 15(a). Effect of boiler size on SO₂ emissions.

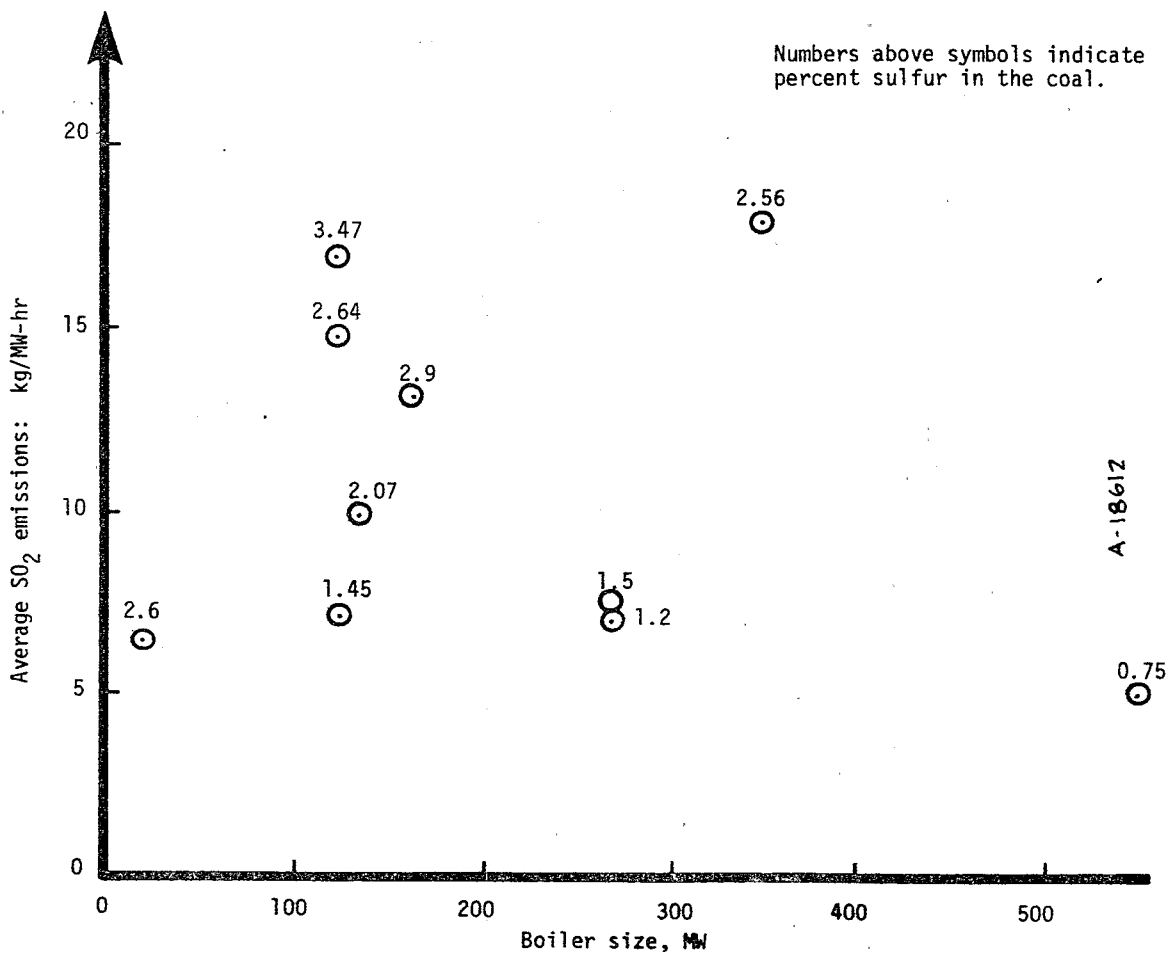


Figure 15(b). Effect of boiler size for bituminous coals.

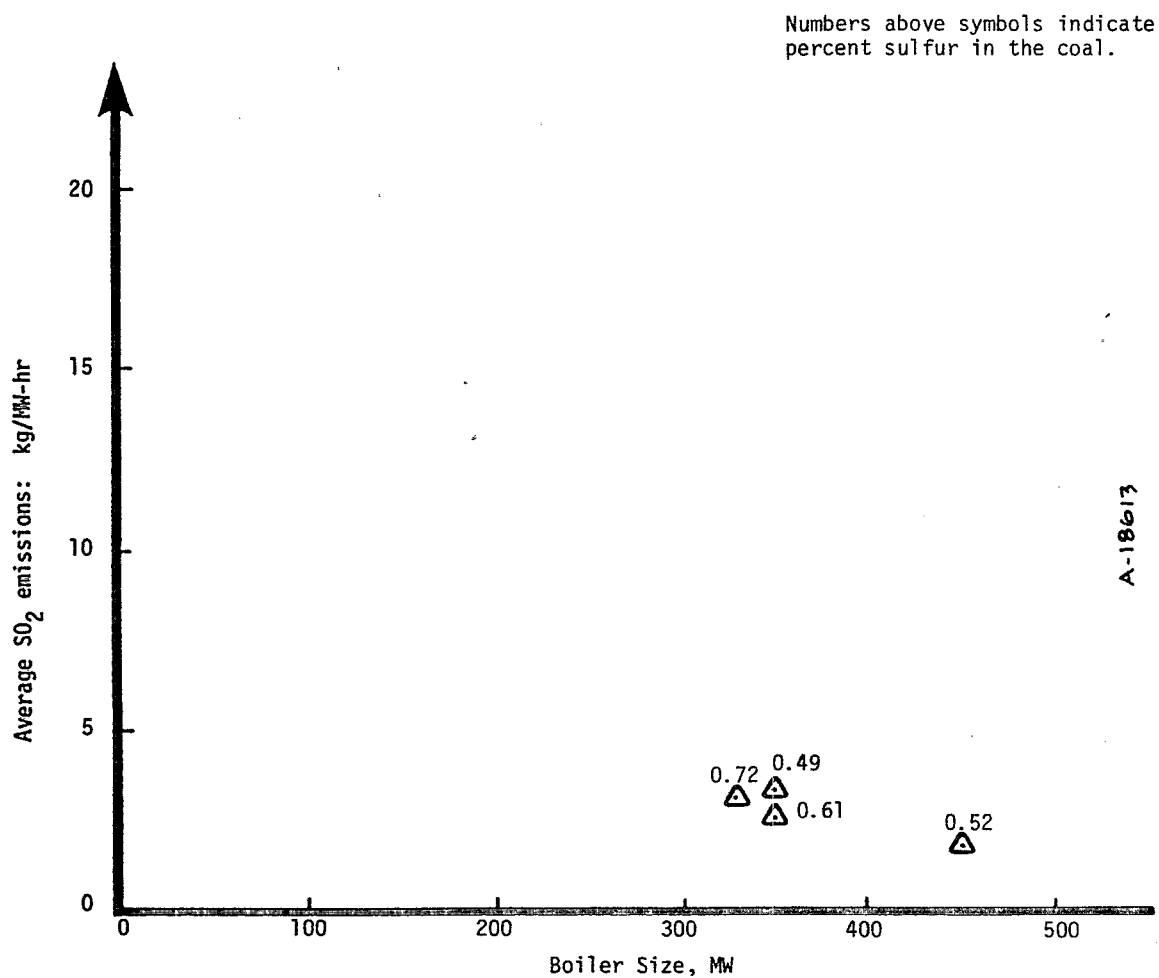


Figure 15(c). Effect of boiler size for subbituminous coals.

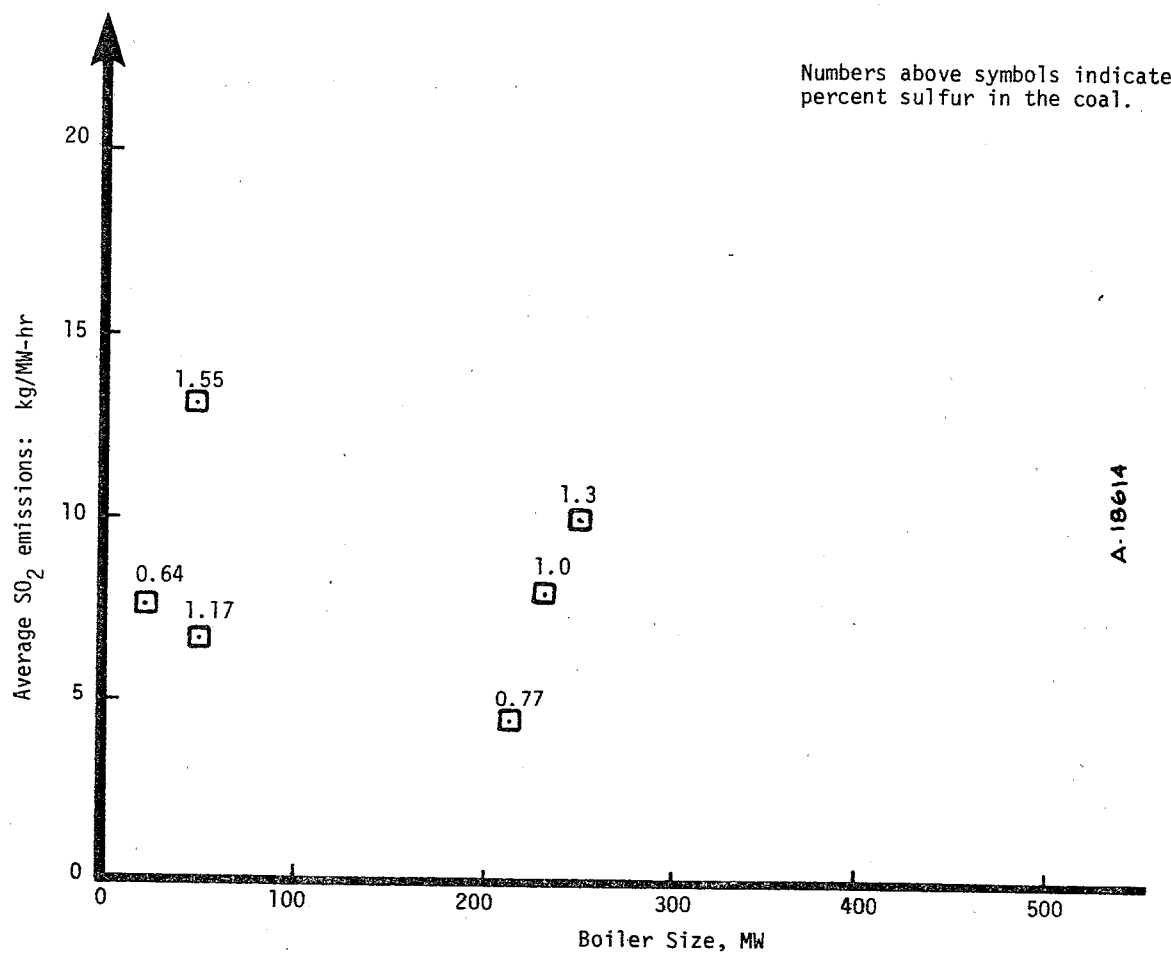


Figure 15(d). Effect of boiler size for lignite coals.

These relationships are seen more clearly in Figure 16 (a qualitatively determined "best-fit" straight line has been added as a visual aid; it cannot be used too rigorously because a straight line relationship between emissions and sulfur content is valid only for "constant" coal and boiler efficiency). In some cases, the smaller units appear above the larger ones (for a given sulfur content and coal type), whereas in other cases, they fall below.

One reason there may be no clear relation between size and sulfur emissions is that boiler unit efficiencies do not vary much with size for boilers larger than 100 MW (Reference 16). The variation in efficiency is typically only between 87 and 90 percent. Even this variation is probably due more to age than size, because the larger units tend to be the newer ones. With the current trend toward the installation of medium-sized boilers rather than the very large ones, this dependence of efficiency on size will diminish.

Figure 16 also suggests that the lignitic coals cause higher SO_2 emission rates, when referenced to energy output, than do the bituminous coals with the same sulfur content. No comparisons can be drawn with sub-bituminous coals, however, because of a lack of data.

Unlike SO_2 emission rates, which depend directly on fuel sulfur content, fuel heating value, boiler firing rate, and possibly boiler firing configuration, SO_2 conversion rates do not necessarily depend on boiler type/size. It was shown in Figure 7, however, that SO_2 conversion increases with fuel sulfur content up to 1.5 percent because of the change in coal characteristics. To see if this effect carries over when emissions are related to boiler size, Figure 17 was prepared. This plot shows SO_2 conversion as a function of boiler output size. Examination of the figure suggests that SO_2 conversion increases somewhat for the bituminous coals as boiler size increases. A similar conclusion appears to hold for lignite. The strongest correlation, however, still is with sulfur content and type of coal. A much larger data base would be required to more rigorously evaluate the dependence of SO_2 conversion on boiler size.

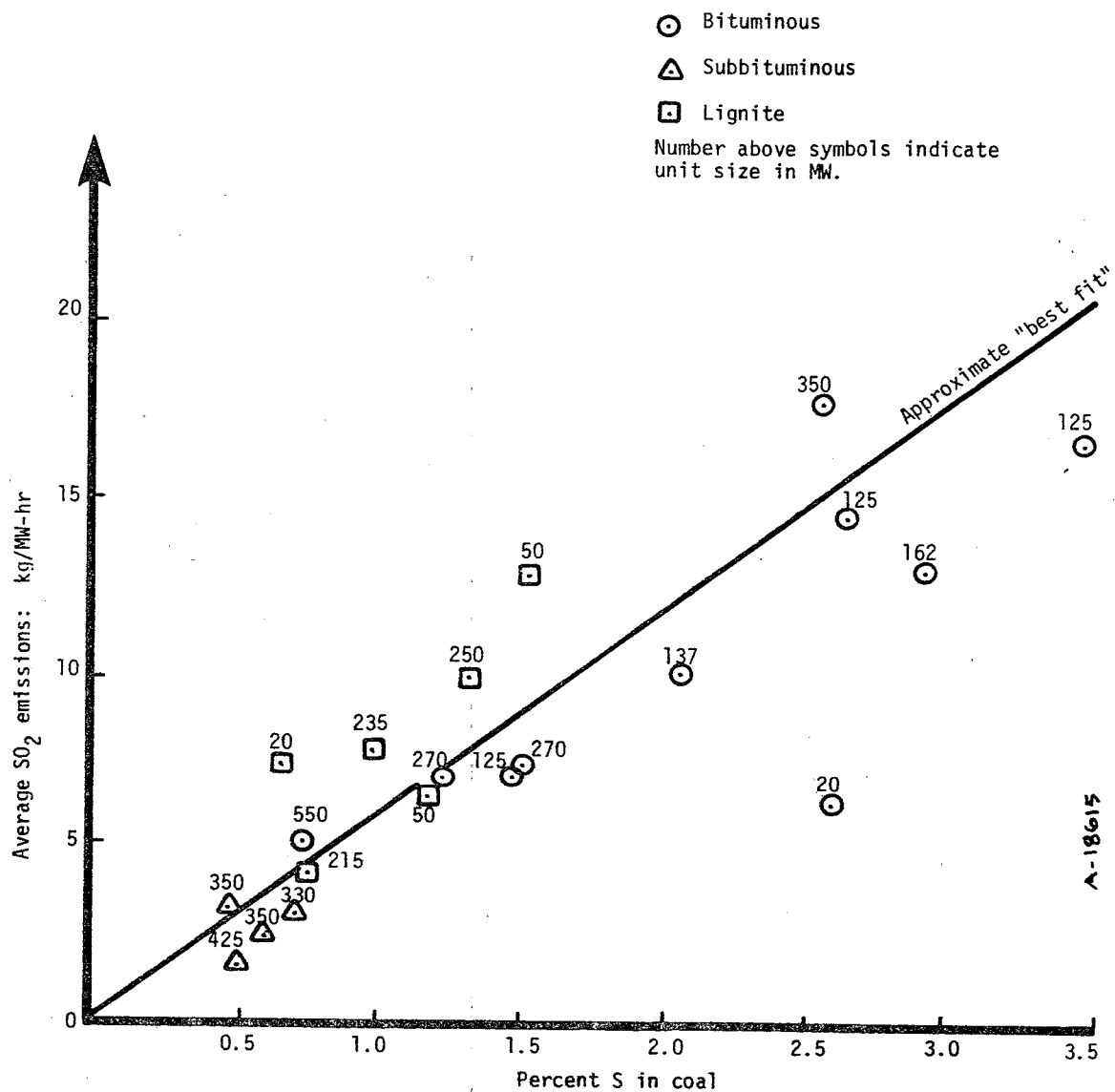


Figure 16. Effect of sulfur content on SO₂ emissions.

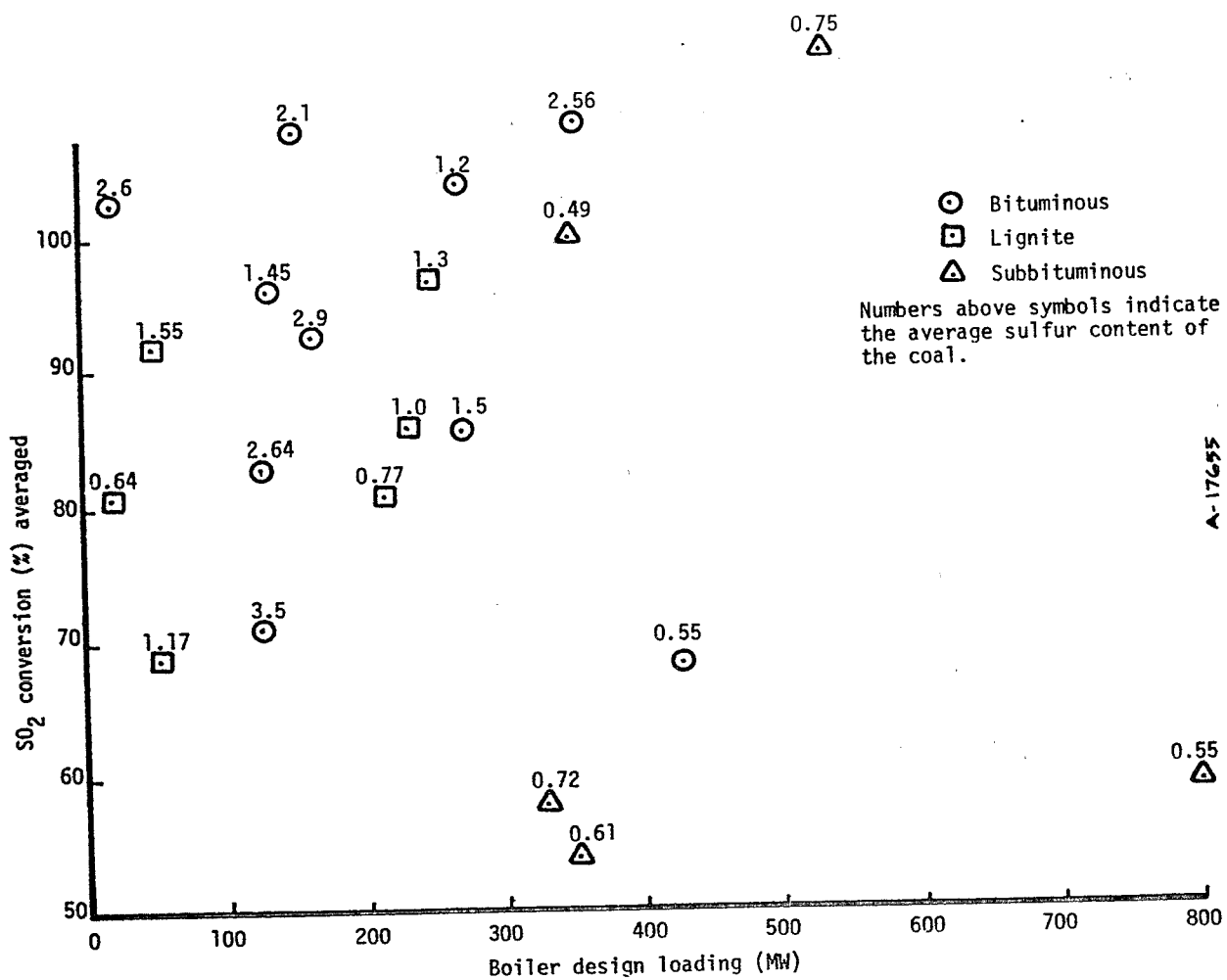


Figure 17. Effect of boiler size on SO₂ emissions.

SECTION 4

GASEOUS SULFUR EMISSION ACROSS PARTICULATE COLLECTION DEVICES

Virtually all coal-fired power plants are equipped with particulate control devices to capture the flyash they emit. From the perspective of SO_x control, therefore, the typical boiler — the so-called "uncontrolled" unit — is one with particulate controls. Since the data reported in Section 3 were measured in the ducts ahead of any control devices, the actual SO_x emissions from the plant could be different than the measured values. To determine whether this is true, in fact, data were collected for SO_x emission rates on both sides of particulate control devices; these data are reported here.

The results of four series of tests (Reference 6) in which sulfur oxides were measured at both the inlet and the outlet of particulate collection devices are summarized in Tables 6(a) and 6(b). Each test series is for a different power plant and control system. Two boilers (Units "A" and "C") have a cyclone followed by an electrostatic precipitator (ESP), one (Unit "B") has only an ESP, and the last one (Unit "D") has only a cyclone.

It is interesting to note that the average inlet SO_2 mass loadings for three of the units was nearly the same. On the average, the SO_2 mass loading across the collection devices decreased slightly for units "C" and "D", however, they increased significantly for unit "B". SO_2 emissions are not expected to change significantly across these collection devices. Large differences in emissions across these collectors can be attributed more to measurement errors than effects of the collectors.

In the case of sulfur trioxide emissions, units "B", "C", and "D" had nearly the same concentration at the inlet, but unit "A" produced a considerably larger quantity of SO_3 . The exit streams for all four collector devices had similar concentrations of SO_3 . As a result, the concentration of SO_3 across the mechanical dust collector-electrostatic precipitator for unit "A" was greatly reduced, while the other three units showed slight increases. These small increases are probably within the uncertainty of the measurement techniques, therefore it is difficult to identify trends. Evidently the collecting devices for unit "A" were successful in removing some SO_3 from the flue gas. This substantial reduction could be due to leakage and temperature decrease of the gas stream across the collectors. The cooling of the flue gas could have resulted in condensation of the SO_3 and formation of sulfuric acid mist. The resulting mist as well as some sulfur trioxide gas could be adsorbed on the flyash particulates. Then upon removal of these particles, the concentration of SO_3 would be reduced. In addition, for the case of an electrostatic precipitator the acid mist particles could be ionized and collected in the precipitator.

In conclusion, the data do not show any trends. SO_2 emission decreased in two cases (by 6.5 percent on the average) and increased in two other cases, where similar collection devices were used (by 24 percent on the average). In one case with relatively high SO_3 emissions, the combination of an ESP and mechanical collector removed over 80 percent of the SO_3 . Inconsistencies in the SO_2 emission data across particulate collection devices can be attributed to the measuring technique used. These techniques consisted of single point grab samples from large and split ducts. A discussion of measurement techniques is presented in Appendix C.

TABLE 6(a). SULFUR OXIDE EMISSIONS ACROSS PARTICULATE COLLECTION DEVICES^a

Collection Device	Test No.	Inlet				Outlet				Change in SO ₂ Across Collector (percent)	Change in SO ₃ Across Collector (percent)	Remarks
		SO ₂		SO ₃		SO ₂		SO ₃				
		Mass Loading (ng/l)	Percent Conversion	Mass Loading (ng/l)	SO ₃ (SO ₂ +SO ₃) Percent	Mass Loading (ng/l)	Net Percent Conversion	Mass Loading (ng/l)	SO ₃ (SO ₂ +SO ₃) Percent			
Mechanical dust collector in series with electrostatic precipitator	1	1756	106	95	5.1	2209	133	17.3	0.8	+25.8	-81.8	Boiler — Unit A vertically fired. High volatile bituminous coal.
	2	1364	78	23	1.7	1464	83.7	0.0	0.0	+7.3	-100.0	
	3	1192	74	123	9.4	1500	93	17.4	1.1	+25.8	-85.8	
	4	1946	115	81	4.0	1757	104	7.5	0.4	-9.7	-90.7	
	5	1501	94	35	2.3	1574	98.6	18.1	1.1	+4.9	-48.3	
	Avg	1552	93	71	4.5	1700	102	12.1	0.7	+9.5	-83.0	
Electrostatic precipitator	1	2310	164	4.8	0.2	3918	278	24.5	0.6	+69.6	+410	Boiler — Unit B front wall fired bituminous coal. Original data given in lb/1000 ft ³ of flue gas. Refer to Appendix A for conversion testators.
	2	1257	88	1.2	0.1	951	66	0.48	0.05	-24.3	-60.0	
	3	1858	118	27.9	1.5	3220	204	22.9	0.7	+73.3	-17.9	
	5	780	103	5.8	0.7	481	63	2.9	0.6	-38.3	-50.0	
	Avg	1551	118	9.9	0.6	2142	153	12.7	0.5	+38.1	+28.3	
Cyclone separator in series with electrostatic precipitator	1	1445	105	8.9	0.6	1319	95.8	12.2	0.9	-8.7	+37.0	Boiler — Unit C tangentially fired. High volatile bituminous coal.
	2	1258	92	15	1.2	1182	86	13.9	1.2	-6.0	-7.3	
	3	1143	91	8	0.7	1198	95.4	13.7	1.1	-4.8	+71.0	
	4	526	89	9	1.7	553	93.6	14.9	3.2	+5.1	+100	
	5	677	103	5.6	0.8	534	81	11.2	1.5	-21.1	+50.0	
	Avg	1010	96	9.3	1.0	957	90.4	13.2	1.6	-5.2	+41.9	
Cyclone separator	3	1738	104	15.6	0.9	1561	93.4	11.7	0.7	-10.2	-25.0	Boiler — Unit D horizontally opposed. High volatile bituminous coal. Flyash reinjection.
	4	1864	100	7.4	0.4	1824	97.8	7.4	0.4	-2.1	-0.0	
	5	1590	98.7	8.3	0.5	1448	89.9	11.8	0.8	-8.9	+42.2	
	6	1233	98.4	5.4	0.4	1086	86.7	-	-	-11.9	-	
	Avg	1606	100	9.2	0.6	1480	92.0	10.3	0.6	-7.8	+12.0	

^aData from Reference 6

TABLE 6(b). Concluded

Collection Device	Test No.	Inlet				Outlet				Change In SO ₂ Across Collector (percent)	Change In SO ₃ Across Collector (percent)	Remarks
		SO ₂		SO ₃		SO ₂		SO ₃				
		Mass Loading (lb/HBtu)	Percent Conversion	Mass Loading (lb/HBtu)	SO ₃ (SO ₂ +SO ₃) Percent	Mass Loading (lb/HBtu)	Percent Conversion	Mass Loading (lb/HBtu)	SO ₃ (SO ₂ +SO ₃) Percent			
Mechanical dust collector in series with electrostatic precipitator	1	4.08	106	0.22	5.1	5.14	133	0.04	0.8	+25.8	-81.8	Boiler — Unit A vertically fired. High volatile bituminous coal.
	2	3.17	78	0.05	1.7	3.40	83.7	0.0	0.0	+7.3	-100.0	
	3	2.77	74	0.29	9.4	3.49	93	0.04	1.1	+25.8	-85.8	
	4	4.53	115	0.19	4.0	4.08	104	0.017	0.4	-9.7	-90.7	
	5	3.49	94	0.08	2.3	3.66	98.6	0.042	1.1	+4.9	-48.3	
	Avg	3.61	93	0.17	4.5	3.95	102	0.028	0.7	+9.5	-83.0	
Electrostatic precipitator	1	5.37	164	0.01	0.2	9.11	278	0.057	0.6	+69.6	+410	Boiler — Unit B front wall fired bituminous coal. Original data given in lb/1000 ft ³ of flue gas. Refer to Appendix A for conversion testors.
	2	2.92	88	0.003	0.1	2.21	66	0.001	0.05	-24.3	-60.0	
	3	4.32	118	0.06	1.5	7.49	204	0.053	0.7	+73.3	-17.9	
	5	1.81	103	0.01	0.7	1.12	63	0.0067	0.6	-38.3	-50.0	
	Avg	3.61	118	0.02	0.6	4.98	153	0.029	0.5	+38.1	+28.3	
Cyclone separator in series with electrostatic precipitator	1	3.36	105	0.02	0.6	3.07	95.8	0.028	0.9	-8.7	+37.0	Boiler — Unit C tangentially fired. High volatile bituminous coal.
	2	2.93	92	0.03	1.2	2.75	86	0.032	1.2	-6.0	-7.3	
	3	2.66	91	0.018	0.7	2.79	95.4	0.032	1.1	-4.8	+71.0	
	4	1.22	89	0.021	1.7	1.28	93.6	0.035	3.2	+5.1	+100	
	5	1.57	103	0.013	0.8	1.24	81	0.026	1.5	-21.1	+50.0	
	Avg	2.35	96	0.022	1.0	2.23	90.4	0.031	1.6	-5.2	+41.9	
Cyclone separator	3	4.04	104	0.036	0.9	3.63	93.4	0.027	0.7	-10.2	-25.0	Boiler — Unit D horizontally opposed. High volatile bituminous coal. Flyash reinjection.
	4	4.33	100	0.017	0.4	4.24	97.8	0.017	0.4	-2.1	-0.0	
	5	3.70	98.7	0.019	0.5	3.37	89.9	0.027	0.8	-8.9	+42.2	
	6	2.87	98.4	0.012	0.4	2.53	86.7	—	—	-11.9	—	
	Avg	3.73	100	0.021	0.5	3.44	92.0	0.024	0.6	-7.8	+12.0	

Data from Reference 6

SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The most important result documented by this survey is that the conversion of sulfur in the coal to SO_2 emissions depends more on the coal type and its ash characteristics than on any boiler or design variable considered. Specific findings are listed below:

1. Sulfur conversion to SO_2 ranged from 86 to 108 percent for bituminous coals, from 54 to 114 percent for subbituminous coals, and from 69 to 97 percent for lignitic coals.
2. Excess air in the furnace and percent firing rate did not seem to control the conversion of coal sulfur to SO_2 .
3. The mass emission rate of SO_2 per energy output (g/MW-hr) does not appear to depend on boiler size; SO_2 conversion, however, does seem to increase slightly with boiler size for bituminous and lignitic coals.
4. The percent sodium in the coal ash has a significant effect on sulfur retention in the boiler ash. This is a very important parameter since the more sulfur retained in the ash, the less gaseous SO_2 leaves the boiler. The conversion of sulfur to SO_2 was reduced from approximately 85 to 50 percent when the sodium content was increased from 0.9 to 9 percent by weight in a lignitic coal. Of course, this high sodium content of the ash causes boiler tube fouling.
5. Cyclone boilers retained the least amount of sulfur in the ash when burning lignite. Therefore, the SO_2 emissions from the cyclone

boilers burning lignite are generally higher than those from other lignite-fired boilers with different burner configurations.

6. Gaseous SO_3 emissions were higher for the vertically-fired boiler than from any other boiler. However, this trend is not definitive since more data would have to be analyzed to make this result conclusive.
7. The gaseous SO_3 content of flue gases is minimum for lignitic coals due to the formation of sulfate particulates. Gaseous SO_3 emission are about the same for bituminous and subbituminous coals.

5.2 RECOMMENDATIONS FOR FURTHER INVESTIGATIONS

The data compiled in this report give some very interesting results for coal sulfur conversion to SO_2 , SO_3 , and sulfates. However, in the short time allowed for this project, all the available data could not be obtained rapidly enough to allow us to conduct a more detailed and in-depth analysis of the effect of boiler design and process variables on the emissions. A substantial amount of additional data was identified and requested, but not received by the completion date of this task. Sources of the data were contacted to evaluate the quality and usefulness of their data. They are listed in Table 7 along with the estimated quantity of sulfur emission data they could provide.

In addition to the analysis of more emission data, the quality of the data should be analyzed in more detail to attempt to explain some of the scatter in the results.

A preliminary investigation was conducted of the sampling techniques and instrumentation used to collect the data presented in this report (see Appendix C). Unfortunately the information was too qualitative to identify sources of error and quantify measurement uncertainties.

TABLE 7. ADDITIONAL DATA SOURCES

Source	No. of Boilers	Emissions Reported	No. of Test Runs	Remarks
1. Selker et al. Reference 11	1	SO ₂	28	Low NO _x data - Boiler fired with over fire air and burners out of service. Substoichiometric conditions in the furnace. (Tangential furnace)
2. Hollinden et al. Reference 6	1	SO ₂	40	Low NO _x data. Boiler fired with burners out of service. Substoichiometric conditions in the furnace. ^a
3. York Research Corp.	10-30	SO _x	NA	Need 2-4 weeks of work to retrieve the data. ^b
4. Pennsylvania Electric Co.	3	Total S Balance	NA	Some data have been sent to Aerotherm, but not in time to be included in this report. The remainder of the data will be sent when final results are obtained. ^c
5. Oak Ridge National Labs Report No. ORNL-NSF-EP-43	1	NA	NA	Identified as containing sulfur emission data from pulverized coal-fired power plants. Ordered through Aerotherm library.
6. APCA-1974 67th Meeting	1	NA	NA	
7. Mitre "Baseline Measurements" Test Results for Cat-Ox Demonstration Program	1	NA	NA	

^aNeil D. Moore of Power Research Staff at TVA has sent (June 1, 1977) fuel analysis data for their tests on Widows Creek No. 5 conducted in 1974-75.

^bMr. B. Epstein of York was contacted (May 16, 1977) in order to obtain data. York would be willing to send these data to Aerotherm only if York were reimbursed for the large amount of time they claim it would take to collect the test data and obtain permission to release them.

^cTelephoned Mr. D. Fyock, Director of Environmental Affairs, Pennsylvania Electric Company on May 20, 1977, to request their data. Followed telephone call by a letter.

T-400

REFERENCES

1. J. A. Cavallero, M. T. Johnston, A. W. Dembrouck, "Sulfur Reduction Potential of the Coals of the United States, a Revision of Report of Investigation 7633," Bureau of Mines Report of Investigation 8118, 1976.
2. J. F. Kircher, A. A. Putnam, D. A. Bull, H. H. Krause, J. M. Genca, R. W. Content, J. O. Y. Wendt & R. Leag, "A Survey of Sulfate, Nitrate and Acid Aerosol Emissions and Their Control," Battelle Columbus Laboratory Draft Report for W. Steve Lanier of EPA-RTP, September 1976.
3. Homlya, et al., "A Characterization of the Gaseous Sulfur Emissions from Coal and Oil-Fired Boilers," Fourth National Conference on Energy and Environment, October 1976, Cinc., Ohio.
4. Richard L. Davison, David F. S. Natush, John R. Wallace and Charles A. Evans, Jr., "Trace Elements in Flue Ash, Dependence of Concentration on Particle Size," Env. Sci. Tech., 8 (13), pp. 1107-1113, December 1974.
5. Telephone conversation with M. H. Schwartz — Chemical Engineering Department — Shell Development Company, Houston, Texas, May 16, 1977.
6. Cuffe, S. T., et al., "Air Pollutants Emissions from Coal-Fired Power Plants," Reports 1 & 2, 56th Annual Meeting APCA, Detroit, Michigan, 1963.
7. Hollinden, G. A., et al., "Control of NO_x Formation in Wall Coal-Fired Boilers," Preceedings of the Stationary Source Combustion Symposium Vol. II, EPA-600/2-76-152b, June 1976, Atlanta, Georgia.
8. Cowherd, C., et al., "Hazardous Emission Characterization of Utility Boilers," EPA-650/2-75-066, July 1975.
9. Crawford, A. R., Manny, E. H., Bartok, W., Exxon Draft Report - To be released.
10. Grouhoud, et al., "Some Studies on Stack Emissions from Lignite-Fired Power Plants," Technology and Use of Lignite, Bu-Mines-IC 8650, Oct. 1, 1974.
11. Mesich, F. G., et al., "Coal-Fired Power Plant Trace Element Study, Station 1, 2 & 3," Radian Corporation, EPA Contract No. 68-01-2663, 1975.
12. Selker, A. P., "Program for Reduction of NO_x from Tangential Coal-Fired Boilers — Phase II," EPA-650/2-73-005, June 1975.
13. U.S. Federal Register Vol. 36, No. 247, December 23, 1971.
14. Burnington, R. L., et al., "Field Test Program to Study Staged Combustion Technology for Tangentially Fired Utility Boilers Burning Western U.S. Coal Types," Draft Report, Combustion Engineering, Inc.

15. Ctvrtnicek, T. E., et al., "Evaluation of Coal-Sulfur Western Coal Characterization, Utilization, and Distribution Experience," Monsanto Research Corp. EPA 650/2-75-046, May 1975.
16. Crawford, A., et al., "Field Testing: Application of Combustion Modifications to Control NO_x Emission from Utility Boilers," EPA-650/2-74-066, June 1974.
17. Gregory, M. W., et al., "Determination of the Magnitude of SO₂, NO, CO₂, and O₂ Stratifications in the Ducting of Fossil Fuel-Fired Power Plants," Exxon Research and Engineering Co., Presented at the 69th Annual Conference of the APCA, June 27-July 1, 1976.
18. Personal Communication with Frank Sustino, Combustion Engineering Inc., September 23, 1977.
19. Beck, A. A., and Burdick, "A Method of Test for SO₂ and SO₃ in Flue Gases," Bureau of Mines Report of Investigations 4818, January 1950.
20. Smith, W. S., and Gruber, C., "Atmospheric Emissions from Coal Combustion — An Inventory Guide," PHS Rep. 999-AP-24.
21. Smith, J. F., "Sampling and Analytical Modifications of the Beck and Burdick Method For SO₂ and SO₃ Analysis," Bureau of Mines.
22. Goksøyz, H., and Ross, K., "The Relation Between Acid Dew Point and Sulfur Trioxide Content of Combustion Gases," Thornton Research Center, Shell Research, Ltd., 1962.
23. Lisle, E.S., and Sensenbaugh, J. D., "The Determination of Sulfur Trioxide and Acid Dew Point in Flue Gases," Combustion Engineering, Inc., Combustion, January 1965.
24. Wohlschlegel, P., "Guidelines for Development of A Quality Assurance Program: Volume XV — Determination of Sulfur Dioxide Emissions From Stationary Sources By Continuous Monitors," EPA-650/4-74-005-0, March 1976.

APPENDIX A

MATHEMATICAL RELATIONSHIPS USED

1. 100 percent fuel sulfur conversion to SO₂

$$SO_2 \left(\frac{ng}{J} \right) = 8.598 \times 10^6 \frac{S}{HV}$$

S = percent sulfur in the coal

HV = heating value of the coal as fired (Btu/lb)

2. Conversion of sulfur dioxide emissions from lb/HR to ng/J

$$SO_2 \left(\frac{ng}{J} \right) = 4.299 \times 10^8 \left(SO_2 \frac{lb}{hr} \right) \left(\frac{1}{HV} \right) \left(\frac{1}{FF} \right)$$

HV = heating value of the coal as fired (Btu/lb)

FF = coal flow (lb/hr)

3. Conversion of ppm SO₂ to ng/J

$$SO_2 \left(\frac{ng}{J} \right) = 4.299 \times 10^2 (MSO_2) (ppm SO_2) \frac{nf_{gd}}{HV}$$

MSO₂ = molecular weight of SO₂ = 64

HV = heating value of the coal (Btu/lb)

nf_{gd} = moles of dry flue gas per pound of fuel (dry basis)

$$nf_{gd} = \frac{4.762 (nc + ns) + 0.9405 nH - 3.762 no_2 \text{ fuel}}{1 - 4.762 \frac{\%O_2}{100}}$$

$$nc = \frac{\% \text{ carbon in the coal (as fired)}}{1200}$$

$$ns = \frac{\% \text{ sulfur in the coal (as fired)}}{3200}$$

$$nH = \frac{\% \text{ hydrogen in coal (as fired)}}{100}$$

$$No_2 = \frac{\% O_2 \text{ in the coal (as fired)}}{3200}$$

$\% O_2$ = percentage excess oxygen in the stack

$$SO_2 \left(\frac{ng}{J} \right) = 2.751 \times 10^4 \text{ (ppm } SO_2) \frac{nfgd}{HV}$$

$$SO_2 \left(\frac{ng}{J} \right) = 3.439 \times 10^4 \text{ (ppm } SO_3) \frac{nfgd}{HV}$$

$$4. \quad SO_2 \left(\frac{ng}{J} \right) = 4.299 \times 10^2 \frac{1b \ NO_x}{MBtu} \frac{ppm \ SO_2}{ppm \ NO} \frac{MW \ SO_2}{MW \ NO}$$

MW SO_2 = molecular weight of SO_2 = 64

MW NO = molecular weight of NO = 30

5. Percent fuel sulfur from ash free basis to total weight percent basis:

$$\%S = \%S(\text{ash free basis}) \left(\frac{100 - \%ash}{100} \right)$$

$$6. \quad SO_x \frac{ng}{J} = \frac{430 \times 10^3}{HV} \left[1 + 206 (n_C + n_S) + 42.5 n_H \right] \frac{1b \ SO_x}{1000 \ 1b \ dry \ flue \ gas \ 50\%/EA}$$

APPENDIX B
COMPARISON OF SO₂ EMISSION FACTORS

Table B-1 presents the emission factors listed in U.S. EPA AP-42 together with the emission factors obtained in this study. The two sets of data compare favorably except for the emission factors for the high sodium ash lignite fired boilers. The emission factor reported in this study for lignite represents an average of all the readily available data from high sodium lignitic coal. If only the data from the Hoot Lake boiler (Figure 6) are considered, then the conversion becomes approximately 50 percent. The resulting emission factor of 20 S compares more favorably with the EPA value. It is believed that the Hoot Lake data might be more reliable than the overall average, since the tests were conducted specifically to measure the effect of sodium in the ash on SO₂ emissions.

TABLE B-1. COMPARISON OF SULFUR OXIDE EMISSION FACTORS

Coal Type	AP-42		Aerotherm		Difference lb/ton
	lb/ton	Equivalent Conversion Ratio	lb/ton	Equivalent Conversion Ratio	
Bituminous	38 S ^b	95	38.8 S	97	+0.8 S
Anthracite	38 S	95	NA	NA	NA
Lignite — low sodium ash sodium oxide <2%	35 S	87.5	33 S	83	-2.0 S
Medium sodium ash lignite	30 S	75	31 S	78	+1.0 S
High sodium ash lignite (sodium oxide >8%)	17 S	42.5	26 S	66	+9.0 S
Subbituminous	38 S	95	34 S	84	-4.0 S

^aData represent average values

^bS = Sulfur content of fuel (percent by weight)

APPENDIX C

INSTRUMENTATION AND SAMPLING TECHNIQUES

Table C-1 lists the instrumentation and sampling techniques used to insure gaseous sulfur emissions data reported in Section 3. The equipment varied significantly among the test programs, thereby introducing another variable when comparing sulfur oxides data.

The methods used can be divided into two main groups:

- Wet chemistry (grab sample)
- Electronic monitors (continuous sample and intermittent grab sample)

The wet chemistry methods include the EPA Reference Method No. 6, the Berk and Burdick and the Lisle and Sensenbough methods. The continuous monitoring techniques include the extractive ultraviolet absorption and the non-dispersive infrared (NDIR) methods.

All these methods are comparable in measurement accuracy; however, they all require different sampling procedures, which can be the source of possible errors if appropriate precautions are not taken.

For example, the wet chemical methods involve the use of sampling trains which grab a predetermined flue gas sample for chemical analysis, usually by titration method. The grab sample is most often taken from a single location in the stack, usually 2 to 3 feet from stack walls. This single point sample can be nonrepresentative of the average sulfur oxide concentration due to gaseous stratification. Typical errors caused by single point sampling are ± 20 percent but can be as high as ± 48 percent of the measured value (Reference 17). Sulfur oxide data from single point sampling were reported in References 6, 10, 12 and 14.

TABLE C-1. INSTRUMENTATION AND TECHNIQUES USED FOR GASEOUS SULFUR EMISSION MEASUREMENTS

Boiler ID and Firing Type	Gaseous Sulfur Emission Measurement	Type of Source	Instrumentation of Equipment Used	Comments	Reference
Unit "A" - Vertical Unit "B" - Front wall Unit "C" - Tangential Unit "D" - Horizontally opposed	SO ₂ , SO ₃	Grab	Method of Berk and Burdick	Modification made to eliminate interference on SO ₂ readings. Hydrochloric acid titration for SO ₂ analysis and standard benzene method for SO ₃ analysis.	6
Widows Creek No. 5 Rear wall	SO ₂	Intermittent Grab	Extractive ultraviolet absorption SO ₂ Analyzer DuPont No. 400.	Two flue gas ducts. Size of each duct is 6' by 20' 8". Three probes in each duct evenly spaced 3' into the duct.	7
Widows Creek No. 5 Rear wall	SO ₂	Grab	EPA Method 6, using and modified EPA Method 5 sampling train.	SO ₂ was collected in impinger No. 3 which contained 10% sodium carbonate.	8
Mercer No. 1 - Front wall E. G. Gaston No. 2 - Horizontally opposed Navejo No. 2 - Tangential Comanche No. 1 - Tangential	SO ₂ , SO ₃	Grab	EPA Method 6 modified by Exxon Research and Engineering Company	Location of grab sample was at boiler outlet before air pre-heater. A minimum of 12 sampling points per boiler were used.	9
Wm. J. Neal - Front wall Leland Olds No. 8 - Horizontally opposed Milton R. Young - Cyclone Hoot Lake - Tangential	SO ₂ , SO ₃	Grab	Sulfur oxide condenser described by Lisle and Sensenbough.	Single point sampling. Usually samples were collected in the duct between boiler exit and the air heater. In one case (not specified) SO ₂ samples were collected from stack.	10
Stations No. 1 - Tangential No. 2 - Tangential No. 3 - Cyclone	SO ₂	Grab	EPA Method 6. Hydrogen peroxide bubblers used to absorb SO ₂ .	For Stations No. 1 and No. 2 samples were collected from the stack downstream of the scrubber (Station No. 1) or ESP (Station No. 2). For Station No. 3 sample was collected from stack leaving cyclone collectors.	11
Berry No. 2 - Tangential Berry No. 4 - Tangential	SO ₂	Grab for Berry No. 2 Continuous for Berry No. 4	Method 6 for Berry No. 2 samples. Beckman infrared for Berry No. 4.a	Sample collected from economizer outlet from a single average point using a heated sample line (for Berry No. 2). Twelve sample points were used to collect SO ₂ samples from Berry No. 4.	12
Columbia No. 1 - Tangential Huntington Canyon No. 2 - Tangential	SO ₂	Grab	Wet chemistry	Single point sample from left economizer outlet duct using a heated sample line.	14

^aReport specified only "wet chemistry" Reference 18.

Multiple point sampling using EPA Method No. 6 was used during test programs reported in References 8, 9, and 11.*

In these test programs, a combined EPA Method 5 (particulate test) and Method 6 were combined by changing the situations in the impingers from distilled water to hydrogen peroxide and isopropyl alcohol (as described in EPA Reference Method 8 — Reference 13).

Another source of error associated with grab sampling comes from sample handling and analysis. Errors due to these operations can be very significant if contamination is not avoided and prescribed sample procedures are not followed closely. Unfortunately these errors are impossible to identify and quantify because fully documented procedures for each of these test programs are not available.

Continuous monitors were used to collect SO₂ data from only two sources, namely Barry No. 4 (Reference 12) and Willows Creek No. 5 (Reference 7). In the case of Barry No. 4, the use of continuous monitors permitted the measurement of sulfur dioxide from a composite of 12 individual flue gas samples. In the case of the Willows Creek No. 5 tests, it is believed that intermittent grab samples were taken from six individual test points. This assumption of continuous grab samples is based on the fact that the ultra-violet adsorption instrument analyzes one grab sample at a time.

One common source of error for these two analyzers, as with all electronic analyzers in general, is in the calibration of the instrument. Proper calibration procedures are necessary to account for changes in instrument response caused by drift, instrument wear and analyzer contamination. Another source of error associated with the NDIR alone is in the sample handling and conditioning interface necessary with the use of this instrument. The interface removes particulate and moisture from the flue gas sample prior to exposing the sample to the sensor. This interface can be a source of errors because of leaks or doesn't provide sufficient conditioning.

* EPA Method 6 does not specifically require traversing the stack. However, composite samples might have been taken because Methods 5 and 6 were combined to measure particulate and sulfur emissions during these test programs.

The UV analyzer is usually located next to the stack; therefore, it avoids the use of long, potentially leaky sample lines. Furthermore, this instrument does not require the removal of moisture from the flue gas as long as the sample is maintained above its water dew point.

In conclusion, measuring error probably caused many of the data to show conversion of over 100 percent. The most easily identified error is that due to single point grab sampling instead of multiple point sampling or traversing. Other errors stemming from instrument operation, sample handling, and fuel sampling and analysis are difficult to identify, so they can only be speculated upon.

A brief description of the type of instrumentation used in each of the field tests investigated follows.

Modified Berk and Burdick Method

The Berk and Burdick Method used in Reference 6 uses an acidimeter type of analysis for determining SO_2 and SO_3 emissions in power plant effluents. The original method described in Reference 19 was shown to have interferences in the analysis of SO_2 when acid gases such as NO_2 , HCl , NH_3 and organic acid were also present in the measured gases.* This interference caused the SO_2 readings to be 15 to 50 percent higher than the theoretically expected values.

However, the reported SO_2 , SO_3 emissions from Units "A" through "D" in Reference 6 were measured using a modified version of the Berk and Burdick Method. The modification consisted of using hydrochloric and benzidine solutions when titrating the flue gas samples. These solutions eliminate the interference of Cl , NO_2 and organic acid gases (Reference 21).

Lisle and Sensenbough Method

For the tests performed on the Hoot Lake, Milton N. Young, Leland Olds and William J. Neal boilers (Reference 10), a modified sulfur oxide condenser was used. This condenser was first devised by Goksoyn and Ross (Reference 22) and later investigated by Lisle and Sensenbough (Reference 23).

*These acids are quite frequently found in flue gases from combustion of coal (Reference 20).

The intake apparatus consists of a glass heated probe followed by a helical glass coil and a glass fit. The coil is immersed in a heated water jacket which permits moisturizing the condenser temperature between the acid dew point and the water dew point. Since the acid dew point can be defined as "the temperature at which the combustion gases are saturated with sulfuric acid," then the dew point-acid concentration relationship can be determined for known amounts of sulfur oxide inlets to the condenser. This relationship is then used to determine unknown concentrations of sulfur oxide based on the flue gas dew points. The demonstrated accuracy of this apparatus for SO_3 measurement has been reported to be ± 0.3 ppm in the range of concentrations normally encountered in stack flue gases.

Ultraviolet Absorption Method

The extractive ultraviolet absorption method employed in Reference 7 consists of measuring electrical signals generated by wavelength phototubes which measure intensity of light beams. The instrument uses a sample and a reference light beam. Sample gases containing SO_2 are passed through the sample beam. SO_2 absorbs light at certain wavelength causing a change in intensity of the beam. The change in intensity is detected by the phototube which in turn releases an electrical signal proportional to the concentration of the SO_2 in the gas.

Nondispersive Infrared Method

The nondispersive infrared analyzer (NDIR) used to measure SO_2 emissions from Barry No. 2 (Reference 12) is the most common continuous monitoring technique for SO_2 measurement.

The NDIR technique consists of either one light source with a light chopper or two identical sources whose beams are directed through two different cells. One of the cells contains a gas which does not absorb infrared energy at the same wavelengths at which sulfur dioxide absorbs infrared energy. Passing through the other cell is the sampled stack gas. The beams pass through both of these cells and into different half sections of a reference chamber. Separating the two half sections of the reference chamber is a flexible metal diaphragm. Both sections contain the

same amount of SO_2 vapor kept at the same atmospheric pressure. The degree of absorption of infrared energy by the sample gas is directly proportional to the amount of SO_2 in the sample gas. The absorption by the sample gas will proportionally reduce the absorption by the SO_2 vapor in the corresponding half section of the reference chamber. The difference between the energy absorptions in the two halves on the reference chamber, then, is a measurement of the concentration of SO_2 in the sample gas.

The primary sources of error in the NDIR method are the blocking of the transmission of the light beam by particulates and the inadvertent absorption of infrared energy by moisture in the sample gas. Both of these sources of error can be minimized by adequate interfacing equipment.

The sampling interface used with an NDIR analyzer must be capable of removing flyash and particulate matter as well as removing or determining the quantity of moisture in the sample. Particulate matter will tend to collect on the windows of the sample cell. Water vapor will interfere inasmuch as the SO_2 absorption band is overlapped by a water system in the 1200-cm^{-1} to 1400-cm^{-1} region (Reference 24).

U.S. EPA Method 6

This method uses a glass probe followed by a set of four impingers immersed in an ice bath. A gas sample is extracted from the sampling point in the stack. The sulfuric acid mist, including SO_3 and SO_2 , are separated. SO_3 is collected in the first impinger bubbles containing isopropyl alcohol solution, while SO_2 is collected in the following two impingers containing an hydrogen peroxide solution. Possible interference due to cations and fluorides in the flue gas are eliminated by inserting a glass wool filter in the probe. The probe is maintained at a temperature higher than the dew point of the water in the flue gas. The samples are titrated with the Barium-thorin method to measure SO_2 and SO_3 .

APPENDIX D

TABLE OF CONVERSION UNITS

SI Metric to English Conversion Factors

<u>To Convert From</u>	<u>To</u>	<u>Multiply by</u>
J/g	Btu/lb	4.299×10^{-1}
MJ/S	10^6 Btu/hr	3.412
ng/J	lb/ 10^6 Btu	2.326×10^{-3}
kg/S	10^3 lbs/hr	7.936

English to SI Metric Conversion Factors

<u>To Convert From</u>	<u>To</u>	<u>Multiply by</u>
Btu	J	1.0548×10^3
Btu/lb	J/g	2.326
10^6 Btu/hr	MJ/S	2.9307×10^{-1}
lb/ 10^6 Btu	ng/J	4.299×10^2
10^3 lbs/hr	kg/S	1.26×10^{-1}
MW (electrical)	J/hr	1.0548×10^{10} (assumes 34 percent plant efficiency)

J = Joule

g = gram

S = second

W = watts

M = mega (10^6)

n = nano (10^{-9})

k = kilo (10^3)

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Boiler Design and Operating Variables Affecting Uncontrolled Sulfur Emissions from Pulverized Coal-Fired Steam Generators		5. REPORT DATE February, 1978
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Carlo Castaldini & Meredith Angwin		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Acurex Corporation/Aerotherm Division 485 Clyde Avenue Mountain View, California 94042		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-02-2611
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Protection Agency Office of Air Quality Planning and Standards (MD-13) Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED Final
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The report presents an analysis of the data from eight field test reports for twenty-one steam generator/coal type combinations. The data were analyzed to determine boiler design and operating variables which affect SO₂ emissions, the extent to which emissions were affected, and trends in conversion of sulfur in coal to SO₂, SO₃, and solid sulfates.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT Release Unlimited	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 80
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

