SULFUR SOLUBILITY IN SLAGS FOR CYCLONE COAL COMBUSTORS

by

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I. INTRODUCTION

This study was conducted to select potential slag compositions for use in a slagging, staged, cyclone coal combustor, and to obtain the necessary data to evaluate the desulfurizing ability of the combustor. The first stage of such a combustor would be operated quite reducing to facilitate sulfur removal by a slag formed from the coal ash and inorganic additives (e.g., lime). A tangential motion imparted to the gas would throw ash, coal, and additives to the combustor wall where they would combine to form a molten slag. This slag, containing some dissolved sulfur, would continually drain out of a taphole at the exit end of the horizontally-placed cylindrical combustor. Advantages of this type of combustor are removal of some sulfur, low particulate emissions, and low NO_x emissions.

This paper will be divided into three parts. First, the selection of slag compositions will be outlined. Second, sulfide capacity measurements of these slags will be discussed. Third, the desulfurizing potential of a slagging, cyclone combustor will be evaluated using these measurements.

II. SLAG COMPOSITION SELECTION

The strategy was first to select possible additives, then locate phase diagrams for systems of major ash components plus additives, and finally, select low-melting eutectic compositions as candidate slags. Additives were chosen for their known ability to form low-melting silicates (e.g., the alkalis) or for their known ability for desulfurization (e.g., the alkaline earth elements). An eastern coal was used for tests of a pilot combustor. Its ash composition, used to calculate additive compositions, is given in Table I. Major components, SiO_2, Al_2O_3, and Fe_2O_3, account for approximately 80% of the ash.

Ternary phase diagrams for the SiO_2-Al_2O_3-additive and SiO_2-FeO-additive systems were investigated for possible slag compositions. Unless otherwise noted, all phase diagrams were taken from Levin, et al (1-3) or Roth, et al (4). The selected compositions which were tested are given in Table II, as are estimated liquidus temperatures. Obviously, the liquidus temperature of the slag consisting of coal ash and the additive will be different from those given by the phase diagrams because of the minor components of the ash. However, the phase diagrams provide reasonable initial selections. Additive compositions and quantities are given in Table III.

III. SULFIDE CAPACITY MEASUREMENTS

Sulfide capacities of the selected slag compositions were measured to rate the slags and to provide data for evaluation of the operation of a combustor with these slags.

Chemistry of Sulfur in Slags: There has been considerable research on the chemistry of sulfur in slags reported in the literature. Most was aimed toward understanding and improving the desulfurization of iron and steel. These studies (5-7) have shown that at high oxygen potentials sulfur dissolves in slags as a sulfate, and at low oxygen potentials, the condition relevant to the two-stage combustor, sulfur dissolves as a sulfide. This can be represented by the reaction,

$$1/2\ S_2(g) + \left(O^{2-}\right) = 1/2\ O_2(g) + \left(S^{2-}\right). \qquad 1)$$

A quantity called the sulfide capacity (6) can be defined as:

$$C_S \equiv (\text{wt \% S}) \left(\frac{P_{O_2}}{P_{S_2}}\right)^{1/2} \qquad 2)$$

where wt % S refers to sulfur dissolved in the slag, and P_{O_2} and P_{S_2} are the partial pressures of oxygen and sulfur in the atmosphere with which the slag is equilibrated. The sulfide capacity for many slags has been found (5,6) to be independent of sulfur and oxygen potentials for wide ranges, and therefore is a useful quantity for rating slags. One exception relevant to this study is that, for slags containing FeO, C_S is expected to change with oxygen potential as the ratio of ferrous to ferric ions in the slag changes.

A review of the literature (5-22) showed that virtually all work on sulfur in slags was on systems relevant to the desulfurization of iron and steel and at temperatures ranging from 1400-1600°C. No data were found for low-melting slags (liquidus temperatures, approximately 1000-1100°C), and particularly for the iron-alkali-aluminosilicates from which many of the proposed compositions are composed. Therefore, experimental measurements were necessary to obtain the data needed for selection of slags.

Experimental Method: An equilibration technique was chosen to measure the sulfide capacities of the candidate slags. Slag samples were equilibrated with a $CO-CO_2-SO_2$ gas mixture having fixed oxygen and sulfur potentials, quenched to room temperature, and analyzed for sulfur. Sulfide capacities were then calculated from the sulfur concentrations using Equation 2. This technique was chosen because it is a direct method, and because the oxygen and sulfur potentials could be accurately controlled, and, if necessary, these could be set to match the activities for oxygen and sulfur which were anticipated in the actual coal combustor. The apparatus used for sulfide capacity measurements is shown schematically in Figure 1.

Slags were prepared by mixing preweighed amounts of additives and coal ash. The coal ash was obtained from Bituminous Coal Research, Inc. It was prepared by ashing Loveridge Seam, West Virginia coal in air at 750°C, followed by a reduction in a 60%CO-40%CO_2 gas at 1000°C, then cooled under nitrogen.

The gas compositions for each experiment were chosen to obtain as low an oxygen potential as possible, without reducing FeO to Fe metal. They were also chosen to obtain as low a sulfur potential as possible to match anticipated conditions in the actual combustor, yet large enough so that they could be prepared by mixing gases. The equilibration time for slag samples was determined by periodic analyses of the gas exiting the reactor. Quenched slag samples were analyzed for sulfur using a Leco titrator, and were analyzed for Si, Al, Fe, Na, K, Ca, Mg, Ti, and P by atomic absorption.

Results: Table IV gives the results for all sulfide capacity measurements. Figures 2 and 3 show ternary phase diagrams for selected systems on which the results are shown. Compositions shown were obtained by taking the three major components from the slag analyses and normalizing to 100%. The sulfide capacities are shown as a function of basicity in Figure 4, which summarizes all results of this study. Molar basicities (Σmole fraction bases/Σmole fraction acids) were calculated from the slag analyses.

It was found that after equilibration with the sulfurizing gas, certain slags in the $FeO-Al_2O_3-SiO_2$ system consisted of two immiscible liquids at 1100°C. One phase was a glass. The other phase had a metallic appearance and will be referred to as the "matte phase". The sulfide capacities for these slags should be considered as "apparent" because the sulfide capacity is defined for a single liquid phase. The matte phase in all of these double-phased slags contained 27-31% S, while the glass phase contained from 0.2 to 13% S. X-ray diffraction analyses showed the glass phase to be amorphous and the matte phase to contain FeS and FeS_2.

Discussion: Slag compositions 2-A-1, 2-A-7, 2-B-2, 2-C-1, 2-D-2, and 2-E-1 were closest to the coal ash composition given in Table I, containing 25-38% additive. As seen from Table IV, log C_S ranged from approximately -3.8 to -5.5 at 1100°C. Using the basicity of the ash calculated from Table I and the data shown in Figure 4, the sulfide capacity for pure ash is estimated to be approximately log C_S = -5.2. This is quite low as compared to results obtained for slags containing significant quantities of additives. As will be demonstrated later in the report, sulfur captured by coal ash slag with this sulfide capacity would be insignificant even at very favorable conditions - very low oxygen potential and low temperature.

There is a general correlation between sulfide capacity and basicity for a given system, as shown in Figure 4. There is a sharp drop in sulfide capacity between basicities of 1.0 to 0.5, which corresponds to the metasilicate to disilicate compositions in a binary silicate. For a given basicity, systems 2-A (FeO) and 2-C (FeO, CaO) have significantly higher sulfide capacities than systems 2-D (Na_2O) and 2-E (CaO), so that for a given basicity, FeO is superior to CaO and Na_2O as an additive. This is not what would be expected considering the standard free energies of formation of the sulfides and oxides of Fe, Ca, and Na.

Considering standard free energies for the formation of metal sulfides from metal oxides, FeO and CaO should be approximately equivalent desulfurizers and Na_2O should be superior. However, slags are far from ideal solutions because of the strong interactions among species -- particularly with SiO_2. This is why experimental measurements of sulfide capacities were needed. Free energy of mixing data (24) for Na_2O, CaO, and FeO binary silicates show that the chemical interaction with silica decreases in the order Na_2O, CaO, FeO, and for a given basicity, the activity of the basic oxide in the silicates increase in the order Na_2O, CaO, and FeO. On this basis, FeO should be a better desulfurizer than CaO or Na_2O. This is consistent with the present results. Not surprisingly, the metal oxide-silica interaction is a major factor in the desulfurization ability of the slag.

Several modifications of slags based on the $FeO-Al_2O_3-SiO_2$ system were tested to determine if a less expensive additive could be substituted for some of the iron or if additives could be used to reduce liquidus temperatures. Figure 4 shows that replacing a portion of the iron oxide in slags of the $FeO-Al_2O_3-SiO_2$ system with CaO (5 wt %) or MgO (12 wt %) had no effect on the sulfide capacities. Results for composition 2-C-1 also support this conclusion, because for this composition approximately 14% of the FeO of an equivalent composition in the $FeO-Al_2O_3-SiO_2$ system was replaced by CaO, with only a slight decrease in sulfide capacity. Replacement of portions of the SiO_2 in $FeO-Al_2O_3-SiO_2$ slags by B_2O_3 or P_2O_5 has no effect on sulfide capacities; therefore, these additives are potentially useful for reducing slag liquidus temperatures.

Figure 5 compares some results of this study to those found in the literature for similar slags at higher temperatures. These literature data were adjusted to a basicity of 1.65 using data given in Figure 4. The data from this study are quite consistent with the literature data. The linearity of the sulfide capacity with inverse temperature is consistent with the theoretical relationship,

$$\frac{d \ln C_S}{d(1/T)} = -\Delta H^\circ/R + H^M_{FeO}/R - H^M_{FeS}/R \qquad 3)$$

where ΔH° is the standard enthalpy change for the reaction,

$$1/2\ S_2(g) + FeO = 1/2\ O_2(g) + FeS \qquad 4)$$

and H^M_{FeO} and H^M_{FeS}

are the partial molar enthalpies of mixing of FeO and FeS in the slag. This relationship can be derived from Equation 2, the equilibrium constant for Equation 4 and the Gibbs-Helmholtz equation.

Most of the slags tested were found to have been partially or completely melted at 1100°C. However, at 1000°C, all slags from the $FeO-Al_2O_3-SiO_2$ system were not molten. It is thought that for these compositions the entire additive reacted with sulfur species in the atmosphere while none reacted with the SiO_2 or with other components in the ash. Hence, sulfide capacities measured from this experiment are not true sulfide capacities of the slags. Another point which supports this is that the "measured" sulfide capacities at 1000°C are greater than those at 1100°C, while Figure 5 shows the opposite trend for results for molten slags. Also, other literature data show that sulfide capacities generally increase with temperature.

This points out an inherent disadvantage in using a coal ash slag for desulfurization. When silica reacts with the desulfurizing agent, e.g., lime, the effectiveness of the desulfurizing compound is greatly reduced. Hence, it is desirable to design a desulfurizing combustor in which the ash does not react with the desulfurizing material.

IV. EVALUATION OF A PILOT COMBUSTOR

Calculations: The measured sulfide capacities were used to estimate sulfur emissions from a staged, slagging, cyclone combustor operating close to equilibrium. To calculate sulfur emissions, an equation for gas-slag chemical equilibrium for sulfur (Equation 2) and a mass balance for sulfur are solved simultaneously. First, the equilibrium gas compositions were calculated for the combustion of coal with air for a range of sulfur concentrations in the coal. This was done using Alcoa's Chemical Equilibrium Computer Program (23). Next, the concentrations of sulfur in the slags for equilibrium with the combustion gases were calculated. Finally, the quantity of additives needed to obtain these compositions were calculated from sulfur mass balances.

Results: Figure 6 shows an example of the results for these calculations, for combustion with 55% of stoichiometric air (stage 1) at 1100°C. A reasonable goal for the sulfur capture, considering projections of future EPA regulations, is 70%. The slag mass can vary between 85 and 350 g/kg coal (the upper limit was

established from a heat balance for Alcoa's pilot combustor), so the necessary log C_S for a 70% sulfur removal is between -2.75 and -3.3. A sulfide capacity of log C_S = -3.3 at 1100°C was obtained for certain slags based on the $FeO-Al_2O_3-SiO_2$ system, e.g., compositions 2-A-3 or 2-A-10.

As the combustion stoichiometry is decreased, the curves in Figures 6 are rotated counterclockwise about the origin, i.e., the sulfur removal is increased. An increase in temperature will have the opposite effect. The curves are rotated clockwise about the origin. However, for a particular slag composition the sulfide capacity increases with temperature, as shown in Figure 5. The net result of the two opposing effects (using the temperature behavior shown in Figure 5) is that the sulfur removal decreases with increasing temperature. In the range of coal-sulfur contents investigated, 2-6%, the fraction of sulfur removed by slag does not change with sulfur content in the coal. The total sulfur emitted increases with increasing sulfur concentration in the coal, but the sulfur removal by the slag also increases.

A final point to note regarding sulfur removal is that as the concentration of hydrogen in the combustion gases is decreased, the sulfur removal by the slag will increase. This is due to the high stability of the hydrogen-sulfur species, such as $H_2S(g)$, as compared to the carbon-sulfur species, such as COS. Thus, drying and charring of coal would significantly increase the theoretical removal of sulfur by the slag.

These calculations assume gas-slag equilibrium with respect to sulfur. This is probably only approached at the gas-slag surface near the exit of the first stage. At the entrance end of the combustor, the conditions would probably be more oxidizing than conditions calculated from the overall combustion stoichiometry, Ø, and thus sulfur solubility in the slag would be less than that calculated. At some depth below the slag surface near this entrance end of the first stage, the conditions would be more reducing than those calculated from the overall combustion stoichiometry. This would result in increased sulfur solubility. The actual combustion process and sulfur removal processes are quite complex, and the extent of sulfur removal will depend on the combustion kinetics. For example, consider two extreme situations. In one, where most coal is combusted after it hits the slagged wall, sulfur removal should be relatively good. In the other extreme, where all the coal is combusted before it reaches the slagged wall, sulfur removal would be relatively poor because it would be dependent on mass transport through the gas phase, and the gas has a relatively short residence time.

In summary, the kinetics of the combustion process is important with regard to sulfur removal. The kinetics must be considered either by modelling or experimentation before a final judgment on desulfurization in a slagging, cyclone combustor can be made. The results of this study show that it is theoretically possible.

V. CONCLUSIONS

Sulfide capacity measurements of relatively low melting (approximately 1100°C in most cases) slags based on the $FeO-Al_2O_3-SiO_2$, $FeO-Na_2O-SiO_2$, $FeO-CaO-SiO_2$, $Na_2O-Al_2O_3-SiO_2$, and $CaO-Al_2O_3-SiO_2$ systems but composed of coal ash + additives, have shown that the $FeO-Al_2O_3-SiO_2$-based slags had the highest sulfide capacities. For a given basicity, the sulfide capacities could be ranked in the following order: $FeO-Al_2O_3-SiO_2 > FeO-CaO-SiO_2 > FeO-Na_2O-SiO_2 > CaO-Al_2O_3-SiO_2 > Na_2O-Al_2O_3-SiO_2$. The chemical interaction of the basic oxides with silica appears to be a dominant factor controlling the sulfide capacity. There was good correlation between sulfide capacity and slag basicity, and sulfide capacities increased with temperature.

Calculations of the equilibrium sulfur removal for a commercial combustor using the measured sulfide capacities, showed that it was theoretically possible to remove 70% or more of the sulfur in coal. The sulfur removal increases with decreasing temperature, decreasing combustion stoichiometry in the first stage of the burner, increasing slag flow, and decreasing content of hydrogen in the fuel. This work showed that a slagging, cyclone combustor can remove sulfur into the slag, but kinetic modelling and/or experimentation is needed to prove whether or not the concept will work.

VI. ACKNOWLEDGEMENT

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TABLE I. ASH FROM LOVERIDGE SEAM (WEST VIRGINIA) COAL

Component	Ash Analysis: Wt Pct.	Ash Analysis: Normalized (excluding sulfur and taking iron as FeO)
Al_2O_3	18.4	24.1
SiO_2	44.5	47.8
Fe_2O_3	15.9	17.4 (FeO)
CaO	4.56	4.9
MgO	1.08	1.2
Na_2O	1.10	1.5
K_2O	1.11	1.3
TiO_2	1.20	1.1
SO_3	9.02	--
P_2O_5	0.33	0.5

TABLE II. NORMALIZED COMPOSITIONS OF CANDIDATE SLAGS - MAJOR COMPONENTS ONLY

Slag No.	Composition, Wt. Pct. SiO_2	Al_2O_3	FeO	Na_2O	CaO	Liquidus Temperature (°C) (Major Components Only)
2-A-1	46.0	19.9	34.1			1205
2-A-2	40.0	12.0	48.0			1083
2-A-3	18.1	5.9	76.0			1148
2-A-7	43.3	19.8	36.9			1220
2-A-8	35.3	14.1	50.6			1200
2-A-9	27.0	8.3	64.4			1150
2-A-10	23.6	5.9	70.4			1155
2-B-1	39.3		48.0	12.7		1000
2-B-2	56.4		21.8	21.8		?
2-B-3	33.2		26.2	40.6		1050
DSE-1	42.5		28.9	28.6		900
DSE-2	37.0		26.0	37.0		
2-C-1	37.7		46.4		15.7	1093
2-D-1	43.8	18.2		37.9		915
2-D-2	62.7	23.2		14.0		1063
2-D-3	61.6	12.2		26.2		732
2-E-1	42.1	20.1			37.8	1265
2-I-1	55.3	21.5	10.0	13.1		990

TABLE III. ADDITIVE COMPOSITIONS FOR CANDIDATE SLAGS

Slag No.	Additive Mass g/g Ash	Additive Composition, Wt. Pct.					
		SiO_2	Al_2O_3	Fe_2O_3	Na_2CO_3	CaO	Other
2-A-1	0.34	22.9		77.1			
2-A-2	1.20	27.0		73.0			
2-A-3	3.52	7.4		92.6			
2-A-4	3.74	7.0		87.2			5.8 % CaF_2
2-A-5	3.52	1.6		92.6			5.8 % B_2O_3
2-A-6	3.52	1.6		92.6			5.8 % P_2O_5
2-A-7	0.36	13.9		86.1			
2-A-8	0.89	13.9		86.1			
2-A-9	2.19	13.9		86.1			
2-A-10	3.47	13.9		86.1			
2-A-10b	4.07	11.8		73.5			14.7 % MgO
2-A-11	3.49	7.5		86.7		2.5	3.4 % CaF_2
2-A-12	4.99	13.9		86.1			
2-B-1	0.69			65.7	34.2		
2-B-2	0.30			3.9	96.1		
2-B-3	1.20			18.9	81.1		
DSE-1	0.69			24.2	75.8		
DSE-2	0.97			18.5	81.5		
2-C-1	0.61			75.5		24.5	
2-D-1	0.93	10.9			89.1		
2-D-2	0.40	43.8			56.2		
2-D-3	1.60	46.3			53.7		
2-E-1	0.43	6.3				93.7	
2-I-1	0.99	49.1	13.5		37.4		

TABLE IV. SULFIDE CAPACITY MEASUREMENTS

Exp't. No.	T (°C)	Run Time (h)	Slag Composition	Wt % S	Log C_S	Comments
2*	1100	24	DSE-1	4.22	-4.31	
			"	5.34	-4.21	
			2-B-1	6.05	-4.16	
			2-B-2	0.26	-5.52	
			2-D-1	0.96	-4.96	
			2-D-2	0.87	-5.00	Did not melt
			2-D-3	0.69	-5.10	
4**	1100	115	DSE-1	4.31	-4.06	
			2-A-1	4.80	-4.01	
			2-A-2			Sample crept out
			2-A-3	22.5	-3.34	2 phases
			2-A-4	23.5	-3.32	2 phases
			2-C-1	7.91	-3.79	
5**	1100	144.6	2-A-5	20.2	-3.38	2 phases
			2-A-6	13.4	-3.56	2 phases
			2-A-7	5.06	-3.99	
			2-A-8	9.81	-3.70	
			2-A-9	16.6	-3.47	2 phases
			2-A-10	19.1	-3.41	2 phases
			2-A-11			Sample crept out
			2-B-3	2.65	-4.27	
7***	1000	168.75	2-A-3	25.4		Did not melt
			2-A-4	25.1		" " "
			2-A-5	25.5		" " "
			2-A-6	24.1		" " "
			2-A-10	23.6		" " "
			2-A-11	24.2		" " "
			2-A-12	25.8		" " "
			2-A-3a	26.3		" " "
			2-I-1	0.44	-5.04	
11****	1300	70.0	2-A-3	2.67	-2.86	
			2-A-10	1.97	-3.00	
			2-A-10b	3.10	-2.80	

* Gas Composition - 70%CO-29.5% CO_2-0.5%SO_2

$X_{O_2} = 7.2 \times 10^{-14}$, $X_{S_2} = 5.4 \times 10^{-4}$

** Gas Composition - 70.2%CO-29.6%CO_2-0.25%SO_2

$X_{O_2} = 6.8 \times 10^{-14}$, $X_{S_2} = 1.6 \times 10^{-4}$

*** Gas Composition - 74.5%CO-25.3%CO_2-0.18%SO_2

$X_{O_2} = 6.8 \times 10^{-14}$, $X_{S_2} = 1.6 \times 10^{-4}$

**** Gas Composition - 66.3%CO-33.6%CO_2-0.14%SO_2

$X_{O_2} = 4.9 \times 10^{-11}$, $X_{S_2} = 1.9 \times 10^{-4}$

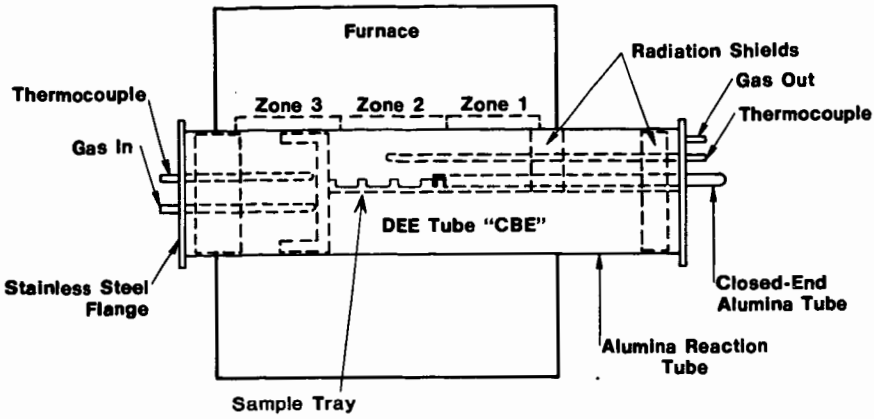

FIGURE 1. REACTOR USED FOR SULFIDE CAPACITY MEASUREMENTS.

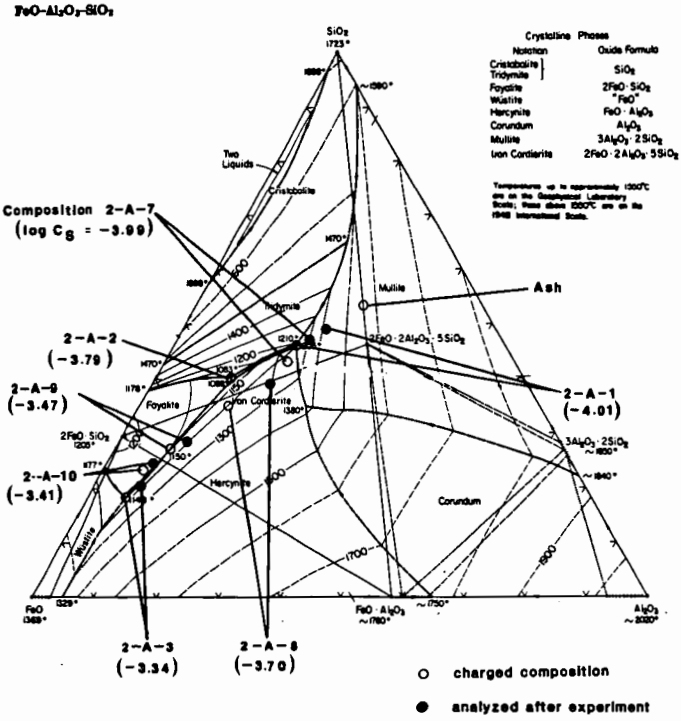

FIGURE 2. THE $FeO-Al_2O_3-SiO_2$ SYSTEM (2-A) WITH MEASURED SULFIDE CAPACITIES INDICATED. PHASE DIAGRAMS TAKEN FROM REFERENCE (1). OXIDE PHASES IN EQUILIBRIUM WITH METALLIC IRON.

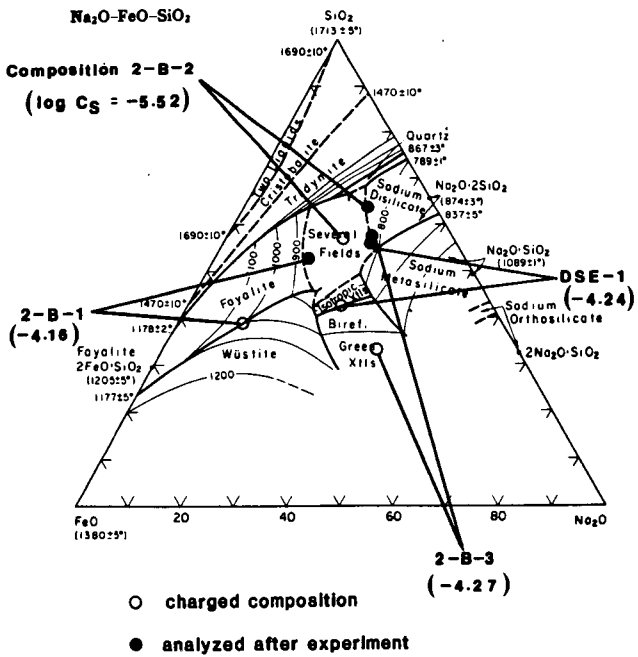

FIGURE 3. THE $FeO-Na_2O-SiO_2$ SYSTEM (2-B) WITH MEASURED SULFIDE CAPACITIES INDICATED. PHASE DIAGRAM TAKEN FROM REFERENCE (2). OXIDE PHASES IN EQUILIBRIUM WITH METALLIC IRON.

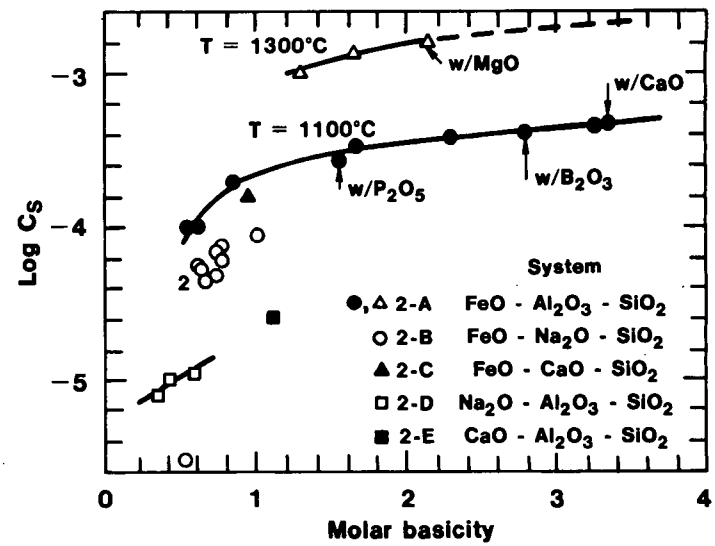

FIGURE 4. MEASURED SULFIDE CAPACITIES OF CANDIDATE SLAGS. BASICITY CALCULATED FROM CHEMICAL ANALYSES. POINTS DENOTED BY w/P_2O_5 AND w/B_2O_3, REPRESENT SLAGS IN WHICH 5% SiO_2 WAS REPLACED BY 5% OF THESE OXIDES. POINT DENOTED BY w/CaO IS FOR SLAG TO WHICH 5% CaF_2 WAS ADDED, BUT ALL FLUORINE WAS LOST DURING EXPERIMENT. POINT DENOTED BY w/MgO FOR SLAG TO WHICH 12% MgO WAS ADDED.

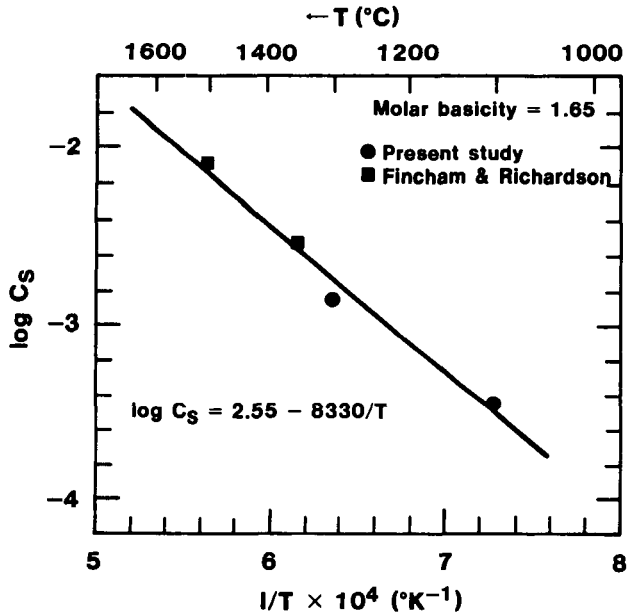

FIGURE 5. COMPARISON OF RESULTS FROM THIS STUDY TO THOSE OF FINCHAM AND RICHARDSON (6) FOR AN IRON SILICATE WITH MOLAR BASICITY OF 1.65. DATA FROM FINCHAM AND RICHARDSON WERE FOR PURE IRON SILICATES WHILE THESE FROM THE PRESENT STUDY CONTAINED SOME COAL ASH. DATA FROM FINCHAM AND RICHARDSON WERE CORRECTED FOR BASICITY USING DATA FROM THE PRESENT STUDY.

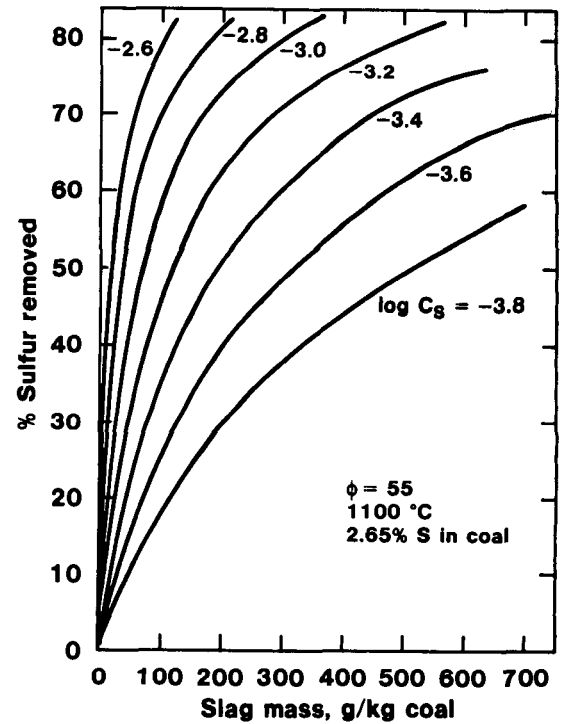

FIGURE 6. EQUILIBRIUM SULFUR REMOVAL BY SLAG FOR A COMBUSTOR OPERATING WITH LOVERIDGE SEAM (WEST VIRGINIA) COAL.