

THERMOCHEMISTRY OF THE Fe-O-S SYSTEM AS A
DESULFURIZER IN COAL COMBUSTION ATMOSPHERES:
PART I - Fe-FeO-LIQUID EQUILIBRIUM

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Key words: Iron oxysulfide, slagging burner, desulfurization

INTRODUCTION

Development in slagging combustors for utility coal combustion is being driven by several factors:

- * Removal of coal combustion residues as dense constituents at the source of combustion to reduce ash transfer to heat exchangers and down-stream fly ash capture devices,
- * Incorporation of staged-combustion to minimize NO_x emissions,
- * Utilization of added sorbents to reduce SO_x emissions,
- * Capability of operation at elevated pressures suitable for combined cycle operation.

A recent survey¹ indicated that lime or limestone was currently the only sorbent being injected in slagging utility burners for those systems close to, or currently undergoing commercial development. Some researchers, notably Avco² have experimented with added iron as a sorbent material with initial success. The results of some preliminary studies by AMAX on iron oxide additions to the reducing stage of a small coal burner was reported³ to result in up to 90 percent sulfur removal into a compact residue. This residue appeared to be relatively inert with respect to sulfur re-emission when exposed to moisture. Avco confirm these preliminary findings in experiments conducted late in 1989.

This paper is written entirely from a thermodynamic point of view. It compares the degree of desulfurization which can be achieved using an iron system with a calcium-based system operating under both reducing conditions (to produce calcium sulfide) and oxidizing conditions (to produce calcium sulfate). For this study calculations were made on an Illinois #2 coal as the fuel. They are restricted to those sulfur potentials which occur for the four phase equilibrium: gas + iron + wustite (FeO) + liquid iron oxysulfide.

Iron may be considered a potential competitor to lime as a sorbent for several reasons:

- * It forms a series of low-melting-point liquid solutions with iron and oxygen under reducing conditions. These liquids should be highly reactive with respect to absorption of sulfur in the gases which they contact. Because they are liquids rather than solids, good internal mixing under the high shear conditions of cyclonic burners should enhance the kinetics of absorption and also achieve sulfur absorption closer to the predicted stoichiometry than would occur with a solid sorbent.

- * However, lime, being a solid, has been shown to require from two-to-five times the stoichiometric ratio of calcium-to-sulfur⁴ in order to produce a high degree of desulfurization.
- * Iron in the form of taconite concentrates (magnetite) is cost-competitive with lime at locations close to Great Lakes' ports (approximately \$30/short ton, FOB).

THERMODYNAMIC ANALYSIS

Calculations are based upon a Western Illinois Coal (Illinois No. 2), described as "Colchester, low ash, high pyritic sulfur" from sample IBC 102⁵. This coal, of the assay given below, was factored into the calculations as 100 grams of coal on dry basis plus 14.2 grams moisture:

<u>Constituent</u>	<u>% by Wt.</u>
Carbon	73.92
Hydrogen	5.29
Nitrogen	1.52
Total sulfur	3.29
Oxygen	9.02 (not included in ash)
Ash	<u>6.9</u>
Total	100.0 (dry basis)
 Moisture	 14.2
BTU/lb	13,582

An interactive computer program was developed which enables coal assays to be varied as well as combustion conditions including temperature, total pressure coal composition, moisture content, volume of air, etc. Data were taken from Kubaschewski and Alcock⁶ for the thermodynamics of the gas phase interactions and for the stabilities of the calcium compounds. The iron oxygen-sulfur systems incorporates data from Darken and Gurry⁷, Bog and Rosenqvist⁸, Rosenqvist and Hartvig⁹, and Burgmann et al.¹⁰ as reported by Turkdogan and Kor.¹¹

The results of these calculations are shown in Figure 1 for the system Ca-S-O. This figure is a predominance diagram in which the equilibrium phase regions are designated on a logarithmic plot of partial pressures of sulfur (taking the dimer as the predominant elemental sulfur species) on the ordinate and log oxygen partial pressure as a measure of the chemical potential of oxygen on the abscissa. The solid lines represent conditions at 1000° C. and the dashed lines at 1300° C., respectively. As is expected, calcium sulfide is oxidized upon increasing the oxygen potential to the sulfate form and can only be maintained under the reducing conditions shown. As temperature is increased (dashed lines) the transition from sulfide to sulfate occurs under more oxidizing conditions. Also as temperature is increased the equilibrium between sulfide and oxide occurs at lower sulfur pressures in the equilibrium between CaS and CaO; however, the sulfur pressures for the equilibrium between CaO and CaSO₄ phases occur for higher sulfur pressures as temperature is raised.

Using the interactive program and the coal composition given above, the calculations in Figure 2 on the CaO/CaS/gas system show the anticipated equilibrium sulfur concentration reported as pounds of SO₂ per million BTU against temperature. For this plot the partial pressure of oxygen was arbitrarily taken at 10⁻¹² atmospheres with a total gas pressure of 1 atmosphere. The thermodynamic conditions are for the reducing stage of a two-stage combustor; however, the calculations for the sulfur dioxide emissions (ordinate) are based upon stoichiometric conditions existing in the second stage of the combustor. Figure 2 substantiates the conditions borne out in Figure 1; that is, high temperatures for the calcium sulfide system yield better desulfurization.

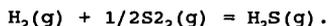
The converse is true for lime used as a sorbent under oxidizing conditions; i. e., with calcium sulfate as the product of reaction. Figure 3 shows that for temperatures much above 1150° C., the sulfur pressure rises rapidly. The conditions chosen were for an oxygen pressure of 0.05 atmospheres, or a slight excess of oxygen over stoichiometric requirements. In Figures 2 and 3 the theoretical dosage of lime is also plotted. As the lime reacts with sulfur, the dosage of lime required, of course, increases (Figure 1); whereas, the converse is true for Figure 3 where lime becomes less effective as a desulfurizer.

Figure 4 is a ternary projection of the liquidus surfaces in the Fe-O-S system showing the phase pyrrhotite (FeS) at the lower right hand corner. The liquid phase is seen to be in the thermal "trough" with a ternary eutectic of 920° C. From this ternary eutectic the labeled isotherms diverge outward to form the steep walls of this valley. The region in this paper for which calculations were made is the heavy diagonal line toward the left-hand wall of this trough which marks the boundary between the regions of iron/wustite/and liquid.

Data summarized by Turkdogan and Kor have been employed in our calculations. Figure 5 is a plot of the conditions of oxygen and sulfur potential as a function of temperature to maintain this four phase equilibrium (three condensed phases plus gas). This plot is not for a system of constant composition but for the composition along the solid line shown in the previous figure. As temperature rises, the oxygen partial pressure is shown to rise, but interestingly, the sulfur partial pressure shown on a log scale drops sharply. Part of this drop can be attributed toward the increasing solubility limit of the liquid phase (closer to lower sulfur concentrations); nevertheless, the rapid drop in sulfur partial pressure is steeper than would be predicted merely by a shift in composition to lower sulfur contents. Even at 1300°C the chemical potential of sulfur, as measured by the parameter, $-RT \ln P_{S_2}$, is about 45,000 calories per gram mole corresponding to a partial pressure of sulfur of 5.58×10^{-7} atm. This is a fortuitous aspect of the iron-oxygen-sulfur system; i. e., the thermodynamic calculations on desulfurization show improvement with higher temperatures. Figure 6 is a plot for the Fe-O-S system similar to those for the lime-based systems in which this improved degree of desulfurization with increasing temperature is shown. The increased dosage of iron is also shown. For example at 1300°C an iron dosage for the coal composition for these calculations would be 15 grams per 100 grams of coal.

One of the objectives of this study is to develop an interactive computer program such that an operator of a slagging combustor can enter coal compositions and combustion conditions and determine the optimum process conditions required. Figure 7 shows the air requirements for 100 grams of dry coal and the theoretical percent sulfur removal which can be achieved.

Figure 8 shows the calculated concentrations of the major gas species as a function of temperature for the equilibrium between Fe/FeO/liquid/gas. The predominant species for these reducing conditions (corresponding to a combustion stoichiometry of approximately 55% of the required air for complete combustion) are N₂ and CO followed by CO₂, H₂, and H₂O in that order. The total sulfur pressure is the sum of all the sulfur-bearing species with H₂S being the predominant sulfur carrier. Lower rank coals with higher hydrogen water vapor contents would be expected to carry more sulfur into the gas phase. Since the pressure of the sulfur species, S₂, is fixed by the Fe-O-S equilibria, the actual amount of sulfur in the gas phase is determined principally by the equilibrium:



This equilibrium has an equilibrium constant somewhat greater than unity. Also the pressure of H₂S is proportional only to the square root of the sulfur pressure but varies linearly with hydrogen pressure. It follows, then, that iron oxysulfide would perform best on dry, high-rank coals.

CONCLUSIONS

The following can be concluded from this analysis:

- * In the Fe-O-S system for the four-phase contact, Fe/FeO/liquid/gas, higher temperatures result in greater degrees of desulfurization for the range of temperatures studied.
- * Lime added under oxidizing conditions to form sulfate as a reaction product is not practical as a sulfur sorbent at temperatures above 1175°C.
- * Inference is made that for iron oxysulfide as a sorbent, this liquid phase should exhibit a higher degree of utilization in liquid droplets than solid lime sorbents. Furthermore the kinetics of liquid/gas interactions should be more favorable than solid/gas interactions. This hypothesis will require further study in a dynamic burner system.
- * Further calculations are required to determine the process conditions to achieve effective sulfur removal for the two phases, liquid/gas. These calculations should be made for a range of coals of varying hydrogen and water contents.

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ACKNOWLEDGEMENT

The authors wish to express their appreciation to the Department of Energy contract #DOE/DE-FG22-89PC89778 for funding this study.

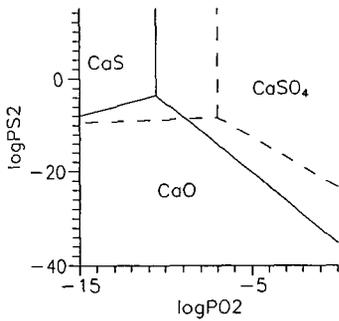


Figure 1. Predominance Diagram
Ca-S-O System.

Solid Lines - 1000° C.
Dashed Lines - 1300° C.

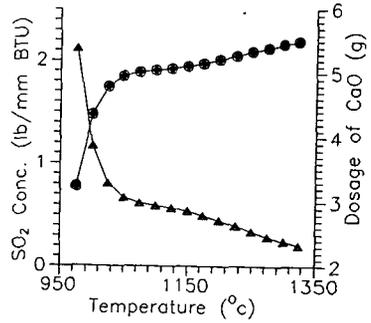


Figure 2. CaO/CaS/Gas
Stoichiometric SO₂
Conc. vs. Temp
at Oxygen Pressure: 10⁻¹²
Atm.

△ SO₂
○ Dosage of CaO

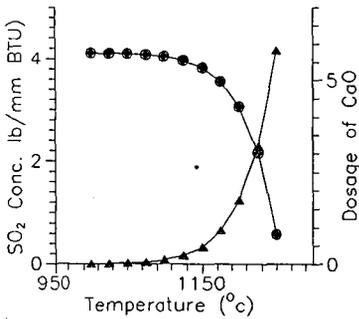


Figure 3. CaO/CaSO₄/Gas
Stoichiometric SO₂
at Oxygen Pressure: 0.05
Atm.

△ SO₂
○ Dosage of CaO

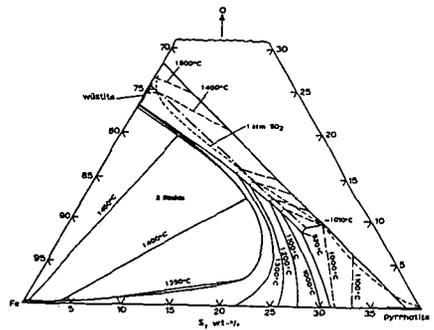


Figure 4. Ternary Section Fe/FeS/O System:
Projection Liquidus Surface.

After: Bog and Rosenqvist⁸
Hilty and Crafts¹²

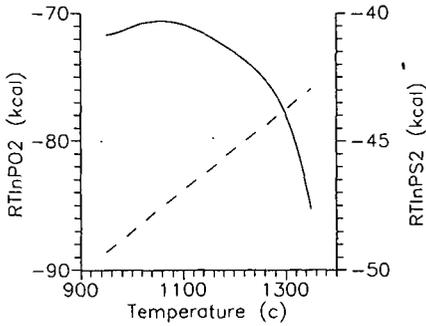


Figure 5. Fe/FeO/Liquid/Gas System
Chemical Potentials S, O.
— Sulfur
--- Oxygen

After: Turkdogan et al.¹¹

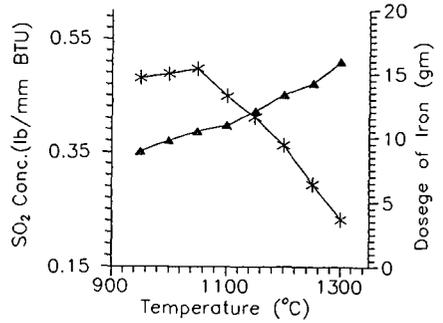


Figure 6. Fe/FeO/Liquid/Gas System
Stoichiometric SO
Conc. vs. Temp.
* SO₂ Concentration
△ Dosege of Iron

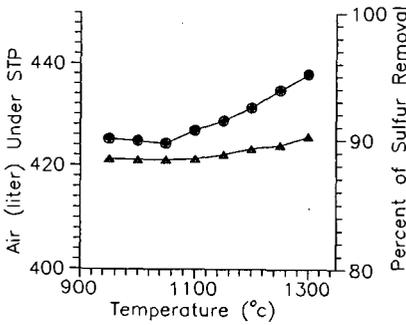


Figure 7. Fe/FeO/Liquid/Gas System
△ Air Dosage/100g Dry Coal &
○ % Sulfur Removal vs. Temp.

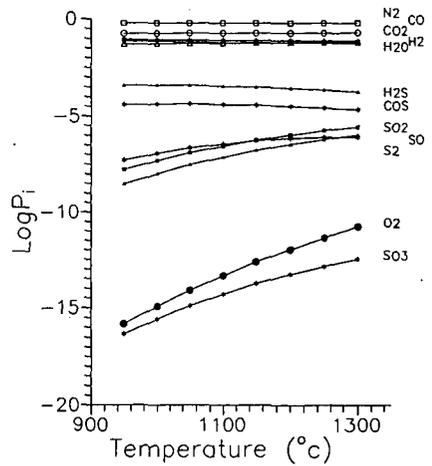


Figure 8. Calculated Partial Pressure (atm.)
vs. Temperature for Coal Combustion
Products in Equilibrium with
Fe/FeO/Liquid