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Technical Progress Report

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MOLTEN IRON OXYSULFIDE AS A SUPERIOR SULFUR SORBENT

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by

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ABSTRACT*

Slagging combustors with injected lime or limestone are being considered as replacements for conventional coal burners. They have advantages in that they can be staged to reduce NO_x and SO_x emissions. Iron oxide, as an alternative to lime or limestone may be effective not only as a desulfurizing agent, but under the right conditions of oxygen potential and after combination with sulfur, the reaction products of coal gases with iron oxide can act as a flux to produce a fluid phase. The thermodynamic conditions for optimum removal of sulfur from the first stage of a coal combustor are being determined by experiment and by use of existing data. Contour plots in which the pounds of SO₂ per million Btu of calorific power are plotted on isothermal ternary phase diagrams of the iron-oxygen-sulfur system. These contour plots determine the most favorable conditions for coal combustion in the presence of added iron oxide. Lowest SO₂ pressures are close to the phase boundary limit between iron saturation and the oxysulfide liquid phase. Experimental studies confirm the observations of previous investigators that the oxysulfide liquid exhibits a tendency to creep up and over the walls of containing vessels presumably as a result of surface tension effects. These effects, which make equilibration measurements difficult, may be favorable with respect to producing a high degree of reactivity of the oxysulfide with coal gases and resultant rapid reaction kinetics. Kinetic measurements, which are now being undertaken, will help to provide information on any such favorable effects.

*Underlined are key words.

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INTRODUCTION

In the prior quarterly reports, the combustion conditions were calculated on six Illinois Basin coals to determine what dosage of iron oxide and combustion stoichiometries are required in order to achieve a high degree of sulfur removal. Several sorbent systems were considered. These included the calcium-based system under reducing conditions to produce the phases $\text{CaS}/\text{CaO}/\text{gas}$ and under oxidizing conditions to produce $\text{CaSO}_4/\text{CaO}/\text{gas}$ as well as an iron-based system. This latter system is the primary subject of this research program. Prior calculations were for the four-phase equilibrium $\text{Fe}/\text{FeO}/\text{liquid (iron oxysulfide)}/\text{gas}$, for which data are available in the literature.^{1,2} These calculations were part of an interactive program which enabled the coal combustion conditions to be entered by an operator. The program then calculated the optimum conditions of air dosage to achieve desulfurization with lime or iron oxides.

In this past quarter, effort has been directed toward a determination of the combustion conditions which would yield the lowest levels of SO_2 in the gas phase in terms of the activities of oxygen, sulfur, and system temperature. These data are then superimposed upon an isothermal section of the iron-oxygen-sulfur system to determine the most favorable conditions for coal combustion and iron oxide dosage in order to achieve the lowest sulfur levels. The prior restriction that the gas phase be in equilibrium with the three condensed phases: $\text{FeO}/\text{Fe}/\text{Liquid}$ - is removed, and instead, calculations are now extended to the more general case of gas in equilibrium with the oxysulfide liquid. Data by Stofko *et al.*³ were incorporated into the calculations.

SUMMARY AND CONCLUSIONS

- Equilibrium measurements of gas compositions over the liquid iron-oxysulfide phase have been made; however, analysis of the quenched liquids indicate that they exhibit a tendency to creep up and over the walls of containing vessels presumably as a result of surface tension effects. These effects, which make equilibration measurements difficult, may be favorable with respect to producing a high degree of reactivity of the oxysulfide with coal gases and resultant rapid reaction kinetics.

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- 1 Turkdogan, E.T. and Kor, G.J.W., "Sulfides and Oxides in the Fe-Mn Alloys: Part I, Phase Relations in the Fe-Mn-S-O System," Metallurgical Transactions, Vol. 2, June 1971, pps. 1561-1578.
 - 2 Turkdogan, E.T., Physico-Chemical Properties of Molten Slags and Glasses, The Metals Society, London (1983), pps. 143-151.
 - 3 Stofko, M., Schmiedl, J., and Rosenqvist, T., "Thermodynamics of Iron-Sulfur-Oxygen Melts at 1200°C," Scand. J. Metallurgy, Vol. 3, (1974), pps. 113-118.

- A series of contour maps as equi-composition locii expressed as pounds of SO_2 per million Btu of coal calorific power (at stoichiometric combustion) have been calculated as a function of oxygen and sulfur chemical potentials for the gas atmospheres which would arise for combustion of an Illinois Basin Coal. These calculations have been made at 1200°, 1300°, 1400°, and 1450° C. These contour maps show steep increases in sulfur dioxide emissions will occur as oxygen pressure (in atmospheres) increases to values above 10^{-8} at 1450°C and to values above 10^{-10} at 1200°C.
- Using a solution model and existing data on the Fe-O-S system at 1200° C, activity data on sulfur and oxygen have been calculated for a range of compositions in the oxysulfide single condensed phase region. These calculations extend the data which were determined in the quarterly report of the period prior to the last quarterly report. These calculations have resulted in a contour map for sulfur dioxide levels which would be produced upon burning an Illinois Coal (IBC-102C) to stoichiometric combustion with the first stage of the combustor (reducing stage) operating predetermined oxygen and sulfur chemical potentials.
- The most favorable conditions for lowest sulfur levels at 1200°C occur at compositions close to iron saturation. For example: a level of SO_2 of 0.644 lbs/millions Btu's occurs at an oxysulfide concentration of 49.3 atom % iron, 27.2 atom% oxygen and 23.5 atom % sulfur. This represents an added magnetite level of 8.34% and an air rate of 410 liters STP per 100 g of dry coal. Increasing the sulfur content by only 3% nearly doubles the SO_2 level.
- Kinetic experiments are underway to expose single particles of magnetite to a pulse of a gas of sulfidizing and reducing gas, simulating coal combustion conditions. Upon quenching the exposed particle, it is examined for the extent of liquid phase formation around the magnetite core and the sulfur level of the liquid which is formed.

PLANS FOR NEXT QUARTER

In the next quarter, emphasis will be primarily on the kinetic studies, described in the paragraph above, and also extending the equilibrium calculations to higher temperatures, including 1400° and 1450°C. Effort will also be directed toward overcoming the anomalous surface tension effects in order to collect a sufficient sample of liquid phase for subsequent analysis for its resistance to aqueous and acid attack.

THERMODYNAMIC ANALYSIS

Four Cases are under examination:

- Case 1: Liquid oxysulfide, solid wustite (FeO)⁴ and solid iron in equilibrium with liquid oxysulfide;
- Case 2: Liquid oxysulfide in equilibrium with solid iron as a phase;
- Case 3: Liquid without the restriction of the presence of solid iron;
- Case 4: Gas phase equilibria without the presence of any condensed phase.

Restrictive Cases 1 and 2 were the subject of earlier Quarterly Reports. Case 3 is the general case where coal gases are in contact with a liquid phase, which acts as the sulfur sorber, and Case 4 is one in which the partial pressure of sulfur is a function entirely of the oxygen pressure and the type of coal being burned.

We have been using in our analysis an Illinois Basin Coal (IBC-102). Information on this coal is given in Table 1.

Table 1 Composition of IBC -102 Coal

<u>Constituent</u>	<u>% by Wt of IBC-102 Coal.</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

In this present report, we will review the results presented in Case 2, and then explore the results of Case 4 before developing Case 3, the particular case of interest to this program.

⁴ Actual composition is not stoichiometric FeO , but a compound containing iron, oxygen and sulfur.

Case 2: Liquid oxysulfide in equilibrium with solid iron as a phase.

Figure 1 is an isothermal section of the Fe-O-S System at 1200°C along a path of iron saturation. This plot is not the conventional ternary isothermal section, in that the axes are at right angles rather than an angle of 60 degrees. The pure iron corner of the diagram is off the paper at the lower left with oxygen content increasing along the abscissa, and similarly sulfur content increasing along the ordinate. The circles represent the phase boundary between the two condensed phase regions of iron plus liquid at the lower left of the figure (below and to the left of the line marked with circles). The region to the upper right, therefore, is the single-(condensed) phase region of liquid oxysulfide of variable composition. Along the diagonally slanted line (marked with circles) is the phase boundary. The left-hand axis should be read with this latter line. Toward the end of this line at the lower right the liquid comes into equilibrium with the solid phase *wustite*, a phase of stoichiometry close to FeO; however, the stoichiometry of this compound varies with oxygen potential as well at its melting point (ranging between 1371°C to 1242°C). The W-shaped curve, marked with triangles is the calculated value of SO₂ concentration (expressed as pounds SO₂ per million Btus for completely burned coal gases). The values are to be read with the right-hand axis. From this curve, one should note that the minimum in sulfur content of the gas phase occurs as compositions close to wustite saturation. As one proceeds to higher oxygen contents (beyond 30 percent oxygen), the phase *magnetite* is reached, which has much higher oxygen potentials, and as a result, the sulfur content in equilibrium with the liquid phase in contact with magnetite rises sharply.

The region of sulfur activity which we wish to explore in Case 3 is to the right of and above the slanting phase boundary line in this figure and preferably near the composition where the calculated SO₂ content shows a minimum.

Before this is undertaken, it is instructive to explore Case 4.

Case 4: Gas phase equilibria without the presence of any condensed phase.

Using literature values from the thermodynamic data and previously described⁵ interactive program, contour maps were generated for the temperatures 1200°, 1300°, 1400°, and 1450°C. These maps, which are given in Figures 2-5, are equi-compositional locii expressed as pounds of SO₂ per million Btu of coal calorific power, calculated for conditions of stoichiometric composition for IBC-102 coal under the reducing conditions of a first stage combustor operating at the sulfur and oxygen chemical potentials shown by the axes. The oxygen chemical potential given by the abscissa is represented by the logarithm of the oxygen partial pressure in atmospheres ($\log_{10} P_{O_2}$), and the ordinate is similarly the chemical potential of sulfur for the species S₂(gas) represented by $\log_{10} P_{S_2}$.

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Quarterly Report on this project (DOE/DE-FG22-89PC89778); Period: September 1 - November 30, 1990.

Figure 1. Isothermal Section Fe-O-S System at 1200°C along a Path of Iron-Saturation. Calculated Concentrations of SO₂ are for Conditions of Stoichiometric Combustion of IBC -102 Coal.

Figure 2. Equi-Composition Curves for Combustion Atmospheres of IBC-102 Coal at 1200°C. Pressures of Sulfur and Oxygen in Atmospheres, Equi-Compositional Loci in Units of Pounds SO₂/million Btu Calculated for Conditions of Stoichiometric Combustion of the Coal.

Figure 3. Equi-Composition Curves for Combustion Atmospheres of IBC-102 Coal at 1300°C. Pressures of Sulfur and Oxygen in *Atmospheres*, Equi-Compositional Loci in Units of *Pounds SO_2 /million Btu* Calculated for Conditions of Stoichiometric Combustion of the Coal.

Figure 4. Equi-Composition Curves for Combustion Atmospheres of IBC-102 Coal at 1400°C. Pressures of Sulfur and Oxygen in *Atmospheres*, Equi-Compositional Loci in Units of *Pounds SO_2 /million Btu* Calculated for Conditions of Stoichiometric Combustion of the Coal.

Figure 5. Equi-Composition Curves for Combustion Atmospheres of IBC-102 Coal at 1450°C . Pressures of Sulfur and Oxygen in *Atmospheres*, Equi-Compositional Loci in Units of *Pounds SO_2 /million Btu* Calculated for Conditions of Stoichiometric Combustion of the Coal.

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In examining Figure 2 (map at 1200°C), one can see that the lowest iso-SO₂-composition curve for 0.1 lbs SO₂ per million Btu is in the lower center of the plot at logP_{O₂} values near -10.5. At this temperature, the values of logP_{S₂} are approximately -7. As more oxidizing conditions are approached, i.e. less negative values of logP_{O₂}, the concentrations of SO₂ in the off-gas emerging from the second (stoichiometric) stage of combustion rises rapidly. In other words, slightly more oxidizing conditions increase the sulfur dioxide content of the gas. There is more flexibility for allowing more reducing conditions since the rise in value of the SO₂ concentration is much more gentle in that direction. As the temperature is increased (Figures 3-5), the locii shift to slightly higher values of SO₂ concentration (i.e., the curves move downward with increasing temperature.) Also the minimum values for SO₂ concentration move toward the right on the abscissa, i.e., toward higher oxygen potentials. It is possible now to superimpose these contour plots on isothermal sections of the iron-oxygen-sulfur system in order to maintain the minimum SO₂ concentrations which will satisfy the equilibria in the oxysulfide liquid phase.

In order to obtain an appreciation of the significance of the chemical potentials of oxygen which are shown on these four figures, Figure 6 is presented which is a calculation of the equivalence ratio⁶ at three temperatures (1000°, 1150°, and 1300°C) as a function of logP_{O₂}. By comparison of Figure 6 with the prior four figures, it is possible to see that the range of oxygen pressures for optimum sulfur removal is above but close to an equivalence ratio of unity. Lower temperatures require higher equivalence ratios (more reducing conditions).

In the review of a recently published paper⁷ on the first year's effort, the question arose regarding whether it were possible to operate a coal burner under conditions of high equivalence ratio and still maintain enough heat to sustain combustion. Figure 7 is the result of calculations on flame temperatures for as-received (moist) IBC-102 coal for the two conditions:

- No heat loss (adiabatic flame temperature) and
- 20 percent of the coal calorific power lost.

Clearly, there is no difficulty in attaining temperatures above 1500°C even with 20 % heat losses for equivalence ratios less than 2.0, a value much higher than that required for desulfurization with iron.

⁶ Equivalence Ratio defined as the fuel to oxygen molal ratio such that the ratio approaches unity for stoichiometric combustion to carbon dioxide and water

⁷ Hepworth, M. T. and Zhong, S.: "Thermodynamic Comparison of Lime as a Desulfurizer with Iron in Coal Combustion Atmospheres: Fe-FeO-Liquid Equilibrium," Energy and Fuels, 1991, 5 pp. 237-243.

Figure 6 Equivalence Ratio as a Function of Oxygen Potential for Three Temperatures, Calculated for IBC-102 Coal (Oxygen Pressure in Atmospheres).

Figure 7. Flame Temperature and Equivalence Ratio Calculated for Combustion of IBC-102 Coal.

Case 3: *Liquid oxysulfide in equilibrium with solid iron as a phase.*

Returning to Figures 2-5, the optimum conditions for lowest sulfur levels in an off-gas are seen in each contour map of iso-SO₂-composition curves as a low point in the "trough" in the lower center of the diagrams. The role of the iron oxysulfide phase as a sorbent is to establish a set of oxygen and sulfur chemical potentials which establish conditions in this "trough".

Figure 8 is the result of calculations and experimental conditions which yield these conditions. The results of calculations which were detailed in the appendix of the prior quarterly report⁸ are shown in this as a three-dimensional plot. In this plot the front corner of the diagram is the iron-corner with sulfur contents increasing from right to left and oxygen contents increasing from left to right. The vertical axis represents the calculated locus of off-gas sulfur concentrations. The lowest values of SO₂ content are seen to be in the leading edge of the surface, which is also the limit of the liquid phase where it is in equilibrium with iron. Only here are values of SO₂ concentrations significantly below unity. For concentrations moving toward the back of the diagram, the sulfur contents are seen to rise dramatically. Clearly there is a narrow region of optimum composition at this temperature. In the next quarter, we plan to expand the range of these diagrams to higher temperatures to determine how wide the compositions range may be. Clearly at higher temperatures, the region of liquid phase stability increases.

EXPERIMENTAL STUDIES

Equilibrium Measurements: Equilibrium measurements of gas compositions over the liquid iron-oxysulfide phase have been attempted at higher temperatures, e. g. 1400°C; however, analysis of the quenched liquids indicate that they exhibit a tendency to creep up and over the walls of containing vessels presumably as a result of surface tension effects. These effects, which make equilibration measurements difficult, may be favorable with respect to producing a high degree of reactivity of the oxysulfide with coal gases and resultant rapid reaction kinetics.

Experimental studies have already begun; however, initial work was temporarily suspended until an improved ventilation system was developed to avoid the possibility of leaks in the gas system which contains hydrogen and hydrogen sulfide. These modifications have been completed, and studies are now continuing with emphasis on extending the temperature range to higher values such as 1300° and 1400°C.

Kinetic Studies: Kinetic experiments are underway to expose single particles of magnetite to a pulse of a reactive gas of sulfidizing and reducing gas, simulating coal combustion conditions. This pulse ranges from 2 to 7 seconds in length after which time the reactive gas

⁸ Quarterly Report on this project (DOE/DE-FG22-89PC89778); Period: September 1 - November 30, 1990.

Figure 8. Isothermal Section of Ternary Phase Diagram for Fe-O-S System at 1200°C. Shown is a Portion of the Liquid OxySulfide Phase with Superimposed Iso-SO₂ Concentration Curves (lbs SO₂/MM Btu) Calculated for Stoichiometric Combustion of IBC-102 Coal.

is replaced by an inert gas and the sample is rapidly quenched in this latter atmosphere. Upon quenching the exposed particle, it is examined for the extent of liquid phase formation around the magnetite core and the sulfur level of the liquid which is formed. Analysis is by optical and electron microscopy and by microprobe analysis to determine sulfur contents of the particle.

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