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University of Minnesota

Final Report
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David Hunter, Contract Specialist
MOLTEN IRON OXYSULFIDE AS A SUPERIOR
SULFUR SORBENT
DOE/DE-FG22-89PC89778
by
Malcolm T. Hepworth, Principal Investigator
March 31, 1993

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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 operating under gasifier conditions and using added iron oxide as a sorbent have been determined by experiment and by use of existing data. Analysis of the phase equilibria in the multi-component system: C, H, O, Fe, S indicates that optimum conditions for deployment of the reducing stage of a multi-stage burner operating with iron injection are close to the boundary of the liquid iron oxysulfide phase as iron-saturation is approached, but avoiding the presence of iron. Three sets of experiments have been conducted:

- Equilibration at 1400°C between gas atmospheres containing oxygen and sulfur at controlled chemical potentials over oxysulfide melts to determine activity/composition relationships for the ternary isotherm in the Fe-O-S system,
 - Kinetic studies on reactions on milligram-scale between magnetite in a thermogravimetric device in simulated coal/gas atmospheres which are optimum for desulfurization
- and
- Studies on a 3 million btu per hour Dynamic Containment Burner located at a local utility plant (Northern States Power, High-Bridge Plant in Saint Paul, MN) in which magnetite is to be injected into simulated coal gas atmospheres (produced by combustion of hydrogen sulfide-spiked acetylene [C₂H₂]) under reducing conditions.

Experimental results of the equilibration studies confirm the solution model for oxygen and sulfur chemical potentials.

Results of small-scale kinetic experiments (100 mg samples) indicate that the kinetics of magnetite contained in small crucibles, when exposed to gas atmospheres in a thermo-gravimetric apparatus are slow (requiring tens of minutes rather than seconds) to approach 90% of sulfur-saturation. However, a model has been developed to explore reaction kinetics on much finer (30 micro-meter) particles which are characteristic of taconite concentrates which represent a potentially low-cost source of iron oxide. This model predicts that the reactivity of these fine particles is much higher than stagnant liquids contained in crucibles, indicating that they could effect desulfurization within the

residence time of a flame in a gasifier/burner system. Although prior studies¹ using a small bench-scale entrained-type burner have shown 90% desulfurization as feasible for feed rates of approximately 50 to 100 grams coal per minute, a 3 million Btu per hour burner has been set up at the Northern States Power High Bridge plant in Saint Paul, MN. This burner has a unique design and is termed a Dynamic Containment Burner. Although it has been operated on acetylene (C_2H_2) to simulate the hydrogen-carbon atomic ratio which would be encountered upon combustion of coal, it has not yet been tested on actual coal feeds nor with iron oxide additions during the combustion of high-sulfur coal. This burner would serve the purpose of contacting iron oxide and sulfur-bearing coal gases in a reducing vortex flame and then effecting the removal of the iron oxysulfide phase from the coal gases. Further studies are required with either this burner or a similar-type gasification device to determine the effectiveness of iron oxides as sorbents.

* Underlined are key words.

¹"Coal Slagging Burner for Producing Clean Low-Sulfur Fuel Gas," *U.S. Patent 4,599,955*, 7/15/86; and "Coal Combustion to Produce Clean Low-Sulfur Exhaust Gas," *U.S. Patents 4,598,652 and 4,572,085*, dated 7/8/86 and 2/25/86, respectively.

INTRODUCTION and SUMMARY

The studies which are described in this report cover the period from September 1989 to the present and had as their original objective an analysis of the conditions required to utilize iron oxysulfide, a liquid phase of variable composition, as a desulfurizing agent during the gasification of coal. Ancillary to this analysis was a comparison of iron oxysulfide with lime as sorbents both under conditions where lime reacts with sulfur-bearing gases to form calcium sulfate or alternately to form calcium sulfide as products. However, the primary thrust of the program is to determine the thermodynamic requirements necessary to achieve desulfurization by iron additions (for example low-cost taconite concentrate) during the combustion process in gasifiers operating at high equivalence ratios.

The program can be divided into four separate parts.

- Thermodynamic analysis of lime-based systems to determine the theoretical degree of desulfurization possible when gypsum or calcium sulfide is present as a reaction product.
- Thermodynamic analysis of iron-based systems to determine the optimum conditions required during the gasification of actual coals to achieve desulfurization.
- Bench-scale experiments on 100 milligram-scale specimens of iron oxide exposed to fuel-gas atmospheres to determine desulfurization kinetics
- Design and construction of a 3 mm Btu burner using a simulated fuel gas (hydrogen sulfide-spiked acetylene [C_2H_2]) to which iron oxide could be added to test the desulfurization kinetics. This latter study was added during the final year of the program in an extension, but at this time of writing, it has not been finally tested on gas/iron oxide mixtures.

Details are given in two Appendices: Appendix A is a thesis by Dr. Shaolin Zhong, in which the first three parts of the study are developed; Appendix B is a summary of work to date in developing the Dynamic Containment Burner.

The studies can be summarized as follows:

Since desulfurization with lime or limestone results in a solid product of fixed composition (i. e. CaS or $CaSO_4$), the process conditions required for utilization of lime as a desulfurizer are relatively simple to determine from existing thermodynamic data. These conditions are presented in a computer program, (see Appendix A), in which an operator of a combustor or gasifier can program in the coal compositions and determine

optimum conditions for coal desulfurization. At either low or high equivalence ratios (depending upon temperature and coal composition) lime is effective in sulfur removal; however, at intermediate equivalence ratios, neither calcium sulfide nor calcium sulfate is stable. As a consequence, lime is ineffective in these regimes which are fully developed in this report. The kinetics of desulfurization are for a gas/solid reaction, which may have potential disadvantages compared with gas/liquid desulfurization, but reaction problems with furnace enclosures and heat exchangers is not as great a consideration as would be the case if one were to desulfurize with a liquid phase.

On the other hand, the conditions for desulfurization with iron oxide to form a liquid iron oxysulfide phase of variable composition are more complex since another degree of thermodynamic freedom is involved in the analysis. This report details the procedures for determining optimum desulfurization with the surprising result that higher temperatures promote a higher degree of desulfurization in iron based systems up to the upper temperature of our calculations (1500°C). (This compares with a maximum temperature in lime-based systems in which sulfate is formed of 1100°C, above which temperature sulfate decomposes). Since a liquid containing sulfide-sulfur is formed, it is necessary to form and then remove this phase from the fuel gas prior to utilization of the fuel gas in complete (stoichiometric) combustion. If carry-over of liquid droplets of iron oxysulfide to an oxidizing regime were to occur, then oxidation of the sulfide sulfur to sulfur dioxide would occur with its release into the fuel gas. Therefore an effective gasification/combustion system is required which gasifies coal under conditions of high equivalence ratios at relative high temperatures. Also, during the gasification of the coal contact between the added iron oxides by this gas is required. Reduction of the solid iron oxides and their contact with sulfide-bearing gases to form oxysulfides must also occur, and subsequently the liquid oxysulfide products which are formed must be removed from the gas prior to its utilization in stoichiometric combustion. This sequence required the development of a specialized burner system which is detailed in Appendix B of this report.

Next, bench scale tests were conducted on individual small particles of magnetite in Thermogravimetric equipment and also on hot substrates. These tests indicated that the kinetics of such reactions were orders of magnitude slower than were required for effective desulfurization in a flame. Although disappointing, they led to the development of a model which predicted the actual kinetics of reactions on iron oxide particles to be reduced, reacted with sulfur and form liquid form droplets. The models gave encouragement for further scale-up testing in an actual burner system to determine the actual reaction kinetics.

As mentioned in the abstract, tests at 50 to 200 grams per minute feed rates of coal added to a crude laboratory burner system in a prior study had shown that greater than 90 % removal of sulfur was achievable from high-sulfur coals.

As a result of these earlier successful efforts, a six-month extension of time under the original Grant Budget was requested to determine if it would be possible to set up, test and apply a "Dynamic Containment Burner", a system under development by Wilhelm Reindl at the University of Minnesota. A description of this device and some operating conditions is found in Appendix B of this report. We were successful in setting up the burner at a local utility (Northern States Power Company: High Bridge Power Plant in Saint Paul, MN). Also tests were conducted on simulated gas atmospheres for coal combustion as detailed in Appendix B of this report. Unfortunately, funding was not sufficient to carry this added study beyond the tests detailed in the Appendix. In other words, we have not yet at the time of writing this report introduced iron oxide (taconite concentrates) into the burner to determine whether combustion, desulfurization, and separation of the iron oxysulfide can be accomplished in one unit operation. We continue to devote effort in early 1993 to perform some definitive tests on this burner. At present this burner system is being readied for experimental studies in which acetylene spiked with hydrogen sulfide will be used as a fuel. (Acetylene, C_2H_2 , was chosen since it approximates the atomic ratio of hydrogen to carbon in coal). Combustion will be partial at equivalence ratios ranging from 1.5 to 2.9 so that the product gases will contain about 5000 ppm H_2S . Iron oxide will then be introduced and the product gases will be measured before and during the iron additions.

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Appendices A and B to this final report detail the experimental studies and analysis which have been undertaken. An attempt will be made here only to state the conclusions and recommendations for future work which is required.

Conclusions

- The thermodynamic analysis of the lime-oxygen sulfur system shows why lime is generally injected in a burner system operating under oxidizing conditions at restricted upper temperatures. Injection of lime under reducing conditions to form calcium sulfide required removal of the reaction product (calcium sulfide) otherwise oxidation and release of sulfur will occur. At intermediate oxidation potentials, lime is not effective as a desulfurizing agent.
- Iron as the oxysulfide liquid has a range of stability and can be used as a desulfurizing agent provided that operation of the burner/gasifier is in a sufficiently reducing regime (high equivalence ratio). The exact operating range is given in this report and is calculable via an interactive computer program for any given coal composition, temperature, and stoichiometry.
- High moisture contents and/or high hydrogen contents of the coal yield a poorer degree of desulfurization as measured by percent sulfur removal.

- Kinetic tests on individual iron oxide particles placed upon substrates or in platinum cups with a TGA apparatus fail to predict reaction rates which represent actual operating conditions within a burner system.
- Preliminary tests on the Dynamic Containment Burner give some promise that this system may have the capability of producing the proper conditions of coal gasification for use of added iron as a sulfur sorbent; however, tests have not been carried forward proving its utility.

Recommendations for future work

The following points should be addressed:

- The Dynamic Containment Burner should be operated on actual coals of high sulfur content and with added iron oxide to determine its capabilities for gasification and sulfur removal.
- The predicted regimes of temperature and equivalence ratio should be examined to determine whether not an existing burner system could be used under the conditions predicted for sulfur sorbency.

PUBLICATIONS RESULTING FROM THIS WORK

Hepworth, M. T. and Zhong, S: "Iron Oxide as A Desulfurizing Agent in a Slagging Coal Combustor" Paper presented June, 1992 at *DOE/PETC Symposium on Clean Coal Technology*, Pittsburgh, PA.

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*, Vol 5, No. 2, March/April, 1991 pp. 237-243.

Hepworth, M. T., Reid, K. J., Wang, J. C. and Zhong, S.: "Thermochemistry of the Fe-O-S System as a Desulfurizer in Coal Combustion Atmospheres: Part I - Fe-FeO-Liquid Equilibrium", *Proceedings of Clean Coal Technology Symposium*, Amer Chem Soc, Pittsburgh, August 29, 1990 pp 1433-1439.

APPENDIX A

**THESIS OF DR. SHAOLIN ZHONG: COMPARATIVE STUDIES ON SULFUR
SORBENTS (LIME, IRON OXY-SULFIDE) AND STUDIES ON THERMODYNAMICS
AND KINETICS OF FE-O-S SYSTEM IN CONJUNCTION WITH GASIFIER
ATMOSPHERES**

**MOLTEN IRON OXYSULFIDE
AS A SUPERIOR SULFUR SORBENT**

A Thesis

**Submitted to the Faculty of the Graduate School
of the University of Minnesota**

by

Shaolin Zhong

**In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy**

March 1993

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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 also the reaction product of coal gases with iron oxide, a molten phase with variable composition, termed "iron oxysulfide", can act as a flux to produce a liquid.

A comparison is made between lime and iron oxide as desulfurizing agents. With lime, the thermodynamic conditions are chosen: a set of conditions where the compound calcium sulfide is the product and a set of conditions where calcium sulfate is the product. The temperature limits of the sulfate forming and sulfide forming reactions are defined.

The thermodynamic conditions for optimum removal of sulfur with iron oxide from the first stage of a coal combustor have been determined by the thermodynamic analysis. Contour curves of the pounds of SO_2 per million Btu of calorific power and percentage of sulfur removal are plotted on isothermal ternary phase diagrams of the Fe-S-O system. These contour plots determine the most favorable conditions for coal combustion in the presence of added iron oxide. Lowest SO_2 concentrations are close to the phase boundary limit between iron saturation and the oxysulfide liquid phase. Thermodynamic performance of iron oxysulfide is improved at higher temperature. The experimental test program utilizes thermogravimetric analysis (TGA) to establish this region of optimum burner performance and check the calculated thermodynamic values.

Kinetic experiments on single particles of magnetite show that relatively pure taconite concentrate reacts with sulfidizing gases with relatively fast kinetics and that high purity mineral-grade magnetite appears not to react with sulfidizing gases. The TGA experiments show that the whole process, from magnetite Fe_3O_4 to liquid iron oxysulfide, consists of a reduction stage during which magnetite is reduced to wustite, and a sulfidation stage of product wustite. During the latter stage the mass transport of dissolved sulfur and oxygen in the liquid phase is rate-controlling. In a real burner, the droplets of iron oxysulfide are expected to have a fast rate compared with the conditions in TGA experiments. The results of diffusion modelling analysis show that when the operating temperature in burner is above

1400°C, for example, a high degree of desulfurization with iron oxysulfide can be obtained with less than one-second residence time.

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I. INTRODUCTION

Exploitation of coal provided the first large-scale, low-cost source of energy and made the industrial revolution possible. Coal remained the dominant world energy source until the rapid growth of crude oil and natural gas production. However, the large reserves of coal world-wide ensure that, in the forthcoming era of energy shortage, coal will remain a crucially important energy source. Technologies to produce clean gas and/or liquid fuels from coal may spur increased use of this energy source, which is predicted to be sufficient for the next 600 years.^[1]

Coal is an inhomogeneous organic fuel, formed largely from partially decomposed and metamorphosed plant materials. As mined, coal contains three components: moisture, mineral matter, and dry, mineral-matter-free coal which consists mainly of the elements carbon, hydrogen, oxygen, nitrogen, and sulfur. Depending on the fixed carbon content and energy value, coals are classified into four primary ranks: anthracite, bituminous, subbituminous, and lignite.^[1,2] Table 1.1 shows the compositions of typical coals.

Table 1.1 Compositions of Typical Coals

Group	Proximate Analysis %			Gross Heating Value Btu/lb (dry)
	Volatile Matter	Fixed Carbon	Ash	
Anthracite	1.2-13.0	74.6-90.7	8.1-12.4	13690
Bituminous	16.0-36.4	54.5-79.1	4.9-9.1	14430
Subbituminous	38.9-42.8	47.4-56.4	4.7-13.2	12650
Lignite	41.8	49.4	8.8	11034

Group	Ultimate Analysis %				
	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
Anthracite	78.3-86.8	1.6-3.6	0.6-1.4	0.9-2.0	2.0-2.3
Bituminous	73.1-85.4	4.8-5.2	1.4-1.6	0.8-2.6	2.6-8.9
Subbituminous	64.2-75.1	4.4-5.0	1.2-1.4	0.4-1.0	12.8-16.6
Lignite	64.4	4.2	1.1	0.8	20.7

The major inorganic constituents of coal ash are SiO_2 (40-90%), Al_2O_3 (20-60%), Fe_2O_3 (5-25%), CaO (1-15%), MgO (0.5-4%), Na_2O (0.5-3%), K_2O (0.5-3%), SO_3 (0.5-10%), P_2O_5 (0-1%), and TiO_2 (0-2%).

The United States has more coal, on any basis of comparison, than combined petroleum, natural gas, and oil shale reserves; yet the use of coal is disproportionately low because of the high sulfur contents.^[3] The total coal production between 1970 and 1987 in U.S.A. is listed in Table 1.2. The combustion of coal for the generation of electric power and process heat necessitates the control of pollutants which are partially harmful to man and the environment. Although the control of emissions of particulate, nitrogen oxides, and trace elements is receiving attention, much effort has been directed towards the control of emissions of sulfur in the form of sulfur dioxide. Essentially all (95%) of the sulfur in the coal is converted to SO_2 and leaves with the flue gases. Presence of rare metals such as platinum and vanadium in the ash can catalyze the conversion of SO_2 to SO_3 which combine with water vapor to form acid mist. Coal combustion accounts for about 67% of man-made sulfur pollution and about 23% of all sulfur air emissions.^[4]

Table 1.2 Total U.S. Coal Production (Thousand Short Tons)

1970	1975	1980	1984	1985	1986	1987
812661	854641	829700	896921	883638	890315	918762

Sulfur is recognized as one of the major impurities in coal. Its concentration in world coal resources varies between 0.19% and 10%^[5] although the range for the world's economically recoverable coal reserves is narrower, at 0.38 to 5.32%.^[6]

Sulfur occurs in coal as pyritic sulfur, organic sulfur, sulfate salt, and elemental sulfur. Pyritic and organic sulfur together account for the large majority of sulfur in coal. Sulfate sulfur occurs chiefly as gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) and iron sulfate, the latter normally resulting from the oxidation of iron pyrite. The concentration of sulfate sulfur in coal is generally less than 0.1%. This, together with its solubility in water, means that form of sulfur is of little concern during coal cleaning. The concentration of elemental sulfur in coal is also small, generally less than 0.2%.^[6]

Emissions of sulfur dioxide from coal combustion may be controlled by one of several ways:

1. the use of low-sulfur coal;
2. the pretreatment of coal to remove sulfur;
3. the removal of sulfur during combustion;
4. the post-combustion treatment of flue gases;
5. the conversion of coal into a liquid or gaseous form.

In the USA, according to the 1971 New Source Performance Standards (NSPS), SO_2 emissions must be less than or equal to 1.2 lb/MM Btu (0.52 kg/GJ). The SO_2 concentration is expressed in pounds of SO_2 emission per million Btu of gross calorific heat of the coal burned under stoichiometric conditions. An emission of 1.2 lb/MM Btu is approximately equivalent to burning a coal containing between 0.6 and 0.7 % sulfur without emission control equipment.^[6] Reserves of coals containing sufficiently low concentration of sulfur are limited and restricted to specific geographical locations. To prevent the rapid depletion of the reserves of low-sulfur coals and their transportation over long distances, the NSPS were revised in 1979. For new steam generators whose capacity is greater than 73.3 MW, SO_2 emission must be less than 1.2 lb/MM Btu (0.52 kg/GJ). And for new steam-electric power plants whose capacity is less than 73.3 MW, either SO_2 reduction of 70% is required when SO_2 emission is below 0.6 lb/MM Btu (0.26 kg/GJ) or SO_2 reduction of 90% is required when SO_2 emission is below 1.2 lb/MM Btu (0.52 kg/GJ).

The removal of sulfur prior to combustion as part of a coal cleaning process includes physical, chemical, and microbiological desulfurization. Physical coal desulfurization techniques are applicable only to the removal of inorganic sulfur. The majority of commercial physical coal cleaning processes are gravity separation, froth flotation and oil agglomeration. Studies of several hundred samples of coals revealed that even with a 50% rejection of coal during preparation, 68% of the coal could not be cleaned sufficiently to comply with the SO_2 emission standard of 0.52 kg/GJ.^[7] Chemical desulfurization of coal has the potential advantage of removing both inorganic and organic sulfur. With almost complete removal of pyritic sulfur and partial removal of organic sulfur, the majority of the chemical processes are potentially capable of desulfurizing a large number of coals to the

NSPS standard for SO_2 emission of 1.2 lb/MM Btu.^[6] Microbiological desulfurization of coal is only of academic interest at present. Atmospheric oxidation or weathering of coal can result in a significant reduction in its sulfur content.^[8] It is theoretically possible to catalyze this oxidative dissolution of pyrite, FeS_2 , in coal by use of microorganisms.^[9]

The potential for absorption of SO_2 by a sorbent during the fluidized bed combustion of coal is widely known as one of the advantages of this combustion technique.^[10] By removing the sulfur in the form of SO_2 , the technique is not dependent on the form or chemical nature of sulfur in coal. Reduction in SO_2 emissions of greater than 90% can be achieved for most coals.^[11,12]

Flue gas desulfurization has been the most popular method of controlling SO_2 emissions. The processes can consistently remove more than 90% of the SO_2 from flue gases.^[13,14] The removal of SO_2 from industrial waste gases and boiler flue gases can be achieved by wet and dry gas scrubbing processes.

In order to remove both organic and inorganic sulfur with a high efficiency, the chemical conversion of coal into a gaseous or liquid fuel is necessary.^[15] In coal conversion processes, the sulfur is removed from the liquid or gaseous products at some stage of the operation to control sulfur emissions. There are numerous methods of removing sulfur from flue gases at ambient temperatures. Sulfur removal efficiencies of 99 per cent are usually possible.^[16]

There are a large number of operating processes for direct combustion of coal or its conversion into other products. These processes can be classified as direct combustion, gasification, liquefaction, carbonization, and coking, by process type and coal particle size or temperature, etc.^[17] Most of the coal presently being burned is by direct combustion in large-scale utility furnaces for the generation of electric power. In a conventional power station, coal is burned with air at atmospheric pressure to raise superheated high pressure steam (typically 540°C and 160 atm); the electricity is produced by the expansion of steam in turbogenerators.^[18] An example of an air-heater design operating in a simple gas turbine cycle is shown in Figure 1.1.

Fluidized bed combustion is one of a limited number of alternatives available to fuel consumers in the industrial and electric utility sectors wishing to employ high sulfur coal.

Fluidized bed combustion has many advantages ^[4,19,20,21]. The fluidized bed combustor has a near-ideal configuration for combustion reactions and heat transfer. The thorough mixing within the bed ensures good contact between sorbent and combustion gases and a uniform bed temperature. A fluidized bed combustor is tolerant to the varying properties of the feed coal and is particularly advantageous for coals of high, low, or variable ash content, or of low ash fusion temperature. It has relatively low power station capital costs and low power costs. Sulfur dioxide emissions may be largely suppressed due to good limestone and SO₂ reaction temperature, good contacting between the sorbent particles and the combustion gases, and long residence times of the sorbent in the combustion zone. The formation of nitrogen oxides may be reduced because of the relatively low operating temperatures. However fluidized bed combustion systems create potential environmental problems during the disposal of spent SO₂-control sorbent. Rainwater leaching of spent sorbent in disposal site is inevitable thus leading to groundwater contamination.

Gasification is the first step for advanced power cycles. A potentially important use of coal gasification is the manufacture of a clean gas for power generation. The gas produced is clean and its low-Btu content results in a large mass flow through the gas turbine and improves the efficiency of this step. By employing advanced combined cycle systems, the efficiency of the overall system is high and the emissions of sulfur oxides and nitrogen oxides are controlled below the required standards cheaply and effectively. A typical combined gas-steam-turbine system for use with coal gasification is illustrated in Figure 1.2.^[19] Air is compressed and is used to burn a clean, desulfurized flue gas in the combustion chamber. The hot combustion gases are expanded through the gas turbine. The exhaust gases from the turbine are directed to a waste heat boiler to raise steam and to generate further power in the conventional steam cycle. If the raw gas from the gasifier is cooled in a heat exchanger before cleaning, then heat may be recovered for reheating the gas and for use in the steam cycle. The overall efficiency in the combined-cycle power generation is about 51%, considerably higher than that of a conventional power station which usually does not exceed 38%.

The important factor affecting the efficiency of the combined cycle system is the gas turbine inlet temperature.^[19] The higher the inlet temperature to a gas turbine, the greater

Figure 1.1 Steam Turbine System

Figure 1.2 Combined Gas-Steam Turbine System

the amount of work that can be obtained from the gas during its expansion to atmospheric pressure. In order to operate an efficient steam cycle, sufficient heat must be recovered at high temperature. An important factor affecting the amount of high temperature heat available in a gasification combined cycle is the gas turbine inlet temperature as this, in turn, affects the temperature of the turbine exhaust gases. In the combined gas-steam-turbine system, a greater efficiency would result if the fuel gas could be cleaned without significant cooling in order to take advantage of the sensible heat in the gases leaving the gasifier.

Desulfurization processes can be either post-gasification treatment of hot reducing coal gases or retention of sulfur during the gasification process. The main post-gasification treatment method of hot reducing coal gases is the use of metal/metal oxide systems as sulfur sorbents in a fixed-bed under controlled or a contained temperature region (500-1000°C).^[24,25,26] Iron oxides are conventionally used for the removal of sulfur from hot reducing gases at moderate temperatures (827-977°C) in a fixed bed by the formation of iron sulfides; the sorbent can be regenerated by oxidation. Two absorber beds in parallel are used, one being regenerated while the other is in use. The sulfur is recovered from the regenerator off-gas. Up to 96% sulfur removal is claimed.^[20,27] Calcium-oxide based sorbents have also been studied but appear to be less efficient in absorbing H_2S which is the dominant sulfur species under gasification conditions.^[20] Manganese oxide pellets were used to desulfurize hot reducing gases. The pellets made of a mixture of finely ground manganese oxide ore and alumina in a fixed bed were readily sulfided at temperatures above 800°C. The regeneration of Mn_3O_4 by air oxidation of MnS from the sulfidation cycle was very rapid. In addition, at regeneration temperatures below 1200°C, the pellets did not lose their reactivity upon repeated recycle.^[28] A combination of two oxides, zinc ferrite ($ZnO \cdot Fe_2O_3$) can be used for desulfurization and regenerated by oxidation with steam and air. The zinc ferrite sorbent is capable of removing sulfur from hot coal gas to a level of 1 to 10 ppm by volume.^[29,30,31]

The ideal desulfurization system would operate at temperatures ranging from 1200 to 1400°C which are usually required for efficient coal gasification and the subsequent use of product gas for electric power generation. Operation above 1200°C causes the ash to form

a molten slag. Developments in slagging combustors for utility coal combustion are being driven by several factors:

- Removal of coal combustion residues as dense constituents at the source of combustion to reduce ash transfer to heat exchanger 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.

Recent surveys^[32,33,34,35] indicate that lime or limestone is currently the only sorbent being injected in slagging utility burners for those systems close to, or currently undergoing commercial development. An alternative to lime as a high temperature desulfurizing agent is iron oxide. Studies on iron oxide additions to the reducing stage reported 90 percent sulfur removal in the form of a compact residue. This residue appears to be inert with respect to sulfur re-emission when exposed to moisture.^[35,36,37,38,39]

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

- (1) It forms a series of low melting-point liquid solutions with sulfur and oxygen under reducing conditions. These liquids should be highly reactive with respect to absorption of sulfur in the gasification product gases. Because they are liquids rather than solids, good internal mixing is likely to enhance the kinetics of absorption and achieve desulfurization levels closer to those thermodynamically feasible than a solid sorbent would be expected to achieve.
- (2) Iron oxysulfide solutions are stable under reducing conditions over a wide range of temperatures (950-1650°C) and are effective as a molten system in removing sulfur via the formation of highly-dispersed fine droplets. The sulfur activity in these solutions is significantly less than the activity of sulfur gases in contact with pyrrhotite.
- (3) In contrast, lime or limestone is a solid and reacts with H_2S or SO_2 on the surface. The interior of the lime or limestone particles is typically unreacted. Therefore the stoichiometric ratio of calcium to sulfur from two to five times may be required in

order to produce a high degree of desulfurization.

- (4) Iron oxide 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 can act as a flux to produce a fluid phase.
- (5) The injection of limestone increases the fly ash burden.
- (6) In addition, all added lime or limestone with 2-4 times of stoichiometric excess contributes the release of CO_2 via the dissociation of limestone, and as a result, adds unnecessarily to the greenhouse effect.

The objective of this project is to compare the degree of desulfurization by using an iron system with a calcium-based system. The investigations consist of theoretical and experimental studies of the thermodynamics and kinetics of desulfurization using iron oxides. The goal of the thermodynamic studies is to determine the relationship between composition of iron oxysulfide and isoactivity curves for sulfur and oxygen on an isothermal section for the Fe-S-O system. Based on these thermodynamic data, an interactive computer program will be developed which enables an operator of a gasification plant to adjust the air/fuel rates and other process conditions to optimize the degree of desulfurization with iron-based sulfur sorbent. A series of kinetic experiments will be undertaken. The kinetic study will show that the iron oxysulfides are effective desulfurizing agents under conditions similar to that encountered in coal combustion. With the results reported in this study it is hoped that a commercial burner developer will seize the initiative and continue the examination of this likely candidate system for its desulfurizing potential.

II. Thermodynamic Analysis

In the following thermodynamic analysis, calculations will be carried out to determine the gas phase composition, SO_2 emission concentration, percentage of sulfur removal, NO_2 emission concentration, dosage of sorbent, equivalence ratio, and dosage of air, which can be expected under equilibrium conditions upon a gasification with in situ desulfurization. The Ca-S-O system and Fe-S-O system which includes Fe-FeO-liquid system and single iron oxysulfide liquid system will be examined.

A Western Illinois #6 Coal^[40], designated IBC (Illinois Basin Coal) - 107 having the analysis given in Table 2.1 and 2.2 is employed for the following calculations (except for specified situations). The analyses which are incorporated into the calculations are for 100 g of dry coal plus 9.3 g moisture.

Table 2.1 Analysis of IBC-107 Coal
(Moisture Free Values)

Content	Weight %
Proximate Analysis	
Volatile Matter	40.0
Fixed Carbon	48.6
Ash	11.5
Moisture	9.3
Ultimate Analysis	
Carbon	68.11
Hydrogen	5.00
Nitrogen	1.20
Oxygen	10.56
Sulfatic Sulfur	0.26
Pyritic Sulfur	0.48
Organic Sulfur	2.94
Total Sulfur	3.87
Calorific Heat (Btu/lb)	12224

Table 2.2 Composition of Ash

Content	Weight %
SiO ₂	51.01
Al ₂ O ₃	19.00
Fe ₂ O ₃	11.78
CaO	5.22
MgO	1.00
K ₂ O	2.39
Na ₂ O	1.20
TiO ₂	0.89
P ₂ O ₅	0.04
MnO	0.07
SrO	0.04
BaO	0.05
SO ₃	5.85

2.1 Method of Calculation

Analysis of a thermodynamic state in a complex system necessarily involves solution of several simultaneous equations, some representing the equilibrium conditions, some expressing the atomic mass balances, and one giving the total pressure. The elements considered in the calculations are N, C, O, H, and S which are the main components in coal. These elements along with the predominant gas species of N₂, CO, CO₂, H₂O, H₂, H₂S, S₂, S, S₄, COS, SO, SO₂, SO₃, O₂, CS, CS₂, NO, NO₂, CH₄, and NH₃ are incorporated in the calculations to yield fifteen independent equations for the gas phase equilibria plus six additional equations for the five element atomic mass balances and total pressure.

The relevant equations for gas phase equilibria are expressed as:

$$2CO + O_2 = 2CO_2 \quad K_1 = \frac{P_{CO_2}^2}{P_{CO}^2 \cdot P_{O_2}} \quad (2.1.1)$$

$$2H_2 + O_2 = 2H_2O \quad K_2 = \frac{P_{H_2O}^2}{P_{H_2}^2 \cdot P_{O_2}} \quad (2.1.2)$$

$$2H_2 + S_2 = 2H_2S \quad K_3 = \frac{P_{H_2S}^2}{P_{H_2}^2 \cdot P_{S_2}} \quad (2.1.3)$$

$$S_2 + 2O_2 = 2SO_2 \quad K_4 = \frac{P_{SO_2}^2}{P_{S_2} \cdot P_{O_2}^2} \quad (2.1.4)$$

$$2SO_2 + O_2 = 2SO_3 \quad K_5 = \frac{P_{SO_3}^2}{P_{SO_2}^2 \cdot P_{O_2}} \quad (2.1.5)$$

$$2CO + S_2 = 2COS \quad K_6 = \frac{P_{COS}^2}{P_{CO}^2 \cdot P_{S_2}} \quad (2.1.6)$$

$$S_2 + O_2 = 2SO \quad K_7 = \frac{P_{SO}^2}{P_{S_2} \cdot P_{O_2}} \quad (2.1.7)$$

$$S_2 = 2S \quad K_8 = \frac{P_S^2}{P_{S_2}} \quad (2.1.8)$$

$$2S_2 = S_4 \quad K_9 = \frac{P_{S_4}}{P_{S_2}^2} \quad (2.1.9)$$

$$\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO \quad K_{10} = \frac{P_{NO}}{P_{N_2}^{\frac{1}{2}} \cdot P_{O_2}^{\frac{1}{2}}} \quad (2.1.10)$$

$$\frac{1}{2}N_2 + O_2 = NO_2 \quad K_{11} = \frac{P_{NO_2}}{P_{N_2}^{\frac{1}{2}} \cdot P_{O_2}} \quad (2.1.11)$$

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3 \quad K_{12} = \frac{P_{NH_3}}{P_{N_2}^{\frac{1}{2}} \cdot P_{H_2}^{\frac{3}{2}}} \quad (2.1.12)$$

$$\frac{1}{2}S_2 + 2CO = CS + CO_2 \quad K_{13} = \frac{P_{CS} \cdot P_{CO_2}}{P_{S_2}^{\frac{1}{2}} \cdot P_{CO}^2} \quad (2.1.13)$$

$$S_2 + 2CO = CS_2 + CO_2 \quad K_{14} = \frac{P_{CS_2} \cdot P_{CO_2}}{P_{S_2} \cdot P_{CO}^2} \quad (2.1.14)$$

$$2H_2 + 2CO = CH_4 + CO_2 \quad K_{14} = \frac{P_{CH_4} \cdot P_{CO_2}}{P_{H_2}^2 \cdot P_{CO}^2} \quad (2.1.15)$$

The atomic mass balance equations are given by:

$$n_C = n_{CO} + n_{CO_2} + n_{COS} \quad (2.1.16)$$

$$n_S = n_{H_2S} + n_{SO_2} + n_{SO_3} + 2n_{S_2} + n_{COS} + n_{SO} \quad (2.1.17)$$

$$n_H = 2n_{H_2O} + 2n_{H_2} + 2n_{H_2S} \quad (2.1.18)$$

$$n_O = n_{CO} + 2n_{CO_2} + 2n_{O_2} + n_{COS} + n_{SO} + 2n_{SO_2} + 3n_{SO_3} \quad (2.1.19)$$

$$n_N = 2n_{N_2} \quad (2.1.20)$$

And the equation for total pressure is represented as:

$$\begin{aligned}
 P_T = & P_{N_2} + P_{CO} + P_{CO_2} + P_{H_2O} + P_{H_2} + P_{H_2S} \\
 & + P_{S_2} + P_S + P_{S_4} + P_{COS} + P_{SO} + P_{SO_2} + P_{SO_3} \\
 & + P_{O_2} + P_{CS} + P_{CS_2} + P_{NO} + P_{NO_2} + P_{CH_4} + P_{NH_3}
 \end{aligned} \quad (2.1.21)$$

Equations (2.1.17) and (2.1.19) are valid only for conditions in which no sorbent is present since they are for sulfur and oxygen mass balances in the gas phase. For conditions in which a sorbent is present, then these two equations are omitted from the calculations and superseded by additional equilibria between sorbent and gas phase.

For the Ca-S-O system, there are two separate and mutually exclusive phase equilibria, CaS-CaO-gas and CaSO₄-CaO-gas.

When lime is present as a sorbent in the phase combination CaO-CaS under reducing condition, the following equilibrium applies:

In the mass balance resulting from this equilibrium, the change in the number of moles of oxygen released is equal to the change in the number of moles of sulfur captured as shown in equation (2.1.23):

$$\Delta n_{O_2} = -\Delta n_{S_2} \quad (2.1.23)$$

When lime is present as a sorbent in the phase combination CaO-CaSO₄ under oxidizing conditions, the following equilibrium (2.1.24) applies:

And in the mass balance resulting from the above equilibrium, the moles of sulfur captured are related to the moles of oxygen taken up by lime to form sulfate as expressed by the following stoichiometric constraint:

$$\Delta n_{O_2} = 3\Delta n_{S_2} \quad (2.1.25)$$

For the Fe-S-O system, two-phase equilibria are considered. One applies to the gas in equilibrium with Fe-FeO-liquid, that is, the composition of liquid iron oxysulfide in contact with wustite (FeO) and metallic iron varies with temperature. Another deals with the gas in equilibrium with single liquid iron oxysulfide. The properties of the latter phase vary with both temperature and composition. These equilibria are in the form below because the diatomic sulfur and oxygen species dissolve monoatomically in the liquid iron oxysulfide as:

$$\frac{1}{2}S_{2(g)} = \underline{S} \quad K_{17} = \frac{a_s}{P_{S_2}^{1/2}} \quad (2.1.26)$$

$$\frac{1}{2}O_{2(g)} = \underline{O} \quad K_{18} = \frac{a_o}{P_{O_2}^{1/2}} \quad (2.1.27)$$

where $\underline{S}$ and $\underline{O}$ refer to sulfur and oxygen, respectively, dissolved in the oxysulfide liquid at equilibrium. For Fe-FeO-liquid-gas system, the partial pressures of oxygen and sulfur depend on temperature only. However, for the liquid-gas system, the partial pressures of oxygen and sulfur depend not only on temperature but also on the composition of liquid iron oxysulfide.

The thermodynamic data are taken from various sources^[18,41] to calculate the equilibrium constants for the gas-phase reactions. The method of calculation is via an iterative approach for complex equilibria.^[42] The iterative procedure is outlined below:

- (1) According to the given conditions, the atom ratio of carbon to hydrogen, $RCH = (C/H)_{\text{initial}}$ can be computed from the number of gram-moles or the partial pressures of the species involved.
- (2) Initial guesses of the partial pressures of CO and H₂ are made.
- (3) Using the estimated values for the partial pressures, the corresponding "equilibrium" partial pressures are calculated for the remaining species by making use of the equilibrium-constant expressions (2.1.1) to (2.1.15).
- (4) The new total pressure P_T' and the new atom ratio $RCH' = (C/H)_{\text{equilibrium}}$ are computed.
- (5) The atom-ratio conservation equation is expressed as:

$$RCH = (C/H)_{\text{initial}} = (C/H)_{\text{equilibrium}} \quad (2.1.28)$$

The inequalities $|P_T - P_T'|/P_T < 0.00001$ and $|RCH - RCH'|/RCH < 0.00001$ are considered as convergence criteria. If these two conditions are satisfied simultaneously, the desired convergence is achieved and the results are printed out.

- (6) The new values of P_{CO} and P_{H_2} are defined by the following convergence formulas:^[42]

$$(P_{\text{CO}})_{\text{new}} = (P_{\text{CO}})_{\text{old}} (P_T/P_T') (RCH/RCH')^{\frac{1}{2}} \quad (2.1.29)$$

$$(P_{\text{H}_2})_{\text{new}} = (P_{\text{H}_2})_{\text{old}} (P_T/P_T') (RCH'/RCH)^{\frac{1}{2}} \quad (2.1.30)$$

- (7) Return to step 3, continue until convergence criteria are met.

Upon solving the twenty one equations, the composition of the gas in equilibrium

with the solid or liquid phases can be determined.

Figure 2.1.1 illustrates the primary process of coal conversion. The primary air, coal, and sorbent are fed into a gasification system to produce clean fuel gas and slag. An interactive computer program has been developed (Figure 2.1.2) which will be discussed subsequently. The input permits coal assays and moisture content to be entered as variables as well as temperature of the system, total pressure, and sorbent properties. The output of the program gives the partial pressures of all gaseous species in the gas phase, the total moles of sulfur involved in the gas phase, sulfur concentration expressed as pounds of SO_2 per million BTU, the percentage of sulfur removal, the nitrogen oxide concentration reported as pounds NO_2 per million BTU, the dosage of air as liters at STP, equivalence ratio, and the dosage of sorbents as gram per 100 g of dry coal.

**Figure 2.1.1 Primary Process of Coal Conversion
with In-Situ Desulfurization**

Figure 2.1.2 Structure of Computer Program

2.2 Analysis of Lime-Based Sorbent System

The solid phase CaS or CaSO_4 will equilibrate with CaO when lime is used as a sulfur sorbent. Figure 2.2.1 is a predominance diagram of the Ca-S-O system in which the equilibrium phase regions are outlined on a plot of common logarithm of the partial pressures of $\text{S}_2(\text{g})$ versus that of $\text{O}_2(\text{g})$. As is expected, the sulfide form exists under more reducing conditions and the sulfate form under more oxidizing conditions. As temperature is increased, the transition from sulfide to sulfate occurs under more oxidizing conditions which means the CaSO_4 is less stable under high temperature. One of the important properties of the Ca-S-O system is that as the partial pressure of oxygen increases, the equilibrium partial pressure of sulfur between sulfide and oxide increases while that between sulfate and oxide equilibrium decreases. It must be noted that increasing values of the partial pressure of sulfur are accompanied by increasing sulfur dioxide emission.

A listing of the interactive computer program for coal combustion in the presence of lime is attached in Appendix A. The results for equilibrium calculations under three different temperatures (800°C , 1000°C , and 1200°C) and four different partial pressures of oxygen (10^{-14} , 10^{-10} , 10^{-6} , and 10^{-2}) are listed in Tables 2.2.1-2.2.3. These results consist of the partial pressures of all gaseous species, the total molar sulfur involved in the gas phase, sulfur concentration expressed as pounds of SO_2 per million BTU, the percentage of sulfur removal, the nitrogen oxide concentration reported as pounds of NO_2 per million BTU, the dosage of air as liters at STP, equivalence ratio, and the dosage of lime CaO as grams per 100 of dry coal.

The calculated equilibrium sulfur concentration reported as pounds of SO_2 per million Btu and the percentage of sulfur removal are plotted against the common logarithm of the partial pressure of oxygen in atmospheres for six temperatures 800, 900, 1000, 1100, 1200, and 1300°C in Figure 2.2.2 and Figure 2.2.3, respectively. The horizontal line at the top of the diagram in Figure 2.2.2 is the sulfur dioxide concentration level which would be present if no desulfurization is effected by the sorbent. Under reducing conditions, the sorbent CaO reacts with H_2S to form CaS ($\text{CaO} + \text{H}_2\text{S} = \text{CaS} + \text{H}_2\text{O}$); under oxidizing conditions, the product CaSO_4 is formed by the reaction among the sorbent CaO , SO_2 , and O_2 ($\text{CaO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{CaSO}_4$). As the temperature is increased, the desulfurization

Figure 2.2.1 Stability Diagram for Ca-S-O System

Table 2.2.1 Effect of P_{O_2} on Gas Composition
in Equilibrium with Ca-S-O System at 800 °C

Species	Partial Pressure, atmosphere			
PO_2	1.00×10^{-14}	1.00×10^{-10}	1.00×10^{-6}	1.00×10^{-2}
PCO	1.02×10^{-3}	1.02×10^{-5}	1.02×10^{-7}	9.70×10^{-10}
PCO_2	1.66×10^{-1}	1.66×10^{-1}	1.66×10^{-1}	1.58×10^{-1}
PH_2	6.44×10^{-4}	6.46×10^{-6}	6.46×10^{-8}	6.15×10^{-10}
PH_2O	8.74×10^{-2}	8.77×10^{-2}	8.77×10^{-2}	8.36×10^{-2}
PN_2	7.44×10^{-1}	7.46×10^{-1}	7.46×10^{-1}	7.48×10^{-1}
PH_2S	5.69×10^{-5}	5.71×10^{-13}	5.71×10^{-21}	5.44×10^{-29}
PSO_2	9.77×10^{-4}	9.77×10^{-6}	9.77×10^{-8}	9.77×10^{-10}
$PCOS$	5.10×10^{-6}	5.10×10^{-14}	5.10×10^{-22}	4.86×10^{-30}
PSO	3.75×10^{-7}	3.75×10^{-11}	3.75×10^{-15}	3.75×10^{-19}
PS_2	1.83×10^{-6}	1.83×10^{-18}	1.83×10^{-30}	1.83×10^{-42}
PSO_3	8.40×10^{-11}	8.40×10^{-11}	8.40×10^{-11}	8.40×10^{-11}
PCS_2	1.34×10^{-11}	1.34×10^{-27}	1.35×10^{-43}	0
PCS	5.60×10^{-13}	5.61×10^{-23}	5.61×10^{-33}	5.34×10^{-43}
PS	8.35×10^{-11}	8.35×10^{-17}	8.35×10^{-23}	8.35×10^{-29}
PS_4	3.53×10^{-15}	3.53×10^{-39}	0	0
PNO	1.57×10^{-11}	1.57×10^{-9}	1.57×10^{-7}	1.58×10^{-5}
PNO_2	1.13×10^{-19}	1.13×10^{-15}	1.13×10^{-11}	1.14×10^{-7}
PCH_4	1.73×10^{-14}	1.75×10^{-22}	1.75×10^{-30}	1.51×10^{-38}
S in Gases	3.55×10^{-2}	3.34×10^{-4}	3.34×10^{-6}	3.80×10^{-8}
SO_2 Conc.	1.93	1.82×10^{-2}	1.82×10^{-4}	2.07×10^{-6}
%S Removal	70.6	99.7	99.997	100
NO_x Conc.	2.09×10^{-8}	2.10×10^{-6}	2.10×10^{-4}	2.23×10^{-2}
Air Dosage	716.5	721.7	721.8	760.1
Eq. Ratio	0.9983	0.9911	0.9911	0.9412
CaO Dosage	4.781	6.751	6.769	6.769

Table 2.2.2 Effect of P_{O_2} on Gas Composition
in Equilibrium with Ca-S-O System at 1000 °C

Species	Partial Pressure, atmospher			
PO_2	1.00×10^{-14}	1.00×10^{-10}	1.00×10^{-6}	1.00×10^{-2}
PCO	1.02×10^{-1}		1.47×10^{-5}	1.40×10^{-7}
PCO_2	1.15×10^{-1}		1.66×10^{-1}	1.58×10^{-1}
PH_2	4.12×10^{-2}		4.95×10^{-6}	4.72×10^{-8}
PH_2O	7.30×10^{-2}		8.78×10^{-2}	8.36×10^{-2}
PN_2	6.69×10^{-1}		7.46×10^{-1}	7.48×10^{-1}
PH_2S	1.86×10^{-4}		1.77×10^{-13}	1.68×10^{-21}
PSO_2	4.14×10^{-7}		3.28×10^{-4}	3.28×10^{-6}
$PCOS$	2.37×10^{-5}		2.71×10^{-14}	2.58×10^{-22}
PSO	3.02×10^{-8}		2.39×10^{-9}	2.39×10^{-13}
PS_2	1.15×10^{-7}		7.18×10^{-18}	7.18×10^{-30}
PSO_3	6.73×10^{-15}		5.33×10^{-8}	5.33×10^{-8}
PCS_2	5.28×10^{-10}		4.79×10^{-28}	4.62×10^{-44}
PCS	1.91×10^{-9}		2.18×10^{-22}	2.08×10^{-32}
PS	1.30×10^{-9}		1.03×10^{-14}	1.03×10^{-20}
PS_4	4.59×10^{-18}		1.80×10^{-38}	0
PNO	7.33×10^{-11}		7.73×10^{-7}	7.75×10^{-5}
PNO_2	1.90×10^{-19}		2.00×10^{-11}	2.01×10^{-7}
PCH_4	1.10×10^{-8}		2.29×10^{-24}	1.98×10^{-32}
S in Gases	5.51×10^{-3}		1.12×10^{-2}	1.19×10^{-4}
SO_2 Conc.	0.30		0.609	6.50×10^{-3}
%S Removal	95.4		90.7	99.9
NO_x Conc.	7.51×10^{-8}		1.03×10^{-3}	0.109
Air Dosage	496.3		721.16	760.06
Eq. Ratio	1.44		0.9919	0.9412
CaO Dosage	6.461		6.142	6.763

Table 2.2.3 Effect of P_{O_2} on Gas Composition
in Equilibrium with Ca-S-O System at 1200 °C

Species	Partial Pressure, atmosphere			
PO_2	1.00×10^{-14}	1.00×10^{-10}	1.00×10^{-6}	1.00×10^{-2}
PCO	3.12×10^{-1}	4.67×10^{-2}		5.25×10^{-6}
PCO_2	9.41×10^{-3}	1.41×10^{-1}		1.58×10^{-1}
PH_2	1.58×10^{-1}	1.16×10^{-2}		1.11×10^{-6}
PH_2O	1.19×10^{-2}	8.71×10^{-2}		8.36×10^{-2}
PN_2	5.09×10^{-1}	7.12×10^{-1}		7.47×10^{-1}
PH_2S	6.87×10^{-5}	5.05×10^{-4}		4.74×10^{-16}
PSO_2	1.22×10^{-9}	1.22×10^{-3}		1.19×10^{-3}
$PCOS$	6.54×10^{-6}	9.80×10^{-5}		1.08×10^{-16}
PSO	4.05×10^{-9}	4.05×10^{-5}		3.97×10^{-9}
PS_2	1.08×10^{-8}	1.08×10^{-4}		1.04×10^{-20}
PSO_3	5.89×10^{-18}	5.89×10^{-10}		5.76×10^{-6}
PCS_2	5.84×10^{-10}	8.75×10^{-9}		9.40×10^{-33}
PCS	6.44×10^{-8}	9.65×10^{-9}		1.06×10^{-24}
PS	8.11×10^{-9}	8.11×10^{-7}		7.93×10^{-15}
PS_4	1.83×10^{-20}	1.83×10^{-12}		1.68×10^{-44}
PNO	2.04×10^{-10}	2.41×10^{-8}		2.47×10^{-4}
PNO_2	2.50×10^{-19}	2.96×10^{-15}		3.03×10^{-7}
PCH_4	6.80×10^{-7}	5.50×10^{-12}		5.69×10^{-28}
S in Gases	1.33×10^{-3}	6.27×10^{-2}		4.29×10^{-2}
SO_2 Conc.	7.24×10^{-2}	3.416		2.334
%S Removal	98.9	48.03		64.5
NO_x Conc.	1.41×10^{-7}	2.85×10^{-5}		0.346
Air Dosage	253.5	608.4		757.7
Eq. Ratio	2.821	1.176		0.9441
CaO Dosage	6.695	3.251		4.366

Figure 2.2.2 Calculated SO_2 Concentration for CaS/CaO or CaSO_4/CaO Equilibria at Six Temperatures as a Function of Partial Pressure of Oxygen

Figure 2.2.3 Calculated Sulfur Removal for CaS/CaO or CaSO_4/CaO Equilibria at Six Temperatures as a Function of Partial Pressure of Oxygen

product transition from sulfide to sulfate occurs under more oxidizing conditions. At a fixed temperature, under highly reducing conditions, since the partial pressure of sulfur equilibrated with calcium oxide and calcium sulfide increases with increasing oxygen pressure, the sulfur concentration increases and percentage of sulfur removal decreases. When the partial pressure of sulfur from the coal combustion is less than the sulfur pressure equilibrated with CaO-CaS, the sulfide phase is less stable and dissociates to the oxide; therefore, the sulfur concentration reaches the maximum concentration and the percentage of sulfur removal is nil. At this stage no further desulfurization occurs because lime rather than the sulfide is stable. When the oxygen partial pressure is greater than the transition partial pressure of oxygen between calcium sulfide and sulfate, the lime can again act as a sorbent to form CaSO_4 . However, the sulfate phase is still unstable and dissociates to the oxide causing the sulfur concentration to be at its maximum value. This is true until the partial pressure of sulfur from the coal combustion is larger than the sulfur pressure equilibrated with CaO- CaSO_4 , at which point the sulfate is stable. Because the partial pressure of sulfur between sulfate and oxide equilibrium decreases with increasing oxygen partial pressure, the sulfur concentration decreases and the percentage of sulfur removal increases. Finally, when the partial pressure of oxygen is very high ($>10^{-0.75}$ atm.), the removal of sulfur decreases again since the air dosage increases very rapidly. The final gas volume is very large, since, according to the ideal gas law: $n = PV/RT$; the total amount of sulfur in atmosphere shows an increase, although the concentration of SO_2 decreases.

On the other hand, under fixed low partial pressures of oxygen, as temperature is increased, the degree of desulfurization with lime in the form of calcium sulfide increases due to a decreasing sulfur partial pressure. However, for the CaO- CaSO_4 equilibrium under high oxygen pressure, as temperature is increased the calcium sulfate phase is less stable and tends to dissociate. Therefore, the degree of desulfurization with lime decreases. Finally as the temperature increases to 1300°C , CaSO_4 is completely dissociated and consequently becomes ineffective as a sulfur sorbent.

The theoretical dosage of lime is plotted as a function of oxygen partial pressure for various temperatures in Figure 2.2.4 which looks quite similar to Figure 2.2.2. As more sulfur reacts with lime, the sulfur removal and dosage of lime required increase, as is

Figure 2.2.4 Lime Dosage g/100 g Coal for CaS/CaO or CaSO_4/CaO Equilibria at Six Temperatures as a Function of Partial Pressure of Oxygen

expected.

Equivalence ratio, widely used in combustion research, is the actual amount of fuel expressed as a fraction percent of the stoichiometrically correct amount of fuel.^[92] Figure 2.2.5 shows the equivalence ratio against the partial pressure of oxygen for various temperatures. Under more reducing conditions, the main gas species are CO, CO₂, H₂, and H₂O. At higher temperatures CO₂ and H₂O have greater tendency to decompose; therefore, at a fixed equivalence ratio, the partial pressure of oxygen increases with increasing temperature. Under more oxidizing conditions, the main gas species are CO₂, H₂O, and O₂. Therefore, at a fixed equivalence ratio, the temperature will not affect the partial pressure of oxygen. For intermediate situations the equivalence ratio is close to unity.

The main application of adding a calcium-based sorbent during coal combustion is in fluidized bed combustion. Calcium carbonate calcines under combustion conditions resulting calcium oxide which is porous with relatively large internal surface area, which, in turn, promotes the sulfation of calcium oxide. But the calcium sulfate which has a larger molar volume than the original CaCO₃ eventually forms an impervious skin around the particle which effectively isolates the remaining CaO from SO₂, then stops any further reaction.^[43] Rarely is more than 50% of CaO present in limestone or dolomite converted to CaSO₄. The addition of the theoretical requirement of limestone results in the retention of less than 50% of the sulfur. The extent of sulfur retention by limestone increases with Ca/S ratio in the charge. To retain 85% of the sulfur would typically require a calcium to sulfur mole ratio of 2 to 4.^[44]

The operating temperature of fluidized bed combustor lies in the range 775 to 950°C. The bed temperature also has an important effect on the sulfur retention efficiency. The optimum bed temperature at which the sulfur removal efficiency is a maximum lies between 820 and 840°C.^[45] The thermodynamic calculations (Figures 2.2.2 and 2.2.3) indicate that the lower the fluidized bed temperature, the better the sulfur removal efficiency. However, comparing the equilibrium constant of the CaCO₃ dissociation reaction (Table 2.2.4) and the partial pressure of carbon dioxide for different temperatures and oxygen partial pressures (Figure 2.2.6), it is evident that the partial pressure of carbon dioxide is larger than the equilibrium constant of the dissociation reaction at low bed temperatures.

Figure 2.2.5 Equivalence Ratio as a Function of Oxygen Pressure (atm.) and Temperature

Figure 2.2.6 Partial Pressure of Carbon Dioxide for Combustion System at Four Temperatures as a Function of Partial Pressure of Oxygen

Therefore, the sulfur retention will be inhibited by poor calcination of limestone and at the same time desulfurization is restrained by a slow rate of sulfation.

Table 2.2.4 Thermodynamic Data^[41] for the Dissociation of Limestone

$\text{CaCO}_3 = \text{CaO} + \text{CO}_2(\text{g})$	
Temperature °C	Equilibrium Constant of Reaction
700	0.06168
710	0.07639
720	0.09419
730	0.1156
740	0.1413
750	0.1720
760	0.2086
770	0.2519
780	0.3031
790	0.3633
800	0.4339
810	0.5165
820	0.6127
830	0.7244
840	0.8538
850	1.003

At high bed temperature, although the sulfation reactivity tends to increase slightly with increasing temperature, the calcium sulfate become less stable causing the extent of sulfur retention to decrease. The upper temperature limit is mainly determined by the need to avoid ash sintering.

At atmospheric pressure, limestone and dolomite calcine initially to form CaO and CaO*MgO, then the calcium oxide reacts with sulfur dioxide to form the sulfates CaSO₄ and

$\text{CaSO}_4 \cdot \text{MgO}$. Limestone is preferred to dolomite because a smaller amount of materials is required to retain a given amount of sulfur.

At high pressures, since calcium carbonate is stable at the temperature used in fluidized bed combustion and does not calcine, the porosity of the limestone remains low and gas cannot penetrate easily to the interior of the particles. Therefore, limestone is found to be unreactive and less effective than at low pressures. After the formation of the surface layer of sulfate the reaction effectively ceases because no more active sites are accessible. When dolomite is used, the calcination of the magnesium component opens up the pore structure as a result of noble volume effects so that the reactivity of the stone is high and sulfation is not limited to the exterior surface of the particles. Therefore, dolomite is a preferred sulfur acceptor at high pressures.

Much of the current research and development effort on sulfur removal in fluidized bed combustors (FBCs) is directed at increasing the efficiency of limestone utilization, thereby decreasing the quantities required. Ultimately, the goal must be a sorbent which can be regenerated and reused through many cycles of loading and regeneration. However, limited success in this approach has led to investigation of other processes in which spent sorbent is reactivated and reused for a limited number of passes through the FBC. The efficiency of limestone utilization can also be increased by careful control of the operating parameters (limestone particle size, bed temperature, fluidizing velocity, bed height, fine recycle, and pressure) in a FBC and by pretreatment of the limestone.^[12]

Fluidized bed combustion systems also create potential environmental problems in the form of spent SO_2 - control sorbent disposal/utilization, and of possible rainwater leaching and groundwater contamination from spent sorbent disposal sites.

The calculation of Gibbs' free energy shows that elemental calcium has a very strong affinity for sulfur. Thermodynamic calculations indicate that under reducing conditions calcium oxide is a perfect sulfur sorbent and that the degree of desulfurization with lime increases with increasing temperature. The slagging coal burners as coal gasifier with injected lime or limestone are being considered as replacements for conventional coal burners. Lime, being a solid, may require from 2 to 5 times the stoichiometric ratio of calcium to sulfur in order to effect a high degree of desulfurization, since an impervious skin

of product CaS formed around the particle effectively isolates the remaining CaO from H_2S , then stops any further reaction.^[46] However, desulfurization at calcium-to-sulfur ratio near unity is also reported.^[47]

Nitric oxide NO and nitrogen dioxide NO_2 are formed during coal combustion. After release to the atmosphere, more NO is oxidized to NO_2 , which is an air pollutant and participates in smog formation.^[19] A mixture of NO and NO_2 as pollutants in the atmosphere is usually referred to as NO_x . The NO_x concentration (lb NO_2 /MM Btu) is plotted against oxygen pressure under different temperatures in Figure 2.2.7. The NO_x concentration increases with increasing temperature and oxygen partial pressure. The techniques that have been used to modify the combustion conditions to reduce NO_x emissions often involve both reduction in combustion temperature and staged oxygen supply. The higher temperature and smaller coal particle size substantially increase firing rates and boiler efficiencies. Unfortunately, economically optimum firing conditions produce excessive nitrogen oxide emissions and ultimately have to be modified to control the flame temperature and to maintain reducing conditions throughout most of the combustion process. Multistage burners are employed in which coal is burned under sub-stoichiometric conditions and the gaseous combustion products are then burned to completion with a controlled air excess. Fluidized bed combustion is a low combustion temperature operation process.

Figure 2.2.7 Concentration of Nitrogen Oxide for Combustion System at Six Temperatures as a Function of Partial Pressure of Oxygen

2.3 Analysis of Iron-Based Sorbent System

Iron oxide, as an alternative to lime or limestone may be effective not only as a high-temperature desulfurizing agent, but also the reaction product of coal gases with iron oxide, iron oxysulfide, can act as a flux to produce a fluid phase.

2.3.1 The Thermodynamic Properties of the Fe-S-O System

The Fe-S-O system includes iron-oxygen, iron-sulfur, and iron-sulfur-oxygen systems.

2.3.1.1 The Iron-Oxygen System

A number of investigators^[48,49,50] have studied the phase relationships in the iron-oxygen system. The phase diagram showing composition of different condensed phases over a wide range of temperatures is displayed in Figure 2.3.1.

The solubility of oxygen in liquid iron is neither large nor negligible. In liquid iron saturated with liquid oxide, the solubility increases from about 0.18 wt.% at 1550°C to about 0.36 wt.% at 1700°C. Solid iron, in any of its modifications, dissolves virtually no oxygen.

Three solid oxide phases occur in the system: wustite (Fe_yO), magnetite (Fe_3O_4), and hematite (Fe_2O_3). The wustite phase exhibits a sizable range of homogeneity. In contrast, magnetite and hematite have small range of homogeneity.

A noteworthy feature of the system is the relative instability of the monoxide phase having the exact stoichiometric composition, FeO . It readily dissociates into the more stable configuration composed of Fe and Fe_yO , where y is smaller than unity. The wustite phase, even when fully saturated with iron, remains deficient in iron. Wustite has the same crystal structure as NaCl; oxygen sites in the lattice are fully occupied, but some iron sites remain vacant. At 1000°C, in the Fe_yO phase in equilibrium with $\gamma\text{-Fe}$, the value of y is 0.952; at the opposite end of the range of homogeneity, in Fe_yO in equilibrium with magnetite, the value of y falls to 0.877.

A family of oxygen isobars referring to the partial pressure of oxygen in the gas phase in equilibrium with condensed phases is shown. In a single-condensed-phase field, the system has one degree of freedom; the partial pressure of oxygen is a function of temperature. On the other hand, in a two-condensed-phase field, the system coexists with a gas phase of given

Point	°C	% O	p_{CO_2}/p_{CO}	Point	°C	% O	p_{CO_2}/p_{CO}	p_{O_2} (atm)
A	1536°			Q	560	23.26	1.05	
B	1528	0.16	0.209	R	1553	28.30		1
C	1528	22.60	0.209	R'	1553	28.07		1
G	1392°	22.84	0.263	S	1424	27.64	16.2	
H	1424	25.60	16.2	V	1597	27.64		0.0575
I	1424	25.31	16.2	Y	1457	28.36		1
J	1371	23.16	0.282	Z	1457	30.04		1
L	911°	23.10	0.447	Z'		30.06		
N	1371	22.91	0.282					

* Values for pure iron.

Figure 2.3.1 Phase Diagram for Iron-Oxygen System^[48]

partial pressure of oxygen only at one temperature. The oxygen isobar changes direction at a phase boundary. Higher oxygen pressures are consistent with higher temperatures.

2.3.1.2. The Iron-Sulfur System

The iron-sulfur phase diagram^[51] is shown in Figure 2.3.2. Only a portion of the system Fe-FeS (36.48 wt.%S) is discussed in the following section. Fe and FeS alloy in all proportions and form a eutectic. The eutectic temperature is 989°C and the eutectic composition is at 31.6 wt.%S. At the eutectic temperature the FeS phase contains about 35.8 wt.%S, indicating that the solubility of Fe in FeS is only very little. There is a miscibility gap in the liquid state extending from 3 to 29 wt.%S at 1400 °C.

2.3.1.3. The Iron-Sulfur-Oxygen System

The phase equilibria and liquidus surfaces in the Fe-O-S system shown in Figure 2.3.3 were determined by Hilty and Crafts^[52], and Bog and Rosenqvist^[53]. The system is shown to have a ternary eutectic located at 67% Fe, 24% S, 9% O and approximately 920°C. For temperatures above the eutectic temperature, the region of the molten phase is limited by the equilibrium with metallic iron at high iron content, by the equilibrium with wustite and magnetite at high oxygen content, and by the equilibrium with solid iron sulfide (pyrrhotite) at high sulfur content. A liquid miscibility gap extends into the system from the Fe-O side to a sulfur content of 21.5% with a minimum point at approximately 81.5% Fe, 16.5% S, 2% O and 1345°C.

Equilibrium calculations involve the Fe-FeO-liquid-gas system. The region under study is the liquid in equilibrium with iron and wustite, which would be for compositions along the line running from the upper right to the lower left, ending at the ternary eutectic. For the analysis involving the single liquid phase (Fe-S-O) and gas, the liquid region termed iron oxysulfide is the single-phase liquid range of composition for the desulfurizing slag phase which is beyond the liquid boundaries saturated with iron. For effective desulfurization, temperature and composition should be controlled to create conditions in the melt such that the sulfur activities are low but the sulfur solubilities are high to make good utilization of the sorbent.

Figure 2.3.2 Phase Diagram for Iron-Sulfur System^[51]

Figure 2.3.3 Phase Diagram for Fe-O-S System^[52]

2.3.2 Fe-FeO-Liquid-Gas System

There are six condensed phases in the Fe-S-O system: gamma iron (γ), wustite (W), magnetite (M), pyrrhotite (P), liquid oxysulfide (l_1), and metallic liquid (l_2). Using the Morey-Williamson theorem which describes the univariant equilibrium in terms of chemical potential, or activity, at constant pressure as a function of temperature, enthalpy, and composition, Turkdogan and Kor^[54] constructed the sulfur and oxygen potential versus temperature in Figures 2.3.4 and 2.3.5, respectively. There are three stable invariant equilibria within the oxide-sulfide region of this system: (I) iron, wustite, magnetite, pyrrhotite, gas; (II) iron, wustite, pyrrhotite, liquid, gas; and (III) wustite, magnetite, pyrrhotite, liquid, gas, and nine univariant equilibria: (a) iron, wustite, pyrrhotite; (b) iron, wustite, magnetite; (c) iron, wustite, pyrrhotite; (d) wustite, magnetite, pyrrhotite; (e) iron, wustite, liquid; (f) iron, pyrrhotite, liquid; (g) wustite, pyrrhotite, liquid; (h) wustite, magnetite, liquid; and (i) pyrrhotite, magnetite, liquid. The phase diagram in the Fe-S-O system (Figure 2.3.3) shows the composition ranges for these invariant, univariant, bivariant, and trivariant phase equilibria. The possible systems for the application of liquid iron oxysulfide as a sulfur sorbent in equilibrium with an univariant system are Fe-FeO-liquid-gas and FeO-Fe₃O₄-liquid-gas systems. Pre-calculated results indicate that the SO₂ concentration from a coal-gas desulfurization system in equilibrium with FeO-Fe₃O₄-liquid-gas yields values of SO₂ concentration significantly above the EPA New Source Performance Standards. Therefore, it is necessary to examine the equilibrium of Fe-FeO-liquid-gas system.

Figure 2.3.6 is a pseudo-binary section following the boundary of the three condensed-phase region Fe-FeO-liquid, as was shown in Figure 2.3.3. This plot (Figure 2.3.6) is for data taken by the diagonally slanting line, which passes through the point labeled 920°C in Figure 2.3.3. The compositions expressed in terms of weight percent of sulfur and weight percent of oxygen are functions of temperature for the Fe-FeO-liquid-gas system. As temperature increases, the weight percent of sulfur decreases while that of oxygen increases. Figure 2.3.7 displays the values of the partial pressures of sulfur and oxygen in a gas at equilibrium with the Fe-FeO-liquid-gas system. As temperature rises, the oxygen partial pressure is shown to rise linearly due to the increase in oxygen content, but interestingly, the

Figure 2.3.4 Sulfur Potentials for Univariant Equilibria in the Fe-S-O System^[54]

- (a) iron, wustite, pyrrhotite;
- (b) iron, wustite, magnetite;
- (c) iron, wustite, pyrrhotite;
- (d) wustite, magnetite, pyrrhotite;
- (e) iron, wustite, liquid;
- (f) iron, pyrrhotite, liquid;
- (g) wustite, pyrrhotite, liquid;
- (h) wustite, magnetite, liquid; and
- (i) pyrrhotite, magnetite, liquid.

Figure 2.3.5 Oxygen Potentials for Univariant Equilibria in the Fe-S-O System^[54]

- (a) iron, wustite, pyrrhotite;
- (b) iron, wustite, magnetite;
- (c) iron, wustite, pyrrhotite;
- (d) wustite, magnetite, pyrrhotite;
- (e) iron, wustite, liquid;
- (f) iron, pyrrhotite, liquid;
- (g) wustite, pyrrhotite, liquid;
- (h) wustite, magnetite, liquid; and
- (i) pyrrhotite, magnetite, liquid.

Figure 2.3.6 The Composition of the Three Condensed-Phase Fe-FeO-Liquid System as a Function of Temperature

Figure 2.3.7 Partial Pressure of Sulfur and Oxygen in Equilibrium with the Fe-FeO-Liquid System as a Function of Temperature

sulfur partial pressure rises with decreasing slope because of reduced sulfur content.

Incorporating the above thermodynamic data for Fe-FeO-liquid-gas system into the interactive computer program listed in appendix A for coal gasification in the presence of an iron-based sorbent, one obtains the results reported in Table 2.3.1. The predominant species for these reducing conditions (corresponding to a combustion stoichiometry of approximately 52% of the required air for complete combustion) are N_2 and CO followed by CO_2 , H_2 , and H_2O . Figure 2.3.8 shows the calculated concentrations of the major sulfur containing gaseous species in equilibrium with the Fe-FeO-liquid-gas system as a function of temperature. The total sulfur pressure is the sum of all the sulfur-bearing species with H_2S and COS being the predominant sulfur species.

The sulfur concentration (SO_x lb/MM BTU) and percentage of sulfur removal are plotted against temperature in Figure 2.3.9 for the Fe-FeO-liquid-gas system, as was previously done with the lime-based system. It is a fortuitous aspect of Fe-FeO-liquid-gas system that the thermodynamic predictions for desulfurization show improvement with higher temperatures.

The required dosage of magnetite in g/100g of dry coal and the equivalence ratio are shown in Figure 2.3.10. Although the weight percent of iron in composition of the Fe-FeO-liquid system decreases with increasing temperature, the higher desulfurization efficiency still needs more magnetite addition. At higher temperatures, the larger partial pressures of oxygen equilibrated with the Fe-FeO-liquid-gas system cause the equivalence ratio to remain at values only slightly smaller than those at lower temperatures.

The iron oxysulfide as sulfur sorbent is employed in gasification processes in which coal is burned under sub-stoichiometric conditions which do not favor significant NO_x emission.

The effect of moisture of an IBC-107 coal, based on 100 g of dry coal, on the emission levels of SO_2 and percentage of sulfur removal is shown in Figure 2.3.11. The SO_2 concentration is expressed in pounds of SO_2 per million BTUs of gross calorific power of the coal burned under stoichiometric conditions at $1200^\circ C$. Figure 2.3.12 shows the four major sulfur containing species in the gas phase which occur at $1200^\circ C$ in a gas at equilibrium with Fe-FeO-liquid system, as a function of moisture content of the coal. The

Table 2.3.1 Effect of Temperature on the Composition of Gas
in Equilibrium with the Fe-FeO-liquid System

Temperature	1000°C	1100°C	1200°C	1300°C
PO ₂	1.16x10 ⁻¹⁵	4.53x10 ⁻¹⁴	1.08x10 ⁻¹²	1.71x10 ⁻¹¹
PCO	1.87x10 ⁻¹	1.93x10 ⁻¹	1.98x10 ⁻¹	2.02x10 ⁻¹
PCO ₂	7.18x10 ⁻²	6.64x10 ⁻²	6.20x10 ⁻²	5.82x10 ⁻²
PH ₂	8.50x10 ⁻²	8.07x10 ⁻²	7.69x10 ⁻²	7.37x10 ⁻²
PH ₂ O	5.13x10 ⁻²	5.59x10 ⁻²	6.00x10 ⁻²	6.37x10 ⁻²
PN ₂	6.05x10 ⁻¹	6.04x10 ⁻¹	6.03x10 ⁻¹	6.02x10 ⁻¹
PH ₂ S	3.74x10 ⁻⁴	3.42x10 ⁻⁴	2.74x10 ⁻⁴	1.72x10 ⁻⁴
PSO ₂	4.68x10 ⁻⁸	7.20x10 ⁻⁸	1.07x10 ⁻⁶	2.72x10 ⁻⁶
PCOS	4.24x10 ⁻⁵	4.06x10 ⁻⁵	3.39x10 ⁻⁵	2.21x10 ⁻⁵
PSO	1.00x10 ⁻⁸	7.20x10 ⁻⁸	3.44x10 ⁻⁷	1.03x10 ⁻⁶
PS ₂	1.09x10 ⁻⁷	3.50x10 ⁻⁷	7.23x10 ⁻⁷	7.98x10 ⁻⁷
PSO ₃	2.59x10 ⁻¹⁶	4.89x10 ⁻¹⁵	5.40x10 ⁻¹⁴	3.34x10 ⁻¹³
PCS ₂	2.71x10 ⁻⁹	2.95x10 ⁻⁹	2.38x10 ⁻⁹	1.16x10 ⁻⁹
PCS	1.00x10 ⁻⁸	2.02x10 ⁻⁸	3.21x10 ⁻⁸	3.69x10 ⁻⁸
PS ₄	4.14x10 ⁻¹⁸	2.77x10 ⁻¹⁷	8.15x10 ⁻¹⁷	7.17x10 ⁻¹⁷
PS	1.27x10 ⁻⁹	1.14x10 ⁻⁸	6.63x10 ⁻⁸	2.35x10 ⁻⁷
PNO	2.37x10 ⁻¹¹	2.76x10 ⁻¹⁰	2.31x10 ⁻⁹	1.47x10 ⁻⁸
PNO ₂	2.09x10 ⁻²⁰	1.02x10 ⁻¹⁸	2.94x10 ⁻¹⁷	5.51x10 ⁻¹⁶
PCH ₄	2.52x10 ⁻⁷	4.45x10 ⁻⁸	9.84x10 ⁻⁹	2.64x10 ⁻⁹
S in Gases	9.13x10 ⁻³	8.39x10 ⁻³	6.78x10 ⁻³	4.36x10 ⁻³
SO ₂ Conc.	0.497	0.457	0.369	0.237
%S Removal	92.43	93.05	94.38	96.39
NO _x Conc.	2.04x10 ⁻⁸	2.36x10 ⁻⁷	1.97x10 ⁻⁶	1.25x10 ⁻⁵
Air Dosage	375.2	373.7	372.3	371.2
Eq. Ratio	1.906	1.914	1.921	1.927
Fe ₃ O ₄ Dosage	16.34	18.27	22.15	26.33

Figure 2.3.8 Partial Pressures of the Major Sulfur-Containing Gaseous Species in Equilibrium with the Fe-FeO-Liquid System as a Function of Temperature

Figure 2.3.9 Calculated SO₂ Concentration and Percentage of Sulfur Removal with Fe-FeO-Liquid Sorbent System as a Function of Temperature

Figure 2.3.10 Magnetite Dosage g/100g Dry Coal and Equivalence Ratio versus Temperature with Fe-FeO-Liquid Sorbent System

Figure 2.3.11 SO₂ Concentration and Percentage of Sulfur Removal versus Moisture Content (g/100 g Dry Coal) at 1200°C in the Presence of Fe-FeO-Liquid System

Figure 2.3.12 Partial Pressures of the Major Sulfur-Containing Gaseous Species as a Function of Moisture Content (g/100 g Dry Coal) in the Presence of the Fe-FeO-Liquid System at 1200°C

partial pressure of the predominant sulfur-containing species, hydrogen sulfide, is seen to increase with increasing moisture content of the coal while those of COS, SO₂, S₂ remain virtually constant. Since the partial pressures of sulfur and oxygen are fixed by the following two reactions: $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ and $2\text{H}_2 + \text{S}_2 = 2\text{H}_2\text{S}$, the addition of moisture increases the partial pressure of hydrogen, which, in turn, increases the partial pressure of H₂S. Therefore, gasification of coals with higher moisture content would be expected to cause higher sulfur levels in the gas phase. It is thus beneficial to the desulfurization process to dry the coal prior to gasification.

The effect of total pressure on SO₂ concentration at 1200°C is shown in Figure 2.3.13., provided the total pressure has very little effect on chemical potentials of sulfur and oxygen of the Fe-FeO-liquid system. It is seen that increasing the total pressure results in virtually no effect on the extent of desulfurization. Although, from a thermodynamic stand point, the pressure effect is minimal, except for pressures significantly below one atmosphere, total pressure is likely to affect reaction kinetics.

The coal seam which has been studied most extensively in clean-coal programs is Illinois #6. Four other representative coals from this seam are characterized with respect to their assays and calorific values in Table 2.3.2.

These data are incorporated into the interactive program to predict the equilibrium sulfur pressures of the predominant gaseous species which would be present in a gas in equilibrium with the Fe-FeO-liquid-gas system. The results of these calculations are reported in Table 2.3.3. Figures 2.3.14 and 2.3.15 give the equilibrium values of SO₂ under conditions of stoichiometric combustion and the percentage of sulfur removal versus temperature, respectively. The moist IBC-108 coal which contains 45 percent moisture (essentially a slurry) shows the highest SO₂ content of the combustion products, as is expected. The lowest sulfur content is for IBC-109 which has a starting composition of only 1.14% sulfur compared with the other coals which range up to 4.52% sulfur for IBC-105 coal. Using iron oxysulfide as sulfur sorbent, however, the percentage of sulfur removal is higher for high-sulfur coals than for low-sulfur coals. Since the partial pressures of sulfur and oxygen are fixed by the iron oxysulfide melts, the partial pressures of all sulfur-bearing species involved in the gas phase are also fixed. The higher the initial sulfur content of the

Figure 2.3.13 Effect of Total Pressure on the Concentration of SO_2 in a Gas at equilibrium with the Fe-FeO-Liquid System at 1200°C

Table 2.3.2 Compositions of Several Illinois #6 Coals

Illinois #6 Coal (Moisture Free Value)				
Lots	IBC-104	IBC-105	IBC-108	IBC-109
Moisture %	10.5	9.4	45.0	9.2
V Matter %	28.3	36.7	41.3	34.9
Fixed C %	33.3	44.8	54.9	56.8
H-T Ash %	38.4	18.5	3.8	8.3
Carbon %	46.78	63.6	76.2	74.95
Hydrogen %	3.41	4.58	5.41	4.95
Nitrogen %	0.88	1.19	1.56	1.76
Oxygen %	8.25	7.55	10.39	8.93
Sulfur %	4.17	4.52	2.63	1.14
BTU/lb	8522	11540	13700	13301

coal, the higher the percentage of sulfur removal. According to the 1979 revised NSPS (New Source Performance Standard), there are limits not only for the SO_2 concentration but also for the percentage of sulfur removal. Therefore the above analysis indicates clearly that iron oxysulfide as a sulfur sorbent would perform best on dry, high-sulfur coals.

Table 2.3.3 Gas Compositions Resulting from the Gasification
of Four Different Illinois #6 Coals in the Presence
of the Fe-FeO-liquid System at 1200 °C

	IBC-104	IBC-105	IBC-108	IBC-109
PO ₂	1.08x10 ⁻¹²	1.08x10 ⁻¹²	1.08x10 ⁻¹²	1.08x10 ⁻¹²
PCO	2.01x10 ⁻¹	1.97x10 ⁻¹	1.97x10 ⁻¹	1.97x10 ⁻¹
PCO ₂	6.32x10 ⁻²	6.17x10 ⁻²	6.18x10 ⁻²	6.17x10 ⁻²
PH ₂	8.67x10 ⁻²	7.64x10 ⁻²	1.19x10 ⁻¹	6.88x10 ⁻²
PH ₂ O	6.77x10 ⁻²	5.96x10 ⁻²	9.25x10 ⁻²	5.37x10 ⁻²
PN ₂	5.80x10 ⁻¹	6.05x10 ⁻¹	5.29x10 ⁻¹	6.19x10 ⁻¹
PH ₂ S	3.08x10 ⁻⁴	2.72x10 ⁻⁴	4.21x10 ⁻⁴	2.45x10 ⁻⁴
PSO ₂	1.07x10 ⁻⁶	1.07x10 ⁻⁶	1.07x10 ⁻⁶	1.07x10 ⁻⁶
PCOS	3.46x10 ⁻⁵	3.37x10 ⁻⁵	3.38x10 ⁻⁵	3.37x10 ⁻⁵
PSO	3.44x10 ⁻⁷	3.44x10 ⁻⁷	3.44x10 ⁻⁷	3.44x10 ⁻⁷
PS ₂	7.23x10 ⁻⁷	7.23x10 ⁻⁷	7.23x10 ⁻⁷	7.23x10 ⁻⁷
PSO ₃	5.40x10 ⁻¹⁴	5.40x10 ⁻¹⁵	5.40x10 ⁻¹⁴	5.40x10 ⁻¹³
PCS ₂	2.43x10 ⁻⁹	2.37x10 ⁻⁹	2.37x10 ⁻⁹	2.37x10 ⁻⁹
PCS	3.27x10 ⁻⁸	3.19x10 ⁻⁸	3.20x10 ⁻⁸	3.19x10 ⁻⁸
PS ₄	8.15x10 ⁻¹⁷	8.15x10 ⁻¹⁷	8.15x10 ⁻¹⁷	8.15x10 ⁻¹⁷
PS	6.63x10 ⁻⁸	6.63x10 ⁻⁸	6.63x10 ⁻⁸	6.63x10 ⁻⁸
PNO	2.26x10 ⁻⁹	2.31x10 ⁻⁹	2.16x10 ⁻⁹	2.34x10 ⁻⁹
PNO ₂	2.89x10 ⁻¹⁷	2.95x10 ⁻¹⁷	2.76x10 ⁻¹⁷	2.98x10 ⁻¹⁷
PCH ₄	1.27x10 ⁻⁸	9.66x10 ⁻⁹	2.33x10 ⁻⁸	7.84x10 ⁻⁹
S in Gases	5.09x10 ⁻³	6.32x10 ⁻³	1.12x10 ⁻²	6.80x10 ⁻³
SO ₂ Conc.	0.407	0.363	0.565	0.342
%S Removal	96.09	95.52	86.31	80.87
NO _x Conc.	1.91x10 ⁻⁶	1.95x10 ⁻⁶	1.91x10 ⁻⁶	2.04x10 ⁻⁶
Air Dosage	241.3	350.8	366.4	422.3
Eq. Ratio	2.041	1.928	2.169	1.826
Fe ₃ O ₄ Dosage	24.30	26.18	13.77	5.59

Figure 2.3.14 Fe-FeO-Liquid-Gas System
The Comparative Effect of Temperature upon
SO₂ Concentration for Four Illinois Coals

Figure 2.3.15 Fe-FeO-Liquid-Gas System
The Effect of Temperature upon the Percentage
of Sulfur Removal for Four Illinois '6 Coal

2.3.3 Equilibrium between Liquid (Fe-S-O) and Gas

Bog and Rosenqvist^[53] also determined the partial pressures of oxygen and sulfur by equilibrating the iron oxide-iron sulfide melts with a ternary gas mixture, $H_2 + H_2O + H_2S$, at 1120°C and 1400°C. Dewing and Richardson^[55] made measurements of equilibria involving molten mixtures of iron sulfide and iron oxide and gas mixtures consisting of N_2 , S_2 , and SO_2 of known sulfur and oxygen fugacities at temperatures ranging from 1100 to 1433°C. Subsequently, Nagamori and Kameda^[56] extended these measurements to higher activities of sulfur by equilibrating the homogeneous Fe-S-O melts with ternary gas mixtures of $CO-CO_2-SO_2$ at 1200°C. Stofko, Schmiedl, and Rosenqvist^[57] also extended the equilibrium measurements at 1200°C to more oxidizing conditions, corresponding to SO_2 pressures approaching one atmosphere, and until saturation with solid magnetite. By using these equilibrium data available in the literature and extrapolating from higher temperatures, Naldrett^[58,59] presented diagrams showing the liquid field in a portion of the system Fe-S-O contoured in terms of partial pressures of sulfur and oxygen and the activity of iron oxide for a number of temperatures, the highest of which was 1200°C (Figure 2.3.16). Shima and Naldrett^[60] also extrapolated the isoactivities of iron oxide (a_{FeO}), sulfur ($\log P_{S_2}$), and oxygen ($\log P_{O_2}$) in the Fe-S-O melts at 1450°C, assuming a straight line relationship between $\log P_i$ and $1/T$ (Figure 2.3.17). It is clearly seen that the liquid region beyond the liquid boundaries saturated with iron which covers the isoactivity curves is the same as that at 1200°C.

The isothermal sections can be readily constructed from the available data on phase equilibria (Figure 2.2.3) in the Fe-S-O system. Figure 2.3.18 is an isothermal section at 1200°C showing composition ranges for two univariant equilibria (three condensed phases), four two-phase equilibria, and one liquid phase. Figure 2.3.19 is a similar isothermal section at 1450°C showing regions of the univariant miscibility gap as well as other phase equilibria. Iron-saturated liquid boundary shifts towards iron-rich region with increasing temperature. Except at 1200°C, the partial pressures of sulfur and oxygen in the composition region beyond the liquid boundary not covered by the existing data have to be studied for the analysis of desulfurization with single iron oxysulfide liquid.

For the potential use of iron oxysulfide as a sulfur sorbent for a coal gasification

Figure 2.3.16 Isoactivities, a_{FeS} , $\log P_{S_2}$, and $\log P_{O_2}$ in Fe-S-O melts at 1200°C^[59]

Figure 2.3.17 Isoactivities, a_{FeS} , $\log P_{\text{S}_2}$, and $\log P_{\text{O}_2}$ in Fe-S-O melts at 1450°C^[59]

Figure 2.3.18 Isotherm for Fe-S-O System at 1200°C
 γ , gamma iron; W, wustite; M, magnetite;
 P, pyrrhotite; L_1 , liquid oxysulfide.

Figure 2.3.19 Isotherm for Fe-S-O System at 1450°C

δ , delta iron; W, wustite;
M, magnetite; P, pyrrhotite;
 L_1 , liquid oxysulfide; L_2 , liquid iron.

system operating at temperatures ranging from 1200 to 1450°C which are usually required for efficient combustion and conversion to electrical power, it becomes necessary to extend the data from the literature to regions not tested experimentally. This objective can be realized by using a solution model which includes a mathematical description of the activity coefficients of sulfur and oxygen in the iron oxysulfide melts. The solution model can then be used in conjunction with the interactive computer program for a thorough thermodynamic analysis of coal combustion in presence of an iron-based sulfur sorbent.

2.3.3.1 Development of a Thermochemical Model

The goal of this model is to develop mathematical descriptions of the activity coefficients of sulfur and oxygen in iron oxysulfide melt that will:

- (a) reproduce the reported and measured data; and
- (b) serve to interpolate or extrapolate the system behavior, with some confidence, to regions not tested experimentally.

(I) Data Source for Solution Model

Under the conditions of fixed composition of the iron oxysulfide and total pressure, the partial pressures of sulfur and oxygen equilibrated with liquid oxysulfide as a function of temperature can be expressed as:^[42,61]

$$\left(\frac{\partial \ln P_i}{\partial T} \right)_{P, n_i} = \frac{\Delta H^\circ}{RT^2} \quad (2.3.1)$$

where the $P_i = P_{S_2}$ or P_{O_2} .

Integration gives

$$\int_{P_{i,1}}^{P_i} d \ln P_i = \int_{T_1}^T \frac{\Delta H^\circ}{RT^2} dT \quad (2.3.2)$$

When the temperature range involved is not appreciable, and in the absence of any phase change in the participating species, ΔH° can be treated as being independent of temperature,

and the above equation is directly integrated to yield equation 2.3.3.

$$\ln \frac{P_i}{P_{i,1}} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right) \quad (2.3.3)$$

By using the data of the iron oxysulfide liquid at 1200°C and 1450°C to obtain the values of the ΔH° at fixed liquid compositions, equation (2.3.4) can be derived and used to calculate the partial pressures of sulfur and oxygen at different temperatures.

$$\ln P_i = \ln(P_i)_{1473} + \ln \left(\frac{(P_i)_{1673}}{(P_i)_{1473}} \right) \frac{\left(\frac{1}{1473} - \frac{1}{T+273} \right)}{\left(\frac{1}{1473} - \frac{1}{1773} \right)} \quad (2.3.4)$$

(II) Solution Model

In searching for the most suitable mathematical form to express the dependence of species activity coefficients on the composition at constant temperature, there is always a trade-off between simplicity and flexibility of the model, - the number of adjustable parameters, and the ability of the model to fit a wide range of the system. Several different types of solution models, either empirical or semitheoretical, have been developed to represent the composition variations of the activities of components in liquid or solid solutions.^[18,42,59,62,63] The author's preferences for modelling of activity coefficients led us to focus on the following two solution models.

Multicomponent regular solution model: A solution is said to be regular, by definition, when the entropy of mixing is equal to the ideal configurational entropy. The general form of the equation for a regular solution model is

$$RT \ln \gamma_i = \sum_j k_{ij} x_j - \frac{1}{2} \sum_j \sum_p k_{jp} x_j x_p \quad (2.3.5)$$

where:

γ_i = activity coefficient of species i

x_i = mole fraction of species i

$k_{ij} = k_{ji}$

$k_{ii} = k_{jj} = k_{pp} = 0$

For the sulfur equilibrium between liquid and gaseous phases, the reaction can be expressed as:

and

$$\ln P_{S_2} = \ln K_s + 2 \ln x_s + 2 \ln \gamma_s \quad (2.3.7)$$

Combining equations (2.3.5) and (2.3.7), one obtains

$$\begin{aligned} \ln p_{S_2} = & \ln k_s + 2 \ln x_s + k_{so} x_o^2 + k_{FeS} x_{Fe}^2 \\ & + (k_{so} + k_{FeS} - k_{FeO}) x_o x_{Fe} \end{aligned} \quad (2.3.8)$$

A Similar expression can be developed for the partial pressure of oxygen. With this model only four parameters (K_s , k_{SO} , k_{FeS} , k_{FeO}) are needed to describe the iron oxysulfide system, so that simplicity is indeed achieved. However, the symmetry $k_{ij} = k_{ji}$ may be too restricting to make the model of any use to fit the reported data.

Three-Suffix Margules' equation: One of the most durable formulas for expressing the activity-composition variation is that due to Margules. The so-called three-suffix Margules' equations for multicomponent systems^[64,65], with zero ternary interactions will be applied to liquid iron oxysulfide. According to this model, at constant temperature each pair of species is characterized by two parameters, k_{ij} and k_{ji} , so that a solution of three species would require six parameters for complete description. The equations that express the composition dependence of the activity coefficients are:

$$\begin{aligned}
\ln \gamma_i = & \frac{1}{2} \sum_j (k_{ij} + k_{ji}) x_j - \frac{1}{2} \sum_j \sum_p k_{jp} x_j x_p \\
& + \sum_j \sum_p (k_{jp} - k_{pj}) x_j^2 x_p \\
& + \sum_j (k_{ij} - k_{ji}) (0.5 x_j - x_i) x_j
\end{aligned} \quad (2.3.9)$$

where $k_{ii} = k_{jj} = k_{pp} = 0$. For the special case when $k_{ij} = k_{ji}$ for all values of i and j , the model reduces to the strictly regular solution model. By admitting both k_{ij} and k_{ji} coefficients, the capability of the model to handle nonsymmetrical activity coefficient is enhanced.

Combining equations (2.3.7) and (2.3.9), one obtains:

$$\begin{aligned}
\ln p_{s_2} = & \ln k_s + 2 \ln x_s + (k_{so} + k_{os}) x_o \\
& + (k_{SFe} + k_{FeS}) x_{Fe} - (k_{so} + k_{os}) x_s x_o \\
& - (k_{SFe} + k_{FeS}) x_s x_{Fe} - (k_{OFe} + k_{FeO}) x_o x_{Fe} \\
& + 2(k_{so} - k_{os}) (0.5 x_o - x_s) x_o \\
& + 2(k_{SFe} - k_{FeS}) (0.5 x_{Fe} - x_s) x_{Fe} \\
& + 2(k_{so} - k_{os}) x_s^2 x_o + 2(k_{SFe} - k_{FeS}) x_s^2 x_{Fe} \\
& + 2(k_{os} - k_{so}) x_o^2 x_s + 2(k_{OFe} - k_{FeO}) x_o^2 x_{Fe} \\
& + 2(k_{FeS} - k_{SFe}) x_{Fe}^2 x_s + 2(k_{FeO} - k_{OFe}) x_{Fe}^2 x_o
\end{aligned} \quad (2.3.10)$$

There are seven unknown parameters ($\ln k_s$, k_{SO} , k_{OS} , k_{SFe} , k_{FeS} , k_{OFe} , k_{FeO}).

As noted previously, a similar expression can be developed for the partial pressure of oxygen.

(III) Determination of Model Parameters

The next step in model development is to determine the values of the four parameters in equation (2.3.8) and the seven parameters in equation (2.3.10) that give a best fit to available reported data as well as to data calculated from equation (2.3.4) at a given temperature.

First, we define an objective function:

$$OBJ = \sum_{i=1}^n [\log(P_i)_{modeled} - \log(P_i)_{measured}]^2 \quad (2.3.11)$$

A modified simplex optimization^[66,67] computer program, a listing of which is provided in Appendix A, is developed to use the data reported or calculated from equation (2.3.4) to obtain the four unknown parameters in equation (2.3.8) or the seven unknown parameters in equation (2.3.10) in order to make the objective function have a minimum value. Following this procedure, the model is used to extrapolate the system to the unmeasured composition range.

(IV) Simplex Method^[66,67]

The simplex method is a sequential optimization method that involves repeated observation of the system response and selection of new values for the variables. This method can be visualized for optimization problems involving just two variables for tracking on the response surface. It corresponds to seeking hills or ridges on a topographical map. A geometric construct called simplex is used as the method for tracking about on the response surface. A simplex in two dimensions is a triangle.

At each iteration, to minimize a function $f(x)$, this function is evaluated at each of the three vertices of the triangle. The direction of search is oriented away from the point with the highest value for the function through the centroid of the simplex. By making the search direction bisect the line between the other two points of the triangle, the direction goes through the centroid. The new point is selected in this reflected direction, preserving the geometric shape (Figure 2.3.20). The objective function is then evaluated at the new point, and a new search direction is calculated. The method proceeds by rejecting one vertex at a time until the simplex straddles the optimum. Various rules are used to prevent excessive repeating of the same cycle or simplexes. As the optimum is approached, the last equilateral triangle will straddle the optimum point or be within a distance of the order of its own size from the optimum (Figure 2.3.21).

(V) Results of Modelling Work

Tables (2.3.4-2.3.11) in Appendix B are the reported and modeled data and

Figure 2.3.20 Reflection to a new point in the Simplex method

Figure 2.3.21 Progression to the Vicinity of the Optimum and Oscillation around the Optimum Using the Simplex Method of Search^[66]

parameters for the partial pressures of sulfur and oxygen at 1200 °C, 1300 °C, 1400 °C, and 1450 °C obtained with the method of Three-Suffix Margules' equation. For the partial pressure of sulfur, the average absolute error and average relative error are about 0.25 and 6%. They are approximately 0.12 and 1% in the case of the partial pressure of oxygen.

The results of modelling calculation and error analysis show the ability of the model to fit the reported data and its use to interpolate or extrapolate the system behavior to regions not tested experimentally.

2.3.3.2 Analysis of Equilibrium between Liquid (Fe-S-O) and Gas

The calculated seven parameters ($\ln k_S$ or $\ln k_O$, k_{SO} , k_{OS} , k_{SFe} , k_{FeS} , k_{OFe} , k_{FeO}) were then used in conjunction with the three suffix Margules' equation to determine the partial pressures of sulfur and oxygen in the gas phase in equilibrium with the liquid iron oxysulfide in plots of wt% S versus wt% O at various temperatures. These values are superimposed on the liquid composition expressed as weight percentages of oxygen and sulfur ranging from 1200 to 1450 °C in Figures 2.3.22 and 2.3.23 at 1200°C, Figures 2.3.28 and 2.3.29 at 1300°C, Figures 2.3.34 and 2.3.35 at 1400°C, and Figure 2.3.40 and 2.3.41 at 1450°C.

As expected, the partial pressure of sulfur increases as the weight percent of sulfur in liquid iron oxysulfide increases at fixed weight percent oxygen, and the partial pressure of oxygen increases with increasing oxygen content of the liquid. At fixed liquid composition, the partial pressures of sulfur and oxygen increase with increasing temperature. The single phase liquid region beyond the liquid boundary saturated with iron covers a wider range of compositions as temperature increases.

A notable feature of the sulfur isoactivity diagrams is that an increase in temperature of 100°C has little effect on raising the partial pressure of sulfur for a given ternary composition; in other words, the isoactivity curves shift only slightly. However, the region of available liquid phase increases significantly with increasing temperature, thus allowing for a region of higher degree of desulfurization, especially at the lower-left liquid region. But the increase in the size of the region of stability of the liquid also requires more iron oxide to be added as a sorbent.

Using the partial pressures of sulfur and oxygen from the solution model under certain compositions of iron oxysulfide melt, the interactive computer program in Appendix A is used to conduct theoretical analysis of coal combustion in the presence of an iron-based sulfur sorbent. The contour lines of calculated sulfur concentration (SO_2 lb/MM BTU), percentage of sulfur removal, dosage of magnetite (Fe_3O_4 g), and equivalence ratio are plotted in Figures 2.3.24, 2.3.25, 2.3.26, 2.3.27 at 1200°C, in Figures 2.3.30, 2.3.31, 2.1.32, 2.3.33 at 1300°C, in Figures 2.3.36, 2.3.37, 2.3.38, 2.3.39 at 1400°C, and in Figures 2.3.42, 2.3.43, 2.3.44, 2.3.45 at 1450°C.

At the same temperature, the lower levels of sulfur concentration and higher

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percentages of sulfur removal are found near the iron-liquid boundary, close to the low oxygen boundary. For the composition further into the iron oxysulfide phase the SO_2 levels rise rapidly, since the partial pressure of sulfur increases as the weight percent of sulfur in liquid iron oxysulfide (Fe-O-S) increases at fixed weight percent oxygen. Essentially, desulfurization is poor for all compositions except those close to the two-phase boundary.

Although at a fixed liquid composition, the partial pressure of sulfur increases with increasing temperature, this system has a fortunate feature: Upon stoichiometric combustion of the fuel gas in contact with the iron-oxysulfide phase, the SO_2 concentration remains relatively constant. For example, at a fixed composition of an iron oxysulfide melt containing 5% oxygen and 25% sulfur, the SO_2 concentration remains at a level of 0.8 lb/MM Btu over a range of temperature from 1200°C to 1450°C. This occurs because of the decomposing tendency of the predominant sulfur-containing species H_2S . This decomposition as expressed by the reverse reaction:

has a tendency to equilibrate to the left as temperature increases. One may observe, therefore, from the equilibrium relationship ($P_{\text{H}_2\text{S}} = K_{\text{H}_2\text{S}} \cdot P_{\text{H}_2} \cdot P_{\text{S}_2}^{1/2}$) that an increase in sulfur pressure over the Fe-O-S liquid will, upon increasing temperature, be offset by the temperature variation of the equilibrium constant. However, with increasing temperature, one feature of this system is that the two-phase boundary retreats toward the abscissa (iron-rich region) as the compositional range of the molten phase increases with increasing temperature. In other words, the region of stability of the single-phase liquid increases with increasing temperature. This feature has a noticeable effect at higher temperatures where the compositional range exhibiting lower values SO_2 concentration widens with increasing temperature (Compare, for example, Figures 2.3.24, 2.3.30). When the temperature is over 1350°C, the region within the curved line is a two-phase region of liquid immiscibility: iron-saturated liquid and iron oxysulfide liquid. The upper boundary shows a wide region of low SO_2 values which accommodates within the single-phase liquid at a wide range of reducing potentials. Levels of greater than 90% sulfur removal are shown to be readily achievable. The thermodynamic calculations for desulfurization demonstrate that the iron oxysulfide can

be used as a sulfur sorbent under the temperature range of 1200-1450 °C with significant improvement with increasing temperature. A fortuitous aspect of the Fe-S-O system is that at higher temperature, the fluidity of iron oxysulfide is increased and the kinetics of sulfur capture is accelerated at higher temperatures. In addition, coal combustion and subsequent conversion to electric power becomes more efficient at higher temperature.

The increase in the extent of desulfurization and weight percentage of iron in iron oxysulfide at higher temperature adds to the cost of the operation. However, the high levels of added iron oxide are not necessary; 15% or less addition of iron oxide is sufficient to meet the EPA standard. For a low SO₂ concentration and a high sulfur removal, the gasification process with the iron oxysulfide liquid as a sulfur sorbent should be operated at the equivalence ratios larger than 2.5.

For a given desulfurization process with iron oxysulfide liquid as a sulfur sorbent, the selection of temperature, composition of iron oxysulfide, dosage of iron oxide, and equivalence ratio can be controlled to achieve the best results according to the above thermodynamic analysis.

Figure 2.3.22 Ternary Isothermal Section of the Fe-S-O System at 1200°C with Isobars of Partial Pressure of Sulfur

Figure 2.3.23 Ternary Isothermal Section of the Fe-S-O System at 1200°C with Isobars of Partial Pressure of Oxygen

Figure 2.3.24 Iso-SO₂ Concentration* Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1200°C
*Under Subsequent Condition of Stoichiometric Combustion

Figure 2.3.25 Iso-Sulfur Removal Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1200°C

Figure 2.3.26 Iso-Dosage of Magnetite Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1200°C

Figure 2.3.27 Iso-Equivalence Ratio Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1200°C

Figure 2.3.28 Ternary Isothermal Section of the Fe-S-O System at 1300°C with Isobars of Partial Pressure of Sulfur

Figure 2.3.29 Ternary Isothermal Section of the Fe-S-O System at 1300°C with Isobars of Partial Pressure of Oxygen

Figure 2.3.30 Iso-SO₂ Concentration* Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1300°C
*Under Subsequent Condition of Stoichiometric Combustion

Figure 2.3.31 Iso-Sulfur Removal Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1300°C

Figure 2.3.32 Iso-Dosage of Magnetite Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1300°C

Figure 2.3.33 Iso-Equivalence Ratio Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1300°C

Figure 2.3.34 Ternary Isothermal Section of the Fe-S-O System at 1400°C with Isobars of Partial Pressure of Sulfur

Figure 2.3.35 Ternary Isothermal Section of the Fe-S-O System at 1400°C with Isobars of Partial Pressure of Oxygen

Figure 2.3.36 Iso-SO₂ Concentration* Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1400°C
*Under Subsequent Condition of Stoichiometric Combustion

Figure 2.3.37 Iso-Sulfur Removal Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1400°C

Figure 2.3.38 Iso-Dosage of Magnetite Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1400°C

Figure 2.3.39 Iso-Equivalence Ratio Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1400°C

Figure 2.3.40 Ternary Isothermal Section of the Fe-S-O System at 1450°C with Isobars of Partial Pressure of Sulfur

Figure 2.3.41 Ternary Isothermal Section of the Fe-S-O System at 1450°C with Isobars of Partial Pressure of Oxygen

Figure 2.3.42 Iso-SO₂ Concentration* Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1450°C
*Under Subsequent Condition of Stoichiometric Combustion

Figure 2.3.43 Iso-Sulfur Removal Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxsulfide at 1450°C

Figure 2.3.44 Iso-Dosage of Magnetite Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1450°C

Figure 2.3.45 Iso-Equivalence Ratio Calculated in Single Phase Region for Desulfurization of Coal Combustion Gases with Iron Oxysulfide at 1450°C

2.3.4 Mass and Heat Balances

All chemical processes involve various kinds of changes of materials and energy interchanges with the surroundings. Mass and heat balances for industrial furnaces are useful in that they provide insight into the supply and utilization of raw materials in determining costs and in determining the success or failure of a process. The developed computer program (Appendix A) yields the equilibrium results for the calculations of mass and heat balances with respect to the gasification stage (first stage of combustion) as well as the second stage (stoichiometric combustion).

Figure 2.3.46 shows the primary process of coal conversion. The mass of coal is taken to be 109.3 kg as-received coal (100 kg dry coal + 9.3 kg moisture) or 100 kg dry coal whose moisture has been removed by drying. The moisture content is ascertained by determining the percentage weight loss sustained by a finely divided sample of the coal when it is heated for 1 hr at a temperature of 107 ± 4 °C in vacuum or in an inert atmosphere. The primary air consists of 21% O₂ and 79% N₂ by volume. The selected composition of iron oxysulfide is 25% S, 5% O, 70% Fe by weight. In the developed interactive computer program for the conversion process, the main parameters for the mass balance calculations include composition of fuel gas, dosage of magnetite, and dosage of air, which are expected under equilibrium conditions. These parameters are given in Table 2.3.12. The mass balance results are summarized in Table 2.3.15.

The heat balance is not calculated directly, since the coal composition is very complex and the thermodynamic data for the elements in coal are unknown. Therefore, an indirect method to calculate the heat of the gasification process is used and is diagrammed in Figure 2.3.47. The calorific value of coal ΔH is the amount of heat released when a unit quantity of the fuel is burned in oxygen to completion and the products of combustion are cooled back to the reference state (25°C) at which the calorific value determination is being made. For the IBC-107, the calorific value ΔH is equal to 12224 Btu/lb (28.415 MJ/kg). The value of ΔH_1 is the released heat during the complete combustion of clean fuel gas and slag with secondary air and cooling its products from 1200°C to the same final temperature under which the calorific value is measured. Using the results of mass balance calculations, the calculation of ΔH_1 is made easily using the HSC program^[68]. The details of calculations for

Figure 2.3.46 Primary Process of Coal Conversion for Calculation of Mass and Heat Balances

Figure 2.3.47 Heat Balance Calculation Scheme

as-received coal and dry coal by the program are listed in Table 2.3.13 and 2.3.14.

Based on the calorific value of coal and the calculated value of ΔH_1 , the heat balance value ΔH_2 for the gasification process is calculated by the following energy conservation equation:

$$\Delta H_2 = \Delta H - \Delta H_1$$

The results of heat balance calculation are also shown in Table 2.3.15.

The distribution of thermal energy between the first and second stages of combustion is an important consideration. If too much energy is expended in the first stage, then the burner walls must be indirectly cooled in order to prevent severe erosion especially from the fluxing properties of the iron oxysulfide liquid. If, however, the first stage is nearly autogenous, then there may be difficulties in maintaining the flame front unless a degree of preheat is applied. The calculations show the first stage is not only autogenous at 1200° C, but that approximately 1 to 2 percent of the thermal energy of the as-received coal is present in excess to maintain the flame. Pre-drying of the coal would, of course, increase the excess heat available. In order to burn these typical coals at temperatures significantly above 1200° C, preheat of the combustion air and/or pre-drying of the coal is necessary; also, drying of the coal is desirable from the viewpoint of reduction of sulfur levels.

One might question whether it is possible to operate a coal burner under conditions of high equivalence ratio and still maintain enough heat to sustain combustion. Similar calculations are processed to give Figure 2.3.48 which shows the flame temperature for the as-received IBC-107 coal for two conditions: no heat loss (adiabatic flame temperature) and 20% of the coal calorific power lost.

Clearly, there is no difficulty in attaining the flame temperatures above 1500 °C even with 20% heat losses for equivalence ratios less than 2.0. The flame temperature increases with decreasing the equivalence ratio, since more of the carbon is converted to CO₂ until it reaches the maximum when the equivalence ratio approaches 1 (stoichiometric combustion). When the equivalence ratio is less than unity, the flame temperature is expected to decrease, since the excess air will remove enthalpy.

**Table 2.3.12 Thermodynamic Results for the
Calculation of Mass and Heat Balances**

Partial Pressure (atm.)	As-Received Coal	Dry Coal
PCO	3.06×10^{-1}	2.80×10^{-1}
PCO ₂	1.30×10^{-2}	1.28×10^{-2}
PH ₂	1.52×10^{-1}	1.23×10^{-1}
PH ₂ O	1.61×10^{-2}	1.31×10^{-2}
PN ₂	5.13×10^{-1}	5.51×10^{-1}
PO ₂	2.00×10^{-14}	2.00×10^{-14}
PH ₂ S	6.35×10^{-4}	5.15×10^{-4}
PSO ₂	2.34×10^{-8}	2.34×10^{-8}
PCOS	6.16×10^{-5}	6.04×10^{-5}
PSO	5.51×10^{-8}	5.51×10^{-8}
PS ₂	1.00×10^{-6}	1.00×10^{-6}
PSO ₃	1.60×10^{-16}	1.60×10^{-16}
PCS ₂	3.74×10^{-8}	3.67×10^{-8}
PCS	4.29×10^{-7}	4.21×10^{-7}
PS ₄	1.56×10^{-16}	1.56×10^{-16}
PS	7.79×10^{-8}	7.79×10^{-8}
PNO	2.89×10^{-10}	3.00×10^{-10}
PNO ₂	5.03×10^{-19}	5.21×10^{-19}
PCH ₄	4.35×10^{-7}	2.81×10^{-7}
SO ₂ Concentration lb/MM Btu	0.6770	0.5665
% of Sulfur Removal	89.70	91.31
NO _x Concentration lb/MM Btu	2.01×10^{-7}	2.11×10^{-7}
Dosage of Air liters	257.44	282.17
Equivalence Ratio	2.779	2.535
Dosage of Fe ₃ O ₄ g	11.56	11.79

Table 2.3.13 Heat Balance in Second Stage Combustion for As-Received Coal

INPUT				
COMPONENT	TEMPERATURE °C	AMOUNT kmol	kg Nm ³	HEAT CONTENT MJ
N ₂ (g)	1200	9.12	204.34	338.99
CO(g)	1200	5.44	121.89	-397.08
CO ₂ (g)	1200	0.23	5.20	-77.61
H ₂ (g)	1200	2.70	60.49	96.03
H ₂ O(g)	1200	0.29	6.42	-55.95
O ₂ (g)	1200	0.00	0.00	0.00
H ₂ S(g)	1200	0.01	0.25	0.33
SO ₂ (g)	1200	0.00	0.00	0.00
COS(g)	1200	0.00	0.02	-0.07
SO(g)	1200	0.00	0.00	0.00
S ₂ (g)	1200	0.00	0.00	0.00
SO ₃ (g)	1200	0.00	0.00	0.00
CS ₂ (g)	1200	0.00	0.00	0.00
CS(g)	1200	0.00	0.00	0.00
S(g)	1200	0.00	0.00	0.00
S ₄ (g)	1200	0.00	0.00	0.00
NO(g)	1200	0.00	0.00	0.00
NO ₂ (g)	1200	0.00	0.00	0.00
CH ₄ (g)	1200	0.00	0.00	0.00
FeS	1200	0.11	9.53	0.97
FeO	1200	0.03	2.40	-6.82
Fe	1200	0.03	1.42	1.15
CaO*SiO ₂	1200	0.01	1.24	-15.90
Al ₂ O ₃ *SiO ₂	1200	0.02	3.47	-50.87
SiO ₂	1200	0.07	3.94	-54.42
O ₂ (g)	25	4.29	96.15	0.00
OUTPUT				
COMPONENT	TEMPERATURE °C	AMOUNT kmol	kg	HEAT CONTENT MJ
CO ₂ (g)	25	5.68	127.22	-2233.54
N ₂ (g)	25	9.12	204.34	0.00
SO ₂ (g)	25	0.12	2.71	-35.89
H ₂ O(g)	25	3.02	67.62	-729.53
Al ₂ O ₃	25	0.02	2.19	-35.98
CaO	25	0.01	0.60	-6.79
Fe ₂ O ₃	25	0.01	1.35	-6.98
SiO ₂	25	0.10	5.87	-88.74
Fe ₃ O ₄	25	0.05	11.56	-55.84
HEAT IS RELEASED / MJ				-2972.04

Table 2.3.14 Heat Balance in Second Stage Combustion for Dry Coal

INPUT				
COMPONENT	TEMPERATURE °C	AMOUNT kmol	kg Nm ₃	HEAT CONTENT MJ
N ₂ (g)	1200	11.42	255.89	424.51
CO(g)	1200	6.22	139.32	-453.86
CO ₂ (g)	1200	0.27	5.94	-88.65
H ₂ (g)	1200	2.55	57.23	90.86
H ₂ O(g)	1200	0.27	6.08	-52.99
O ₂ (g)	1200	0.00	0.00	0.00
H ₂ S(g)	1200	0.01	0.24	0.32
SO ₂ (g)	1200	0.00	0.00	0.00
COS(g)	1200	0.00	0.03	-0.11
SO(g)	1200	0.00	0.00	0.00
S ₂ (g)	1200	0.00	0.00	0.00
SO ₃ (g)	1200	0.00	0.00	0.00
CS ₂ (g)	1200	0.00	0.00	0.00
CS(g)	1200	0.00	0.00	0.00
S(g)	1200	0.00	0.00	0.00
S ₄ (g)	1200	0.00	0.00	0.00
NO(g)	1200	0.00	0.00	0.00
NO ₂ (g)	1200	0.00	0.00	0.00
CH ₄ (g)	1200	0.00	0.00	0.00
FeS	1200	0.11	9.70	0.98
FeO	1200	0.03	2.44	-6.94
Fe	1200	0.03	1.45	1.17
CaO*SiO ₂	1200	0.01	1.24	-15.90
Al ₂ O ₃ *SiO ₂	1200	0.02	3.47	-50.87
SiO ₂	1200	0.07	3.94	-54.42
O ₂ (g)	25	4.06	90.95	0.00
OUTPUT				
COMPONENT	TEMPERATURE °C	AMOUNT kmol	kg Nm ₃	HEAT CONTENT MJ
CO ₂ (g)	25	5.68	127.22	-2233.54
N ₂ (g)	25	11.42	255.89	0.00
SO ₂ (g)	25	0.12	2.71	-35.89
H ₂ O(g)	25	2.50	56.04	-604.60
Al ₂ O ₃	25	0.02	2.19	-35.98
CaO	25	0.01	0.60	-6.79
Fe ₂ O ₃	25	0.01	1.35	-6.98
SiO ₂	25	0.10	5.87	-88.74
Fe ₃ O ₄	25	0.05	11.79	-56.95
HEAT IS RELEASED / MJ				-2863.57

Table 2.3.15 Mass and Heat Balances for the Gasification Stage

Substance	As-Received	Dry
MASS BALANCE		
INPUT		
Coal (kg)	109.3	100.0
C	68.11	68.11
H	5.0	5.0
N	1.2	1.2
O	10.56	10.56
S	3.87	3.87
H ₂ O	9.3	
Al ₂ O ₃	2.19	2.19
CaO	0.60	0.60
Fe ₂ O ₃	1.35	1.35
SiO ₂	5.87	5.87
Others	1.49	1.49
Primary Air		
O ₂	77.18	84.59
N ₂	254.05	278.45
Sulfur Sorbent		
Fe ₃ O ₄	11.56	11.79
TOTAL	452.09	474.84
OUTPUT		
Clean Flue Gas		
CO	152.265	152.263
CO ₂	10.208	10.208
H ₂	5.397	4.467
H ₂ O	5.159	4.270
N ₂	255.25	279.65

O ₂	1.14x10 ⁻¹¹	1.16x10 ⁻¹¹
H ₂ S	3.84x10 ⁻¹	3.18x10 ⁻¹
SO ₂	2.66x10 ⁻⁵	2.72x10 ⁻⁵
COS	6.58x10 ⁻²	6.58x10 ⁻²
SO	4.71x10 ⁻⁵	4.80x10 ⁻⁵
S ₂	1.14x10 ⁻³	1.16x10 ⁻³
SO ₃	2.28x10 ⁻¹³	2.32x10 ⁻¹³
CS ₂	5.05x10 ⁻⁵	5.05x10 ⁻⁵
CS	3.66x10 ⁻⁴	3.66x10 ⁻⁴
S ₄	3.55x10 ⁻¹³	3.62x10 ⁻¹³
S	4.43x10 ⁻⁵	4.52x10 ⁻⁵
NO	1.54x10 ⁻⁷	1.63x10 ⁻⁷
NO ₂	4.11x10 ⁻¹⁶	4.35x10 ⁻¹⁶
CH ₄	1.24x10 ⁻⁴	8.15x10 ⁻⁵
Iron Oxysulfide		
Fe	9.346	9.514
O	0.5341	0.5437
S	3.471	3.534
Slag		
CaO·SiO ₂	1.244	1.244
Al ₂ O ₃ ·SiO ₂	3.470	3.470
SiO ₂	3.938	3.938
Others	1.494	1.494
TOTAL	452.23	474.98
Heat Balance		
ΔH (MJ)	-2841.49	-2841.49
ΔH ₁ (MJ)	-2972.04	-2863.57
ΔH ₂ (MJ)	130.55	22.08

Figure 2.3.48 Calculated Flame Temperature versus Equivalence Ratio

2.3.5 Thermodynamic Experiments

A series of thermodynamic experiments were undertaken to verify the calculated thermodynamic values predicted by the solution model experimentally. The focus of this study is to determine the composition of the iron oxysulfide melts in equilibrium with gas mixtures having known partial pressures of oxygen and sulfur.

2.3.5.1 Experimental Procedure and Equipment

(I) Procedure

Pure magnetite or a mixture of iron and iron sulfide is carefully weighed and placed in a pre-weighed platinum crucible, suspended in a Stanton Redcroft STA 780 thermogravimetric analysis (TGA) furnace (Figure 2.3.49). The sample is then heated in an argon atmosphere to a temperature in the range 1200 to 1400°C. After reaching the desired temperature, the sample is exposed to a mixed gas stream in which the partial pressures of sulfur and oxygen are controlled by mixing CO, CO₂, and H₂S or CO, CO₂, H₂, and H₂S in proportions indicated by calculations involving the computation of complex equilibria by an iterative method. Each charge is equilibrated until there is no further weight change of sample, quenched rapidly, and then the sulfur content of the total charge determined by analysis in Model 3220 Total Sulfur Apparatus and Model 3200 Sulfur Culometer. Since no losses of iron are possible, the oxygen content is determined by difference using the known mass of iron and the sulfur assay.

(II) Thermogravimetric Analysis

The Stanton Redcroft STA 780 Simultaneous Thermal Analyzer Series is designed to give simultaneous thermogravimetric analysis (TGA) records and differential thermal analysis (DTA) curves. The inner ceramic cup system and outer hangdown ceramic tube which surround the sample head allow very accurate atmosphere control. The furnace which is water-cooled permits both rapid heating and cooling.

(III) Analysis of Sulfur

The sample and crucible are weighed in a ceramic combustion boat and covered with vanadium pentoxide (V₂O₅). The sample is introduced into Model 3220 Total Sulfur Apparatus (COULOMETRICS, Inc.). Oxygen is introduced into the system by a nitrogen carrier gas. The combustion products are passed over a copper oxide catalyst to ensure

Figure 2.3.49 Schematic Thermogravimetric Analysis System

complete decomposition, and are then passed over reduced copper quantitatively converting all oxides of sulfur to SO_2 . The SO_2 -containing gas is then swept into the Model 3200 Sulfur Coulometer.

The anode compartment of the coulometer cell is filled with a proprietary solution containing methanol, pyridine, water, and tetrabutyl ammonium iodide. Positioned in the anode compartment are a platinum anode and a dual platinum detector electrode. The cathode compartment contains a buffered acidic solution and platinum cathode.

When a gas stream passes through the anode solution, SO_2 is quantitatively absorbed and oxidized by free iodine (I_2) in solution. As the I_2 is consumed, the detector electrode becomes more polarized and the detector current decreases. This detector current decrease is monitored by the sulfur detector board, which in turn automatically activates the titration current. The titration current stoichiometrically generates I_2 at a rate which is inversely proportional to the detector current. When the majority of SO_2 has been titrated, the free iodine concentration increases, causing the detector electrode to become depolarized and detector current to increase. When the original I_2 concentration is reached, the detector current returns to its initial value, and the titration stops.

The Total Sulfur Apparatus can be used for either solid and liquid. Sulfur levels from less than 1% to 100% can be effectively determined with the Coulometric system. Accuracies are better than $\pm 0.03\%$ in ten minutes.

(IV) Determination of the Gas Composition

According to the required partial pressures of sulfur and oxygen, the ratios of CO/CO_2 and $\text{H}_2/\text{H}_2\text{S}$ under different temperatures are determined from Figures 2.3.50 and 2.3.51 which are plotted according to the reactions.

and

For a fixed partial pressure of oxygen, the ratio of the partial pressure of CO to that of CO_2 increases with increasing temperature. Similarly, as temperature increases the ratio of partial pressure of H_2 to that of H_2S increases at fixed partial pressure of sulfur.

When a gas mixture of CO , CO_2 , and H_2S or CO , CO_2 , H_2 , and H_2S is heated to high

Figure 2.3.50 Partial Pressure Ratio of Carbon Monoxide to Carbon Dioxide versus Temperature at Various Partial Pressures of Oxygen

Figure 2.3.51 Partial Pressure Ratio of Hydrogen to Hydrogen Sulfide versus Temperature at Various Partial Pressures of Sulfur

temperature (1200-1400 °C), the following predominant gas species are produced by interaction or dissociation: O₂, S₂, CO, CO₂, H₂O, H₂, H₂S, COS, and SO₂. Incorporating the gas phase equilibrium equations, atom mass balances, and total pressure, the partial pressures of sulfur and oxygen are calculated by an iterative method for the computation of complex equilibria.

The calculated results obtained for selected experimental series are given in Table 2.3.16.

Table 2.3.16 Experimental Conditions for
Equilibration Studies on Fe-O-S Melt Equilibria

Test Number	Gas Flowrate (ml/min)				Chemical Potential	
	CO	CO ₂	H ₂	H ₂ S	logP _{S₂}	logP _{O₂}
1200 °C						
35	15	30	20	2	-2.72	-11.35
47	15	30	0	1.5	-2.04	-10.87
1300 °C						
41	20	20	20	2	-2.55	-10.66
45	50	18	19.55	0.45	-3.93	-11.12
49	15	30	20	1	-2.89	-10.12
51	50	10	19.85	0.15	-4.99	-11.69
53	50	15	19.58	0.42	-4.03	-11.30
1400 °C						
61	20	30	20	2	-2.29	-9.18
63	15	30	20	1	-2.68	-9.06
65	50	20	19.5	0.5	-3.49	-9.95
67	50	15	19.65	0.35	-3.84	-10.23
69	50	10	19.85	0.15	-4.63	-10.63

2.3.5.2 Experimental Results

Some of the existing data of Bog and Rosenqvist^[53] are given in Table 2.3.17 for actual measurements made at 1200°C. Table 2.3.18 reports all the experimental data, while Table 2.3.19 summarizes the partial pressures of sulfur and oxygen obtained both experimentally and via modelling. The partial pressures of sulfur and oxygen obtained experimentally and fugacity data on liquids in the Fe-S-O system at 1200 °C from Bog & Rosenqvist^[53] are plotted on Figures 2.3.52 and 2.3.53, respectively. The solution model is used to produce the isoactivity curves for the partial pressures of sulfur and oxygen. All data points are marked with test numbers on each figure. The remaining data in Table 2.3.19 are then plotted on Figures 2.3.54, 2.3.55, 2.3.56, and 2.3.57 which show the isoactivity curves for sulfur and oxygen on the ternary section at 1300°C and 1400°C, respectively. Curve fittings are made using the solution model.

Table 2.3.17 Fugacity Data on Liquids in the Fe-S-O System from Bog & Rosenqvist^[53] at 1200 °C

#	Weight Percent			Measured		Modeled	
	Fe%	S%	O%	logP _{S₂}	logP _{O₂}	logP _{S₂}	logP _{O₂}
1	69.0	30.0	1.0	-5.1	-13.3	-4.96	-12.92
2	69.0	28.0	3.0	-5.2	-12.7	-5.34	-13.05
3	69.0	27.0	4.0	-5.2	-12.5	-5.29	-13.06
4	69.0	26.0	5.0	-5.3	-12.4	-5.16	-12.94
5	68.0	30.0	2.0	-4.8	-12.9	-4.76	-12.70
6	67.0	31.0	2.0	-4.4	-12.7	-4.31	-12.46
7	67.0	30.0	3.0	-4.4	-12.3	-4.27	-12.26
8	66.0	32.0	2.0	-4.0	-12.1	-3.91	-12.23

The average absolute error and relative error for the calculated partial pressure of sulfur with the solution model prediction are about 0.19 and 6.5%. They are about 0.21 and 1.8% for the partial pressure of oxygen. The results of error analyses on the present

experimental data and data reported by Shima and Naldrett^[60] are very close. The thermodynamic experiments verify the calculated thermodynamic values and suggest further confidence in the use of the solution model to interpolate or extrapolate to regions not tested experimentally.

Table 2.3.18 Results of Thermodynamic Experiments

Test	Initial Mass mg			Final Mass mg		Melt Composition mg		
	Fe ₃ O ₄	Fe	FeS	total	sulfur	S	Fe	O
1200°C								
#35	46.72	0	0	52.11	16.17	16.17	33.18	2.76
#47	49.56	0	0	54.97	15.98	15.98	35.86	3.13
1300°C								
#41	65.2	0	0	72.50	22.34	22.34	47.20	2.96
#45	0	15.6	44.0	65.00	18.94	18.94	43.60	2.46
#49	62.7	0	0	69.20	19.73	19.73	45.40	4.07
#51	0	10.1	51.6	61.90	14.88	14.88	42.90	4.12
#53	0	20.8	34.3	62.7	16.94	16.94	42.60	3.16
1400°C								
#61	54.6	0	0	59.86	17.06	17.06	39.51	3.29
#63	52.3	0	0	56.02	13.80	13.80	37.84	4.38
#65	0	16.2	41.4	62.76	16.50	16.50	42.50	3.76
#67	0	14.7	39.3	57.69	13.99	13.99	39.67	4.03
#69	0	14.3	39.1	56.21	12.78	12.78	39.14	4.29

Table 2.3.19 Comparison of Measured and Modeled Data

Test	Weight Percent			Measured		Modeled	
	Fe%	S%	O%	logP _{S2}	logP _{O2}	logP _{S2}	logP _{O2}
1200°C							
#35	64.88	31.03	4.09	-2.72	-11.35	-3.00	-10.98
#47	65.23	29.07	5.70	-2.04	-10.87	-2.48	-10.36
1300°C							
#41	65.10	30.81	4.09	-2.55	-10.66	-2.58	-10.66
#45	67.08	29.14	3.78	-3.93	-11.12	-3.96	-11.57
#49	65.61	28.51	5.88	-2.89	-10.12	-2.28	-9.84
#51	69.30	24.04	6.66	-4.99	-11.69	-4.97	-12.06
#53	67.94	27.02	5.04	-4.03	-11.30	-4.30	-11.57
1400°C							
#61	66.00	28.50	5.50	-2.29	-9.18	-2.24	-9.25
#63	67.55	24.63	7.82	-2.68	-9.06	-2.55	-9.14
#65	67.72	26.29	5.99	-3.49	-9.95	-3.27	-9.98
#67	68.76	24.25	6.99	-3.84	-10.23	-3.84	-10.25
#69	69.63	22.74	7.63	-4.63	-10.63	-4.49	-10.61

Figure 2.3.52 Ternary Isothermal Section of the Fe-O-S System at 1200°C with Isobars of Partial Pressure of Sulfur: Isobars Calculated from Solution Model, Equilibration Data Superimposed

Figure 2.3.53 Ternary Isothermal Section of the Fe-O-S System at 1200°C with Isobars of Partial Pressure of Oxygen: Isobars Calculated from Solution Model, Equilibration Data Superimposed

Figure 2.3.54 Ternary Isothermal Section of the Fe-O-S System at 1300°C with Isobars of Partial Pressure of Sulfur: Isobars Calculated from Solution Model, Equilibration Data Superimposed

Figure 2.3.55 Ternary Isothermal Section of the Fe-O-S System at 1300°C with Isobars of Partial Pressure of Oxygen: Isobars Calculated from Solution Model, Equilibration Data Superimposed

Figure 2.3.56 Ternary Isothermal Section of the Fe-O-S System at 1400°C with Isobars of Partial Pressure of Sulfur: Isobars Calculated from Solution Model, Equilibration Data Superimposed

Figure 2.3.57 Ternary Isothermal Section of the Fe-O-S System at 1400°C with Isobars of Partial Pressure of Oxygen: Isobars Calculated from Solution Model, Equilibration Data Superimposed

III. EXPERIMENTAL KINETIC STUDIES

A basic knowledge of the rate-controlling mechanisms is necessary for the design of an efficient large scale combustion-desulfurization process. The study of small scale laboratory systems can be useful for determining kinetic data which may be extended to a scale-up reactor.

The desulfurization reactions of coal-derived fuel gases with iron oxysulfide as sulfur sorbent are heterogenous. The two phases involved are gas and iron oxysulfide liquid or magnetite solid. The kinetic studies are usually performed by exposing the sample to a gas stream within a controlled temperature environment. The progress of the reaction may be monitored in a variety of ways. Perhaps the most commonly used technique is gravimetric analysis.^[69] The weight gain or loss of the sample is monitored during the reaction by a micro-balance. Other techniques of studying the progress of the reaction include visual examination of the partially-reacted sample and chemical analysis of the sample. In the present experimental program, the single-particle studies are conducted first, then experiments on thermogravimetric analysis equipment follow.

3.1 Single Particle Studies on Magnetite Sulfidation

The equipment used for the magnetite sulfidation reaction is shown schematically in Figure 3.1.1. A series of different range and different grade of particles of magnetite are placed on an alumina plaque. The sample is heated in argon to a temperature of 1300°C and then subjected to a flow of mixing hydrogen, water vapor, and hydrogen sulfide for 10 to 20 seconds. Then the gas flow is immediately shifted to argon and the sample is quenched to room temperature. The sample is either mounted in an epoxy compound and examined optically or by direct visual examination.

The flow rates of hydrogen and hydrogen sulfide are carefully monitored by calibrated flowmeters. The hydrogen is water-saturated in a constant temperature bath to the required dew point to produce a desired partial pressure of oxygen and sulfur. The water saturation in a gas stream is calibrated by the weight change of a drying agent (SiO_2) when the gas stream flows through the drying agent in a certain time and flowrate.

Four experimental approaches have been explored:

- The first approach is to examine the kinetics of the reaction of individual small slabs

Figure 3.1.1 Schematic Diagram of Apparatus Used for Kinetic Studies

of pure crystalline magnetite to a sulfidizing atmosphere of a simulated fuel gas. These slabs are cut by a fine diamond saw into rectangular prisms measuring 5mm x 2mm x 2mm in dimension. They are mounted with the long axis perpendicular to a ceramic plaque with the minor axis perpendicular to the flow of gas. After being subjected to a mixture of hydrogen, water vapor, and hydrogen sulfide for 20 seconds, the samples are quenched in argon to room temperature. The samples are then mounted in epoxy compound with the long axis perpendicular to the mounting surface and sectioned to examine the cross section. A reacted surface layer showing the iron oxysulfide is expected, however, even through the experiment conditions are well within the liquid region, according to the phase diagram for the Fe-S-O system, no liquid is observed.

- The second approach is to place small crystallites ($\approx 1\text{mm}$) of Minnesota taconite concentrate on an alumina plaque. The composition of taconite concentrate is listed in Table 3.1.1. This analysis corresponds to a magnetite content (Fe_3O_4) of 97.337%. These taconite samples are subjected to the same conditions as described in the first approach above. They are observed to undergo partial melting with the original surface material fusing and slumping onto the plaque under the conditions of a twenty-second exposure to the sulfidizing gas. The original crystallite, diminished by approximately half its height and approximately double its diameter, stands in relief above the plane of plaque as seen in the photograph in Figure 3.1.2. Upon cutting the sample with a diamond saw through its midsection in the plane parallel to the flow of gas, two distinct phases are noted. In the central column is the original taconite sample cemented to the plaque by the liquid phase which has slumped off the crystallite and run out from the central column in a dendritic phase. The dendritic phase is presumably iron oxysulfide. At a magnification of 100 times, the dendritic phase can be seen in Figure 3.1.3 running diagonally from lower left to upper right against the alumina substrate in the lower right hand portion of photomicrograph.
- The third approach is to sprinkle fine ($\approx 50\text{ }\mu\text{m}$) high-grade ($\approx 99.9\%$ Fe_3O_4) specimens of magnetite on an alumina plaque as well as the same size of taconite

EXPOSURE TO ARGON

EXPOSURE TO SULFIDIZING GAS

Figure 3.1.2 Photograph of Taconite Concentrate on Alumina Plaque
Prior to and After Exposure to Sulfurizing Gas

Figure 3.1.3 Photomicrograph (100x) Dendritic Liquid
Phase on Alumina Plaque

concentrate on a second plaque. These two plaques are placed adjacent to each other at the same conditions of temperature and gas composition in the same furnace tube for the conditions given above. Upon cooling and making an optical examination, the first specimen (high-grade magnetite) shows no apparent reaction; whereas, the second (taconite concentrate) shows melting. From these observations, it is clear that relatively pure taconite concentrate reacts with the sulfidizing gas with relatively fast kinetics; however, high purity mineral-grade magnetite appears not to react with the sulfidizing gas. The reactivity of the taconite concentrate may be a result of the minor impurities which exert a catalytic effect on their reactivity with sulfur.

Table 3.1.1 Composition of Taconite Concentrate

Constituent	Weight %
SiO ₂	0.645
P ₂ O ₅	0.35
TiO ₂	0.47
MgO	0.1145
Al ₂ O ₃	0.257
CaO	0.413
FeO	28.39
Fe ₂ O ₃	66.84
Other	2.52

- The fourth approach is to place three size ranges of particles of taconite concentrate and high-grade ($\approx 99.9\%$ Fe₃O₄) specimens of magnetite on plaques to determine whether or not the size of the particles is a major factor in the kinetics or alternatively the purity. These particles are 2.36 to 1.68 mm, 1.65 to 0.833 mm, and 0.833 to 0.710 mm in diameter, respectively. The same conditions in prior experiments are repeated. All size ranges of taconite concentrates react with the sulfidizing gas; whereas the pure magnetite shows negligible reaction. Figure 3.1.4

exhibits three photo-micrographs at 30x, 20x, and 6x (from top to bottom). The top figure shows a single particle which has been exposed to the sulfidizing gas mixture, the liquid phase has flowed down onto the plaque leaving an unreacted core of crystallites showing relief in a complex interaction pattern. The second photomicrograph, taken at intermediate magnification shows the original expose sample on the right adjacent to a fresh non-exposed sample to the left. The smooth conchoidal fracture characteristics of a fresh mineral specimen on the left is in contrast to the etched appearance of the reacted specimen on the right. The third photomicrograph shows the same sample in the upper-right hand corner with the other adjacent sample. Decrepitation has caused the adjacent sample to explode off the surface leaving behind a strained plaque. These results which are repeated many times show that large specimens tend to break down and expose much more surface than the original sample, which is an encouraging development with respect to desulfurization.

6X

20X

Figure 3.1.4 Scanning Electron
Photomicrographs

30X

3.2 Kinetic Studies of Desulfurization With Iron Oxysulfide Melts

Based on the experimental results of sulfidation of single magnetite particles, 325 - 400 mesh Minnesota taconite concentrate is used as samples in the kinetic experiments on thermogravimetric analysis. Similar to the thermodynamic experiments, the kinetic studies are performed on samples exposed to sulfidizing atmosphere in platinum crucibles. These crucibles which contain up to 100 mg of material are suspended from a sensitive balance arm within a vertical tube furnace where operating temperature and gas flowrates and compositions can be maintained constant. The weight change of the sample against the reaction time is recorded. Tests are conducted between 1200 and 1400 °C with gas flow rates, initial masses of magnetite, and particle sizes as reported in Table 3.2.1. The curves for different temperatures, different flowrates, and different gas phase concentrations are used to determine the rate-controlling process for desulfurization with iron oxide. A reaction model will be developed to describe the kinetics of magnetite sulfidation.

3.2.1 Previous Results of TGA Kinetic Studies

Since the sequence of steps in the formation of iron oxysulfide from magnetite Fe_3O_4 is complex, two different approaches are used to determine the mechanism of the reaction.

The first set of experimental conditions which is applied in test 101 (Figure 3.2.1) is to expose the magnetite to a reducing gas ($\text{CO} + \text{CO}_2$) without the presence of hydrogen sulfide, and upon reduction to wustite FeO , hydrogen sulfide and hydrogen are added and the experiment continued. The dashed line in Figure 3.2.1 represents the prior condition of reduction, during which time oxygen is transferred from the solid phase to the gas phase by the controlled reducing atmosphere over a 20-minute period of exposure (see Table 3.2.2). The ratio of mass of sample to the starting mass (labeled as "Mass Ratio") undergoes a change of -0.07 (or a 7% loss of weight) which agrees with the value of weight loss for magnetite reduction to wustite. Upon addition of H_2S and H_2 to the same gas atmosphere, no weight increase is observed for approximately the first 20 minutes. The unexpected outcome indicates that there is a long incubation period prior to desulfurization associated with freshly reduced wustite (FeO). Further examination of Figure 3.2.1 shows a steady increase in weight after the initial incubation period consistent with the exchange of sulfur (having an atomic weight approximately twice that of oxygen) with oxygen expressed as equation.

Figure 3.2.1 Kinetic Studies via TGA: Test 101
Prior Reduction of Magnetite

After approximately 150 minutes no further weight gain is observed. The composition of liquid iron oxysulfide approaches the equilibrium composition under the controlled gas atmosphere.

Table 3.2.1. Conditions for Kinetic Experiments

Test	Gas Flowrate (ml/min)				Temperature °C	Initial Mass of Magnetite	Particle Size	
	CO	CO ₂	H ₂	H ₂ S			mesh	micron
101	30	30	30	1	1200	78.90 mg	325-400	37-44
103	30	30	w0	1	1200	78.50 mg	325-400	37-44
106	45	45	45	1.5	1200	79.20 mg	325-400	37-44
108	30	30	30	1	1300	77.86 mg	325-400	37-44
109	30	30	30	1	1400	78.34 mg	325-400	37-44
112	30	30	30	1	1200	78.30 mg	230-270	53-63
115	30	30	30	0.5	1200	78.80 mg	325-400	37-44

The second experiment conditions is applied in test 103 (Figure 3.2.2) are essentially the same as those in test 101, except the initial reduction was avoided. Hydrogen sulfide and hydrogen are added from the beginning as part of the reducing gas mixture (CO + CO₂ + H₂ + H₂S). The initial drop with a 7% loss of weight again indicates the loss of oxygen with reduction of magnetite to wustite prior to sulfur pickup, however, a short flat incubation stage is present. After approximately 5 minutes, the specimen again gains weight at about the same rate as the prior test.

Upon examination of a sample from similar experimental conditions in test 101 after reduction, but prior to the addition of hydrogen sulfide, it is found to be sintered and densely compacted in a platinum crucible. Another sample subjected to similar conditions (i. e. exposure to a reducing, sulfidizing atmosphere) was quenched immediately after the lag period. Microscopic examination showed it to have undergone fusion thus explaining the lag observed in the TGA experiments. This lag is not only associated the time required for

Figure 3.2.2 Kinetic Studies via TGA: Test 103
No Prior Reduction of Magnetite

fusion but also the requirement that sulfur replace oxygen to produce the liquid phase. The long lag time shown in Figure 3.2.1 (Test 101) is explained by the requirement that sulfur exchanges with oxygen via diffusion in the dense solid product (FeO). An incubation period is to be expected until the initial iron oxysulfide liquid appears. However, for the experimental conditions in test 103 (sulfidizing from the beginning) sulfur pickup occurs during the reduction process when the sample is still fine-grained. Therefore the initial iron oxysulfide is formed without any pronounced incubation period.

The initial experiments show that the whole process of transformation from magnetite Fe_3O_4 to liquid iron oxysulfide mainly consists of the reduction process of magnetite to wustite and the sulfidation process of the intermediate product, wustite. Therefore the kinetic studies are divided into two parts. The kinetics of the reduction process is studied by exposing the magnetite to the reducing gas mixture ($\text{CO} + \text{CO}_2$). The combined kinetics of transfer of oxygen from magnetite to form wustite followed by substitution of oxygen by sulfur is studied by exposing the magnetite to the reducing gas mixture ($\text{CO} + \text{CO}_2 + \text{H}_2 + \text{H}_2\text{S}$) from the beginning.

Table 3.2.2. Results of TGA Experiments

#101			#101			#103		
Time	Mass (mg)	Mass ratio	Time	Mass (mg)	Mass Ratio	Time	Mass (mg)	Mass Ratio
0	78.90	1.000	0	74.12	0.939	0	78.50	1.000
0.5	78.60	0.996	5	74.12	0.939	1	78.00	0.994
1	77.38	0.981	10	74.12	0.939	2	77.50	0.987
1.5	76.31	0.967	20	74.12	0.939	3	75.50	0.962
2	75.31	0.954	30	74.12	0.939	4	74.00	0.943
2.5	74.64	0.946	35	74.12	0.939	5	73.90	0.941
3	74.29	0.942	36	74.15	0.940	6	73.80	0.940
3.5	74.21	0.941	37	74.30	0.942	7	73.80	0.940
4	74.16	0.940	38	74.35	0.942	8	73.80	0.940
5	74.12	0.939	39	74.45	0.944	9	73.90	0.941
10	74.12	0.939	40	74.50	0.944	10	73.92	0.942
15	74.12	0.939	41	74.60	0.946	15	74.00	0.943
20	74.12	0.939	42	74.70	0.947	20	74.30	0.946
			43	74.83	0.948	25	74.70	0.952
			44	74.95	0.950	30	75.10	0.957
			45	75.05	0.951	35	75.50	0.962
			46	75.15	0.952	40	76.00	0.968
			47	75.22	0.953	50	77.00	0.981
			48	75.30	0.954	60	78.00	0.994
			49	75.45	0.956	70	78.90	1.005
			50	75.55	0.958	80	80.05	1.020
			51	75.70	0.959	90	81.10	1.033
			52	75.81	0.961	100	82.10	1.046
			53	75.88	0.962	110	83.35	1.060
			54	75.95	0.963	120	84.40	1.075

			55	76.02	0.963	130	85.25	1.086
			56	76.12	0.965	140	85.80	1.093
			57	76.15	0.965	150	85.95	1.095
			58	76.20	0.966	160	86.00	1.096
			59	76.30	0.967	170	86.04	1.096
			60	76.46	0.969	180	86.07	1.096
			61	76.55	0.970	190	86.10	1.097
			62	76.65	0.971	200	86.10	1.097
			63	76.73	0.972	250	86.10	1.097
			64	76.85	0.974	300	86.10	1.097
			65	76.90	0.975			
			66	76.98	0.976			
			67	77.10	0.977			
			68	77.15	0.978			
			69	77.25	0.979			
			70	77.35	0.980			
			75	77.80	0.986			
			80	78.25	0.992			
			85	78.70	0.997			
			90	79.25	1.004			
			100	80.20	1.016			
			110	81.15	1.029			
			120	82.20	1.042			
			140	84.25	1.068			
			170	86.05	1.091			
			210	86.10	1.091			
			250	86.12	1.092			
			300	86.08	1.091			

Mass Ratio of Sample = Mass of Sample / Initial Mass of Magnetite

3.2.2 Reduction Kinetics of Iron Oxides

As the first step of desulfurization with molten iron oxysulfide as sulfur sorbent, the reduction of iron oxide is investigated by exposing the magnetite to a controlled reducing gas mixture consisting of CO and CO₂.

3.2.2.1 Thermodynamics of Reduction of Iron Oxide

The reduction reactions of iron oxides are as follows:

A thermodynamic stability diagram (Figure 3.2.3) for the Fe-O system is constructed using linear free energy equations for the various species involved.

The phases Fe₃O₄, FeO, and Fe coexist at 568°C. This temperature is the lowest at which stable FeO can exist. Below 568°C, the wustite, FeO, phase decomposes into magnetite, Fe₃O₄, and iron. The reduction of hematite, Fe₂O₃, by carbon monoxide or hydrogen, occurs:

The same conclusions can be deduced from the phase diagram for the iron-oxygen system (Figure 2.3.1).

Under the operating conditions of desulfurization with molten iron oxysulfide as sulfur sorbent, the gas mixtures are sufficiently oxidizing that metallic iron is not formed; the reduction product of magnetite is wustite.

3.2.2.2 Literature Review of Reduction of Iron Oxide

The reduction of iron ore by carbon monoxide or hydrogen is a complicated process involving a great many variables, both physical and chemical in characteristics. The reduction sequence of hematite - hematite, magnetite, wustite and iron - is given by the following equations:

Figure 3.2.3 Equilibria and Predominance Areas for the Fe-O System

Starting with a dense sphere of hematite, an initial reaction with CO will produce a shell or layer of metallic iron in contact with a layer of wustite beyond which there will be a layer of magnetite surrounding the core of hematite. Under the reducing conditions prior to desulfurization, the partially reduced particle of Fe_3O_4 will exhibit a layered structure as shown schematically in Figure 3.2.4.^[70]

During transformation, only hexagonal hematite undergoes structural metamorphosis to cubic close-packed magnetite lattice, the structure of the wustite being similar to that of magnetite. Wustite ($\text{Fe}_{0.95}\text{O}$) is an iron deficient non-stoichiometric compound with iron ion vacancies. During transformation of hematite to magnetite, the structural metamorphosis from hexagonal to cubic gives rise to lattice distortions, volume expansion, increased porosity, cracks and fissures. In the disturbed lattice the diffusion of iron ions is accelerated and a large vacancy concentration can arise where mass is lost. The creation of voids is thus facilitated in the defect structure and all these factors contribute to a considerable pore formation. The reduction of hematite produces a porous product and the large surface area thus generated results in a much higher reduction rate of hematite compared to magnetite.^[71,72]

The reduction of iron oxides takes place in a series of sequential steps. The overall rate will be determined by the slowest of the process or processes in the series. The possible consecutive steps are^[72]:

- (i) transport of gaseous reductant from the bulk gas phase to the particle surface through a boundary gas film;
- (ii) molecular diffusion of the gaseous reductant through the product layer to the reaction interface;
- (iii) adsorption of the gaseous reductant at the interface;
- (iv) reaction at the interface (reaction between adsorbed reductant and oxygen of the lattice);
- (v) desorption of the gaseous products from the interface;
- (vi) mass transport of iron and oxygen ions and transformations in the solid phase; formation and growth of the reaction products, viz., magnetite, wustite and

- iron;
- (vii) molecular diffusion of the gaseous products through the product layer to the particle surface;
 - (viii) transport of the gaseous products from the particle surface through the boundary gas film to the bulk gas phase.

The rate limiting cases are:

chemical control = steps (iii) to (vi)

diffusion control = step (i) and (viii); (ii); (vi) and (vii)

3.2.2.3 "Shrinking Unreacted-Core" Model

The reduction of metal oxides may in general be described by the following:

Figure 3.2.5 illustrates how the reaction progresses. The overall process can be divided into three steps: external mass transfer, diffusion through the product layer, and the chemical reaction at the interface between the unreacted and completely reacted zones. The analysis will be made for an isothermal system on a first order, irreversible reaction occurring in an initially nonporous spherical particle.^[69,73,74,75]

At steady state the interfacial chemical reaction and mass transfer processes must occur at the same rate. Thus, in terms of species A the following three rates are equal:

Interfacial chemical reaction

$$-N_A = 4\pi r_c^2 k C_{Ac} \quad (3.2.1)$$

Diffusion through the product layer

$$-N_A = 4\pi r^2 D_e \frac{\partial C_A}{\partial r} \quad (3.2.2)$$

External mass transport

Figure 3.2.4 Partially Reduced Magnetite Particle

Figure 3.2.5 Schematic Diagram of a Shrinking Unreacted Core System

$$-N_A = 4\pi r_p^2 k_m (C_{Ab} - C_{As}) \quad (3.2.3)$$

where

$-N_A$ is the total rate of transport of A into the sphere,

r_c is the radius of the unreacted core,

C_{Ac} is the concentration of A at r_c ,

D_e is the effective diffusivity of A in the product layer,

r_p is the radius of the sphere at any time,

k_m is the external mass transfer coefficient,

C_{Ab} is the concentration of A in the bulk gas phase, and

C_{As} is the concentration of A at the sphere surface.

The solution is obtained by applying the pseudo-steady-state approximation, that is, the movement of r_c is much slower compared with the time scale for establishing the concentration profile of A. Thus, as far as the diffusion of A is concerned, the position of r_c appears to be stationary and N_A is independent of position. Then, equation 3.2.2 can be integrated for constant N_A with equations 3.2.1 and 3.2.3 as boundary conditions to give the concentration profile as a function of r_c . According to the chemical reaction equation, the consumption of A can be related to that of solid B through the following relationships:

$$N_A = \frac{4\pi r_c^2 \rho_B}{b} \frac{dr_c}{dt} \quad (3.2.4)$$

where

b: the number of moles of solid B reacted by one mole of fluid reactant A,

ρ_B : the number of moles of species B per unit volume of the entire solid mixture.

The procedure for solving equations 3.2.1-3.2.3 together with equation 3.2.4 is straightforward. The result can be expressed in terms of r_c as follows:^[73]

$$\begin{aligned}
t = & \frac{\rho_B r_p}{bkC_{Ab}} \left[1 - \frac{r_c}{r_p} \right] \\
& + \frac{\rho_B r_p^2}{6bD_e C_{Ab}} \left[1 - 3\left(\frac{r_c}{r_p}\right)^2 + 2\left(\frac{r_c}{r_p}\right)^3 \right] \quad (3.2.5) \\
& + \frac{\rho_B r_p}{3bk_m C_{Ab}} \left[1 - \left(\frac{r_c}{r_p}\right)^2 \right]
\end{aligned}$$

The fractional conversion of the solid X is defined as follows:

$$X = \frac{W_0 - W}{W_0} = 1 - \left(\frac{r_c}{r_p}\right)^3 \quad (3.2.6)$$

where

W_0 : weight of unreacted solid B, and

W : weight of unreacted core B.

The rate equation expressed in terms of fraction reacted is as follows:

$$\begin{aligned}
t = & \frac{\rho_B r_p}{bkC_{Ab}} \left[1 - (1-X)^{\frac{1}{3}} \right] \\
& + \frac{\rho_B r_p^2}{6bD_e C_{Ab}} \left[1 - 3(1-X)^{\frac{2}{3}} + 2(1-X) \right] \quad (3.2.7) \\
& + \frac{\rho_B r_p}{3bk_m C_{Ab}} \left[1 - (1-X)^{\frac{2}{3}} \right]
\end{aligned}$$

It is seen in equation 3.2.7 that the time required to attain a certain conversion is the sum of the times to reach the same conversion under the control of the three separate steps, the first being that of chemical reaction, the second that of product-layer diffusion, and the third that of external mass transport.

3.2.2.4 Kinetics of Iron Oxide Reduction

The mass transfer of reductant from the bulk gas to the reaction interface and vice

versa, steps (i) and (viii) have been included as possible rate-limiting factors. However, this is not the case in practice since in a moving system the linear gas velocity far exceeds the critical velocity and the influence of boundary gas film disappears.

If the product layer is very porous permitting unrestricted access of the reductant molecules to the reaction interface, at any moment the partial pressure of the reductant on the particle surface and at the reaction interface will be identical. Therefore, gaseous transport will not be rate-controlling and depending on the energy of activation the rate of reaction will increase exponentially with temperature. The rate expression can be approximated by considering the second and third terms in equation 3.2.7 negligible:

$$t = \frac{\rho_B r_p}{bkC_{Ab}} [1 - (1-X)^{\frac{1}{3}}] \quad (3.2.8)$$

In many studies on iron ore reduction, it has been found that rate of reduction is proportional to the partial pressure of CO or H₂. Most investigators have reported an activation energy for interfacial reaction of about 10-15 kcal/mole for the reduction of iron oxide by CO or H₂.^[76,77,78]

Once an iron layer is formed on the oxide, further removal of oxygen from the oxide surface occurs by transport of the reductant and withdrawal of the gaseous product to and from the surface through the pores in the iron layer. In case the supply rate is less than its consumption, the chemical reaction rate exceeds the supply rate of the reductant gas, then gaseous diffusion becomes rate-controlling. The reductant gas concentration is about the same as the equilibrium concentration at the interface. By eliminating the first and third terms in equation 3.2.7, the rate expression is as follow:

$$t = \frac{\rho_B r_p^2}{6bD_e C_{Ab}} [1 - 3(1-X)^{\frac{2}{3}} + 2(1-X)] \quad (3.2.9)$$

Apparent activation energy of gas diffusion is about 2-5 kcal/mole.

When the chemical and the diffusion rates are comparable, the overall reduction processes are controlled by both diffusion and chemical reaction. The rate equation for mixed control by reaction and diffusion can be expressed as follow:

$$t = \frac{\rho_B r_p}{bkC_{Ab}} [1 - (1-X)^{\frac{1}{3}}] + \frac{\rho_B r_p^2}{6bD_e C_{Ab}} [1 - 3(1-X)^{\frac{2}{3}} + 2(1-X)] \quad (3.2.10)$$

Some examples have been investigated to obey the equation.^[79,80] Apparent activation energy is about 6-10 kcal/mole.

3.2.2.5 Analysis of Experimental Results

The aim of the kinetic studies of the reduction reaction of magnetite to wustite is to determine the rate-controlling step and to interpret the experimental data.

The reduction of magnetite to wustite is investigated by exposing the magnetite to a controlled reducing gas mixture (CO + CO₂) on TGA equipment. The weight loss of sample with time is recorded. Since there is only loss of oxygen with the sample during the reduction reaction ($\text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2$), the mass of unreacted magnetite and fractional conversion of magnetite are easily obtained from the original sample mass and the weight loss. The experimental data from test #92 and their conversion values are listed in Table 3.2.3. The mass of sample, mass of unreacted magnetite, and fractional conversion of magnetite are plotted against time in Figures 3.2.6, 3.2.7, and 3.2.8, respectively. The experimental data show that the reaction rate is fast in the first two minutes and then slows down.

To determine the rate-controlling step, the relationships of $[1 - (1-X)^{1/3}]$ and $[1 - 3(1-X)^{2/3} + 2(1-X)]$ with time are shown in Figures 3.2.9 and 3.2.10, respectively. The plot of $[1 - (1-X)^{1/3}]$ against time yields a straight line up to approximately 80% reaction. This means that at the initial stage of reaction, the reaction product layer is porous and the process is controlled by chemical reaction at the interface. Beyond 80% reaction, since the layer of product layer is thick, the chemical and diffusion rates are comparable, the reduction

Figure 3.2.6 Mass of Sample versus Reaction Time for Reduction of Magnetite to Wustite with a CO-CO₂ Gas Mixture at 1200°C

Figure 3.2.7 Mass of Unreacted Magnetite versus Time for Reduction of Magnetite to Wustite with a CO-CO₂ Gas Mixture at 1200°C

Figure 3.2.8 Fraction Conversion versus Reaction Time
for Reduction of Magnetite to Wustite Using
a CO-CO₂ Gas Mixture at 1200°C

Figure 3.2.9 Term $[1-(1-X)^{1/3}]$ versus Reaction Time for Reduction of Magnetite to Wustite Using a CO-CO₂ Gas Mixture at 1200°C

Figure 3.2.10 Term $[1-(1-X)^{2/3}+2(1-X)]$ versus Reaction Time for Reduction of Magnetite to Wustite Using a CO-CO₂ Gas Mixture at 1200°C

process is controlled by both diffusion and chemical reaction (mixed control). Finally, the rate-controlling process becomes diffusion.

The effect of temperature on reaction rate of reduction of magnetite to wustite is performed under identical conditions with the exception of temperature being varied. The experimental results are listed in Table 3.2.4. The plot of the fractional conversion of magnetite with time (Figure 3.2.11) shows that the reaction rate increases with increasing temperature. The values of the term $[1-(1-X)^{1/3}]$ for different temperatures are plotted against time in Figure 3.2.12. During the initial stages of reaction, these relationships can be approximated by straight lines. Since the rate controlled by chemical reaction increases exponentially with temperature, the range which fits the straight line of $[1-(1-X)^{1/3}]$ against time decreases with increasing temperature. From Figure 3.2.12, the relationship of $\ln(\text{slope})$ versus $1/T$ is shown in Figure 3.2.13. The slope of the straight line obtained is used to calculate the apparent activation energy according to Arrhenius' equation:

$$K = K_0 e^{-\frac{E_a}{RT}} \quad (3.2.11)$$

The apparent activation energy for the first stage of the reduction reaction of magnetite to wustite is 11.39 kcal/mole, which is consistent with the reported values of about 10-15 kcal/mole. The calculation of apparent activation energy also confirms that the first stage of the reaction process is controlled by chemical reaction.

Table 3.2.3 Experimental Data from Test #92

Time	Sample	Fe ₃ O ₄	X	g_{Fp}^*	p_{Fp}^{**}
0.00	78.90	76.80	0.00	0.00	0.00
0.50	78.61	72.60	0.05	0.02	0.00
0.75	78.06	64.64	0.16	0.06	0.01
1.00	77.42	55.38	0.28	0.10	0.03
1.25	76.91	48.00	0.37	0.15	0.06
1.50	76.38	40.33	0.47	0.19	0.10
1.75	75.88	33.09	0.57	0.24	0.15
2.00	75.41	26.29	0.66	0.30	0.22
2.25	75.02	20.65	0.73	0.35	0.29
2.50	74.75	16.74	0.78	0.40	0.35
2.75	74.61	14.76	0.81	0.42	0.39
3.00	74.49	12.98	0.83	0.45	0.42
3.25	74.41	11.82	0.85	0.46	0.45
3.50	74.34	10.81	0.86	0.48	0.47
3.75	74.29	10.08	0.87	0.49	0.49
4.00	74.24	9.36	0.88	0.50	0.51
4.50	74.18	8.49	0.89	0.52	0.53
5.00	74.14	7.91	0.90	0.53	0.55
6.00	74.11	7.48	0.90	0.54	0.56
7.00	74.09	7.19	0.91	0.55	0.57
8.00	74.07	6.90	0.91	0.55	0.58
9.00	74.06	6.76	0.91	0.56	0.58
10.00	74.05	6.61	0.91	0.56	0.59

$$* g_{\text{Fp}} = 1-(1-X)^{1/3}$$

$$** p_{\text{Fp}} = 1-3(1-X)^{2/3}+2(1-X)$$

Table 3.2.4 Experimental Data for the Reduction of Magnetite to Wustite at Different Temperatures

Time, min	Sample	Fe ₃ O ₄	X	1-(1-X) ^{1/3}
1200 °C				
0.00	78.90	76.80	0.00	0.00
0.50	78.61	72.57	0.06	0.02
0.75	78.06	64.66	0.16	0.06
1.00	77.42	55.39	0.28	0.10
1.25	76.91	48.00	0.38	0.15
1.50	76.38	40.32	0.48	0.19
1.75	75.88	33.10	0.57	0.24
2.00	75.41	26.23	0.66	0.30
2.25	75.02	20.66	0.73	0.35
2.50	74.75	16.79	0.78	0.40
2.75	74.61	14.75	0.81	0.42
3.00	74.49	12.98	0.83	0.45
1300 °C				
0.00	77.80	75.73	0.00	0.00
0.50	77.46	70.81	0.07	0.02
0.75	76.51	57.10	0.25	0.09
1.00	75.77	46.42	0.39	0.15
1.25	75.18	37.79	0.50	0.21
1.50	74.54	28.63	0.62	0.28
1.75	74.11	22.34	0.71	0.33
2.00	73.82	18.10	0.76	0.38
2.25	73.60	14.92	0.80	0.42
2.50	73.44	12.57	0.83	0.45
2.75	73.34	11.21	0.85	0.47

3.00	73.22	9.39	0.88	0.50
1400 °C				
0.00	79.70	77.58	0.00	0.00
0.50	79.25	71.00	0.08	0.03
0.75	78.10	54.46	0.30	0.11
1.00	77.35	43.50	0.44	0.18
1.25	76.54	31.86	0.59	0.26
1.50	76.03	24.44	0.69	0.32
1.75	75.71	19.78	0.75	0.37
2.00	75.45	16.14	0.79	0.41
2.25	75.21	12.65	0.84	0.45
2.50	75.07	10.55	0.86	0.49
2.75	74.99	9.39	0.88	0.51
3.00	74.91	8.30	0.89	0.53

Figure 3.2.11 Fraction Conversion versus Reaction Time for Reduction of Magnetite to Wustite at 1200, 1300, and 1400°C Using a CO-CO₂ Gas Mixture

Figure 3.2.12 Term $[1-(1-X)^{1/3}]$ versus Reaction Time for Reduction of Magnetite to Wustite at 1200, 1300, and 1400°C Using a CO-CO₂ Gas Mixture

Figure 3.2.13 Effect of Temperature on the Kinetics of the Reduction of Magnetite to Wustite

3.2.3 Mechanism of Magnetite Sulfidation

As indicated in previous TGA experiments, following the reduction of magnetite to wustite by CO, the remaining process from magnetite Fe_3O_4 to liquid iron oxysulfide is the sulfidation process of reduction product, wustite. The mechanism of the remaining process consists of the reaction expressed as equation $\text{H}_2\text{S} + \text{FeO}_x\text{S}_y = \text{H}_2\text{O} + \text{FeO}_{x-1}\text{S}_{y+1}$ and the mass transfer of sulfur and oxygen species. The process takes place in a series of sequential steps. Similar to the reduction process of iron oxide, the possible consecutive steps are:

- (I) transport of the reaction reactant hydrogen sulfide from the bulk gas phase to the liquid surface through a boundary gas film;
- (II) chemical reaction at the interface;
- (III) mass transport of dissolved sulfur from interface to inside and oxygen from inside to surface in liquid phase; and
- (IV) transport of the reaction product water vapor from surface through the boundary gas film to the bulk gas phase.

The overall rate will be determined by the slowest of the steps involved in the series. The rate limiting cases are a chemical control step (II) and a mass transfer control step (I), or (III), or (IV).

The mechanism of sulfidation process of reduction product wustite is studied by exposing the magnetite to a reducing gas mixture ($\text{CO} + \text{CO}_2 + \text{H}_2 + \text{H}_2\text{S}$) on TGA equipment. The effects of various parameters including flowrate, temperature, particle size, and reactant concentration in gas phase are used to decide the rate-controlling step during the process of desulfurization with iron oxide. The experimental data are reported in Table 3.2.5.

(I) Effect of Gas Flowrate on Sulfidation Kinetics

Results from test 103 and 106 are compared in Figure 3.2.14 in which the only varied parameter is the total flow rate. For test 106 the flowrate is 50% greater than that for test 103. The solid line (test 103) and the dashed line (test 106) are essentially congruent indicating that the rate-controlling step of the process is neither the transport of the reactant hydrogen sulfide from the bulk gas phase to the liquid surface through a boundary gas film nor the transport of the reaction product water vapor from the surface through the boundary

Figure 3.2.14 Kinetic Studies via TGA: Test 103 and 106
Effect of Overall Flow Rate on the Reaction
Rate for the Magnetite Sulfidation

gas film to the bulk gas phase. Instead, the process is governed either by chemical reaction at the interface of melt/gas interface or inter-diffusive mass transport of sulfur and oxygen within the bulk liquid. Therefore, the kinetic study of the sulfidation process must focus only on the gas-liquid interaction and mass transport of sulfur and oxygen in the liquid iron oxysulfide.

(II) Effect of Temperature on Sulfidation Kinetics

The effect of temperature on the sulfidation process is studied as a function of temperature in test 103 (1200 °C), test 108 (1300 °C), and test 109 (1400 °C). Figure 3.2.15 shows a large increase in the rate of reaction with increasing temperature which will be discussed in section 3.2.4.2.

(III) Effect of Particle Size on Sulfidation Kinetics

A comparison is made between two particle size fractions: the size range 37-44 micrometers for test 103 and 53-63 micrometers for test 112 in Figure 3.2.16. The finer-size particles with a larger surface area exhibit more rapid kinetics, as is expected.

(IV) Effect of Gaseous Composition on Sulfidation Kinetics

The effect of gas composition is studied by using two different concentrations of hydrogen sulfide in the reacting gas mixture. The concentration of other constituents in gas phase are held constant. The flow rate of H_2S for test 103 is twice that for test 115. In Figure 3.2.17, there is a divergence between the two slope values: the sulfur composition of the liquid phase is expected to be greater for the higher sulfur concentration in the gas stream than for the lower one, resulting in a sulfur concentration gradient difference. The sensitivity of slopes of two curves with the concentration of reactant indicates that the rate-controlling step of the process is not likely to be chemical reaction at the interface.

Analysis of experimental results shows that the rate-controlling step of the process is inter-diffusive mass transport of dissolved sulfur and oxygen within the liquid phase.

Figure 3.2.15 Kinetic Studies via TGA: Test 103, 108, and 109, Effect of Temperature on the Reaction Rate for the Magnetite Sulfidation

Figure 3.2.16 Kinetic Studies via TGA: Test 103 and 112
Effect of Particle Size of Magnetite on the
Reaction Rate for the Magnetite Sulfidation

Figure 3.2.17 Kinetic Studies via TGA: Test 103 and 115
Effect of Hydrogen Sulfide Concentration on
Reaction Rate for the Magnetite Sulfidation

Table 3.2.5 Results of TGA Kinetic Experiments

Time	#103	#106	#112	#115	Time	#108	#109
0	1.000	1.000	1.000	1.000	0	1.000	1.000
1	0.994	0.993	0.996	0.993	1	0.990	0.985
2	0.987	0.989	0.989	0.987	2	0.968	0.962
3	0.962	0.962	0.964	0.962	3	0.955	0.945
4	0.943	0.948	0.945	0.943	4	0.941	0.941
5	0.941	0.944	0.942	0.942	5	0.940	0.939
6	0.940	0.942	0.940	0.941	6	0.940	0.940
7	0.940	0.942	0.939	0.940	7	0.942	0.950
8	0.940	0.941	0.939	0.939	8	0.945	0.979
9	0.941	0.941	0.939	0.939	9	0.950	1.010
10	0.942	0.942	0.940	0.940	10	0.957	1.040
15	0.943	0.943	0.941	0.942	11	0.963	1.068
20	0.946	0.947	0.942	0.944	12	0.970	1.075
25	0.952	0.952	0.945	0.950	13	0.978	1.078
30	0.957	0.958	0.951	0.955	14	0.985	
35	0.962	0.965	0.957	0.960	15	0.992	
40	0.968	0.972	0.964	0.966	16	1.000	
50	0.981	0.984	0.975	0.978	17	1.009	
60	0.994	0.996	0.987	0.989	18	1.016	
70	1.005	1.009	1.001	1.000	19	1.023	
80	1.020	1.021	1.013	1.010	20	1.030	
90	1.033	1.033	1.028	1.022	21	1.038	
100	1.046	1.046	1.040	1.033	22	1.044	
110	1.062	1.060	1.055	1.046	23	1.050	
120	1.075	1.073	1.068	1.054	24	1.057	
130	1.086	1.084	1.081	1.066	25	1.061	
140	1.093	1.094	1.090	1.074	30	1.078	
150	1.095	1.096	1.093	1.083			

3.2.4 Kinetic Model of Sulfidation

For moving fluids, mass transfer occurs both by convection and by diffusion. Under these conditions the mass conservation equation within the system boundary may be formulated^[81,82]:

$$\text{accumulation} = \text{diffusion} + \text{convection} + \text{generation} \\ \text{transport} \quad \text{transport} \quad \text{of species}$$

$$\frac{\partial C}{\partial t} = D \nabla^2 C - v \nabla C + r \quad (3.2.11)$$

where C is the concentration of the species,

D is the diffusion coefficient,

v is the fluid flowrate,

r is the rate at which species is being generated due to homogeneous chemical reaction.

In many metallurgical processes operating at extremely high temperatures, interfacial steps are generally very rapid in comparison with the rates of bulk transport of the reacting or product species. Two important consequences follow^[83]:

- (1) The reaction may be considered to be transport-controlled.
- (2) Chemical equilibrium of the species dissolved in both phases may be assumed at the interface.

The experimental results show that the rate-controlling step of the sulfidation process of iron oxysulfide is the inter-diffusional mass transport of dissolved sulfur and oxygen within the liquid phase. Under the experimental conditions of thermogravimetric studies, iron oxysulfide liquid is motionless ($v=0$) and within the system boundary there is no chemical reaction ($r=0$). Therefore the transport-controlling step is a diffusion process. Only the diffusion transport term is considered in the right-hand side of equation 3.2.11.

3.2.4.1 Theory of Diffusion

Diffusion is a process which leads to an equalization of concentration. The laws of diffusion connect the rate of flow of the diffusing substance with the concentration gradient

responsible for the flow.

The diffusion flow or current J of a substance in a mixture with other substances is defined as the amount of this substance passing perpendicularly through a reference surface of unit area during a unit time. Fick's first law of diffusion states that the diffusion flow J is in the opposite direction to the concentration gradient and is proportional to its absolute value.

$$J = -D \left(\frac{\partial C}{\partial x} + \frac{\partial C}{\partial y} + \frac{\partial C}{\partial z} \right) \quad (3.2.12)$$

where D is the diffusion coefficient.

Generally, it is not possible to investigate diffusion under conditions of constant concentration gradient, which implies the establishment of a steady state. Therefore the change of concentration caused by diffusion with time has to be determined. From Fick's first law, Fick's second law of diffusion can be derived in the form.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} \right) \quad (3.2.13)$$

Most important for practical purpose are the cases of cylindrical or spherical symmetry, where c depends on the radius r only. The equation can be transformed

$$\frac{\partial C}{\partial t} = \left(\frac{1}{r} \right) \frac{\partial}{\partial r} \left(r D \frac{\partial C}{\partial r} \right) \quad \text{Axial Symmetry} \quad (3.2.14)$$

and

$$\frac{\partial C}{\partial t} = \left(\frac{1}{r^2} \right) \frac{\partial}{\partial r} \left(r^2 D \frac{\partial C}{\partial r} \right) \quad \text{Spherical Symmetry} \quad (3.2.15)$$

Much of the theoretical work on diffusion has been concerned with solving, for

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various initial and boundary conditions, the partial differential equation (3.2.13), and more complex equations for systems in which diffusion occurs in more than one direction.^[84]

There are two types of diffusion.^[85] Self-diffusion includes all atomic migration processes which occur without the presence of a gradient in chemical concentration. It not only includes diffusion of solvent atoms in a pure solvent but also solute atoms in trace quantities in solvent. Chemical diffusion implies atomic migration processes with the presence of a concentration gradient. The experiments in this investigation where chemical compositions vary with position in the specimen fall into the chemical diffusion category.

Diffusion coefficients greatly vary with temperature. Numerous experimental studies of diffusion over a wide temperature range confirm the following theoretically derived exponential relationship between the diffusion coefficient and temperature^[86]

$$D = D_0 e^{-\frac{E_d}{RT}} \quad (3.2.16)$$

where D_0 is frequency factor, and E_d is the activation energy of diffusion. Activation energies of diffusion in metals are up to 20 kcal/mole and depend mainly on the nature of solvent. Values for diffusion in slags are considerably higher, perhaps approaching 100 kcal/mole, probably reflecting the greater range of viscosity in slags.^[87] The diffusion coefficients of sulfur in iron^[88] are listed in Table 3.2.6.

Table 3.2.6 Diffusion Coefficients of Sulfur in Iron^[88]

Element	Concentration, %	Temperature, °C	D, cm ² /sec
S	---	1050	7.0x10 ⁻⁹
S	0.08-0.64	1560	3.0x10 ⁻⁴

3.2.4.2 Diffusion Model

According to the TGA experimental conditions and results, several explanations and assumptions are made:

- (1) Initially, magnetite reacts with carbon monoxide and hydrogen sulfide to produce the iron oxysulfide melt whose concentrations of sulfur and oxygen are almost uniform throughout ($\text{Fe}_3\text{O}_4 + \text{CO} + \text{H}_2\text{S} = \text{FeSO} + \text{CO}_2 + \text{H}_2\text{O}$). The initial concentrations of sulfur and oxygen are denoted as C_s^0 and C_o^0 .
- (2) Since the rate-controlling step is diffusion transfer, the resistance to transfer in the medium surrounding the liquid is negligible.
- (3) The rate of interfacial reaction is very rapid; chemical equilibria of the sulfur and oxygen between liquid and gas phases are reached. The surface concentrations of sulfur and oxygen are constant at C_s^s and C_o^s .
- (4) Since the ion diameter of sulfur is greater than that of oxygen, the diffusion rate of sulfur in iron oxysulfide liquid is slower than that of oxygen. Therefore the rate limiting step is the sulfur diffusion transfer step from the top of the melt in the crucible where chemical equilibrium is achieved to the bottom of the melt in the crucible where the concentration of sulfur is the initial one, C_s^0 . The process continues until the concentration of sulfur on the bottom of the crucible achieves the equilibrium concentration. The whole procedure is shown in Figure 3.2.18.
- (5) Ignoring the effect of the corner of the crucible, the level of iron oxysulfide liquid in the crucible is the same.
- (6) The diffusion coefficient is only a function of temperature and does not vary with the change in composition of iron oxysulfide.

Based on the above explanations and assumptions, the mass conservation of the transferred sulfur within the system boundary is given by the Fick's second law equation (3.2.13), and the initial and boundary conditions are in the form:

$$\begin{aligned}
 \frac{\partial C}{\partial t} &= D \frac{\partial^2 C}{\partial y^2} \\
 C|_{t=0} &= C^o \\
 C|_{y=0} &= C^s \\
 \left. \frac{\partial C}{\partial y} \right|_{y=H} &= 0
 \end{aligned}
 \tag{3.2.17}$$

Figure 3.2.18 Scheme of Diffusion Process

where y is the coordinate chosen perpendicular to the surface, C is the concentration of diffusing sulfur, C^o is the initial concentration of sulfur, C^s is the interfacial concentration of sulfur, and H is the thickness of iron oxysulfide melts. The second boundary condition is due to the crucible impermeable bottom surface, so that the concentration gradient $\partial C/\partial y$ is zero at the bottom surface.

The method of separation of variables^[89,90] is used to solve the above diffusion equation. By superposition, the $C(y,t)$ is equal to

$$C(y,t) = C^s + W(y,t) \quad (3.2.18)$$

Substitution of $C(y,t)$ in equation (3.2.17) yields

$$\begin{aligned} \frac{\partial W}{\partial t} &= D \frac{\partial^2 W}{\partial y^2} \\ W|_{t=0} &= C^o - C^s \\ W|_{y=0} &= 0 \\ \frac{\partial W}{\partial y} \Big|_{y=H} &= 0 \end{aligned} \quad (3.2.19)$$

In the linear case, the solution is assumed to be in the following form in order to separate the variables:

$$W(y,t) = Y(y)T(t) \quad (3.2.20)$$

where Y is function of y only, and T is function of t only. Upon substitution into equation (3.2.19), we get

$$\frac{Y''(y)}{Y(y)} = \frac{T'(t)}{DT(t)} \quad (3.2.21)$$

Since the left-hand side of equation (3.2.21) is independent of t and the right-hand side is

independent of y , they can be set equal to the same constant, independent of y and t , as follows:

$$\frac{Y''(y)}{Y(y)} = \frac{T'(t)}{DT(t)} = -\lambda \quad (3.2.22)$$

where λ is a separation constant.

Thus the ordinary differential equations are obtained

$$\begin{aligned} Y''(y) + \lambda Y(y) &= 0 \\ Y(0) &= 0 \\ Y'(H) &= 0 \end{aligned} \quad (3.2.23)$$

and

$$T'(t) + \lambda DT(t) = 0 \quad (3.2.24)$$

The solution of the differential equation (3.2.23) is

$$Y(y) = A \cos(\sqrt{\lambda} y) + B \sin(\sqrt{\lambda} y) \quad (3.2.25)$$

Because of the boundary condition $Y(0)=0$, constant A must be equal to zero. Also to satisfy the second boundary condition, the following must be true

$$\cos \sqrt{\lambda} H = 0 \quad (3.2.26)$$

or

$$\begin{aligned} \sqrt{\lambda} H &= \left(n + \frac{1}{2}\right) \pi \quad n=0,1,2,3,\dots \\ \lambda &= \frac{(2n+1)^2 \pi^2}{4H^2} \end{aligned} \quad (3.2.27)$$

Thus,

$$Y(y) = B \sin \frac{(2n+1)\pi y}{2H} \quad (3.2.28)$$

Next, equation (3.2.27) is substituted into equation (3.2.24) to get:

$$T'(t) + D \frac{(2n+1)^2 \pi^2}{4H^2} T(t) = 0 \quad (3.2.29)$$

which has the following solution

$$T(t) = E e^{-\frac{(2n+1)^2 \pi^2 D t}{4H^2}} \quad (3.2.30)$$

Hence, the nontrivial solution of equation (3.2.19) which satisfies the boundary conditions is given by:

$$W(y,t) = F e^{-\frac{(2n+1)^2 \pi^2 D t}{4H^2}} \sin \frac{(2n+1)\pi y}{2H} \quad (3.2.31)$$

where $F = B \cdot E$ is an arbitrary constant.

To find the solution to this problem, a series is formally formed

$$W(y,t) = \sum_{n=0}^{\infty} F_n e^{-\frac{(2n+1)^2 \pi^2 D t}{4H^2}} \sin \frac{(2n+1)\pi y}{2H} \quad (3.2.32)$$

which satisfies the initial condition.

$$\sum_{n=0}^{\infty} F_n \sin \frac{(2n+1)\pi y}{2H} = C^o - C^s \quad (0 < y < H) \quad (3.2.33)$$

$(C^o - C^s)$ can be represented in a Fourier sine series

$$C^o - C^s = \sum_{n=0}^{\infty} \left[\frac{2}{H} \int_0^H (C^o - C^s) \sin \frac{(2n+1)\pi y}{2H} dy \right] \sin \frac{(2n+1)\pi y}{2H} \quad (3.2.34)$$

Comparison of equations (3.2.33) and (3.2.34) yields

$$F_n = \frac{2}{H} \int_0^H (C^o - C^s) \sin \frac{(2n+1)\pi y}{2H} dy = \frac{4(C^o - C^s)}{(2n+1)\pi} \quad (3.2.35)$$

and

$$W(y,t) = \sum_{n=0}^{\infty} \frac{4(C^o - C^s)}{(2n+1)\pi} e^{-\frac{(2n+1)^2 \pi^2 D t}{4H^2}} \sin \frac{(2n+1)\pi y}{2H} \quad (3.2.36)$$

Hence

$$C(y,t) = C^s - \sum_{n=0}^{\infty} \frac{4(C^s - C^o)}{(2n+1)\pi} e^{-\frac{(2n+1)^2 \pi^2 D t}{4H^2}} \sin \frac{(2n+1)\pi y}{2H} \quad (3.2.37)$$

is the formal solution of the diffusion equation (3.2.17).

In practical experiments, the total amount of substance which is taken up is measured, but not the local concentration. From such measurements the average concentration may be derived at once. The average concentration is obtained from equation (3.2.37)

$$\begin{aligned}\bar{C}(t) &= \frac{1}{H} \int_0^H C(y, t) dy \\ &= C^s - \sum_{n=0}^{\infty} \frac{8(C^s - C^o)}{(2n+1)^2 \pi^2} e^{-\frac{(2n+1)^2 \pi^2 D t}{4H^2}}\end{aligned}\quad (3.2.38)$$

By rearranging equation (3.2.38), a slightly simplified formula is obtained.

$$\frac{C^s - \bar{C}}{C^s - C^o} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\frac{(2n+1)^2 \pi^2 D t}{4H^2}} \quad (3.2.39)$$

For sufficiently large t , the first term in the series (3.2.39) gives a good approximation

$$\frac{C^s - \bar{C}}{C^s - C^o} = \frac{8}{\pi^2} e^{-\frac{t}{\tau}} \quad \tau = \frac{4H^2}{\pi^2 D} \quad (3.2.40)$$

One approach is to take the natural logarithm on both sides of the above equation, as follows:

$$\ln\left(\frac{C^s - \bar{C}}{C^s - C^o}\right) = \text{const} - \frac{t}{\tau} \quad (3.2.41)$$

Consequently, τ and D may be obtained from the slope of the straight part of the curve plotted using the experimental data.

A simpler approach is applicable when the absolute value of exponential t/τ is much less than one, equation (3.2.40) is approximated by a linear equation using the approximation $e^x = 1 + x$, when $x \ll 1$.

$$\begin{aligned}\bar{C}(t) &= [C^s - \frac{8(C^s - C^o)}{\pi^2}] + \frac{2(C^s - C^o)D}{H^2}t \\ &= A + Bt\end{aligned}\quad (3.2.42)$$

where

$$\begin{aligned}\text{intercept} &= A = [C^s - \frac{8(C^s - C^o)}{\pi^2}] \\ \text{slope} &= B = \frac{2(C^s - C^o)D}{H^2}\end{aligned}$$

3.2.4.3 Analysis of Experimental Results

The experiments using TGA equipment on the kinetics of the sulfidation process of the intermediate reduction product wustite are conducted by exposing the magnetite to a reducing gas mixture ($\text{CO} + \text{CO}_2 + \text{H}_2 + \text{H}_2\text{S}$). The flow of sulfidizing gas mixture is initiated after the magnetite sample reaches the desired temperature. This time is also taken as the starting point of the experiments in subsequent analysis. The analyses of experimental results under various flowrates, temperatures, particle sizes, and concentrations of gaseous species show that the rate-controlling step of the process is diffusion transport of dissolved sulfur from the gas/liquid interface to the interior of the liquid phase.

Since the values of initial concentration C^0 and average concentration in equation 3.2.40 are difficult to obtain directly from the experimental data, the simplified approach discussed earlier is applied. The steady increase in weight after the reduction period of magnetite to wustite is due to the replacement of sulfur with oxygen (the atomic weight of sulfur is twice as large as that of oxygen). The higher the concentration of sulfur in iron oxysulfide, the greater is the mass of sample. Therefore, the weight of sample is proportional to the average concentration of sulfur in the liquid phase. With 1-mm thick iron oxysulfide melts and the normal ranges of diffusion coefficients $10^{-6} - 10^{-8} \text{ cm}^2/\text{sec}$ in molten matte, the value of τ is estimated to be in the range from 1080 to 108000 minutes. Given that the duration of each experiment did not exceed 100 minutes, the assumption that absolute value of exponential t/τ is much less than unity is quite valid. Therefore, the linear equation 3.2.42 is applicable to analyze the experimental results. All the curves of mass change of the sample with time under different conditions tend to be linear at time periods beyond the reduction of magnetite to wustite.

The most important parameter is the slope of the straight line which is proportional to the diffusion coefficient D and the difference of concentration ($C^s - C^0$) and is inversely proportional to the depth H of iron oxysulfide liquid in the crucible.

With the diffusion transport of dissolved sulfur in the liquid phase being rate-controlling, the flowrate of gas mixture has no effect on the sulfidation kinetics (Figure 3.2.14). Since the activation energy of diffusion in molten matte is relatively high, the diffusion coefficient and the slope of straight line are expected to increase rapidly with

increasing temperature. Therefore, the TGA curves (Figure 3.2.15) show a substantial increase in the rate of reaction. Since the surface area per unit mass is inversely proportional to the particle size, the particle size of sample does affect the reaction rate of reduction of magnetite or the incubation period. Beyond the incubation period, all samples melt. Therefore, the particle size will have no effect on the sulfidation process of the iron oxysulfide liquid. The experimental results (Figure 3.2.16) illustrate that both curves are linear and have the same slope. The equilibrium compositions of iron oxysulfide vary little with the changes of concentration of the gaseous species. The TGA curves (Figure 3.2.17) show that there is a little change in slope with the difference in concentration (C^s-C^o).

Experimental results illustrate that temperature has the most significant effect on the kinetics of the sulfidation process of the iron oxysulfide liquid. The slopes of straight lines for various temperatures are reported in Table 3.2.7.

Table 3.2.7 Slopes of Straight Line for Different Temperatures

Temperature (°C)	Slope (1/min)
1200	0.00131
1250	0.00318
1300	0.00738
1350	0.01110
1400	0.02330

Given that during each experiment the same amount of sample was added into the same type of crucible, the depth of iron oxysulfide liquid is held constant. By maintaining the gas composition constant, the effect of temperature on the difference of concentration (C^s-C^o) is negligible. Therefore, only the change in slope is affected by the temperature. The relationship of $\ln(\text{slope})$ versus $1/T$ is shown in Figure 3.2.19. The slope of the straight line is used to calculate the apparent activation energy according to equation 3.2.16. The estimated apparent activation energy for the diffusion of dissolved sulfur in iron oxysulfide is 70.98 kcal/mole.

Figure 3.2.19 Effect of Temperature on the Rate of the Diffusion Process in Iron Oxysulfide Liquid

3.2.4.4 Application of Kinetic Model in Practice

The limitations of equipment and method indicates that TGA testing does not simulate the actual test conditions in a burner system such as those which have been previously reported by Hepworth and Wicker^[36]. In their burner system (Figure 3.2.20), the mixture of magnetite and coal pulverized to 325 - 400 mesh was injected with primary air into a vertical down-fired chamber where the coal was burned with oxygen-deficient air at 1200 to 1500 °C and magnetite reacted with hydrogen sulfide to produce iron oxysulfide. Slag and iron oxysulfide were separated from the off-gas by gravity and accumulated at the bottom of the assembly. The off-gases were burned to completion with secondary air in an afterburner. With this kind of entrained-phase gasifier, the gas and solids residence times are similar, each being of the order of seconds.^[19] For this reason entrained-phase gasifiers generally operate at slagging temperatures in order to obtain high reaction rates and carbon conversions.

Similar to the TGA experiments, the entire process of desulfurization with magnetite as sulfur sorbent in a burner will include a reduction reaction of magnetite to wustite and a sulfidation process of liquid iron oxysulfide. Because of the relatively fast reaction rate and high CO concentration in the gas phase, the time required to complete the reduction process is much less than that for the sulfidation process. Therefore the discussion is focused on the kinetics of the sulfidation process of iron oxysulfide.

The sulfidation process of the reduction product, wustite, can be expressed by the equation:

The iron oxysulfide liquid is dispersed as droplets in reacting gases. The mechanism consists of mass transport of reactant hydrogen sulfide and product water vapor between bulk gas phase and liquid surface through a boundary gas film, chemical reaction at the interface, and mass transports of dissolved sulfur and oxygen in the liquid phase.

In practice the burner is a moving system and the linear gas flow velocity is much greater than the critical velocity where the influence of boundary gas film is negligible. Therefore the mass transport of reactant hydrogen sulfide and product water vapor between bulk gas phase and liquid surface through a boundary gas film is not considered as a

Figure 3.2.20 Test Facility for Slagging Desulfurizing Burner^[36]

possible rate-limiting step. At the same time the desulfurization process operates at high temperatures (1200-1500°C); the rate of chemical reaction at the interface is very rapid in comparison with the rate of mass transport of the dissolved sulfur and oxygen. Chemical equilibrium of the species dissolved in both gas and liquid phases at the interface is reached. The whole process is considered to be transport-controlled.

The mass conservation equation in the iron oxysulfide droplet is obtained from equation 3.2.11:

$$\frac{\partial C}{\partial t} = D \nabla^2 C - v \nabla C \quad (3.2.43)$$

For the spherical geometry, spherical polar coordinate is used. There is a spherical symmetry, where C depends on the radius r only. Unsteady state diffusion of a dissolved species in a droplet is considered initially with concentration C^0 , when the surface concentration is raised to C^s at $t=0$. In this situation, the equation is simplified to:

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) + v \frac{\partial C}{\partial r} \quad (3.2.44)$$

Comparing with the TGA experiment, the time required to reach the equilibrium for the iron oxysulfide liquid droplet in burner is expected to be much shorter than that for the sample in the crucible in the TGA tests.

The dimension of the reactant has a very important effect on the reaction rate. It decides not only the distance for the species to diffuse but also the area of interface for reacting molecules to transfer from one phase to the other. The rate of desulfurization of the droplet with a diameter of about 40 micron in the burner will be a thousand times as fast as that of a slab with a 5-mm diameter and a 1-mm depth in the TGA equipment.

Geometry of the interface also plays a role in determining the rate of a process. Figure 3.2.21^[93] shows fractional saturations $(C_m - C_o)/(C_m - C_s)$ as a function of time for a sphere, cylinder, and slab with uniform initial concentration C_o , surface concentration C_s ,

Figure 3.2.21 Fractional Saturations for a Sphere, Cylinder, and Slab with Uniform Initial Concentration C_0 and Surface Concentration C_s . C_m is the Mean Concentration at Time t . L is radius of Sphere and Cylinder and Half Thickness of Slab. Other Dimensions are infinite.^[93]

and mean concentration C_m at time t . With the same dimensional size, the rate of radial diffusion in a spherical droplet is twice as fast as that of diffusion in a slab in a crucible.

With a dispersed droplet it is evident from high-speed cine-films that a great deal of movement goes on in both the surface and the interior. The convection will accelerate the mass transfer of dissolved sulfur and oxygen in the droplet and improve the desulfurization efficiency.^[93]

It is, however, very difficult to estimate the fluid flowrate r in the interior of the liquid droplet. This is because there is no way of knowing the degree of circulation set up within the droplet. Another complication is that the flow rate is a function of the radius r . Several assumptions are made for quantitative analysis:

- (1) There is no convection in the liquid droplet;
- (2) the initial concentrations of sulfur and oxygen, expressed as C_s^o and C_o^o , are uniform throughout the droplet;
- (3) chemical equilibrium of the sulfur and oxygen in both liquid and gas phases is reached. The surface concentrations of sulfur and oxygen are constant at C_s^s and C_o^s ;
- (4) the diffusion coefficient is only a function of temperature and does not vary with the change in composition of iron oxysulfide;
- (5) there is no temperature difference between the droplet and the gas phase;
- (6) the partial pressures of sulfur and oxygen in the gas phase are constant during the process; and
- (7) the dimension of droplet does not change; there is no aggregation.

Based on the above assumptions, the equation for mass transfer of dissolved sulfur in the droplet and the initial and boundary conditions become:

$$\begin{aligned}
 \frac{\partial C}{\partial t} &= \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \\
 C|_{t=0} &= C^o \\
 C|_{r=r_0} &= C^s \\
 \frac{\partial C}{\partial r} \Big|_{r=0} &= 0
 \end{aligned}
 \tag{3.2.45}$$

where the origin of coordinates is at the center of the droplet; the radius of the droplet is r_0 .

By using the method of separation of variables, the formal solution of the above equation is

$$C(r,t) = C^s + \sum_{n=1}^{\infty} (-1)^n \frac{2(C^s - C^0)r_0}{n\pi r} e^{-\frac{n^2\pi^2 D t}{r_0^2}} \sin \frac{n\pi r}{r_0} \quad (3.2.46)$$

The average concentration is obtained from equation (3.2.46)

$$\begin{aligned} \bar{C}(t) &= \frac{1}{\frac{4}{3}\pi r_0^3} \int_0^{r_0} 4\pi r^2 C(r,t) dr \\ &= C^s - \sum_{n=1}^{\infty} \frac{6(C^s - C^0)}{n^2\pi^2} e^{-\frac{n^2\pi^2 D t}{r_0^2}} \end{aligned} \quad (3.2.47)$$

By rearranging equation (3.2.47), a slightly simplified formula is obtained:

$$\frac{C^s - \bar{C}}{C^s - C^0} = \sum_{n=1}^{\infty} \frac{6}{n^2\pi^2} e^{-\frac{n^2\pi^2 D t}{r_0^2}} \quad (3.2.48)$$

For sufficiently large t , the first term in the series (3.2.48) gives a good approximation

$$\frac{C^s - \bar{C}}{C^s - C^0} = \frac{6}{\pi^2} e^{-\frac{t}{\tau}} \quad \tau = \frac{r_0^2}{\pi^2 D} \quad (3.2.49)$$

Comparing equations 3.2.40 and 3.2.49, the ratio of time required to approach certain fractional conversion in the burner and the TGA equipment is obtained by rearranging:

$$\frac{t_{\text{burner}}}{t_{\text{TGA}}} = \frac{r_o^2}{4H^2} \frac{(\ln C^* - 0.210)}{(\ln C^* - 0.498)} \quad (3.2.50)$$

Where C^* is the fractional saturation $(C^s - C)/(C^s - C^o)$.

With the depth $H = 1$ mm and the radius $r_o = 40$ μm , the time ratio is plotted against the fractional saturation C^* in Figure 3.2.22. The rate of desulfurization of the droplet in the burner is about thousand times as fast as that of slab in the TGA equipment. The time ratio increases with increasing fractional saturation. Using the calculated time ratio, the time of the droplet in the burner required for desulfurization can be obtained from the TGA experimental data (Figure 3.2.15) for various temperatures and fractional saturation. The results are listed in Table 3.2.8.

Table 3.2.8 Residence Times Required for TGA and Burner under Different Fractional Saturations and Temperatures

C^*	1200 °C		1300 °C		1400 °C	
	t_{TGA} min	t_{Burner} sec	t_{TGA} min	t_{Burner} sec	t_{TGA} min	t_{Burner} sec
0.95	130	6.56	35	1.76	15	0.76
0.90	122	5.60	31	1.42	14	0.64
0.85	115	4.89	28	1.19	11.5	0.49
0.80	110	4.39	26	1.04	10.8	0.43

The calculation results show that when the operating temperature in burner is over 1400 °C, the time of droplet required for high desulfurization in the burner is less than one second, which agrees with the experimental results reported by Hepworth and Wicker^[36]. In a real burner, the assumptions that the dimension of the droplet does not change and there is no convection in the liquid droplet are not valid. The aggregation of droplets between the iron oxysulfide liquid and the molten slag will increase the dimension of the droplet and reduce the surface area, thus decelerating the desulfurization process. However, the

Figure 3.2.22 The Time Ratio versus the Fractional Saturation

convection in droplet will accelerate the mass transfer of dissolved sulfur and oxygen and improve the desulfurization efficiency. These two opposite effects will be balanced to a certain degree which depends on the design of the burner and the actual operating conditions.

IV. SUMMARY AND CONCLUSIONS

The following can be deduced from the theoretical and experimental studies of the thermodynamics and kinetics of desulfurization:

- (1) Interactive computer programs are developed to determine combustion conditions, sorbent dosages, and potentials for desulfurization.
- (2) Lime added to combustion gases is effective as a desulfurizer under both oxidizing conditions to form sulfate CaSO_4 as a reaction product, and reducing conditions to form the sulfide CaS . It is not practical under equilibrium conditions as a sulfur sorbent at temperatures above 1175°C when conditions are oxidizing. It is effective up to temperatures well above 1500°C . When temperature increases, the compound CaS can exist under more oxidizing conditions.
- (3) In the Fe-O-S system, the desulfurization with Fe-FeO-liquid-gas system shows greater extent at higher temperatures for the range studied. Moisture and hydrogen in the coal have adverse effects on the degree of desulfurization.
- (4) Three-suffix Margules' equation is used to interpolate or extrapolate the iron oxysulfide system to regions not tested experimentally. Equilibrium measurements of gas compositions over the liquid iron oxysulfide phase have been made to verify the calculated thermodynamic data.
- (5) A series of contour maps expressing SO_2 concentration have been calculated as functions of partial pressures of oxygen and sulfur. These calculations have been made at 1200°C , 1300°C , 1400°C , and 1450°C . These contour maps show that substantial increases in sulfur dioxide emissions occur as oxygen pressure increases to values above 10^{-8} at 1450°C and to values above 10^{-10} at 1200°C . Thermodynamic performance of oxysulfide is improved at higher temperature. Calculations indicate that degrees of desulfurization in excess of 92% are feasible with iron oxide additions. With the thermodynamic calculations, the thermodynamic conditions for optimum removal of sulfur from the first stage of a coal combustor are determined. Analysis of phase equilibria indicates that the optimum conditions for deployment of the reducing stage of a multi-stage burner operating with iron oxide injection are close to the boundary of the liquid iron oxysulfide phase with iron saturation.

- (6) Mass and heat balance calculations indicate that combustion is nearly autogenous. To sustain combustion at higher temperatures, heat exchange between the combustion products and inlet air would be required. It is also possible to attain flame temperatures above 1500°C with 20% heat loss for equivalence ratios less than 2.0.
- (7) Kinetic experiments of single particles of magnetite are made by exposing the particle to a pulse of sulfidizing and reducing gas. Relatively pure taconite concentrate reacts with sulfidizing gases with relatively fast kinetics; however high purity mineral-grade magnetite appears not to react with the sulfidizing gases. This reactivity of the taconite concentrate may be a result of the minor impurities which exert a catalytic effect on their reactivity with sulfur.
- (8) The experiments by TGA show that the whole process from magnetite Fe_3O_4 to liquid iron oxysulfide consists of the reduction process of magnetite to wustite and the sulfidation process of reduction product wustite. By using "shrinking unreacted-core" model, it is confirmed that the first stage of the reduction reaction of magnetite to wustite is controlled by chemical reaction kinetics. The analyses of TGA experimental results show that the sulfidation process of iron oxysulfide is controlled by the mass transport of dissolved sulfur and oxygen in the liquid phase.
- (9) A diffusion model is developed to analyze the TGA experimental results. The diffusion model is applied to actual test conditions in a burner. Comparing with the conditions in TGA experiments, the droplets of iron oxysulfide in burner with their dimensions, geometry, and inside convection are expected to have a fast rate. When the operating temperature in burner is above 1400°C, a high degree of desulfurization with iron oxysulfide can be obtained with less than one second residence time.

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VI. APPENDIX A

Interactive Computer Programs

**Interactive Computer Program for Coal
Combustion in the Presence of a Lime-Based Sorbent**

```

1000 DIM G(25),K(25)
1010 PRINT "CaO As Sulfur Sorbent"
1020 PRINT "The Composition of Coal Based On 100 g Dry Coal"
1030 INPUT "C=";C:INPUT "S=";S:INPUT "O=";O
1040 INPUT "H=";H:INPUT "N=";N:INPUT "M=";M
1050 GOSUB 4000
1060 INPUT "T=";T:T=T+273.15
1070 INPUT "P=";P
1080 GOSUB 6000
1090 PRINT "The Partial Pressure of Oxygen"
1100 INPUT "PO2=";PO2
1110 GOSUB 8000

2000 PRINT "Analysis of The Result"
2010 PRINT "The Amount of Air Under SPT=";A
2020 AIR=(C/12.01+S/32.06+H/4/1.008-O/2/16)/.21*22.415
2030 PRINT "Equivalence Ratio=";A/AIR
2040 PST=PS2+PH2S+PSO2+PCOS+PSO+PSO3+PS+PS4+PCS+PCS2
2050 PRINT "The Total Pressure (atm) of Sulfur Species=";PST
2070 PSST=2*NST*PN2/NN*1000000
2090 PRINT "The Total Sulfur (Moles) Evolved in The Gas=";NST
2100 PRINT "The Total Pressure of Equivalent SO2 (ppm)=";PSST
2110 PRINT "The Percent of Sulfur Removal="; (NS-NST)/NS*100;"%"
2120 NCV=(145.8*C+612*(H-O/8)+39.6*S-10.52*(9*H+M))/1000000
2130 SSS=(NST/NS)*(S/100)*(64.06/32.06)
2140 PRINT "Oxygen Amount (atom moles) into System=";NOA+NOC-NOOT
2150 PRINT "Sulfur Amount (atom moles) into System=";NS-NST
2160 IF SSS>S*2/100 THEN 2190

```



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2170 WCaO=(NS-NST)*56.08
2180 GOTO 2210
2190 SSS=S*2/100
2200 WCaO=0
2210 PRINT "The Dosage of CaO=";WCaO
2220 PRINT "SO2 Emission Rate (LB SO2/MM BTU)=";SSS/NCV
2230 NNN=(PNO+PNO2)/(PCO+PCO2+PCS+PCS2+PCH4+PCOS)*NCC*.4601
2240 PRINT "NOx Emission Rate (LB NO2/MM BTU)=";NNN/NCV
2250 END

```

```

4000 NCC=C/12.01:NSC=S/32.06:NOC=O/16+M/18.016
4010 NHC=H/1.008+M/9.008:NNC=N/14.01
4020 RCH=NCC/NHC
4030 RETURN

```

```

6000 G(1)=-67500+20.75*T
6010 G(2)=-58900+13.1*T
6020 G(3)=-21580+11.805*T
6030 G(4)=-86620+17.31*T
6040 G(5)=-22860+18.7*T
6050 G(6)=-15400-1.4*T
6060 G(7)=-26700-20.95*T
6070 G(8)=-94200-.2*T
6080 G(9)=40800-41.7*T
6090 G(10)=-109220+38.67*T
6120 IF (T-273.15)<1195 THEN 6150
6130 G(13)=-216800+73.92*T
6140 G(11)=-194800+72.79*T:GOTO 6180
6150 G(11)=-196810+74.19*T
6170 G(13)=-218810+75.32*T

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6180 G(12)=22000-1.13*T
6200 G(16)=-42540+39.32*T
6210 G(17)=-810+19.87*T
6220 G(18)=-61570+67.32*T
6230 G(19)=56085-19.275*T
6240 G(20)=-15000+27.6*T
6250 G(21)=21610-3.03*T
6260 G(22)=7720+15.14*T
6270 FOR I=1 TO 22
6280 K(I)=EXP(-G(I)/1.987/T)
6290 NEXT I
6300 RETURN

8000 K=1:PCO=1E-5:PH2=1E-5
8010 IF PO2<(1/K(13))^.5 THEN 8050
8020 PRINT "CaO-CaSO4 SYSTEM"
8030 PS2=1/(K(11))^2/(PO2)^3
8040 GOTO 8140
8050 PRINT "CaO-CaS SYSTEM"
8060 PS2=PO2/K(12)^2
8140 PCO2=K(1)*PCO*(PO2)^.5
8150 PH2O=K(2)*PH2*(PO2)^.5
8160 PH2S=K(3)*PH2*(PS2)^.5
8170 PSO2=K(4)*PO2*(PS2)^.5
8180 PCOS=K(5)*PCO*(PS2)^.5
8190 PSO=K(6)*(PS2*PO2)^.5
8200 PSO3=K(10)*(PS2)^.5*(PO2)^1.5
8210 PCS2=K(16)*PS2*(PCO)^2/PCO2
8220 PCS=K(17)*(PS2)^.5*(PCO)^2/PCO2
8230 PCH4=K(18)*(PCO)^2*(PH2)^2/PCO2

```

$$8240 \text{ PS} = \text{K}(19) * (\text{PS2})^{.5}$$

$$8250 \text{ PS4} = \text{K}(20) * (\text{PS2})^2$$

$$8260 \text{ NST} = \text{NCC} * (2 * \text{PS2} + \text{PH2S} + \text{PSO} + \text{PSO2} + \text{PSO3} + \text{PCOS} + 2 * \text{PCS2} + \text{PCS} + \text{PS} + 4 * \text{PS4}) / (\text{PCO} + \text{PCO2} + \text{PCOS} + \text{PCS} + \text{PCS2} + \text{PCH4})$$

$$8270 \text{ NOOT} = \text{NCC} * (\text{PCO} + 2 * \text{PCO2} + \text{PH2O} + 2 * \text{PSO2} + \text{PCOS} + \text{PSO} + 2 * \text{PO2} + 3 * \text{PSO3}) / (\text{PCO} + \text{PCO2} + \text{PCOS} + \text{PCS} + \text{PCS2} + \text{PCH4})$$

$$8275 \text{ IF } \text{PO2} < (1 / \text{K}(13))^{.5} \text{ THEN } 8290$$

$$8280 \text{ NOA} = \text{NOOT} + 3 * (\text{NSC} - \text{NST}) - \text{NOC}$$

$$8285 \text{ NO} = \text{NOA} + \text{NOC} - 3 * (\text{NSC} - \text{NST}); \text{GOTO } 8305$$

$$8290 \text{ NOA} = \text{NOOT} - (\text{NSC} - \text{NST}) - \text{NOC}$$

$$8300 \text{ NO} = \text{NOA} + \text{NOC} + (\text{NSC} - \text{NST})$$

$$8305 \text{ NNA} = \text{NOA} * 0.79 / 0.21$$

$$8310 \text{ NN} = \text{NNA} + \text{NNC}$$

$$8320 \text{ NH} = \text{NHC}$$

$$8330 \text{ NS} = \text{NSC}$$

$$8340 \text{ NC} = \text{NCC}$$

$$8350 \text{ RNH} = \text{NN} / \text{NH}$$

$$8360 \text{ RNC} = \text{NN} / \text{NC}$$

$$8370 \text{ RSN} = \text{NS} / \text{NN}$$

$$8380 \text{ PN2} = \text{RNC} * (\text{PCO} + \text{PCO2} + \text{PCOS} + \text{PCS} + \text{PCS2} + \text{PCH4}) / 2$$

$$9382 \text{ PNO} = \text{K}(21) * (\text{PN2} * \text{PO2})^{.5}$$

$$9388 \text{ PNO2} = \text{K}(22) * (\text{PN2})^{.5} * \text{PO2}$$

$$8390 \text{ PT} = \text{PCO} + \text{PH2} + \text{PO2} + \text{PS2} + \text{PCO2} + \text{PH2O} + \text{PH2S} + \text{PSO2} + \text{PCOS} + \text{PSO} + \text{PN2} + \text{PSO3} + \text{PCS2} + \text{PCS} + \text{PCH4} + \text{PS} + \text{PS4} + \text{PNO} + \text{PNO2}$$

$$8400 \text{ RCHC} = .5 * (\text{PCO} + \text{PCO2} + \text{PCOS} + \text{PCS2} + \text{PCS} + \text{PCH4}) / (\text{PH2O} + \text{PH2S} + \text{PH2} + 2 * \text{PCH4})$$

$$8410 \text{ ZZA} = \text{ABS}((\text{PT} - \text{P}) / \text{P}); \text{ZZB} = \text{ABS}((\text{RCHC} - \text{RCH}) / \text{RCH})$$

$$8420 \text{ IF } (\text{ZZA} <= 1\text{E-}5) \text{ AND } (\text{ZZB} <= 1\text{E-}5) \text{ THEN } 8500$$

$$8430 \text{ PCO} = \text{PCO} * (\text{P} / \text{PT}) * (\text{RCH} / \text{RCHC})^{.5}$$

$$8440 \text{ PH2} = \text{PH2} * (\text{P} / \text{PT}) * (\text{RCHC} / \text{RCH})^{.5}$$

8450 K=K+1

8460 GOTO 8140

8500 A=NOA*22.415/.21/2

8510 IF $\text{PCO}^2/\text{PCO}_2 > \text{K}(9)$ THEN 9000

8600 PRINT "The result of calculation"

8610 PRINT "PCO=";PCO;" PH2=";PH2

8620 PRINT "PCO2=";PCO2;"PH2O=";PH2O

8630 PRINT "PN2=";PN2;" PO2=";PO2

8640 PRINT "PH2S=";PH2S;"PSO2=";PSO2

8650 PRINT "PCOS=";PCOS;"PSO=";PSO

8660 PRINT "PS2=";PS2;" PSO3=";PSO3

8670 PRINT "PCS2=";PCS2;"PCS=";PCS

8680 PRINT "PS=";PS;"PS4=";PS4

8690 PRINT "PNO=";PNO;"PNO2=";PNO2

8700 PRINT "PCH4=";PCH4

8710 RETURN

9000 PRINT "There is excess carbon in system."

9010 END

**Interactive Computer Program for Coal
Combustion in the Presence of an Iron-Based Sorbent**

```

1000 DIM G(25),K(25)
1010 PRINT "Iron Oxysulfide As Sulfur Sorbent"
1020 PRINT "The Composition of Coal Based On 100 g Dry Coal"
1030 INPUT "C=";C:INPUT "S=";S:INPUT "O=";O
1040 INPUT "H=";H:INPUT "N=";N:INPUT "M=";M
1050 GOSUB 4000
1060 INPUT "T=";T:T=T+273.15
1070 INPUT "P=";P
1080 GOSUB 6000
1090 PRINT "COMPOSITION(Wt%) AND PO2, PS2"
1100 INPUT "WtO=";WtO
1110 INPUT "WtS=";WtS
1120 WtFe=100-WtO-WtS
1130 INPUT "PO2=";PO2
1140 INPUT "PS2=";PS2
1150 GOSUB 8000

2000 PRINT "Analysis of The Result"
2010 PRINT "The Amount of Air Under SPT=";A
2020 AIR=(C/12.01+S/32.06+H/4/1.008-O/2/16)/.21*22.415
2030 PRINT "Equivalence Ratio=";A/AIR
2040 PST=PS2+PH2S+PSO2+PCOS+PSO+PSO3+PS+PS4+PCS+PCS2
2050 PRINT "The Total Pressure (atm) of Sulfur Species=";PST
2090 PRINT "The Total Sulfur (Moles) Evolved in The Gas=";NST
2110 PRINT "The Percent of Sulfur Removal="; (NS-NST)/NS*100;"%"
2120 NCV=(145.8*C+612*(H-O/8)+39.6*S-10.52*(9*H+M))/1000000
2130 SSS=(NST/NS)*(S/100)*(64.06/32.06)
2140 PRINT "Oxygen Amount (atom moles) into System=";NOA+NOC-NOOT

```

```

2150 PRINT "Sulfur Amount (atom moles) into System=";NS-NST
2160 IF SSS>S*2/100 THEN 2190
2170 WFe3O4=(NS-NST)*WtFe/WtS*44.304
2180 GOTO 2210
2190 SSS=S*2/100
2200 WFe3O4=0
2210 PRINT "The Dosage of Fe3O4=";WFe3O4
2220 PRINT "SO2 Emission Rate (LB SO2/MM BTU)=";SSS/NCV
2230 NNN=(PNO + PNO2)/(PCO + PCO2 + PCS + PCS2 + PCH4 + PCOS)*NCC*.4601
2240 PRINT "NOx Emission Rate (LB NO2/MM BTU)=";NNN/NCV
2250 END

```

```

4000 NCC=C/12.01:NSC=S/32.06:NOC=O/16+M/18.016
4010 NHC=H/1.008+M/9.008:NNC=N/14.01
4020 RETURN

```

```

6000 G(1)=-67500+20.75*T
6010 G(2)=-58900+13.1*T
6020 G(3)=-21580+11.805*T
6030 G(4)=-86620+17.31*T
6040 G(5)=-22860+18.7*T
6050 G(6)=-15400-1.4*T
6060 G(7)=-26700-20.95*T
6070 G(8)=-94200-.2*T
6080 G(9)=40800-41.7*T
6090 G(10)=-109220+38.67*T
6200 G(16)=-42540+39.32*T
6210 G(17)=-810+19.87*T
6220 G(18)=-61570+67.32*T
6230 G(19)=56085-19.275*T

```

6240 $G(20) = -15000 + 27.6 * T$

6250 $G(21) = 21610 - 3.03 * T$

6260 $G(22) = 7720 + 15.14 * T$

6270 FOR I=1 TO 22

6280 $K(I) = \text{EXP}(-G(I)/1.987/T)$

6290 NEXT I

6300 RETURN

8000 $PCO = 1E-5; PH2 = 1E-5$

8140 $PCO2 = K(1) * PCO * (PO2)^{.5}$

8150 $PH2O = K(2) * PH2 * (PO2)^{.5}$

8160 $PH2S = K(3) * PH2 * (PS2)^{.5}$

8170 $PSO2 = K(4) * PO2 * (PS2)^{.5}$

8180 $PCOS = K(5) * PCO * (PS2)^{.5}$

8190 $PSO = K(6) * (PS2 * PO2)^{.5}$

8200 $PSO3 = K(10) * (PS2)^{.5} * (PO2)^{1.5}$

8210 $PCS2 = K(16) * PS2 * (PCO)^2 / PCO2$

8220 $PCS = K(17) * (PS2)^{.5} * (PCO)^2 / PCO2$

8230 $PCH4 = K(18) * (PCO)^2 * (PH2)^2 / PCO2$

8240 $PS = K(19) * (PS2)^{.5}$

8250 $PS4 = K(20) * (PS2)^2$

8260 $NST = NCC * (2 * PS2 + PH2S + PSO + PSO2 + PSO3 + PCOS + 2 * PCS2 + PCS + PS + 4 * PS4) / (PCO + PCO2 + PCOS + PCS + PCS2 + PCH4)$

8270 $NOOT = NCC * (PCO + 2 * PCO2 + PH2O + 2 * PSO2 + PCOS + PSO + 2 * PO2 + 3 * PSO3) / (PCO + PCO2 + PCOS + PCS + PCS2 + PCH4)$

8280 $NOO = (NSC - NST) * 32.06 * (WtFe / WtS * 0.0238735 - WtO / WtS * 0.0625)$

8285 $NOA = NOOT - NOO - NOC$

8290 $NNA = NOA * .79 / .21$

8300 $NO = NOA + NOC + NOO$

8310 $NN = NNA + NNC$

```

8320 NH = NHC
8330 NS = NSC
8340 NC = NCC
8350 RCH = NC / NH
8360 RNC = NN / NC
8370 RSN = NS / NN
8380 PN2 = RNC * (PCO + PCO2 + PCOS + PCS + PCS2 + PCH4) / 2
9382 PNO = K(21) * (PN2 * PO2) ^ .5
9388 PNO2 = K(22) * (PN2) ^ .5 * PO2
8390 PT = PCO + PH2 + PO2 + PS2 + PCO2 + PH2O + PH2S + PSO2 + PCOS + PSO
      + PN2 + PSO3 + PCS2 + PCS + PCH4 + PS + PS4 + PNO + PNO2
8400 RCHC = .5 * (PCO + PCO2 + PCOS + PCS2 + PCS + PCH4)
      / (PH2O + PH2S + PH2 + 2 * PCH4)
8410 ZZA = ABS((PT - P) / P); ZZB = ABS((RCHC - RCH) / RCH)
8420 IF (ZZA <= 1E-5) AND (ZZB <= 1E-5) THEN 8500
8430 PCO = PCO * (P / PT) * (RCH / RCHC) ^ .5
8440 PH2 = PH2 * (P / PT) * (RCHC / RCH) ^ .5
8450 K = K + 1
8460 GOT( ) 8140

8500 A = NOA * 22.415 / .21 / 2
8510 IF ! CO ^ 2 / PCO2 > K(9) THEN 9000

8600 PRINT "The result of calculation"
8610 PRINT "PCO = "; PCO; " PH2 = "; PH2
8620 PRINT "PCO2 = "; PCO2; "PH2O = "; PH2O
8630 PRINT "PN2 = "; PN2; " PO2 = "; PO2
8640 PRINT "PH2S = "; PH2S; "PSO2 = "; PSO2
8650 PRINT "PCOS = "; PCOS; "PSO = "; PSO
8660 PRINT "PS2 = "; PS2; " PSO3 = "; PSO3

```



```
8670 PRINT "PCS2=";PCS2;"PCS=";PCS
8680 PRINT "PS=";PS;"PS4=";PS4
8690 PRINT "PNO=";PNO;"PNO2=";PNO2
8700 PRINT "PCH4=";PCH4
8710 RETURN

9000 PRINT "There is excess carbon in system."
9010 END
```

**Computer Program for Best
Fitting of Data in Iron Oxysulfide Solution**

```
5 PRINT "N, T, U, E, L0"
6 INPUT N, T, U, E, L0
10 DIM X(N,N+3), S(N+3), Q(N+3)
11 DIM O(100), SS(100), F(100), PS2(100), PSS(100), O1(100), SS1(100)
20 OPEN "A:IN.DAT" FOR INPUT AS #1
21 OPEN "A:OUT.DAT" FOR OUTPUT AS #2
22 OPEN "A:DATA.DAT" FOR OUTPUT AS #3
23 INPUT "NUM=";NUM
24 FOR J=1 TO NUM
25 INPUT #1, O1(J), SS1(J), PS2(J)
26 ZSL=100/(O1(J)/16+SS1(J)/32.064+(100-O1(J)-SS1(J))/55.847)
27 SS(J)=SS1(J)/32.064*ZSL:O(J)=O1(J)/16*ZSL:F(J)=100-SS(J)-O(J)
28 NEXT J
29 PRINT "X(I,0)"
30 FOR I=1 TO N
35 INPUT X(I,0)
40 NEXT I
45 PRINT
50 FOR J=1 TO N
55 FOR I=1 TO N
60 IF I=J GOTO 75
65 LET X(I,J)=X(I,0)
70 GOTO 80
75 LET X(I,J)=X(I,0)+L0
80 NEXT I
85 NEXT J
90 FOR J=0 TO N
95 GOSUB 540
```

```
100 LET Q(J)=S(J)
105 NEXT J
110 LET J0=0
112 LET J2=0
115 FOR J=1 TO N
120 IF Q(J)<=Q(J0) GOTO 130
125 LET J0=J
130 IF Q(J)>=Q(J2) GOTO 140
135 LET J2=J
140 NEXT J
145 LET J1=J2
150 FOR J=0 TO N
155 IF J=J0 GOTO 180
160 IF Q(J)<=Q(J1) GOTO 180
170 LET J1=J
180 NEXT J
183 LET Q0=Q(J0)
186 LET Q1=Q(J1)
189 LET Q2=Q(J2)
192 FOR I=1 TO N
195 FOR J=1 TO N
198 IF ABS(X(I,J)-X(I,0))>E GOTO 225
201 NEXT J
204 NEXT I
207 IF Q2>1 GOTO 220
210 IF (Q0-Q2)<E GOTO 505
215 GOTO 225
220 IF(Q0-Q2)<(E*Q2) GOTO 505
225 FOR I=1 TO N
230 LET X(I,N+1)=0
```

```
235 FOR J=0 TO N
240 LET X(I,N+1)=X(I,N+1)+X(I,J)
245 NEXT J
250 LET X(I,N+1)=2*(X(I,N+1)-X(I,J0))/N-X(I,J0)
255 NEXT I
260 LET J=N+1
265 GOSUB 540
270 LET Q(N+1)=S(J)
275 IF Q(N+1)<Q(J1) GOTO 410
280 IF Q(N+1)<Q(J0) GOTO 310
285 FOR I=1 TO N
290 LET X(I,N+2)=X(I,N+1)
295 LET X(I,N+1)=X(I,J0)
300 LET X(I,J0)=X(I,N+2)
305 NEXT I
310 FOR I=1 TO N
315 LET X(I,N+2)=(1-T)*X(I,J0)+T*X(I,N+1)
320 NEXT I
325 LET J=N+2
330 GOSUB 540
335 LET Q(N+2)=S(J)
340 IF Q(N+2)<Q(J1) GOTO 380
345 FOR J=0 TO N
350 FOR I=1 TO N
355 LET X(I,J)=(X(I,J)+X(I,J2))/2
360 NEXT I
365 NEXT J
370 PRINT "+":
375 GOTO 90
380 FOR I=1 TO N
```

```
385 LET X(I,J0)=X(I,N+2)
390 NEXT I
395 LET Q(J0)=Q(N+2)
400 PRINT "-";
405 GOTO 110
410 IF (1-U)*Q0+U*Q(N+1)<Q2 GOTO 440
415 FOR I=1 TO N
420 LET X(I,N+2)=X(I,N+1)
425 NEXT I
430 LET Q(N+2)=Q(N+1)
435 GOTO 380
440 FOR I=1 TO N
445 LET X(I,N+3)=(1-U)*X(I,J0)+U*X(I,N+1)
450 NEXT I
455 LET J=N+3
460 GOSUB 540
465 LET Q(N+3)=S(J)
470 IF Q(N+3)<Q(N+1) GOTO 480
475 GOTO 415
480 FOR I=1 TO N
485 LET X(I,0)=X(I,N+3)
490 NEXT I
500 GOTO 50
505 FOR I=1 TO N
510 PRINT #3, X(I,J2)
512 NEXT I
518 PRINT #3, Q(J2)
520 FOR Z=1 TO NUM
522 PSS(Z)=X(7,J2)+2*LOG(SS(Z))+(X(1,J2)+X(2,J2))*O(Z)+(X(3,J2)
    +X(4,J2))*F(Z)-(X(1,J2)+X(2,J2))*SS(Z)*O(Z)
```

```

523 PSS(Z)=PSS(Z)-(X(3,J2)+X(4,J2))*SS(Z)*F(Z)-(X(5,J2)+X(6,J2))
      *O(Z)*F(O)+2*(X(1,J2)-X(2,J2))*(.5*O(Z)-SS(Z))*O(Z)
524 PSS(Z)=PSS(Z)+2*(X(3,J2)-X(4,J2))*(.5*F(Z)-SS(Z))*F(Z)+2*(X(
      1,J2)-X(2,J2))*SS(Z)^2*O(Z)+2*(X(3,J2)-X(4,J2))*SS(Z)^2*F(Z)
525 PSS(Z)=PSS(Z)+2*(X(2,J2)-X(1,J2))*O(Z)^2*SS(Z)+2*(X(5,J2)
      -X(6,J2))*O(Z)^2*F(Z)
526 PSS(Z)=PSS(Z)+2*(X(4,J2)-X(3,J2))*F(Z)^2*SS(Z)+2*(X(6,J2)
      -X(5,J2))*F(Z)^2*O(Z)
528 PSS(Z)=PSS(Z)/log(10)
529 PRINT #2, O1(Z), SS1(Z), PSS(Z), PS2(Z)
530 NEXT Z
531 CLOSE
535 GOTO 630
540 S(J)=0
560 FOR Z=1 TO NUM
590 PSS(Z)=X(7,J)+2*LOG(SS(Z))+(X(1,J)+X(2,J))*O(Z)+(X(3,J)
      +X(4,J))*F(Z)-(X(1,J)+X(2,J))*SS(Z)*O(Z)
592 PSS(Z)=PSS(Z)-(X(3,J)+X(4,J))*SS(Z)*F(Z)-(X(5,J)+X(6,J))
      *O(Z)*F(O)+2*(X(1,J)-X(2,J))*(.5*O(Z)-SS(Z))*O(Z)
594 PSS(Z)=PSS(Z)+2*(X(3,J)-X(4,J))*(.5*F(Z)-SS(Z))*F(Z)+2*(X(
      1,J)-X(2,J))*SS(Z)^2*O(Z)+2*(X(3,J)-X(4,J))*SS(Z)^2*F(Z)
596 PSS(Z)=PSS(Z)+2*(X(2,J)-X(1,J))*O(Z)^2*SS(Z)+2*(X(5,J)
      -X(6,J))*O(Z)^2*F(Z)
598 PSS(Z)=PSS(Z)+2*(X(4,J)-X(3,J))*F(Z)^2*SS(Z)+2*(X(6,J)
      -X(5,J))*F(Z)^2*O(Z)
600 TEMP=(PS2(Z)-PSS(Z)/log(10))^2
608 S(J)=TEMP+S(J)
610 NEXT Z
620 RETURN
630 END

```

VI. APPENDIX B

Reported and Modeled Data for Solution Model

Table 2.3.4
The Reported and Modeled Data and the Parameters
for Partial Pressure of Sulfur at 1200 °C

Composition wt%			log(P _{S2})	
O	S	Fe	Modeled	Reported
0	28.50	71.50	-5.55	-5.5
1	28.25	70.75	-5.84	-5.5
2	27.70	70.30	-5.97	-5.5
3	27.00	70.00	-5.95	-5.5
4	26.15	69.85	-5.87	-5.5
5	25.30	69.70	-5.69	-5.5
6	24.45	69.55	-5.44	-5.5
7	23.50	69.50	-5.27	-5.5
8	22.50	69.50	-5.17	-5.5
9	21.50	69.50	-5.14	-5.5
10	20.50	69.50	-5.19	-5.5
0	30.95	69.05	-4.43	-5
1	30.30	68.70	-4.83	-5
2	29.50	68.50	-5.00	-5
3	28.60	68.40	-5.00	-5
4	27.60	68.40	-4.91	-5
5	26.40	68.60	-4.87	-5
6	25.30	68.70	-4.74	-5
7	24.10	68.90	-4.72	-5
8	22.95	69.05	-4.72	-5
9	21.80	69.20	-4.80	-5
10	20.75	69.25	-4.88	-5
0	33.75	66.25	-3.45	-4
1	32.95	66.05	-3.80	-4
2	31.90	66.10	-3.94	-4
3	30.75	66.25	-3.92	-4
4	29.60	66.40	-3.77	-4
5	28.25	66.75	-3.66	-4
6	26.85	67.15	-3.58	-4
7	25.10	67.90	-3.86	-4
8	23.80	68.20	-3.90	-4
9	22.30	68.70	-4.26	-4
10	21.00	69.00	-4.59	-4
0	35.00	65.00	-3.11	-3
1	34.30	64.70	-3.39	-3
2	33.40	64.60	-3.42	-3
3	32.20	64.80	-3.32	-3
4	30.95	65.05	-3.11	-3
5	29.40	65.60	-2.99	-3

6	27.90	66.10	-2.88	-3
7	26.20	66.80	-2.98	-3
8	24.60	67.40	-3.17	-3
9	23.00	68.00	-3.53	-3
10	21.60	68.40	-3.89	-3

$$k_{\text{SO}} = -3.722 \times 10^{-2}$$

$$k_{\text{OS}} = -3.685 \times 10^{-2}$$

$$k_{\text{SFe}} = -1.708 \times 10^{-2}$$

$$k_{\text{FeS}} = -1.712 \times 10^{-2}$$

$$k_{\text{OFe}} = -2.072 \times 10^{-2}$$

$$k_{\text{FeO}} = -2.080 \times 10^{-2}$$

$$\ln K_s = -97.957$$

Average absolute error = 0.257

Average relative error = 6.28%

Table 2.3.5
The Reported and Modeled Data and Parameters
for Partial Pressure of Oxygen at 1200 °C

Composition wt%			log(P _{O2})	
O	S	Fe	Modeled	Reported
1.20	36	62.80	-12.31	-12
1.45	35	63.55	-12.14	-12
1.80	34	64.20	-11.97	-12
2.15	33	64.85	-11.90	-12
2.55	32	65.45	-11.87	-12
3.00	31	66.00	-11.89	-12
3.50	30	66.50	-11.94	-12
4.05	29	66.95	-12.00	-12
4.60	28	67.40	-12.09	-12
5.20	27	67.80	-12.15	-12
5.80	26	68.20	-12.20	-12
6.40	25	68.60	-12.25	-12
7.15	24	68.85	-12.09	-12
7.80	23	69.20	-11.99	-12
3.00	34	63.00	-10.86	-11
3.35	33	63.65	-10.86	-11
3.80	32	64.20	-10.83	-11
4.20	31	64.80	-10.89	-11
4.70	30	65.30	-10.91	-11
5.15	29	65.85	-11.00	-11
5.70	28	66.30	-11.02	-11
6.25	27	66.75	-11.04	-11
6.80	26	67.20	-11.07	-11
7.40	25	67.60	-11.02	-11
8.10	24	67.90	-10.80	-11
8.75	23	68.25	-10.60	-11
5.15	31	63.85	-9.89	-10

5.60	30	64.40	-9.93	-10
6.05	29	64.95	-10.00	-10
6.55	28	65.45	-10.02	-10
7.05	27	65.95	-10.06	-10
7.60	26	66.40	-10.02	-10
8.10	25	66.90	-10.05	-10
8.75	24	67.25	-9.83	-10
7.25	28	64.75	-9.12	-9
7.80	27	65.20	-9.04	-9
8.30	26	65.70	-9.03	-9
8.80	25	66.20	-9.01	-9
9.40	24	66.60	-8.82	-9
7.90	28	64.10	-8.22	-8
8.40	27	64.60	-8.18	-8
8.90	26	65.10	-8.14	-8
9.40	25	65.60	-8.09	-8
10.00	24	66.00	-7.85	-8

$$k_{\text{OS}} = -5.888 \times 10^{-3}$$

$$k_{\text{SO}} = -5.638 \times 10^{-3}$$

$$k_{\text{OFe}} = -9.705 \times 10^{-3}$$

$$k_{\text{FeO}} = -1.023 \times 10^{-2}$$

$$k_{\text{SFe}} = -1.256 \times 10^{-2}$$

$$k_{\text{FeS}} = -1.254 \times 10^{-2}$$

$$\ln K_{\text{O}} = -30.715$$

Average absolute error = 0.108

Average relative error = 1.04%

Table 2.3.6

The Reported and Modeled Data and the Parameters
for Partial Pressure of Sulfur at 1300 °C

O	Composition wt%		log(P_{S_2})	
	S	Fe	Modeled	Reported
0	29.75	70.25	-5.03	-5
1	29.25	69.75	-5.34	-5
2	28.60	69.40	-5.45	-5
3	27.80	69.20	-5.44	-5
4	26.80	69.20	-5.42	-5
5	25.90	69.10	-5.20	-5
6	24.90	69.10	-4.98	-5
7	23.70	69.30	-4.88	-5
0	31.60	68.40	-4.16	-4.5
1	30.90	68.10	-4.45	-4.5
2	30.00	68.00	-4.61	-4.5
3	29.10	67.90	-4.59	-4.5
4	28.00	68.00	-4.56	-4.5
5	26.80	68.20	-4.51	-4.5
6	25.60	68.40	-4.40	-4.5

7	24.40	68.60	-4.26	-4.5
8	23.30	68.70	-4.01	-4.5
0	33.00	67.00	-3.53	-4
1	32.20	66.80	-3.78	-4
2	31.30	66.70	-3.86	-4
3	30.25	66.75	-3.85	-4
4	29.10	66.90	-3.79	-4
5	27.80	67.20	-3.76	-4
6	26.50	67.50	-3.68	-4
7	25.00	68.00	-3.75	-4
8	23.70	68.30	-3.65	-4
9	22.25	68.75	-3.70	-4
0	34.75	65.25	-2.78	-3
1	34.00	65.00	-2.89	-3
2	33.00	65.00	-2.92	-3
3	31.80	65.20	-2.91	-3
4	30.60	65.40	-2.80	-3
5	29.20	65.80	-2.75	-3
6	27.70	66.30	-2.75	-3
7	26.00	67.00	-2.91	-3
8	24.50	67.50	-2.94	-3
9	22.90	68.10	-3.09	-3
10	21.40	68.60	-3.20	-3
0	36.00	64.00	-2.27	-2
1	35.20	63.80	-2.34	-2
2	34.20	63.80	-2.30	-2
3	33.00	64.00	-2.22	-2
4	31.70	64.30	-2.10	-2
5	30.20	64.80	-2.06	-2
6	28.70	65.30	-2.00	-2
7	26.80	66.20	-2.26	-2
8	25.20	66.80	-2.33	-2
9	23.60	67.40	-2.44	-2
10	22.00	68.00	-2.60	-2

$$k_{\text{SO}} = -2.245 \times 10^{-2}$$

$$k_{\text{SFe}} = -5.403 \times 10^{-3}$$

$$k_{\text{OFe}} = 1.433 \times 10^{-2}$$

$$\ln K_s = -39.086$$

$$\text{Average absolute error} = 0.218$$

$$\text{Average relative error} = 6.94\%$$

$$k_{\text{OS}} = -2.233 \times 10^{-2}$$

$$k_{\text{FeS}} = -5.482 \times 10^{-3}$$

$$k_{\text{FeO}} = 1.412 \times 10^{-2}$$

Table 2.3.7
The Reported and Modeled Data and Parameters
for Partial Pressure of Oxygen at 1300 °C

Composition wt%			log(P _{O2})	
O	S	Fe	Modeled	Reported
2.80	32	65.20	-11.63	-11.5
3.20	31	65.80	-11.47	-11.5
3.60	30	66.40	-11.41	-11.5
4.05	29	66.95	-11.42	-11.5
4.55	28	67.45	-11.46	-11.5
5.05	27	67.95	-11.57	-11.5
5.70	26	68.30	-11.61	-11.5
6.30	25	68.70	-11.71	-11.5
7.05	24	68.95	-11.66	-11.5
3.00	33	64.00	-11.23	-11
3.35	32	64.65	-11.06	-11
3.75	31	65.25	-10.94	-11
4.20	30	65.80	-10.87	-11
4.65	29	66.35	-10.88	-11
5.15	28	66.85	-10.92	-11
5.65	27	67.35	-11.02	-11
6.30	26	67.70	-11.00	-11
6.90	25	68.10	-11.06	-11
7.60	24	68.40	-11.00	-11
4.25	32	63.75	-10.03	-10
4.65	31	64.35	-9.96	-10
5.10	30	64.90	-9.92	-10
5.60	29	65.40	-9.88	-10
6.10	28	65.90	-9.90	-10
6.60	27	66.40	-9.97	-10
7.20	26	66.80	-9.95	-10
7.75	25	67.25	-10.01	-10
8.45	24	67.55	-9.87	-10
9.15	23	67.85	-9.70	-10
5.60	31	63.40	-8.79	-9
5.95	30	64.05	-8.89	-9
6.35	29	64.65	-8.98	-9
6.80	28	65.20	-9.05	-9
7.30	27	65.70	-9.10	-9
7.90	26	66.10	-9.04	-9
8.55	25	66.45	-8.92	-9
9.20	24	66.80	-8.78	-9
7.40	28	64.60	-8.27	-8
7.95	27	65.05	-8.23	-8
8.50	26	65.50	-8.21	-8
9.05	25	65.95	-8.20	-8
9.70	24	66.30	-8.03	-8

10.30	23	66.70	-7.91	-8
	$k_{OS} = -8.261 \times 10^{-3}$		$k_{SO} = -7.878 \times 10^{-3}$	
	$k_{OFe} = -1.003 \times 10^{-2}$		$k_{FeO} = -1.062 \times 10^{-2}$	
	$k_{SFe} = -9.471 \times 10^{-3}$		$k_{FeS} = -9.382 \times 10^{-3}$	
	$\ln K_O = -35.259$			
	Average absolute error = 0.103			
	Average relative error = 1.07%			

Table 2.3.8
The Reported and Modeled Data and the Parameters
for Partial Pressure of Sulfur at 1400 °C

Composition wt%			log(P_{S_2})	
O	S	Fe	Modeled	Reported
0	29.50	70.50	-4.47	-4.5
1	29.10	69.90	-4.77	-4.5
2	28.40	69.60	-4.93	-4.5
3	27.60	69.40	-4.92	-4.5
4	26.75	69.25	-4.79	-4.5
5	25.80	69.20	-4.63	-4.5
6	24.90	69.10	-4.35	-4.5
7	23.80	69.20	-4.22	-4.5
0	31.50	68.50	-3.57	-4
1	30.90	68.10	-3.88	-4
2	30.00	68.00	-4.05	-4
3	29.10	67.90	-4.02	-4
4	28.00	68.00	-3.96	-4
5	26.90	68.10	-3.82	-4
6	25.80	68.20	-3.64	-4
7	24.40	68.60	-3.69	-4
8	23.20	68.80	-3.63	-4
0	33.90	66.10	-2.65	-3
1	33.10	65.90	-2.94	-3
2	32.00	66.00	-3.08	-3
3	31.00	66.00	-3.00	-3
4	29.80	66.20	-2.88	-3
5	28.50	66.50	-2.75	-3
6	27.10	66.90	-2.67	-3
7	25.60	67.40	-2.69	-3
8	24.10	67.90	-2.80	-3
9	22.70	68.30	-2.92	-3
10	21.20	68.80	-3.25	-3
0	36.20	63.80	-1.93	-2
1	35.20	63.80	-2.18	-2
2	34.00	64.00	-2.25	-2

3	32.60	64.40	-2.24	-2
4	31.10	64.90	-2.17	-2
5	29.60	65.40	-2.07	-2
6	28.20	65.80	-1.90	-2
7	26.50	66.50	-1.99	-2
8	24.80	67.20	-2.19	-2
9	23.20	67.80	-2.43	-2
10	21.75	68.25	-2.66	-2

$$k_{SO} = -3.099 \times 10^{-2}$$

$$k_{OS} = -3.072 \times 10^{-2}$$

$$k_{SFe} = -1.221 \times 10^{-2}$$

$$k_{FeS} = -1.226 \times 10^{-2}$$

$$k_{OFe} = -1.325 \times 10^{-2}$$

$$k_{FeO} = -1.338 \times 10^{-2}$$

$$\ln K_S = -71.914$$

$$\text{Average absolute error} = 0.212$$

$$\text{Average relative error} = 7.12\%$$

Tabl : 2 3.9

The Reported and Modeled Data and Parameters
for Partial Pressure of Oxygen at 1400 °C

Composition wt%			log(P _{O2})	
O	S	Fe	Modeled	Reported
3.25	31	65.75	-10.41	-10.5
3.60	30	66.40	-10.41	-10.5
3.95	29	67.05	-10.47	-10.5
4.35	28	67.65	-10.56	-10.5
4.90	27	68.10	-10.57	-10.5
5.45	26	68.55	-10.63	-10.5
6.05	25	68.95	-10.68	-10.5
6.65	24	69.35	-10.74	-10.5
3.05	33	63.95	-10.05	-10
3.30	32	64.70	-10.05	-10
3.60	31	65.40	-10.06	-10
4.00	30	66.00	-10.04	-10
4.50	29	66.50	-9.98	-10
5.00	28	67.00	-9.99	-10
5.60	27	67.40	-9.95	-10
6.20	26	67.80	-9.95	-10
6.80	25	63.20	-9.97	-10
7.40	24	68.60	-10.00	-10
3.75	32	64.25	-9.56	-9.5
4.10	31	64.90	-9.55	-9.5
4.60	30	65.40	-9.45	-9.5
5.15	29	65.85	-9.36	-9.5
5.65	28	66.35	-9.37	-9.5
6.25	27	66.75	-9.32	-9.5

6.75	26	67.25	-9.40	-9.5
7.45	25	67.55	-9.30	-9.5
4.65	31	64.35	-8.97	-9
5.10	30	64.90	-8.93	-9
5.60	29	65.40	-8.90	-9
6.10	28	65.90	-8.91	-9
6.65	27	66.35	-8.91	-9
7.10	26	66.90	-9.04	-9
7.75	25	67.25	-8.98	-9
8.40	24	67.60	-8.92	-9
9.10	23	67.90	-8.80	-9
5.90	30	64.10	-8.07	-8
6.35	29	64.65	-8.10	-8
6.80	28	65.20	-8.17	-8
7.35	27	65.65	-8.16	-8
7.95	26	66.05	-8.12	-8
8.50	25	66.50	-8.15	-8
9.15	24	66.85	-8.06	-8

$$k_{\text{OS}} = -7.858 \times 10^{-3}$$

$$k_{\text{SO}} = -7.586 \times 10^{-3}$$

$$k_{\text{OFe}} = -6.630 \times 10^{-3}$$

$$k_{\text{FeO}} = -7.024 \times 10^{-2}$$

$$k_{\text{SFe}} = -1.050 \times 10^{-2}$$

$$k_{\text{FeS}} = -1.047 \times 10^{-2}$$

$$\ln K_{\text{O}} = -32.008$$

$$\text{Average absolute error} = 0.0877$$

$$\text{Average relative error} = 0.933\%$$

Table 2.3.10
The Reported and Modeled Data and the Parameters
for Partial Pressure of Sulfur at 1450 °C

Composition wt%			log(P_{S_2})	
O	S	Fe	Modeled	Reported
0	30.90	69.10	-3.16	-3.5
1	30.40	68.60	-3.41	-3.5
2	29.70	68.30	-3.49	-3.5
3	28.80	68.20	-3.49	-3.5
4	27.80	68.20	-3.43	-3.5
5	26.70	68.30	-3.37	-3.5
6	25.55	68.45	-3.30	-3.5
0	28.65	71.35	-3.90	-4
1	28.30	70.70	-4.27	-4
2	27.80	70.20	-4.41	-4
3	27.25	69.75	-4.35	-4
4	26.50	69.50	-4.25	-4
5	25.60	69.40	-4.13	-4
6	24.60	69.40	-4.03	-4

7	23.65	69.35	-3.85	-4
8	22.65	69.35	-3.70	-4
9	21.50	69.50	-3.69	-4
10	20.65	69.35	-3.41	-4
0	32.50	67.50	-2.70	-3
1	31.90	67.10	-2.86	-3
2	31.00	67.00	-2.91	-3
3	29.90	67.10	-2.92	-3
4	28.80	67.20	-2.84	-3
5	27.50	67.50	-2.84	-3
6	26.20	67.80	-2.82	-3
7	24.80	68.20	-2.90	-3
8	23.50	68.50	-2.94	-3
9	22.10	68.90	-3.12	-3
10	21.00	69.00	-3.06	-3
0	34.40	65.60	-2.21	-2
1	33.70	65.30	-2.26	-2
2	32.80	65.20	-2.18	-2
3	31.70	65.30	-2.06	-2
4	30.30	65.70	-2.02	-2
5	29.00	66.00	-1.90	-2
6	27.55	66.45	-1.88	-2
7	26.00	67.00	-1.97	-2
8	24.30	67.70	-2.25	-2
9	22.80	68.20	-2.46	-2
10	21.30	68.70	-2.75	-2

$$k_{\text{SO}} = -2.498 \times 10^{-2}$$

$$k_{\text{SFe}} = -8.029 \times 10^{-3}$$

$$k_{\text{OFe}} = -1.174 \times 10^{-2}$$

$$\ln K_{\text{S}} = -51.204$$

$$\text{Average absolute error} = 0.176$$

$$\text{Average relative error} = 5.87\%$$

$$k_{\text{OS}} = -2.484 \times 10^{-2}$$

$$k_{\text{FeS}} = -8.067 \times 10^{-3}$$

$$k_{\text{FeO}} = -1.192 \times 10^{-2}$$

Table 2.3.11

The Reported and Modeled Data and Parameters
for Partial Pressure of Oxygen at 1450 °C

Composition wt%			log(P_{O_2})	
O	S	Fe	Modeled	Reported
4.40	25	70.60	-10.58	-10
4.00	26	70.00	-10.34	-10
3.50	27	69.50	-10.19	-10
3.00	28	69.00	-10.08	-10
2.66	29	68.34	-9.95	-10
2.25	30	67.75	-9.90	-10

1.95	31	67.05	-9.87	-10
1.55	32	66.45	-9.96	-10
1.35	33	65.65	-9.99	-10
1.15	34	64.85	-10.07	-10
1.00	35	64.00	-10.16	-10
7.10	23	69.90	-9.72	-9.5
6.50	24	69.50	-9.64	-9.5
5.90	25	69.10	-9.57	-9.5
5.30	26	68.70	-9.51	-9.5
4.70	27	68.30	-9.48	-9.5
4.20	28	67.80	-9.39	-9.5
3.70	29	67.30	-9.35	-9.5
3.20	30	66.80	-9.35	-9.5
2.80	31	66.20	-9.33	-9.5
2.40	32	65.60	-9.37	-9.5
2.00	33	65.00	-9.47	-9.5
1.70	34	64.30	-9.56	-9.5
1.50	35	63.50	-9.62	-9.5
9.30	21	69.70	-8.80	-9
8.60	22	69.40	-8.88	-9
7.95	23	69.05	-8.89	-9
7.33	24	68.67	-8.88	-9
6.66	25	68.34	-8.91	-9
6.05	26	67.95	-8.90	-9
5.50	27	67.50	-8.86	-9
4.95	28	67.05	-8.84	-9
4.45	29	66.55	-8.80	-9
3.95	30	66.05	-8.81	-9
3.45	31	65.55	-8.86	-9
3.05	32	64.95	-8.87	-9
2.70	33	64.30	-8.90	-9
2.33	34	63.67	-9.00	-9
2.00	35	63.00	-9.13	-9
10.00	21	69.00	-7.99	-8
9.50	22	68.50	-7.87	-8
8.90	23	68.10	-7.87	-8
8.30	24	67.70	-7.88	-8
7.70	25	67.30	-7.89	-8
7.10	26	66.90	-7.92	-8
6.60	27	66.40	-7.86	-8
6.05	28	65.95	-7.87	-8
5.50	29	65.50	-7.90	-8
5.00	30	65.00	-7.92	-8
4.50	31	64.50	-7.97	-8

4.10	32	63.90	-7.97	-8
3.70	33	63.30	-8.01	-8
10.75	21	68.25	-7.08	-7
10.20	22	67.80	-7.04	-7
9.55	23	67.45	-7.13	-7
9.00	24	67.00	-7.10	-7
8.35	25	66.65	-7.20	-7
7.85	26	66.15	-7.14	-7
7.33	27	65.67	-7.11	-7
6.80	28	65.20	-7.12	-7
6.25	29	64.75	-7.17	-7
5.75	30	64.25	-7.20	-7
5.25	31	63.75	-7.26	-7
4.85	32	63.15	-7.25	-7

$$k_{OS} = -1.256 \times 10^{-2}$$

$$k_{SO} = -1.249 \times 10^{-2}$$

$$k_{OFe} = -6.848 \times 10^{-4}$$

$$k_{FeO} = -9.814 \times 10^{-4}$$

$$k_{SFe} = -9.344 \times 10^{-3}$$

$$k_{FeS} = -9.339 \times 10^{-3}$$

$$\ln K_O = -25.190$$

$$\text{Average absolute error} = 0.124$$

$$\text{Average relative error} = 1.45\%$$

APPENDIX B

DYNAMIC CONTAINMENT BURNER

NARRATIVE

Wilhelm Reindl, has been the primary inventor of a device which he has termed a "Dynamic Containment Combustor". This burner holds promise not only to minimize the production of pollutants, but also to be capable of removing particulates from the hot gas or flame, before leaving the combustor. It may allow flame desulfurization with a number of different sorbent substances, without the danger of damage to the water-cooled of the burner walls. The possibility of using this novel combustor on sulfur-containing fuels depends upon several factors in its design. This design incorporates internal flow patterns which are able to convert thermal energy, released during the combustion process into kinetic energy. A portion of this kinetic energy is used to drive the internal mixing processes. Also the combustor appears to operate in a manner similar to a premix-burner and can probably also be used for dual fuel firing, such as natural gas and waste materials. When properly installed, the combustor exhibits stable fluid dynamics.

The original development work on the novel combustor was begun in 1982 with the initial objective to develop a gasification system providing high specific gas output in a system which burned a fuel consisting of sawdust and sand. Requirements for the burner system were: a minimum of erosion on the burner walls due to abrasion, minimal thermal loads due to convective heat transfer, good solids retention within the system, and good separation between gases and as with good ash/slag rejection.

These objectives were finally achieved utilizing a technique that was subsequently called "dynamic containment of confined vortices" or, in short "Dynamic Containment". It has been shown that dynamic containment can be achieved by controlling the leakage flow that normally occurs in the end-wall boundary layers and is mainly responsible for any particle escape from a confined vortex.¹ The two end-walls usually found in a combustor (the front wall, incorporating the burner mouth and the back wall) assume different fluid dynamic functions in the dynamic containment scheme and therefore are controlled differently. As described by Leaner et al.¹, any confined vortex creates, through centrifugal forces, a pressure maximum along the periphery of the confinement vessel. The resulting forces are balanced throughout the vessel by centrifugal forces, except in the end-wall boundary layers. Here, by definition, the tangential velocity vanishes and therefore the peripheral pressure can accelerate the fluids radially inward.

This leakage flow, under certain, conditions can be substantial² and is the primary cause for the escape of matter from confined vortices. The radial acceleration in the front end-wall can be reversed in its direction by applying internal suction along the end-wall periphery. This can be accomplished (based on ejector technology) through a ring-jet entering the combustor along the periphery of the front wall, with an axial momentum component directed towards the opposite end. This jet, by entraining gasses from the immediate surrounding, will generate a secondary flow at its base with a flow direction 90° to that of the jet. In other words, the entrained flow will come predominantly from

the boundary-layer region. This effect is desirable in that it reverses the normally occurring flow from radially-inwards to radially-outward. It has been observed that this suction can be strong enough to entrain air along the entire front wall through the burner mouth.

This effect also has the additional benefit of cooling the burner mouth and alleviating the necessity of refractory materials in that area. As in conventional ejector technology, it is also here important to match the fluid dynamic conditions of the combined flow (primary and secondary flow) to those prevalent in the surrounding bulk fluid. In the dynamic containment combustor this is achieved in two ways:

- By impressing on the primary jet a rotational velocity higher than that of the surrounding gas. (This will tend to keep the primary jet from dissipating its momentum too rapidly into the surrounding gas column.)
- By designing the burner side-walls in a conical form, with the apex of the truncated cone at the front end of the combustor. (It was shown by Volchkov et al.³, that the ideal contour of the side walls does not take on the form of a straight cone, but follows a hyperbolic function. To date, because of their simplicity, only straight cones have been tested. This geometry appears to increase the suction pressure close to the burner mouth, reduce the overall effect of the front end wall and improve the "coupling" of the "front ejector" flow to the bulk flow within the combustor.)

As the flow from the burner front reaches the back wall, it will be decelerated by friction and spiral towards the center. Simultaneously during this process, the predominantly potential-flow will be converted into a rotating flow for which, by definition, the vorticity is unequal to zero throughout the fluid.

This conversion process establishes the vortex core, whose diameter appears to depend to an equal degree on the burner mouth opening. Control over the fluid dynamic conditions within the core and by extension, over the flow within the back wall boundary layer, can be gained by injecting vorticity into the core. Through a rotating axial jet, fluid is entrained from the surrounding boundary layer and accelerated towards the front end of the combustor. Also the geometry and momenta of this primary jet are chosen such that the resulting mixed-flow will couple easily with the bulk of the gases in the burner with a minimum of losses.

This description of a dynamic containment flow-field can be summarized as superposition of three distinct circulation patterns:

- the confined vortex flow,
- the front-to-back recirculation along the burner wall

- and the back-to-front recirculation, increasing the vortex core diameter and simultaneously re-dispersing the matter flowing through the rear wall boundary layer (In other words, two perpendicularly rotating recirculation patterns.)

The existence and control of the so-called dynamic-containment flow-regime have been experimentally and practically proven during the course of several years of development work. The actual processes appear complicated, and in order to describe the behavior of the system as a combustor, a number of different models will have to be used to highlight specific aspects of the system. These models have been formulated based on well-established information gathered from various branches of fluid dynamic and combustion research. Although some of the observed burner characteristics can, in principle, be described with reference to these models, it is necessary to investigate these phenomena in detail in order to fully develop the dynamic containment combustor to its perceived practical potential.

Some of the highlights of the dynamic containment combustor and the respective, possible processes involved, can be described with the following three models:

1) **Uniform Internal Mixing through Micro Vortices and Acoustic Resonance.**

A good analog to the two rotating fluid columns generated by the front jet on the outside and the core, largely driven by the rotating center jet, can be represented by two concentric rotating cylinders. The flow pattern generated under various operating conditions between these cylinders have been studied extensively^{4,5}, and are known as Taylor vortices or Couette flow, depending on the respective dynamic conditions. In essence, Taylor vortices can be described as double vortex cells stacked one on top of the other along the entire length of the cylinders. At sufficiently high rotational velocities of the cylinders, these cells begin to show different structures, described in the literature as standing or traveling waves⁵. Similar patterns have been observed in a dynamic containment combustor operating with propane as fuel. These observations were accompanied by strong acoustic emissions. Largely due to the strength of these emissions and the apparent correlation with the flame structure, it is postulated that these vibrations appear to be in resonance with the flame itself. The benefits accruing to the combustion process from these phenomena can be deduced from experiences gained with pulse combustors⁶. The high specific energy release, as observed in the dynamic containment combustor, can also be related to the above-mentioned flow patterns. In the dynamic containment burner, the size of the flame, external to the burner, can be influenced to the point that it can be totally withdrawn into the combustor. This requires the capability of intense and rapid internal mixing, which again can be explained by the formation of Taylor vortices and their various structures. At least, in case of gaseous fuels, the burner, under these operating circumstances, appears to perform similar to, what is normally described as

premix burner.

2) Gas Acceleration by Direct Conversion of Thermal Energy Released in the Flame into Kinetic Energy.

Measurements taken on the dynamic containment combustor with- and without flame indicated that the core depression did not change significantly between the two conditions. Assuming, conservatively, a gas expansion of at least 3 to 4 times its original volume, the combustion gases must be accelerated substantially in order maintain the core pressure constant. The associated increase in kinetic energy appears to be derived from the thermal energy released by the flame. The velocity increase is also easily discernable through an observed accompanying rise in sound frequency and level. The occurrence of gas accelerations, due to direct heat release within the gas, have been predicted and verified in a number of reports^{7,8,9,10}. Two conclusions can be made:

- A substantial portion of the mixing process is directly driven by the flame itself, without additional power input; and
- the containment of matter in general, but especially the retention of particles, is increased after ignition.

The first point again indicates that the burner operates in a similar fashion as a premix burner, with the mixing occurring within the flame itself. This eliminates the addition of secondary or tertiary air and the associated mixing problems and should prove beneficial in dual fuel operations. The second point has been observed during the initial dynamic containment combustor development, which showed that especially fine particles, that tended to escape from the combustor under a particular set of dynamic conditions, appeared to be completely retained after the flame had been established.

3) Integral Ejector Drive of the Dynamic Containment Combustor with High Pressure Steam or Hot Water.

High pressure steam, and to a lesser degree, high-pressure hot water, are frequently used to provide reliable, maintenance-free suction or compressor services, if, of course, low cost steam is available^{11,12,13}. It has been shown that the dynamic containment burner can be driven successfully with high-pressure, high-temperature saturated or unsaturated steam. This made it possible to achieve very high dynamic containment velocities without the necessity of expensive and maintenance intensive compressor equipment.

Using well-designed ejectors properly matched to and integrated with the fluid dynamics of the rest of the dynamic containment system, a rough calculation indicates that the energy consumption can be expected to be favorable, compared with that needed in case mechanical equipment is used. The steam, after spending its free energy accelerating the combustion air, is reheated in the combustor to flame temperatures that are substantially higher than the original steam temperature. It enters the heat exchange portion of the burner with the

rest of the combustion gases where it emits most of its heat and finally is discharged at the stack temperature with very little remaining enthalpy.

It is reasonable to compare this process with an "integrated top cycle". In order to reduce operating costs even further, the steam can be used to heat water, as it is usually available in cooling towers, under sufficiently high pressure, which in turn will flash into steam in the ejector nozzle. This concept was successfully employed in France to drive very economically high velocity wind tunnels. The water that did not flash into steam, or recondensed prior to entering the combustor proper, can of course, be recirculated. If wet scrubbing of the exhaust gases is employed, no additional net water consumption is required, since the combustion gases ultimately are released to the atmosphere under saturated conditions.

Besides expected reduced initial and operating costs this approach promises additional benefits. It can easily be seen that the fluid dynamic effects, discussed earlier, can be substantially increased, without the penalty of substantial equipment and operating costs. Therefore more power can be made available within the combustor itself for pollution control purposes. It was also shown in the literature^{14,15,16} that injection of steam into combustors can reduce the production of NO_x and CO simultaneously. This is not entirely contributable to a lowering of the flame temperature but seems to be connected with the oxidizing properties of water at high temperature.

The dynamic containment combustor, due to its dynamic and related properties, some of which have been pointed out above, appears to be well suited for a broad range of industrial and commercial applications. Since it is expected that a great deal of pollution can be eliminated within this burner itself, it seems to be well suited for dual-fuel or multi-fuel applications.

STATUS OF WORK CONDUCTED ON PETC PROGRAM

The schematic principles described in the prior narrative are shown in Figure 1, which depicts a single-stage cylindrical cross-section of the Dynamic Containment Burner. In this Figure the burner is shown in a horizontal position, but it was actually operated in a vertical configuration with the flame emitted from the top (right shown in Figure). Air and fuel is injected along the center-line of the burner at the left (bottom of the burner) with a swirling action. The fuel was originally propane, but for later tests², propane plus acetylene (C_2H_2) were used. Acetylene was employed for two reasons:

- to simulate the hydrogen-to-carbon molal ratio in coal;
- since acetylene has a higher enthalpy of combustion than propane, the additional enthalpy enables steady-state operation at temperatures approaching $1400^{\circ}C$ to be reached even under the highly sub-stoichiometric conditions required for subsequently planned tests on desulfurization.

Although coal should be the fuel which is to be utilized by this burner, the tests which were planned for this work were for a gaseous fuel rather than a solid one in order to avoid the additional problems of combustion of coal. This additional complication should be studied in future studies and is not part of this originally proposed work.

Shown in the diagram below the injection point of the air/fuel mixture is "air/slag" removal. This exit port is designed to act as a outflow of quenched (iron-oxysulfide) products from the feeding of iron oxide to the acetylene/air flame. If and when coal is fed as a fuel in later studies, the oxysulfide will be combined with the ash constituents of the coal.

The fuel/primary air mixture follows the swirling trajectory shown by the lack arrows in the center of the burner in Zone 1 where it is met toward the end of the path by the primary air stream added tangentially by a header piece with tangentially-bored holes for ingress air. The motion of the air is shown by the hollow arrow marker "air". The motion of the combustion products is shown schematically in Figure 2.

Subsequent tests on this prototype cylindrical burner demonstrated that a conical configuration was more stable and hence a glass version was constructed to view the flow patterns. The dimensions of this glass version are given below:

Top I.D.	4.5 inches
Bottom I. D.	9.0 inches
Cone length	18.0 inches
Cone angle	$\approx 30^{\circ}$

²However only one test with acetylene is reported in this appendix and is described in Table 1.

The outer-drive nozzle assembly has:

- Tangential velocity control: scroll type diffuser with adjustable nozzle ring;
- Axial velocity control: adjustable gap between inlet section and cone.

The inner-drive nozzle assembly has:

- One and a half inch Whirljet spray nozzle from Spraying Systems, Inc;
- Several different jet geometries (axial versus rotational flow) which can be obtained with different nozzle geometries.

Cold testing using magnetite particles were conducted in the glass model. Figure 3 is a photograph of the assembly. Figure 4 is a photograph of cold testing with sawdust showing the swirling action produced. Figure 5 is a test at temperature (flame temperature approximately 1500°C) in which the pyrex glass walls remained relatively cool.

The experience and information obtained from this glass model can be summarized as follows:

1) Establishment of Dynamic Containment Zone, Particle Retention, Wall Abrasion, Convective Heat Transfer:

In prior tests using sand-contaminated sawdust as fuel, the inside of the burner walls appeared to be covered with a thin carbon deposit (black sheen) with no scouring marks observable. From this observation, one can deduce that the fuel as well as the ash/slag particles did not touch the wall but were, however, suspended within the so-called Dynamic Containment Zone. There is also the possible inference that convective heat transfer does not occur between the flame zone and burner side-walls.

2) Visual Observations on the Dynamic Containment Zone and Convective Heat Transfer.

A 4-inch diameter, 12-inch long combustor, using compressed air and propane was operated at an output of about 1 million Btu. After an operating time of about 0.5 hours, the outside wall of the combustor still showed no sign of heat-up but remained cool to the touch. Immediately after shut-down, condensed water from the compressed air line collected at the burner mouth in the form of droplets without any visible sign of boiling or rapid evaporation. The visual observations of the flame zone indicated a well-defined containment zone. It was also noted that the front jets not only expanded the flame diameter in the vicinity of the burner mouth, but also entrained outside air through the burner exit opening along its wall in a flow counter-current to the exiting gases. Again this observation explains the lack of heat build-up on the combustor wall and corroborated the above-mentioned observations and deductions.

3) Direct Conversion of Heat into Kinetic Energy

Pressure measurements taken before and after ignition from a location on the rear section of the core region showed no appreciable change. The measurements were taken outside the immediate influence of the rear nozzle assembly. Assuming a conservative expansion of the combustion gases due to the flame temperature rise (about three times their original volume before ignition), a core pressure rise should be expected; however, this pressure rise was not observed. It was also noted that the inlet pressures remained constant before and after ignition; therefore, the gas/air flow rates through the nozzle assemblies remained constant. One conclusion that can be drawn from this observation is that the rotating velocity of the burned gases increased in such manner so as to counterbalance any volumetric increase resulting from the temperature rise. The energy to accomplish this can only come from the thermal energy released in the combustion process.

4) Fuel Residence Time and Total Fuel Loading

In the model described above, the combustor was loaded with about one pound of sawdust and operated for about one hour without flame (See Figure 4.) During this operating time, no significant loss of solids was detected. The amount of solids suspended at any time was clearly dependent upon the gas/air velocities at the end-wall (situated opposite to the burner exit), and therefore was dependent upon the outer jet velocities. The distribution of the suspended particles through the Dynamic Containment zone is also a function of the dynamic conditions.

5) Alternative Nozzle Drive

An alternative to compressed-air jet-drives for both nozzles is high pressure steam. Properly designed steam ejectors can supply the required air for combustion purposes and deliver this air with the necessary momentum to both nozzle assemblies. By carefully designing the ejector as well as the interconnecting ducts and the nozzles themselves, the efficiency of such a system can be maximized. Such an approach has several advantages, some of which are:

- i) Reduced overall combustor complexity and service requirements.
- ii) Reduced NO_x production during combustion.
- iii) Excellent particulate control and corresponding fly ash reduction due to potentially very high jet momenta.

A 4-inch diameter combustor with a cylindrical 12-inch long burner tube was used in the proof of this principle. Although the 180 psi steam which was used was saturated and no provisions were available to remove any condensate prior to entry of the steam into the ejector, a stable operation of the burner was achieved with propane as a fuel. As expected, all moisture was fully evaporated in the flame.

This approach would not be appropriate for use in systems in which iron oxide is the sorbent because of the adverse effect with elevated hydrogen levels have on the sorption associated with the equilibrium between sulfur and hydrogen sulfide in the gas atmosphere.

Results of Work undertaken at the High-Bridge Plant of Northern States Power.

In order to conduct tests using a conical test burner rig capable of burning propane plus acetylene in a range of 1 to 3 million Btu, testing was moved to the High Bridge power plant of the Northern States Power Company, which provided us space in one of the unused sections of the plant.

The system consisted of a vertical conical burner having the dimensions described previously. Provision for adding fuel and air in various combinations both to the bottom of the burner (see Figure 1) and the top of the burner. Off-gas analyses were performed using infra-red spectrometry with a mobile probe. The probe positions with respect to exit location enabled assays to be taken with the results being mapped as shown in Figures 6-13.

The results of these burner tests are presented in Tables 1-12. The chart below outlines burner conditions and relates them to the maps.

Table #	Effect Measured	Comments	Map: Figure
1	Variation of Air Fuel Added with Bottom Air	Propane + Acetylene	
2	Variation of Fuel Fuel added with Top Air	Propane	
3	Variation of Fuel Fuel added with Top Air	Propane	
4	Variation of Fuel Fuel Added with Top Air	Propane	
5	Variation of Air Fuel Added with Bottom Air	Propane 6 SCFM	Figure 6

6	Variation of Air Fuel Added with Bottom Air	Propane 7 SCFM	Figure 7
7	Variation of Air Fuel Added with Bottom Air	Propane 8 SCFM	Figure 8
8	Variation of Air Fuel Added with Bottom Air	Propane 9 SCFM	Figure 9
9	Variation of Air Fuel added with Top Air	Propane 6 SCFM	Figure 10
10	Variation of Air Fuel Added with Top Air	Propane 7 SCFM	Figure 11
11	Variation of Air Fuel Added with top Air	Propane 8 SCFM	Figure 12
12	Variation of Air Fuel Added with Top Air	Propane 9 SCFM	Figure 13

Figures 6-13 contain a matrix of black square markers which represent actual data points. The curves through the data are locii of equi-volume ratios of CO/CO_2 and therefore represent regions of constant oxygen potential. These plots can enable one to operate the burner at oxygen potentials required to maintain the pre-calculated operating conditions for the formation of an iron oxysulfide phase and optimizing the pickup and retention of sulfur by liquid droplets.

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DYNAMIC CONTAINMENT COMBUSTER (SINGLE STAGE)

Figure 1: Schematic Dynamic Containment Burner

Figure 2 Flow Patterns Dynamic Containment Burner

Figure 3 Glass Model of Burner System

Figure 4 Photograph of Flow Patterns in Glass Model using Sawdust as Media

Figure 5 Photograph of Flame in Glass Model

Table 1

**Burner Conditions: Effect of Variation of Air
Fuel Added with Bottom Air**

Fuel: Propane plus Acetylene; Flows Maintained Constant

Propane: 2.4SCFM + Acetylene: 3.6SCFM

Stoichiometric Air Requirements:

Propane: 2.4SCFM Acetylene: 3.57SCFM

Air: 57.1SCFM Air: 42.5SCFM

SCFM Air		Assay Vol %		Ratio
Bottom	Top	CO	CO2	CO/CO2
50	70	0.01	4.77	0.00
40	70	0.01	5.31	0.00
30	70	0.01	5.13	0.00
50	60	0.01	5.86	0.00
40	60	0.01	6.23	0.00
30	60	0.01	5.86	0.00
40	50	0.09	6.80	0.01
30	50	0.33	6.42	0.05
30	40	1.80	5.49	0.33
30	30	3.01	4.77	0.63

Combustion Constant Data:

	Density lb/ft3	Enthalpy Btu/ft3
Propane	0.120	2590
Acetylene	0.070	1499

Table 2

Burner Conditions: Effect of Variation of Fuel
Fuel Added with Top Air

Fuel: Propane

Bottom Air: 50SCFM + Top Air: 50SCFM

Air Flows Maintained Constant

SCFM	Assay Vol%		Ratio
Fuel	CO	CO2	CO/CO2
8.7	13.28	6.42	2.07
8	11.01	5.86	1.88
7	8.91	6.99	1.27
6.6	5.25	8.36	0.63
6	3.35	10.21	0.33
5	0.09	10.84	0.01
4	0.01	7.97	0.00
3	0.01	5.67	0.00

Table 3

**Burner Conditions: Effect of Variation of Fuel
Fuel Added with Top Air**

Fuel: Propane

Bottom Air: 60SCFM + Top Air: 60SCFM

Air Flows Maintained Constant

SCFM Fuel	Assay Vol%		Ratio
	CO	CO2	CO/CO2
8.5	8.42	6.61	1.27
8	7.45	7.19	1.04
7	2.08	10.21	0.20
6.6	0.85	11.70	0.07
6	0.05	11.27	0.00
5	0.02	8.67	0.00
4	0.01	6.42	0.00

Table 4

**Burner Conditions: Effect of Variation of Fuel
Fuel Added with Top Air**

Fuel: Propane

Bottom Air: 80SCFM + Top Air: 80SCFM

Air Flows Maintained Constant

SCFM Fuel	Assay Vol%		Ratio CO/CO ₂
	CO	CO ₂	
8.8	1.80	11.05	0.16
8	0.49	11.92	0.04
7	0.09	11.05	0.01
6	0.01	6.80	0.00

Table 5

Burner Conditions: Effect of Variation of Air
Fuel Added with Bottom Air

Fuel: Propane; Flows Maintained Constant
Propane: 6SCFM

SCFM Air		Assay Vol%		Ratio
Bottom	Top	CO	CO2	CO/CO2
80	80	0.01	7.28	0.00
80	70	0.01	6.90	0.00
70	80	0.01	7.48	0.00
60	80	0.01	8.27	0.00
50	80	0.01	8.77	0.00
40	80	0.89	12.47	0.07
30	80	7.22	8.67	0.83
70	70	0.01	7.87	0.00
60	70	0.01	8.67	0.00
50	70	0.01	9.89	0.00
40	70	0.01	11.05	0.00
30	70	0.01	10.52	0.00
60	60	0.01	8.77	0.00
50	60	0.01	10.73	0.00
40	60	0.01	12.35	0.00
30	60	0.01	13.02	0.00
50	50	0.01	11.05	0.00
40	50	0.57	12.69	0.04
30	50	1.93	11.59	0.17
40	40	2.22	10.42	0.21
30	40	8.17	7.38	1.11
30	30	11.01	5.86	1.88

Figure 6

Table 6

Burner Conditions: Effect of Variation of Air
Fuel Added with Bottom Air

Fuel: Propane; Flows Maintained Constant
Propane: 7SCFM

SCFM Air		Assay Vol%		Ratio
Bottom	Top	CO	CO2	CO/CO2
90	100	0.01	8.46	0.00
80	100	0.01	8.87	0.00
70	100	0.01	9.17	0.00
60	100	0.01	11.70	0.00
50	100	0.49	12.24	0.04
40	100	5.66	8.57	0.66
90	90	0.01	8.87	0.00
80	90	0.01	9.79	0.00
70	90	0.01	9.79	0.00
60	90	0.01	10.52	0.00
50	90	0.01	12.03	0.00
40	90	3.70	9.58	0.39
80	80	0.01	9.07	0.00
70	80	0.01	9.17	0.00
60	80	0.01	10.00	0.00
50	80	0.01	10.42	0.00
40	80	1.66	11.05	0.15
30	80	6.76	8.07	0.84
70	70	0.01	10.21	0.00
60	70	0.01	11.16	0.00
50	70	0.01	11.92	0.00
40	70	0.27	12.14	0.02
30	70	2.52	10.52	0.24
60	60	0.15	12.91	0.01
50	60	0.66	12.58	0.05
40	60	4.45	10.00	0.44
30	60	7.69	8.36	0.92
50	50	5.45	9.17	0.59
40	50	8.03	7.77	1.03
30	50	9.68	7.09	1.37
40	40	10.47	6.52	1.61
30	40	11.84	5.90	2.01

Figure 7

Table 7

**Burner Conditions: Effect of Variation of Air
Fuel Added with Bottom Air**

**Fuel: Propane; Flows Maintained Constant
Propane: 8SCFM**

SCFM Air		Assay Vol%		Ratio
Bottom	Top	CO	CO ₂	CO/CO ₂
90	90	0.01	12.80	0.00
80	90	0.09	12.69	0.01
70	90	0.49	12.47	0.04
60	90	5.25	9.38	0.56
50	90	8.42	7.57	1.11
40	90	11.01	6.14	1.79
90	80	0.02	12.24	0.00
80	80	0.33	12.69	0.03
70	80	2.08	11.59	0.18
60	80	4.07	10.00	0.41
50	80	6.09	8.77	0.70
40	80	9.94	6.80	1.46
30	80	12.13	5.31	2.28
80	70	0.02	11.92	0.00
70	70	0.20	12.69	0.02
60	70	2.08	12.35	0.17
50	70	5.25	11.37	0.46
40	70	9.94	6.42	1.55
30	70	10.21	6.33	1.61
60	60	9.42	6.42	1.47
50	60	10.74	6.14	1.75
40	60	11.01	5.86	1.88
30	60	11.01	5.86	1.88
50	50	11.01	5.86	1.88
40	50	11.56	5.49	2.11
30	50	11.56	5.31	2.18
40	40	12.13	5.13	2.37

Figure 8

Table 8

Burner Conditions: Effect of Variation of Air
Fuel Added with Bottom Air

Fuel: Propane; Flows Maintained Constant
Propane: 9SCFM

SCFM Air		Assay Vol%		Ratio
Bottom	Top	CO	CO2	CO/CO2
100	100	0.01	12.69	0.00
90	100	0.15	12.91	0.01
80	100	0.57	12.35	0.05
70	100	2.08	10.73	0.19
60	100	3.88	10.31	0.38
50	100	9.17	7.28	1.26
90	90	1.06	12.03	0.09
80	90	2.08	11.16	0.19
70	90	4.64	9.27	0.50
60	90	7.69	7.87	0.98
50	90	10.21	6.80	1.50
40	90	11.29	5.95	1.90
80	80	2.84	10.52	0.27
70	80	5.25	8.97	0.59
60	80	9.68	6.99	1.38
50	80	9.84	6.80	1.45
40	80	10.74	6.33	1.70
30	80	10.74	6.33	1.70
70	70	9.68	6.90	1.40
60	70	11.29	5.86	1.93
50	70	12.41	5.58	2.22
40	70	12.70	5.77	2.20
30	70	12.41	5.86	2.12
60	60	11.84	5.77	2.05
50	60	12.41	5.40	2.30
40	60	12.99	5.22	2.49
30	60	12.99	5.04	2.58
50	50	12.70	5.04	2.52
40	50	14.18	4.68	3.03
30	50	14.18	4.68	3.03
40	40	14.80	4.14	3.57

Figure 9

Table 9

**Burner Conditions: Effect of Variation of Air
Fuel Added with Top Air**

**Fuel: Propane; Flows Maintained Constant
Propane: 6SCFM**

SCFM Air		Assay Vol%		Ratio
Bottom	Top	CO	CO ₂	CO/CO ₂
80	80	0.01	7.38	0.00
80	70	0.01	8.57	0.00
80	60	0.01	9.38	0.00
80	50	0.01	9.89	0.00
80	40	0.01	10.10	0.00
70	80	0.01	8.07	0.00
60	80	0.01	7.97	0.00
50	80	0.01	9.17	0.00
40	80	0.01	10.25	0.00
70	70	0.01	8.97	0.00
60	70	0.01	9.07	0.00
50	70	0.01	10.16	0.00
40	70	0.01	11.70	0.00
70	60	0.01	9.58	0.00
70	50	0.01	10.31	0.00
70	40	0.41	11.48	0.04
60	60	0.01	10.31	0.00
50	60	0.01	11.48	0.00
40	60	0.09	12.47	0.01
30	60	3.35	10.00	0.33
60	50	0.09	11.27	0.01
60	40	0.09	9.79	0.01
50	50	0.33	12.47	0.03
40	50	3.01	10.52	0.29
30	50	7.45	7.97	0.94
50	40	1.80	11.16	0.16

Figure 10

Table 10

Burner Conditions: Effect of Variation of Air
Fuel Added with Top Air

Fuel: Propane; Flows Maintained Constant
Propane: 7SCFM

SCFM Air		Assay Vol%		Ratio
Bottom	Top	CO	CO ₂	CO/CO ₂
90	90	0.05	10.63	0.00
90	80	0.02	11.27	0.00
90	70	0.18	11.81	0.02
90	60	0.31	11.70	0.03
80	90	0.02	10.59	0.00
70	90	0.02	11.31	0.00
60	90	0.02	11.70	0.00
80	80	0.09	11.05	0.01
80	70	0.07	11.66	0.01
80	60	0.33	11.59	0.03
80	50	0.49	11.48	0.04
70	80	0.01	9.58	0.00
60	80	0.01	10.52	0.00
50	80	0.01	11.92	0.00
70	60	0.41	12.14	0.03
70	50	5.04	9.27	0.54
70	40	8.66	6.80	1.27
60	70	0.15	12.58	0.01
50	70	0.95	11.81	0.08
40	70	3.01	10.52	0.29
60	60	2.08	10.21	0.20
60	50	6.09	8.46	0.72
60	40	9.68	6.71	1.44
60	30	10.74	5.58	1.92
50	60	3.88	9.96	0.39
40	60	6.99	7.57	0.92
50	50	8.91	6.99	1.27
50	40	12.41	5.53	2.25
50	30	12.82	4.91	2.61
40	40	12.41	5.49	2.26

Figure 11

Table 11

**Burner Conditions: Effect of Variation of Air
Fuel Added with Top Air**

**Fuel: Propane; Flows Maintained Constant
Propane: 8SCFM**

SCFM Air		Assay Vol%		Ratio
Bottom	Top	CO	CO2	CO/CO2
90	90	0.01	7.48	0.00
80	90	0.01	8.36	0.00
70	90	0.01	10.00	0.00
60	90	0.01	10.95	0.00
50	90	0.03	12.91	0.00
40	90	2.37	9.58	0.25
30	90	4.84	8.97	0.54
90	80	0.01	8.77	0.00
80	80	0.01	10.31	0.00
70	80	0.01	11.37	0.00
60	80	0.01	12.91	0.00
50	80	1.29	12.35	0.10
40	80	4.45	10.21	0.44
30	80	7.45	8.27	0.90
80	70	0.01	11.27	0.00
70	70	0.05	12.58	0.00
60	70	0.66	12.80	0.05
50	70	3.70	10.63	0.35
40	70	6.54	8.97	0.73
30	70	10.47	6.80	1.54
70	60	0.33	12.58	0.03
60	60	1.29	2.53	0.51
50	60	5.88	9.27	0.63
40	60	8.66	7.57	1.14
30	60	12.13	4.59	2.64
60	50	4.84	9.58	0.51
50	50	9.94	6.80	1.46
40	50	11.01	6.23	1.77
30	50	12.70	5.31	2.39
50	40	12.13	5.49	2.21
40	40	10.47	6.52	1.61
30	40	13.28	4.95	2.69

Table 12

Burner Conditions: Effect of Variation of Air
Fuel Added with Top Air

Fuel: Propane; Flows Maintained Constant
Propane: 9SCFM

SCFM Air		Assay Vol%		Ratio
Bottom	Top	CO	CO ₂	CO/CO ₂
100	100	0.01	6.61	0.00
90	100	0.01	6.99	0.00
80	100	0.01	7.77	0.00
70	100	0.01	9.48	0.00
60	100	0.05	10.95	0.00
50	100	1.17	11.70	0.10
40	100	3.88	10.10	0.38
100	90	0.01	9.58	0.00
90	90	0.01	10.52	0.00
80	90	0.01	10.95	0.00
70	90	0.01	11.81	0.00
60	90	0.20	12.80	0.02
50	90	2.52	11.16	0.23
40	90	5.25	9.38	0.56
90	80	0.01	10.84	0.00
80	80	0.01	11.48	0.00
70	80	0.02	12.80	0.00
60	80	1.06	12.03	0.09
50	80	4.45	9.89	0.45
40	80	8.66	7.28	1.19
30	80	11.01	5.95	1.85
80	70	0.02	11.16	0.00
70	70	1.80	11.48	0.16
60	70	4.84	9.48	0.51
50	70	9.68	6.61	1.46
40	70	11.01	5.77	1.91
30	70	12.70	5.04	2.52
70	60	0.66	11.92	0.06
60	60	9.42	6.80	1.39
50	60	10.21	6.42	1.59
40	60	11.84	5.13	2.31
30	60	2.08	1.80	1.16

60	50	8.42	7.38	1.14
60	40	5.25	6.61	0.79
50	50	10.47	6.05	1.73
40	50	11.84	4.77	2.49
30	50	4.84	4.06	1.19
50	40	10.21	5.58	1.83
50	30	8.42	5.40	1.56
40	40	11.56	4.95	2.34
30	40	7.93	4.86	1.63
40	30	9.58	4.95	1.94

Figure 13

END DATE
9-16-93