Hot Coal Gas Desulfurization With Manganese-Based Sorbents

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ABSTRACT

The focus of much current work being performed by the Morgantown Energy Technology Center (METC) of the Department of Energy on hot coal-derived fuel gas desulfurization is in the use of zinc-based sorbents. Extensive research, however, casts doubt that these sorbents can be utilized even for the mild conditions associated with fixed-bed operation. Accordingly, METC has shown interest in formulating and testing manganese-based pellets as alternative effective sulfur sorbents in the 700 to 1200 °C temperature range.

To substantiate the potential superiority of Mn-based pellets, a systematic approach toward the evaluation of the desulfurizing power of single-metal sorbents is developed based on thermodynamic considerations. This novel procedure considered several metal-based sorbents and singled out manganese oxide as a prime candidate sorbent capable of being utilized under a wide temperature range, irrespective of the reducing power (determined by CO_2/CO ratio) of the fuel gas. Then, the thermodynamic feasibility of using Mn-based pellets for the removal of H_2S from hot-coal derived fuel gases, and the subsequent oxidative regeneration of loaded (sulfided) pellets was established. It was concluded that MnO is the stable form of manganese for virtually all commercially available coal-derived fuel gases. In addition, the objective of reducing the H_2S concentration below 150 ppmv to satisfy the integrated gasification combined cycle system requirement was shown to be thermodynamically feasible.

A novel process is developed for the manufacture of Mn-based spherical pellets which have the desired physical and chemical characteristics required during the long-term cyclic sulfidation and regeneration in a high-temperature desulfurization operation. Screening sulfidation tests on a number of formulations, consisting of a Mn-containing compound (ore or MnCO_3), alundum (Al_2O_3), and organic or inorganic binders, were carried out using H_2S - H_2 gas mixtures in a thermogravimetric (TGA) apparatus at temperatures ranging from 700 to 1000 °C. A formulation, designated FORM4-A, was found to possess the best combination of sulfur capacity, reactivity, and strength. Regeneration tests determined that for $T \geq 900$ °C, loaded pellets can be fully regenerated with air in 10 to 15 minutes, without sulfate formation, in strict accordance with thermodynamic guidelines. Repeated cycling of the leading sorbent formulation (FORM4-A) was then conducted in the TGA apparatus, up to 5 consecutive cycles. One important finding was that the capacity of the pellets for sulfur pickup from fuel gas and the kinetics of reduction, sulfidation, and regeneration reactions improved with recycling without compromising the strength.

Testing of the leading Mn-based sorbent pellets was carried out in a 2-inch fixed-bed reactor to evaluate the long-term durability and regenerability of the sorbent using a Tampella-U fuel gas for sulfidation and air for regeneration. Consistent with TGA results on individual pellets, the fixed-bed tests show small improvement in capacity and kinetics with the sulfur capacity being about 22% by weight of the original pellet, which corresponds to approximately 90% bed utilization. In addition, the effect of temperature on sulfidation reaction equilibrium is determined in the range 800 to 1000 °C. A re-assessment of the equilibrium states of reactions in the Mn-S-O system is then presented based on the results obtained and a recent study by Turkdogan.

The shrinking unreacted-core model was found to approximate the kinetic

behavior of Mn-based pellets during both the sulfidation and regeneration stages. Kinetic analysis of TGA experimental data determined that beyond approximately 35% reaction completion, sulfidation and regeneration reaction rates were controlled primarily by gaseous counter-diffusion through the porous product layer.

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CHAPTER I: INTRODUCTION

1.1 Introduction

In the Clean Air Act of 1990 legislation is directed toward cleanup of coal gases by development of processes for removal of sulfur and particulates from coal combustion products. Since such gas cleanup is expensive, more efficient utilization of coal is required to offset these costs. One approach toward the more efficient use of coal is via gasification processes to produce a fuel gas which can be used in combined cycle operations in which a gas turbine utilizes the gasifier product. Another approach is directed toward the development of processes in which coal gases can be used directly in fuel cell applications to avoid the inefficiencies inherent in the Rankine cycle (conversion of heat into electricity). In this latter application, sulfur must be removed from the gasification products to avoid deterioration of the cell. One approach to cleanup of gasification products is to contact the hot coal gases with a sorbent capable of removing the sulfur.

The focus of much current work being performed by the Morgantown Energy Technology Center (METC) of the Department of Energy (DOE) on hot coal-derived fuel gas desulfurization is primarily in the use of zinc ferrite and zinc titanate sorbents. These zinc-based sorbents have received much attention over the past twelve years because, from a theoretical point of view, they have desirable properties: high sulfur capacity, ability to remove H_2S from coal-derived fuel gas to levels of a few ppmv (parts per million by volume), and the feasibility of regeneration with air. Because it is economically necessary to recycle sulfur sorbents for at least 100 cycles, research has focused almost entirely on making the zinc-based sorbents durable. Unfortunately, extensive research carried out by METC casts doubt that zinc ferrite or zinc titanate can be utilized even for the mild conditions associated with fixed-bed operation.

One major problem associated with zinc-based sorbents is sulfate formation which is found to occur whenever SO_2 is present in the regeneration gas. Sulfation leads to volume expansion and swelling of sorbent pellets eventually causing them to spall and crack. Certainly, in a fixed-bed operation some of the pellets will be saturated with sulfur and the regeneration gas will contain some SO_2 . Therefore, sulfate formation is unavoidable along with accompanying spalling and cracking. Another serious problem associated with zinc-based sorbents is the loss of the reactive component zinc in the form of $ZnCl_2$ caused by the presence of HCl in the fuel gas produced under reducing conditions. $ZnCl_2$ has a relatively low boiling point of $1005^\circ K^1$ ($732^\circ C$) which makes it susceptible to volatilization and losses from the sorbent surfaces.

Given the limited success of the zinc-based sorbents, METC has shown interest in formulating and testing manganese-based sorbent pellets.² There are a number of studies that led to the consideration of Mn-based sorbents,^{3,4,5,6,7} perhaps the most important one of which is that by Turkdogan and Olsson⁵ which established the practical feasibility of using manganese oxide pellets to

desulfurize hot H_2S-H_2 gas mixtures.

A fortuitous feature of the manganese-sulfur-oxygen (Mn-S-O) system is its resistance to reduction to elemental manganese under the range of most of the fuel compositions for which it would be utilized as a sulfur sorbent. Although the thermodynamics for sulfur removal by manganese predicts somewhat higher hydrogen sulfide over-pressures than can be accomplished with zinc-based sorbents, zinc tends to be reduced to the metallic state under coal gasification conditions resulting in loss of capacity and activity by volatilization of reactive surfaces. This volatilization phenomenon limits the temperatures to which desulfurization can be effectively accomplished to less than 550 °C for zinc ferrite and 700 °C for zinc titanate;^{8,9} whereas, manganese-based sorbents can be utilized at temperatures well in excess of 700 °C. Manganese chloride ($MnCl_2$) has a boiling point of 1504 °K¹ (1231 °C); therefore, even in the presence of HCl, no physical loss of reactive component should occur. Another favorable feature of the Mn-S-O system is its resistance to fusion as a result of temperature excursions which may occur in the exothermic step of regeneration since the system is relatively refractory and non-volatile (i.e., lacks low-melting point phases). It must be noted that operation of the desulfurization step at higher temperatures increases the efficiency of power generation via the Integrated Gasification Combined Cycle (IGCC) process. High water vapor contents are currently encountered in gasifier systems because these gases had to be quenched with water in order to (a) avoid reduction of iron, which destroys the zinc ferrite sorbent planned for use with these gases and (b) reduce the temperature below the 982 to 1093 °C (1800 to 2000 °F) level which the gasifiers would achieve if they were to operate directly without a water quench. The importance of the Mn-based system is that it eliminates the quenching step altogether since there is no need to lower the temperature of the fuel gas prior to desulfurization.

The objective of this study is to develop manganese-based sorbent pellets for the effective desulfurization of coal-derived fuel gases at high temperature (700 to 1200 °C). A number of formulations are prepared and screened first by testing in a thermogravimetric apparatus (TGA) in which individual pellets are weighed in mixtures of simulated coal-derived fuel gases at atmospheric pressure and high temperatures, and then in a bench-scale fixed-bed reactor. Sorbent screening criteria include measurement of sorbent (fresh, used, and regenerated) crush strength, chemical reactivity by thermogravimetric analysis, surface area, porosity, etc... The superior formulation is tested for long-term durability and chemical reactivity in the TGA apparatus and the bench-scale unit.

The developed information will be of value to METC in determining whether or not a manganese-based regenerable sorbent holds real promise for sulfur pick up from hot fuel gases. This information is necessary before pilot-scale testing leading to commercial development is undertaken. This final report is comprised of several chapters as briefly summarized below.

A brief literature review is presented in the second chapter to explain the

advantages associated with the desulfurization of fuel gases at high temperature. Particular emphasis is placed on the potential usefulness of a manganese-based sorbent system. In the third chapter, a systematic approach for the evaluation of the behavior of single and mixed-metal sorbents for removing hydrogen sulfide from hot coal-derived fuel gases is developed based on thermodynamic considerations. This theoretical study singled out manganese oxide as a prime candidate sorbent capable of being utilized under a wide temperature range, irrespective of the reducing power (determined by CO_2/CO ratio) of the fuel gas.

The fourth chapter of this study addresses the physical and chemical behavior of several sorbent formulations fabricated from manganese-containing compounds, alundum (alumina) as a supporting matrix, and a binder. The thermodynamic feasibility of H_2S removal from hot simulated coal gases is then established and an analysis of the sulfidation reaction kinetics based on thermogravimetric experimental results is presented.

The fifth chapter is concerned with the thermodynamic feasibility of regeneration which occurs by oxidation of manganese sulfide to produce manganese oxide and a concentrated sulfur dioxide product gas. The effect of temperature on the kinetics of regeneration of the leading Mn-based formulation is then given and the TGA results analyzed kinetically. The effect of repeated loading/regeneration cycling on the chemical reactivity and physical durability of this superior formulation is also quantified.

The sixth chapter focuses on the multicycle testing of the leading formulation in a 2-inch fixed-bed reactor using a simulated Tampella-U fuel gas for sulfidation and air for regeneration. This commercially produced gas contains 5% by volume water vapor and its selection for use with Mn-based pellets is explained. In addition, the effect of temperature on sulfidation reaction equilibrium is determined in the range 800 to 1000 °C. A re-assessment of the equilibrium states of reactions involving solid MnO , MnS , Mn_3O_4 , and MnSO_4 is then presented based on the results obtained and a recent investigation by Turkdogan.¹⁰

Appendix A documents the methods employed for sorbent pellet manufacture based on a recent patent application filed by the author. This appendix also reports the chemical analyses of the different raw materials used in preliminary work as well as those selected for experimentation. Appendix B presents mathematical derivations of relevant time-fractional conversion expressions used in the kinetic analysis of the sulfidation and regeneration reactions. Appendix C includes interpretations of experimental results based on an extensive microscopic study carried out by the Twin Cities Research Center of the U.S. Bureau of Mines.

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CHAPTER II: LITERATURE REVIEW

2.1 Introduction

Although the choice of energy sources has widened with the advent of new forms of renewable clean energy, fossil fuel remains the main source of supply. Fossil fuels, e.g. coal, petroleum, and natural gas, still provide approximately 90% of the total energy consumed in the U.S. Coal is by far the most plentiful, low-cost domestic fuel source which has played a very important role in the U.S. industrial expansion. Recoverable reserves of coal in the U.S. amount to 243 billion tonnes which, at current consumption rates, would last for over 240 years. It is projected that the use of coal will double by the year 2030, achieving a level of 1.8 billion tonnes per year, and will be predominantly for power generation.¹ Coal supplies about 23% of the U.S. energy; in addition, coal-fired power plants currently account for 56% of the electricity used in the U.S.

The general term "coal" describes a wide range of solid fossil fuels derived from the partial degradation of plants. Table 2.1 shows the characteristics of the major classes of coal, differentiated largely by percentage of fixed carbon.² Table 2.2 gives the ultimate analysis of an Illinois No. 6 coal which is a type of bituminous coal. Coal consists primarily of carbon with scattered atoms of hydrogen, oxygen, nitrogen, and sulfur. In addition, coal contains ash which consists primarily of silica, alumina, iron and calcium oxides, and traces of virtually every mineral. Ash usually accounts for 5 to 10 % on a dry weight percent basis. The major mineral 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%).³ Sulfur in coal is known to exist in two forms: pyritic (FeS_2) and organic. In the pyritic form, sulfur is combined with iron in finely dispersed particles that are physically distinct from the coal; whereas, in the organic form, sulfur is chemically bound to the carbon atoms of coal.

Anthracite is a low-sulfur coal with a relatively high heating value, and as a result, is the most desirable of all coals. It is thus not surprising that approximately half of the anthracite originally present in the U.S. has been mined. Bituminous coal is found in the Appalachian and North Central coal fields, and is the most widely used because of its high heating value. Unfortunately, most bituminous coals have a high sulfur content (an average of 2 to 3%) which makes their continued use less and less attractive from an environmental standpoint. Enormous reserves of virtually untouched subbituminous and lignite coals are found in the Rocky Mountain states and in the northern plains of the Dakotas, Montana, and Wyoming. These coals have a relatively high oxygen content, high moisture, and high ash content, causing them to have a considerably lower heating value than other types of coal. However, subbituminous coals have a low sulfur content which is the reason why they are increasingly being used in power plants which would not otherwise meet stringent sulfur dioxide emission standards.

Table 2.1 Major Types of Coal Found in the U.S.²

Proximate Analysis, Weight Percent					
Type of Coal	Fixed Carbon	Volatile Matter	Moisture	Ash	Range of Heating Value (Btu/lb)*
Anthracite	82	5	4	9	13,000 - 16,000
Bituminous:					
Low-volatile	66	20	2	12	11,000 - 15,000
Medium-Volatile	64	23	3	10	
High-Volatile	46	44	6	4	
Subbituminous	40	32	19	9	8,000 - 12,000
Lignite	30	28	37	5	5,500-8,000

Table 2.2 Ultimate Analysis of a Typical Bituminous Coal (Illinois No. 6)

Constituent	Percent by Weight
Carbon	67.87
Hydrogen	5.0
Nitrogen	1.2
Total Sulfur	3.87
Oxygen	10.56 (not included in ash)
Ash	11.5
Total	100.0 (dry basis)
Moisture	9.3
Gross Heating Value	28415 kJ/kg

With diminishing petroleum supplies, public concern regarding the overall safety of nuclear power, and unavailability of alternative large-scale sources of energy, coal is gaining much more importance in the total energy picture. The most economical use of coal in the future is likely to continue to be the generation of electricity, as has been the case for decades.

* to convert Btu/lb to the S.I. unit of kJ/kg, multiply by 2.326

Current methods for the conversion of chemical energy in coal to electrical energy tend to be cumbersome, wasteful, and environmentally unsound. Conventional technology of power generation consists of reacting coal in a burner system which exchanges heat to a boiler to generate steam. This steam then passes through a turbine to drive a generator and produce electricity. This process wastes about 60% of the energy originally present in the coal.² Energy is also lost in transmitting the generated electricity through power lines to users causing the process to be, overall, only 30 to 35% efficient. In addition, solid waste streams are generated and must be disposed of in increasingly expensive landfill space.

During coal combustion, sulfur is released mainly in the form of sulfur dioxide (SO_2) in the flue gas. Sulfur emissions are very damaging to the environment since SO_2 combines with water moisture to form sulfuric acid which then falls as acid rain. The threat from acid rain is increased by the burning of high-sulfur coal as a substitute for diminishing petroleum. The removal of SO_2 from the flue gas prior to discharge into the atmosphere is thus essential to prevent air pollution. For these reasons, government regulations for sulfur emissions have been introduced and are becoming progressively more stringent since they are often based on the best available technology of SO_2 scrubbing. It follows that conventional technology is required to adopt available technology for sulfur removal so that its increased use of coal is done in an environmentally acceptable manner.

Ash and sulfur removal may be achieved through a number of ways which include: (a) pre-combustion cleaning, i.e. removal of ash and sulfur compounds prior to burning; (b) combustion or in-situ cleaning, i.e. removal of pollutants in the boiler during coal combustion; (c) post-combustion cleaning, i.e. flue gases released from coal boilers are cleaned in the ductwork leading to the smokestack or in scrubbers.¹

Physical and chemical processes can be used to remove ash and sulfur from coal before it is burned. Unfortunately, only pyritic sulfur may be removed in this manner; organic sulfur is chemically bound to the complicated structure of coal and cannot be removed except by converting coal to a liquid or a gas fuel, as discussed subsequently.

As more high-sulfur coal is used and because of stricter and stricter government regulations, stack-gas desulfurization has been practiced more commonly to meet air pollution emission standards. A number of systems have been developed to remove SO_2 from flue gas. These include both dry systems, in which a dry solid is used to absorb SO_2 from stack gas, and wet systems, in which a solution, or slurry, is used. Some systems are throwaway systems, in which the spent absorbing substance is discarded; others are recovery systems, in which the absorbing substance is regenerated and recirculated and sulfur is recovered. The most commonly used system is lime slurry scrubbing, which uses a slurry of $\text{Ca}(\text{OH})_2$ suspended in water to absorb SO_2 , as represented by reactions (2.1) and (2.2). The production of the compound $2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

causes considerable scaling and other problems in the scrubber mechanism. In

addition, huge amounts of lime waste are produced as the scrubber operates. For example, about one tonne of limestone is required to make the lime needed to scrub the stack gas from each five tonnes of coal burned. A large 9,080-tonne per day power plant requires 1,816 tonnes per day of limestone. The lime wastes from the scrubber are in the form of a watery sludge and are stored in holding ponds which are environmentally undesirable. Furthermore, although the wet limestone process and other flue gas cleaning systems help the utilities comply with new, more stringent environmental requirements, they lower plant operating efficiency and reliability, while increasing both capital and operating costs. Such limitations have been the main driving force behind technological innovations which aim at improving both the efficiency and environmental performance of power generation.

2.2 Emerging Technologies for Power Generation

2.2.1 Introduction

Both gas and liquid fuels can be prepared from coal through gasification and liquefaction, respectively. These conversion methods depart significantly from the traditional method of coal combustion. Gasification or the production of gaseous fuels from coal is closest to widespread commercial development. During gasification, coal containing carbon, hydrogen, and oxygen, as well as impurities such as sulfur, nitrogen, ash, and trace metals reacts with steam and either air or oxygen to produce a fuel and/or synthesis gas.¹ The reactions which occur are represented by the following equations.

Reaction (2.3) generates heat which maintains coal hot; reaction (2.4) produces two combustible (e.g. fuel) gases, H_2 and CO . Gasifier operating conditions must be carefully controlled to obtain the desired product fuel gas. The proportion of the various gaseous components exiting the gasifier (CO , CO_2 , CH_4 , H_2 , N_2 , etc.) is influenced by the type of coal, the composition of the feed gases (steam + air/oxygen), the type of reactor (fixed-bed, fluidized-bed, or entrained flow), and

operating conditions (temperature, equivalence ratio^{**}, flow, and pressure). The compositions of some commercially-produced fuel gases are reported in Table 4.1 in Chapter IV.

2.2.2 Advantages of Hot Gas Desulfurization

Advanced power generation systems which are reaching the commercial stage are principally based on coal gasification and include the integrated gasification combined cycle (IGCC), the molten carbonate fuel cell (MCFC), and the pressurized fluidized-bed combustor (PFBC). In a coal gasifier, unlike coal combustion processes, the sulfur in coal is released in the form of hydrogen sulfide, H_2S , rather than sulfur dioxide, SO_2 . These emerging technologies must thus employ hot gas cleanup techniques to remove sulfur and other impurities in the fuel gas stream, mainly to meet stringent government regulations for sulfur emissions and also to protect system components from the corrosive action of H_2S . Hydrogen sulfide should be removed by purifying the product gas while it is still hot so that the gas can be used directly without loss of heat values. This completely eliminates the more costly, less efficient method of low-temperature, liquid-based, fuel gas scrubbing systems, and the subsequent reheat of cleaned gas which gives this design a better overall efficiency and reduces the capital costs associated with expensive heat recovery systems. In addition, since the volume of the fuel gas is significantly less than that of the flue gas stream, the removal of H_2S at high temperature results in considerably lower hardware costs than would be required by a conventional SO_2 scrubbing method at low temperature. Since hot gas desulfurization is a dry process, it does not require expensive waste water treatment plants to handle process condensate from quenching processes. Also, since hot gas cleanup occurs at high pressures, the volume of gases that must be processed is greatly reduced. The desulfurizing agent (e.g. sorbent) is reusable over many sulfur capture cycles which, in turn, improves process economics and reduces the amount of solid waste generated and ultimately landfilled. In addition, saleable byproducts, such as sulfuric acid and elemental sulfur, can be produced.

Fuel cells, which convert chemical energy directly to electricity, are most desirable.⁴ A fuel cell uses the chemical combination of H_2 and O_2 to produce electricity directly from electrochemical reactions which release the chemical energy that bonds the oxygen and hydrogen atoms together. This device consists of two porous graphite electrodes dipped into a solution of potassium hydroxide, KOH. At the anode, H_2 is oxidized, giving up electrons, and at the cathode, O_2 is reduced, taking up electrons. The overall reaction provides a non-polluting source of energy, since the only product is water. Unfortunately, pure hydrogen (which is extracted from coal gas made by a coal gasifier) and oxygen are both rather expensive to generate.

^{**} This parameter is defined in Chapter III

Fluidized-bed combustion with in-situ desulfurization (i.e., slagging combustion) offers one approach to the use of high-sulfur coal. With such a system, coal and air are injected into a bed of granular absorbing solid, such as lime. The force of the air pressure fluidizes the solid, making it behave as a liquid. The solid absorbs SO_2 , and the relatively clean, hot exhaust gases rising from the fluidized-bed of solids are used to convert water to steam in a boiler. One major drawback of this method is that it is necessary to either dispose of the solid or recycle it. Recycling is expensive, and disposal poses some problems because of the high sulfur content of the solid and the quantities involved.⁵

The IGCC process is the most promising and attractive technology being considered by the electric utility industry. In this emerging technology the mixture of carbon monoxide and hydrogen produced through gasification is burned; the very hot exhaust is routed through a gas turbine to generate electricity; and the residual heat in the exhaust is used to boil water for a conventional steam-turbine generator thus producing more electricity. IGCC systems have superior efficiency and environmental performance compared to other technologies widely used for coal-based power generation. IGCC systems also effectively utilize varied coal feedstocks with high or low sulfur content.⁶ For these reasons, only detailed description of the IGCC system is considered in the remainder of this chapter.

A schematic diagram of a typical IGCC plant is shown in Figure 2.1. In this system, fuel gas, which is composed primarily of hydrogen and carbon oxides, is generated in a gasifier by the reaction of coal with high-temperature steam and oxygen or air. This low-Btu product gas is then sent to a gas cleanup system for purification. The clean gas is then combusted in a high-efficiency gas turbine with a compressed oxidant to provide a stream of hot, high pressure gas which drives the turbine to generate electricity. The exhaust gases from the turbine pass through a waste heat boiler where steam at high pressure and temperature is produced by heat exchange with the boiler feed water. This steam is used in a steam turbine to generate additional electricity. The term "integrated" stems mainly from the fact that process flows from one plant subsystem may be used in another. For example, the steam for gasification and for sorbent regenerated is produced by the heat recovery steam generator.⁷ The combination of gas and steam turbines accounts for the name "combined cycle."

Aging power generation facilities, coupled with a steady growth in the demand for electricity will force utility generators to build new power plants, as well as, repower some existing ones. Repowering is the replacement of the major portion of an existing plant (such as the boiler) with a gasifier, cleanup system, and a gas turbine, while keeping certain other portions (such as the steam cycle equipment). It is projected that a plant repowered with IGCC technology will: 1) lower its emissions below possible future regulatory levels, 2) produce 50-150% more power, and 3) extend the life of the plant by 20 to 30 years, while costing far less to build than a new plant.⁷ IGCC plants being demonstrated can achieve efficiencies of 42% (HHV) and with continuous

Figure 2.1 Schematic diagram of a typical integrated gasification combined cycle (IGCC) power generation plant.'

improvements over the next 15 to 20 years, 52% efficiency is achievable.⁸ The efficiency level of a power plant is measured by the amount of electrical energy produced per amount of coal energy used to create it, and the baseline efficiency of a conventional coal-fired plant is 34% at best.

IGCC systems differ from those commercially available in that they may use hot gas cleanup at 427-649 °C, with air-blown gasifiers operating at 982 °C. There is a need to optimize the system by finding the right balance between higher temperature gas cleanup which improves efficiency, and lower temperature components and materials which improve cost. In addition, when compared to existing coal plants with flue gas desulfurization, IGCC technology is capable of achieving 35% reduction in CO₂ emission (because less coal is required to generate an equivalent power), 94% reduction in SO₂, 93% in NO_x, and 40-50% reduction in solid waste.⁹

2.2.3 Coal Gasifiers for IGCC Application

Gasifiers for IGCC application fall into three main categories: moving/fixed bed, fluidized bed, and entrained flow, as shown in Figure 2.2. The moving-bed gasifier typically consists of a pressure vessel containing a grate which supports a coal charge that moves slowly downward, through a series of counter-current reaction zones, while reacting with gases (oxidant and steam) moving upward from the bottom. Ash products are removed from below the grate. The temperature of the product gas is usually between 427 and 649 °C.⁷ In fluidized-bed reactors, coal is fed into the bottom or side of the unit, and steam and oxidant are injected at the bottom and allowed to percolate up through at a velocity sufficient to cause turbulent mixing of the bed. A fluid-bed gasifier operates at moderate temperatures from 927 to 1038 °C.⁷ Entrained-flow gasifiers are characterized by higher velocities (shorter residence times) and higher temperatures (> 1260 °C),⁷ which are above the ash melting point. The coal feed to most of these gasifier types can be dry or slurry, and the oxidant can be oxygen or air.

2.2.4 Particulate Removal System

The particulate removal system is an integral part of an IGCC system, not only because it is undesirable to emit particles into the atmosphere, but also, because many gas cleanup and turbine systems are intolerant of fines in the fuel gas. Impurities present in the fuel gas may cause chipping or erosion of the turbine blades. Particulate removal systems may include one or a combination of the following: cyclones, electrostatic precipitators, rigid ceramic filters, moving granular collectors, and ceramic-fabric filter systems.⁷ A typical design arrangement is to use one or two cyclones for primary-fines removal and a ceramic filter for capture of the remaining fines.

2.2.5 Hot Gas Desulfurization

The purpose of the gas cleanup system is to remove unwanted gas and

Figure 2.2 Schematic diagrams of main categories of gasifiers for IGCC application.

vapor compounds, primarily sulfur, from the raw fuel gas to meet gas turbine requirements and to comply with environmental regulations. To improve removal efficiency and lessen the burden on the downstream hot gas cleanup system, a sorbent is added to some gasifier systems to remove a portion of the sulfur.⁷ This in situ removal of sulfur is accomplished by mixing sorbent with the coal prior to gasification or the combustion process. The spent sorbent is removed from the reactor vessel with the ash and disposed of in a conventional manner. For these single-use sorbents, the reagents which are of practical consideration must be inexpensive and, as a result, are confined to calcium- or magnesium-based sorbents.¹⁰ Limestone and dolomite, a naturally-occurring mixture of calcium and magnesium carbonates (CaCO_3 and MgCO_3), are often used as in-bed sorbents. The MgCO_3 in dolomite remains chemically inert, although it serves to maintain a high degree of porosity within the sorbent during the sulfidation reaction.¹¹

Currently, however, the focus of cleanup system development is on hot gas desulfurization processes that are external and require fewer vessels and are more efficient than conventional flue gas desulfurization. These approaches consist of passing the hot fuel gases through beds of regenerable sorbents. These sorbents are invariably oxides which are converted to sulfides during a sulfur loading stage under reducing hot fuel gas conditions and then regenerated by oxidation of the sulfides to oxides and a concentrated byproduct stream of SO_2 .¹⁰ Regeneration is important to the commercial feasibility of external sorbents since they are made from relatively expensive materials. The sorbent bed can be a fixed-bed, a moving-bed, or a fluidized-bed design, as shown in Figure 2.3.

In a fixed-bed design, there are two parallel vessels, one of which will be capturing sulfur, while the other is regenerating. When the sorbent in the capturing vessel becomes fully saturated, the fuel gas flow is diverted to the other bed, so that the vessels can exchange roles. In a moving-bed design, the sorbent is exchanged between the two vessels continuously or in a batch manner, so that the reactors always have the same role.⁸

The fluidized-bed design is similar to the moving-bed, in that the sorbent exchange is continuous, but, in this case, the bed is fluidized to improve its mixing and heat transfer characteristics. In the absorber, the sorbent becomes sulfided as a result of removing sulfur species from a fuel gas stream. In the regenerator, the captured sulfur in the sulfided sorbent is burned off with air and the activity of the sorbent is restored to enable its re-use in the process.⁷

For fluidized-bed processing, sorbent particle sizes are small, generally in the range 20-500 μm . Hot gas desulfurization processes utilizing fluidized beds offer the following potential advantages over those processes using fixed or moving beds: they provide steady-state operation (simplifies system control strategies and need for auxiliary equipment during cyclic operation); they improve temperature control (reduce sorbent deactivation due to overheating, which results in longer sorbent life); they enhance process heat integration (increases system efficiency); and they add flexibility with respect to sulfur recovery options (wide range of achievable SO_2 concentrations).

(a) Fixed-Bed Desulfurization

(c) Moving-Bed Desulfurization

(c) Fluidized-Bed Desulfurization

Figure 2.3 Schematic diagrams of different types of hot gas cleanup systems for IGCC application.^a

External desulfurization techniques are also used for the removal of residual sulfur in systems employing primary in-situ desulfurization. The implementation of in-situ desulfurization in conjunction with external desulfurization may offer an economically effective process for sulfur removal.

To be applicable to advanced IGCC combustion turbine systems, hot gas desulfurization has to operate at high pressures (600 psia) and high-temperatures. A system operating at higher temperatures is more compatible with fluidized-bed gasifiers since there is no need for costly heat exchanger equipment for lowering the fuel gas temperature entering the hot gas cleanup system. Gasification also produces dry ash which is suitable for landfills and eliminates the need for liquid waste disposal. In addition, The air-blown system does not require a costly oxygen separation system.⁷

2.3 Review of Hot Gas Desulfurization Sorbents

2.3.1 Introduction

An integral feature common among advanced power generation systems is hot gas cleanup. Early work on hot gas desulfurization utilized pure metal oxide (MeO) sorbents because metal oxides tend to be reactive at high temperature where desulfurization is desirable to conserve the sensible heat in gasifier fuel gas.¹² Because during the process of gasification sulfur in the coal is converted predominantly to H_2S , the general sulfidation reaction may be represented by the following equation:

Desulfurization with sorbents is essentially a process of removal of the species H_2S from the gas phase. As H_2S is removed, the other minority sulfur-bearing species, such as COS, equilibrate in the gas phase and also are proportionately reduced. The high temperature desulfurization can be successfully accomplished by using solid sorbents such as oxides of those metals that form stable sulfides. The effectiveness of a desulfurizing agent in treating coal gases is related to the predicted equilibrium partial pressure of sulfur which will be present in a phase combination of the reduced form of sulfide and oxide phases. A sulfur concentration limitation of approximately 150 ppmv has been established for IGCC systems; therefore, a sorbent system capable of reducing H_2S concentration from about 5000 to 150 ppmv is sought.¹³

The focus of much current work on hot coal-derived fuel gas desulfurization is primarily in the use of three basic types of sorbents: iron oxides, zinc ferrite, and zinc titanate. Iron oxides react with the fuel gas to remove sulfur primarily in the form of H_2S . SO_2 in the regenerator off-gas is treated for the production of elemental sulfur. Fixed- and fluidized-bed schemes have been developed with 90-96% sulfur removal efficiencies.⁸

The choice of zinc oxide is typically based on the thermodynamic considerations that indicated very low concentration levels of H_2S in equilibrium

with ZnO, ZnS, and H₂O vapor.¹⁴ The addition of zinc oxide component was found to greatly improve the performance of iron oxide sorbents. The resulting sorbent (zinc ferrite, ZnFe₂O₄) exhibits the favorable properties of the individual oxides and increased its operating temperature to the 500-650 °C range with sulfur capture efficiencies in excess of 99% and outlet sulfur concentrations less than 10 ppmv.⁷ This reduction in required gas cooling is significant since it allows more sensible heat to be extracted in an efficient gas turbine which increases plant efficiency considerably. Zinc ferrite was, however, limited with respect to its maximum operating temperature of about 649 °C. Above this temperature, the sorbent suffered a loss of pore volume during reduction and a subsequent loss of reactivity during sulfidation.¹⁵

In efforts to improve zinc ferrite sorbents, titanium oxide (TiO₂) was chosen as an inert additive due to its ability to stabilize zinc oxide at high temperatures. Its addition increased the upper sulfidation temperature limit of these sorbents to 725 °C and decreased losses due to sorbent decrepitation. Though the addition reduces sulfur capture capacity relative to zinc ferrite, zinc titanate system efficiencies greater than 99.9% are obtainable.⁷

To improve the process economics further, it is required to have an easily regenerable sorbent which would not only reduce the cost of sorbent but also the costs associated with frequent loading and unloading of the reactors with sorbent and the costs associated with disposal of the spent sorbent.¹⁴ Furthermore, the sulfur produced by regeneration of the sorbent should be recoverable in a form which is readily saleable or storable. This means that the regeneration step should be flexible and be able to produce elemental sulfur or sulfuric acid depending on the demand at the location of the gasification plant.¹⁶

With these restrictions in mind, research has focused almost entirely on making the zinc-based sorbents durable. However, extensive research, carried out mainly by the Morgantown Energy Technology Center (METC), casts doubt that zinc ferrite or zinc titanate can be utilized even for the mild conditions associated with fixed-bed operation.¹² The practical limitations of zinc-based sorbents are discussed in detail in Chapter IV.

2.3.2 Manganese-based Systems

Based on thermodynamic considerations alone, Westmoreland and Harrison¹⁷ screened the high-temperature desulfurization potential of twenty-eight (28) solids, primarily metal oxides. They concluded that eleven candidate solids based upon the metals Fe, Zn, Mo, Mn, V, Ca, Sr, Ba, Co, Cu, and W showed thermodynamic feasibility for high-temperature desulfurization. Manganese oxide stability and high fractional desulfurization were predicted to temperatures in excess of 1000 °C. Importantly, manganese shows desulfurization potential in the temperature range of 600 to 700 °C where metal oxides currently known to be reactive with H₂S are unsatisfactory.

Westmoreland et al.¹⁸ also determined the initial rates for the reaction between H₂S and MnO, CaO, ZnO, and V₂O₃ over a temperature range of 300 to

800 °C, in a thermobalance reactor. The relative magnitude of reaction rates decreased in the order $\text{MnO} > \text{CaO} \approx \text{ZnO} > \text{V}_2\text{O}_3$. They concluded that MnO possessed favorable properties for a high-temperature desulfurization process and highly recommended that further studies be carried out.

Turkdogan and Olsson¹¹ studied the practical feasibility of using calcined dolomite to desulfurize hot reducing gases in a regenerative cyclic process. They also investigated four different methods of regeneration of the loaded calcined dolomite. Calcined dolomite is often advocated as a suitable material for desulfurization of gases. There are, however, limitations to its use for this purpose. The freshly calcined dolomite is capable of absorbing H_2S rapidly from hot reducing gases. However, treatment of the sulfided dolomite with $\text{CO}_2\text{-H}_2\text{O}$ mixtures under pressure and at temperatures below 700°C results in only poor regeneration of $\text{CaCO}_3(\text{MgO})$. After the second or third cycle, the level of regeneration is too low for any practical applications. After repeated cycles of sulfidation and regeneration, the H_2S -absorbing capacity of the material decreases. With regeneration by oxidative calcination at around 1050°C, the calcined dolomite may be recycled 7 to 10 times without too great a loss in reactivity for H_2S absorption at the anticipated operating temperatures of 750 to 950°C.

Turkdogan and Olsson¹⁹ studied the practical feasibility of using manganese oxide pellets to desulfurize hot reducing gases. The results of this investigation substantiated the practical feasibility of desulfurizing hot reducing gases with manganese oxide pellets in a regenerative cyclic process with SO_2 -enriched exhaust gas as a by-product. It was found that $\text{MnO-Al}_2\text{O}_3$ pellets were much better than calcined dolomite in enduring this regenerative cyclic process. The best results were obtained with pellets made from a mixture of 75 parts of finely ground high-grade Comilog ore and 25 parts of alumina powder, sintered in air at 1200 °C. The pellets in a packed bed can be sulfided and regenerated almost completely at relatively high speeds and recycled without loss of reactivity or strength. The regeneration is done readily by one of several methods of oxidative calcination using air, $\text{O}_2\text{-SO}_2$, or $\text{CO}_2\text{-H}_2\text{O-O}_2$ mixtures. The $\text{MnO-Al}_2\text{O}_3$ pellets maintained their reactivity and strength in this regenerative cyclic process much better than the calcined dolomite.

Efforts to overcome the temperature limitations of this first zinc ferrite formulation led to the development of other mixed metal oxide sorbents as well as improved formulations of zinc ferrite. For example, the addition of an inorganic binder, bentonite, to the original zinc ferrite formulation provided a sorbent with comparable reactivity and capacity but with capability of withstanding temperatures up to 692 °C.

Hepworth and Jha²⁰ have shown that a durable, porous sulfur sorbent useful in removing hydrogen sulfide from hot coal gases can be prepared by pelletizing zinc oxide and iron oxide powders with binders and activators to produce crush-resistant pellets. These pellets are effective in removing hydrogen sulfide in coal gases down to levels of less than 200 ppm when operated at temperatures around 550°C. Upon regenerating the sorbent in the temperature

range of 700° to 800°C, in a steam-air mixture, the contained sulfur in the form of sulfur dioxide was evolved in concentrations ranging up to 10% sulfur at sulfur loadings up to 25% by weight of the sorbent.

These studies were based upon prior work of Oldaker et al.²¹ and Grindley and Steinfeld.²² The goal of this prior work was to produce a sorbent which was capable of multiple loading and regeneration cycles. It is striking that of the four sorbents which were cited in the patent, the best results in terms of durability, regenerability, and terminal sulfur levels, originated from a zinc ferrite sorbent in which about 6% by weight manganese oxide was substituted for the iron oxide. Further studies on the use of a sorbent which contained higher levels of manganese were not pursued, however, even though this initial manganese oxide-containing sorbent showed considerable promise.

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CHAPTER III: THERMODYNAMIC COMPARISON OF SEVERAL SORBENT SYSTEMS FOR HOT COAL-DERIVED FUEL GAS DESULFURIZATION

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Thermodynamic Comparison of Several Sorbent Systems for Hot Coal-Derived Fuel-Gas Desulfurization

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A systematic approach toward the evaluation of the behavior of single-metal sorbents for removing sulfur from hot coal-derived fuel-gases is developed from thermodynamic considerations. A procedure is developed (and represented in graphical form) to compare a range of metal-based sorbents (Fe, Ni, Mg, Ca, Mn, Cu, and Zn) with respect to their ability to remove sulfur from fuel gases produced over a range of equivalence ratios. The examples which are given are for a specific Illinois No. 6 coal; however, the calculation method can readily be extended for any coal and other sorbent, such as mixed-metal systems using referenced standard computer programs.

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3.1 Introduction

The U. S. Department of Energy has been exploring several approaches to clean coal combustion to produce electrical energy. These approaches range from single-use sorbent additions to slagging gasifiers during combustion to the passage of hot fuel gases through beds of regenerable sorbents.^{1,2,3,4} In the latter instance, these sorbents are invariably oxides which are converted to sulfides during a sulfur "loading" stage under reducing hot fuel gas conditions and then regenerated by oxidation of the sulfides to oxides and a concentrated byproduct stream of sulfur dioxide. For single-use sorbents, the reagents which are of practical consideration must be inexpensive and, as a result, are confined to calcium- or magnesium-based oxides; however, recently iron-based sorbents have been considered.⁵ In this paper single-metal oxide/sulfide systems are discussed as potential desulfurization sorbents. A method of evaluating the ultimate desulfurizing power of sorbents and their capabilities for regeneration is shown from entirely thermodynamic considerations. In addition, conditions quantifying the extent of desulfurization, in terms of the percentage of sulfur removal and H₂S terminal levels, are mapped as a function of partial pressures of sulfur and oxygen in the cleaned gas and a wide range of temperature values. This procedure can easily be extended to mixed-metal sorbent compounds and solutions, provided the thermodynamic data are known.

Previously, Westmoreland *et al.*⁶ screened the high-temperature desulfurization potential of 28 solids, primarily metal oxides, based on thermodynamic considerations alone. This earlier work, which was subsequently followed by kinetic studies,⁷ was based on a free energy minimization method to determine equilibrium sulfur removal and solid compound stability. The purpose of this paper is to demonstrate the wide applicability of a thermodynamic program developed by Zhong and Hepworth,⁵ and that of the STEPSOL software package,⁸ a chemical equilibrium program for the simulation of semibatch metallurgical reactors on an IBM-PC or compatible. STEPSOL is capable of handling systems up to 14 elements, 84 species, and 19 phases through up to 24 steps and is thus valuable in the calculation of chemical equilibria in complex systems.

3.2 Analytical Approach

In order to illustrate the thermodynamic method used in this analysis, a typical high-sulfur Illinois No. 6 coal has been used as the coal producing a gaseous product. The assay of this coal is given in Table 3.1. The gaseous species considered include N₂, CO, CO₂, H₂O, H₂, H₂S, S₂, COS, SO₂, SO₃, O₂, S, S₄, SO, CS, CS₂, NO, NO₂, CH₄, and NH₃. For a system in which coal gases are equilibrated with a combination of two solid phases (for example metal oxide and metal sulfide), the Gibbs phase rule predicts the number of degrees of freedom as $F = C + 2 - P$, where C is the number of components and P is the number of phases (three in our analysis, gas plus two solids). The components are metal, oxygen, and sulfur. Most of the examples which will be considered are for a three-phase, three-component system. For such a system, the number of degrees of

freedom (F) is two, and therefore at a fixed total pressure of 1 atm, the chemical potential of oxygen and sulfur are uniquely determined at a given temperature. The two components of sulfur and oxygen are most conveniently represented by the logarithms of their partial pressures.

Table 3.1 Analysis of Illinois No. 6 Coal Used in Calculations, Basin Coal IBC-107 (Herrin)

constituent	% by weight
carbon	67.87
hydrogen	5.0
nitrogen	1.2
total Sulfur	3.87
oxygen	10.56 (not included in ash)
ash	11.5
total	100.0 (dry basis)
moisture	9.3
gross heating value	28415 kJ/kg

Figure 3.1, however, shows the oxygen potential which results from establishing a given equivalence ratio for the single-phase gas composition (absence of any solid phase) resulting from gasification of the referenced coal (at a series of fixed temperatures and 1 atm pressure). This figure defines the gasification conditions of equivalence ratio as a function of oxygen potential and temperature for the above-referenced coal by a method described in the next section of this paper. This figure shows that at a given equivalence ratio, the product gas becomes less reducing with increasing temperature. This figure also shows that higher equivalence ratios are required at higher temperatures to achieve the same oxygen pressure. For example, an equivalence ratio of almost 3 is required to establish an oxygen pressure of 10^{-16} at 1450 °C. This would be equivalent to burning coal to produce only hydrogen and carbon monoxide, without carbon dioxide or water vapor, as is usually the case for gasification aimed at the production of synthesis gas.

Figures 3.2a through 3.2c give the calculated concentrations of the majority of sulfur species as determined by standard computer programs (e.g., SOLGASMIX). In examination of these figures, one can see that for equivalence ratios associated with gasification (i.e. > 1), oxidized sulfur in the species SO_2 becomes negligible with respect to lower-valent sulfur in COS and H_2S , the latter being the majority species as shown. Because of the presence of hydrogen in the coal, H_2S concentrations are very much larger than the species S_2 . Desulfurization with sorbents, then, is essentially a process of removal of the species H_2S from the

gas phase. Of course, as H_2S is removed, the other minority species equilibrate in the gas phase and also are proportionately reduced.

Figure 3.3 is a predominance equilibrium diagram for a hypothetical metal-sulfur-oxygen system (M-S-O) at a given temperature, as a function of the oxygen and sulfur partial pressures (the two components chosen for the analysis). According to this figure, desulfurization can be accomplished by two possible reactions, depending on whether the elemental metal or the oxide is stable.

If the metal is stable, desulfurization may be represented by reaction (3.1)

It must be noted, however, that metallic sorbents cannot usually be used for desulfurization, primarily because of the difficulty of converting the sulfide to the metal for recycle, which is the fundamental reason why sulfides are first converted to oxides prior to smelting in metallurgical processing.

If the oxide is stable, desulfurization may be represented by reaction 2

Unfortunately, the choice of oxides is also limited because of the reduction of some oxides during the desulfurization of hot reducing gases. Figure 3.3 shows that the following reactions are also possible. They are undesirable for the sulfidation as well as the regeneration process steps.

With these restrictions in mind, five types of equilibria involving elemental metal (M), metal oxide (MO), metal sulfide (MS), and metal sulfate (MSO_4) are explored in the subsequent analysis. They are elemental metal/metal oxide (M/M_xO_y), metal sulfide/metal sulfate (M_xS/MSO_4), elemental metal/metal sulfide (M/M_xS), metal oxide/metal sulfide (M_xO/M_xS), and metal oxide/metal sulfate (M_xO/M_xSO_4).

3.3 Complex Chemical Systems

Calculation of chemical equilibria in complex systems requires computer methods because of their complexity when more than a small number of reactions must be considered. Calculations require solution of simultaneous, nonlinear equations which are constrained by the mass balance of the system and would, if

conducted by hand calculator require multiple iterations. In recent years the program SOLGASMIX⁹ has been widely used in the calculation of chemical equilibria, including the calculation of predominance diagrams.^{10,11,12,13} The program uses Lagrange's method of undetermined multipliers coupled with the method of steepest descent to find the minimum free energy of a constrained system, which is, by definition, the equilibrium composition. SOLGASMIX is the basis for the FACT EQUILIB program,¹⁴ as well as the CHEMIX program of CSIRO's (Commonwealth Scientific and Industrial Research Organization) THERMODATA¹⁵ system.

Flynn *et al.*¹⁶ have coupled these programs to formulate a powerful yet easy-to-use equilibrium program package which is suitable for use with IBM personal computers or compatibles. STEPSOL was written to model multistep, semibatch reactors for conditions in which equilibrium is reached in each step. This menu-driven system includes an interactive editor which simplifies the work of typing the data needed by the calculation module. In addition to processing data from compounds, it also includes activity models for solutions including the Bale Pelton Interaction Parameter model,¹⁷ the regular solution model, subregular three-suffix and four-suffix Margules models, the ideal model, and free-form entry model.¹⁸

Based on an iterative approach developed by Rao,¹⁹ Zhong and Hepworth⁵ developed an interactive computer program which permits coal assays to be entered as variables as well as the temperature of the system, total pressure, moisture content, oxygen partial pressure, and sulfur partial pressure. The program output includes the gas phase composition, SO₂ emission concentration, percentage of sulfur removal, NO₂ emission concentration, and equivalence ratio, which can be expected under equilibrium conditions upon gasification of a given coal, followed by desulfurization of the product fuel-gas. (The equivalence ratio is a means of expressing the fuel-to-air ratio, which is defined as the actual amount of fuel expressed as a decimal ratio of the stoichiometrically correct amount of fuel²⁰.) The results reported in this paper can be obtained using either STEPSOL or this program, provided the same thermodynamic data base is used.

3.4 Evaluation of Degree of Desulfurization for Several Metal Sorbent Systems

For the analysis which follows, only thermodynamic considerations are taken into account. Reagent cost, physical stability of substrates, fusion, kinetics, and inherent regenerability based upon physical stability are separate factors which are not addressed here. These factors, however, must be taken into consideration prior to making the ultimate choice among candidate sorbent systems. The purpose of this analysis is to provide a format for analysis of the chemical stability of metal oxide sorbents. The thermodynamic databases used in the following figures are referenced below.^{21,22,23,24,25,26}

In this analysis the significance of the remaining diagrams will first be developed, and then two examples will be given to illustrate the sequence of steps required to fix the optimum equivalence ratio required to desulfurize a given coal-

derived fuel gas. The diagrams are standardized by writing the reactions in terms of 1 mol of oxygen or sulfur gas. This procedure enables comparisons to be made on the same molal basis.

3.5 Graphical Procedure

In Figure 3.4, the phase stability for nine metal oxides (iron and manganese oxides in two forms MO and M_2O_3 , where M designates elemental metal) is shown as a function of oxygen partial pressure and temperature. Each line represents a boundary above which the metal oxide is stable. This diagram is useful in the prediction of metal or oxide stability during the sulfidation stage.

In Figure 3.5, the stability of the sulfate with respect to the sulfide is shown in terms of oxygen pressure and temperature. For example, for manganese sulfate to be stable, oxygen pressures above the middle line on the diagram would be required; below that line, the sulfide would be stable. This diagram is useful in the assessment of sulfide or sulfate stability during the sulfidation or regeneration stages.

Figure 3.6 shows the standard Gibbs free energy of formation of sulfides from sulfur and the metal as a function of temperature. The sulfur pressure can readily be determined from the Gibbs free energy by the equation $\ln P_{S_2} = (1/RT)\Delta G^\circ$. From this relationship, one notes that along the ordinate, less negative Gibbs free energies of formation are directly related to increasing sulfur partial pressures. Therefore the analysis is similar to that in Figure 3.4 for the metal/metal oxide equilibrium. The usefulness of such a representation, which employs the free energy instead of the sulfur partial pressure, will be pointed out later.

Figure 3.7 compares the relative stability of sulfide with oxide in a plot similar to Figure 3.6. The sulfide is stable above the line and the oxide below the line. Accordingly, the most stable sulfide shown, compared with the oxide, is copper sulfide, whereas, the least stable sulfide compared with the oxide is magnesium sulfide. Equilibria for CaO/CaS and MnO/MnS are shown approximately midway in the diagram and cover the entire temperature range studied. The diagram shows that the oxide phases are generally more stable than the sulfide except for copper. For the system $Fe-O-S$ stoichiometric compounds FeO and FeS have no practical significance since this system contains a melt having a wide range of compositions; i. e., sulfur has a solubility range within the melt $Fe-O-S$.²⁷

Figure 3.8 compares the stabilities of sulfate with oxide systems with the sulfide being stable above the line of each equilibrium shown. Higher (less negative) values of the standard Gibbs free energy change occur for less stable sulfates (top of diagram). This figure is especially useful in predicting whether the oxide or sulfate is stable during regeneration of the loaded (spent) sorbent.

Figure 3.9 is a composite representation of Figures 4-8 in which the quantity P_i on the right-hand side of the diagram represents one of the three terms as shown in the legend. For example, for $P_i = P_{S_2}/P_{O_2}$, which corresponds

to a metal oxide/metal sulfide equilibrium, each slanting line is drawn as a function of temperature at the various values indicated on the right-hand side and top of diagram. A ratio of unity, in this example, along a line passing through an ordinate value of zero, would occur for the situation in which the metal sulfide and the metal oxide have an equal stability.

3.6 Example 1

Again making reference to the previously-described Illinois No. 6 coal which is subject to gasification at a equivalence ratio of 1.05 at 800 °C., removal of 95% of the sulfur from the fuel gas at 1 atm total pressure is desired. Reference at 800 °C to Figure 3.1 shows that for an equivalence ratio of 1.05, the oxygen pressure is approximately 10^{-15} atm. Figure 3.10a indicates that for 95% sulfur removal and for P_{O_2} having a value of 10^{-15} , the partial pressure of sulfur, P_{S_2} , is fixed at approximately $10^{-6.15}$ atm. Providing hydrogen sulfide (H_2S) is the only sulfur-bearing species (an excellent approximation as previously established in Figure 3.2a), Figure 3.10b shows that the sulfur content of the cleaned gas corresponds to somewhat less than 200 ppm. Inspection of Figure 3.4 shows that the phase combinations NiO/Ni , Cu_2O/Cu , and MnO/Mn_3O_4 all exhibit oxygen partial pressures greater than this requirement. Consequently, the metal oxides Mn_3O_4 , Cu_2O , and NiO will be reduced to MnO , Cu , and Ni , respectively, and therefore are not suitable as sulfur acceptors under these conditions. On the other hand, the rest of the metal oxides shown in Figure 3.3 would be suitable, i.e. thermodynamically stable.

It must be noted that this example was predicated upon hydrogen sulfide gas (H_2S) being the only sulfur species. As a more exact approach, Figures 10-13, however, are based upon calculations made upon the Illinois No. 6 coal in Table I in which all sulfur-bearing species, as indicated earlier, are taken into account. During the process of gasification, sulfur in the coal is converted predominantly to H_2S . These figures are calculations at the temperatures shown (ranging from 800 to 1400 °C) on plots of sulfur vs oxygen pressure (both in atmospheres), all at a total pressure of 1 atm. The curves (part a) represent lines of equal percentage of sulfur removal, thus quantifying the extent of desulfurization achieved. The curves (part b) represent lines of constant ppm H_2S in the cleaned gas as a function of O_2 and S_2 partial pressures.

A comparison is made between Figures 10a and 13a (800 and 1400 °C). The range of oxygen partial pressures below the 95% sulfur removal line is wide for the higher temperature and very limited for the lower temperature. Reference to Figure 3 shows that in order to achieve such a high degree of desulfurization, operation must be restricted to equivalence ratios ranging for the lower temperature (800 °C) from approximately 1.0 to 1.1 and for the higher temperature (1400 °C) from 1.2 to 3.0. Upon examination of Figure 3.13a, one notes that at higher oxygen pressures ranging up to 10^{-8} atm, the range of satisfactory desulfurization is wide; however, above this pressure, there is a rapid loss of desulfurizing capability. An examination of the above Figures shows that 95% sulfur removal requires a sorbent system which exhibits equilibrium sulfur

partial pressures below approximately $10^{-6.5}$ atm at both temperatures (800 and 1400 °C). Reference to Figure 3.7 indicates that both the CaO/CaS and MnO/MnS systems meet the above criteria for the realization of the desired extent of desulfurization. However, for the system MnO/MnS, operation beyond the eutectic point of 1232 °C may not be possible, although Turkdogan and Olsson⁴ indicate that this system performed well even at temperatures as high as 1300 °C.

3.7 Example 2

The following example will illustrate the proposed procedure for coal gasification followed by product gas desulfurization with manganese oxide or a manganese-based sorbent. Consider a gasification process carried out at 1200 °C for the Illinois No. 6 coal at an equivalence ratio of 2.5. Figure 3.3 indicates that P_{O_2} is fixed at a value of approximately $10^{-13.2}$ atm. Figure 3.4 shows clearly that among Mn, MnO, and Mn_3O_4 , MnO is the stable phase under the specified thermodynamic conditions. Figure 3.5 shows that MnS is stable with respect to $MnSO_4$ formation. Since MnO is the stable desulfurizing agent (and not Mn), there is no need to examine Figure 3.6 and consider the Mn/MnS equilibrium as the desulfurization reaction. Instead, one should examine Figure 3.7 and the MnO/MnS equilibrium, for which the standard free energy may be read from the ordinate as 190 kJ per mol of S_2 . Figure 3.8 need not be considered in this specific case because of the above-discussed relative instability of the sulfate. Based upon Figure 3.9 and the value of the free energy change for the desulfurization reaction deemed appropriate at the given temperature, one can estimate the ratio of P_{S_2}/P_{O_2} to be approximately 10^7 . Since P_{O_2} is known, one can calculate P_{S_2} as $10^{-6.2}$ atm. Knowing P_{S_2} and P_{O_2} values one may now examine Figures 3.12a and 3.12b to estimate the percentage of sulfur removal and H_2S concentration (ppm), respectively. These values are approximately 91.1% sulfur removal and 489.5 ppm H_2S .

3.8 Summary

The figures presented in this analysis enable an operator of a slagging combustor or coal gasifier, operating on a specific coal, to determine the equivalence ratio and temperature required for a given set of sorbents. This analysis is readily changed by use of the computer programs stated for any coal composition. Similar figures can be generated for another coal composition which would enable new desulfurization conditions to be evaluated. (However for the present examples, since results are presented in terms of percent sulfur removal, they will not be significantly different so long as the coal rank remains similar to the chosen Illinois No. 6 coal.) Extension of this approach to mixed-metal systems (e. g. zinc ferrite) requires input of the data for such a system into the database.

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Figure 3.1 Equivalence ratio vs oxygen partial pressure (atmosphere) at several temperatures for an Illinois No. 6 coal.

Figure 3.2a Concentration of H_2S (ppm) resulting from the gasification of an Illinois No. 6 coal, as a function of temperature and equivalence ratio.

Figure 3.2b Concentration of COS (ppm) resulting from the gasification of an Illinois No. 6 coal, as a function of temperature and equivalence ratio.

Figure 3.2c Concentration of SO₂ (ppm) resulting from the gasification of an Illinois No. 6 coal, as a function of temperature and equivalence ratio.

Figure 3.3 Stability diagram for a hypothetical divalent metal-sulfur-oxygen (M-S-O) system at a fixed temperature.

Figure 3.4 Stability of several metal/metal oxide combinations as a function of oxygen partial pressure (atmosphere) and temperature ($^{\circ}\text{C}$).

Figure 3.5 Stability of several metal sulfide /metal sulfate combinations as a function of oxygen partial pressure (atmosphere) and temperature (°C).

Figure 3.6 Free energy (in kJ/mol S_2) vs temperature ($^\circ\text{C}$) stability diagram for several metal/metal sulfide combinations.

Figure 3.7 Free energy (in kJ/mol S_2) vs temperature ($^\circ C$) stability diagram for several metal oxide/metal sulfide single-metal systems.

Figure 3.8 Free energy (in kJ/mol S_2) vs temperature ($^\circ C$) stability diagram for several metal oxide/metal sulfate systems.

Figure 3.9 Composite representation of free energy (in kJ/mol) vs temperature (°C) stability diagram for metal/metal sulfide, metal oxide/metal sulfide, and metal oxide/metal sulfate systems.

Figure 3.10a

Percentage of sulfur removal from fuel gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 800 °C (Illinois No. 6 coal).

Figure 3.10b Concentration of H_2S (ppm) in the cleaned gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 800 °C (Illinois No. 6 coal).

Figure 3.11a Percentage of sulfur removal from fuel gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 1000 °C (Illinois No. 6 coal).

Figure 3.11b

Concentration of H_2S (ppm) in the cleaned gas as a function of partial pressures of oxygen and sulfur (atmosphere) at $1000\text{ }^{\circ}\text{C}$ (Illinois No. 6 coal).

Figure 3.12a

Percentage of sulfur removal from fuel gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 1200 °C (Illinois No. 6 coal).

Figure 3.12b

Concentration of H_2S (ppm) in the cleaned gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 1200 °C (Illinois No. 6 coal).

Figure 3.13a

Percentage of sulfur removal from fuel gas as a function of partial pressures of oxygen and sulfur (atmosphere) at 1400°C (Illinois No. 6 coal).

Figure 3.13b

Concentration of H_2S (ppm) in the cleaned gas as a function of partial pressures of oxygen and sulfur (atmosphere) at $1400\text{ }^{\circ}\text{C}$ (Illinois No. 6 coal).

**CHAPTER IV: DESULFURIZATION OF HOT COAL-DERIVED FUEL GASES
WITH MANGANESE-BASED REGENERABLE SORBENTS. 1. LOADING
(SULFIDATION) TESTS**

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Desulfurization of Hot Coal-Derived Fuel Gases with Manganese-Based Regenerable Sorbents. 1. Loading (Sulfidation) Tests

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In earlier studies, zinc ferrite and zinc titanate were developed as regenerable sorbents capable of removing hydrogen sulfide from hot coal-derived fuel gases. Manganese ore as well as manganese carbonate, precipitated from aqueous solutions, combined with alumina to form indurated pellets is shown to hold promise of being a highly-effective, inexpensive, regenerable sulfur sorbent for hot fuel gases. Although the thermodynamics for sulfur removal by manganese predicts somewhat higher hydrogen sulfide over-pressures than can be accomplished with zinc-based sorbents, zinc tends to be reduced to the metallic state under coal gasification conditions resulting in loss of capacity and activity by volatilization of reactive surfaces. This volatilization phenomenon limits the temperatures to which desulfurization can be effectively accomplished to less than 550 °C for zinc ferrite and 700 °C for zinc titanate; whereas, manganese-based sorbents can be utilized at temperatures well in excess of 700 °C. This paper addresses the physical and chemical behavior of several sorbent formulations fabricated from manganese and alumina, establishes the thermodynamic feasibility of hydrogen sulfide removal from hot simulated coal gases using these sorbents, and presents an analysis of the sulfidation reaction kinetics based on thermogravimetric experimental results.

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4.1 Introduction

The Integrated Gasification Combined Cycle (IGCC) is one of the most promising proposed processes for advanced electric power generation that is likely to replace conventional coal combustion. This emerging technology not only will improve considerably the thermal efficiency but will also reduce or eliminate the environmentally adverse effects normally associated with coal combustion. The IGCC process gasifies coal under reducing conditions with essentially all the sulfur existing in the form of hydrogen sulfide (H_2S) in the product fuel gas. The need to remove H_2S from coal-derived fuel gases is a significant concern which stems from stringent government regulations and also, from a technical point of view, a need to protect turbines from corrosion. Westmoreland *et al.*¹ and Hepworth *et al.*² carried out comparative studies on several proposed sorbent systems which consisted almost entirely of metal oxides. Metal oxides have been proposed because they tend to be more reactive at high temperature where desulfurization is desirable to conserve the sensible heat in gasifier fuel gas. A sulfur concentration limitation of approximately 150 ppmv (parts per million by volume) for IGCC systems has been established; therefore, a sorbent system capable of reducing H_2S concentration from about 5000 to 150 ppmv is sought.³

Zinc ferrite and zinc titanate have received much attention over the past twelve years because, from a theoretical point of view, they have desirable properties: high sulfur capacity, ability to remove H_2S from coal-derived fuel gas to levels of a few ppmv, and the feasibility of regeneration with air. Because it is economically necessary to recycle sulfur sorbents for at least 100 cycles, research has focused almost entirely on making the zinc-based sorbents durable. Unfortunately, extensive research carried out by the Morgantown Energy Technology Center (METC) of the Department of Energy (DOE) casts doubt that zinc ferrite or zinc titanate can be utilized even for fixed-bed operation. The desirable properties of Zn-based sorbents as well as their practical limitations will be discussed in detail in a later section of this paper.

Given the limited success of the zinc-based sorbents, METC has shown interest in formulating and testing manganese-based sorbent pellets.⁴ There are a number of studies that led to the consideration of Mn-based sorbents. Westmoreland *et al.*¹ screened the high-temperature desulfurization potential of 28 solids, primarily metal oxides, based upon thermodynamic considerations alone. This earlier work, which was subsequently followed by kinetic studies,⁵ predicted manganese oxide stability and a high degree of desulfurization to temperatures in excess of 1000 °C. In addition, manganese showed desulfurization potential in the range of 600 to 700 °C where traditional metal oxides known to be reactive with H_2S proved unsatisfactory. These kinetic studies determined the initial rates for the reaction between H_2S and MnO , CaO , ZnO , and V_2O_3 over a temperature range of 300 to 800 °C. The relative magnitude of reaction rates decreased in the order: $MnO > CaO \approx ZnO > V_2O_3$. They concluded that MnO possessed favorable properties for a high temperature desulfurization process and highly recommended that further studies be carried out.

Turkdogan and Olsson⁶ examined the feasibility of using manganese oxide pellets to desulfurize hot reducing gases. They found that a mixture of manganese ore and alumina formed into pellets in a 3:1 weight ratio readily accepted sulfur from hot (800 °C) H₂-H₂S gas mixtures and that the pellets could be regenerated with air, or other oxidizing gases. They explored the cyclic loading and regeneration of these pellets through 18 consecutive cycles. Their pellets exhibited high strength and rapid loading kinetics which did not show a decline in reactivity or capacity through the regimes which they explored. Interestingly, repeated cycling of the pellets resulted in improved sulfidation and regeneration kinetics, unlike the situation with Zn-based sorbents, as will be discussed later. This desirable phenomenon with manganese pellets was attributed to transport between pellet pores, possibly by development of cracks.

During their investigation of zinc ferrite Jha and Hepworth⁷ substituted MnO for some of the zinc oxide as a means of enhancing the durability and reactivity of the zinc ferrite and reported favorable results. In a recent study Hepworth et al.² developed a systematic approach for the evaluation of the behavior of single and mixed-metal sorbents for removing sulfur from hot coal-derived fuel gases, based on thermodynamic considerations. A range of metal systems including iron, nickel, magnesium, calcium, manganese, copper, sodium, and zinc were examined. This study singled out manganese oxide as a prime candidate sorbent capable of being utilized under a wide temperature range, irrespective of the reducing power (determined by CO₂/CO ratio) of the fuel gas. This paper addresses the physical and chemical behavior of several sorbent formulations fabricated from manganese and alumina, establishes the thermodynamic feasibility of H₂S removal from hot simulated coal gases, and presents an analysis of the sulfidation kinetics based on thermogravimetric experimental results.

4.2 Thermodynamic Considerations

There are four stable oxides of manganese: MnO, Mn₃O₄, Mn₂O₃, and MnO₂. Figure 4.1 is a stability diagram for the Mn-O system as a function of oxygen potential and temperature with superimposed equilibrium CO₂/CO ratios in the gas phase. A very desirable feature of this system is its resistance to reduction to elemental manganese by CO or H₂ because of the unavoidable presence of trace amounts of CO₂ and H₂O in the reducing gas. In addition, the higher oxides of manganese are readily reduced to MnO even in very slightly reducing atmospheres. This implies that MnO is the stable form of manganese for virtually all commercially available coal-derived fuel gases.

The reducing coal-derived fuel gas is desulfurized by MnO according to reaction 1

The equilibrium ratio of H₂O/H₂S for this reaction has been determined by

Turkdogan and Olsson,⁶ and is expressed by

$$\text{Log} \left[\frac{pH_2O}{pH_2S} \right] = \frac{3330}{T} - 0.310 \quad (4.2)$$

In the desulfurization of hot reducing gases by Mn-based pellets, the extent of desulfurization achieved depends on temperature and gas composition. The residual H_2S concentration in the desulfurized gas, calculated using SOLGASMIX²⁸, for the conditions of gas-solid equilibrium in the reactor, is shown in Figure 4.2 as a function of temperature for various typical oxygen-blown and air-blown gasifier gases, the compositions of which are reported in Table 4.1.* It is seen from this figure that the lower the operating temperature and the lower the H_2O/H_2S ratio, the lower is the residual sulfur in the cleaned gas. Noting that the amount of water vapor produced in the exhaust gas is equal to the quantity of H_2S reacted, the concentration of H_2S in the exhaust gas can be expressed as a function of temperature and H_2O content of the clean gasifier fuel gas. This is given by equation 3, where T denotes absolute temperature in °K.

$$[H_2S] \text{ (ppmv)} = \frac{(\%H_2O)_{\text{fuel gas}}}{10^{\frac{3330}{T} - 4.310}} \quad (4.3)$$

This equation may be used to predict the concentration of H_2S in a fuel gas following equilibration with MnO . It is seen that the objective of reducing the concentration of H_2S below 150 ppmv to satisfy the IGCC system requirement is thermodynamically feasible. See inset in Figure 4.2 for the Tampella-U and Shell (oxygen-blown) gases.

4.3 Experimental Investigations and Results

4.3.1 Sorbent Pellet Preparation. The prior studies by Turkdogan and Olsson⁶ were conducted on an African rich pyrolusite (MnO_2) ore which assayed 63%

* Gas compositions A through E were provided by METC; those of F through K were supplied by R. Gupta from Research Triangle Institute.

Table 4.1 Typical Gasifier Exit Gas Compositions (Vol.%): (typical air-blown gasifier: GE fixed-bed (A & G), KRW fluid-bed (B & F), Texaco entrained-bed (C & H), and Lurgi fixed-bed (D), Tampella U-gas (I); and typical oxygen-blown gasifiers: Texaco entrained-bed (J) and Shell (K).

Vol.%	A	B	C	D	E	F	G	H	I	J	K
CO	8	10.55	16.13	11.9	40	15	8	15.2	24.33	39.1	64
CO ₂	11	4.64	7.55	10	12.5	5	11	8.28	5.16	12.25	.8
H ₂	16	8.26	10.7	17.4	27.84	10	15	10.7	13.19	30.13	31.6
H ₂ O	30	27.52	10.94	28.1	18.5	15	30	10.7	5.35	17.52	1.5
H ₂ S	3	.06	.42	1	1.08	.5	.5	.5	.118	1	1.4
COS	-	-	.03	-	.08	-	-	-	-	-	-
N ₂	29	48.73	54.22	28.7	-	53.7	32.2	53.9	49.9	-	.7
CH ₄	3	.24	-	3	-	.5	3	-	1.84	-	-
NH ₃	.5	.2	.16	.5	.2	.3	.3	-	.111	-	-
CO/CO ₂	.73	2.27	2.14	1.19	3.2	3	.73	1.84	4.72	3.19	80
H ₂ /H ₂ O	.53	.3	.98	.62	1.5	.67	.5	1	2.47	1.72	21

Mn (primarily as Mn_2O_3) upon calcination in air at 1000 °C. A significant domestic source of manganese in Minnesota is being explored for an in-situ leach process⁹ which has potential for producing large tonnages of solutions which may be ideal for precipitation and recovery of pure manganese as a carbonate¹⁰ in a reactive form. For these reasons, the present investigation employed similar materials: Moanda manganese ore,^{*} regular manganese carbonate,^{*} alundum,^{**} bentonite,^{**} and dextrin.^{***}

Four pellet formulations were prepared using combinations of a manganese-containing compound, an alumina-based matrix, and a binder, based on desired compositions determined on a dry weight-percent basis. The amount of binder used was as low as possible, not only to save on the cost, but also to provide a greater amount of chemically active sorbent. After each blend is mixed, an appropriate amount of water is added prior to pelletizing. The composition of the initial make up of the formulations prepared using this procedure is reported in Table 4.2.

Twenty-four induration campaigns were conducted. Preliminary tests indicated that Moanda ore-based pellets required a temperature of 1200 °C and manganese carbonate-based pellets required an induration temperature of 1250 °C, to produce a required strength of greater than 22 N per mm of pellet diameter (5 lbs/mm). In addition, two time periods for induration were explored,

^{*} Moanda manganese ore (77% MnO_2 , 3.36% MnO , 6% Al_2O_3 , 2.81% Fe, 2.56% SiO_2 , 5.16% H_2O (bound)) was obtained from the Prince Manufacturing Company in Quincy, IL.

^{*} Regular manganese carbonate (approximately 93-95% pure) was obtained from Chemetals, Inc. in Baltimore, MD.

^{**} Alundum (96.6% Al_2O_3 , 2.6% TiO_2) was obtained from Industrial Ceramics Corporation (Norton Materials) in Worcester, MA.

^{**} Bentonite, an inorganic binder, was obtained from the Aldrich Chemical Company, Inc. in Milwaukee, WI.

^{***} Dextrin (type IV), an organic binder, was obtained from the Sigma Chemical Company in St. Louis, MO.

Table 4.2 Initial Make up of Formulations

Formulation No.	Raw Material Content in initial make-up, wt. %				
	Moanda Ore	Alundum	MnCO ₃ ^{***}	Bentonite	Dextrin
1	68.18	22.73	-	-	9.09
2	73.53	24.51	-	1.96	-
3	-	15.51	75.4	-	9.09
4	-	16.73	81.31	1.96	-

namely, 1 hour and 2 hours. The strongest formulations are bentonite-bonded as expected. At the conclusion of these tests, four formulations were selected for thermogravimetric analysis (TGA). They were given the following designations: FORM1-A, FORM2-A, FORM2-B, and FORM4-A. Letter "A" corresponds to induration for 2 hours at 1200 °C for the ore-based pellets, and 1250 °C for carbonate-based pellets; whereas, letter "B" corresponds to an induration time of 1 hour.

Table 4.3 summarizes the manganese assays and strengths of the formulations which were subjected to TGA analysis. In addition, BET surface area tests on indurated pellets have shown them to have a surface area less than 0.2 m²/g, which is below the sensitivity of our equipment and therefore required krypton as a carrier gas in an outside laboratory. Typical specific surface area values are 0.055 and 0.127 m²/g for FORM2-A and FORM1-A, respectively. These low specific surface area values are caused by rapid sintering which occurs during induration at high temperature. Porosity tests made by combination of aqueous and mercury pycnometry on crushed pellets from formulation 2 showed the pellets to have a porosity of about 36%.

*** Calcination of manganese carbonate effectively reduces its mass upon loss of carbon dioxide. Precalcination mass was chosen to produce 75% by wt. MnO.

Table 4.3 Manganese Assays and Strengths of Formulations Studied.

Sample Designation	Weight %Mn	Strength, N/mm
FORM1-A	41.14	25.5
FORM2-A	37.48	64.7
FORM2-B	39.83	52.4
FORM4-A	44.22	23.8

4.3.2 Pellet Reactivity via Thermogravimetric Analysis (TGA). The TGA testing is divided into two campaigns the first being only comparative loading for one cycle, and the second for regeneration studies and repeated cyclic loading and regeneration. The second campaign activity will be described in a following paper.

During the first campaign, emphasis was placed upon studying the kinetics of sulfidation using the above four sorbents. The reaction variables included temperature (700 to 1000 °C), fuel gas H₂S content (1%, 2%, and 3% in H₂/H₂S gas mixtures), and pellet diameter in the range 5-10 mm. As was established earlier, the reducing power of the fuel gas is not sufficient to cause the reduction of MnO to elemental Mn. Accordingly, it was not considered important in these loading tests to place any particular emphasis on the kinetics of reduction since there are no losses to be expected by evaporation as would be the situation with zinc-based sorbents.

Figure 4.3 is a schematic diagram of the experimental equipment employed for TGA testing. The upper right-hand portion of the diagram shows the Cahn 1000-Series automatic recording balance assembly which holds up to twelve pellets in a nichrome wire-mesh basket suspended with a nichrome chain from the left pan of the balance. The reactor consists of an alumina tube positioned in a high-temperature molybdenum-wound furnace. The reaction temperature was monitored by using a Pt/Rd thermocouple positioned directly below the sorbent pellets. The weighing unit was constantly blanketed with nitrogen during each test. The gas delivery and data acquisition systems are as depicted. Vent gases are scrubbed in a sodium hypochlorite solution prior to flaring and venting.

For each test, pellets were selected at random from a large batch of indurated pellets. The furnace pressure was 1 atm and the total flowrate was 500 cc/min. Before the heat was turned on, the reactor chamber was evacuated to 0.03 atm and then backfilled with nitrogen. The reactor was heated in a nitrogen atmosphere flowing at 1 L/min to the desired operating temperature before the balance platform was lowered to position the pellets in the center of the 10-cm-long hot zone. Five minutes after the sample was lowered into the hot zone, the nitrogen flow was shut off and the reactive gas mixture was started. Chemically pure (>99.9 %) hydrogen and hydrogen sulfide were metered into the TGA apparatus; flows were regulated by needle valves using calibrated rotameters.

Finally, the nitrogen flow was turned on and the pellets were raised into the cold zone. The results of these TGA tests are shown in Figures 4 through 9, which are studies on loading of pellets as described below.

Figure 4.4 shows the results of TGA analysis at 1000 °C on the four selected sorbents which were described above. In this plot and the plots which follow, the weight of the pellets divided by the initial weight is expressed on the ordinate as a weight ratio: W/W_0 . Initially, this ratio for all pellets is unity; however, there is a decline in this value (reduction of Mn_3O_4 to MnO) when the pellets are exposed to hydrogen during the initial reduction period. Each reduction phase lasted 45 minutes although all pellets remained constant in weight for at least 20 minutes. Each of the sorbents appears to have lost the expected percentage of its original weight; FORM4-A pellets, which contain high manganese concentrations lost appreciably more weight than did the pellets containing lower proportions of manganese. Total percent loss at the conclusion of the reduction period ranged from 2% to 5% for FORM2-B and FORM4-A, respectively.

As indicated on the figures describing sorbent screening tests, hydrogen sulfide is added at 3% by volume to the gas which is flowing at a rate of 500 cc per minute. In the lower right-hand corner of the diagram are the theoretical maximum weight ratios which the pellets could exhibit based upon total conversion of the manganese in the pellet, as determined by chemical analysis, to the stoichiometry: MnS . Upon examining these calculated values, one should note that the formulation which resulted from manganese originating from purified carbonate (i. e., FORM4-A) has a greater capacity for sulfur than the formulations which originate from the ore because of the higher manganese content of the calcined carbonate. (see Tables 4.2 and 4.3). Furthermore, dextrin-based formulations also yield higher sulfur capacities based upon the fact that dextrin volatilizes upon induration of the pellet; whereas, bentonite is a non-volatile impurity which effectively lowers the manganese content of the pellet.

The asymptote for time periods exceeding 90 minutes for formulation 4-A at 1000 °C actually exceeds the calculated value for sulfur capacity, which may indicate that the original sulfur assay is slightly on the low-side. The asymptotic value for formulation 1-A is very close to the calculated value; whereas, the asymptote for 2-A (Moanda ore plus bentonite) falls below the calculated value indicating that some of the manganese may be chemically combined with silicate compounds in the ore and therefore not available to react with hydrogen sulfide. In general, however, and at longer reaction times, each curve would approach its final weight corresponding to complete sulfidation.

In continuing the examination of Figure 4.4, one should note the rapid kinetics upon switching to the loading gas, which is most pronounced in formulation 4-A, i. e. manganese carbonate plus bentonite. Formulation 1-A (ore plus dextrin) has somewhat slower kinetics followed by formulation 2-A (ore plus bentonite). Figure 4.5 shows similar results for tests conducted at 900 °C. Again

formulation 4-A shows the highest sulfur capacity and the most rapid kinetics of the four pellet groups. From Figure 4.6 it is seen that tests conducted at 800 °C show somewhat slower kinetics again with the pellet groups showing similar trends in kinetics. Pellet groups 1-A, 2-B, and 2-A do not reach their asymptotic values for complete loading within the time frame shown (i.e., three hours).

Results from similar loading tests at 700 °C indicated that the kinetics are significantly slower so that only a fraction of the pellet capacity is utilized for all four formulations within the time-frame of the three-hour test regime.

Figure 4.7 is a composite of the data for formulation 4-A, the best of all the formulations studied, for the temperatures 760, 800, 900, and 1000 °C. The theoretical capacity for this formulation is shown as a dashed line on the plot with reactivity rates for all temperatures being rapid. It should be noted that earlier pellet strength tests on manganese pellets originating from the carbonate and indurated at 1200 °C were even superior in reactivity to similar pellets indurated at 1250 °C; however, the strengths of these pellets indurated at the lower temperature were not sufficient to maintain the strength requirements which were imposed as pre-selection criteria.

Figure 4.8 shows the effect of fuel gas H_2S content, over the range 1 to 3% by volume and a constant temperature of 900 °C, on sulfidation kinetics of FORM1-A pellets. The results are as expected, with the sulfidation rate increasing with the H_2S content. At 1% H_2S , the reaction was about 88% complete when the run was terminated after the 2-hr period. However, the reaction was progressing normally, and it appears that complete sulfidation would be achieved if the reaction time had been extended.

Figure 4.9 shows the effect of pellet diameter on sulfidation kinetics at 900 °C for FORM1-A. As expected, the smaller pellets reacted faster, but differences are not too appreciable.

4.4 Kinetic Considerations

As established by the previous thermodynamic analysis, the sulfidation reaction is represented by equation (4.1). This reaction is heterogeneous in which a gas contacts a solid, reacts with it, and then transforms it into products. During sulfidation the pellets contain sufficient amounts of non-reactive impurities (alumina matrix and inorganic binder in some instances) which remain as non-flaking materials. Sulfidation reaction also forms firm product material of somewhat similar specific volume as the reactant : i.e., oxide (MnO) to sulfide (MnS). Accordingly, the sorbent pellets may be assumed to remain unchanged in size during sulfidation although they undergo structural changes. Such an assumption is made in the modeling of metallurgical processes such as the roasting of sulfide ores and the subsequent reduction of the resulting oxides to metals. In addition, the sulfidation reaction is controlled to a large extent by diffusion and may thus be considered irreversible. An additional assumption may be made about the reaction being elementary (i.e., first-order with respect to H_2S)

and the concentration gradients being linear to simplify the mathematical treatment of the problem.^{11,12}

Evidence from a wide variety of situations indicates that the shrinking-core model approximates the behavior of real particles closely in most cases.¹¹ In this model the reaction proceeds at a narrow front which moves into the solid particle and the reactant is completely converted as the front progresses.

In the following analysis, rate equations (time-conversion) describing the progress of the sulfidation reaction with time have been derived, with reference to Figure 4.10, using the following steps which are conceptualized to occur in series:

Step 1: Diffusion of gaseous reactant H_2S through the gas film surrounding the pellet to the exterior surface of the pellet.

Step 2: Penetration and diffusion of H_2S through the newly-formed product layer, MnS , to the surface of the unreacted core.

Step 3: Reaction of H_2S with the reactive component of the pellet, MnO , at the reaction front to exchange sulfur with oxygen and release H_2O .

Step 4: Diffusion of the gaseous product, H_2O , through the product layer, MnS , to the exterior surface of the pellet.

Step 5: Diffusion of H_2O through the gas film to the bulk of the reducing fuel gas.

It must be noted that diffusion steps 2 and 4 could be considered as one step as a countercurrent diffusion in a binary gas mixture. The resistances of the different steps usually vary greatly from one another and the step with the highest resistance is taken as the rate-controlling step.

Time-Conversion performance equations for the sulfidation reaction obtained using the shrinking-core model are given by equations (4.4), (4.5), and (4.6) for diffusion through gas film control, diffusion through product layer control, and surface reaction control, respectively. The symbols used in these equations and their units are as follows: t : time (s); R_p : radius of reduced pellet (cm); k_g : mass transfer coefficient between reducing fuel gas and sorbent pellet (cm/s); k_s : first-order rate constant for the surface reaction (cm/s); superscript o : initial value of parameter; superscript e : equilibrium value of parameter; ρ_i : molar density of component i in pellet (mol/cm^3); F_i : fractional conversion of component i in reduced pellet (dimensionless); D_e : effective diffusivity (cm^2/s); R : universal gas constant ($\text{cm}^3\text{-atm}/\text{mol}\text{-}^\circ\text{K}$); T : absolute temperature ($^\circ\text{K}$); P : total pressure (atm); P_i : partial pressure of gaseous component i (atm), and C_1 , C_2 , and C_3 : constants of integration.

$$F_{MnO} = \frac{3k_s(P^{\circ}_{H_2S} - P^{\circ}_{H_2S})}{RT\rho_{MnO} R_p} t + C_1 \quad (4.4)$$

$$3 - 2F_{MnO} - 3(1 - F_{MnO})^{2/3} = \frac{6D_e(P^{\circ}_{H_2S} - P^{\circ}_{H_2S})}{RT\rho_{MnO} R_p^2} t + C_2 \quad (4.5)$$

$$1 - (1 - F_{MnO})^{1/3} = \frac{k_s(P^{\circ}_{H_2S} - P^{\circ}_{H_2S})}{RT\rho_{MnO} R_p} t + C_3 \quad (4.6)$$

The sulfidation rate is likely to be controlled primarily by countercurrent diffusion through the porous layer of manganese sulfide (MnS) formed. Therefore, the rate data for the sulfidation reaction of FORM4-A pellets at 800, 900, and 1000 °C are plotted in Figure 4.11 in accordance with equation (4.5). It is seen that beyond about 35% reaction, when the product layer becomes sufficiently thick, the results follow closely the limiting rate equation. The effective gas diffusivity, D_e , is then calculated from the slopes of the regression lines the equations of which are indicated in the legend. Figure 4.12 displays D_e (on a log scale) as a function of reciprocal temperature. In the range 850 to 1000 °C the temperature dependence of the effective diffusivity is given by the following equation.

$$\text{Log}(D_e) = \frac{-1656}{T} + 2.2 \quad (4.7)$$

4.5 Mn-Based Sorbents vs Zn-Based Sorbents

The theoretical capacity of manganese-based pellets for sulfur compares favorably with zinc ferrite and zinc titanate as shown in Table 4.4. In generating this table, the overall reactions of the active components of manganese-based pellets, zinc ferrite, and zinc titanate with the major sulfur-bearing species in gasifier gases, H_2S , are as represented by equations (4.1), (4.8), and (4.9), respectively.

It is also assumed that Fe_3O_4 is the stable form of Fe after reduction of ZnFe_2O_4 , and that the optimized zinc titanate formulation is composed of 1.5 ZnO:1.0 TiO_2 . Furthermore, the manganese ore-based formulation is based upon Moanda ore containing 51.2% Mn by weight.

Clearly, even the manganese ore-based sorbent pellet, which has a lower capacity than the Mn carbonate-based formulation, compares favorably with the optimized formulation of zinc titanate which was used extensively in pilot-scale and process development work.

The ultimate degree of desulfurization of manganese-based pellets is less favorable than would be achieved with Zn-based sorbents. For example, for a

Table 4.4 Theoretical Sorbent Capacities

Sorbent	Theoretical Capacity, g S/100 g of sorbent
Zinc ferrite	39.8
Zinc titanate	23.8
Mn Ore-based	24.0
Mn carbonate-based	25.8

fuel gas containing 5% H_2O and 1% H_2S , desulfurization at 1000 °K (727 °C) achieves 57 ppmv H_2S with MnO and 6 ppmv H_2S with ZnO, based on data compiled by Turkdogan.¹³

To compare the rate of sulfidation of Mn-based pellets with that of Zn-based sorbents, the results from sulfidation tests on L-3140 sorbent³ at 760 and 870 °C are superimposed on the results reported above in Figure 4.7, as shown in Figure 4.13. The goal of exposing the Zn-based sorbent to the H_2S -free reducing gas is to quantify the weight loss which is solely due to ZnO depletion. At 760 °C this physical loss of reactive component is negligible; however, at 870 °C this phenomenon becomes noticeably more severe leading to lower sorbent capacity for sulfur. More importantly, the rate of sulfur pick-up from hot coal-derived fuel gases using Mn-based pellets compares favorably with that which is obtained using Zn-based sorbents.

One major problem associated with zinc-based sorbents is sulfate formation which is found to occur whenever SO_2 is present in the regeneration

gas. Sulfation leads to volume expansion and swelling of sorbent pellets eventually causing them to spall and crack. For example: a 5 to 6-mm diameter loaded pellet expands to 9 mm after regeneration when sulfate was formed.¹⁴ Certainly, in a fixed-bed operation some of the pellets will be saturated with sulfur and the regeneration gas will contain some SO_2 . Therefore, sulfate formation is unavoidable along with accompanying spalling and cracking.

The role of chlorides in the gas system should be considered in any study because of the potential volatility of metal chlorides. The presence of HCl in the coal gas causes extensive volatilization of zinc in the form of ZnCl_2 . All fuel gases contain some hydrochloric acid, under reducing conditions. Zinc chloride (ZnCl_2) has a boiling point of 1005 °K (732 °C); whereas, manganese chloride (MnCl_2) has a boiling point of 1504 °K¹⁵ (1231 °C). The higher boiling point of manganese makes it much less susceptible to volatilization and losses from the sorbent than zinc. Losses of zinc as high as 5-10% by weight from the exit of a fixed-bed reactor have been reported,¹⁴ even after one cycle of loading and

regeneration. It follows that any gas system which is used as an environment for comparing the cyclic loading and regeneration behavior between manganese oxide and zinc-based sorbents should take into account the presence of chlorides in the fuel gases.

A fortuitous feature of the manganese-oxygen-sulfur system is its resistance to reduction to elemental manganese under the range of most of the fuel gas compositions for which it would be utilized as a sorbent. Furthermore the sulfidation and regeneration can be carried out at the same temperature, for example (800 °C) without the formation of sulfates. Another favorable feature of the manganese-oxygen-sulfur system is its resistance to fusion as a result of temperature rises which may occur in the exothermic step of regeneration since the system is relatively refractory and non-volatile (i.e., lacks low melting-point phases) even in the presence of trace chloride impurities. For the case of zinc ferrite, it was found that temperature excursions as small as 50 °C could destroy the sorbent reactivity.¹⁶ Exit gas temperatures from commercial gasifiers are likely to be in excess of 650 °C; in addition, operation of the desulfurization process at higher temperatures increases the overall IGCC plant efficiency. Manganese-based pellets appear to be capable of much higher temperatures of loading and regeneration than zinc without degradation; however, this question remains to be fully explored.

4.6 Summary and Conclusions

Four sorbent formulations have been prepared using Moanda ore and manganese carbonate as starting materials in combination with alumina. Both dextrin and bentonite have been employed as bonding materials for pellet formation; however, dextrin, which appears to produce favorable porosity and is volatilized upon induration is a preferred binder. All pellets made met strength requirements. The carbonate required an induration temperature of 1250 °C;

whereas, the oxide (ore) required an induration temperature of 1200 °C.

Single loading tests via TGA analysis at temperatures ranging from 700 to 1000 °C show that the manganese carbonate source material bonded with bentonite exhibits the best combination of loading capacity and kinetics. The manganese ore-based formulation (FORM1-A) exhibited the best combination of sulfidation capacity, kinetics, and strength. Both formulations, however, are deemed to be successful in reducing the H₂S concentration in the coal-derived fuel gas to less than 150 ppmv.

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Figure 4.1 Oxygen potential diagram for the Mn-O system showing lines of constant CO_2/CO ratios.

Figure 4.2 Equilibrium H_2S concentration in desulfurized gas as a function of temperature for typical air-blown and oxygen-blown gasifiers.

Figure 4.3 Schematic of the ASTRO thermogravimetric (TGA) apparatus.

Figure 4.4 Normalized weight vs time for reduction and sulfidation of four manganese-based formulations at 1000 °C in a 3% H_2S - H_2 gas mixture.

Figure 4.5 Normalized weight vs time for reduction and sulfidation of four manganese-based formulations at 900 °C in a 3% H_2S - H_2 gas mixture.

Figure 4.6 Normalized weight vs time for reduction and sulfidation of four manganese-based formulations at 800 °C in a 3% H_2S - H_2 gas mixture.

Figure 4.7 Effect of temperature on sulfidation kinetics of FORM4-A pellets.

Figure 4.8 Effect of H_2S concentration on sulfidation kinetics of FORM4-A pellets at $T = 900\text{ }^{\circ}\text{C}$.

Figure 4.9 Effect of pellet diameter on sulfidation kinetics of FORM1-A sorbent at $T = 900\text{ }^{\circ}\text{C}$.

Figure 4.10 Representation of a reacting Mn-based sorbent pellet when rate controlling steps are: a) diffusion through the gas film, b) diffusion through the product layer, and c) surface reactions

Figure 4.11 Reaction rate data for sulfidation of 4.8-mm diameter FORM4-A pellets at 800, 900, and 1000 °C, plotted according to equation (4.5) for diffusion through product layer control

Figure 4.12 Effective diffusivity (D_e) dependence on temperature (i.e., Arrhenius plot.)

Figure 4.13 Comparison of sulfidation kinetics via thermogravimetric analysis of FORM4-A Mn-based pellets and L-3140 Zn-based sorbents.

**CHAPTER V: DESULFURIZATION OF HOT COAL-DERIVED FUEL GASES
WITH MANGANESE-BASED REGENERABLE SORBENTS.
2. REGENERATION AND MULTICYCLE TESTS**

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Desulfurization of Hot Coal-Derived Fuel Gases with Manganese-Based Regenerable Sorbents. 2. Regeneration and Multicycle Tests

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In a previous paper, the reduction and sulfidation thermodynamic and kinetic characteristics of four manganese-based high-temperature desulfurization sorbents were investigated. A formulation, FORM4-A, which consisted of Mn carbonate, alundum, and bentonite exhibited the best combination of capacity and reactivity; whereas, FORM1-A, which consisted of Mn ore, alundum, and dextrin exhibited the best combination of strength, capacity, and reactivity. In this paper the thermodynamic feasibility of regeneration is discussed. The kinetics of regeneration of sulfided (loaded) pellets with air is studied in the 800 to 1000 °C temperature range. Repeated cycling of the leading sorbent formulation (FORM4-A) was then conducted in a thermogravimetric apparatus (TGA), up to 5 consecutive cycles. One important finding was that the capacity of the pellets for sulfur pickup from fuel gas and the kinetics of reduction, sulfidation, and regeneration improved with recycling without compromising the strength. This appears to be a result of radial micro-crack formation which reduced the solid-state diffusion path within the pellet.

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5.1 Introduction

Current methods for the conversion of chemical energy to electrical energy tend to be cumbersome, wasteful, and environmentally unsound. In a typical system, depicted in Figure 5.1, coal is burned in a boiler to generate steam which passes through a turbine to drive a generator and produce electricity. This process wastes more than 60% of the energy originally present in the coal.¹ Energy is also lost in transmitting the generated electricity through power lines to users causing the process to be, overall, only 30 to 35% efficient. In addition, solid waste streams are generated and must be disposed of in increasingly expensive landfill space.

Stricter government regulations on pollutant emissions and the need to improve process efficiency led to the development of advanced power generation systems. For example, in the Clean Air Act of 1990 legislation is directed toward cleanup of coal gases by development of processes for removal of sulfur and particulates from coal combustion products. Since such cleanup is expensive, more efficient utilization of coal is required to offset these costs. One approach toward the more efficient use of coal is via combustion in gasification processes to produce a fuel gas which can be used in combined cycle operations in which a gas turbine utilizes the gasifier product; however, to achieve maximum efficiency by this approach, the fuel gases should not be cooled to remove sulfur, but rather, they must be desulfurized when still hot to conserve their sensible heat. Another approach is directed toward the development of processes in which coal gases can be used directly in fuel cell applications to avoid the inefficiencies inherent in the Rankine cycle (conversion of heat into electricity). In this latter application, sulfur must be removed from the gasification products to avoid deterioration of the cell. An approach to cleanup of gasification products which conserves their sensible heat is to contact the hot coal gases with a sorbent capable of removing the sulfur.

Emerging technologies which are reaching the commercial stage include the integrated gasification combined cycle (IGCC), the molten-carbonate fuel cell (MCFC), and the pressurized fluidized-bed combustor (PFBC). These technologies are principally based on coal gasification, i.e. the production of gaseous fuels from coal. During gasification, coal containing carbon, hydrogen, and oxygen, as well as impurities such as sulfur, nitrogen, ash, and trace metals reacts with steam and either air or oxygen to produce a fuel gas. To obtain the desired product, gasifier operating conditions must be carefully controlled. The proportion of the various gaseous components exiting the reactor (CO , H_2 , CH_4 , N_2 , etc.) is influenced by the type of coal, the composition of the feed gases (steam + air/oxygen), the type of reactor (fixed-bed, fluidized-bed, or entrained flow), and operating conditions (temperature, equivalence ratio,^{2,3} flow, and pressure). The compositions of some commercially-produced fuel gases were previously reported.⁴

One of the most promising and attractive new technologies being considered by the electric utility industry is the IGCC process.⁵ A configuration of

an ideal* system is depicted in Figure 5.2. In this emerging technology the mixture of carbon monoxide and hydrogen produced through gasification is burned; the very hot exhaust is routed through a gas turbine to generate electricity; and the residual heat in the exhaust is used to boil water for a conventional steam-turbine generator thus producing more electricity. In a coal gasifier, unlike coal combustion processes, the sulfur in coal is released in the form of hydrogen sulfide, H_2S , rather than sulfur dioxide, SO_2 . The IGCC process must employ hot gas cleanup techniques to remove sulfur and other impurities in the fuel gas stream, principally to meet stringent government regulations for sulfur emissions and also to protect turbine components from the corrosive action of H_2S . The H_2S should be removed by purifying the product gas while it is still hot so that the gas can be used directly without loss of heat values. This completely eliminates the more costly, less efficient method of low-temperature, liquid-based, fuel gas scrubbing systems. In addition, since the volume of the fuel gas stream is a lot smaller than that of the flue gas stream, the removal of H_2S at high temperature results in considerably lower hardware costs than would be required by a conventional SO_2 scrubbing method at low temperature.

The focus of current work being performed by the Morgantown Energy Technology Center (METC) of the Department of Energy (DOE) on hot coal-derived fuel gas desulfurization is primarily in the use of zinc ferrite and zinc titanate sorbents; however, prior studies by Turkdogan and Olsson⁶ indicated that an alternate sorbent, manganese dioxide-containing ore in mixture with alumina, may be a viable alternative to zinc-based sorbents. Manganese, for example, has a significantly lower vapor pressure in the elemental state than zinc hence it is not as likely to undergo depletion from the sorbent surface upon loading and regeneration cycles. Also manganese oxide is less readily reduced to the elemental state than iron hence the range of reduction potentials for oxygen is somewhat greater than for zinc ferrite. A more thorough comparison of Mn-based sorbents and Zn-based sorbents has been given by Ben-Slimane and Hepworth.⁴ In addition, the following thermodynamic analysis of the manganese-sulfur-oxygen (Mn-S-O) system shows it to be much less amenable to sulfation than zinc-based sorbents. Potential also exists for utilization of manganese at higher temperatures than zinc ferrite or zinc titanate which would boost the efficiency of power generation from coal.

In a previous paper,⁴ the thermodynamic feasibility for the use of manganese-based sorbents for the removal of hydrogen sulfide (H_2S) from hot coal-derived fuel gases was established. Screening sulfidation tests were carried out on individual sorbent pellets via thermogravimetric analysis (TGA). It was concluded that sorbents prepared with the organic binder, dextrin, on Moanda manganese ore offered the best combination of strength, reactivity, and capacity.

* An ideal IGCC system is one in which there are *no* designed changes in gas pressure or temperature as the gas flows through the system.

Sorbents prepared with bentonite on manganese carbonate possessed the best combination of capacity and reactivity. The loading characteristics of these two leading Mn-based pellets were shown to be superior to those obtained using Zn-based sorbents.

Economics dictates that the sulfur sorbent employed be regenerable, i.e. the loaded sorbent may be restored to its original (fresh) condition. The regeneration step is indicated on Figure 5.2 as a process in parallel with the hot gas desulfurization step. In this paper, the feasibility of regeneration of manganese-based pellets is discussed from thermodynamic considerations. Experimental tests, utilizing the best formulation, FORM4-A, were carried out to study the kinetics of regeneration. The reaction parameters which were varied included temperature and oxygen content in O₂-N₂ gas mixtures. Repeated sulfidation and regeneration tests were then carried out to investigate the effect of pellet recycling on its chemical reactivity, physical durability, and capacity for sulfur pickup from fuel gases.

5.2 Thermodynamic Considerations

The goal of regeneration is to restore the loaded (sulfided) sorbent to its original fresh condition. Hence, regeneration involves the oxidation of manganese sulfide to manganese oxide using an oxidizing gas. Regeneration conditions (temperature and nature of regeneration gas) must be carefully controlled to maintain the reactivity and physical durability of the sorbent pellets. Excessive temperatures may lead to sintering, causing the pellet reactivity to diminish considerably through substantial loss of porosity. Relatively low temperatures and the presence of SO₂ in the regeneration product gas may lead to sulfate formation. Sulfation must be avoided because once sulfate is formed, its decomposition is slow. In addition to the above restrictions, the SO₂ concentration in the regeneration product gas must be high enough to meet the requirement of a sulfuric acid plant ($\approx 6\%$ SO₂ by volume).

Sulfur sorbents may be regenerated after sulfidation by reacting the sulfide with H₂O-containing gas mixtures. This is desirable because, in the case of zinc ferrite or zinc titanate, for example, steam addition provides a highly effective oxygen diluent to limit the maximum sorbent temperature reached during regeneration.⁵ If the regeneration gas consisted of pure H₂O or CO₂, the regeneration of Mn-based pellets may be represented by the following reactions:

However, these two routes may be thermodynamically unlikely and also not practical because of the low SO₂ concentration in the product gases.

The regeneration of MnO must be oxidative, i.e. involving air, pure oxygen, oxygen-enriched air, oxygen-deficient air, or SO₂-O₂ mixtures. Further discussion

of regeneration thermodynamics must thus be made with reference to the phase equilibria in the Mn-S-O system in the temperature range of interest. Figure 5.3 is a stability equilibrium diagram for the Mn-S-O system at 800, 1000, and 1200 °C. The phase equilibria among the various solid compounds involved are shown as a function of the logarithms of the equilibrium partial pressures of two components in the gas phase, namely SO₂ and O₂. In this diagram each phase is stable within a predominance region, bordered by lines that represent the coexistence with other phases.⁷ The slope of each curve is determined by the stoichiometry of the corresponding reaction. As the temperature increases, the equilibrium lines shift up and to the right, further constricting the region of stability of the sulfate.

The effect of temperature is best displayed by plotting Log(P_{O₂}) versus reciprocal temperature at constant SO₂ partial pressure, as shown in Figure 5.4. In this figure the solid lines are for P_{SO₂} = 1 atm and the dashed lines are for P_{SO₂} = 0.14 atm. This latter value was selected because it represents the maximum SO₂ partial pressure attained during the early stages of regeneration with air. As the SO₂ partial pressure decreases, the regions of oxide stability expand while those of the sulfide and sulfate diminish. It is also clear that MnO/Mn₃O₄ and Mn₃O₄/Mn₂O₃ equilibria are independent of the SO₂ partial pressure, as expected. Theoretical guidelines may be deduced from Figure 5.4 to avoid the possibility of sulfate formation during regeneration. For example, for a regeneration product gas containing 10% SO₂, it can be shown that sulfate formation is not thermodynamically feasible above approximately 915 °C. The location of this operating point on the diagram is marked with a circle and is probably the lowest possible temperature to avoid sulfate formation.

The regeneration reaction proceeds initially according to the following reaction:

Then MnO is readily converted to Mn₃O₄ because of the availability of O₂ in the gas:

Consequently, under these conditions the overall regeneration reaction is given by

The above reaction is thermodynamically favorable and proceeds essentially to completion in the temperature range 800 to 1200 °C. Thus, the

oxygen in the reactant gas is virtually converted to SO_2 . The regenerated manganese oxide would be in the form of Mn_3O_4 which would be immediately reduced to MnO upon exposure to the hot reducing fuel gas during the sulfidation stage. The maximum temperature of both sulfidation and regeneration may be as high as 1232°C , the eutectic temperature of the pseudo-binary MnO-MnS system.⁶

It should be noted, however, that the oxidative regeneration of the oxide is highly exothermic. Reaction (5.5), for example, has a heat of reaction of -527.2 kJ per mole of MnS reacted in the temperature range 900 to 1200°C .⁸ Accordingly, practical problems may be encountered in the control of the reactor temperature. Turkdogan and Olsson⁶ suggested that this may be overcome by using a $\text{CO}_2\text{-H}_2\text{O-O}_2$ gas mixture where, in addition to the exothermic oxidation of MnS by O_2 , a number of endothermic reactions may occur. By appropriate adjustment of the composition of the feed gas $\text{CO}_2\text{-H}_2\text{O-O}_2$, it is possible to control the reactor temperature at the desired level during regeneration. Consequently, a thermodynamic model was developed to calculate the composition of the feed gas for the operation of the reactor at a desired temperature of regeneration with an exhaust gas containing sufficient SO_2 for recovery in the sulfuric acid plant. This was done by combining SOLGASMIX⁹ and THERBAL,¹⁰ mass balance and heat balance software packages, respectively. The calculation procedure using these computer programs is outlined in Figure 5.5. The gaseous species considered include N_2 , CO , CO_2 , H_2O , H_2 , H_2S , S_2 , COS , SO_2 , SO_3 , O_2 , S , S_4 , SO , CS , CS_2 , NO , NO_2 , CH_4 , and NH_3 . Pure oxygen or air is added to the product gas above the bed to convert all sulfur-bearing species to SO_2 . At the same time, the H_2 and CO present are oxidized so that the final product gas contains only SO_2 , H_2O , and CO_2 . With the assumption of complete equilibrium in the reactor, the calculated data in Figure 5.6, for the feed gas preheated to 800°C and regeneration carried out isothermally at 1100°C , give the concentration of SO_2 in the product gas (wet and dry basis) as a function of the composition of the feed gas. The additional amount of oxygen needed for complete combustion of the regeneration product gas above the bed is also given. Similar plots may readily be made for other combinations of preheat and regeneration temperatures.

The above thermodynamic model is useful in making predictions which may be essential prior to the design of a regeneration reactor. For example, it may be estimated that for a feed gas at 800°C containing equimolar amounts of CO_2 and H_2O , the composition of the feed gas required to maintain the regeneration isothermal at 1100°C is 6.08% O_2 , 46.96% (i. e., $[100-6.08]/2$) CO_2 , and 46.96% H_2O . In addition, the diagram shows that to ensure complete combustion of the regeneration product gas, 2.59 mols of O_2 per 100 mols of feed gas (or 2.52%) must be added in the after burner above the bed. The final regeneration product gas will contain 11% and 5.78% SO_2 on a dry and wet basis, respectively. Both of these SO_2 concentrations satisfy the requirements of a typical sulfuric acid plant.

5.3 Experimental Investigations and Results

The test work reported here was directed to formulation FORM4-A which was shown to possess the most favorable loading characteristics of the four formulations selected for screening sulfidation tests. This formulation is made up of 81.31% by weight manganese carbonate (containing 93-95% MnCO_3), 16.73% alundum (containing 96.6% Al_2O_3), and 1.96% bentonite (an inorganic binder). Upon forming pellets, they were first dried to a constant weight at 110 °C, then heated to 350 °C to allow for dissociation of the manganese carbonate.* They were then heated to 1250 °C and indurated for 2 hours in an air atmosphere before removal from the furnace. The average size of the pellets was 4.8 mm and they had an average strength of 23.8 N/mm of diameter (5.4 lbs/mm). The final manganese assay of the indurated pellets was 44.22% by weight, which corresponds to a theoretical sulfur capacity of 25.8%, i.e., 25.8 gS/100g of indurated pellet.

5.3.1 Regeneration Tests

The equipment used in the thermogravimetric (TGA) experimental work has been previously described in detail.⁴ The TGA tests focused on studying the effects of regeneration parameters (temperature and O_2 content) and on repeated loading and regeneration of the selected FORM4-A pellets. Since up to fifteen pellets may be used in each reduction/sulfidation test, various tests were needed to provide enough fully-loaded pellets for the various regeneration tests planned. This provided an opportunity to determine the reproducibility of the sulfidation tests. The reduction and sulfidation were carried out under standard conditions of 950 °C and 3% $\text{H}_2\text{S-H}_2$ gas mixtures at 500 cc/min delivery for a total of approximately 2 grams of pellets. Reduction was carried out with pure hydrogen for the first 45 minutes and then the hydrogen sulfide was added.

Figure 5.7 shows the reproducibility of loading tests resulting from five separate tests on fresh pellets (i.e., first loading cycle) at 950 °C with 3% by volume hydrogen sulfide in hydrogen. This figure gives the error bars on the data to indicate the range of the results. In all subsequent figures, W_0 refers to the mass of the indurated pellet and W to the mass of the reacting pellet as a function of time. Although not shown for the reduction portion of the curve the reproducibility is particularly good, with reduction essentially completed in fifteen minutes. Figure 5.7 shows that deviations in extent of loading occur even though during each test the macroscopic properties (mass and size) of the pellets were kept as constant as possible. These deviations may be due to the difficulty associated with controlling temperature, flow rates, etc. However, the reproducibility of sulfidation is excellent beyond the first 30 minutes after the initial reduction period (total lapse time of 75 minutes). The solid line represents the average values and therefore serves as an indication for future test results.

A total of five regeneration tests were then carried out using five pellets

* MnCO_3 dissociates to MnO and CO_2 at 343 °C with CO_2 evolving at 1 atm.

during each test. The regeneration gas was air flowing at 500 cc per minute and regeneration temperature varied between 800 and 1000 °C in increments of 50 °C. The purpose was to determine the temperature at which loaded pellets could be fully regenerated in reasonable time. The results from these tests are reported in Figure 5.8. The loading curve corresponds to the solid line shown in Figure 5.7; however, the right-hand portion of this figure shows the regeneration portion after a total time lapse of 165 minutes. These results appear to be in strict accordance with thermodynamic predictions which were outlined above, viz.: at 800 °C the loaded pellets first oxidize (and hence lose weight) for about 3 minutes at which time sulfation with an concurrent weight gain becomes predominant. When approximately 60% of the MnS is converted to MnSO_4 , sulfate decomposition starts and the pellets begin to show a weight loss. Continuing at higher temperatures, at 850 °C, the same trend is observed; however, the oxidation of the pellets appears to be faster than sulfation; this is reasonable since the driving force for the decomposition of sulfate is greater. Regeneration kinetics appear to be a weak function of temperature over the range 900 to 1000 °C. In this range regeneration is essentially complete in 10 to 15 minutes and sulfation does not occur, as concluded from the prior thermodynamic analysis of the Mn-S-O system. It must be noted, however, that full regeneration (i.e., $W/W_0 = 1$) apparently requires a temperature of 1000 °C or higher.

Figure 5.9 shows the effect of oxygen content in N_2 /air gas mixtures on regeneration kinetics for four oxygen levels: 5, 10, 15, 21% (air) by volume. Even for the lowest oxygen level, the flow rates and mass of samples were chosen so that the rate of gas delivery was not rate-limiting. The results are as expected, with the regeneration rate increasing with the O_2 content of the regeneration gas. It appears that a duration of 10 minutes is required for full regeneration with air, while at the 5% O_2 level the reaction is essentially complete in 50 minutes. These results are of consequence to the operation of a fixed-bed where temperature control may be essential to prevent overheating and resulting sintering and deterioration of pellet reactivity during regeneration.

5.3.2 Multicycle Tests

Over a five-day period, one loading and regeneration cycle was completed each day at 950 °C for reduction and sulfidation and 1000 °C for regeneration. The TGA data for these five tests are shown in Figure 5.10. The arrows show the direction of increasing cycle sequence numbers, i. e. for loading, the capacity and reaction kinetics improve for each of the five cycles with the change between the first and second cycles being the most pronounced. For the tail of the curve terminating the regeneration step, the weight loss drop is steepest for the fifth cycle: again showing that the rate of regeneration increases with pellet re-use. An optical examination at 30 magnifications with a binocular microscope as well as petrographic thin sections examined at 100x showed the presence of radial cracks. The penetration distance of the sulfur as exhibited by the higher reflectivity of the manganese sulfide phase was densest adjacent to these cracks, indicating that the

diffusion distance for permeation of sulfur (and counter-transport of oxygen) was decreased by the change in diffusion geometry occasioned by the cracking. Whereas the original pellet experiences diffusion for a gross pellet size of ≈ 2.5 mm in radius; upon cracking of the pellet, the solid-state diffusion distance is somewhat reduced. This permits gaseous species to be transported by the relatively faster mechanism of gaseous diffusion into the cracks compared with the slower process of solid state counter diffusion of oxygen out of the pellet to exchange for sulfur into the pellet. This diffusional kinetics will be developed subsequently.

This is a unique feature of manganese-based pellets, i. e. their retained strength upon micro-cracking and improved kinetics compared with competing sorbents, e. g., zinc titanate, in which the reaction kinetics and sorbent loading capacity and pellet strength decrease upon cyclic loading.

5.3.3 Discussion

The results reported here and in a previous paper⁴ relate to the use of manganese-based sorbent pellets for the desulfurization of H_2S - H_2 gas mixtures in the 700 to 1000 °C temperature range, and the subsequent regeneration of the loaded pellets with air. It must be noted that the use of a very aggressive reduction period (in pure H_2) is intended to ensure complete reduction of Mn_3O_4 to MnO ; the reduction of MnO to elemental Mn is not feasible, as was previously explained in detail⁴. The use of an H_2S plus H_2 mixture may seem unrealistic as a process simulation, and further work should be carried out to see if the same results could be obtained with a different gas mixture that approximates more closely the composition of a coal-derived fuel gas. The authors realize that currently there is very limited incentive for desulfurization at temperatures much above 900 °C due mainly to the difficulty of maintaining low alkali content in the fuel gas fed to the gas turbine. At higher temperatures a significant portion of the alkali is in the vapor phase and not easily removed from the gas; whereas at lower temperatures most of the alkali will have condensed on entrained particulate and thus, removing the dust also significantly lowers the alkali content. In addition, current gas turbine fuel flow control valve technology is well below 900 °C and extending it above 800 °C is regarded as a major challenge by the industry.

Both the desulfurization and regeneration processes should desirably be carried out at a level somewhat above gas turbine combustor pressures so that further and very significant equipment cost savings can result. Since the regeneration process must take place above 900 °C (which is reasonable) and since the overall oxidation reaction is highly exothermic, the ability to efficiently recover the released heat of regeneration offers a potential system performance enhancement. This is particularly true if a so-called after-burner becomes part of the regeneration process. The ability to accomplish this heat recovery is also normally improved to the degree the sorbent's crush strength is improved (e.g., producing an ability to use fluidized beds and enhanced sorbent/heat transfer

media or surface contacting).

While the results reported in this paper are obtained using thermogravimetric (TGA, widely recognized as a good research tool) testing on small batches of pellets, practical processes aim to minimize required reactor and sorbent volume. This translates to the processes of most potential interest having a need to "move" the sorbent in some fashion between the desulfurization and regeneration vessels. Consequently, both the crush strength of the sorbent and its sorption capacity after repeated cycling are of critical interest. Normally, and especially in the Zn-based sorbents, the onset of small cracks leads to sorbent spalling and reduced usable life (due to increased "dust" loadings in an exit gas stream). With the manganese-based sorbents the presence of these small cracks apparently led to improvement in the reaction rate for sulfidation and regeneration without adversely affecting the strength. At the conclusion of each of the five consecutive cycles reported earlier, the weight of the regenerated pellets was almost identical to the original weight of pellets indicating that no spalling took place. In addition, the crush strengths of five separate pellets ranged from 21.2 to 23.6 N/mm of pellet diameter (4.8 to 5.2 lbs/mm).

5.4 Kinetic Considerations

Previously,⁴ the shrinking-unreacted core model was found to approximate the kinetic behavior of Mn-based sorbent pellets during the sulfidation stage. Rate equations (time-fractional conversion) were derived for diffusion through gas film control, diffusion through product layer control, and surface reaction control. Kinetic analysis of thermogravimetric experimental data determined that beyond approximately 35% reaction completion, the sulfidation rate was controlled primarily by countercurrent diffusion through the porous MnS product layer.

The regeneration reaction is irreversible; in addition, its highly exothermic nature makes it even more likely to be controlled by countercurrent diffusion of oxygen and sulfur through the porous Mn_3O_4 product layer. For these reasons, only the derivation of the equation when diffusion through product layer is rate-limiting is deemed worthwhile. As was established in the previous thermodynamic analysis, the overall regeneration reaction is represented by equation (5.5). The symbols used in the following equations and their units are as follows: t : time (s); J : total molar flux ($\text{mol}/\text{cm}^2\text{-s}$); J_i : molar flux of gaseous component i ($\text{mol}/\text{cm}^2\text{-s}$); D_e : effective diffusivity (cm^2/s); C_i : molar concentration of gaseous component i (mol/cm^3); r : arbitrary position within radius of pellet (cm); y_i : mole fraction of component i in the gas phase (dimensionless); F_{MnS} : fractional conversion of MnS in loaded pellet (dimensionless); P : total pressure (atm); R : universal gas constant ($\text{cm}^3\text{-atm}/\text{mol}\text{-}^\circ\text{K}$); T : absolute temperature ($^\circ\text{K}$); ρ_{MnS} : molar density of component MnS in pellet (mol/cm^3); R_p : radius of loaded or sulfided pellet (cm); superscript e : equilibrium value of parameter; superscript o : initial value of parameter; P_i : partial pressure of gaseous component i (atm); and C_i : constant of integration.

The molar flux of O_2 through the newly-formed Mn_3O_4 layer is expressed by Fick's law, as follows:

The first term on the right-hand side of the above equation is termed molecular

$$J_{O_2} = -D_s \frac{dC_{O_2}}{dr} + y_{O_2} J \quad (5.6)$$

diffusion flux and is produced by a concentration gradient; the second term represents the flux resulting from the bulk motion of the regeneration gas. J is the total flux, and is given by:

$$J = J_{O_2} + J_{SO_2} \quad (5.7)$$

From the stoichiometry of the overall regeneration reaction, the following relation applies:

$$J_{SO_2} = -\frac{3}{5} J_{O_2} \quad (5.8)$$

Substituting for J in terms of J_{O_2} in equation (5.6) and rearranging, we get:

$$\left(1 - \frac{2}{5} y_{O_2}\right) J_{O_2} = -D_s \frac{dC_{O_2}}{dr} \quad (5.9)$$

Using mass balance considerations, it can be shown that:

$$3 - 2F_{MnS} - 3(1 - F_{MnS})^{2/3} = \frac{9D_s P}{RT \rho_{MnS} R_p^2} \ln \left[\frac{5P - 2P^*_{O_2}}{5P - 2P^0_{O_2}} \right] t + C_1 \quad (5.10)$$

The rate data for the regeneration reaction of FORM4-A pellets with air at 1000 °C are plotted in Figure 5.11 in accordance with equation (5.10). The results follow the limiting rate equation closely, indicating that diffusional product layer is present and controls the rate of reaction. Also shown in Figure 5.11 are rate data for the sulfidation reaction at 1000 °C (with 3% H_2S - H_2 as previously described). For example, for a 90% reaction completion, the sulfidation reaction requires about 30 minutes; whereas, regeneration requires about 10 minutes.

5.5 Summary and Conclusions

Sorbent pellets composed of high purity manganese carbonate, alundum, and bentonite as a binder were found to be potentially highly effective for the removal of sulfur from simulated fuel gases at high temperature (800 to 1000 °C). These sorbents were also found to be capable of being regenerated after sulfidation by reacting the sulfide with air or oxygen-deficient air. Pellets which underwent loading and regeneration over five consecutive cycles showed a slight improvement in capacity and reaction kinetics. This unique phenomenon is attributed to the formation of radial cracks which reduced the diffusion distance required for transport of sulfur into the pellet and oxygen out of the pellet. These cracks did not have a significant effect upon pellet strength which continued to be

no less than 21.2 N/mm of pellet diameter (4.8 lbs/mm). Although the pellets may be loaded at temperatures below 800 °C, regeneration must be accomplished above 900 °C to avoid sulfate formation.

5.6 References

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Figure 5.1 Schematic of a conventional power generation system with pre- and post-combustion physical and chemical cleaning.

Figure 5.2 Schematic of an ideal integrated gasification combined cycle (IGCC) system.

Figure 5.3 Predominance area diagram for the Mn-S-O system at 800, 1000, and 1200 °C.

Figure 5.4 Effect of temperature on phase equilibria in the system Mn-S-O at constant SO_2 partial pressure. $P_{\text{total}} = 1 \text{ atm}$.

Figure 5.5 Schematic of heat and mass balance calculations on the isothermal regeneration of manganese oxide from sulfide.

Figure 5.6 SO_2 content of regeneration product gas (on wet and dry basis) as a function of feed gas composition. Regeneration gas is fed at 800°C and regeneration is carried out at 1100°C .

Figure 5.7 Reproducibility of loading tests at 950 °C with 3% H_2S-H_2 gas mixtures showing average value and error bars.

Figure 5.8 Effect of temperature on regeneration kinetics of FORM4-A Mn-based pellets. Reduction and sulfidation were carried out at 950°C in H_2 and $3\% \text{H}_2\text{S}-\text{H}_2$ gas mixtures, respectively.

Figure 5.9 Effect of O_2 concentration in $\text{O}_2\text{-N}_2$ gas mixtures on regeneration kinetics of FORM4-A pellets at $1000\text{ }^{\circ}\text{C}$.

Figure 5.10 Effect of repeated cyclical loading and regeneration on the reaction kinetics and capacity of FORM4-A pellets.

Figure 5.11 Reaction rate data for sulfidation and regeneration of FORM4-A pellets at 1000 °C.

**CHAPTER VI: DESULFURIZATION OF HOT COAL-DERIVED FUEL GASES
WITH MANGANESE-BASED REGENERABLE SORBENTS.
3. FIXED-BED TESTING**

This chapter is a slightly edited version of a paper to be submitted for review to the American Chemical Society Journal "Energy & Fuels."

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Desulfurization of Hot Coal-Derived Fuel Gases with Manganese-Based Regenerable Sorbents.

3. Fixed-Bed Testing

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In recent studies, the thermodynamic feasibility of using manganese-based sorbent pellets for the removal of H_2S from hot-coal derived fuel gases, and the subsequent regeneration of loaded (sulfided) pellets with air was established. Screening sulfidation tests on a number of formulations, consisting of a manganese-containing compound (ore or $MnCO_3$), alundum (Al_2O_3), and organic or inorganic binders, were carried out using H_2S - H_2 gas mixtures in a thermogravimetric apparatus (TGA) at temperatures ranging from 700 to 1000 °C. A formulation, designated FORM4-A, was found to possess the best combination of sulfur capacity, reactivity, and strength. Regeneration tests determined that for $T \geq 900$ °C, loaded pellets can be fully regenerated with air in 10 to 15 minutes, without sulfate formation. This paper reports on fixed-bed testing of the leading Mn-based sorbent pellet formulation (i.e., FORM4-A). Experiments are carried out to test the long-term durability and regenerability of the sorbent using a simulated Tampella-U fuel gas for sulfidation and air for regeneration. In addition, the effect of temperature on sulfidation reaction equilibrium is determined in the range 800 to 1000 °C. A re-assessment of the equilibrium states of reactions involving solid MnO , MnS , Mn_3O_4 , and $MnSO_4$ is then presented based on the results obtained and a recent study by Turkdogan.

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6.1 Introduction

The rationale for desulfurizing coal-derived fuel gases at high temperature is a result of concerns within the U. S. Department of Energy to burn coal to produce electrical power more efficiently and also to meet government regulations for sulfur emissions which have become progressively more stringent. Conventional technology of power generation is inherently inefficient and consists of reacting coal in a burner system which exchanges heat to a boiler to generate steam. This steam then passes through a turbine to drive a generator and produce electricity. The sulfur in the coal is released in form of sulfur dioxide (SO_2) in the flue gas. The removal of SO_2 from the flue gas prior to discharge into the atmosphere is essential to prevent air pollution mainly in the form of acid rain. Conventional processes for sulfur recovery are well established and require that the coal gas be cooled to less than 100°C in order to contact it with scrubbing reagents.

The loss of thermal efficiency in the cooling process lowers the energy available for electrical conversion compared with the higher efficiencies which would be obtained if the coal gas were desulfurized while hot. In addition, since the volume of the fuel gas stream is significantly less than that of the flue gas stream, the removal of sulfur-bearing species at high temperature results in considerably lower hardware costs than would be required by a conventional SO_2 scrubbing method at low temperature; also, conventional scrubbing results in the formation of gypsum sludge, which requires costly management. A regenerable sorbent avoids this problem since the sulfur can be recovered as sulfur dioxide or other sulfur products. The cleaned hot fuel gas may then be useful in a number of applications such as an integrated gasification combined cycle (IGCC), an emerging energy conversion system to produce electrical power at higher efficiencies than those experienced in conventional steam plants. Power generation may also be rendered more efficient by ultimately by-passing Rankine efficiencies completely and using the generated fuel gases in fuel cells for the direct conversion of heat into electricity. With increasing international concern over the green-house effect, fuel cells have the added advantage of potentially reducing emissions of carbon dioxide from power plants by factors ranging from two- to three-fold.¹ The problem with operation of fuel cells or IGCC systems, which are principally based on coal gasification, is that sulfur must be removed at high temperature to prevent its corrosive effects.

For the reducing conditions which are encountered in gasifiers operating on coal combustion systems, the predominant sulfur-bearing gaseous species is H_2S .^{2,3,4} The conventional technology of scrubbing the gas for H_2S is not practical in these situations because the scrubbing processes operate at low temperature and, therefore, impose a severe thermal penalty, because thermal efficiencies are directly dependent upon the difference in temperature between the process heat and the heat sink. Thus the IGCC process must employ hot-gas cleanup techniques to remove sulfur and other impurities in the fuel gas stream. This approach completely eliminates the more costly, less efficient method in which a

liquid-based scrubbing system is employed at low-temperatures for scrubbing the flue gas.

Desulfurization with sorbents is essentially a process of removal of the species H_2S from the gas phase. As H_2S is removed, the other minority sulfur-bearing species, such as COS, equilibrate in the gas phase and also are proportionately reduced.² The high temperature desulfurization can be successfully accomplished by using solid sorbents such as oxides of those metals that form stable sulfides. The effectiveness of a desulfurizing agent in treating coal gases is related to the predicted equilibrium partial pressure of sulfur which will be present in a phase combination of the reduced form of sulfide and oxide phases. A sulfur concentration limitation of approximately 150 ppmv (parts per million by volume) for IGCC systems has been established; therefore, a sorbent system capable of reducing H_2S concentration from about 5000 to 150 ppmv is sought.⁵ The focus of much current work on hot coal-derived fuel gas desulfurization is primarily in the use of zinc ferrite and zinc titanate sorbents. The choice of zinc oxide is typically based on the thermodynamic considerations that indicated very low concentration levels of H_2S in equilibrium with ZnO, ZnS, and H_2O vapor.⁶

To improve the process economics further, an easily regenerable sorbent is required which would not only reduce sorbent costs but also costs associated with frequent loading and unloading of the reactors with sorbent and disposal of the spent sorbent. Furthermore, the sulfur produced by regeneration of the sorbent should be recoverable in a form which is readily saleable or storable. This means that the regeneration step should be flexible and be able to produce elemental sulfur or sulfuric acid depending upon the demand at the location of the gasification plant. With these restrictions in mind, research has focused almost entirely on making the zinc-based sorbents durable. However, extensive research, carried out mainly by the Morgantown Energy Technology Center (METC), casts doubt that zinc ferrite or zinc titanate can be utilized even for the mild conditions associated with fixed-bed operation. The desirable properties of Zn-based sorbents as well as their practical limitations have been discussed in detail by Ben-Slimane and Hepworth.^{7,8}

Given the limited success of the zinc-based sorbents, interest has been shown in formulating and testing manganese-based sorbent pellets.⁹ The thermodynamic feasibility of using such sorbent pellets for the removal of H_2S from hot coal-derived fuel gases, and the subsequent regeneration of loaded (sulfided) pellets with air has been previously discussed in detail.^{7,8} Screening sulfidation tests on a number of formulations were carried out using H_2S - H_2 gas mixtures in a thermogravimetric apparatus (TGA) in the temperature range 700 to 1000 °C. These formulations consisted of a manganese-containing compound (ore or $MnCO_3$), alundum (Al_2O_3), and organic or inorganic binders. A formulation, FROM4-A as described below, was found to possess the best combination of sulfur capacity, reactivity, and strength. Regeneration tests were carried out on loaded pellets and determined that for $T \geq 900$ °C, FORM4-A

pellets could be fully regenerated with air in 10 to 15 minutes.

Repeated cycling of the leading sorbent formulation (FORM4-A) was conducted in the TGA apparatus, up to five consecutive cycles. One important finding was that the capacity of the pellets for sulfur pickup from fuel gas and the kinetics of reduction, sulfidation, and regeneration improved with recycling without compromising the strength. This desirable phenomenon was attributed to radial micro-crack formation which reduced the solid-state diffusion path within the pellet. Normally, and especially in the case of Zn-based sorbents, the onset of small cracks leads to sorbent spalling and reduced usable life due to increased "dust" loadings in an exit gas stream.¹⁰ With the Mn-based sorbents, the presence of these small cracks apparently led to improvement in the reaction rate for sulfidation and regeneration without adversely affecting the strength.

While the results reported earlier^{7,8} were obtained using thermogravimetry, the potential usefulness of Mn-based pellets may be more realistically assessed by simulating practical processes of fuel gas desulfurization, which fall into three main categories: fixed-bed, fluidized-bed, or moving-bed technology. This paper reports on fixed-bed testing of the leading Mn-based sorbent pellet formulation (i.e., FORM4-A). Experiments are carried out to test the long-term (up to 14 cycles) durability and regenerability of the sorbent using a simulated Tampella-U fuel gas for sulfidation and air for regeneration. In addition, the effect of temperature on sulfidation reaction equilibrium is determined in the range 800 to 1000 °C. A re-assessment of the equilibrium states of reactions involving solid MnO, MnS, Mn₃O₄, and MnSO₄ is then presented based on the results obtained and a recent study by Turkdogan.¹¹

6.2 Experimental Investigations and Results

6.2.1 Introduction

The procedures for sorbent pellet making, drying, and induration are fully documented in a recent patent application filed by the authors.¹² However, the test work reported in this paper is directed only to formulation FORM4-A which was shown to possess the most favorable loading characteristics of the four formulations selected for screening sulfidation tests. This formulation is made up of 81.31% by weight manganese carbonate (containing 93-95% MnCO₃), 16.73% alundum (containing 96.6% Al₂O₃ and 2.6% TiO₂), and 1.96% bentonite (an inorganic binder). Upon forming pellets, they were first dried to a constant weight at 110 °C, then heated to 350 °C to allow for dissociation of the manganese carbonate. The pellets were then heated to 1250 °C and indurated for 2 hours in an air atmosphere before removal from the furnace. The average size of the pellets was 4.8 mm and they had an average strength of 23.8 N/mm of diameter (5.4 lbs/mm). The final manganese assay of the indurated pellets was 44.22% by weight, which corresponds to a theoretical sulfur capacity of 25.8%, i.e.,

* MnCO₃ dissociates to MnO and CO₂ at 343 °C with CO₂ evolving at 1 atm.

25.8 gS/100g of indurated pellet.

6.2.2 Fixed-Bed System Description and Testing Procedures

The schematic diagram of the overall experimental arrangement for fixed-bed tests is shown in Figure 6.1. The split or two-zone furnace is positioned with respect to the bed to accomplish gas preheating and careful control of the bed temperature. Gas combinations for flows are produced via control of bottled gases through the valves and flowmeters shown in the diagram. The water content of the system is controlled by a metering pump acting on distilled water which is discharged into a heated stainless steel tube to induce the vaporization of liquid water and provide the gas composition required for the simulation of a slightly modified form of the Tampella-U gas (from a Tampella-U air-blown gasifier), as reported in Table 6.1. Hydrogen sulfide is mixed with the other gases and water vapor immediately before the introduction of the complete mixture into the reactor to minimize corrosion of system components. The reactive gas feed line was heat-traced to prevent subsequent condensation. In addition, the exhaust gas line was also heated from the top of the reactor to the cold trap to prevent any formation and subsequent freezing of elemental sulfur.

The primary modification made in the gas composition is an increase in the

Table 6.1 Gas Composition for the Simulation of the Tampella-U Fuel Gas.

Gas	Volume Percent
Hydrogen (H ₂)	13
Nitrogen (N ₂)	50
Carbon monoxide (CO)	24
Carbon dioxide (CO ₂)	5
Water vapor (H ₂ O)	5
Hydrogen sulfide (H ₂ S)	3

amount of H₂S, which is typically contained at about 1% by volume in Tampella U-gas. The modified composition included 3% by volume of H₂S to decrease the amount of time required to achieve "breakthrough", arbitrarily defined at [H₂S] = 500 ppmv in the exit gas. Tampella-U gas also contains 0.111% NH₃ and 1.84% CH₄, which are not taken into consideration in the present study.

The Tampella-U gas was selected for experimentation, in part, because of its relatively low water vapor content ($\approx$ 5% by volume). The extent of desulfurization attainable with a Mn-based sorbent is dependent on the water vapor content of the feed gas, i.e., lower water vapor content results in higher levels of desulfurization. In addition, the choice of a fuel gas having a low water vapor content should, actually, be indicative of the performance of the sorbent pellets because gasifier systems typically add water vapor to the exit gas stream to stabilize zinc oxide and render the desulfurization with zinc-based sorbents

possible. Also, in order to prevent carbon formation in the desulfurizer, a large quantity of steam must be added to the fuel gas. If a Mn-based sorbent is used, the water addition can be eliminated altogether, which would provide additional advantages as addition of water vapor poses two major disadvantages. First, the heating value of the exit gas is significantly reduced with the introduction of water vapor and, second, the volume of the gas is increased which requires corresponding increases in the size and cost of the equipment in the desulfurization system and other equipment downstream.¹³

The details of the fixed-bed reactor system are depicted in Figure 6.2. This figure shows the two-inch (I.D.) closed-end alumina reactor tube equipped with an alumina perforated-disc plate suspended over alumina chips. The coal-derived fuel gas simulating the Tampella-U gas is passed through a small central tube (without contacting the reaction zone of manganese-based pellets) through the perforated disc and into a preheat zone of alumina chips which supports the disc. The gas is then discharged from the small central tube into the larger tube and moves upward into a gas preheat zone of the two-zone furnace. The gas, now at the desired temperature, ranging from 800 to 1000 °C, then contacts the sorbent bed consisting of FORM4-A pellets ranging in size from 4 to 5 mm in diameter. The off-gas is then flared and passed through a cold trap to condense water vapor before being scrubbed in a sodium hypochlorite solution and then discharged into a hood. A gas sample is taken via a sampling bag prior to scrubbing and is analyzed for H₂S using detector tubes which have been calibrated using pre-mixed H₂S-N₂ gas mixtures. Detector tube readings were also checked by an independent wet chemistry method which consisted of determining the H₂S concentration in the exhaust gas by periodically bubbling the gas through an aqueous solution of lead acetate and measuring the quantity of material precipitated. In addition, feed and exit gas flowrates were calibrated using a wet test meter.

The fixed-bed was made with 292.7 grams of FORM4-A pellets packed to a height of 15.24 cm (6 inches) in the 2-in (I.D.) reactor tube. In a typical test, the reactor was purged with nitrogen to expel air. During the purge, reactive gas flows were adjusted and routed directly to the scrubber solution. The reactive gases were then introduced into the reactor and the loading test timed. In such a fixed-bed desulfurization reactor H₂S removal would first occur near the bottom of the bed where reduction of Mn₃O₄ to MnO and the immediate conversion of MnO to MnS occur. The majority of the unreacted pellets are then exposed to the sulfur-free reducing gas for varying times as the reaction front progressed through the bed.

At the conclusion of the sulfidation test, the bed is flushed with nitrogen in order to expel remaining combustible gases and a regeneration gas consisting of air is initiated with the product gas being periodically analyzed for SO₂ using detector tubes. The regeneration step is discontinued when the concentration of SO₂ is measured below 500 ppmv.

A minor problem arose in preliminary regeneration tests which were

carried out with air at 3 L/min in that sulfur tended to deposit in the exhaust lines. Its accumulation during the early stages of regeneration caused plugging of the exit tube (close examination revealed that it was elemental sulfur). This indicates that the oxygen in the regeneration air was completely consumed. In addition, examination of the pellets showed them to have experienced extreme overheating which led to sintering and loss of reactivity. These problems were overcome by reducing the air flowrate in order to limit the rate of heat release by the highly exothermic regeneration reaction. The addition of an after-burner on top of the pellet bed resulted in more oxidizing conditions and hence less tendency for sulfide sulfur (S^{2-}) to oxidize to the intermediate elemental form (S^0) rather than to the 4-valent (S^{+4}) form.

6.2.3 Results and Discussion

The breakthrough curve for sulfidation at 900 °C on the first cycle is shown in Figure 6.3. The concentration of H_2S in the exhaust gas (on wet basis) appears to reach a steady state value of approximately 222.5 ppmv for at least the first 7 hours of the loading test. This value is close to that of the MnO/MnS equilibrium, which may be calculated using subsequent analysis as 256 ppmv, based on results obtained in this study (see equation (6.8)). The vertical dashed line corresponds to the theoretical time required for breakthrough and is a function of the quantity of sorbent pellets in the reactor, the loading gas flowrate or space velocity, and the equilibrium pH_2O/pH_2S in the exhaust gas, i.e. reaction temperature since the amount of water vapor in the feed gas is fixed at 5% by volume. If breakthrough is arbitrarily defined at 500 ppmv in the exhaust gas, then breakthrough occurred after a total reaction time of 8 hours which corresponds to 21.12% loading or 81.86% bed utilization.

The concentration of SO_2 in the regeneration product gas is shown in Figure 6.4 as a function of reaction time. Again, the theoretical time for complete regeneration is displayed as a vertical dashed line which is a function of air flowrate, the quantity of pellets in the reactor, and temperature to a lesser extent since the reaction occurs essentially to completion. In addition, the theoretical maximum SO_2 concentration in the product gas (before mixing with after-burner gas) is shown in Figure 6.4 as a horizontal dashed line. This 13.76% value corresponds to regeneration with air and the complete consumption of oxygen in the air, and is calculated based on the stoichiometry of the overall regeneration reaction, as previously outlined in detail.⁸ As can be seen in Figure 6.4, the breakthrough occurred rapidly when the bed was almost completely regenerated.

A relatively short series of complete sulfidation/regeneration cycles was then carried out at 900 °C to verify the sorbent as a viable candidate for a fixed-bed fuel gas desulfurization. Six consecutive cycles over a 15-day period were deemed adequate for this purpose. The results of sulfidation tests from cycles 1,2,3, and 6 are reported in Figure 6.5. Before breakthrough the H_2S concentration in the cleaned gas approaches more closely the equilibrium value,

which is an indication of an improvement in pellet reaction kinetics with increasing cyclic loading. These results are consistent with the previous results from TGA tests on individual pellets.⁸

A series of twenty-two cycles of tests was then completed to demonstrate the durability and regenerability of FORM4-A sorbent formulation. Each sulfidation and regeneration repeated the initial run conditions. The results are reported in Figure 6.6 which shows the effect of cycling on the sulfur capacity of FORM4-A pellets at 900 °C upon repeated loading and regeneration. The sulfur loading capacity (defined as grams of sulfur per 100 grams of original pellet mass) shows a slight improvement with each cycle. This effect is noticeable in the second cycle, but is much less pronounced in subsequent cycles. The sulfur capacity ranged from 21.12% to 23.12%, which corresponds to approximately 90% sorbent bed utilization. This sulfur capacity is calculated using mass balances, based upon gas analyses for H₂S entering and leaving the reactor. In subsequent tests, not reported here, no significant diminution in sorbent capacity was observed after over thirty loading and regeneration cycles.

6.3 Re-assessment of Reaction Equilibria in the Solid Mn-S-O System

Turkdogan¹¹ has recently made a critical assessment on previous experimental data on reactions involving solid MnO, MnS, Mn₃O₄, and MnSO₄ in relation to those calculated from the thermochemical tables. His goal was to resolve some of the inconsistencies between the experimentally determined equilibrium constant of a reaction and that calculated from the thermochemical tables which may sometimes be so significant that the estimated value is uncertain by factors of two or more. Levels of uncertainty of this magnitude are not acceptable in the assessment of the equilibrium states of reactions in an industrial process such as the high temperature desulfurization of hot coal-derived fuel gases with manganese-based pellets.

The results from the various studies^{14,15,16} used in Turkdogan's analysis are reproduced in Figure 6.7, where the logarithm of the equilibrium constant (pH₂O/pH₂S) is plotted as a function of reciprocal temperature. By combining the experimental free energy data (ΔG_r) for MnO-MnS reactions in the three studies outlined above and two additional studies^{17,18} with tabulated ΔG° values for SO₂, H₂O, and H₂S, the ΔG_r values for the reaction

are obtained. These values are plotted in Figure 6.8 and are represented by lines A through D. Lines E and F are derived using the ΔG°_{MnO} data assessed by Coughlin¹⁹

$$\Delta G^\circ_{\text{MnO}} = -384840 + 73.14T, \quad J \text{ mol}^{-1} \quad (6.2)$$

and two different assessments of $\Delta G^\circ_{\text{MnS}}$:

- (i) values assessed by Cooper and Scarpiello²⁰ and by Pankratz and King²¹
- (ii) values derived from the thermodynamic data on inorganic sulfides, selenides, and tellurides compiled by Mills.²²

Turkdogan¹¹ gave more credence to line F since it lies in the middle range of the experimental results from two independent investigations using entirely different experimental techniques. The equation for line F is given by:

$$\Delta G_r = 106900 - 9.18T, \quad J \text{ mol}^{-1} \quad (6.3)$$

Combining this equation with tabulated values for $\Delta G^\circ_{\text{H}_2\text{S}}$ and $\Delta G^\circ_{\text{H}_2\text{O}}$ gives the following equilibrium relation for the governing sulfidation reaction

$$\log \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{S}}} \right) = \frac{2557}{T} + 0.204 \quad (6.5)$$

This equation is used for the solid line in Figure 6.7.

Several equilibrium measurements have been made of the dissociation partial pressures of SO_2 and O_2 in the reaction:

The results from different investigations^{16,18,23,24} are in general agreement, and the average of all the data may be represented by the following equation for temperatures in the range 900 to 1300 °K:¹¹

$$\log k = \log P_{\text{SO}_2} (P_{\text{O}_2})^{1/2} = -\frac{15625}{T} + 11.888 \quad (6.7)$$

This equation is useful for the assessment of the thermodynamic feasibility of sulfate formation and may also be used to update previous thermodynamic analyses outlined by the authors.^{7,8}

A number of MnO/MnS equilibration tests were conducted using fresh FORM4-A pellets. The sulfidation gas consisted of a 3% H_2S - H_2 mixture flowing at 2 L/min and the temperature was varied from 800 to 1000 °C. The average value of the logarithm of the equilibrium constant ($p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{S}}$) obtained at the

three temperatures studied is represented by a star-marked line on Figure 6.9. This figure also displays the error bars on the data to indicate the range of the results. The data from the present investigation may be represented by the following equation:

$$\log \left(\frac{P_{H_2O}}{P_{H_2S}} \right) = \frac{2151}{T} + 0.659 \quad (6.8)$$

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Figure 6.1 Schematic diagram of overall experimental arrangement for fixed-bed tests.

Figure 6.2 Schematic diagram of fixed-bed reactor details.

Figure 6.3 Breakthrough curve for sulfidation at 900 °C (cycle No. 1) of FORM4-A pellets using a Tampella U fuel gas at 3 L/min.

Figure 6.4 Breakthrough curve for regeneration at 900°C (cycle No. 2) of loaded FORM4-A pellets using air at 1 L/min.

Figure 6.5 Breakthrough curves for sulfidation at 900 °C (cycles 1,2,3 and 6) of FORM4-A pellets using a Tampella U fuel gas at 3 L/min and air at 1 L/min for regeneration.

Figure 6.6

Effect of cyclic loading and regeneration on sulfur capacity of FORM4-A pellets at 900 °C.

Figure 6.7. Comparison of experimental data on reaction equilibrium $MnO + H_2S = MnS + H_2O$ with those calculated from compiled thermochemical tables.¹¹

Figure 6.8. Experimental (A,¹⁷ B,¹⁸ C,^{15,16} D¹⁴) and calculated (E,^{20,21} F²²) free energy data for the reaction $\text{MnO} + 1/2\text{S}_2 = \text{MnS} + 1/2\text{O}_2$ ¹¹

Figure 6.9 Comparison of experimental data obtained in this investigation on sulfidation reaction equilibrium with those of Turkdogan and Olsson¹⁵ and the equation recently recommended by Turkdogan.¹¹

CHAPTER VII: SUMMARY AND SUGGESTIONS FOR FUTURE WORK

7.1 Summary

The present study revealed several points of value for summary:

- A systematic approach toward the evaluation of the behavior of single-metal sorbents for removing hydrogen sulfide (H_2S) from hot coal-derived fuel gases is developed based on thermodynamic considerations. This new method of comparative analysis singled out manganese oxide as a prime candidate sorbent capable of being utilized under a wide temperature range to reduce H_2S concentrations in the fuel gas to less than 150 ppmv (parts per million by volume).
- A novel pelletization process is developed for the manufacture of manganese-based spherical pellets which have the desired physical and chemical characteristics required during the long-term cyclic sulfidation and regeneration in a high-temperature desulfurization operation.
- Single sulfidation (loading) tests via thermogravimetric (TGA) analysis at temperatures ranging from 700 to 1000 °C showed that FORM4-A pellets ($MnCO_3$ + alundum + bentonite) exhibits the best combination of sulfur capacity and reaction kinetics; FORM1-A pellets (Mn ore + alundum + dextrin) exhibits the best combination of strength, sulfur capacity, and reaction kinetics. Both formulations, however, are deemed to be successful in reducing the H_2S concentration in the coal-derived fuel gas to less than 150 ppmv.
- Although the pellets may be loaded at temperatures below 800 °C, regeneration with air or oxygen-deficient air must be conducted above 900 °C to avoid sulfate formation; under these conditions the regeneration reaction is essentially complete in 10 to 15 minutes.
- Repeated cycling of the leading pellet formulation (FORM4-A), up to five consecutive cycles, revealed that the capacity of these pellets for sulfur pickup from fuel gases and the kinetics of reduction, sulfidation, and regeneration improve with recycling. This unique phenomenon is attributed to the formation of radial micro-cracks which reduced the diffusion distance required for transport of sulfur into the pellet and oxygen out of the pellet. These cracks did not have a significant effect upon pellet strength which continued to be no less than 5 lbs/mm of diameter.
- Fixed-bed tests using FORM4-A pellets and a simulated Tampella-U gas (with 3% H_2S) for sulfidation and air for regeneration (both at 900 °C) indicated improvement in capacity and kinetics with the sulfur loading capacity ranging from 21.1% to 23.1% by weight of the original bed, which corresponds to > 90%

of bed utilization. These results are consistent with the above results obtained from TGA sulfidation and regeneration tests on individual pellets.

- Rate equations (time-fractional conversion) were derived for diffusion through gas film control, diffusion through product layer control, and surface reaction control. The shrinking-unreacted core model was found to approximate very closely the kinetic behavior of manganese-based pellets during both the sulfidation and the regeneration reactions. Analysis of TGA experimental data determined that beyond about 35% reaction, when the product layer becomes sufficiently thick, the sulfidation reaction rate is controlled primarily by countercurrent diffusion of sulfur and oxygen through the porous layer of manganese sulfide (MnS) formed.

- A re-assessment of the equilibrium states of reactions involving solid MnO, MnS, Mn₃O₄, and MnSO₄ is presented based on the results obtained and a recent study by Turkdogan.

7.2 Suggestions for Future Work

Leach solutions from bench-scale in-situ mining tests of core samples from manganese deposits in the Emily District of Minnesota are currently being produced by the Twin Cities Research Center of the U. S. Bureau of Mines. These solutions are made by leaching the manganese contained in the cores with acidic solution saturated with sulfur dioxide. A typical composition of such solution is as reported in Table 7.1

Table 7.1 Typical Composition of In-Situ Mined Manganese Leach Solution from Mn deposits in the Emily District of Minnesota

Mn (g/l)	Fe (g/l)	K (ppm)	Al (ppm)	Ca (ppm)
28.075	2.3775	675	357.5	267.5
Si (ppm)	Na (ppm)	Mg (ppm)	Ba (ppm)	
85.0	80.00	67.5	4.00	

To ensure the economic viability of this innovative and environmentally sound mining method, the resulting solution must be treated with focus on the development of a useful and more valuable product from the in situ-leached manganese product than would be possible if it were simply utilized as a manganese steel additive. The possibility of manganese being employed as a sulfur sorbent in coal-gasification cleanup processes is the potential market which should be explored. The present study on the manganese-sulfur-oxygen (Mn-S-O) system indicated that a Mn-based sorbent pellet has considerable potential application in the area of desulfurization of coal-derived fuel gases at high temperature. In addition, the comparative experimental investigations concluded that a MnCO₃-based sorbent pellet offers the best combination of reaction kinetics and sulfur loading capacity. For these reasons, the treatment of

the leach solution mentioned above should aim at the production of manganese in the form of carbonate.

The author was initially involved in a study to effect a separation of manganese from the other constituents in solution, primarily iron. The removal of iron is particularly required since it forms low melting point systems which may cause the pellets to lose their reactivity. Studies on the recovery of manganese from these solutions have been conducted and involved oxidation and selective precipitation of iron followed by precipitation of manganese in the form of manganese carbonate.

Considerable success in obtaining a pure manganese product in accordance with the above procedure (see Figure 7.1) has been reported by the Salt Lake Research Center (SLRC) of the U. S. Bureau of Mines. The manganese carbonate resulting from this procedure will very likely be an excellent feed material for sulfur sorbent pellets since they will, upon calcination and loss of carbon dioxide, have potential for a high degree of porosity and resulting high surface area. As mentioned above, a somewhat similar manganese carbonate material which is commercially available was found to be a critical component in the manufacturing of regenerable manganese-based sorbent pellets for the desulfurization of coal-derived fuel gases at high temperature. The desulfurization process constitutes a crucial sub-system in the Integral Gasification Combined Cycle (IGCC), an emerging innovative method of power generation.

A typical assay of product filter cake resulting from studies conducted by the SLRC is shown in Table 7.2.

Table 7.2 Assays (in Percent unless Otherwise Noted) of Manganese Carbonate Filter Cake Product.

Species	Conc.	Species	Conc.	Species	Conc.
Mn	40	V	<0.01	Na	0.2
CO ₂	47	Sr	0.016	K	0.2
As	0.0002	Co	0.0004	Ca	0.16
Sb	<0.002	Ni	<0.001	Mo	<0.01
Cr	<0.0006	Pb	<0.0034	Hg	<0.13ppm

If cyclic testing during loading (sulfur pickup from fuel gases) and regeneration (oxidation to produce a gas of high sulfur dioxide content) demonstrate that pellets made from in-situ mined Minnesota manganese yields a superior sorbent, then the potential exists to produce a high value-added product having a sale price ranging 2 to 3 dollars per pound compared with prices of cents per pound for manganese in competition with manganese ore as additives to steel.

Figure 7.1 Schematic diagram of the Salt Lake City Research Center MnCO_3 recovery process.

VIII. APPENDIX A
Raw Materials Used and Method of Pellet Manufacture

8.1 Introduction

The processes used to manufacture manganese-based pellets used in this study essentially comprise mixing combinations of manganese-containing compounds and an alumina-based matrix material with organic or inorganic binders. The mixed powder is then fed to a pelletizer, along with a fine spray of water to form spherical pellets. These pellets are dried to impart green strength for further handling. The dried pellets are then indurated at high temperature to obtain the desired combination of physical properties such as crush strength and porosity.

The raw materials used to form the pellets comprise a source of manganese as either a carbonate or an oxide ore and an alumina-based matrix to provide the strength needed to maintain porosity and provide the mechanical structure in the pellets. In the compositions employing manganese carbonate, preliminary work indicated that it is preferred to also include an inorganic binder to provide further cementing actions to increase strength in the pellets as well as to facilitate formation into spherical pellets. In compositions employing manganese oxides, the raw materials can include an organic binder to provide additional porosity to the pellets as the organic binder volatilizes during induration as well as to provide a mechanism for formation of the raw materials into pellets. Organic binders can also be included in formulations using manganese carbonates, but are typically not needed because of the porosity-enhancing effects of MnCO_3 dissociation.

The leading formulation (FORM4-A), a combination of technical grade manganese carbonate, alundum, and bentonite as an inorganic binder, provides excellent sulfidation and regeneration characteristics. No further modifiers or surface area or porosity promoters are needed since the carbonate, upon dissociation and volatilization of the contained carbon dioxide during induration of the pellets, produces the required porosity.

The spherical shape of the pellets and the high crush strength imparted to them by the presence of the inorganic binder result in desirable handling and packing characteristics. The inorganic binder also preferably provides a strong, permanent bridging action between manganese oxide and matrix materials. It should be noted that the amount of inorganic binder is preferably limited, not only to reduce the cost of the finished pellets, but also to provide a greater amount of chemically active sorbent to maximize both sorption capacity and reaction rates.

Another problem faced by many of the pellet-based sorbent systems is that the pellets are typically formed through extrusion processes which provide essentially cylindrical-shaped pellets. Although cylindrical pellets are expedient from a manufacturing standpoint, they do not provide optimum packing efficiency. Furthermore, the cylindrical pellets have edges at either end which are the center of stress and the site of degradation of the pellets, resulting in the loss of sorbent capacity.

The preferred inorganic binder comprises bentonite, although other

inorganic binders, such as kaolin or Portland cement could be substituted for bentonite. The presence of the organic binder dextrin also enhances the porosity as this material burns away during the induration process. Other organic binders which could be used in the process include starches, methyl cellulose, and molasses.

In the formulations comprising manganese carbonate, precalcination mass of the MnCO_3 was chosen to produce 75% by weight MnO in the finished pellets because calcination of manganese carbonate effectively reduces its mass upon loss of carbon dioxide.

The preferred particle sizes of both the manganese compounds and matrix compounds is less than about 100 μm , and more preferably less than about 50 μm to facilitate pellet formation.

8.2 Pellet Preparation Procedure

Feed is prepared by adding a binder to the dry mix of manganese-containing compound and alumina-based matrix and mulling the mixture while slowly adding water to produce a cohesive, but not sticky, consistency. The amount of water needed is typically in the range of about 5 to 10% by weight.

The mix is then rubbed through a 10-mesh sieve to form fines.

Pelletization is accomplished using a balling tire at a 40 to 60° inclination to the horizontal and a rotational speed of 30 to 50 rpm. Initially, the tire interior is moistened and then wiped clean. About 7% by weight of the prepared feed in the form of fines is slowly sprinkled into the rotating tire. When seeds begin to form (as evinced by micro-pellets), moisture is added in discrete increments (of about 0.1% by weight of the original solids) via a finely atomized hand-held sprayer (spray droplets 5 to 15 μm in diameter) along with additional fines to allow the seeds to grow. After growth, the seeds are removed and screened to pass a 6-mesh screen, and the fines are returned to the tire.

This procedure is continued until approximately one-third of the original feed (which is set aside) is converted to agglomerates which would ideally range in size from 2 to 5 mm in diameter. At this point, the feed is divided into three portions. In the subsequent pellet making operation, a portion of the seeds is returned to the tire and sprayed with the above fine spray of water until the glistening point is noted. This glistening point is a visual observation of a shiny reflective surface appearance on pellets which originally appeared as "flat", i.e. non-glossy. Fines are then added in small increments to cause the seeds to grow.

The rate of addition of fines is controlled so as to avoid sticking and also to promote the free-rolling of the pellets. Too slow a rate of addition causes the seeds to stick together; whereas, too rapid an addition causes the formation of unnecessary new seeds in competition with the desired growth of the original seeds. Immediately after this procedure of addition of the fines, water is sprayed once again to bring the pellets to the glistening point. This procedure of spraying pellets to the glistening point and the subsequent addition of fines is

repeated until the pellets grow to the desired final size. At this point, the pellets are removed from the pelletizer and screened; the 7- to 10-mm fraction is stored in desiccators pending evaluation of their strength and appearance, and the undersize pellets are returned to the tire for further growth.

The required moisture content for the feed depends on its average density. Balling is optimal at about 30-35% moisture on a volume basis, i.e., the approximate void fraction in dried pellets. For 33% moisture on a volume basis, it can be shown that the required amount of water to be added is given by the following equation:

$$Wt. \%(H_2O) = \frac{100}{\left[1 + \frac{67}{33} \rho_{av} \right]} \quad (8.1)$$

where ρ_{av} is the average density of the feed.

The green pellets are then dried to a constant weight at 110 °C and then indurated. Induration was conducted for a 12 hour cycle in air and involved heating from 25 °C to about 300 °C over one hour; heating from about 300 °C to about 400 °C over a period of about five hours and then holding the Moanda ore based pellets at 1200 °C for one to two hours while the manganese based pellets were heated to about 1250 °C and held there for one to two hours.

The pellets produced using the above procedures had the desired strength of greater than 22 N/mm of pellet diameter (5 lbs/mm).

8.3 Discussion

Some of the research discussed in Chapter 2 above has indicated that manganese based pellets may provide a useful sorbent for coal gas desulfurization at high temperature. None of the research, however, has provided a formulation of pellets and a process of manufacturing them which is economically feasible and provides pellets which have the characteristics necessary for successful commercial application. The durability provided both by the materials used to manufacture the pellets as well as their spherical shape allows the pellets to maintain their desired physical and chemical characteristics in long-term cyclic sulfidation and regeneration in a high-temperature desulfurization operation. The desired physical characteristics of pellets include high crush strength, resistance to attritioning or physical disintegration, and high porosity. The desired chemical characteristics are: a high sulfur sorption capacity (gS/100 g pellets) during the sulfidation step; and a high reaction rate and extent for both sulfidation and regeneration. The sorbent pellets are also produced by a relatively inexpensive process which uses commercially available reagents. The pelletizing operation requires the following commercially available equipment: mix-muller, pelletizer, drying oven, and induration furnace.

The spherical shape of the pellets manufactured by the process described above and the high crush strength imparted to them by the presence of the

inorganic binder, bentonite, result in desirable handling and packing characteristics. The increased packing density of spherical pellets as compared to typical cylindrical pellets allows more sorbent material to be contained within a reactor. That results in increased capacity as well as reaction rate. The spherical shape also eliminates the edges which are the site of degradation due to stresses during use as well as handling of typical cylindrical pellets.

8.4 Raw Materials Used and Their Assays

- 1) Regular Manganese Carbonate: Obtained from Chemetals, Inc. in Baltimore, MD. This product contains approximately 93-95% MnCO_3 ; no typical analysis is available at the present time.
- 2) Alundum Fepa F, Size 600, Code 7102: Obtained from Industrial Ceramics Corporation (Norton Materials) in Worcester, MA.

Table 8.1 Typical Chemical Analysis of Alundum

Species	Al_2O_3	TiO_2	SiO_2	Fe_2O_3	CaO	MgO	S	K_2O
Wt. %	96.60	2.60	0.60	0.20	0.10	0.40	0.02	0.02

- 3) Manganous Oxide (MnO) Ore, Industrial Grades: Received from Chemetals, Inc. This product contains approximately 60% manganese.

Table 8.2 Chemical Analysis of Manganous Oxide Ore Used in Preliminary Work.

Ingredient	Approximate %
Manganese Oxide	55 - 83
Manganese Tetroxide	75 - 85
Iron as Iron Oxide	4 (max.)
Silica as Silicon Oxide	5 (max.)
Aluminum Dioxide	8 (max.)
Barium as Barium Compounds	4 (max.)

- 4) Bentonite, an inorganic binder, was obtained from the Aldrich Chemical Company, Inc. in Milwaukee, WI.
- 5) Dextrin (type IV), an organic binder, was obtained from the Sigma Chemical Company in St. Louis, MO.
- 6) "Moanda" Ore (African Manganese Dioxide Ore) and "GE" Ore (Australian Manganese Dioxide Ore): Obtained from The Prince Manufacturing Company in Quincy, IL.

IX. APPENDIX B
Derivation of Relevant Kinetic Expressions

9.1 Definition of symbols used and their units

S_{ex} : exterior surface of pellet (fresh, fully-loaded, or recycled), cm^2

S_c : exterior surface of unreacted pellet core, cm^2

r_i : reaction rate per unit surface area, $\text{mol}/\text{cm}^2\text{-s}$

N : number of moles of reactive component (MnO or MnS), mol

t : reaction time, s

R_p : radius of reduced or regenerated pellet, cm

k_g : mass transfer coefficient between gas phase and sorbent pellet, cm/s

k_s : first-order rate constant for the surface reaction, cm/s

C_i : concentration of gaseous component i , mol/cm^3

Superscript s : value of parameter at surface

Superscript o : initial value of parameter

Superscript e : equilibrium value of parameter at reaction site

ρ_i : molar density of reactive component i in pellet, mol/cm^3

V : volume of pellet, cm^3

r : arbitrary position within radius of pellet, cm

r_c : radius of unreacted pellet core, cm

τ_g : time for complete reaction when diffusion through gas film is rate-limiting, s

τ_{pl} : time for complete reaction when diffusion through product layer is rate-limiting, s

τ_{sr} : time for complete reaction when surface reaction is rate-limiting, s

F_i : fractional conversion of reactive component i as a function of time, dimensionless

J_i : molar flux of gaseous component i , $\text{mol}/\text{cm}^2\text{-s}$

D_e : effective diffusivity, cm^2/s

y_i : mole fraction of component i in the gas phase, dimensionless

R : universal gas constant, $\text{cm}^3\text{-atm}/\text{mol}\text{-}^\circ\text{K}$

T : absolute reaction temperature, $^\circ\text{K}$

P : total pressure, atm

J : total molar flux, $\text{mol}/\text{cm}^2\text{-s}$

P_i : partial pressure of gaseous component i , atm

9.2 Introduction

The sulfidation reaction is represented by equation (9.1):

while the overall regeneration reaction is represented by equation (9.2):

Both reactions are heterogeneous in which a gas contacts a solid, reacts with it, and transforms it into products. In both cases the pellets contain sufficient

amounts of non-reactive (inert) impurities (alundum matrix and inorganic binder in some instances) which remain as a non-flaking materials. Both reactions also form firm product material, i.e., sulfide or oxide of somewhat similar specific volumes. Accordingly, the sorbent pellets may be assumed to remain unchanged in size during sulfidation and regeneration, although they undergo structural changes. Such an assumption is made in the modeling of metallurgical processes such as the roasting of sulfide ores and the subsequent reduction of the resulting oxides to metals. In addition, the sulfidation and regeneration reactions are controlled to a large extent by diffusion and may thus be considered irreversible. An additional assumption may be made about the reaction being elementary (i.e., first-order with respect to H_2S) and the concentration gradients being linear to simplify the mathematical treatment of the problem and obtain an analytical solution.

For the non-catalytic reactions of particles with surrounding gas two simple idealized models have been conceptualized: the *progressive-conversion model* and the *shrinking-core model*. In the former model the reactant gas enters and reacts throughout the particle at all times, i.e., the solid reactant is converted continuously and progressively throughout the particle. In the latter model the reaction proceeds at a narrow front which moves into the solid particle and the reactant is completely converted as the front progresses.

Evidence from a wide variety of situations indicates that the shrinking-core model approximates the behavior of real particles more closely in most cases than does the progressive-conversion model. Therefore, in the following analysis, rate equations (time-conversion) describing the progress of the sulfidation reaction with time have been derived (with reference to Figure 4.10 in Chapter 4). Those equations describing the progress of the regeneration reaction with time were also derived using the same approach, but only the case where gaseous diffusion through the product layer is rate-limiting is considered.

9.3 Application of the Shrinking-Core Model for Spherical Pellets During Sulfidation

Five steps are conceptualized to occur in series during the sulfidation reaction:

Step 1: Diffusion of gaseous reactant H_2S through the gas film surrounding the pellet to the exterior surface of the pellet;

Step 2: Penetration and diffusion of H_2S through the newly-formed product layer, MnS , to the surface of the unreacted core;

Step 3: Reaction of H_2S with the reactive component, MnO , at the reaction front to exchange sulfur with oxygen and release H_2O ;

Step 4: Diffusion of the gaseous product, H_2O , through the product layer, MnS , to the exterior surface of the pellet; and

Step 5: Diffusion of H_2O through the gas film to the bulk of the reducing fuel gas.

It must be noted that diffusion steps 2 and 4 could be considered as one

step as a countercurrent diffusion in a binary gas mixture. The resistances of the different steps usually vary greatly from one another and the step with the highest resistance is taken as the rate-controlling step.

9.3.1 Diffusion through gas film controls:

In this case the concentration profile for gaseous reactant H_2S is as depicted in Figure 4.10(a) which shows that no reactant is present at the exterior surface of the pellet (S_{ex}) or at the surface of the unreacted core (S_c). When diffusion through the gas film is rate-limiting, diffusion through the product layer and the surface reaction are relatively fast that the exit reactant gaseous component is immediately consumed as soon as it gets to the surface.

It is convenient to derive the relevant kinetic expressions based on the unchanging exterior surface of the pellet (S_{ex}). The following procedure is initiated by the selection of one reaction component; the reaction rate is then defined in a meaningful way in terms of this component. Although initially the manganese exists as Mn_3O_4 in the indurated fresh pellet, the reactive constituent of the pellet, MnO , serves the purpose of defining the reaction rate best. It must be pointed out that MnO is the thermodynamically stable form of manganese in the pellet upon its exposure to the reducing fuel gas, as established in Chapters 3 and 4. Based on unit exterior surface of the pellet in this gas-solid system the reaction rate is given by:

$$r''_{MnO} = -\frac{1}{S_{ex}} \frac{dN_{MnO}}{dt} = \frac{\text{Moles of MnO reacted}}{(\text{exterior surface of pellet}) (\text{time})} \quad (9.3)$$

$$-\frac{1}{S_{ex}} \frac{dN_{MnO}}{dt} = -\frac{1}{4\pi R_p^2} \frac{dN_{MnO}}{dt} = -\frac{1}{4\pi R_p^2} \frac{dN_{H_2S}}{dt} = k_s(C^o_{H_2S} - C^e_{H_2S}) \quad (9.4)$$

If we let ρ_{MnO} be the molar density of MnO in the pellet and V the volume of the *reduced* pellet, then the number of moles of MnO present in the reduced pellet is given by:

$$N_{MnO} = \rho_{MnO} V \quad (9.5)$$

The change in the number of moles of reactive component MnO which causes the volume or the radius of unreacted core to decrease is then given by:

$$-dN_{MnO} = -dN_{H_2S} = -\rho_{MnO} dV = -\rho_{MnO} d\left(\frac{4}{3}\pi r_c^3\right) = -4\pi\rho_{MnO} r_c^2 dr_c \quad (9.6)$$

The rate of reaction can then be written in terms of the shrinking radius of unreacted core as follows:

$$-\frac{1}{S_{\alpha}} \frac{dN_{MnO}}{dt} = -\frac{\rho_{MnO} r_c^2}{R_p^2} \frac{dr_c}{dt} = k_g (C_{H_2S}^o - C_{H_2S}^e) \quad (9.7)$$

We then separate the variables and integrate to get an expression describing the shrinkage of the unreacted core with time:

$$-\frac{\rho_{MnO}}{R_p^2} \int_R^{r_c} r_c^2 dr_c = k_g (C_{H_2S}^o - C_{H_2S}^e) \int_0^t dt \quad (9.8)$$

from which we can deduce time t as follows:

$$t = \frac{\rho_{MnO} R_p}{3k_g (C_{H_2S}^o - C_{H_2S}^e)} \left[1 - \left(\frac{r_c}{R} \right)^3 \right] \quad (9.9)$$

The time τ_{gr} for complete reaction of the pellet is obtained by setting $r_c=0$:

$$\tau_{gr} = \frac{\rho_{MnO} R_p}{3k_g (C_{H_2S}^o - C_{H_2S}^e)} \quad (9.10)$$

Equation (9.9) may then be written in terms of τ_{gr} , as follows:

$$\frac{t}{\tau_{gr}} = 1 - \left(\frac{r_c}{R_p} \right)^3 \quad (9.11)$$

The fractional conversion of MnO is defined as:

$$F_{MnO} = \frac{N_{MnO}^o - N_{MnO}}{N_{MnO}^o} = 1 - \frac{\frac{4}{3} \pi r_c^3 \rho_{MnO}}{\frac{4}{3} \pi R_p^3 \rho_{MnO}} = 1 - \left(\frac{r_c}{R_p} \right)^3 \quad (9.12)$$

It follows that:

$$\frac{t}{\tau_{gr}} = 1 - \left(\frac{r_c}{R_p} \right)^3 = F_{MnO} \quad (9.13)$$

An important relationship between time, pellet size (radius), and fractional conversion for the case where diffusion of H_2S through the gas film controls is given by:

$$F_{MnO} = \frac{3k_g(C_{H_2S}^\infty - C_{H_2S})}{\rho_{MnO} R_p} t + C_1 \quad (9.14)$$

where C_1 is a constant of integration.

Given that:

$$C_1 = \frac{P_1}{RT} \quad (9.15)$$

equation (9.14) becomes:

$$F_{MnO} = \frac{3k_g(P_{H_2S}^\infty - P_{H_2S})}{RT\rho_{MnO} R_p} t + C_1 \quad (9.16)$$

9.3.2 Diffusion through product layer controls:

During the consideration of the concentration gradient of gaseous reactant H_2S , it is reasonable to assume that the unreacted core is stationary. With this steady state assumption the rate of reaction of H_2S at any instant is given by its rate of diffusion to the reaction site, as given by the following equation:

$$-\frac{dN_{H_2S}}{dt} = 4\pi r^2 J_{H_2S} = 4\pi R_p^2 J_{H_2S}^s = 4\pi r_c^2 J_{H_2S}^c \quad (9.17)$$

If we let the flux of H_2S through the product layer (MnS) be expressed by Fick's law for equimolar counterdiffusion, then we obtain:

$$J_{H_2S} = D_e \frac{dC_{H_2S}}{dr} \quad (9.18)$$

where D_e is the effective diffusion coefficient (diffusivity) of gaseous reactant H_2S in the product layer. Combining equations (17) and (18), we get:

$$-\frac{dN_{H_2S}}{dt} = 4\pi r^2 D_e \frac{dC_{H_2S}}{dr} \quad (9.19)$$

Integrating across the product layer, we get:

This reduces to the following differential equation which describes the conditions

$$-\frac{dN_{H_2S}}{dt} \int_{R_p}^{r_c} \frac{dr}{r^2} = 4\pi D_e \int_{C_{H_2S}^e}^{C_{H_2S}^o} dC_{H_2S} \quad (9.20)$$

of a reacting particle at any time t :

$$-\frac{dN_{H_2S}}{dt} \left(\frac{1}{r_c} - \frac{1}{R_p} \right) = 4\pi D_e (C_{H_2S}^o - C_{H_2S}^e) \quad (9.21)$$

This equation contains three variables: t , N_{H_2S} , and r_c , one of which must be eliminated or expressed in terms of the other variables before integration can be performed to obtain an analytical solution. N_{H_2S} may be eliminated by writing it in terms of r_c , as follows:

$$-\rho_{MnO} \int_{r_c=R_p}^{r_c} \left(\frac{1}{r_c} - \frac{1}{R_p} \right) r_c^2 dr_c = D_e (C_{H_2S}^o - C_{H_2S}^e) \int_0^t dt \quad (9.22)$$

or

$$t = \frac{\rho_{MnO} R_p^2}{6D_e (C_{H_2S}^o - C_{H_2S}^e)} \left[1 - 3\left(\frac{r_c}{R_p}\right)^2 + 2\left(\frac{r_c}{R_p}\right)^3 \right] \quad (9.23)$$

For complete conversion of the pellet, $r_c=0$, and the time required is:

$$\tau_{pl} = \frac{\rho_{MnO} R_p^2}{6D_e (C_{H_2S}^o - C_{H_2S}^e)} \quad (9.24)$$

Equation (23) can then be expressed in terms of τ_{pl} , as follows:

$$\frac{t}{\tau_{pl}} = 1 - 3\left(\frac{r_c}{R_p}\right)^2 + 2\left(\frac{r_c}{R_p}\right)^3 \quad (9.25)$$

or in terms of fractional conversion, we get:

$$\frac{t}{\tau_p} = 1 - 3(1 - F_{MnO})^{2/3} + 2(1 - F_{MnO}) \quad (9.26)$$

$$3 - 2F_{MnO} - 3(1 - F_{MnO})^{2/3} = \frac{6D_s(C^o_{H_2S} - C^e_{H_2S})}{\rho_{MnO} R_p^2} t + C_2 \quad (9.27)$$

where C_2 is a constant of integration. Combining equation (9.27) and equation (9.15), we get:

$$3 - 2F_{MnO} - 3(1 - F_{MnO})^{2/3} = \frac{6D_s(P^o_{H_2S} - P^e_{H_2S})}{RT\rho_{MnO} R_p^2} t + C_2 \quad (9.28)$$

9.3.3. Chemical (surface) reaction controls:

In this case the progress of reaction is independent of the existence of the gas film or the product layer. The reaction rate is thus proportional only to the available surface of the unreacted core. Therefore, the rate of reaction is given by:

$$-\frac{1}{4\pi r_c^2} \frac{dN_{MnO}}{dt} = -\frac{1}{4\pi r_c^2} \frac{dN_{H_2S}}{dt} = k_s(C^o_{H_2S} - C^e_{H_2S}) \quad (9.29)$$

where k_s is the first-order rate constant for the surface reaction. N_{MnO} is then expressed in terms of the shrinking radius r_c , as follows:

$$-\frac{1}{4\pi r_c^2} \rho_{MnO} 4\pi r_c^2 \frac{dr_c}{dt} = -\rho_{MnO} \frac{dr_c}{dt} = k_s(C^o_{H_2S} - C^e_{H_2S}) \quad (9.30)$$

Separating variables and integrating, we get:

$$-\rho_{MnO} \int_{R_p}^{r_c} dr_c = k_s(C^o_{H_2S} - C^e_{H_2S}) \int_0^t dt \quad (9.31)$$

The time τ_{sr} for complete conversion is determined by setting $r_c=0$:

$$t = \frac{\rho_{MnO}}{k_s(C_{H_2S}^o - C_{H_2S}^e)}(R_p - r_c) \quad (9.32)$$

$$\tau_{sr} = \frac{\rho_{MnO} R_p}{k_s(C_{H_2S}^o - C_{H_2S}^e)} \quad (9.33)$$

$$\frac{t}{\tau_{sr}} = 1 - \frac{r_c}{R_p} = 1 - (1 - F_{MnO})^{1/3} \quad (9.34)$$

Again, a more useful equation is in the form:

$$1 - (1 - F_{MnO})^{1/3} = \frac{k_s(C_{H_2S}^o - C_{H_2S}^e)}{\rho_{MnO} R_p} t + C_3 \quad (9.35)$$

where C_3 is a constant of integration.

$$1 - (1 - F_{MnO})^{1/3} = \frac{k_s(P_{H_2S}^o - P_{H_2S}^e)}{RT\rho_{MnO} R_p} t + C_3 \quad (9.36)$$

9.4 Application of the Shrinking-Core Model for Spherical Pellets During Regeneration

The regeneration reaction is irreversible; in addition, its highly exothermic nature makes it even more likely to be controlled by countercurrent diffusion of oxygen and sulfur through the porous Mn_3O_4 product layer. For these reasons, only the derivation of the equation when diffusion through product layer is rate-limiting is deemed worthwhile. As was established above, the overall regeneration reaction is represented by equation 9.2.

The molar flux of O_2 through the newly-formed Mn_3O_4 layer is expressed by Fick's law, as follows:

$$J_{O_2} = -D_s \frac{dC_{O_2}}{dr} + y_{O_2} J \quad (9.37)$$

The first term on the right-hand side of the above equation is termed molecular diffusion flux and is produced by a concentration gradient; the second term represents the flux resulting from the bulk motion of the regeneration gas. J is the total flux, and is given by:

$$J = J_{O_2} + J_{SO_2} \quad (9.38)$$

From the stoichiometry of the overall regeneration reaction, the following relation applies:

$$J_{SO_2} = -\frac{3}{5} J_{O_2} \quad (9.39)$$

Substituting for J in terms of J_{O_2} in equation (9.37) and rearranging, we get:

$$\left(1 - \frac{2}{5} y_{O_2}\right) J_{O_2} = -D_e \frac{dC_{O_2}}{dr} \quad (9.40)$$

With the assumption of steady state (i.e., stationary unreacted core), the rate of reaction of O_2 as a function of time is given by its rate of diffusion to the reaction site, as expressed by the following equation (similar to equation (9.17)):

$$\frac{-dN_{O_2}}{dt} = 4\pi r^2 J_{O_2} = 4\pi r^2 \left[\frac{-D_e}{1 - \frac{2}{5} y_{O_2}} \right] \frac{dC_{O_2}}{dr} \quad (9.41)$$

Integrating across the product layer, we get:

$$\frac{dN_{O_2}}{dt} \left(\frac{1}{r_c} - \frac{1}{R} \right) = -4\pi D_e \int_{C_{O_2}^c}^{C_{O_2}^r} \left[\frac{dC_{O_2}}{1 - \frac{2}{5} y_{O_2}} \right] \quad (9.42)$$

Recognizing that:

$$C_{O_2} = \frac{P_{O_2}}{RT} \quad (9.43)$$

and that:

$$y_{O_2} = \frac{P_{O_2}}{P} \quad (9.44)$$

we obtain the following differential equation which describes the conditions of the pellet during the course of the regeneration reaction:

Following a similar procedure as the one above for the case of the sulfidation

$$\frac{dN_{O_2}}{dt} \left(\frac{1}{r_c} - \frac{1}{R} \right) = \frac{10\pi D_e P}{RT} \ln \left[\frac{5P - 2P^e_{O_2}}{5P - 2P^o_{O_2}} \right] \quad (9.45)$$

reaction, it can be shown that N_{O_2} may be eliminated by writing it in terms of r_c , as follows:

$$dN_{O_2} = \frac{20}{3} \rho_{MnS} \pi r_c^2 dr_c \quad (9.46)$$

Separating variables and integrating, we get the following equation in terms of the fractional conversion of manganese sulfide in the sulfided (loaded) pellet (F_{MnS}):

$$3 - 2F_{MnS} - 3(1 - F_{MnS})^{2/3} = \frac{9D_e P}{RT \rho_{MnS} R_p^2} \ln \left[\frac{5P - 2P^e_{O_2}}{5P - 2P^o_{O_2}} \right] t + C_4 \quad (9.47)$$

where C_4 is a constant of integration.

The time-conversion equations derived above are summarized in the following table.

Table 9.1 Time-Conversion Performance Equations for Sulfidation and Regeneration Reactions Using the Shrinking Unreacted-Core Model.

Rate-Limiting	Sulfidation Reaction	Regeneration Reaction
Gas Film	$F_{MnO} = \frac{3k_s(P^{\circ}_{H_2S} - P^{\circ}_{H_2S})}{RT\rho_{MnO} R_p} t + C_1$	
Product Layer	$3 - 2F_{MnO} - 3(1 - F_{MnO})^{2/3} = \frac{6D_s(P^{\circ}_{H_2S} - P^{\circ}_{H_2S})}{RT\rho_{MnO} R_p^2} t + C_2$	$3 - 2F_{MnS} - 3(1 - F_{MnS})^{2/3} = \frac{9D_s P}{RT\rho_{MnS} R_p^2} \ln \left[\frac{5P - 2P^{\circ}_{O_2}}{5P - 2P^{\circ}_{O_2}} \right] t + C_4$
Surface Reaction	$1 - (1 - F_{MnO})^{1/3} = \frac{k_s(P^{\circ}_{H_2S} - P^{\circ}_{H_2S})}{RT\rho_{MnO} R_p} t + C_3$	

X. APPENDIX C

Petrographic Study of Mn Oxide and Sulfide Pellets

Acknowledgements. The author thanks Dr. Rolland Blake of the Twin Cities Research Center of the U.S. Bureau of Mines for carrying out this study. This appendix is based entirely on Dr. Blake's report.

10.1 Introduction

Manganese-based pellets, in the fresh (oxide) and loaded (sulfide) conditions, are characterized by using light optical microscopy (LOM), X-ray diffraction (XRD), and electron microprobe analyses (EMP). The purpose of this study is to determine macro- and micro-structure and macro- and micro-texture, the crystalline phases and degree of non-crystallinity, and the microchemistry of the pellets. The ultimate goal is to gain further understanding of the behavior of the pellets and improve their performance in the desulfurization of coal-derived fuel gases at high temperature.

The oxidation heating or induration would drive off any remaining moisture and CO_2 (in the case of MnCO_3 pellets) and result in an apparent chemistry of Mn_3O_4 crystals in an Al_2O_3 -rich matrix for the oxide pellets.

10.2 Pellet Macrophotography and Macrocharacteristics

The size, shape, and color of FORM4-A pellet samples in the fresh and loaded condition are depicted in Figure 10.1. Fresh pellet: dull black color, spherical, and 3-4 mm in diameter. The sulfide pellet has a greenish-gray color. The same properties for FORM1-A pellets are depicted in Figure 10.2. Fresh pellet: dull brownish black, slightly oval 4-6 mm in diameter. The sulfide pellet has dull gray black color.

Pellet surface texture and fractures are shown in Figures 10.3 and 10.4. Most pellets showed one or more macrocracks, but one of the FORM4-A loaded pellets exhibited only one minor crack with a small hole; the other showed no surface cracks. The very fine texture of FORM4-A pellets is indicative of very fine grind of starting pelletizing materials.

10.3 Pellet Preparation

The pellets were briquetted in a monomer and hardened at room temperature with a catalyst. The polymerized briquette surface was ground on a resin- or metal-bonded lap until the pellet center was exposed. It was then polished by hand using 30, 16, 5, and finally 3 micron diamonds in a paste on a cloth lap. Pellet cavities exposed on the sectioned surface were purposely not filled with resin in order to reduce the number of grinding and polishing steps so as to preserve the actual texture and structure. Several pellet surfaces showed depressed areas where initial polishing marks were visible, but further polishing pressure had caused the surface to collapse as a result of the weak, highly porous pellet structure.

10.4 Pellet Photomicrography and Microcharacteristics

The polished pellet sections are shown in photomicrographs as Figures 10.5 through 10.8 (part a). Pellet structure is readily seen at this low magnification (34x) as highly porous and permeable (i.e., interconnected pores), with concentric ring agglomeration structure. Figure 10.5 (a) shows small to large black cavities and a collapse area within the large cavity of FORM4-A at the 9 to 10 o'clock

position. The white phase (highly reflective) appears to be scattered and somewhat interconnected within the medium gray matrix. The texture (grain to grain relationship) looks fairly uniform from edge to center. Figure 10.6 (a) of the partially reacted FORM4-A pellet shows a highly variable pellet texture. The center appears to be mostly a gray phase, the outer rim a mixture of light phase within a gray phase, and the mid-rim area has both many cavities and clumps of lighter phase within a matrix of gray phase. Figure 10.7 (a) shows FORM1-A pellet with a series of partly interconnected concentric cavities from the outer rim to near the center, plus an irregular central cavity. The white phase appears to be rather uniformly distributed as isolated irregular blebs. Figure 10.8 (a) shows that the partially sulfided FORM1-A pellet has a contiguous concentric cavity, central separated cavities, and slightly patchy distribution of white and gray phases. FORM4-A pellets appear to have a more even distribution and uniformity of size of white phase than FORM1-A pellets.

At moderate magnification (118x) Figures 10.5 through 10.8 (part b) show pellet fine texture. Figure 10.5 (b) shows that FORM4-A fresh pellet, at a location about 1/3 of the distance from edge to center, has the white phase highly interconnected at the smallest scale, but mostly separated by gray matrix at a larger scale. Some of the white phase is at cavity walls and much is within the gray phase. Figure 10.6 (b) shows that FORM4-A partially-reacted pellet (at about mid-rim location) has a more diffuse white phase in gray phase than in the fresh pellet. Figure 10.7 (b) for FORM1-A fresh pellet shows a somewhat smaller white phase with less interconnection than in the FORM4-A fresh pellet. FORM4-A partially-reacted pellet shows a much more uniform and smaller size of cavities and of dendritic pellet material than the FORM1-A partially-reacted pellet, as shown in Figure 10.8 (b). Also, the white phase in this FORM4-A pellet seems more concentrated near cavity walls than in the FORM1-A sulfided pellet.

10.5 X-ray Diffraction of Whole Pellets

One pellet from each sample was pulverized and subjected to x-ray diffraction (XRD) analysis to determine what crystalline phases were present and the degree of crystallinity of the phases. Figures 10.9 through 10.12 show for each pellet an XRD pattern trace and stick patterns of comparable standard phases found in each sample, showing location and intensity of peaks. Figures 10.9 and 10.11 show that the only crystalline phase in both fresh pellets is Mn_2AlO_4 . Other phases searched for include: galaxite (MnAl_2O_4), $(\text{Li,Al})\text{Mn}_2\text{O}_4$, hausmannite (Mn_3O_4), corundum (Al_2O_3), and bixbeyite (Mn_2O_3). Figure 10.10 shows that the major crystalline phase of the FORM4-A sulfided pellet is alabandite (MnS), as expected, that a minor crystalline phase, galaxite (MnAl_2O_4) is present, that Mn_2AlO_4 is absent, and that two unidentified small peaks occur at 40.6 and 66.5 degrees two-theta. Figure 10.12 shows the same for FORM1-A sulfided pellet except that only the unidentified small peak at 40.6 degree two-theta appears.

10.6 Interpretation of Results

10.6.1 Cracks

cracks create major gas channels which would help gas diffuse into the pellet, but too many might defeat diffusion of gas into smaller pores and would weaken pellets. The few cracks observed in figures presented above do not appear excessive. The figures also show very few surface cracks extending into the pellet interior, so they are apparently not a problem.

10.6.2 Cavities

Large (about 0.1 diameter of pellet) cavities in a pellet could weaken the structure and represent loss of volume of reactive material, so that they should be minimized during pellet formation and heat hardening (induration). These pellets had occasional to frequent large cavities. Both larger and smaller cavities are observed in these pellets. Smaller cavities, especially those below 100 microns (0.1 mm), would seem beneficial in conducting gas throughout a pellet. These pellets had mostly a good distribution of smaller cavities. The structure of the FORM4-A sulfided pellet shows the most desirable smaller-cavity size and distribution of the four pellets.

10.6.3 Particle Size

Particle size affects the diffusion of gas into pellet particles such that gas has to penetrate farther into larger pellet particles than smaller ones to reach the center of the particle. Also, a reaction rim (front) near the surface of a large particle may prevent further gas penetration. Larger particles in a pellet will most likely cause larger pores between particles, but the percent porosity is mostly independent of particle size and is more dependent on particle size distribution because smaller particles can fill in cavities between bridged larger particles. Permeability (interconnection of pores) is affected by particle size distribution and other factors. Pellets in this study appeared to have good porosity and permeability.

10.6.4 Phases

FORM1-A fresh pellet shows a white phase that is interpreted as Mn oxide in a gray phase that is Al_2O_3 -rich and probably a non-crystalline matrix. The Mn oxide shows much interconnection within finer texture, and lesser interconnection within coarser texture. Details are much clearer at high magnification where the Mn oxide shows subhedral (partly bounded by crystal faces) grains that make contact with adjacent grains of Mn oxide. The rather coarse grain size and degree of crystal development of the Mn oxide phase is indication that the oxidation reaction to form Mn oxide went to completion. The gray phase appears less prominent because it is partly below the surface and reflects less light than at the lower magnification. Microscopy will not reveal if any Al, Ti, or Si is present in the Mn oxide phase, or if any Mn is in the gray phase. EMP element maps or point analyses are needed to determine this.

FORM4-A fresh pellet looks different from the FORM1-A fresh pellet at

low and intermediate magnification, but at higher magnification the textures of both pellets look nearly identical. The difference can be partly explained by a finer initial particle size for the FORM4-A pellet, and partly by more fusion of the Mn_2AlO_4 in the FORM1-A pellet, as if it were formed at a higher temperature or had more of a fluxing composition.

The FORM1-A sulfided pellet in Figure 10.8 shows a white phase interpreted as alabandite (MnS) and two gray phases: a lighter gray phase which appears to be the only matrix in contrast to the Mn sulfide in parts of the texture, and elsewhere appears as irregular shapes in a darker gray matrix. The gray phases are suspected to be Al_2O_3 - and SiO_2 -bearing, poorly- to non-crystalline material. It is noteworthy that the expected Mn sulfide phase is usually near cavity walls where it would have most access to sulfur-containing gas. It may be that the sulfidation process for this pellet did not go to equilibrium as attested by the two gray phases. Figure 10.8 shows that the rim and some distance into the pellet the texture appears fused, as though the temperature was too hot, resulting in preventing the gas from penetrating to the middle of the pellet, which looks in Figure 10.8 (b) to be unreacted from its similarity to the oxide pellet of Figure 10.7.

The FORM4-A sulfided pellet of Figure 10.6 appears to have much less fusion and more uniform penetration of sulfur-containing gas than occurred with FORM1-A sulfided pellet.

Phases in the fresh and sulfided FORM4-A pellets are similar to those observed in the two corresponding FORM1-A pellets discussed above.

10.7 X-ray Diffraction of Whole Pellets

Rather than identifying Mn_3O_4 (hausmannite) in the fresh ore- and MnCO_3 -based pellets, the phase Mn_2AlO_4 was identified by x-ray diffraction analysis as the only crystalline phase. The original patterns, not those of figures 10.9 - 10.12, show that the peaks are only moderately sharp and the background is moderately high, an indication that: (1) the crystalline phase is not very well crystallized, and (2) there is a non-crystalline phase present that probably is the matrix. The crystalline Mn_2AlO_4 is compatible with the 1975 phase diagram for Mn_3O_4 - Al_2O_3 in air, in which the cubic phase of $(\text{Mn,Al})_3\text{O}_4$ is called spinel, and the tetragonal phase of this composition is called hausmannite. The phase produced at equilibrium in these Mn oxide pellets contains approximately two atoms of Mn and one of Al for each formula unit. It is not surprising that Al^{3+} can substitute for Mn since their ionic radii are not very different, and possibly Ti^{3+} or Ti^{4+} could substitute for Mn.

10.8 Conclusions

The important findings can be summarized as follows: cracks in the pellets do not appear to be a problem. Large cavities in the pellets during formation could cause fired pellet weakness and loss of reactive material. Aluminum is an active part of the crystalline manganese oxide phase, forming Mn_2AlO_4 , or

$\text{Mn}_{2.5}\text{Al}_{0.5}\text{O}_4$. MnS is the crystalline phase of the sulfide pellets. Both aluminum and the small amount of titanium disperse throughout the pellets, and are present in both matrix and the phases Mn_2AlO_4 and MnS.

The matrix contains much Mn in both oxide and sulfide pellets and much S in the sulfide pellets. The matrix is interpreted as non-crystalline, has a rather variable composition and is believed to both support the structure and to be chemically reactive during elevated temperature reactions. The finer particle size and texture of FORM4-A pellets examined seem to favor good gas penetration and reaction, while FORM1-A pellets examined were observed to have coarser particles and texture and possibly a problem with gas penetration.

Figure 10.1

Macrophotograph of FORM4-A pellets in the (a) fresh condition and (b) partially loaded (sulfided) condition. Scale: 2.7 x actual size.

Figure 10.2

Macrophotograph of FORM1-A pellets in the (a) fresh condition and (b) partially loaded (sulfided) condition. Scale: 2.7 x actual size.

Figure 10.3

Surface texture and structure of FORM4-A pellets in the (a) fresh condition and (b) partially-loaded condition. Magnification = 12 X.

Figure 10.4

Surface texture and structure of FORM4-1 pellets in the (a) fresh condition and (b) partially-loaded condition. Magnification = 12 X.

Figure 10.5

Light optical photomicrograph of a FORM4-A fresh pellet, center sectioned, polished surface. Magnification= 34 X (a) and (b) an enlargement of area shown on (a). Magnification= 118 X. [white= Mn oxide; gray= matrix; black= cavities]

Figure 10.6

Light optical photomicrograph of a FORM4-A partially-sulfided pellet, center sectioned, polished surface. Magnification = 34 X (a) and (b) an enlargement of area shown on (a). Magnification = 118 X. [white = Mn sulfide; gray = matrix; black = cavities]

Figure 10.7

Light optical photomicrograph of a FORM1-A fresh pellet, center sectioned, polished surface. Magnification = 34 X (a) and (b) an enlargement of area shown on (a). Magnification = 118 X. [white = Mn oxide; gray = matrix; black = cavities]

Figure 10.8

Light optical photomicrograph of a FORM1-A partially-sulfided pellet, center sectioned, polished surface. Magnification = 34 X (a) and (b) an enlargement of area shown on (a). Magnification = 118 X. [white = Mn sulfide; gray = matrix; black = cavities]

Figure 10.9 Fresh FORM4-A whole pellet XRD pattern. The only crystalline phase present is Mn_2AlO_4 .

Figure 10.10 XRD pattern of partially-reacted FORM4-A pellet. Major phase is alabandite (MnS).

Figure 10.11 Fresh FORM1-A whole pellet XRD pattern. The only crystalline phase present is Mn_2AlO_4 .

Figure 10.12 XRD pattern of partially-reacted FORM1-A pellet.
Major phase is alabandite (MnS).