

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 $1005\text{ }^\circ K^1$ ($732\text{ }^\circ C$) 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.

1.2 References

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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.

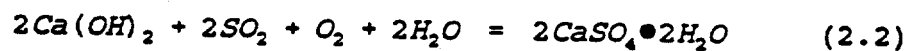
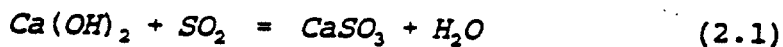
During coal combustion, sulfur is released mainly in the form of sulfur dioxide (SO_2) in the flue gas. Sulfur emissions are very damaging to the environment since SO_2 combines with water moisture to form sulfuric acid which then falls as acid rain. The threat from acid rain is increased by the burning 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

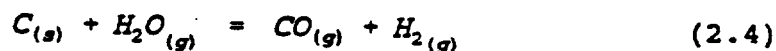


addition, huge amounts of lime waste are produced as the scrubber operates. For example, about one tonne of limestone is required to make the lime needed to scrub the stack gas from each five tonnes of coal burned. A large 9,080-tonne per day power plant requires 1,816 tonnes per day of limestone. The 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, H₂ 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, CO₂, CH₄, H₂, N₂, 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

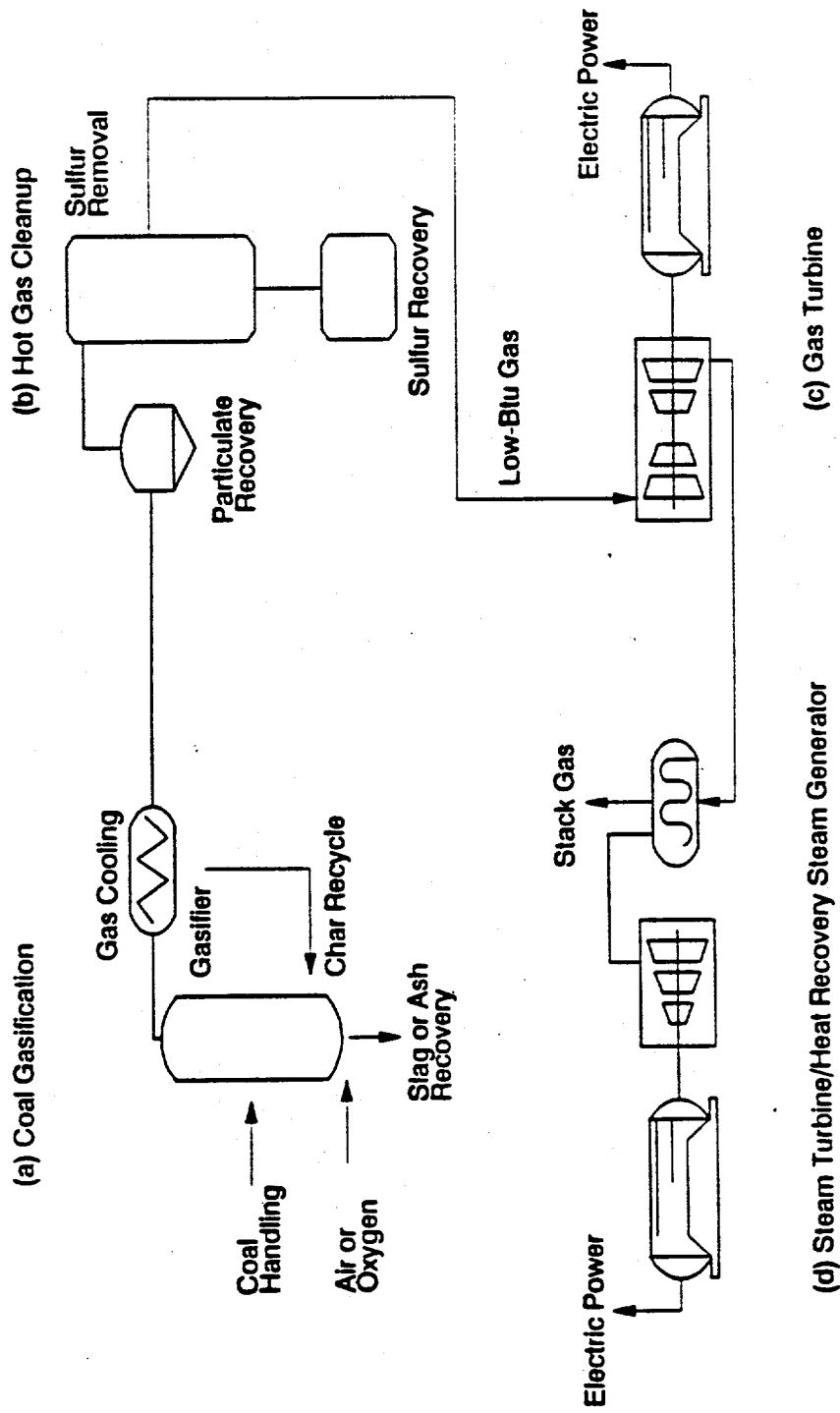


Figure 2.1 Schematic diagram of a typical integrated gasification combined cycle (IGCC) power generation plant.

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

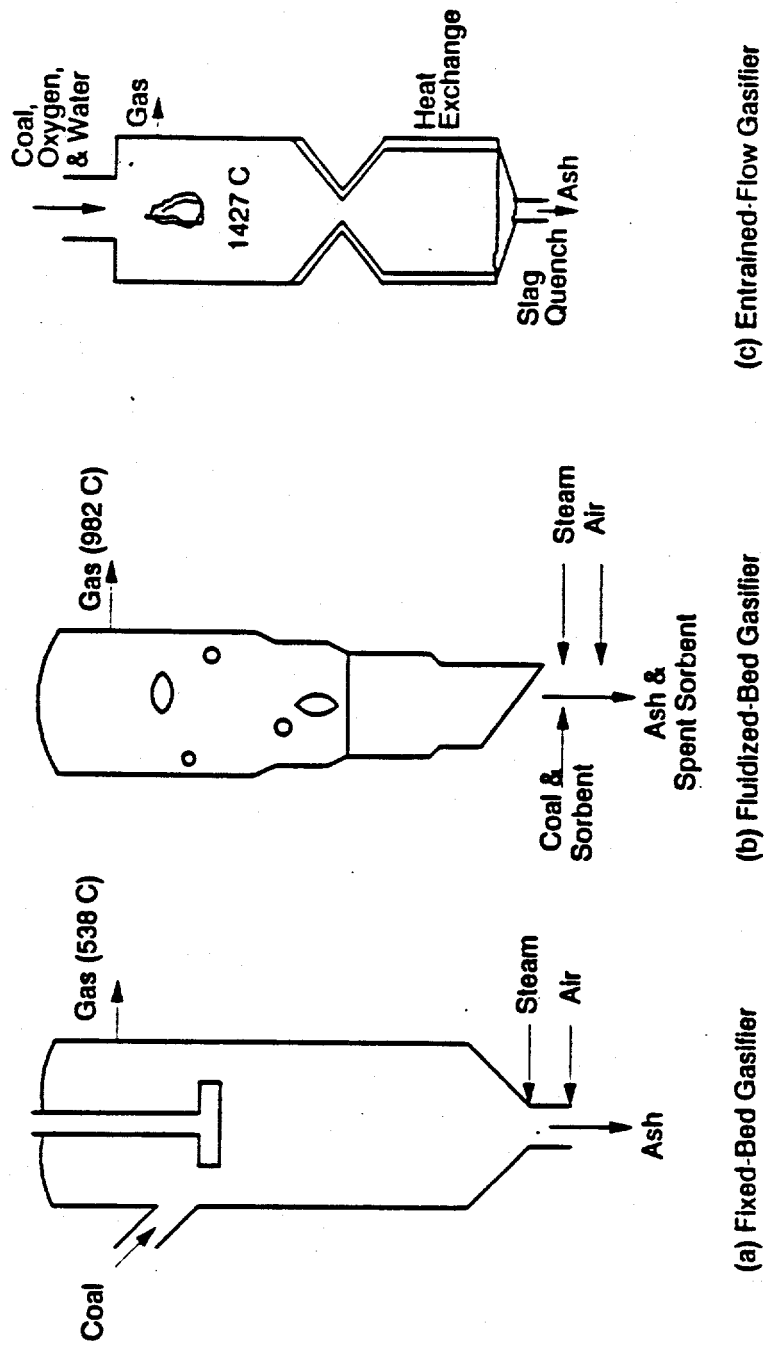
Gasifiers for IGCC application fall into three main categories: moving/fixed bed, fluidized bed, and entrained flow, as shown in Figure 2.2. The moving-bed gasifier typically consists of a pressure vessel containing a grate which supports a coal charge that moves slowly downward, through a series of 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



(a) Fixed-Bed Gasifier (b) Fluidized-Bed Gasifier (c) Entrained-Flow Gasifier

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

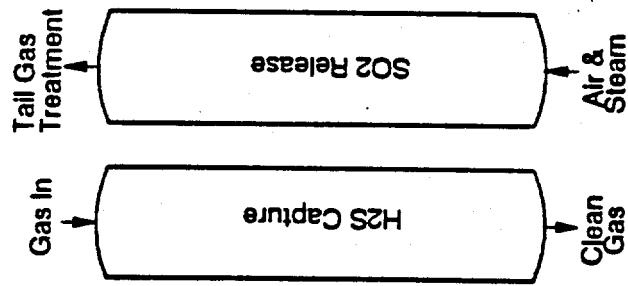
vapor compounds, primarily sulfur, from the raw fuel gas to meet gas turbine requirements and to comply with environmental regulations. To improve removal efficiency and lessen the burden on the downstream hot gas cleanup system, a sorbent is added to some gasifier systems to remove a portion of the 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.

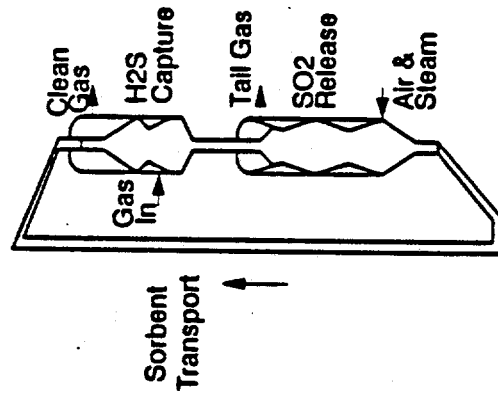
In a fixed-bed design, there are two parallel vessels, one of which will be capturing sulfur, while the other is regenerating. When the sorbent in the capturing vessel becomes fully saturated, the fuel gas flow is diverted to the other bed, so that the vessels can exchange roles. In a moving-bed design, 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

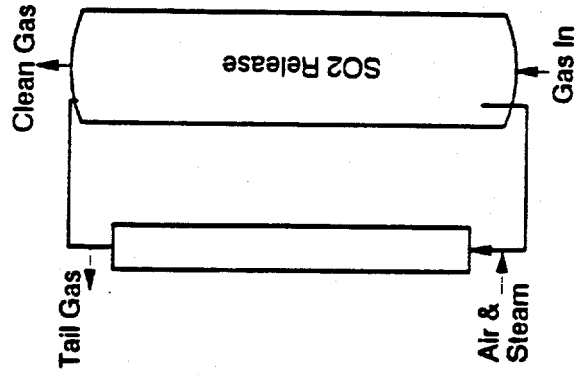
For fluidized-bed processing, sorbent particle sizes are small, generally in the range 20-500 μm . Hot gas desulfurization processes utilizing fluidized beds offer the following potential advantages over those processes using fixed or moving beds: they provide steady-state operation (simplifies system 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.

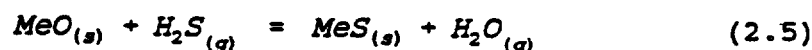
External desulfurization techniques are also used for the removal of residual sulfur in systems employing primary in-situ desulfurization. The implementation of in-situ desulfurization in conjunction with external desulfurization may offer an economically effective process for sulfur removal.

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 H₂S, the general sulfidation reaction may be represented by the following equation:



Desulfurization with sorbents is essentially a process of removal of the species H₂S from the gas phase. As H₂S 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 H₂S 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 H₂S. SO₂ 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 H₂S 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 CO_2 - H_2O 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, O_2 - SO_2 , or CO_2 - H_2O - 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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