FLUIDIZED BED FLUE GAS DESULFURIZATION WITH GAMMA ALUMINA

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In Partial Fulfillment
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Master of Science

by
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CHAPTER I
THE SULFUR DIOXIDE PROBLEM

Sulfur dioxide is one of the most dangerous air pollutants known to man. Sulfur dioxide aggravates existing respiratory disease and contributes to its development. The upper respiratory tract is irritated by sulfur dioxide gas, and when absorbed on dusts, the gas can be carried deep into the respiratory tract often resulting in lung tissue damage (1).

The combination of sulfur dioxide and fine particulate matter produces various synergistic effects. For example, certain types of particulate matter catalyze the oxidation of sulfur dioxide to sulfate aerosol particulates, which many authorities now consider to be more harmful to human health than sulfur dioxide alone (2, 4).

Documented air pollution crises have shown a definite correlation between increased average death rates and exceptionally high concentrations of air pollutants. In these instances, the very young, the elderly, and those afflicted with pre-existing cardio-respiratory illness were most affected. Existing data indicates that excessive death rates may occur in cities having an annual average sulfur dioxide concentration level of 0.15 p.p.m. or more (1).

Information concerning morbidity could conceivably have substantially more influence on future decisions concerning acceptable levels of sulfur dioxide emissions than evidence of increased mortality. Consider the
social costs of suffering for twenty years with chronic bronchitis. When dealing with mortality statistics, this affliction would only be recorded as a death premature by perhaps as little as one week (5).

The sharp rise in the emissions of sulfur and nitrogen oxides to the atmosphere has significantly contributed to the phenomenon of acid rain (acid rain is defined as rain or snow at a pH below 5.6.) Over the past two hundred years, the acidity of precipitation has changed from a nearly neutral solution to a dilute solution of sulfuric and nitric acid. Parts of the eastern United States and Western Europe are most severely affected by this occurrence. The most severe case of acid rain recorded occurred in Scotland in 1974 when the rain had a measured pH of 2.4 (3).

The effects of acid rain on the environment are not fully understood as yet, but it is known that the acidification of lakes and streams often results in a slower rate of organic matter decomposition and a reduced population density of phytoplankton, zooplankton and fishes. Many of the adverse effects of acid rain are thought to be hidden, especially those associated with synergistic effects between the acid and the additional environmental stresses placed on the organism. For example, these effects may be manifested in terms of increased susceptibility of the organism to pathogens and predators (3).

Acid precipitation has been identified as one of the two major global environmental problems facing the world today by the President's Commission on Health and Environmental Effects of Increased Coal Utilization (3). The only way to control the acid precipitation problem is to decrease the emissions of sulfur and nitrogen oxides to the atmosphere. But, at present, it appears as though the United States' future energy
policies will dictate the increased use of the nation's abundant coal reserves in lieu of dwindling and costly foreign oil supplies. This mandate will aggravate the existing acid precipitation problem unless more stringent measures are taken to control sulfur and nitrogen oxide emissions.

Sulfur dioxide also exhibits adverse effects on various types of vegetation, buildings and many materials. In areas polluted by large concentrations of sulfur dioxide, vegetation cannot survive at all. The conversion of sulfur dioxide to sulfuric acid makes it especially dangerous to plant life. Sulfur dioxide concentrations as low as 0.1 to 0.2 P. P. M. are phytotoxic to some plant life (4).

Visibility reduction in urban areas can also be attributed to sulfur dioxide in the atmosphere. The hygroscopicity of sulfur dioxide is responsible for the formation of aerosol droplets in the size range of less than one micron. This size droplet is quite effective in scattering visible light (4).

Seventy billion pounds of sulfur dioxide were emitted in the United States in 1970, 77% of which came from the burning of sulfur-containing fossil fuels. It is estimated that 250 billion pounds of sulfur dioxide will be emitted by the year 2000 if no further corrective actions are taken (6).

Industrial incinerators, sulfuric acid plants, petroleum refineries, coke processing plants, and smelting plants all contribute significantly to sulfur dioxide emissions. But, the major source of sulfur dioxide pollution can be traced to coal burning electric generating plants, which have doubled their output every ten years in the past. In 1976, power plant emissions of sulfur dioxide totalled
46 billion pounds, and these emissions are expected to increase to 68 billion pounds by the year 2000 (7). These estimated figures will likely underestimate the problem because of the anticipated increase in coal utilization resulting from the current energy situation.

As the nation continues to grow economically, so will the demand for electricity. In 1970, 1514 billion kilowatt hours of electricity were generated, 82% of which was produced by fossil fuel burning plants (6).

On October 15, 1978, Congress passed the National Energy Act (NEA) with the intentions of reducing America's oil imports by the year 1985. The Power Plant and Industrial Fuel Use Act, which is one of the five bills composing the NEA, prohibits the use of oil or natural gas in new electric generating plants or in new industrial boilers which have a fuel heat input rate of 100 million BTU's per hour or greater (8).

The preceding two paragraphs point out the current trend towards increased sulfur dioxide emissions. The Clean Air Act Amendments attempt to curtail this problem by establishing a schedule for decreasing sulfur dioxide emissions for both new and existing facilities. The New Source Performance Standards (NSPS) limit sulfur dioxide emissions for power plants to 1.2 pounds per million BTU when solid fuel is burned. This requires 70% sulfur dioxide removal when burning 3% sulfur coal. These standards apply for all power plants for which construction or modification commenced after August 17, 1971. It is likely that more stringent NSPS standards will be imposed in the near future (7).
CHAPTER II
SULFUR DIOXIDE REMOVAL TECHNOLOGIES

In light of the current sulfur dioxide emission standards and the distinct possibility of even more demanding standards arising in the near future, industry has been compelled to face the sulfur dioxide problem. Presently, industrial sources utilizing coal for energy can turn to three basic options. These include physically cleaning coal before combustion, burning low sulfur coals, and employment of one of the flue gas desulfurization (FGD) technologies now commercially available. Emerging technologies may present industry with some alternative sulfur dioxide control technologies by the mid-1980's. The most promising of these emerging technologies are coal gasification, solvent refined coal, coal liquefaction, and fluidized bed combustion (7).

LOW SULFUR COALS

The burning of naturally occurring low sulfur coals would appear to be the simplest method of controlling sulfur dioxide emissions while simultaneously meeting the nation's increasing coal demands. Unfortunately, production of low sulfur coal is limited and most low sulfur coals are found in the western sector of this country. Utilization of low sulfur coals by mid-western and eastern states requires that the coal be transported over long distances, resulting in an overall cost comparable to that incurred when local high sulfur coals are burned in conjunction with some type of flue gas desulfurization
technology. Also, most low sulfur coals can just meet present NSPS standards. If these standards become more stringent in the future, the burning of low sulfur coals would no longer be a viable option in itself (7).

**FLUE GAS DESULFURIZATION TECHNOLOGIES**

Until clean coal-derived fuels become economically competitive with oil, FGD technologies will increase in importance. The ideal FGD system will provide adequate sulfur dioxide control, avoid cooling of stack gases and thereby prevent buoyancy losses, and produce an easily stored, concentrated and saleable byproduct (9). Such an ideal system is quite difficult to develop and, as yet, no one has accomplished this task.

Existing FGD technologies can be grouped into four general categories: dry-absorption systems, wet-absorption systems, catalytic oxidation systems, and wet-and dry-adsorption systems (6).

In all cases, sulfur dioxide removal from stack gases presents many general problems. The amount of stack gas to be processed is one such problem. A 1,000 mega-watt boiler emits over 100,000 tons of gas per day (10). Particulate matter must usually be removed from these gases before a desulfurization process can be employed, thus presenting another problem.

Wet processes generally produce large amounts of wet sludge which present solid waste disposal problem. Dry-absorption processes can eliminate this waste disposal problem, but they also have disadvantages. When designing such a system, it is often difficult to provide adequate gas-solid contact time to allow the
sulfur dioxide to diffuse to the interior of the absorbent particles. Thus sorbent utilization per pass is reduced in comparison to a wet-absorption system (10).

Most dry-absorption systems are regenerable and the regenerated absorbent tends to become less reactive and to physically deteriorate over several cycles. Wet systems generally do not experience deterioration of the absorbent, but wet systems cool the stack gases and thereby necessitate a gas reheat scheme to restore the gases' bouyancy (10).

Many regenerable processes produce elemental sulfur as a byproduct and employ hydrogen sulfide as a reductant. This poses a problem of hydrogen sulfide availability or generation. A regenerative process for a coal-fired power plant with a generating capacity of 1,000 megawatts utilizing 3.5% sulfur coal will require 31 tons of hydrogen sulfide per hour based on a typical Claus type reduction reaction (11).

With the reduced availability of naptha, natural gas, and petroleum residues, some power plants are turning to coal as a source of reducing gas. This can result in up to a 4% increase in coal input (11).

Although FGD processes possess some inherent problems, they are presently one of the few sulfur dioxide control alternatives commercially available. Currently, over 60 different FGD systems are operating or are under development (6). A brief summary of a limited number of FGD processes will be presented in the following pages. The processes will be grouped according to the previously mentioned four categories.

**DRY-ABSORPTION PROCESSES**

Of all the dry absorption processes, injection of limestone or dolomite directly into the furnace is the simplest approach. Unfor-
fortunately, only 25-35% of the sulfur dioxide in the flue gas is removed, and this process greatly increases dust loads. Direct injection of nahcolite, a naturally occurring form of sodium bicarbonate, results in the removal of 70% of the sulfur dioxide present. Problems associated with nahcolite include the cost and availability of nahcolite, as well as the water pollution problems encountered when disposing of the highly soluble salts (sodium salts) in ash disposal areas (6, 12).

The U.S. Bureau of Mines has developed a dry-absorption process which utilizes alkalized alumina as a sulfur dioxide absorbent. Sulfur dioxide is removed from the flue gas in an absorber operating at 625°F. The spent absorbent is regenerated with a reducing gas and elemental sulfur is recovered in a Claus unit. The absorber must be installed between the economizer and the air preheater because of the high reaction temperature. Thus the system is difficult to install in existing power plants. The system also has a high rate of absorbent attrition which greatly increases its operating costs (6, 12, 13).

Japan's Mitsubishi Heavy Industries has developed a sulfur dioxide removal system which uses a dry, activated manganese dioxide as an absorbent. The process, referred to as the DAP-Mn Process, employs an entrainment type absorber at operating temperatures between 212°F and 356°F. The sulfur dioxide reacts with the manganese dioxide to form manganese sulfate which is then regenerated by the addition of ammonia and air. Ammonium sulfate is formed as a byproduct but it is difficult to market (6, 12).

The Grillo Mixed Metal Oxide Process utilizes a mixture of manganese dioxide and magnesium hydroxide deposited on coke as a sulfur dioxide absorbent. Manganese sulfate and magnesium sulfate are the products of the reaction. The spent absorbent is mixed with pulverized
coal and heated to 1650° F. This procedure reduces all sulfur compounds to gaseous sulfur, hydrogen sulfide, and/or carbonyl sulfide and regenerates the absorbent. The gas stream formed during the regeneration step is burned to yield sulfur dioxide which is then fed to a sulfuric acid plant (6).

Ash from the combustion of lignite coal is used as a sulfur dioxide absorbent in the Still Lignite Ash Process. The ash is first hydrated. This step converts the ash to calcium hydroxide because of its high lime content. The sulfur dioxide reacts with the hydrated ash to form calcium sulfites and a small amount of sulfates. The spent ash is thermally regenerated, releasing sulfur dioxide which is subsequently sent to a sulfuric acid plant. This system has the advantage of low absorbent costs, but the absorbent can experience fouling (6).

Copper oxide supported on alumina is the absorbent used by the Shell Flue Gas Desulfurization Process. The copper oxide reacts with the sulfur dioxide in the presence of oxygen to form copper sulfate. This reaction takes place at temperatures between 700° and 800° F. The copper sulfate formed is reduced to release sulfur dioxide which can then be converted into liquid sulfur dioxide or elemental sulfur (6, 14).

WET-ABSORPTION PROCESSES

Wet-absorption is the most common FGD technology commercially employed. The Combustion Engineering Process utilizes an alkaline earth additive which is injected directly into the furnace. The additive, which is calcined to calcium oxide and/or magnesium oxide in the furnace, reacts with the sulfur dioxide in the flue gas to form calcium and magnesium sulfates and sulfites. This reaction
removes 20-30% of the sulfur oxides present, including all of the sulfur trioxide present. Flue gas containing unreacted calcium oxide, magnesium oxide, and sulfur dioxide then enters a wet scrubber where the unreacted additives react with water and the remaining sulfur dioxide. The scrubber removes 90% of the remaining sulfur dioxide and virtually all of the particulate matter contained in the flue gas (6, 12).

The Wellman-Lord Process employs an initial scrubbing of the flue gas with water to remove particulate matter and sulfur trioxide. The gas is then scrubbed with a potassium sulfite solution which reacts with the sulfur dioxide present to form potassium bisulfite. At this point temperature control is crucial. The temperature must be kept within a narrow range to obtain good sulfur dioxide removal. The potassium bisulfite solution formed is then cooled to form a potassium pyrosulfate solution. Steam stripping of this solution yields sulfur dioxide for recovery and potassium sulfite for recycle back to the scrubber (6, 12, 15).

A eutectic mixture of lithium, sodium, and potassium carbonates (32 wt. % lithium carbonate, 33 wt. % sodium carbonate, and 35% potassium carbonate) is the sulfur dioxide absorbent used in the Atomic International Molten Carbonate Process. Dust is first removed in an electrostatic precipitator, and the flue gas is then scrubbed with the molten salt mixture at 800° F. The high scrubbing temperature eliminates the need to reheat the effluent gas stream. The sulfur dioxide reacts with the melt to form sulfates and sulfites. The effluent melt is then preheated to between 1100° and 1400° F before a reduction step is employed. This reduction yields 30%
hydrogen sulfide, 35% carbon dioxide, and 35% water as well as the regenerated melt (6, 10, 12).

Many wet-absorption processes scrub the gas with an ammoniacal solution. In the Mitsubishi Ammonia Process, ammonia reacts with water and sulfur dioxide to form ammonium sulfite. The ammonium sulfite is then oxidized to ammonium sulfate which serves as a saleable byproduct. The Showa Denko Process employs the same type of reaction scheme, but the process produces liquid sulfur dioxide in place of ammonium sulfate because of its better selling potential (6, 12).

The Stone and Webster/Ionics Process utilizes an aqueous caustic soda solution to absorb sulfur dioxide. The sodium bisulfite solution formed in this process is sent to a stripper which yields pure sulfur dioxide. The sulfur dioxide is sent to a sulfuric acid plant. The sodium sulfate solution from the stripper is sent to a special electrolytic cell where caustic soda, sodium acid sulfate, dilute sulfuric acid, oxygen and hydrogen are produced. The caustic soda is recycled to the absorber, the dilute acid and oxygen are sent to the oxygen plant, and the hydrogen is burned in a heater to reheat the effluent gases before entering the stack. The electrolytic cell consumes a great deal of energy, and therefore, this system is best suited for power plant application (6).

The Citrex Process uses a buffered citrate solution at temperatures between 110° and 140° F to scrub the flue gas after particulate removal is accomplished in a countercurrent absorber. Sulfur dioxide is fifty more times soluble in a buffered citrate solution than in water alone. The liquor from the absorber is contacted with hydrogen sulfide in a reactor at 1500° F to produce elemental sulfur. This system produces
.5 pounds of sulfur per pound of sulfur dioxide removed (16, 17).

The Chemico-Basic Process employs an aqueous slurry of magnesium oxide as a sulfur dioxide absorbent. The flue gas, after passing through a particulate remover, enters a scrubber where it contacts the magnesium oxide slurry and forms magnesium sulfite crystals. A bleed stream taken from the slurry circulation loop is sent to a centrifuge where unreacted magnesium oxide and sulfite crystals are separated from the mother liquor. The mother liquor is recycled to the absorber. The sulfite crystals are dried and calcinated to regenerate magnesium oxide and release sulfur dioxide. The sulfur dioxide is then processed in a sulfuric acid plant, claus plant, or liquid sulfur dioxide plant (6, 18).

**CATALYTIC OXIDATION PROCESSES**

Catalytic oxidation processes involve the oxidation of sulfur dioxide to sulfur trioxide. The sulfur trioxide produced can be easily recovered without cooling the effluent gas stream. The main disadvantage associated with this approach is the high reaction temperature required. Most processes operate at or near 850°F. This high reaction temperature requires the catalytic converter to be located ahead of the economizer. The process also requires that most of the particulate matter be removed from the flue gas before it comes in contact with the catalyst to prevent catalyst fouling (6).

The Monsanto-Cat-Ox system utilizes a vanadium pentoxide catalyst. After passing through an electrostatic precipitator, the flue gas enters the converter where the vanadium pentoxide catalyzes the conversion of sulfur dioxide to sulfur trioxide. The sulfur trioxide is then
converted to 78% commercial grade sulfuric acid. The system has only fly ash as a waste product (6, 12, 19).

The Kiyoura Process also uses vanadium pentoxide as a catalyst, but this system produces ammonium sulfate as a byproduct rather than sulfuric acid. Ammonia is injected into the gas stream between the economizer and the air preheater. The ammonia reacts with the sulfur trioxide and water present to form solid ammonium sulfate. The ammonium sulfate is then mechanically collected from the flue gas before it enters the stack (6, 12).

WET-AND DRY-ADSORPTION PROCESSES

In general, wet- and dry-adsorption processes utilize some type of carbon as a sulfur dioxide adsorbent. The adsorbed sulfur dioxide is oxidized by the oxygen contained in the flue gas and then absorbs water to form sulfuric acid in and on the carbon structure.

The Lurgi Sulfacid Process initially cleans and cools the flue gas to between 140° and 150° F. The gas then enters a bed of porous carbon where the sulfur dioxide contained in the flue gas is adsorbed. Oxygen and water are injected into the bed to promote the direct conversion of sulfur dioxide to sulfuric acid. Water spray continually washes out the acid formed on the carbon. The acid is then concentrated for commercial uses (6, 12). The Hitachi Process is very similar to the Sulfacid Process. The main difference occurs in the washing technique used to recover the sulfuric acid (6, 12).

Coke is used as the adsorbent in the Reinluft Process. Flue gas passes through a two-stage countercurrent adsorber. Sulfur dioxide and sulfuric acid mist are adsorbed on the coke in the first stage. The gas is then cooled to enhance sulfur dioxide oxidation, and then
enters the second stage where adsorption continues. The spent adsorbent enters a desorber where it is contacted with a reducing gas at 750°F. This step regenerates the coke and releases sulfur dioxide which is processed in a sulfuric acid plant (6, 12).

The FW-BF (Foster-Wheeler, Bergbau-Forschung) Process utilizes an activated char as an adsorbent. Sulfuric acid is formed within the char pores, and the char is then thermally regenerated at 1200°F. At this temperature all the reactions which occurred in the adsorber are reversed. The regeneration step yields a stream of sulfur dioxide rich gas which is reduced to elemental sulfur (20).

A comprehensive discussion of the chemistry involved in many of the FGD processes just described can be found in a report prepared by the U. S. Bureau of Mines entitled Sulfur Dioxide–Its Chemistry and Removal From Industrial Waste Gases (21).

COAL CLEANING PROCESSES

As an alternative to FGD systems, many individuals have directed their attention to coal cleaning processes. Coal cleaning processes consist of physical or chemical methods of removing impurities from coal before combustion. Presently, only about 40% of the coal used by power generating facilities undergoes any type of precombustion cleaning (22).

Many physical coal cleaning techniques are based upon the difference in specific gravity between coal and inorganic pyrites. New techniques are attempting to separate coal and pyrite particles in a magnetic field. Two such projects utilizing magnetic separation methods are now in progress. At present, only 16-17% of the coal
mined in the United States can be cleaned effectively using physical separation techniques (22).

Chemical separation techniques may prove to be more effective than the current physical separation techniques. One such chemical separation process leaches out pyrite with aqueous ferric sulfate at temperatures between 250° and 265° F and pressures between 50 and 100 psig. Another process oxidizes the pyritic sulfur to sulfate. The sulfate goes into solution and a solids-liquid separation step is employed to remove the sulfate. The use of various strains of bacteria which can desulfurize coal has also been suggested as a potential process (22).

In some instances, the sulfur content of the coal may be as high as 70% organic sulfur. Consequently, various methods capable of removing the organic sulfur present in coal have been tested. Two of the more promising processes are centered around leaching with sodium hydroxide at elevated temperatures, and a system which uses steam and compresses air at temperatures between 300° and 400° F to remove the organic sulfur. Forty percent of the organic sulfur can be removed by these processes (22).

For an in-depth look at coal cleaning technologies, the interested reader is referred to a book edited by Thomas Wheelock entitled Coal Desulfurization: Chemical and Physical Methods (23).

As mentioned earlier, emerging technologies may someday provide economical alternatives to the presently available sulfur dioxide control methods. A brief account of the more promising of these technologies will follow.
FLUIDIZED BED COMBUSTION

Fluidized bed combustion (FBC) is one of the most promising new technologies currently under development. An article recently published by Chemical Engineering entitled "Burning Coal in Fluidized Beds" presents an informative review of present FBC technology (24).

In the FBC process, a bed of inert materials usually consisting of limestone or dolomite is fluidized with air. The bed temperature is raised to between 800° and 1000° by burners. Fuel is fed into the bed and ignites when coming in contact with the hot inerts. Final combustion temperatures range between 1500° and 1600° F (25).

The sulfur dioxide released by the burning coal reacts with the limestone or dolomite during the fluidization process. Dry, solid wastes consisting of calcium oxide, calcium sulfate and ash are the final product of the process. This waste product may have potential for commercial applications. Possibilities include agricultural liming compounds, neutralizing agents for municipal waste-water treatment, and use as a road aggregate and construction material (26).

FBC units can remove up to 90% of the sulfur dioxide produced during the combustion of coal even when 4-5% sulfur coal is burned. The system also reduces nitrogen oxide emissions because of the lower combustion temperatures (25).

FBC units can burn a large variety of fuels without changing the design of the system. Consequently, this technology could possibly be standardized and thereby reduce production costs (25). Some of the current cost estimates predict that FBC units will be more economical than coal fired boilers equipped with scrubbers (26).

One disadvantage of the FBC systems is their high limestone re-
quirements as compared to a wet scrubbing system utilizing limestone. The calcium to sulfur ratio for an FBC unit which removes 90% of the sulfur dioxide is approximately three, while that for a wet scrubbing system is approximately 1.1 (26).

In the near future, clean coal derived fuels could help to reduce America's dependence on foreign oil imports. Presently, many major energy companies are involved with the development of economically feasible coal liquefaction and gasification processes. The diagram on the following page shows the basic routes available for the production of coal derived fuels (29).

Current technology can convert coal to low, medium and high BTU gas, but oil and natural gas are still less expensive at this state of development.

COAL GASIFICATION

Coal gasification processes convert coal to gas by means of a controlled partial oxidation reaction. Slag and ash are the principal byproducts of these processes. The majority of the sulfur contained in the coal is converted to hydrogen sulfide. The hydrogen sulfide can be removed by commercially available methods which are less expensive than sulfur dioxide scrubbing systems. Gasification processes can potentially remove more sulfur from coal than the current scrubbers operating in power plants today (27).

Eighty coal gasification plants, each producing 250 million cubic feet of gas per day, would be required to produce the equivalent of 20% of the current United States' oil consumption. Each of these plants would consume approximately 12,000 tons of high quality eastern coal per day. This would result in an increased coal demand of over
CLEAN FUELS FROM COAL

Coal

Gasification

Low-Btu
CO, H₂, CH₄,
H₂, CO₂, H₂S

Medium-Btu
CO, H₂, CH₄,
CO₂, H₂S

Cleanup

Clean Fuel Gas
Low (100-250) Btu

Clean Fuel Gas
Medium (250-550) Btu

Methanation

Clean Fuel Gas
High (950-1000) Btu

Gas

Pyrolysis

Oils

Char

Dissolution

Filtration and Solvent Removal

Ash
Pyritic Sulfur

Hydrotreating

H₂

H₂S

Hydro-Treating

H₂

Clean Liquid Fuel

Clean Liquid Fuel

Clean Liquid Fuel

Fischer-Tropsch

Clean Solid Fuel

Fig. 2.1 (29)
300 million tons per year (current coal production equals 600 million tons per year.) The environmental impact of such a project is presently being studied. Concerns are centered around the leaching of salts and trace metals from refuse and slag, emissions of gas effluents and waste water clean up (28).

In the future, in-situ gasification of difficult to mine coals may be possible. Presently, 85% of the nation's coal reserves cannot be economically mined by current technologies.

**COAL LIQUEFACTION**

Coal liquefaction processes convert coal to a liquid form. These processes can be grouped into three basic categories: direct liquefaction processes, indirect liquefaction processes, and pyrolysis. Direct liquefaction processes dissolve the coal in a solvent, and ashes which contain pyritic sulfur are then filtered out. The solvent is removed and the resulting heavy crude (syncrude) is reacted with hydrogen. The reaction between the hydrogen and the syncrude removes the organic sulfur and also improves the quality of liquid hydrocarbon. The SRC process can produce a solid fuel by permitting the syncrude to cool before the hydrotreating step (29). Liquid products produced by the direct liquefaction processes contain 65-70% of the energy contained in the original coal feedstock (27).

Indirect liquefaction processes first gasify the coal to produce a synthesis gas consisting of hydrogen and carbon monoxide. The synthesis gas is then converted to liquid hydrocarbons in the presence of a catalyst (Fischer-Tropsch reaction.) Products produced from the indirect liquefaction processes are essentially pollutant free, but the process is characterized by low efficiency (45-60%) and low
yields (27).

Pyrolysis involves heating the coal to drive off the naturally occurring oils contained in it. These oils are condensed and then treated with hydrogen to remove sulfur and improve the quality of the oil. Pyrolysis processes produce large amounts of byproduct gas and char which must be disposed of economically (29).
CHAPTER III
FLUIDIZATION

In recent years the application of fluidization technology to chemical engineering has become increasingly important. Today it is generally accepted as a unit operation of chemical engineering. The petroleum industry employs fluidization processes for the catalytic cracking of petroleum. Fluidization processes are also widely used in drying, the calcination of limestone, catalysis, Fischer-Tropsch reactions, gasification of coal and the transport of a variety of solids (30). As mentioned previously, fluidized bed combustion of coal appears to have the potential for extensive use in the near future.

This chapter is intended to present basic concepts of fluidization. The following pages will be concerned with a description of the fluidized state, as well as a brief account of the concepts of minimum fluidization velocity, gas distribution, bubble phenomenon, and entrainment. The last section of this chapter will discuss the advantages and disadvantages of fluidized bed reactors.

THE FLUIDIZED STATE

To visualize the fluidized state, consider a tube partially filled with a granular solid. Air is admitted through the bottom of the tube. At low velocities, the air passes through the tube without causing any particle movement. As the air velocity is progressively increased, the pressure drop of the air moving through the bed of
particles increases. Eventually, at a specific air velocity, the pressure drop of the air will be equal to the force of gravity acting on the particles. At this point the particles in the tube begin to move (31). A further increase in air velocity results in a slight expansion of the bed, but the particles are still in contact at this point. Increasing the air velocity slightly, the bed porosity increases even more and particles in small localized pockets of the bed may begin to separate. A further increase in air velocity now causes the majority of the particles to separate and the bed is considered to be in the fluidized state (31, 32). At a velocity just slightly above that required for the onset of fluidization the system is said to be in the minimum-fluidization state (also referred to as a quiescent fluidized bed.) Systems at the minimum-fluidization state exhibit very little particle mixing, and even some small pockets of particles may not yet be fluidized (32, 33).

At velocities in excess of that required for the minimum-fluidization state the bed undergoes more expansion and particle mixing occurs. The system is now referred to as a turbulent fluidized bed. Increasing the air velocity considerably in excess of that required for the minimum-fluidization state causes the particles to be entrained by the air and carried up and away with it. At this point the system is described as a dilute fluidized phase system (33).

The characteristics of an ideal fluidized bed can be graphically represented by a log-log plot of pressure drop versus gas flow rate (33).
The line between $E_1$ and $E_2$ represents the fixed-bed pressure drop which occurs at a constant voidage of $E$. At the point $E_1$, bed expansion begins and continues along the horizontal line. When the bed expansion is slightly larger than the value represented by $E_{mf}$, some particle motion begins and the bed is in the quiescently fluidized state. For an ideal fluidized bed a decrease in gas flow rate back to point $E_2$ will result in a fixed bed system again. This perfect reversibility occurs at a pressure drop equal to $P_w$ (33). $P_w$ can be calculated using the following formula:

$$P_w = \frac{\text{weight of solids in the column}}{\text{cross sectional area of the column}} \quad (30).$$

However, for most real systems there is no sharp transition between fixed and fluidized bed, and most systems usually exhibit a rather large "transition region" (32).

Physical properties of the solid particles and the fluid medium, as well as the operating conditions under which the system functions, cannot always be used to predict the behavior of the fluidized system. But, in general, the following list of solid and fluid properties tend to produce a well fluidized system: low particle density, small particle size, small particle size range, spherical particle shape, and a high
fluid density (32). Unfortunately, those properties which lead to a well fluidized system are often the same properties which can make the onset of fluidization difficult. For example, if the material to be fluidized exhibits high surface forces between particles, then smaller particles which have a higher specific surface will also have a higher level of surface forces. Consequently, the separation of particles will be a more difficult task (32).

Channeling is a fluidized bed abnormality which is closely related to the characteristics of the solid to be fluidized. A system which experiences channeling develops flow patterns which cause exceptionally large amounts of the fluid to pass through only one section of the bed (33). In cases of severe channeling, high proportions of the fluid may flow through the channel with the remainder of the bed remaining unfluidized (32).

Channeling can be categorized into two basic types: "through channeling" and "intermediate channeling." "Through channeling" is characterized by the development of a channel which extends throughout the entire bed. A system which undergoes "intermediate channeling" forms a channel in only one section of the bed (33).

Channeling results in a nonhomogeneous bed density. The lack of homogeneous bed density alters local space velocities, and consequently local space velocities may vary from the overall planned space velocity. The final effect is manifested as erratic temperature profiles throughout the bed as well as unequal solid-gas contact time in different areas of the bed. The net result is an inefficient system (33).

Many factors can influence channeling. One of the most important factors is particle size. Generally, smaller particles are more prone
to channel than are larger particles. Vessel diameter and gas inlet
device also strongly influence channeling tendencies. Large vessels
tend to decrease the occurrence of channeling, as well as gas inlet
device which give a uniform gas distribution (33).

Particle diameter and vessel size are also critical factors which
influence the occurrence of wall effects. Wall effects occur when the solid
particles become large in comparison with the radius of curvature of the
reactor vessel. In this situation the particles tend to recede from the
vessel wall and form a concentric ring of higher than average bed voidage
(33). This deviation in bed voidage disrupts flow patterns in the reactor.
A reactor having a particle diameter to vessel diameter ratio of .25 will
have 10% more void than a reactor with no wall effects. The ratio of vessel
diameter to particle diameter should be greater than sixteen to avoid wall
effects (33).

MINIMUM FLUIDIZATION VELOCITY

As discussed previously, minimum fluidization velocity is the upward
fluid velocity through a bed of particles at which the pressure drop of
the fluid is equal to the weight of the bed divided by the cross sectional area of the reactor. This velocity indicates the point of incipient
fluidization. It is often quite useful to be able to reliably predict the
minimum fluidization velocity of a given system. Although most systems
operate well above the minimum fluidization velocity, some systems are most
efficient when operating close to the minimum fluidization velocity. For
example, systems which utilize solid particles which tend to easily
fracture usually operate near the minimum fluidization velocity to
minimize attrition and elutration losses (33).

There are numerous empirical equations in the literature which
predict a reasonable value for the minimum fluidization velocity of a given system. The majority of these equations are based on readily available properties of the fluid and the solid. In general particle diameter, the difference in solid and fluid density, gas viscosity, a gravitational constant, and a experimental constant are the basic parameters involved in the equations (30).

Work done my Miller and Logwinuk has shown that the minimum fluidization velocity is substantially a function of the square of the particle diameter (30). Also, minimum fluidization velocity does not depend upon the height or the weight of the solids in the reactor.

Leva has prepared an equation to predict minimum fluidization velocity which has proved to be quite reliable in a large number of instances. The equation is usually written in the following form:

\[ G_{mf} = \frac{688D_p^{1.82}}{U^{0.88}} \left( e_F (e_S - e_F) \right)^{0.94} \]

where

- \( G_{mf} \) = minimum fluidization velocity in lbs./hr.-ft.\(^2\)
- \( D_p \) = particle diameter in inches
- \( e_S, e_F \) = solid and fluid density respectively in lbs./ft.\(^3\)
- \( U \) = gas viscosity in centipoise (33).

**GAS DISTRIBUTION**

One of the most important factors governing a well fluidized system is the uniform distribution of the entering gas. In the operation of commercial fluidized bed reactors it has been found that the performance of the system is greatly affected by the inlet gas distributor (34). Although particle and fluid properties also exert a significant influence on the behavior of the system, in most instances grid design is
the variable with the greatest degree of freedom (34). Unfortunately, most bench scale reactors have small diameters and consequently, there is little latitude for grid variation.

To insure a well fluidized system, every hole in the gas distributor should be passing gas (34). Also, the greater the grid pressure drop, the more likely are the chances of uniform gas distribution and, hence, a well fluidized system. A grid pressure drop equal to 30% of the bed pressure drop is commonly employed in large scale fluidized bed reactors, although some commercial reactors operate with a grid pressure drop as high as one or two times the bed pressure drop (34).

Porous plate distributors, screen distributors and multi-orifice plate distributors are three of the most commonly employed gas distribution devices. Of the three, porous plate distributors are generally considered to be most efficient (32, 33). Porous plate distributors give uniform gas distribution and they diminish the occurrence of channeling. Also, the point of incipient fluidization is well defined when porous plate distributors are employed. Porous plate distributors have two main disadvantages. They are expensive and they have poor mechanical strength. Consequently, it is not always practical to use porous plate distributors in large reactors (32).

Screen distributors tend to induce channeling because of the tendency for some of the holes in the screen to become blocked (33). Multi-orifice plate distributors also have disadvantages. The most serious disadvantage associated with multi-orifice plate distributors is that they often cause the bottom portion of the bed to be fluidized to a lesser extent than the upper portion of the bed (33).
If the gas flow rate of a fluidized bed reactor is increased above the minimum fluidization flow rate either of two occurrences is likely to take place. The bed can continue to expand and as a result increase the average distance between particles; or bubble formation can occur. Bed expansion is likely to occur in liquid-solid systems or gas-solid systems using very fine solid particles but only over a small velocity range. Bubble formation occurs with all other gas-solid systems (32). In general, if the ratio of solid to fluid densities exceeds ten, the system is likely to bubble (32).

Bubbles which form in fluidized bed reactors are very similar to large gas bubbles which form in boiling liquids. For this reason, there is often an analogy drawn between a boiling liquid and a bubbling fluidized bed. The gas velocity can be compared to the temperature of the liquid because the amount and vigor of the bubbles in a fluidized bed increases with increasing gas velocity. The bubbles formed in a fluidized bed are responsible for solid particle movement and thus are responsible for good particle mixing and high heat transfer coefficients (32).

Bubble shapes are usually assumed to be spherical with an indented base that occupies about one third of the total sphere volume (35). In reality, there are different bubble shapes associated with each individual system. The bubble shape is determined by the type of solid used in the system (32).

Bubbles rise through the bed at a velocity which is determined by the bubble diameter. As the bubbles rise through the bed they tend to elongate as they approach the surface. Bubble velocity can be
calculated using the following equation: \( u_B = 0.78(g a)^{1/2} \), where 
\( u_B \) represents the bubble velocity, \( a \) represents the bubble diameter, and \( g \) represents the acceleration due to gravity (35). Bubbles usually rise through the bed at velocities of the order of magnitude of ten to 1,000 times the minimum fluidization velocity (34). A typical velocity is around two ft./sec. (35).

Bubble diameter can be determined by measuring the size of the eruptions which occur as the bubble breaks the surface of the bed. The bubble diameter is then estimated according to the following relationship: \( d_B = 2/3 \) (eruption diameter), where \( d_B \) represents the bubble diameter (37).

Reported experimental data concerning bubble size indicates an approximately linear increase in bubble diameter with increasing height above the gas distributor (36). Bubbles which coalesce are responsible for this increase in bubble diameter with height above the gas distributor. Bubbles tend to coalesce because of the overall gas expansion resulting from the pressure decrease with height above the distributor (32).

Rowe has prepared a correlation which can be used to predict bubble size at any particular bed height (36). The equation is written in the following form: 
\[
  d_B = \left(\frac{u - u_{MF}}{h + h_o}\right)^{1/2} \left(h + h_o\right)^{3/4} / g^{1/4}
\]
where 
\( d_B \) = average bubble size, 
\( u - u_{MF} \) = excess gas flow (gas velocity minus minimum fluidization velocity) 
\( h \) = height above the distributor,  
\( h_o \) = characteristic constant of the distributor and may be taken as zero for a porous plate distributor.

Using the above equation one can predict the maximum bubble size of a given system operating under specified conditions. Thus, one can
determine whether or not the bubbles will grow large enough to cause the system to slug. Slugging occurs when the gas bubbles coalesce to form a bubble the same size as the diameter of the reactor. Layers of particles will then be trapped between these large gas pockets and move up and down in a fashion similar to that of a moving piston. When the slug reaches a certain height it will disintegrate (32).

Slugging produces a very heterogeneous bed, and therefore affects gas-solid contact patterns. As is the case with channeling, slugging alters local space velocities and consequently causes erratic yields and temperature profiles (32).

Many theories have been generated to explain the occurrence of bubble formation in gas fluidized beds, but as yet, there has been no satisfactory and complete theory (32). The two-phase theory assumes that all the gas flow in excess of the minimum fluidization velocity forms bubbles (38). It also assumes that the interstitial gas moves upward through the dense phase at a velocity approximately equal to the minimum fluidization velocity (35). Thus the total flow through the bed is composed of interstitial gas flowing at the minimum fluidization velocity plus the gas associated with the bubbles traveling at the bubble velocity (35). The gas associated with the bubbles takes on two forms: that associated with the bubble wake and that in the essentially empty space of the bubble (38).

The bubble wake occupies the lower one third of the bubble and is composed of particles which travel with the bubble (32, 35). The bubble wake develops at approximately the same time that the bubble is formed, and consequently the wake consists of particles taken from the bottom of the bed. As a result the bubble wake is responsible
for carrying some material from the bottom of the bed and depositing it on the top of the bed, thus greatly enhancing particle mixing (35).

When the bubble velocity exceeds the upward interstitial gas velocity, the phenomenon referred to as cloud formation occurs (32). The empty gas bubble offers little resistance to gas flow. Consequently the pressure gradient present induces the gas to flow into the bottom of the bubble and out of the top. As the gas emerges from the top of the bubble, it is dragged back down along the bubble's sides by the solid particles which are traveling downward relative to the bubble. At this point, the pressure gradient again induces the gas to flow back up through the bubble (35). Thus, the gas circulates up through the bubble and down its sides forming a spherical "gas cloud" which moves with the bubble (32, 35).

Davidson proposes the following equation to predict the diameter of the spherical gas cloud: 

\[ d_c = d_B \left[ \frac{(a + 2)}{(a - 1)} \right]^{1/3} \]

where \( d_c \) represents the cloud diameter, \( d_B \) represents the bubble diameter, and \( a \) represents the ratio of the bubble velocity to the remote interstitial gas velocity (35).

In the above equation, the cloud diameter decreases as the ratio of the bubble velocity to the interstitial gas velocity increases. A high ratio of bubble velocity to interstitial gas velocity results in a cloud diameter which is only a little larger than the bubble diameter itself. Consequently the gas associated with the bubble is in contact with only a limited amount of solids which should theoretically reduce the efficiency of the reactor (35).

The success of commercial fluidized bed reactors which operate at velocities well in excess of the minimum fluidization velocity
indicates a flaw in the two-phase theory. According to the two-phase theory, these commercial reactors should have a large amount of gas associated with large, rapidly moving bubbles which have small cloud diameters, and consequently there should be poor gas-solid contact resulting in an ineffective system. Obviously, some other type of mechanism must be involved. Other possible contact mechanisms are centered around the concepts of gas diffusion from the bubbles into the dense phase of the system, mixing because of the shifting of large bed masses, and the "raining" of particles into the interior of the bubbles (34).

The "raining" of particles into the interior of the bubble is a concept developed by Zenz. In contrast to the two-phase theory which assumes that the surrounding solids flow around the bubbles, Zenz views bubbles in a gas fluidized bed as pockets of gas into which the surrounding solids can flow. The flow of solids into these pockets of gas displace the gas, and thus are responsible for the rise of the bubbles up through the bed (34). Consequently, Zenz feels that bubble phenomenon should be studied in terms of the flow characteristics of the solid rather than the flow characteristics of the bubbles (34).

**ENTRAINMENT**

As the fluidizing gas velocity is increased above the minimum fluidization velocity the bed becomes more and more turbulent until, at some specific velocity small particles become entrained in the gas (32). Systems which are susceptible to entrainment usually consist of a bed of particles which are varied in size. The bed usually contains a significant portion of large particles which were the original charge, and a lesser portion of smaller particles which are
often formed from attrition of the large particles (33). Particle attrition results principally from high velocity impacts and predominantly occurs in the vicinity of the reactor grid (34).

Two basic conditions must be met before entrainment of particles can occur; the superficial gas velocity must be sufficient to stratify the bed particles and the velocity must be larger than the terminal velocity of the particles entrained (33). The terminal velocity of a particle is the limiting velocity attained by a particle which is allowed to fall through a column of fluid at rest (32).

As the fluidizing gas leaves the top of the bed its point velocities can vary considerably. This non-uniform velocity distribution is caused by the bursting of bubbles as they reach the bed surface. Consequently both large and small particles may be carried away from the bed surface; the larger particles being carried away by some locally high velocity (32). At successively higher levels above the bed, the gas velocity profile becomes more and more uniform until at some specific height above the bed the velocity profile remains essentially constant. This height is referred to as the transport disengaging height or equilibrium disengaging height. The gas velocity at this height is basically equal to the superficial gas velocity (34). At the transport disengaging height all of the larger particles having a terminal velocity greater than the superficial gas velocity reverse their course and return to the bed. The remaining particles will be entrained with the gas (32, 34).

At heights above the transport disengaging height, the rate of entrainment remains constant, while below the transport disengaging height it increases rapidly as the bed surface is approached (34). The transport
Disengaging height appears to be a function of superficial gas velocity and bed diameter. As gas velocity increases, the velocity and frequency of bubble eruptions at the bed's surface increases, thus requiring a greater height to reach a stable velocity profile. The dependence of transport disengaging height on bed diameter is not well understood. But it appears as though wall effects associated with small diameter beds and poor gas distribution associated with large diameter beds may be responsible for this dependence (34).

Zenz and Othmer have prepared an empirical graphical correlation of transport disengaging height which is dependent upon only superficial gas velocity and reactor diameter (32). According to the graph, the transport disengaging height increases with bed diameter and increasing gas velocity.

Entrainment rates are known to vary with a number of factors. Entrainment decreases as the freeboard, which is the distance between the top of the expanded bed and the upper end of the fluidizing apparatus, increases (32, 34). Increasing the velocity of the fluidizing gas will increase entrainment. As the shape of the fines become more irregular, the rate of entrainment decreases and a decrease in the density of the fines results in an increased entrainment rate. Also, decreasing the diameter of the fines results in a rapid increase in entrainment. Entrainment rates should decrease with increasing bed height (33). Some data indicates that entrainment rates are smaller in beds which form small bubbles rather than large bubbles (32). Finally as mentioned previously, entrainment rates increase with increasing gas velocity.
ADVANTAGES AND DISADVANTAGES OF FLUID BED REACTORS

Fluidized bed reactors offer the following advantages over fixed bed reactors:

1) Fluidized bed reactors have a more uniform temperature distribution because of the rapid mixing of solids (35, 39).

2) Fluidized bed reactors exhibit higher heat transfer coefficients because of the movement of particles past internal and external heat transfer surfaces (33).

3) Fluidized bed reactors usually have a smaller pressure drop across the bed of solids than a comparable fixed bed reactor (33).

4) Fluidized bed reactors usually employ smaller size particles and, consequently, the chemical reaction rate is higher because of the smaller degree of resistance to pore diffusion through small particles and the vigorous gas-solid contacting (33, 39).

5) The liquid-like state of the particles in a fluidized bed allows for easy transport of bed particles. Also, the easy addition and removal of particles is a significant advantage when dealing with materials which are characterized by rapid-activity loss (33, 39).

Although fluidized bed reactors offer numerous advantages over fixed bed reactors, they also possess some distinct disadvantages. The following are typical disadvantages of fluidized bed reactors:

1) The flow of gases though a fixed bed reactor approximates plug flow. This is not the case with fluidized bed reactors which have complex flow patterns and often exhibit a good deal of gas bypassing. Consequently, fixed bed reactors offer more efficient gas-solid contacting (39).

2) Since fluid and solid properties determine the flow rate needed for fluidization, there is little freedom in adjusting space velocities (33).

3) If the solids undergo severe attrition, it may be necessary to adjust gas flow rates to maintain "good fluidization" (33).

4) Severe attrition of solids requires the replacement of solids which can be quite expensive (33).
5) Fluidized bed reactors require the installation of fine recovery equipment (33).

6) Fluidized bed reactors may experience significant amounts of equipment erosion (33).
CHAPTER IV
GOALS AND OBJECTIVES

The goal of this research was to provide information which will be necessary for the future development of a dry-phase flue gas desulfurization system which will utilize gamma-alumina as a sulfur dioxide adsorbent. A description of the entire system can be found in a Master's thesis by Mark Hereth (40).

The objective of this research was to compare sulfur dioxide removal rates from a simulated flue gas consisting of nitrogen, oxygen, carbon dioxide, and sulfur dioxide in fixed and fluidized beds of gamma-alumina, and to determine which system would be best suited for a pilot plant operation. The fixed bed data used for comparison was obtained from Hereth's work utilizing gamma-alumina as a sulfur dioxide adsorbent in a bench scale fixed bed reactor (40).

The fluidized bed data was obtained from a three in. I. D. reactor constructed of Pyrex glass. Space velocity, flue gas temperature, and the sulfur dioxide content of the flue gas were varied according to the experimental design discussed in the following chapter.

Emphasis was directed at determining the effect of different experimental conditions on the ability of the gamma-alumina adsorbent to remove between 100 and 90% of the sulfur dioxide present in the gas stream. Results concerning the removal of 90-100% of the sulfur
dioxide present in the flue gas were desired because this is the type of data necessary for the design of a large scale operation which would be competitive with presently available FGD systems, most of which claim to have 85 to 100% sulfur dioxide removal capabilities.
CHAPTER V
EXPERIMENTAL DESIGN

As mentioned previously, the temperature of the flue gas, the space velocity of the gas, and the percent of sulfur dioxide contained in the gas were the three variables investigated in this research. These three variables represent the principle factors which govern the success of failure of a typical dry-phase flue gas desulfurization system found in power plant applications.

A traditional method of investigating the effect of these three variables is to hold two variables at a constant value and vary the third. In this research, the method of factorial design was the basis for the experimental design employed because it is more efficient than the traditional method and it enables the investigator to determine any possible interactions which may occur between variables.

In a factorial design all levels of a given factor are combined with all levels of every other factor in the experiment (41). In this particular set of experiments there were three factors (variables) and two levels (values of the variables) chosen for each factor: a high level and a low level. Thus the experimental design can be represented as a $2^3$ factorial experiment. Eight experimental runs were required to satisfy this design.

Let $A$ represent space velocity, and $A_0$ and $A_1$ represent the lower and upper levels of $A$ respectively. $B$ represents the flue gas temperature and $C$ represents the sulfur dioxide content of the flue
gas. $B_0$ and $C_0$ will then represent the lower levels, and $B_1$ and $C_1$ represent the upper levels of the flue gas temperature and sulfur dioxide content respectively.

The following table shows the various treatment combinations which must be tested in order to satisfy the $2^3$ factorial design (42).

<table>
<thead>
<tr>
<th>$A_0$</th>
<th>$A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_0$</td>
<td>$B_1$</td>
</tr>
<tr>
<td>$C_0$</td>
<td>(l)</td>
</tr>
<tr>
<td>$C_1$</td>
<td>c</td>
</tr>
</tbody>
</table>

Table 5.1
Treatment Combinations For A $2^3$ Factorial Design

In the above table, the following method has been used to designate experimental conditions: a lower case letter represents the factor at a high level and the absence of a letter represents the factor at a low level. Therefore, (l) indicates that all factors are at a low level, and abc indicates that all factors are at a high level.

The following levels were used in the experimental runs taken:

- $A_0 = 1300 \text{ HR}^{-1}$
- $A_1 = 900 \text{ HR}^{-1}$
- $B_0 = 350^\circ \text{ F}$
- $B_1 = 450^\circ \text{ F}$
- $C_0 = 2\% \text{ SO}_2$
- $C_1 = 4\% \text{ SO}_2$

The space velocity levels represent the low and high values of the space velocity used by Hereth (40) and other researchers employing
various metal oxides as sulfur dioxide adsorbents (43, 44). The temperature values were chosen to represent the temperature of the flue gas found before and after the air pre-heaters in a coal-fired boiler. These temperatures are approximately $650^\circ F$ and $350^\circ F$ respectively. Unfortunately, the high level had to be reduced to $450^\circ F$ because of the inability of the Pyrex used in the construction of the reactor to withstand higher temperatures. The sulfur dioxide percentage levels represent the sulfur content of typical high sulfur coals employed in power plant boilers.

**INTERPRETATION OF RESULTS**

The effect of a factor is defined by Hicks (41) as the change of response produced by a change in the level of that factor. A $2^3$ factorial experiment can be represented by the vertices of a cube as shown in the figure below (41).

![Figure 5.1](image)

The high and low levels of A, B and C are represented by 1 and 0, respectively, on the A, B and C axes. The effect of A can be
calculated by the following standard equation:

\[ 4A = (a-1) + (ac-c) + (ab-b) + (abc-bc). \]

The average effect of A is then written as follows:

\[ A = \frac{1}{4}(a-1+ac-c+ab-b+abc-bc) \]  \hspace{1cm} (41, 42).

In the above equation the effect of A was determined by subtracting the experimental values obtained as A is increased from its low level to its high level while the levels of B and C are kept constant. Thus, \( a-1 \) represents the effect of A when B and C are at their low levels and \( abc-bc \) represents the effect of A when B and C are at their high levels. Likewise, \( ac-c \) represents the effect of A when B is low and C is high, and \( ab-b \) represents the effect of A when B is high and C is low.

The average effect of B and C can then be determined in a similar fashion:

\[ B = \frac{1}{4}(b-1+ab-a+bc-c+abc-ac) \]

\[ C = \frac{1}{4}(c-1+ac-a+bc-b+abc-ab) \]

An interaction between two factors means the change in response between levels of one factor is not the same for all levels of the other factor (41). Thus, to determine the effect of any possible interaction between factors the following method can be employed.

First consider the possibility of an interaction between A and B, regardless of C. At the high level of B, the effect of A is \( (ab-b) + (abc-bc) \), and at the low level of B, the effect of A is \( (a-1)+(ac-c) \). If these two effects differ, then there is an interaction between A and B. Thus, the interaction between A and B is the average difference between these two values and can be written as follows:
The interaction between BC and AC can be determined in the same manner and the equations are as follows:

\[ BC = \frac{1}{4}(1 + a - b - ab - c + ac - bc + abc) \]

\[ AC = \frac{1}{4}(1 + a + b - ab - c + ac - bc + abc) \]

The ABC interaction is determined by comparing the BC interaction at the low level of A with the BC interaction at the high level of A. The difference is the ABC interaction. The BC interaction at the low level of A is \((1 - b - c + bc)\), and the BC interaction at the high level of A is \((a - ab - ac + abc)\). Thus, the ABC interaction is as follows:

\[ ABC = \frac{1}{4}[(a - ab - ac + abc) - (1 - b - c + bc)] \]

The same equation is obtained if the AB interaction at the high and low levels of C, or the AC interaction at the low and high levels of B, is considered.

Frank Yates devised a simple technique to calculate the effect of each of the factors and their interactions in a \(2^k\) experiment (41, 42). This technique, known as the Yates Algorithm, is merely a simple mechanical method of calculating the various effects of factors and their interactions without directly substituting values into the previously mentioned equations. Consider the table (following page) which consists of arbitrary data chosen only to illustrate the Yates Algorithm method for a \(2^3\) experiment.

Column 1 indicates the yield of the various treatment combinations. Column 2 is obtained from column 1 by adding adjacent pairs of the yield values to make up the first half of the column, and subtracting adjacent pairs to form the second half of the column. For example, \(336 = 169 + 167, 280 = 145 + 135, -2 = 167 - 169, -10 = 135 - 145\), etc. Note that
<table>
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<th>Treatment Combination</th>
<th>Yield</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5) Avg. Effect</th>
<th>(6) Sum of Squares</th>
</tr>
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<tbody>
<tr>
<td>(1)</td>
<td>169</td>
<td>336</td>
<td>616</td>
<td>1231</td>
<td>I</td>
<td>---</td>
</tr>
<tr>
<td>a</td>
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<td>280</td>
<td>615</td>
<td>-29</td>
<td>A</td>
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</tr>
<tr>
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<td>338</td>
<td>-12</td>
<td>-117</td>
<td>B</td>
<td>-29.25</td>
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<td>-2.25</td>
</tr>
<tr>
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<td>-56</td>
<td>-1</td>
<td>C</td>
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</tr>
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Table 5.2
Yates Algorithm For A $2^3$ Experiment
the differences are always obtained by taking the second minus the first, third minus fourth, etc. Column 3 is obtained from column 2 in the same manner, and likewise, column 4 is obtained from column 3. For a $2^k$ experiment there are $k$ steps of this type. Also note that the order of the treatment combination must always be maintained.

If a fourth factor D were present, the yield values of d, ad, bd, abd, cd, acd, bcd and abcd would be added below the treatment combinations already shown (42).

Column 4 now shows the total effect of the factor or interaction listed in the effect column. Column 5 shows the average effect of these factors or interactions by dividing the total by four, which is the number of differences in each total for a $2^3$ experiment. Column 6 is the sum of the squares for each of the factors or interactions of the experiment (note that the denominator is always the size of the experiment; $2^3 = 8$). By simply looking at the sums of the squares column it is now possible to determine which factors or interactions stand out, and are therefore most significant (42).
CHAPTER VI
REACTOR DESIGN AND EXPERIMENTAL PROCEDURES

REACTOR DESIGN

The fluidized bed reactor was constructed from Pyrex piping purchased from the Corning Glass Company. The reactor was assembled from glass so that the behavior of the fluidized bed could be observed. Thus, fluidization abnormalities could be easily spotted, and hopefully corrected. A sketch of the reactor is shown on the following page.

The main reactor zone (F) was constructed from 3 in. I. D. conical Pyrex pipe (O. D. = 3 13/32 in. + .56 in.). The 3 in. I. D. size was chosen to minimize wall effects, slugging and channeling tendencies. At the same time, the volumetric flow rate of the gas required to fluidize -50 +100 mesh alumina particles was low enough to permit the utilization of compressed gas cylinders as a source of the simulated gas to be desulfurized.

A stainless steel porous plate (E) was chosen as the inlet gas distribution device because of its ability to uniformly distribute the gas and thus contribute significantly to a well fluidized system. Two stainless steel plates (Bₐ), 1/4 in. thick with 3 in. diameter holes cut in the center of each plate, were attached to the top and bottom of the distributor plate. The main reactor pipe (F) and the pre-heat zone pipe (D) were then attached to each plate respectively. Two asbestos gaskets, each with a 3 in. diameter hole in the center,
FLUID BED REACTOR
FIGURE 6.1
were placed between each plate and the distributor to prevent gas leakage.

The main reactor zone (F) was 36 in. in height, 8 in. higher than the theoretical Transport Disengaging Height, thus reducing the amount of entrainment to be processed in the cyclone separator. Thermcraft electric heaters, 18 in. in height were placed around the outside of the main reactor pipe and covered with a 1 in. layer of insulation. The heaters were connected to a powerstat which could be manually adjusted to control the temperature of the heaters.

A cyclone separator was constructed from one 3 in. by 3 in. I. D. Pyrex conical tee (H₂) and a Pyrex conical cap (I) which was attached to the bottom portion of the tee (H₂). A 3 in. to 2 in. low pressure beaded concentric reducer (L) was attached to the upper portion of the tee (H₂). A piece of 1 7/8 in. O. D. Pyrex pipe (J), 20 in. in length, was inserted through the concentric reducer (L) and attached to the reducer by means of an adapter coupling (M). This piece of Pyrex pipe (J) extended to the bottom of the tee (H₂), just parallel with the top of the cap (I). The top of the column (H₁) was sealed off with a 1/4 in. thick stainless steel plate (B₂). This plate had a 1/8 in. O. D. stainless steel thermocouple well (G) welded to the inside portion of the plate. The thermocouple well extended into the fluidized bed, and an iron-constantan thermocouple wire was used in the well.

The cyclone separator attached to the fluidized bed cannot be considered a true cyclone separator because the gas did not enter tangentially. Nevertheless, the cyclone separator did function properly with respect to the larger particles but it was necessary
to install a filter before the gas sample port to remove the extremely fine particles produced by adsorbent attrition. Part of the success of the cyclone separator can be attributed to the impinging separation which occurred when the gas containing the entrained particles collided with the Pyrex pipe (J) installed within the tee (H2).

A polypropylene fitting was placed around the end of the Pyrex pipe (J) extending from the concentric reducer (L). This fitting was drilled and tapped, and a 1/2 in. O. D. piece of PVC tubing (P) was attached. This tubing carried the processed flue gas to a hood. A tee was installed off this tubing which led to the gas sampling port (O). The gas sampling port consisted of a self-sealing septum which was installed at one end of the tee. A PVC line (N), which was connected to an aspirator, was installed at the other end of the tee. A gas filter (O) made from glass wool was installed in the tee before the sampling port. When the reactor was in operation, the aspirator was turned on, thus pulling a continuous gas sample through the filter. A representative gas sample which varied with time could then be obtained by taking gas samples at specified time intervals from the sampling port. A hypodermic syringe was inserted through the sampling port to obtain these samples.

The simulated flue gas was first pre-heated to the desired temperature in the gas pre-heat zone (D). This section of the reactor consisted of a 3 in. I. D. piece of conical Pyrex pipe, 6 in. in height, wrapped with heating tape. A 1/4 in. thick, stainless steel plate (B), which was drilled and taped to accommodate a 1 in. O. D. polypropylene fitting (A), was attached to the bottom of the pre-heat zone.
Each component of the simulated flue gas left its respective gas cylinder by passing through a pressure regulator. PVC tubing was connected to each regulator, and the gases then passed through the tubing into four Fisher and Porter gas flow meters. The gases leaving each flow meter merged into a common piece of tubing which was connected to the fitting (A) attached to the stainless steel plate (B).

A "Master-Mite" heat gun heating element nozzle (C), 4 in. in height and 1 1/4 in. I. D., was installed over the gas entrance port in the bottom plate (B) and connected to a powerstat. The simulated flue gas then passed through the heating element and was heated to the desired temperature by controlling the powerstat setting. An iron-constantan thermocouple, installed above the heating element, was used to monitor the temperature of the gas entering the main reactor zone. Iron-constantan thermocouples were also installed on the outside glass wall of the pre-heat zone and the main reactor zone to monitor the temperature of the glass. The Pyrex piping employed could withstand a maximum temperature of 450° F, and consequently it was necessary to closely monitor the glass temperature to prevent breakage.

All of the conical Pyrex piping was connected together with Corning Conical Style 1, aluminum flanges. The flanges were fitted with soft inserts and connected together with six nuts and bolts. Opposite bolts were tightened one complete turn at a time with a torque wrench until all of the bolts had approximately 3.33 ft.-lbs. of torque placed on them. Solid, Type T, teflon gaskets were installed between all pipe junctions to prevent gas leakage.
Corning Conical Style 1, aluminum flanges were also used to attach the top and bottom stainless steel plates (B₂, B) to the Pyrex pipe as well as the distributor (E) and its plates (B₁) to the Pyrex pipe. Type T, teflon gaskets were also used between these junctions.

A Corning Style 2, cast iron flange was used to attach the second tee (H₂) to concentric reducer (L). A style 2, teflon gasket was installed between these two pieces to prevent gas leakage.

EXPERIMENTAL PROCEDURE

As mentioned previously, -50 +100 mesh alumina particles were used in the fluidized bed reactor. This particle size was chosen to minimize the amount of simulated flue gas required to fluidize the system while simultaneously exhibiting good fluidization behavior. The alumina utilized in all of the experimental runs was an H-151 alumina obtained from Alcoa in the form of 1/8 in. spheres, which had to be ground in a ball mill and sieved through a series of standard mesh screens until the proper particle size was obtained. It was also necessary to dehydrate the alumina in a furnace at 350°F for a period of eight hours before the material could be used in the reactor. The top reactor plate (B₂) was then removed, and the reactor charged with the desired amount of adsorbent.

The minimum fluidization velocity of the system was determined by inspection. Gas flow rates were adjusted until the point of incipient fluidization occurred, and the system was then operated at this level of the gas flow rate which was determined to be 16 ft.³/hr. All experimental runs were operated at this flow rate since the minimum fluidization velocity is not affected by changes in bed height. The system was operated at the minimum fluidization velocity to decrease
the amount of bubbling which occurred within the bed, as well as to
decrease the amount of adsorbent attrition which occurred.

After the reactor had been charged with the desired amount of
alumina, the main reactor heaters and the pre-heat zone heater were
turned on. The temperature was closely monitored by following the
heat build-up measured by the two thermocouples attached to the
main reactor and pre-heat zone walls. These thermocouples were con-
nectected to potentiometers and the millivolt readings recorded by
the potentiometer were converted to temperatures by employing a
standard conversion chart for iron-constantan thermocouples. The
powerstats connected to the heaters were manually adjusted until
steady state was reached at the desired temperature. This procedure
usually consumed two hours.

Once the main reactor and the pre-heat zone walls reached steady
state, the heating element contained within the pre-heat zone was
turned on. Nitrogen, flowing at the minimum fluidization velocity,
was then permitted to enter the reactor. The nitrogen passed through
the heating element and the hot gas then entered the main reactor
zone. The nitrogen temperature was monitored with a thermocouple,
and the powerstat connected to the heating element was adjusted
accordingly. Once again, the entire system was allowed to reach
steady state at the desired temperature, making minor temperature
adjustments whenever necessary. This procedure usually consumed one
hour.

Nitrogen, oxygen, carbon dioxide, and sulfur dioxide were then
permitted to enter the reactor. Each gas, leaving its respective
pressure regulator at 10 psig, passed through Fisher and Porter flow
meters. The desired gas flow rate through each flow meter was ad-
justed by means of a valve installed before each flow meter. Sulfur dioxide was the last gas permitted to enter the reactor. The diagram on the following page illustrates the entire system.

The aspirator was turned on, and gas samples of the effluent gas stream were taken every three minutes. Gas samples were taken with a hypodermic syringe and directly injected into a gas chromatograph. Each sample consisted of .5 cc of gas. The amount of sulfur dioxide contained in the effluent stream was determined by a peak height analysis discussed on the following page. Samples of the inlet gas stream were also intermittently taken to check the gas composition against that indicated by the gas flow meters. Trial and error procedures indicated that the glass wool filter installed before the gas sampling port should be changed every nine minutes to insure that a truly representative gas sample was being taken every three minutes.

Each of the eight experimental runs was operated for a period of sixty minutes. It was not necessary to operate the system for a longer period of time because the desired results were mainly concerned with 100-90% sulfur dioxide removal and in all instances sixty minutes was more than sufficient time to obtain these results.

The spent adsorbent was removed from the reactor by removing the plate (B2) on top of the main reactor zone and inserting a vacuum cleaner hose into the reactor.

**CHROMATOGRAPH OPERATION**

A Gow-Mac, series 550 gas chromatograph was used to analyze all gas samples. The detector temperature was set at 120° C, the column temperature at 90° C, and the bridge current at 150 mA. Helium,
W HOOD
U CYCLONE
M REACTOR
D DISTRIBUTOR

NITROGEN
OXYGEN
CARBON DIOXIDE
SULFUR DIOXIDE
PRESSURE REG.
VALVE
SAMPLE PORT
FLOW METER
HEATER
PREHEAT ZONE
REACTOR SYSTEM

FIG. 6.2
flowing at a rate of 75 cc/min. and at 30 psig pressure, was employed as the carrier gas. A stainless steel column of Porapak Q, 6 ft. in length and 1/8 in. O. D., was used to separate the sulfur dioxide and the carbon dioxide from the nitrogen and oxygen.

The amount of sulfur dioxide contained in the gas samples was determined by a standard procedure described by McNair and Bonelli in a volume entitled Basic Gas Chromatography (45). It was necessary to construct a calibration curve for each gas component by making a plot of volume versus corresponding peak heights. Each plot consisted of a straight line which passed through the origin. When an exact amount of the gas sample was injected into the chromatograph, the various peak heights were measured and the amount of each component present was calculated in the following manner:

\[
\text{Volume \%}_A = \frac{\text{Peak Height}_A \times \text{Slope of Calibration Curve}_A \times 100}{\text{Total Volume Injected}}
\]

Slight changes can occur in detector sensitivity over a period of time and consequently, it was necessary to construct a new set of calibration curves before each experimental run.
APPARATUS

GAS CHROMATOGRAPH
Gow-Mac series 550 Thermal Conductivity dual column gas chromatograph, serial number 46801R, used to analyze all gas samples

RECORDER
Gow-Mac Instrument Co., Model 70-750, Used to record peak heights from the chromatograph

CHROMATOGRAPHIC COLUMNS
Stainless steel column, 6 ft. in length and 1/8 in. O. D., packed with 60-80 mesh Porapac Q, manufactured by the Gow-Mac Instrument Co., used to separate SO$_2$ and CO$_2$ from N$_2$ and O$_2$

CHROMATOGRAPHIC SEPTA
Septa used in gas sampling ports and chromatograph injection port, Supelco Inc., #2-0404

PRESSURE REGULATORS
Nitrogen Air Products; Carbon dioxide-Air Products; Helium-Air Products; Oxygen-Metallizing Co. of America, used to maintain constant back pressure

EXPERIMENTAL GASES

CARRIER GAS FOR GAS CHROMATOGRAPH
Helium-Burdox, Inc.

FLUID BED REACTOR
Conical Pyrex pipe, 3 in. I. D., 3 13/32 $\pm$ .56 in. O. D., 36 in. in length, Corning Glass Co.; #72-7300, used for main reactor zone. Conical Pyrex pipe, 3 in. I. D., 3 13/32 $\pm$ .56 in. O. D., 6 in. in length, Corning Glass Co.; #72-1580 used for gas pre-heat zone

Two conical Pyrex tees, 3 in. by 3 in. I. D., 5 in. in length, Corning Glass Co.; #72-6050, used in construction of cyclone

Conical Pyrex cap, 3 in. I. D., 4 11/16 in. in length, Corning Glass Co.; 72-6283, used in construction of cyclone

Low pressure beaded Pyrex concentric reducer, 3 in. I. D. by 2 in. I. D.,
FLUID BED REACTOR, con't.

5 in. in length, Corning Glass Co.; 
#72-3632, used in construction of cyclone.

Plain end Pyrex pipe, 1 1/2 in. I. D. 
1 7/8 in. O. D., 20 in. in length, 
Corning Glass Co.; #09-ZZ, used in 
construction of cyclone.

Seven style 1-2, type T, teflon 
gaskets, 3 in. I. D., 5/64 in. thick, 
Corning Glass Co.; #72-9257, used 
between pipe junctions.

One style 2 machined envelope, teflon 
gasket, 3 in. I. D., 1/8 in. thick, 
Corning Glass Co.; #72-9557, used 
between concentric reducer and 
Pyrex tee junction.

Nine style 1, aluminum, conical 
flanges, 3 in. I. D., 6 in. O. D., 
7/8 in. thick, Corning Glass Co., 
#72-9036, used to connect conical 
piping.

Two style 2, cast iron, conical to 
beaded flanges, 3 in. I. D., 5 3/16 in. 
square length, 13/16 in. thick, 
Corning Glass Co.; #72-9655, used to 
connect concentric reducer to conical 
tee.

Adapter coupling, Corning Glass Co.; 
#72-9782, used to connect plain end 
Pyrex pipe to reducer.

Porous plate, stainless steel, 6 in. 
diameter, 1/2 in. thick, used for 
gas distributor.

Stainless steel plate, 1/4 in. thick, 
6 in. O. D., drilled and tapped to 
accommodate a 1 in. O. D. fitting, 
used to seal off bottom of pre-heat 
zone.

Stainless steel plate, 1/4 in. thick, 
6 in. O. D., used to seal off top reactor.

Two stainless steel plates, 1/4 in. 
thick, 3 in. diameter hole in center, 
6 in. O. D., used above and below 
porous plate distributor.
FLUID BED REACTOR, con't.
Stainless steel thermocouple well, 1/8 in. O. D., 42 in. long, used to monitor bed temperatures.

ELECTRIC HEATERS
Thermcraft electric heating units, 3 in. I. D., 3 15/16 in. O. D., 18 in. long, model RL-154, 835 watts, 115 volts; two half sections required; used to heat main reactor zone.

HEATING TAPE
BW-61-X high temperature heating tape, 3/4 in. wide, Briscoe Manufacturing Co.; used to heat pre-heat zone.

HEATING COIL
Master-Mite Heat Gun Heating Element Nozzle, 4 in. in height, 1 1/4 in. O. D., Model #20014; used to heat flue gas to desired temperature.

THERMOCOUPLE
Iron-constantan thermocouple wire; used to monitor reactor temperatures.

POTENTIOMETERS
Leeds and Northrup Millivolt Potentiometer, model #8690, and Minneapolis-Honeywell Millivolt Potentiometer; used to register reactor temperatures.

POWERSTAT
Three Superior Edison Co. powerstats, type 116, output 0-140 volts, used to provide current for the electric heaters, heating tape and heating element.

FLOW METERS
Two Fisher and Porter flow meters, Cat. #Fm1044B; used to measure flow rates of SO₂ and O₂.

Two Fisher and Porter flow meters, Tube #3F-3/8-16-5/36; used to measure flow rates of CO₂ and N₂.

VALVES
Three brass valves, manufactured by Hoke, Inc.; used to regulate the amount of N₂, O₂, and CO₂ entering the flow meters.

Three stainless steel valves, manufactured by Whitney Co.; #21RS4, used to regulate the amount of SO₂ entering the flow meter and to permit flue gas to enter reactor or by-pass reactor.
<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>VALVE-SO₂</strong></td>
<td>Stainless steel valve, manufactured by Whitney Co.; #50BR, used to regulate backpressure on SO₂ cylinder.</td>
</tr>
<tr>
<td><strong>GAS SYRINGE</strong></td>
<td>Pressure-Lok gas syringe, series B, .5 cc, manufactured by Precision Sampling Corp.; used to take all gas samples.</td>
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<tr>
<td><strong>STOP WATCH</strong></td>
<td>Clebar 0 to 30 seconds, .1 second divisions, used to measure time between gas samples.</td>
</tr>
<tr>
<td><strong>FURNACE</strong></td>
<td>Lindberg Hevi-Duty Furnace, type 5122i; used to dehydrate alumina.</td>
</tr>
<tr>
<td><strong>JAR</strong></td>
<td>Jar, made of Roulox porcelain, 5 liter capacity, manufactured by Norton Co.; #113-2, used for grinding alumina spheres.</td>
</tr>
<tr>
<td><strong>JAR MILL</strong></td>
<td>Norton Jar Mill, #CK-79160, used for grinding alumina spheres.</td>
</tr>
<tr>
<td><strong>GRINDING MEDIA</strong></td>
<td>Burundum Grinding Media, cylindrical shape, 21 mm O. D. and 21 mm l long, obtained from Fisher Scientific Co.; cat. #8-412-15B, used for grinding alumina spheres.</td>
</tr>
<tr>
<td><strong>SIEVE SCREENS</strong></td>
<td>U. S. Standard Sieve Series, manufactured by Dual Manufacturing Co.; 20, 50 and 100 mesh sizes, used to separate different particle sizes of alumina.</td>
</tr>
<tr>
<td><strong>SIEVE SHAKER</strong></td>
<td>Ro-Tap, model B, Testing Sieve Shaker, #1882, manufactured by Tyler Industrial Products; used to shake sieve screens.</td>
</tr>
<tr>
<td><strong>CATALYST</strong></td>
<td>Activated Alumina, H-151, made by the Aluminum Co. of America; 1/8 in. spheres, used as the SO₂ adsorbent in the experimental runs.</td>
</tr>
<tr>
<td></td>
<td>Activated Alumina, F-1, made by the Alumina Co. of America; -14 +28 mesh, used as the SO₂ adsorbent in the reproducibility runs.</td>
</tr>
</tbody>
</table>
CHAPTER VII
DISCUSSION OF RESULTS

The data obtained from the eight experimental runs was plotted in the form of percent of sulfur dioxide removed from the effluent gas stream versus time of the run in minutes. The experimental data points were fitted to form a smooth curve by employing a computer program which fits the data points to a least square polynomial up to degree ten. As mentioned previously, emphasis was directed at determining the ability of the aluminum oxide to remove between 90 to 100% of the sulfur dioxide present in the inlet gas stream. Figures 7.1 through 7.8 show the experimental results obtained.

The following pertinent observations can be made concerning all of the experimental runs taken:

1) 100% of the sulfur dioxide present in the inlet gas stream was removed for a certain period of time dependent upon the experimental conditions under which the run was taken;

2) Three to six minutes after the 100% removal time, less than 90% of the sulfur dioxide present in the gas stream was removed;

3) The optimum conditions for the removal of the sulfur dioxide present in the gas stream occurred at a flue gas temperature of 350°F, a space velocity of 900 HR⁻¹, and a sulfur dioxide inlet concentration of 2%. Under these conditions, 100% of the sulfur dioxide present in the inlet gas stream was removed for a period of 37 minutes.

ANALYSIS OF RESULTS BY THE YATES METHOD

The experimental results were analyzed by the Yates method dis-
TEMPERATURE - 350 DEG. F
SPACE VELOCITY - 1300/HRS
SO2 CONCENTRATION - 2%
TEMPERATURE - 350 DEG. F
SPACE VELOCITY - 1300/HRS
SO2 CONCENTRATION - 4%
TEMPERATURE - 350 DEG. F
SPACE VELOCITY - 900/HRS
SO2 CONCENTRATION - 2%
TEMPERATURE - 350 DEG. F
SPACE VELOCITY - 900/HRS
SO2 CONCENTRATION - 4%
TEMPERATURE - 450 DEG. F
SPACE VELOCITY - 1300/HR
SO2 CONCENTRATION - 2%
FIG. 7.6

TEMPERATURE - 450 DEG.F
SPACE VELOCITY - 1300/HRS
SO2 CONCENTRATION - 4%
FIG. 7.7

TEMPERATURE - 450 DEG. F
SPACE VELOCITY - 900/hrs
SO2 CONCENTRATION - 2%
FIG. 1.8

TEMPERATURE - 450 DEG. F
SPACE VELOCITY - 900/HR
SO2 CONCENTRATION - 4%
cussed in Chapter VI. The yield values utilized in construction of the Yates Algorithm were the times of 100% sulfur dioxide removal obtained from each experimental run.

The table on the following page shows the effects of each factor and its interactions as determined by the Yates method. By observing the numbers listed in the sum of the squares column, it is quite apparent that the sulfur dioxide concentration (C) had the most significant effect on the 100% removal time. Space velocity (A), temperature (B), and the interactions between space velocity and concentration (AC), and temperature and concentration (BC) were also significant, but to a lesser extent than the sulfur dioxide concentration. The interaction between space velocity and temperature (AB) was determined to have no significance when analyzed by an F test.

In higher order experiments it is customary to dispense with replication and use the highest-order interaction term as the error variance (46). Consequently, the ABC interaction can be considered as an indication of the random error in the experiments. This can be briefly explained by considering the mathematical model for a $2^3$ factorial experiment. The model can be written as follows:

$$Y = U + A + B + C + AB + AC + BC + ABC + E,$$

where $Y$ represents the measured yield, $U$ represents the population means from which all the data came, $A$, $B$, $C$ represent the effects of the three variables and their interactions, and $E$ represents the random error in the experiment (41). There were eight degrees of freedom resulting from the eight experimental runs, but the above equation contains nine terms, each of which represent one degree of
<table>
<thead>
<tr>
<th>Treatment combination</th>
<th>(1) Yield</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>Effect</th>
<th>Avg. Effect</th>
<th>(6) Sum of squares</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>27</td>
<td>64</td>
<td>109</td>
<td>163</td>
<td>I</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>a</td>
<td>37</td>
<td>45</td>
<td>54</td>
<td>19</td>
<td>A</td>
<td>4.75</td>
<td>45.125</td>
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<tr>
<td>b</td>
<td>18</td>
<td>27</td>
<td>19</td>
<td>-19</td>
<td>B</td>
<td>-4.75</td>
<td>45.125</td>
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<tr>
<td>ab</td>
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<td>27</td>
<td>0</td>
<td>-7</td>
<td>AB</td>
<td>-1.75</td>
<td>6.125</td>
</tr>
<tr>
<td>c</td>
<td>12</td>
<td>10</td>
<td>-19</td>
<td>-55</td>
<td>C</td>
<td>-13.75</td>
<td>378.125</td>
</tr>
<tr>
<td>ac</td>
<td>15</td>
<td>9</td>
<td>0</td>
<td>-19</td>
<td>AC</td>
<td>-4.75</td>
<td>45.125</td>
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<tr>
<td>bc</td>
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<td>3</td>
<td>-1</td>
<td>19</td>
<td>BC</td>
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<td>ABC</td>
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<td>3.125</td>
</tr>
<tr>
<td></td>
<td>163</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>567.875</td>
</tr>
</tbody>
</table>

Table 7.1

Analysis of Results by Yates Algorithm
freedom. Consequently, the E term is dropped and the ABC interaction is used as an indication of the random error instead. A more rigorous explanation can be found in Cochran and Cox (47), Fisher (48), and Anderson and Bancroft (49).

The low value of ABC found in Table 7.1 indicates that the amount of random error in the experiments was small and therefore had little effect on the results. The following table lists the various experimental runs and the 100% removal time obtained in each instance.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temp.</th>
<th>Space vel.</th>
<th>% SO₂</th>
<th>100% removal time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>350° F</td>
<td>1300 HR⁻¹</td>
<td>2</td>
<td>27 minutes</td>
</tr>
<tr>
<td>2</td>
<td>350° F</td>
<td>1300 HR⁻¹</td>
<td>4</td>
<td>12 minutes</td>
</tr>
<tr>
<td>3</td>
<td>350° F</td>
<td>900 HR⁻¹</td>
<td>2</td>
<td>37 minutes</td>
</tr>
<tr>
<td>4</td>
<td>350° F</td>
<td>900 HR⁻¹</td>
<td>4</td>
<td>15 minutes</td>
</tr>
<tr>
<td>5</td>
<td>450° F</td>
<td>1300 HR⁻¹</td>
<td>2</td>
<td>18 minutes</td>
</tr>
<tr>
<td>6</td>
<td>450° F</td>
<td>1300 HR⁻¹</td>
<td>4</td>
<td>15 minutes</td>
</tr>
<tr>
<td>7</td>
<td>450° F</td>
<td>900 HR⁻¹</td>
<td>2</td>
<td>27 minutes</td>
</tr>
<tr>
<td>8</td>
<td>450° F</td>
<td>900 HR⁻¹</td>
<td>4</td>
<td>12 minutes</td>
</tr>
</tbody>
</table>

Table 7.2

Experimental Results

Table 7.2 clearly substantiates the results of the Yates Algorithm with respect to the effect of the concentration of sulfur dioxide contained within the flue gas. A doubling of the sulfur dioxide concentration of the gas resulted in a reduction in 100% removal time of approximately one half in all instances but one (compare runs #5 and #6.) The results of run #6 appear to be questionable when they are compared with the results obtained in all other instances. This discrepancy could possibly be attributed to the standard deviation of 5.2 minutes which
applies to all results. The method of determination of this standard deviation will be discussed in the following pages.

The fact that space velocity and temperature had an effect on the 100% removal time was an expected result, but the interaction between temperature and concentration and the interaction between space velocity and concentration had not been anticipated. To clearly understand the significance of these interactions it is helpful to review the concept of factor interactions and the method of their determination.

An interaction between two factors means the change in response between levels of one factor is not the same for all levels of the other factor. Consider the space velocity-concentration interaction (AC). To determine the effect of this interaction it is necessary to calculate the effect of A at the high level of C and the effect of A at the low level of C. Any difference in these two effects indicates an interaction. As discussed previously, the AC interactions can be determined by the following equation:

\[ AC = [(ac-c) + (abc-bc)] - [(a-1) + (ab-b)]. \]

Substituting the experimental results into this equation results in the following:

\[ AC = [(15-12) + (12-15)] - [(37-27) + (27-18)] \]

\[ AC = [0] - [19]. \]

Therefore, space velocity had no effect on the 100% removal time at high concentrations of sulfur dioxide, and a comparatively large effect at low concentrations of sulfur dioxide concentration.

Now, consider the temperature-concentration interaction (BC). Substitution of the experimental values into the equation which calculates the BC interaction effect yields the following results:
The above equation indicates that temperature had no effect on the 100% removal time at high concentrations of sulfur dioxide, but a comparatively large effect at low concentrations of sulfur dioxide. Note the similarity of the results obtained.

In Tables 7.3 and 7.4 the data have been arranged to clearly point out the effects of space velocity and temperature at both high and low levels of sulfur dioxide concentrations. The data agrees with the interpretation of the Yates Algorithm just presented.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Temp.</th>
<th>% SO₂</th>
<th>Space vel.</th>
<th>100% removal time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>350° F</td>
<td>2</td>
<td>1300 HR⁻¹</td>
<td>27 minutes</td>
</tr>
<tr>
<td>3</td>
<td>350° F</td>
<td>2</td>
<td>900 HR⁻¹</td>
<td>37 minutes</td>
</tr>
<tr>
<td>5</td>
<td>450° F</td>
<td>2</td>
<td>1300 HR⁻¹</td>
<td>18 minutes</td>
</tr>
<tr>
<td>7</td>
<td>450° F</td>
<td>2</td>
<td>900 HR⁻¹</td>
<td>27 minutes</td>
</tr>
<tr>
<td>2</td>
<td>350° F</td>
<td>4</td>
<td>1300 HR⁻¹</td>
<td>12 minutes</td>
</tr>
<tr>
<td>4</td>
<td>350° F</td>
<td>4</td>
<td>900 HR⁻¹</td>
<td>15 minutes</td>
</tr>
<tr>
<td>6</td>
<td>450° F</td>
<td>4</td>
<td>1300 HR⁻¹</td>
<td>15 minutes</td>
</tr>
<tr>
<td>8</td>
<td>450° F</td>
<td>4</td>
<td>900 HR⁻¹</td>
<td>12 minutes</td>
</tr>
</tbody>
</table>

Table 7.3

Effect of Space Velocity on 100% Removal Time
<table>
<thead>
<tr>
<th>Run #</th>
<th>Space vel.</th>
<th>% SO\textsubscript{2}</th>
<th>Temp.</th>
<th>100% Removal Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1300 HR\textsuperscript{-1}</td>
<td>2</td>
<td>350°F</td>
<td>27 minutes</td>
</tr>
<tr>
<td>5</td>
<td>1300 HR\textsuperscript{-1}</td>
<td>2</td>
<td>450°F</td>
<td>18 minutes</td>
</tr>
<tr>
<td>3</td>
<td>900 HR\textsuperscript{-1}</td>
<td>2</td>
<td>350°F</td>
<td>37 minutes</td>
</tr>
<tr>
<td>7</td>
<td>900 HR\textsuperscript{-1}</td>
<td>2</td>
<td>450°F</td>
<td>27 minutes</td>
</tr>
<tr>
<td>2</td>
<td>1300 HR\textsuperscript{-1}</td>
<td>4</td>
<td>350°F</td>
<td>12 minutes</td>
</tr>
<tr>
<td>6</td>
<td>1300 HR\textsuperscript{-1}</td>
<td>4</td>
<td>450°F</td>
<td>15 minutes</td>
</tr>
<tr>
<td>4</td>
<td>900 HR\textsuperscript{-1}</td>
<td>4</td>
<td>350°F</td>
<td>15 minutes</td>
</tr>
<tr>
<td>8</td>
<td>900 HR\textsuperscript{-1}</td>
<td>4</td>
<td>450°F</td>
<td>12 minutes</td>
</tr>
</tbody>
</table>

Table 7.4
Effect of Temperature on 100% Removal Time

THEORETICAL INTERPRETATION OF RESULTS

The increase in 100% removal time which resulted from an increase in space velocity at low levels of sulfur dioxide is easily explained. Space velocity was increased by increasing the bed height of aluminum oxide in the reactor. Thus, more aluminum oxide was available for reaction with the sulfur dioxide which resulted in an increase in the 100% removal time.

Table 7.4 indicates that an increase in temperature at low levels of sulfur dioxide resulted in a decrease in the 100% removal time. This could be explained by considering the kinetics of the reaction involved. It may be that there were two competing reactions which occurred; an adsorption reaction and a desorption reaction. Thus at 350° F, the rate of sulfur dioxide adsorption greatly exceeded the rate of desorption. But, an increase in temperature to 450° F may have resulted in a greater increase in the rate of sulfur dioxide desorption than
than adsorption, which caused an overall decrease in the 100% removal time.

An explanation for the lack of effect on 100% removal time observed when the space velocity or the temperature, or both, were increased to their high levels while the sulfur dioxide concentration was at its high level is not as obvious. A possible explanation can be formed if two observations are made. First, the rate of adsorption is substantially a function of temperature and the concentration of the gas species to be adsorbed. Second, the relative increases in levels of the three factors differed. Sulfur dioxide concentration was increased by 100%, while space velocity and temperature were increased by only 44% and 100°F, respectively. Thus, the 100% increase in the rate of sulfur dioxide concentration resulted in a relatively large increase in the rate of sulfur dioxide adsorption. This increase in adsorption was so significant that it overrode the effects of increasing space velocity or temperature, especially since the increases in these factors were substantially less than the increase in sulfur dioxide concentrations.

**COMPARISON OF FIXED AND FLUIDIZED BED RESULTS**

Hereth's results utilizing aluminum oxide as a sulfur dioxide adsorbent in a fixed bed were used to compare the fluidized and fixed bed results (40). Hereth presented two sets of data which can be used for comparison purposes. The other four sets of data produced by Hereth were obtained at temperatures in excess of 450°F, and consequently cannot be used for valid comparisons.

Table 7.5 present a comparison of the two reactors operating under similar conditions.
<table>
<thead>
<tr>
<th>Type</th>
<th>Temp.</th>
<th>Space vel.</th>
<th>% SO$_2$</th>
<th>100% removal time</th>
<th>g. SO$_2$ removed per 100 g. of Al$_2$O$_3$ during 100% removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid</td>
<td>350° F</td>
<td>1300 HR$^{-1}$</td>
<td>2.0</td>
<td>27 minutes</td>
<td>3.50</td>
</tr>
<tr>
<td>Fixed</td>
<td>350° F</td>
<td>1300 HR$^{-1}$</td>
<td>2.6</td>
<td>21 minutes</td>
<td>2.70</td>
</tr>
<tr>
<td>Fluid</td>
<td>350° F</td>
<td>900 HR$^{-1}$</td>
<td>4.0</td>
<td>15 minutes</td>
<td>3.40</td>
</tr>
<tr>
<td>Fixed</td>
<td>350° F</td>
<td>900 HR$^{-1}$</td>
<td>5.0</td>
<td>16.5 minutes</td>
<td>2.81</td>
</tr>
</tbody>
</table>

Table 7.5

Comparison of Fixed and Fluid Bed Reactors
In each of the comparisons listed in Table 7.5, the percent of sulfur dioxide present in the gas steam varied, as well as the amount of sulfur dioxide to be processed, but the temperature and the space velocity were identical. Therefore, attempting to draw some type of comparison between the 100% removal times would not be a valid approach. But, comparing the amount of sulfur dioxide removed per 100 grams of aluminum oxide present in the reactor gives a valid estimate as to the efficiency of each reactor under the specified conditions. It can be observed that in both comparisons, the fluidized bed reactor appears to be more efficient. The first comparison indicates a 23% increase in the amount of sulfur dioxide removed per 100 grams of adsorbent, while the second comparison indicates a 17.6% increase.

Here's optimum conditions for sulfur dioxide removal occurred at 550°F. Consequently, at this point in the process development, no conclusions regarding which system would be best suited for a large scale operation can be drawn since there are no data available concerning the operation of the fluidized bed reactor at temperatures above 450°F.

**REPRODUCIBILITY OF RESULTS**

An additional five runs were taken in an attempt to establish the reliability of the 100% removal times obtained from the factorial design experiments. All five runs were operated under the same experimental conditions: a flue gas temperature of 350°F, a space velocity of 1300 HR⁻¹, and a sulfur dioxide concentration of 2%. All runs were operated at the minimum fluidization velocity of the
system utilizing -50 +100 mesh aluminum oxide. The experimental conditions were arbitrarily chosen since the only objective was to determine the standard deviation of the results obtained. It was necessary to utilize an F-1 aluminum oxide rather than the H-151 aluminum oxide used in the experimental design runs because of a lack of sufficient amounts of the H-151 aluminum oxide to perform five more runs.

The major difference between these two types of alumina lies in their surface areas; H-151 has a surface area of 390 square meters per gram whereas F-1 has a surface area of 210 square meters per gram. Nevertheless, these five runs were intended to give an estimate of the amount of experimental error which occurred while operating the reactor, and consequently a change in adsorbent would not affect the significance of the results.

The results of these five runs indicated a standard deviation of 5.2 minutes. Appendix B presents the results of each run as well as the calculation of the standard deviations.

It is interesting to note that the F-1 alumina performed nearly as well as the H-151 alumina under the same experimental conditions. Figure 7.1 indicates that at 350°F, 2% sulfur dioxide concentration and a space velocity of 1300 HR⁻¹, the H-151 alumina removed 100% of the sulfur dioxide present in the gas stream for a period of 27 minutes. Under these same conditions, the mean of the 100% removal times obtained with the F-1 alumina was 25.2 minutes.

The Yates Algorithm indicated that the factor with the greatest influence on the 100% removal time was the concentration of the sulfur
dioxide present in the inlet gas stream. Consequently, an investigation was conducted to determine whether or not this factor was responsible for the standard deviation of 5.2 minutes.

The nitrogen, oxygen, carbon dioxide, and sulfur dioxide flow meters were adjusted to give the same flow rates used in the five reproducibility runs. An inlet gas sample was then taken. The valves before each flow meter were then closed. Once again all of the flow meters were adjusted to the desired flow rates, and another inlet gas sample was taken. This procedure was repeated five times and the standard deviation of the sulfur dioxide peak heights obtained was determined. A standard deviation of .47 recorder chart paper divisions (each division equals 1/16 in.) was obtained. This corresponded to a difference of ±0.05% sulfur dioxide in the inlet gas streams, which does not appear to be significant enough to account for the standard deviation of 5.2 minutes.

The standard deviation of 5.2 minutes can be attributed to random experimental error. Another possible explanation which could conceivably account for this standard deviation is to attribute the deviation to bubble phenomena. Since bubbles were observed in the fluidized bed, it could be postulated that variations in bubble numbers, size and velocity resulted in slight changes in gas-solid contact time which altered the 100% removal times obtained in the various reproducibility runs.

FLUIDIZATION WITH -100 +200 MESH ALUMINA

One experimental run was taken with -100+200 mesh alumina to
determine if particle size had any effect on the 100% removal time. The minimum fluidization velocity of the system was determined by inspection and an attempt was made to operate the system at this velocity. The experimental conditions employed were the same as the conditions which produced the optimum results in the experimental design runs; a temperature of 350°F, a sulfur dioxide content of 2%, and a space velocity of 900 HR⁻¹.

A large amount of channeling occurred because of the small particles used. Consequently, poor gas-solid contact time resulted and a 100% removal time of only six minutes was obtained. This compares very unfavorably with the 37 minute 100% removal time obtained when -50 +100 mesh particles were used under the same conditions.
CHAPTER VIII
CONCLUSIONS

1) The concentration of sulfur dioxide in the inlet gas stream had the greatest influence on the time required to remove 100% of the sulfur dioxide present.

2) Space velocity affected the 100% removal time at low concentrations of sulfur dioxide. An increase in space velocity resulted in an increase in the 100% removal time.

3) Temperature of the flue gas affected the 100% removal time at low concentrations of sulfur dioxide. An increase in temperatures from 350°F to 450°F resulted in a decrease in 100% removal time.

4) At high concentrations of sulfur dioxide in the inlet gas stream, increases in space velocity and/or temperature had no effect on the 100% removal time.

5) The fluidized bed reactor was more efficient than the fixed bed reactor when both were compared under a limited number of similar experimental conditions.

6) Operation of the fluidized bed reactor with -100+200 mesh alumina in place of -50 +100 mesh alumina resulted in a drastic decrease in 100% removal time. The decrease can be attributed to channeling.
CHAPTER IX
RECOMMENDATIONS

1) The interaction between space velocity and sulfur dioxide concentration, and the interaction between temperature of the flue gas and sulfur dioxide concentration should be further investigated. The levels of all three variables should be increased by the same order of magnitude to determine whether this alters the effects of the interactions.

2) A fluidized bed reactor should be constructed from stainless steel. The reactor could then be operated at temperatures in excess of 450° F, and consequently the results obtained from the operation of the reactor at high temperatures could be used for comparison with the high temperature fixed bed results. A valid conclusion could then be made concerning which type of reactor would be best suited for a large scale operation.

3) Since the scale up of fluidized bed reactors can result in unexpected problems, the stainless steel reactor constructed should be of larger size than the reactor used in these experiments. Thus, an indication as to some of the problems which might be encountered with a large scale reactor may be determined.
REFERENCES


EXPERIMENTAL DATA

Simulated Flue Gas Composition

Nitrogen 80.8- x vol. %
Carbon dioxide 12.0 vol. %
Oxygen 7.2 vol. %
Sulfur dioxide x vol.

Run #1
Temp. = 350° F
S. V. = 1300 HR⁻¹
% SO₂ = 2.0

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% SO₂ in Effluent Stream</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-27</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>30</td>
<td>.2</td>
<td>90</td>
</tr>
<tr>
<td>33</td>
<td>.3</td>
<td>85</td>
</tr>
<tr>
<td>36</td>
<td>.46</td>
<td>77</td>
</tr>
<tr>
<td>39</td>
<td>.66</td>
<td>67</td>
</tr>
<tr>
<td>42</td>
<td>.78</td>
<td>61</td>
</tr>
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<td>45</td>
<td>.78</td>
<td>61</td>
</tr>
<tr>
<td>48</td>
<td>.92</td>
<td>54</td>
</tr>
<tr>
<td>51</td>
<td>.86</td>
<td>57</td>
</tr>
<tr>
<td>54</td>
<td>.92</td>
<td>54</td>
</tr>
<tr>
<td>60</td>
<td>.73</td>
<td>63.5</td>
</tr>
</tbody>
</table>
Run #2

Temp. = 350°F
S. V. = 1300 HR^-1
% SO₂ = 4.0

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% SO₂ in Effluent Stream</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-12</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>15</td>
<td>.22</td>
<td>94.5</td>
</tr>
<tr>
<td>18</td>
<td>1.17</td>
<td>71</td>
</tr>
<tr>
<td>21</td>
<td>1.87</td>
<td>53</td>
</tr>
<tr>
<td>24</td>
<td>1.8</td>
<td>55</td>
</tr>
<tr>
<td>27</td>
<td>.7</td>
<td>82.5</td>
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<tr>
<td>30</td>
<td>.6</td>
<td>85</td>
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<tr>
<td>33</td>
<td>2.1</td>
<td>47.5</td>
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<tr>
<td>36</td>
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<td>1.76</td>
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<td>1.98</td>
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<td>1.32</td>
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<td>54</td>
<td>2.64</td>
<td>34</td>
</tr>
<tr>
<td>63</td>
<td>3.2</td>
<td>20</td>
</tr>
</tbody>
</table>
Run #3
Temp. = 350° F
S. V. = 900 HR
% SO\textsubscript{2} = 2.0

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% SO\textsubscript{2} in Effluent Stream</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-37</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>41</td>
<td>.42</td>
<td>79</td>
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<td>44</td>
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<td>63</td>
<td>.66</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>.90</td>
<td>55</td>
</tr>
</tbody>
</table>
Run #4
Temp.  = 350° F
S. V.  = 900 HR⁻¹
% SO₂  = 4.0

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% SO₂ in Effluent Stream</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-15</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>18</td>
<td>.11</td>
<td>77.3</td>
</tr>
<tr>
<td>21</td>
<td>.55</td>
<td>86.3</td>
</tr>
<tr>
<td>24</td>
<td>1.2</td>
<td>70</td>
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<tr>
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<td>1.76</td>
<td>56</td>
</tr>
<tr>
<td>30</td>
<td>1.8</td>
<td>55</td>
</tr>
<tr>
<td>33</td>
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<td>47.5</td>
</tr>
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<td>39.5</td>
</tr>
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<td>48</td>
<td>2.53</td>
<td>36.8</td>
</tr>
<tr>
<td>54</td>
<td>2.64</td>
<td>34</td>
</tr>
<tr>
<td>57</td>
<td>2.70</td>
<td>32.5</td>
</tr>
<tr>
<td>60</td>
<td>2.64</td>
<td>34</td>
</tr>
</tbody>
</table>
### Run #5

Temp. = 450°F  
S. V. = 1300 HR⁻¹  
% SO₂ = 2.0

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% SO₂ in Effluent Stream</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-18</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>21</td>
<td>.22</td>
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<td>86.5</td>
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<td>1.13</td>
<td>43.5</td>
</tr>
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</tr>
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<td>1.24</td>
<td>38</td>
</tr>
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<td>1.33</td>
<td>33.5</td>
</tr>
<tr>
<td>54</td>
<td>1.33</td>
<td>33.5</td>
</tr>
<tr>
<td>60</td>
<td>1.46</td>
<td>27</td>
</tr>
</tbody>
</table>
### Run #6

Temp. = 450° F  
S. V. = 1300 HR\(^{-1}\)  
\% SO\(_2\) = 4.0

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% SO(_2) in Effluent Stream</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
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<td>100</td>
</tr>
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<td>96.2</td>
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<td>2.76</td>
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<td>2.65</td>
<td>33.8</td>
</tr>
<tr>
<td>62</td>
<td>2.68</td>
<td>33</td>
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</tbody>
</table>
Run #7
Temp. = 450° F
s. V. = 900 HR⁻¹
% SO₂ = 2.0

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% SO₂ in Effuent Stream</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-27</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>30</td>
<td>.15</td>
<td>92.5</td>
</tr>
<tr>
<td>33</td>
<td>.3</td>
<td>85</td>
</tr>
<tr>
<td>36</td>
<td>.35</td>
<td>82.5</td>
</tr>
<tr>
<td>39</td>
<td>.6</td>
<td>70</td>
</tr>
<tr>
<td>42</td>
<td>.6</td>
<td>70</td>
</tr>
<tr>
<td>48</td>
<td>.85</td>
<td>57.5</td>
</tr>
<tr>
<td>51</td>
<td>.85</td>
<td>57.5</td>
</tr>
<tr>
<td>54</td>
<td>.85</td>
<td>57.5</td>
</tr>
<tr>
<td>57</td>
<td>.95</td>
<td>52.5</td>
</tr>
<tr>
<td>60</td>
<td>.95</td>
<td>52.5</td>
</tr>
</tbody>
</table>
Run #8

| Temp. | 450°F |
| S. V. | 900 HR⁻¹ |
| % SO₂ | 4.0 |

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>% SO₂ in Effluent Stream</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-12</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>15</td>
<td>0.18</td>
<td>95.5</td>
</tr>
<tr>
<td>18</td>
<td>1.02</td>
<td>74.5</td>
</tr>
<tr>
<td>21</td>
<td>1.92</td>
<td>52</td>
</tr>
<tr>
<td>24</td>
<td>2.52</td>
<td>37</td>
</tr>
<tr>
<td>30</td>
<td>2.82</td>
<td>29.5</td>
</tr>
<tr>
<td>33</td>
<td>2.94</td>
<td>26.5</td>
</tr>
<tr>
<td>36</td>
<td>2.52</td>
<td>37</td>
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<tr>
<td>39</td>
<td>2.7</td>
<td>32.5</td>
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<tr>
<td>42</td>
<td>2.74</td>
<td>31.5</td>
</tr>
<tr>
<td>45</td>
<td>2.74</td>
<td>31.5</td>
</tr>
<tr>
<td>48</td>
<td>2.82</td>
<td>29.5</td>
</tr>
<tr>
<td>51</td>
<td>2.94</td>
<td>26.5</td>
</tr>
<tr>
<td>54</td>
<td>2.94</td>
<td>26.5</td>
</tr>
<tr>
<td>57</td>
<td>3.12</td>
<td>22</td>
</tr>
<tr>
<td>60</td>
<td>3.12</td>
<td>22</td>
</tr>
</tbody>
</table>
RESULTS OF REPRODUCIBILITY RUNS

<table>
<thead>
<tr>
<th>Run #</th>
<th>100% Removal Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1R</td>
<td>21 min.</td>
</tr>
<tr>
<td>2R</td>
<td>27 min.</td>
</tr>
<tr>
<td>3R</td>
<td>27 min.</td>
</tr>
<tr>
<td>4R</td>
<td>18 min.</td>
</tr>
<tr>
<td>5R</td>
<td>33 min.</td>
</tr>
</tbody>
</table>

Mean 100% removal time = 25.2 min.

Calculation of Standard Deviation

\[
S.D. = \left[ \frac{(X_1 - \bar{X})^2 + (X_2 - \bar{X})^2 + (X_3 - \bar{X})^2 + (X_4 - \bar{X})^2 + (X_5 - \bar{X})^2}{N} \right]^{1/2}
\]

Where \( X_1 - X_5 \) represent the experimental values, \( \bar{X} \) represents the mean of the experimental values, and \( N \) represents the number of experimental runs.

Substituting the appropriate values yields the following:

\[
S.D. = \left[ \frac{(21-25.2)^2 + (27-25.2)^2 + (27-25.2)^2 + (18-25.2)^2 + (33-25.2)^2}{5} \right]^{1/2}
\]

\[S.D. = 5.2 \text{ minutes}\]
RESULTS OF SO\textsubscript{2} PEAK HEIGHT ANALYSIS

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Height of SO\textsubscript{2} Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>1P</td>
<td>16.2 chart divisions</td>
</tr>
<tr>
<td>2P</td>
<td>17.0 chart divisions</td>
</tr>
<tr>
<td>3P</td>
<td>16.1 chart divisions</td>
</tr>
<tr>
<td>4P</td>
<td>15.5 chart divisions</td>
</tr>
<tr>
<td>5P</td>
<td>16.5 chart divisions</td>
</tr>
</tbody>
</table>

Mean Peak Height = 16.2 chart divisions

Calculation of Standard Deviation

\[ S.D. = \sqrt{\frac{(16.5-16.26)^2+(16.2-16.26)^2+(17.0-16.26)^2+(16.1-16.26)^2+(15.5-16.26)^2}{5}} \]

S.D. = .47 chart divisions

Calculation of the possible error in the SO\textsubscript{2}% in the inlet gas

\[ \%SO_2 = \frac{\text{Peak Height} \times \text{Slope of Calibration Curve} \times 100}{\text{Volume of Sample Injection}} \]

\[ \%SO_2 = \frac{.47 \times .00055 \times 100}{.5} \]

\[ \%SO_2 = .05 \]

Therefore, the percent of SO\textsubscript{2} in the inlet gas stream was within .05% of the desired amount.