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David T. Clay* and Scott Lynn

June 1974

Prepared for the U. S. Atomic Energy Commission under Contract W-7405-ENG-48

*Filed as a Ph.D. thesis

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DEVELOPMENT OF A FEASIBLE PROCESS FOR THE SIMULTANEOUS REMOVAL OF NITROGEN OXIDES AND SULFUR OXIDES FROM FOSSIL FUEL BURNING POWER PLANTS.

David T. Clay* and Scott Lynn

Energy and Environment Division
Lawrence Berkeley Laboratory
and
Department of Chemical Engineering
University of California, Berkeley

June 1974

* PhD Thesis
Glenda whose love, encouragement and assistance is entwined throughout this work.
ACKNOWLEDGEMENTS

This Dissertation is more than a record of the work of one individual on a specific problem. Many different inputs were given during its progression. Each of these greatly aided the author by providing new insight into the problem. Professor Lynn provided many practical suggestions and very effective guidance throughout the course of the project. Professors King and Sawyer contributed significantly in the project review and evaluation sessions. Discussions with Derk Vermeer and Stuart Simpson were helpful in dealing with day to day problems.

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ABSTRACT

David T. Clay* and Scott Lynn

A dry solids process has been developed for the simultaneous removal of NO and SO₂ from power plant stack gases. A catalyst/absorbent in a net reducing flue gas effects the removal of SO₂ by absorption as ferrous sulfide or sulfate and the removal of NO by reduction to nitrogen or ammonia. The solid is regenerable; reaction with air produces a rich stream of SO₂ and ferric oxide. The SO₂ may be converted to saleable H₂SO₄ and the solid is recycled to the process.

The process is capable of greater than 90% removal of SO₂ and NO. The emissions of H₂, CO, and NH₃ are well below acceptable emissions levels. The concentration of the solids in the effluent stream is not significantly increased over normal flyash levels. There is no significant increase in the quantity of solids which must be disposed of. No flue gas cooling or reheating is required. There are no large storage vessels or slurry transport lines within the process. The regeneration process is thermally self-sufficient.

Experiments in a flow-through fixed-bed reactor between 370-540°C have confirmed that the process reactions are feasible. Known

* PhD Thesis
calculational techniques were used to extrapolate the fixed-bed rate data to dispersed-phase contactor conditions. The rapid rates result in a relatively short contact time for the highly dilute dispersed-phase contactor. Similar experimental and calculational techniques were used to confirm that regeneration would be feasible at 680°C in a fluidized bed.

An economic analysis of the process for a 1000-Mw coal-fired power plant showed that it is quite competitive with currently existing wet-scrubbing processes which remove only SO₂. The process costs, including the H₂SO₄ plant, are $18.5/kw for the capital investment and 0.91 mills/kw-hr for the operating cost, with no credit taken for the H₂SO₄.
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CHAPTER I
Introduction and Background

A. Problem Statement.

In the middle of the last decade a concentrated effort was begun by government, industry, and university groups to develop technology for control of the emissions of sulfur dioxide from stationary sources. The work concentrated on electrical power generating plants, since at that time, this source accounted for about 45% of the total SO₂ emissions in the US (USDHEW, 1969). SO₂ emissions from US power plants, assuming no control, are expected to increase 270% between 1967 and 1980 (Chilton, 1971). With no SO₂ abatement, by 1980 power plants would emit about 65% of the total SO₂ emissions.

Another important pollutant which was identified as coming from power plants was nitric oxide. When work began in 1968 electrical generating plants emitted about 20% of the total nitric oxide emissions in the US and about 40% of all NO from stationary sources (USDHEW, 1970). Between 1968 and 1980 NO emissions from power plants are expected to increase by 220%, assuming no controls. Bartok (1969) has estimated that, with completely uncontrolled NO emissions, by 1980 the amount of total NO coming from electric utilities will increase to 25% of the total NO emissions. This percent increase is expected to continue in the future, particularly because of emphasis on NO control from mobile sources.

Although both of these pollutants are generated from the same
source, separate control technology was developed for each. This is evidenced by the publication of two separate control documents by DHEW, one in 1969 and the other in 1970 for NO.

In December, 1971, the EPA promulgated Standards of Performance for New Stationary Sources which included limits on the emissions of both $\text{SO}_x$ and $\text{NO}_x$ from power plants. This clearly identified the need to develop processes which controlled both $\text{SO}_2$ and NO emissions. To date there have been only a few processes developed to meet this double goal. An evaluation of these processes (Section D) shows them to be either inefficient or difficult to operate. The broad objective of this study then is the development of a feasible process for the simultaneous removal of nitrogen oxides and sulfur oxides from the effluent gases of fossil-fuel burning power plants.

B. Objectives.

In order to achieve this overall objective, criteria were established for evaluating potential process alternates. These criteria, which should be satisfied by any acceptable process, are described below.

1. Foreseeable government regulations on emission levels of $\text{NO}_x$ and $\text{SO}_x$ must be met.

The proposed 1971 emission standards from EPA have set these
levels at 0.2 lb NO\textsubscript{x}/10\textsuperscript{6} BTU (210 ppm)* for gas-fired units, 0.3 lb NO\textsubscript{x}/10\textsuperscript{6} BTU (310 ppm)* and 0.8 lb SO\textsubscript{2}/10\textsuperscript{6} BTU (390 ppm)* for oil-fired units, and 0.7 lb NO\textsubscript{x}/10\textsuperscript{6} BTU (672 ppm)* and 1.2 lb SO\textsubscript{2}/10\textsuperscript{6} BTU (540 ppm)* for coal-fired units (EST, 1971). Even tighter restrictions can be expected in the future since the majority of new plants built will burn either coal or oil.

The desired process should have the potential of lowering the NO\textsubscript{x} and SO\textsubscript{x} concentrations to less than 100 ppm. The currently accepted technique for lowering NO\textsubscript{x} is by combustion modification (See Section D.2.a). It is generally agreed that the present state-of-the-art in combustion techniques for oil- and coal-fired units only permits the concentration of NO to be reduced to between 300 to 400 ppm. NO itself does not dissolve appreciably in water or basic solutions and its oxidation to the soluble N\textsubscript{2}O\textsubscript{3} is too slow to be practical for large flows. The only feasible method of obtaining NO\textsubscript{x} levels below 100 ppm appears to be by the reduction of NO with CO or H\textsubscript{2} over a solid catalyst. SO\textsubscript{2}, however, reacts quite readily with numerous substances and could be removed by reaction with the NO\textsubscript{x} reduction catalyst. The key to the proposed process is a solid catalyst/absorbent which retains its activity for NO reduction reactions while reacting with and removing the sulfur compounds in the flue gas.

* NO\textsubscript{x} is expressed as NO\textsubscript{2} and the ppm values are based on:

- coal - 0.7 lb C/lb coal, 12,000 BTU/lb coal, 14% CO\textsubscript{2}
- oil - 0.865 lb C/lb oil, NO.0.6 fuel oil, 12% CO\textsubscript{2}
- gas - 0.97 ft\textsuperscript{3} CO\textsubscript{2}/ft\textsuperscript{3} gas, 873 BTU/ft\textsuperscript{3}, 9.1% CO\textsubscript{2}
2. No other type of pollution problem should be created by installation of the process.

This requires that NO\textsubscript{x} and SO\textsubscript{x} either be rendered innocuous or converted to saleable by-products. In the case of NO\textsubscript{x} the latter alternative is highly improbable, and conversion to innocuous products must be achieved. The reduction of NO\textsubscript{x} by CO or H\textsubscript{2} mentioned in the previous section leads to the formation of N\textsubscript{2} or NH\textsubscript{3}. The extent and significance of NH\textsubscript{3} emission from the proposed process is discussed in Chapter VI. On the other hand, there is no compound of sulfur which does not pollute if released on a large enough scale. Saleable by-products worth considering are elemental sulfur and concentrated sulfuric acid.

Sulfur removal schemes are numerous (Davis, 1972). Dry limestone injection was reported as the least expensive SO\textsubscript{x} control technique but was found ineffective for adequate sulfur removal (EPA, 1973). It has the added disadvantage that large amounts of unreacted sulfur-laden solids are discharged. This results in both particulate pollution and solid waste pollution. Wet limestone scrubbing, although it has much higher SO\textsubscript{2} removal rates, has similar problems. It discharges an aqueous stream high in sulfate and calcium ions. The Chemico Magnesium Oxide process (Shah, 1972) has potential for recovering sulfur as concentrated sulfuric acid, but it is ineffective for NO\textsubscript{x} removal. The proposed process has the potential of both effective NO\textsubscript{x} removal and recovering either elemental sulfur or concentrated sulfuric acid without producing other waste products.
3. The removal mechanism for one component should not depend upon the presence or absence of the other.

The nitrogen fixed as NO comes from both the fuel and the air. The significance of the two sources varies, since the extent of NO formation from air N and fuel N depends upon the burning conditions and the composition of the fuel. The NO\textsubscript{x} concentration in the stack gas ranges from 200 to 1400 ppm, most frequently being in the range of 350 to 600 ppm. The source of sulfur oxides, however, is only from the fossil fuel itself. The concentration of SO\textsubscript{x} has no significant dependence on the design of the combustion installation.

There is essentially no sulfur in the natural gas received at power stations, but oil and coal have sulfur levels which generate SO\textsubscript{2} concentrations ranging from 130 to 4000 ppm SO\textsubscript{2}.

Obviously, no correlation is to be expected between the concentrations of NO\textsubscript{x} and SO\textsubscript{2} in the stack gas since they are generated by unrelated mechanisms. Hence a viable control process for both should not depend on the presence or absence of either for it to achieve satisfactory operation.

4. Furnace operation should be independent of the process operation.

The economy of power production is highly dependent upon the operation of the furnace. Large costs can result from a pollution-control process which necessitates suboptimal furnace operation, regardless of other aspects of the process which may be attractive.

The most widely accepted method for reducing the concentration of NO\textsubscript{x} has been combustion modification (Bagwell, 1971; Bartok, 1969).
Included are such techniques as two-stage combustion, low-excess air firing, flue-gas recirculation, burner redesign, some combination of these first four, and water injection. All of these techniques are applied directly in the furnace region of the boiler, where the need to achieve complete and efficient combustion is generally given a higher priority. In order to operate to obtain both high combustion efficiency and low pollution, compromises must be made resulting in neither goal being fully reached.

Combustion modification in addition to being the best way to reduce the bulk of the $NO_x$, has been shown to increase furnace efficiency when properly used (Bartok, 1969). The lower limit achievable in this manner, however, is about 300 ppm $NO_x$ for coal-fueled furnaces. This level is still too high to be acceptable. Removal of the remaining $NO_x$ can be effected by the proposed catalytic process downstream of the furnace section of the boiler. The catalyst/absorbent is used in a dispersed phase after the superheat section so that no problems of slagging, increased system pressure drop, or loss of plume buoyancy will occur.

5. The process should be adaptable to both new and existing power plants.

Two regions in the flue gas path generally accepted as the best points for removing pollutants are either the region between the superheater and the air preheater or the region between the air preheater and the stack. Since solid removal agents react more rapidly at higher temperatures the first position would be preferable. Tempera-
tures in this region are between 370° and 540°C, with residence times of the order of 0.5 second. Longer residence times could be designed into new units or provided in older units by simple duct extensions.

6. The economics should be an improvement over the best currently known processes.

Bartok (1969) shows that investment costs for combustion control of NOₓ for new furnaces range from $0.25/kw for low-excess air firing in 750-mw oil or gas units up to $2.08/kw for 2-stage combustion in 750-mw oil, gas, or coal units. The cost for modifications to existing units would be 20 to 25% higher. Operating costs range from +0.05 mills/kwh (expense) for 2-stage combustion with coal to -0.05 mills/kwh (credit) with low-excess air and 2-stage combustion for oil-fired units.

The most widely applied control for SO₂ is the use of low-sulfur fuel. Fuel oil with 0.3% sulfur sells for roughly $1/bbl higher than its higher sulfur competitors (Shah, 1972). For a 1000-Mw plant this corresponds to roughly 1.6 mills/kwh for the additional fuel expense. Another SO₂ control process which is increasing in its application is Wet Limestone Scrubbing. Reported costs for this technique are about $30-40/kw for installation costs and 2.0-2.5 mills/kwh for operating costs, depending on plant size, operating factors and other variables (Burchard, 1972). Both of these process alternates, when operated properly, can meet the EPA's SO₂ requirements stated earlier.
In comparison with the low cost Dry Limestone Injection Process the proposed process will have the added cost of catalyst/absorbent regeneration, but none of the costs associated with limestone acquisition, crushing, grinding, and disposal. In addition, some credit for sulfur recovery may be obtained. On balance, the costs are expected to be comparable to dry limestone injection. Details of the cost analysis are given in Chapter V.

C. Literature Review

1. Sulfur dioxide control technology.

a. Existing technology.

Flue gas desulfurization processes have traditionally been grouped as either wet or dry systems. The wet processes contact the main flue gas stream with a clear solution or an aqueous slurry which absorbs the SO2 from the gas stream. The liquid composition and type of contactor vary with the process. The dry processes contact the main flue gas stream with a porous solid which either absorbs or adsorbs the SO2. The solid and the type of contactor vary with the process. Slack (1973) has evaluated all of the major process alternatives, both wet and dry systems. Table i-1 summarizes his evaluation.
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<th>WET</th>
<th>DRY</th>
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<td><strong>Advantages:</strong></td>
<td>1. ( \text{SO}_2 ) removals are consistently high when unit is operating.</td>
<td>1. Gas in not cooled.</td>
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<td>2. In regenerable processes the ratio ( \text{SO}_4^{2-}/\text{SO}_3^{2-} ) is much lower than in dry systems</td>
<td>2. No water pollution problem.</td>
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<td><strong>Disadvantages:</strong></td>
<td>1. Flue gas cooling/reheat required.</td>
<td>1. Temperature cycling of absorbent or expensive dampering systems</td>
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<td>2. Scaling.</td>
<td>2. High surface area requirement may mean high attrition.</td>
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<td>3. Slurry transport.</td>
<td>3. Full oxidation generally occurs in solid.</td>
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<td>5. Potential water pollution problem</td>
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</tbody>
</table>

Although a reliable dry process would be preferrable, from the operational point of view, Slack concludes that because of as-yet-unsolved disadvantages of present dry processes the wet systems may be superior. In a recent publication, EPA (Princiotta, 1974) lists six \( \text{SO}_2 \) control processes that are considered the most important for the near-term future. Five of the six processes are wet, concurring with the evaluation of Slack. The sixth is catalytic oxidation, which does not fit well in either group. These processes are grouped according to the type of sulfur product produced.
Table i-2  LEADING SO$_2$ CONTROL PROCESSES.  (Princiotta, 1974).

<table>
<thead>
<tr>
<th>Throwaway Products</th>
<th>Saleable Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime Scrubbing</td>
<td>Magnesium Oxide Scrubbing</td>
</tr>
<tr>
<td>Limestone Scrubbing</td>
<td>Sodium Sulfite Scrubbing</td>
</tr>
<tr>
<td>Double Alkali</td>
<td>Catalytic Oxidation</td>
</tr>
</tbody>
</table>

The original approach taken for the development of a dry process was first to find a metal oxide which when reacted with SO$_2$ would produce a stable metal sulfite under typical flue gas conditions. The metal sulfite would then decompose in a regeneration step to the metal oxide and SO$_2$. Unfortunately, under typical flue gas conditions metal sulfate instead of sulfite was the predominate product. This necessitated higher regeneration temperatures than would be practical if strongly alkaline solids were used, i.e., Ca or Na. Metals such as Fe and Mn could be regenerated at practical temperatures but had high equilibrium partial pressures of SO$_2$ over the solid at typical reaction temperatures, producing low removals (Welty, 1971). The result of this dilemma was to select a process with a solid which could be thrown away. The solid selected was CaCO$_3$.

This original dry process, Dry Limestone Injection (DLIP), had great apparent potential because of its simplicity and low cost. Captial investment and operating costs for this system are approximately half that of the wet processes listed above. Extensive full-scale tests of the DLIP revealed, however, that its major disadvantages were low SO$_2$ removals (20 - 30%) and solids deposition in the superheater portion of the boiler. Despite the simplicity and low cost, the process has been de-emphasized because of these unsolved
problems.

If a solid could be found which would increase the SO₂ removal without substantially increasing the process cost or complexity, this dry system would be competitive with the wet processes. A key to keeping the process cost low is to have an absorbent which absorbs SO₂ at about the same temperature as it can be regenerated. Welty (1971) showed that such an absorbent cannot be found when both the absorption and regeneration steps are carried out under oxidizing conditions. If the absorption step were net reducing, forming a metal sulfide, and the regeneration step, net oxidizing, forming metal oxide and SO₂, temperature cycling would be minimized. A potential sorbent for such a process would be iron. At 650°C it forms a stable sulfide and an unstable sulfate.

b. Selection of absorbent for SO₂ removal.

Thomas (1969), (Also reported in Lowell, 1971), has made an extensive study of the applicability of metal oxides for removing SO₂. The basic removal mechanism for a metal oxide system was the formation of metal sulfate in the removal step and the decomposition of metal sulfate in the regeneration step. The oxides of 47 elements were evaluated based on the following criteria:

1. Stable oxidation states at \( P_{O_2} = 0.02 \) atm.
2. Sulfate decomposition temperatures below 750°C.
3. Decomposition (below 750°C) must yield oxide from sulfate.
4. Low toxicity level of the compound.
5. High \( P_{SO_2} \) at elevated temperature over the oxide.
6. Low cost of material.

Based on the evaluation of the compiled data Thomas reported that
oxides of Al, Bi, Ce, Co, Cr, Cu, Fe, Hf, Ni, Sn, Th, Ti, V, U, Zn, and Zr were the most promising.

The formation of sulfate in both the DLIP and the above mentioned process creates a potential diffusion resistance when the outer layer of sulfate forms around the unreacted core of metal oxide. This effect is believed to be one of the reasons for the low SO₂ removal in the DLIP. If the sulfur were absorbed as the metal sulfide, less surface expansion would occur and the center core would be more accessible. Decreasing the amount of surface change would also cut down on particle attrition. Sulfide formation rather than sulfate formation would occur if the flue gas were made slightly reducing.

Potential metals were screened for sulfide formation with the work of Thomas as a guide. Since the sulfides are more stable than the sulfates in an inert atmosphere, elimination of those oxides which have too unstable a sulfate will be a conservative screening of potentially unstable sulfides. Therefore, the starting point for this screening was the top 16 metals given by Thomas. Table i-3 lists the oxides of these 16 metals with the evaluation data. Ten metals were eliminated for the following reasons.

- Bi₂O₃ -- Cost too high
- Cr₂O₃, CrO -- Toxicity high
- Ce₂O₃, CeO₂ -- +3 valence decomposes with ignition
- HfO₂, ThO₂ -- Radiation danger, no valence change
- UO₂, U₂O₃, UO₃ -- Toxicity
- V₂O₃, VO₂ -- Melting point low or ignites
- Al₂O₃, ZrO₂, ZnO -- No valence change

The remaining potential metals are Fe, Cu, Ni, Co, Ti, and Sn. The sulfides of Ti and Sn are thermodynamically unstable in the presence of H₂O at 1000°K. They hydrolyze to the oxide and H₂S. Since the costs of Fe, Cu, and Ni were significantly less than Co, these three metals were selected as the best potential sorbents for the process.
Table 1-3. METAL OXIDE EVALUATION

<table>
<thead>
<tr>
<th>METAL OXIDE</th>
<th>DECOMP. T OXIDE (°C)</th>
<th>METAL SULFIDE</th>
<th>DECOMP. T SULFIDE(°C)</th>
<th>METAL SULFATE</th>
<th>DECOMP. T SULFATE(°C)</th>
<th>COST $/lb</th>
<th>TOXICITY*</th>
<th>REFERENCES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>2045 mp</td>
<td>Al₂S₃</td>
<td>1100 mp</td>
<td>Al₂(SO₄)₃</td>
<td>770 d</td>
<td>0.14</td>
<td>1 0 2 0</td>
<td>Thomas, 1969</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>820 mp</td>
<td>BiS</td>
<td>680 mp</td>
<td>Bi₂(SO₄)₃</td>
<td>405 d</td>
<td>4.75</td>
<td>1 2 U 1</td>
<td>Sax, 1968</td>
</tr>
<tr>
<td>Bi₂O₅</td>
<td>150 mp</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>1 2 U 1</td>
<td>Oil, Paint &amp; Drug</td>
</tr>
<tr>
<td>CeO₂</td>
<td>2600</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>U 1 U 1</td>
<td>Reporter, 1971</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>200(ignites) Ce₂S₃</td>
<td>2100 d</td>
<td>Ce₂(SO₄)₃</td>
<td>920</td>
<td>---</td>
<td>---</td>
<td>U 1 U 1</td>
<td></td>
</tr>
<tr>
<td>Co₂O₃</td>
<td>895 d</td>
<td>Co₂S₃</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>2.20</td>
<td>1 1 1 1</td>
<td>*Toxicity given on basis of:</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>900 d</td>
<td>---</td>
<td>CoSO₄</td>
<td>735 d</td>
<td>---</td>
<td>---</td>
<td>1 1 1 1</td>
<td>a. acute local</td>
</tr>
<tr>
<td>CoO</td>
<td>1935 mp</td>
<td>CoS</td>
<td>&gt;1116 mp</td>
<td>---</td>
<td>---</td>
<td>&quot;</td>
<td>1 1 1 1</td>
<td>CoO, 1935</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>2435 mp</td>
<td>Cr₂S₃</td>
<td>1350 d</td>
<td>Cr₂(SO₄)₃</td>
<td>460-640</td>
<td>1.83</td>
<td>3 U 3 3</td>
<td>b. Acute systematic</td>
</tr>
<tr>
<td>CrO</td>
<td>---</td>
<td>CrS</td>
<td>1550 mp</td>
<td>---</td>
<td>---</td>
<td>&quot;</td>
<td>3 U 3 3</td>
<td>c. Chronic local</td>
</tr>
<tr>
<td>Cr₂O₅</td>
<td>300 d</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>3 U 3 3</td>
<td>d. Chronic systematic</td>
</tr>
<tr>
<td>CuO</td>
<td>1325 mp</td>
<td>CuS</td>
<td>220 d</td>
<td>CuSO₄</td>
<td>840-935</td>
<td>0.67</td>
<td>1 2 1 1</td>
<td>Where:</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>1235 mp</td>
<td>Cu₂S</td>
<td>1100 mp</td>
<td>Cu₂(SO₄)₂</td>
<td>840-935</td>
<td>&quot;</td>
<td>1 2 1 1</td>
<td>0 - No toxicity</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1565 mp</td>
<td>Fe₂S₃</td>
<td>d</td>
<td>Fe₂(SO₄)₃</td>
<td>781-810</td>
<td>0.08-0.20</td>
<td>1 0 0 0</td>
<td>1 - Slightly toxic</td>
</tr>
<tr>
<td>FeO</td>
<td>1420 d</td>
<td>FeS</td>
<td>1196</td>
<td>FeSO₄</td>
<td>603-810</td>
<td>&quot;</td>
<td>1 0 0 0</td>
<td>2 - Moderate Toxicity</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>1538 d</td>
<td>FeS₂</td>
<td>1171 mp</td>
<td>---</td>
<td>&quot;</td>
<td>1 0 0 0</td>
<td>3 - Severe Toxicity</td>
<td></td>
</tr>
<tr>
<td>HfO₂</td>
<td>2812 mp</td>
<td>---</td>
<td>---</td>
<td>Hf(SO₄)₂</td>
<td>550-650</td>
<td>---</td>
<td>U R</td>
<td>U - Unknown Toxicity</td>
</tr>
<tr>
<td>NiO</td>
<td>1990 mp</td>
<td>NiS, Ni₃S₂</td>
<td>790, 797</td>
<td>NiSO₄</td>
<td>848 d</td>
<td>1.33</td>
<td>1 1 2 2</td>
<td>R - Radiation</td>
</tr>
</tbody>
</table>

Where:
- **a. acute local**
- **b. Acute systematic**
- **c. Chronic local**
- **d. Chronic systematic**
- **0 - No toxicity**
- **1 - Slightly toxic**
- **2 - Moderate Toxicity**
- **3 - Severe Toxicity**
- **U - Unknown Toxicity**
- **R - Radiation**
<table>
<thead>
<tr>
<th>METAL OXIDE</th>
<th>DECOMP. T SULFIDE</th>
<th>METAL OXIDE</th>
<th>DECOMP. T SULFIDE</th>
<th>METAL SULFATE</th>
<th>DECOMP. T SULFATE</th>
<th>COST $/lb</th>
<th>TOXICITY* REFERENCES</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO</td>
<td>1080 d</td>
<td>SnS</td>
<td>882 mp</td>
<td>SnSO4</td>
<td>&gt;360</td>
<td>2.11</td>
<td>---</td>
</tr>
<tr>
<td>SnO2</td>
<td>1127 mp</td>
<td>SnS2</td>
<td>600 d</td>
<td>Sn2(SO4)2</td>
<td>300-587</td>
<td>1.97</td>
<td>---</td>
</tr>
<tr>
<td>ThO2</td>
<td>3050 mp</td>
<td>ThS2</td>
<td>1925 mp</td>
<td>Th(SO4)2</td>
<td>---</td>
<td>U R</td>
<td></td>
</tr>
<tr>
<td>TiO</td>
<td>1750</td>
<td>TiS</td>
<td>---</td>
<td>Ti(SO4)2</td>
<td>150</td>
<td>---</td>
<td>1 U U U U</td>
</tr>
<tr>
<td>TiO2</td>
<td>---</td>
<td>TiS2</td>
<td>---</td>
<td>Ti2(SO4)3</td>
<td>---</td>
<td>---</td>
<td>1 U U U U</td>
</tr>
<tr>
<td>Ti2O3</td>
<td>2130 d</td>
<td>Ti2S3</td>
<td>---</td>
<td>Ti2(SO4)3</td>
<td>---</td>
<td>---</td>
<td>I U U U U</td>
</tr>
<tr>
<td>V2O5</td>
<td>690 mp</td>
<td>V2S5</td>
<td>d</td>
<td>V2(SO4)3</td>
<td>380-408</td>
<td>„</td>
<td>U</td>
</tr>
<tr>
<td>V2O4</td>
<td>1970 mp</td>
<td>---</td>
<td>&quot;</td>
<td>&quot;</td>
<td>U</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>V2O3</td>
<td>---</td>
<td>V2S3</td>
<td>d&gt;600</td>
<td>V2(SO4)3</td>
<td>380-408</td>
<td>&quot;</td>
<td>U</td>
</tr>
<tr>
<td>VO</td>
<td>(ignites)</td>
<td>VS</td>
<td>D</td>
<td>&quot;</td>
<td>&quot;</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>U3O8</td>
<td>1300 d</td>
<td>US3</td>
<td>ignites</td>
<td>&quot;</td>
<td>U</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>UO2</td>
<td>2500 mp</td>
<td>US2</td>
<td>&gt;1100</td>
<td>U(SO4)2</td>
<td>U</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>UO3</td>
<td>d</td>
<td>US</td>
<td>&gt;2000 mp</td>
<td>U</td>
<td>U</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>1975 mp</td>
<td>ZnS</td>
<td>1850 mp</td>
<td>ZnSO4</td>
<td>600 d</td>
<td>0.15</td>
<td>U</td>
</tr>
<tr>
<td>ZrO2</td>
<td>2700 mp</td>
<td>ZrS2</td>
<td>1550 mp</td>
<td>Zr(SO4)2</td>
<td>410 d</td>
<td>&quot;</td>
<td>U U U U U</td>
</tr>
</tbody>
</table>
c. Sulfide formation reactions.

Ryason (1967) reported the catalytic reduction of SO₂ with CO over a copper oxide/alumina catalyst to give S₂. The reaction was

\[ 2\text{CO} + \text{SO}_2 \rightarrow 2\text{CO}_2 + \frac{1}{2}\text{S}_2 \]  

i-1

Qualitative evaluation of the catalyst after reaction suggested that copper sulfide was formed. Since COS was also formed, the sulfidation may have occurred by

\[ \text{CuO} + \text{COS} \rightarrow \text{CuS} + \text{CO}_2 \]  

i-2

Khalafalla (1971) studied the same SO₂ reduction reaction over an iron oxide/alumina catalyst. In a later and more definitive study, Haas and Khalafalla (1973) definitely confirmed the presence of both FeS and FeS₂. They suggested that these sulfides were formed during the initial phases of testing when CO and SO₂ were passed over Fe₂O₃. An important observation made by Haas (1971) was that O₂ above 0.5% poisoned SO₂ reduction to sulfur.

Kasaoka (1973) tested copper oxide/alumina, iron oxide/alumina, nickel oxide/alumina, cobalt oxide/alumina, and iron oxide/chromium oxide/alumina catalysts for reaction i-1 in the presence and absence of water. Traces of COS and H₂S were measured. No discussion of the catalyst composition was given but it would be expected that all of the metals formed a sulfide before there was total sulfur compound elution. The presence of H₂S suggests that H₂, formed probably by the water-gas shift reaction, can also act as a reducer for SO₂. Kasaoka
(1973) also reported that SO\textsubscript{2} reduction decreased when O\textsubscript{2} was in the gas stream. The reduced activity was attributed to the formation of a sulfite or sulfate layer on the catalyst. At 2% O\textsubscript{2} the catalyst was inactive.

Querido (1973) has reported extensive work on reaction i-1 with a copper oxide catalyst. Although he outlined a process to remove SO\textsubscript{2} and maximize S\textsubscript{2} production relative to COS production, no clear discussion of the catalyst composition is given. Based on the work of Haas (1973) and Kasaoka (1973) the active solid is probably copper sulfide.

All of the studies mentioned above reduce SO\textsubscript{2} primarily to S\textsubscript{2} with either COS or H\textsubscript{2}S being produced in varying degrees. Since there is no removal mechanism for either COS or H\textsubscript{2}S after the metal oxide has been sulfided, the potential for total sulfur compound conversion to S\textsubscript{2} is low. Nonhebel (1972), Hopton (1956), and Jordan (1935) discuss the reactions for removing H\textsubscript{2}S from coal gas streams by reaction with iron oxide to give iron sulfide at low temperatures, 55°C. By maintaining an excess of iron oxide in contact with the flue gas the sulfur formation reactions would be suppressed and the sulfide formation reactions enhanced. All forms of reduced sulfur COS, H\textsubscript{2}S, SO\textsubscript{2}, and S\textsubscript{2}, would then be removed from the exit gas stream.

2. Nitric oxide control technology.


An extensive study was done by the Esso Research and Engineering
Company (Bartok, 1969) on methods for the control of NO from stationary sources. The study concluded that the primary NO removal technique for large power plants was combustion modification. This technology can be applied to existing plants as well as new plants at low cost or in some cases at a credit to the plant. Table 1-4 lists the techniques discussed and the amount of NO removal expected.

Table 1-4 ESTIMATED %NO<sub>x</sub> REDUCTION BY COMBUSTION MODIFICATION 1000-Mw UNIT. (Bartok, 1969)

<table>
<thead>
<tr>
<th>Technique</th>
<th>OIL</th>
<th>COAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-excess air firing (LEA)</td>
<td>33</td>
<td>25</td>
</tr>
<tr>
<td>Two-stage combustion (2SC)</td>
<td>40</td>
<td>35</td>
</tr>
<tr>
<td>LEA + 2SC</td>
<td>73</td>
<td>60</td>
</tr>
<tr>
<td>Flue gas recirculation (FGR)</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>LEA + FGR</td>
<td>70</td>
<td>55</td>
</tr>
<tr>
<td>Water Injection</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

Low-excess air firing in combination with two-stage combustion appears to offer the greatest potential for NO removal.

i. Oil-fired units.

Bagwell (1971) reports that with fuel-oil firing on a 175-Mw face-fired unit almost 50% NO removal was achieved with two-stage combustion. The furnace burner design permitted the O<sub>2</sub> concentration to be decreased to 2.6% before smoke formation began. Tomany (1971) reported recent coaxial burner designs for gaseous and liquid fuels which permit a closer approach to stoichiometric firing before the onset of smoking and excessive CO formation. Reman (1963)
claims a burner design that allows liquid fuels to be burned with stoichiometric air without smoking. Bartok (1969) and Turner (1972) report that tangentially-fired oil furnaces have lower NO emissions than horizontally-fired units.

Low-excess air firing on oil units has been commercially demonstrated. Glaubitz (1960, 1961, 1962) reported that a boiler furnace equivalent to approximately a 25-Mw unit was operated satisfactorily for 4 years at 0.2% O₂. Reese (1965) reported an oil-fired, 185-Mw tangential unit that was operated at 0.5% O₂ while still maintaining acceptable carbon levels (99.9% carbon combustion efficiency, CCE) in the flyash.

ii. Coal-fired units.

Limited work has been done on low-excess air firing with pulverized coal-fired units. Bienstock (1966) reported on NO removal and soot formation in a small laboratory coal-fired furnace (1 to 4 lb/hr). When 1% O₂ concentration was maintained in the furnace zone followed by a later injection of 3.4% O₂ (two-stage combustion), 62% NO removal was achieved. The carbon in the ash increased from 2% (99.8% CCE) at 4.4% O₂ to 6.6% (99.2% CCE) with the two-stage combustion. McCann (1970) reports a 70% NO reduction when the O₂ concentration is decreased from 5% to 0.3% in a 500 lb/hr pulverized coal-fired furnace. At the low excess air levels there was 7.8% carbon in the ash (99.0% CCE). This relatively low ash level was achieved by using a 370°C air preheat and a stable air/fuel ratio.

Bartok (1972) reports that two-stage combustion was tested in
three coal units: a 175-Mw front-fired, a 480-Mw tangential-fired, and a 820-Mw horizontally opposed. In the front-fired unit an overall O₂ concentration of about 2% was used. It was reported in all cases that the modifications did not produce unacceptable levels of smoke, CO, or hydrocarbons. These short term tests demonstrate the possibility but have not demonstrated the long term practicality of low-excess air firing in coal-fired furnaces.

iii. Acceptable excess-oxygen firing levels

Industry practice has been to maintain between 1 to 4% O₂ in oil-fired units and 3 to 7% O₂ in coal-fired units (Steam, 1969). The previous paragraphs indicate that commercial oil-fired units have been operated successfully at 0.2% O₂ with the aid of new firing patterns, new burner designs and higher controls. In a similar manner, research on these variables should enable the minimum O₂ level in coal firing to be decreased to about 2% O₂ (Hazard, 1974).

iv. Minimum NO with combustion modification.

Nitrogen oxide is formed in the combustion process from nitrogen in the air and nitrogen in the fuel. Lange (1971) reports that to achieve significant thermal fixation of gaseous N₂ as NO in utility boiler furnaces the temperature must be in the range 1500 - 1900°C. Hammons (1971) reported that fixation of fuel nitrogen in coal to NO can occur between 760 - 870°C. The temperature minimum for the conversion of fuel nitrogen in oil to NO is also expected to be in this range. Since the combustion temperatures for both coal and oil are equal to or above this lower limit, the minimum NO at low excess air will closely correspond to the fraction of fuel N con-
verted to NO. Martin (1972) and Turner (1972) report that the fraction of fuel N converted to NO varies with the level of N in the fuel and the amount of excess O\textsubscript{2} used for combustion. Turner (1972) gives a typical range of fuel N conversion to NO as 30 - 60% for oil-firing. Jonke (1969) reports a typical range of fuel N conversion to NO of 18 - 25% for a fluidized bed of coal. The N content of typical fuel oils ranges between 0.07% (light distillates) and 1.4% (heavy oils). The US crude average is estimated at 0.148% (Ball, 1962). Coal N ranges between 0.8% (Anthracite) and 1.9% (Sub-bituminous A). Most coals average around 1.5% N. Table i-5 lists the expected NO flue gas concentration resulting from the fuel N, given the listed assumptions.

<table>
<thead>
<tr>
<th>Table i-5</th>
<th>CALCULATED MINIMUM NO EMISSIONS EXPECTED FROM OIL AND COAL FIRED UNITS.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wgt % Carbon in Fuel</td>
<td>OIL</td>
</tr>
<tr>
<td>Wgt % Nitrogen</td>
<td>86</td>
</tr>
<tr>
<td>Vol % CO\textsubscript{2} in flue gas</td>
<td>13</td>
</tr>
<tr>
<td>% Conversion fuel N to NO</td>
<td>30</td>
</tr>
<tr>
<td>Concentration NO (ppm)</td>
<td>540</td>
</tr>
</tbody>
</table>

Bartok (1972) reports that NO concentrations in commercial oil-fired and coal-fired units have been lowered to around 150 ppm to 250 ppm with two-stage combustion and low excess air. A 15 - 20% de-rating of the unit capacity was needed in all cases. The lack of % fuel N data in this study does not allow direct comparison with the NO levels reported in Table i-5. It would appear, however,
that commercial units may have lower NO values than laboratory furnaces. It is clear from Bartok (1972) that not all units operated acceptably at the extremes of these modifications. A reasonable estimate of minimum NO emissions under acceptable combustion modification operations appears to be 300 - 400 ppm for both oil and coal at the average N values listed in Table i-5. Therefore, in planning for future emission standards that may limit the NO concentration below 100 ppm, processing techniques in addition to combustion modification need to be developed.

b. Dry NO Removal Processes.

Although combustion modification techniques are effective for removing 60%-80% of the NO formed during combustion, further removal must be accomplished by flue gas treatment processes that are efficient at low NO concentrations. As was the case with SO₂, both wet and dry processes have been proposed for NO removal. Section B.1. discussed the ineffectiveness of wet systems for NO removal. Section C.1. concluded that for SO₂ removal an effective dry system would be preferrable to existing wet processes. This leads to evaluating the potential of dry NO removal processes. These are grouped into three categories.

Solid-gas chemisorption
Heterogeneous catalytic decomposition
Heterogeneous catalytic reduction

i. Solid-gas chemisorption.

Shelef (1971) has given an extensive review of the physical and chemical adsorption of NO on metals. Several different types of bonding
are described ranging from purely ionic to covalent. Ruthenium was the element which gave the largest variety of NO complexes. Iron was the common metal which showed the greatest affinity toward NO. Copper and nickel were other common metals which formed NO complexes.

Otto (1970) studied NO adsorption on supported iron oxides between 26 - 150°C and 1 to 200 Torr. He found the NO adsorption ability of iron oxides to rank: Fe₃O₄ > FeO > Fe₂O₃. With Fe₃O₄ at 26°C and 200 Torr the NO equilibrium loading corresponded to 750 mmoles/m² Fe₃O₄. Similar measurements for supported nickel oxide reported by Gandhi (1972) were 1650 mmoles NO/m² NiO. Gandhi (1973) also reported NO adsorption on supported copper oxide. A maximum of 100 mmoles NO/m² CuO was measured. In contrast to the iron, the more oxidized species, CuO, adsorbs NO more readily than does Cu₂O. A comparison of the chemisorption rates of NO on these three metals shows the ranking to be: iron oxide > nickel oxide > copper oxide.

Otto (1970) reported the initial NO adsorption rate on Fe₃O₄, at 90°C 3.5 Torr, as 1.09 x 10⁻³ mmoles/m² Fe₃O₄-sec. Since he reported 16% reduction of NO to N₂O over Fe₃O₄ at 150°C, 90°C is assumed to be the upper limit for reversible adsorption on Fe₃O₄. Calculations show that if a one-second contact time between a 700 ppm NO flue gas stream and Fe₃O₄ is assumed in a typical power plant, an adsorbant flow rate at least 8 times that of the coal would be required just to remove the NO. This assumes that the flue gas is cooled to 90°C from 150°C and that the presence of
sulfur does not inhibit the adsorption rate. First, cooling the flue gas to 90°C is undesirable since this either results in decreased plume buoyancy or added equipment. Second, Lunsford (1968) has shown by comparing NO adsorption on ZnO and ZnS that placing sulfur on the surface does inhibit NO adsorption. Gidaspow (1972), in contrast, reported NO adsorption rates on platinized FeSO₄ with 780 ppm NO and 82°C after 1 minute of 1.17 mmol NO/m² ads.-sec (270 mmol NO/g ads.-sec.). If this was in fact true adsorption, the adsorbent-to-coal flow rates would be reasonable, around 0.001. Since 2% H₂ in N₂ at 200°C had to be used in regeneration and no NO was measured in the outlet gases, it is apparent that reduction of NO instead of adsorption of NO was occurring at these higher rates.

In summary, adsorption of NO on solids for NO removal from flue gases appears impractical because of the following limitations:

-- Flue gas cooling required.
-- Large adsorbent-to-coal flow rates are required just for NO removal
-- Possible inhibiting interaction between sulfur and NO adsorption.

ii. Heterogeneous catalytic decomposition.

Nitric oxide is thermodynamically unstable relative to the elements in an atmosphere containing 75% N₂ and 1% O₂ below 730°C (Shelef, 1971). At 730°C(75%N₂, 1%O₂) the equilibrium concentration of NO is 7.23 ppm. The presence of NO in power plant exit flue gases (typically 150°C) is a result of kinetically freezing the NO decomposition reaction. Bartok (1969) reports that under typical combustion conditions homogeneous NO decomposition is kinetically
frozen below 1260°C.

Shelef (1969) tested the heterogeneous catalytic decomposition of NO over platinum and five base metal oxide catalysts. Even at 500°C NO decomposition kinetics were not rapid enough for practical application. Winter (1971) tested 40 metal oxides for NO decomposition. He measured rates comparable to those of Shelef. Riesz (1957) performed an extensive screening of 21 commercial and 17 laboratory-prepared catalysts. Platinum, palladium, base metal oxides and base metal sulfides were tested. The general conclusion was also that none of these catalysts produced a sufficiently high decomposition rate to be of importance.

The results of Riesz (1957) work on base metal sulfides as potential catalysts warrants further discussion since this is a system which includes both sulfur and nitrogen oxides. Sulfided iron oxide, sulfided cobalt molybdate, molybdenum sulfide, and molybdenum sulfide activated with potassium carbonate were tested. A stream of 2000 ppm NO in N₂ was passed over a fixed-bed of catalysts.

Table 1-6. DECOMPOSITION OF NO BY SULFIDE CATALYSTS. (Riesz, 1957).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Residence Time (second)</th>
<th>Temperature (°C)</th>
<th>NO Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Sulfide</td>
<td>0.052</td>
<td>500</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>0.041</td>
<td>700</td>
<td>24</td>
</tr>
<tr>
<td>Cobalt-Molybdenum</td>
<td>0.032</td>
<td>500</td>
<td>17</td>
</tr>
<tr>
<td>Sulfide</td>
<td>0.030</td>
<td>700</td>
<td>4</td>
</tr>
<tr>
<td>Molybdenum Sulfide</td>
<td>0.032</td>
<td>500</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>0.030</td>
<td>700</td>
<td>4</td>
</tr>
<tr>
<td>Molybdenum Sulfide +</td>
<td>0.029</td>
<td>500</td>
<td>28</td>
</tr>
<tr>
<td>15% K₂CO₃</td>
<td>0.030</td>
<td>700</td>
<td>17</td>
</tr>
</tbody>
</table>
Although NO removal is relatively high, Riesz found that the catalyst lost activity after extended use. Concurrent with the decreased activity was a loss of sulfur from the surface in the form of SO₂. Riesz, as well as later investigators, eliminated sulfides as potential catalysts because of what they thought would be an unavoidable SO₂ pollution problem. As noted in Section c.1.c., the presence of a reducing agent, CO or H₂, would prevent evolution of SO₂ from FeS.

iii. Heterogeneous catalytic reduction.

(a.) Initial catalytic screening.

The most effective means for NO removal from gas streams is heterogeneous catalytic reduction. Shelef (1971) has reviewed all of the early studies on these reactions. He concludes that, under reducing conditions, a variety of catalysts as well as a variety of reducing agents can be employed to remove NO from gas streams at low gas residence times and relatively low temperatures. Evaluation of these data showed that supported precious metals and supported copper oxide or copper chromite were the catalysts with the most promise. Typical reducing agents were CO, H₂ or a hydrocarbon.

Shelef (1971) emphasized that in addition to the reaction rates between NO and a reducing agent, the competitive reactions between other oxidizing species and the reducing agent are important. Shelef (1968) reported on the competitive oxidation of CO by NO or O₂ over various catalysts. He found that the CO-O₂ reaction proceeded more rapidly over the earlier selected Cu₂O and CuCr₂O₄.
catalysts than did the CO-NO reaction. The reverse was found true for Fe$_2$O$_3$ and Cr$_2$O$_3$ catalysts. In his study, Fe$_2$O$_3$ catalyst showed the highest rate for the CO-NO reaction, and it was therefore viewed as a potential catalyst.

This preference for the CO-NO reaction terminated when O$_2$ was added to the Cr$_2$O$_3$ system. Only when the gas stream was slightly reducing relative to both NO and O$_2$ reduction was there complete removal of both NO and O$_2$. It was assumed that the Fe$_2$O$_3$ system would act similarly. In laboratory tests Jones (1971) demonstrated that neither supported CuCr$_2$O$_4$ nor Fe$_2$O$_3$ catalysts were effective in promoting the NO-H$_2$ reaction in preference to the O$_2$-H$_2$ reaction. Some improvement in reaction selectivity was found with supported Pt-Pd below 205°C. These metals are too expensive and the temperatures too low for practical considerations on power plant flue gases.

From this initial screening, the best NO reduction catalysts for application on power plants would be copper oxides, copper chromite, or iron oxide, all of which should be supported.

(b.) Reduction products and reducing agents.

Kokes (1966) showed that the reduction of NO by H$_2$ on a Pt catalyst led to N$_2$O, NH$_3$ or N$_2$. Shelef (1968) reported the appearance of both N$_2$ and N$_2$O when NO was reduced by CO over Pt and copper chromite catalysts. Jones (1971) and Klimisch (1972) reported on the formation of both N$_2$ and NH$_3$ when NO is reduced by CO in the presence of H$_2$O over both noble and base metal catalysts.

Shelef (1968) reported that N$_2$O is primarily a low-temperature
product over active Fe$_2$O$_3$, CuCr$_2$O$_4$, and Cu$_2$O supported catalysts. The temperature for maximum N$_2$O formation for the NO-CO reaction ranges between 180°C - 220°C when the residence time is about 0.75 sec. Above 300°C there was essentially no N$_2$O. Decreasing the residence time to about 0.07 seconds at 273°C increased N$_2$O formation over supported Fe$_2$O$_3$ catalyst. This suggested that N$_2$O is a possible gas-phase intermediate for the NO-CO reaction.

An extensive study of NH$_3$ formation in the NO-H$_2$ reaction over base metal oxide catalysts was reported by Shelef (1972). He also studied the effect of CO in the NO-H$_2$ system. NH$_3$, N$_2$O and N$_2$ were assumed to be the reduction products in the system with about a 0.18 second residence time. The relative amounts of NH$_3$ and N$_2$ produced varied with the catalyst, temperature, the reducing agent, and the amount of oxygen. Table i-7 shows the effect of different catalysts and temperatures on the percent reduced nitrogen product which is NH$_3$ (this is referred to as the ammonia selectivity).

Table i-7 AMMONIA SELECTIVITY AS A FUNCTION OF THE CATALYST AND TEMPERATURE. (Shelef, 1972)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>370°C</th>
<th>538°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Oxide</td>
<td>20%</td>
<td>20%</td>
</tr>
<tr>
<td>Copper Oxide</td>
<td>88%</td>
<td>80%</td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>16%</td>
<td>80%</td>
</tr>
<tr>
<td>Copper Chromite</td>
<td>95%</td>
<td>90%</td>
</tr>
</tbody>
</table>

Inlet: NO, 0.10 - 0.12%  
H$_2$, 1.4%  
θ, 0.18 sec.
Although nickel oxide has the lowest NH₃ selectivity at both extremes, at an intermediate temperature of 420°C the NH₃ selectivity is 65%. The low selectivity at the higher temperature is caused by NH₃ catalytically being decomposed by NiO (Klimisch, 1973). All of these catalysts will decompose NH₃ to the elements but at higher temperatures (greater than 600°C) than the nickel. Shelef (1972) found that in all cases the addition of CO to the NO-H₂ system resulted in an increase in both the NO removal and in the NH₃ selectivity. The addition of 0.25% O₂ to the 1.4% H₂ - 0.12% NO system decreased both the NO removal and the NH₃ selectivity at a given temperature. A significant finding was that when both O₂ and NO were present, CO reacted preferentially with O₂ while H₂ reacted to the same extent with both NO and O₂.

Klimisch (1972) also noted the higher reactivity in the NO-H₂ system. He demonstrated that the presence of both CO and H₂O in the system allowed the water-gas shift reaction to proceed, producing a more reactive H than molecular H₂ for NO reduction and NH₃ formation. The effect of O₂ on both NO removal and NH₃ selectivity was also confirmed.

Over base metal oxide catalysts the two main reduction products will be NH₃ and N₂. At very low residence times, when neither H₂O nor H₂ is present, N₂O may also be generated. The amounts of NH₃ and N₂ produced will vary depending upon the reducing agent, the temperature, the catalyst, and the amount of O₂ in the gas stream.

(c.) Reduction kinetics.

Shelef (1972) has presented data comparing the kinetics of NO
reduction catalysts. Table i-8 compares the three potential catalysts plus nickel oxide on the basis of the temperature at which 90% NO conversion occurs.

Table i-8. TEMPERATURE OF 90% NO CONVERSION IN NO-H₂-CO SYSTEMS,
°C. (Shelef, 1972)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NO-H₂</th>
<th>NO-H₂-CO</th>
<th>NO-CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper Chromite</td>
<td>275</td>
<td>275</td>
<td>320</td>
</tr>
<tr>
<td>Copper Oxide</td>
<td>280</td>
<td>270</td>
<td>350</td>
</tr>
<tr>
<td>Nickel Oxide</td>
<td>425</td>
<td>420</td>
<td>470</td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>480</td>
<td>430</td>
<td>510</td>
</tr>
</tbody>
</table>

In this study the copper catalysts showed the fastest kinetics and the iron the slowest. In all cases the combined H₂-CO system either accelerated the kinetic rate or kept it at a high value. All of the temperatures listed are below the upper process limit of 540°C, which is the temperature at which the flue gas leaves the superheater section. The 0.18-second residence time of the gas in the catalyst bed is less than the available 0.50-second residence time between the economizer and air preheater in a power plant. These facts imply that catalysts exist which have potential for at least 90% NO removal in flue gas streams.

Since no detailed discussion of the catalyst treatment or oxidation state was given it is not possible to select a catalyst simply. At best it can be said that copper, nickel, and iron oxide catalysts
have potential for sufficiently rapid kinetics for power plant application. Studies under flue gas conditions are needed to confirm each catalysts reactivity.

3. Simultaneous $SO_x$ and $NO_x$ dry process control technology.

Jordan (1935) reported that at 105°C iron oxide removed both $H_2S$ and NO from commercial gas streams. Iron sulfide formed and NO was adsorbed on the solid. The simultaneous removal declined rapidly as the solid became loaded with NO, the atmosphere became oxidizing, or the temperature was raised.

Pierce (1929) reported that the reaction of $H_2S$ and NO proceeded at 27° to 100°C over silica gel and glass wool to give $S$, $N_2$, and $H_2O$. Princeton Chemical Research (1968) has studied a process using this reaction for simultaneous $SO_2$ and NO removal. They propose to recycle a stream of $H_2S$ to an alumina or molecular sieve catalyst where it reacts with the $SO_2$ and NO by the following reactions:

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$  \hspace{1cm} (i-3)
$$NO + H_2S \rightarrow S + \frac{5}{4}N_2 + H_2O$$  \hspace{1cm} (i-4)

The sulfur condenses on the catalyst and must be stripped off at high temperature. Preliminary tests confirm acceptable sulfur removal but the catalyst was poisoned when NO was present. In addition to the poisoning problem the large $H_2S$ recycle stream causes added problems of control.

Bartok (1969) has proposed a dry process that sequentially removes $SO_x$ and $NO_x$. The $SO_x$ in dust-free flue gas is first oxidized to $SO_3$ over a catalyst such as $V_2O_5$ at 455°C. $NH_3$ is injected forming
\((\text{NH}_4)_2\text{SO}_4\) which precipitates from the gas at 400°C. A second injection of \(\text{NH}_3\) is made prior to the flue gas passing over a Pt catalyst at 200°C. The \(\text{NH}_3\) reduces the NO, forming \(\text{N}_2\) and \(\text{H}_2\text{O}\). Two catalyst systems are required in this process, the second being an expensive catalyst easily poisoned by sulfur.

Ryason (1967) reported the simultaneous removal of \(\text{SO}_2\) and NO over a copper oxide catalyst when the net gas stream was reducing. The \(\text{SO}_2\) was reduced to sulfur, which condensed in the reactor outlet and NO was assumed to be reduced to \(\text{N}_2\). The catalyst appeared to be copper sulfide at the end of the run. Traces of \(\text{COS}\) were also measured. Additional work on a process utilizing this concept is reported by University of Massachusetts workers, Querido (1973), Okay (1973), and Quinlan (1973). Three catalyst beds in series are used to reduce \(\text{SO}_2\) to sulfur and NO to \(\text{N}_2\) with an excess of CO in the flue gas stream. The original catalyst charged to each bed is copper oxide on supported alumina. The first bed catalyzes the oxidation of CO with \(\text{O}_2\) to remove all of the \(\text{O}_2\) which could poison the remaining catalyst beds. The flue gas is split into two streams after the first bed. The main flow enters the second bed where \(\text{SO}_2\) is reduced to \(\text{S}_2\) and \(\text{COS}\) and NO to \(\text{N}_2\). The secondary flow bypasses the second bed and goes directly to the third bed. In the third bed \(\text{COS}\) and \(\text{SO}_2\) react to produce \(\text{S}_2\) and \(\text{CO}_2\).

The reactions for \(\text{SO}_2\) removal were first studied at 430 - 540°C with residence times of 0.07 - 0.22 seconds. They reported greater than 90% removal of \(\text{SO}_2\) in less than 0.20 seconds. The addition of NO to the system decreased the \(\text{SO}_2\) removal slightly. NO removals
were always greater than 90%. The assumed reduction product for NO in these experiments was N₂. The simultaneous reduction was studied between 400 - 430°C with residence times around 0.20 seconds. Okay (1973) reported that H₂O had an adverse effect on the SO₂ reduction in the CO-SO₂ system but that the water-gas shift reaction did not proceed. Based on this fact, Quinlan (1973) assumed that in the simultaneous removal of NO₅ and SO₅ no H-containing species such as H₂S or NH₃ would form. In Chapter IV, Section G.1., experimental work is reported in which it was found that both H₂S and NH₃ are formed when NO and SO₂ are reduced with CO in the presence of H₂O over copper catalyst. The H₂S would probably react like COS with the bypassed SO₂ to form sulfur. The NH₃, like the product N₂, would elute.

Even if the basic process chemistry is feasible, the University of Massachusetts process has several practical drawbacks. First, three beds in series will create a large system pressure drop. Second, the bypass stream must be very accurately controlled to provide stoichiometric COS and SO₂. Third, the amount of CO required for the reduction must be closely controlled since only reactions with O₂, SO₂ and NO remove it. Fourth, the flue gas would have to be cooled and then reheated after the bed to insure complete precipitation of the sulfur.

In summary no acceptable dry process for simultaneously removing sulfur compounds and NO has previously been developed.

4. CO and H₂ removal by catalyst/absorbent oxidation.

The removal of SO₂ and NO by the proposed process requires the
presence of a reducing agent, either CO or H₂. By necessity, an excess of CO and H₂ needs to be maintained to insure complete reaction with SO₂ and NO. If this excess CO and H₂ were emitted, it would constitute a pollution problem. Both CO and H₂ can be removed by contacting the gas stream with an excess of Fe₂O₃.

Feinman (1961, 1964) reported on the reduction of Fe₂O₃ with H₂ at temperatures between 540°C and 700°C. The iron was reportedly reduced to both Fe₃O₄ and FeO. O₂ and H₂O were found to retard the rate. A more highly reduced iron was produced at the lower temperature.

Fast (1965) discusses the reduction of iron oxide with CO or H₂ between 560 and 1000°C. This discussion is mainly about equilibrium considerations. Otto (1970) uses the work of Fast as a basis for selecting a CO/CO₂ ratio to give a reduced iron oxide for his adsorption studies.

Baranski (1972) studied the reduction kinetics of an iron catalyst with H₂ in the temperature range of 450° - 550°C. As in the case of the other investigators cited, the major concern was the solid reduction instead of CO or H₂ oxidation. All of these investigators have reported reaction at typical process temperatures but have used much higher CO or H₂ concentrations than would be present in stack gas. Experiments at low concentration will be important in the experimental study which follows.

5. Regeneration of catalyst/absorbent.

The oxidation of metal sulfides at high temperatures (700 - 900°C) to give metal oxides and SO₂ has long been a standard process for removal of sulfur from metal ores. Stollery (1964) reports on the
exothermic oxidation of iron, copper, and zinc ores in fluidized-bed roasters. Less than 0.1% sulfide remained after oxidation in a fluid bed with only 2% O₂ in the exit stream. This represented approximately 99.7% oxidation of the sulfides.

With a regeneration process which produces a rich stream of SO₂, a second process step is needed to obtain a saleable sulfur product. This could be either a sulfur plant or a sulfuric acid plant. It would be preferable for sulfur to be directly produced in the regeneration step. Guha (1972) reports on a high temperature decomposition (500 - 830°C) of FeS₂ to give S₂ and FeS. Since it is necessary to regenerate not only FeS₂, but also FeS, this technique is not applicable. A more realistic approach to producing sulfur directly is the use of low temperatures. Beavon (1968) reports that when a regeneration gas of SO₂ and/or O₂ at 200° to 400°C was passed over iron sulfide, sulfur was produced. The heated regeneration gas vaporizes the sulfur and removes it from the solid. The O₂ content is reportedly between 1% and 3%. No level of SO₂ was given. It is not clear from the patent application whether confirming experiments have actually been run. Thermodynamic considerations (presented in Chapter IV, eqns.iv - 42, 43, 44) show that at 227°C only the reactions of FeS with SO₂ to produce solid sulfur and Fe₂O₃ and that of FeS with O₂ to produce gaseous sulfur and Fe₂O₃ are favored. The reactions of SO₂ with FeS to give gaseous sulfur and Fe₂O₃ is thermodynamically unfavorable at these conditions. In order for a low temperature reaction to proceed, producing gaseous sulfur, only O₂ can be used as the oxidizing agent.
D. Conceptual Design of the Proposed Process.

The literature review presented in the previous section shows that a feasible process for simultaneous SO\(_2\) and NO removal is to absorb SO\(_2\) as a metal sulfide and catalytically reduce NO over the supported metal oxide/metal sulfide to nitrogen or ammonia. The requirements that the solid must be reactive toward both SO\(_2\) and NO, regenerable at a relatively low temperature, have a high surface area per unit weight, have a relatively low rate of attrition, and be reasonably priced were not met by any naturally occurring solid. From the evaluation in section C the solids which had the potential to meet all the criteria established in section B were the oxides of iron, copper, and nickel deposited on a matrix of high surface area alumina or alumina and silica. This section outlines a process meeting these criteria. Iron oxide on alumina is used as the solid to demonstrate the reactions which occur. Following a discussion of the experimental results in Chapter IV, a more precise design discussion is presented in Chapter V.

A simplified diagram of the proposed process is given in Figure i-1. The boiler furnace is to be operated at maximum efficiency. Maximum efficiency is achieved with the minimum net oxidizing atmosphere to completely oxidize the carbon to CO\(_2\), hydrogen to H\(_2\)O and sulfur to SO\(_2\). The minimum required excess air over the stoichiometric amount will be a function of the burner design and the type of fuel used. This process is especially applicable to pulverized coal or oil fueled units with front-fired or tangentially-fired furnaces.
Fig. i-1. Process flow diagram—simultaneous $\text{NO}_x$ and $\text{SO}_x$ removal.
At a point in the upper part of the furnace, most probably the upper row of burners, a stream of CO and H₂ is added to produce a slightly fuel-rich flue gas at the furnace exit. This does not preclude the presence of O₂ but requires that there be enough CO and H₂ present so that at equilibrium all NO would be converted to N₂, all O₂ to CO₂, and all SO₂ to sulfide. The stream of CO and H₂ could be generated in a moving-grate, coal-fueled stoker unit which was operated with a limited air supply. The main furnace must then burn two fuels, coal and CO + H₂. No furnace modifications are needed.

When the flue gas exits from the superheater section of the boiler, at 480-590°C, it will be contacted with a dispersed phase of catalyst/absorbent particles. The dispersed-phase method of contacting is preferred because it minimized the system pressure drop. The particles will consist of iron oxide deposited on an alumina matrix.

The overall reactions are given in Table i-9. Nitric oxide is reduced with CO, H₂ or the CO + H₂O combination to N₂ or NH₃. The sulfur compounds will be absorbed as the iron sulfide or sulfate. The major sulfur compound, SO₂, will react with the iron oxide together with a reducing agent to form ferrous sulfide. Any reduced sulfur species H₂S or COS will react directly with reduced iron oxide to form ferrous sulfide. Iron sulfate will result if some O₂ is present in the flue gas at the point of catalyst/absorbent addition.

The original amount of CO and H₂ added to the system will be
above that required to reduce SO$_2$, NO, and O$_2$.

**Table i-9 OVERALL PROCESS REACTIONS.**

**ABSORPTION/REDUCTION STEP**

2 NO + 2 CO $\rightarrow$ N$_2$ + 2 CO$_2$

2 NO + 2 H$_2$ $\rightarrow$ N$_2$ + 2 H$_2$O

2 NO + 3 H$_2$O + 5 CO $\rightarrow$ 2 NH$_3$ + 5 CO$_2$

FeO + SO$_2$ + 3 CO $\rightarrow$ FeS + 3 CO$_2$

FeO + SO$_2$ + 3 H$_2$ $\rightarrow$ FeS + 3 H$_2$O

FeO + H$_2$S $\rightarrow$ FeS + H$_2$O

FeS + 2 O$_2$ $\rightarrow$ FeSO$_4$

Fe$_2$O$_3$ + CO $\rightarrow$ 2 FeO + CO

Fe$_2$O$_3$ + H$_2$ $\rightarrow$ 2 FeO + H$_2$O

**REGENERATION STEP**

2 FeS + 7/2 O$_2$ $\rightarrow$ Fe$_2$O$_3$ + 2 SO$_2$

2 FeO + 1/2 O$_2$ $\rightarrow$ Fe$_2$O$_3$

2 FeSO$_4$ $\rightarrow$ Fe$_2$O$_3$ + SO$_2$ + SO$_3$

The excess CO and H$_2$ are removed by maintaining an excess of ferric oxide in the catalyst/absorbent feed.

After the contact zone the catalyst/absorbent is separated from the flue gas with cyclones. The major part of these collected solids are returned to the contact zone. A slip-stream diverts a portion of the catalyst/absorbent to the regenerator. Air is added in the regenerator to reoxidize the iron to ferric oxide and to produce a rich SO$_2$ stream suitable for conversion to concentrated H$_2$SO$_4$ or elemental sulfur.
Chapter II

Experimental Program

A. Summary of Phases Planned.

The experimental program was designed to answer two basic questions: 1.) Do the proposed process reactions remove sulfur compounds and nitric oxide when both are present simultaneously? 2.) Are the process rates rapid enough to effect efficient removal of these compounds under typical flue gas conditions?

1. Process chemistry.

a. Overall process confirmation.

The first group of experiments was outlined to provide an initial check on the process feasibility. The reduction of NO over reduced iron oxide and iron sulfide with CO was studied. Simultaneous removal of NO, H₂S and CO was tested with Fe₂O₃. Oxidation of excess CO and H₂ by reaction with Fe₂O₃ was tested. High-temperature catalyst regeneration in a stream of low O₂ concentration was studied.

b. Detailed removal studies.

The second group of experiments studied in detail the removal reactions for sulfur compounds (H₂S, COS, SO₂), oxidizing compounds (NO and O₂), reducing compounds (CO and H₂), and water. Since a multitude of reactions is possible when all of these gases are present, the reaction of each with the catalyst/absorbent was first studied separately. The more complex system of multiple gases was reached by progressively adding these gases to the system. Since
H₂S and SO₂ reacted to produce sulfur in the system feed lines, these two gases were never simultaneously present in the inlet gas. Oxygen was the last gas added to the mixture since the literature (see Chapter I) had reported potential catalyst deactivation with O₂.

The number of gases present in the inlet not only varied from run to run, but also varied within runs. The runs are numbered 1a, 1b, 2a, etc., indicating the actual sequence of reactant addition. Appendix A - 1 is a summary of all experimental runs in chronological order. In Chapter IV the runs are grouped and discussed according to reaction chemistry, since the same reaction may have been studied in several runs. The order in which the reactions were studied was based on their rated importance at that stage of the experimental work. This rating was not only a function of the initial experimental plan, but also of the results obtained in previous runs, literature reviews, and/or calculations made to that date. The reader will note that the experimental results are presented in Chapter IV in a logical order rather than strictly in chronological order.

c. Detailed regeneration studies.

The regeneration studies concentrated on determining the sulfur product from the regeneration and on producing an active catalyst/absorbent. The two potential products are sulfur and sulfur dioxide. As discussed in Chapter I, sulfur is reported to form more readily at low temperature and low oxygen concentration. Sulfur dioxide forms during high temperature regeneration.
The regeneration experiments typically were the last step in a run sequence. Following removal reactions, the catalyst/absorbent bed was purged with the system diluent and then cooled or heated to the selected regeneration temperature. Streams having low O\textsubscript{2} concentrations and air were used for these tests. In some of the low-temperature runs, water was added to see if it could catalyze the formation of sulfur.


a. Temperature, residence time, particle size considerations.

The most likely region in the flue gas path for contacting the flue gas with the catalyst/absorbent is between the inlet of the economizer (about 540°C) and the inlet of the air preheater (about 370°C). The residence time of the flue gas in the region between the economizer and air preheater is about 0.5 seconds.

All of the initial studies of process chemistry were conducted in a fixed bed at about 370°C with a gas residence time in the bed of around 0.50 seconds. The particle size chosen for these studies was the standard 3.2-mm x 3.2-mm pellets of Fe-301-T 1/8 Harshaw Catalyst.

After these studies the results suggested that the experimental conditions should be altered. First, in these experiments some catalyst deactivation was found. This deactivation was predicted to be less of a problem at higher temperatures. Second, the sulfur breakthrough curves for the simultaneous removal runs suggested that the actual reaction times were much less than the gas residence
time in the bed. Third, visual observation of cross-sections of the catalyst/absorbent from the lower temperature runs suggested that there were important diffusion limitations within the 3.2-mm pellets.

These three experimental observations suggested the desirability of runs at higher temperatures with shorter gas residence times and with smaller particles. Consequently, the last part of the simultaneous removal studies was conducted at 540°C with residence times between 0.02 and 0.04 seconds, and with particles-sizes between 0.50-mm and 0.25-mm.

No attempt was made to construct an accurate experimental prototype of the contactor envisioned for an actual plant installation. As described in Chapter I, the actual system would be a dispersed-phase or fluidized-bed type of unit. The experimental approach was to study the process initially in a fixed bed. These experimental data would then be used to predict the expected behavior in the commercial unit. The major differences between the fixed and dispersed-bed systems are related to the bed densities and mass transfer effects. Known correlations, detailed in Chapter V, were used for this purpose. The experimental residence times, gas concentrations, and particle sizes were chosen so that reasonable extrapolations could be made to an actual flue gas contactor to predict the process feasibility.

b. Catalyst/absorbent deactivation.

The other major influence on the process kinetics was the deactivation of the catalyst/absorbent. Studies of this effect
were not planned initially but evolved because this phenomenon occurred in both the lower and the upper temperature ranges. Since the addition of \( \text{O}_2 \) to the gas mixture first caused the deactivation, the \( \text{O}_2 \) level and the ratio of oxidizing gas to reducing gas were chosen as the two main variables in this study. An upper gas concentration of 1% \( \text{O}_2 \) was chosen as an estimate of the potential \( \text{O}_2 \) in a net reducing flue gas due to incomplete mixing (Johnson, 1972).

B. Experimental Equipment.

1. Overall system.

All of the experimental apparatus was housed in a 3.2-m x 2.1-m x 1.2-m walk-in hood. Hood ventilation was provided with two exhaust fans. An overall sketch of the experimental apparatus is shown in Figure II-1. This is a straight flow-through system with gas samples taken at the inlet and outlet of the Burrel Tube Furnace which houses the reactor. The discussion of the Gas Chromatographic System and sampling techniques is given in Chapter III.

2. Reactors/Furnace.

a. Fixed-bed reactors.

Fixed-bed, flow-through reactors were used in this study. The first was a 32-mm I.D. 304 stainless steel (SS) reactor. It is shown in Figure II-2. Other workers had reported that 304 and 316 SS were active catalysts for NO reduction reactions in the absence of sulfur compounds (Kearby, 1971, and Lamb, 1972). Neither
Fig. ii-1. Experimental system.
Fig. ii-2. Experimental reactor—32mm.
steel was found significantly reactive in this study. Two other reactors used are shown in Figure ii -3. The 6.4-mm and 9.5-mm reactors were used in the later part of the experimental study to achieve shorter residence times.

The reactions in this study include both gas-metal absorption and gas-metal catalysis. In order to provide a sufficiently high bed capacity for absorption of the sulfur compounds the length of the fixed-bed corresponded to an integral flow reactor for the catalytic reactions. Even in the smaller bed with residence times around 0.02 seconds, the sulfur breakthrough times were greater than 30 minutes. The major disadvantage to working in a fixed-bed reactor is that the removal results must be corrected for both bed-density and mass-transfer effects before they can be directly applied to an actual flue-gas contactor. The influence of both of these effects on the process design can be estimated. This influence is discussed along with the process-design considerations in Chapter V. As mentioned earlier, a more closely analogous reactor would have been a fluidized bed. Since correlations exist which permit extrapolation of data from fixed to dispersed systems, the fixed bed was selected primarily for its simplicity.

b. Reactor furnace.

The reactors were housed in a Burrell Tube Furnace, Model BT-1-9. A 44.4-mm I.D. Mullite tube surrounded the reactor. The 32-mm I.D. reactor rested on the walls of the tube. (See Figure ii - 2). The other two reactors were not in contact with the tube walls. The maximum temperature limit of the furnace was
9.5 mm I.D. reactors

Outlet  Bed  Thermowell

Glass wool  Inlet

75 mm

Material: 316 stainless steel
Fittings: Swaglock

6.4 mm I.D. reactors

Outlet  Bed  Thermowell

Glass wool  Inlet

89 mm

XBL 746-3388

Fig. ii-3. Experimental reactors.
1450°C. A West Instrument Corporation set-point controller, Model J, was used to maintain the desired temperature level. A platinum/platinum - 13% rhodium thermocouple located in the furnace chamber exterior to the Mullite tube was the sensing element for the controller.

c. Fixed-bed temperature measurement.

A more accurate measure of the catalyst/absorbent temperature was obtained from the Chromel/Alumel thermocouples placed in 316 SS thermowells which extended into the inlet and outlet of the 32-mm reactor. Only an inlet thermocouple was used in the smaller reactors. When inert gas was passing through the bed, the inlet temperature was approximately 3°C degrees less than the outlet at an absolute level around 370°C. Figure ii - 4 shows a trace of the furnace and outlet reactor temperatures as a function of time as the reactor heats up to 370°C. The inlet and outlet reactor thermocouples were monitored with the Leeds and Northrup Recorder used to trace the gas chromatograph (G.C.) peaks. The furnace temperature was initially monitored with a modified Varian Aerograph G-10 Recorder. In the latter part of the experimental program this temperature was also monitored with the Leeds and Northrup Recorder. The switching diagram for this circuitry is shown in Figure iii - 6.

3. Heat-traced flow lines.

a. Reactor exit line.

After Run 15 the 6.4-mm exit tube was wrapped with fiber glass sheathing and heat-traced over the last 220-mm to prevent sulfur
Fig. ii-4. Temperature profiles of furnace chamber and reactor during heat up.
(Data from Run 12)
\[ T_2 = \text{furnace chamber temperature} \]
\[ T_4 = \text{reactor outlet temperature} \]
\[ T_3 = T_4 - 3^\circ C \]
\[ T_3 = \text{reactor inlet temperature}. \]
precipitation. This section was inside the Mullite tube. The Nichrome wire-fiber glass heat tape was powered with a Powerstat Variac, maximum rating 120 volts, 7.5 amps. A setting of 55 volts was used. This setting gave a temperature of 160°C at the exit end of the 6.4-mm tube. The tape burned out following Run 27. A second heat tape was used for the remainder of the experiments. A setting of 15 volts was used. This gave a temperature of 195°C at the exit end of the 6.4-mm tube with the new tape. These temperatures prevented major sulfur precipitation in the exit reactor line. Since the equilibrium partial pressure of sulfur at 150°C in an inert gas at 1 atmosphere is 230 ppm (Tuller, 1954), only a sulfur concentration greater than this would have produced precipitate in the exit reactor line.

b. Outlet and inlet lines.

The exit lines from the condenser to the bubbler and gas chromatographs were heat-traced with fiber glass tape and Nichrome wire after Run 26. Heating pads of fiber glass and Nichrome wire were also placed over the gas sample valve and switch valve located in the gas chromatographs. The line temperature was around 40°C. The valve temperatures were around 35°C. These temperature levels prevented condensation of water in the exit lines but allowed some condensation of ammonium salts and sulfur which were not condensed in the air-cooled condenser between the reactor exit line and the outlet system line. The Nichrome wire was powered with a Variac, maximum rating 110 volts, 5.0 amps. The typical setting to give the above temperature was 90 volts.
The reactor inlet lines, including the gas manifold, were heat-traced in a similar manner after Run 32. The heat tracing was required to prevent slight H\textsubscript{2}O condensation in the inlet line noted during earlier runs. This line was powered with a G.R.C. Variac, maximum setting 110 volts, 5.0 amps. A setting of 110 volts gave line temperatures of 35°C.


A constant-temperature water bath was made with an insulated 300-ml round bottom, 3-neck flask. The He diluent passed through the bubbler and then into the gas manifold where other gases were added. A contact thermometer and relay controller were used to control the water bath temperature. The Glas-Col heater was powered with a Powerstat Variac, maximum rating 110 volts, 3.0 amps. Typically a setting around 10 volts was used. Water bath temperatures were around 22 - 24°C. Since the water level was only 70-mm above the fritted glass bubbler, the He was only about 60 - 70% saturated with water.

5. Gas-feed system.

Each gas was metered from a gas cylinder through a needle valve and a glass capillary tube and then into the gas manifold mixer. Table ii - 1 lists the source and purity of each gas used. Except for the He, all of the cylinders used a 20 psig feed pressure. Pressure taps leading from the inlet and outlet of the capillary were connected to U-tube manometers. From Runs 1 through 16 water was used in the manometers. After Run 16, Silicone Oil (Dow Corning 704 Fluid) was
used. The capillaries were calibrated with either the specific gas or \( N_2 \) at atmospheric pressure and ambient temperature with a soap-bubbler meter. \( N_2 \) was used to calibrate the capillaries used for \( \text{SO}_2 \), \( \text{H}_2\text{S} \), \( \text{NH}_3 \), and NO since all were found reactive with the soap solution. The measured pressure drops were corrected for differences in viscosity between the gases. Since the gases were never fed in all together, some flowmeters were calibrated for more than one gas. For all the gases except \( \text{H}_2 \) and CO, the lines from the gas cylinder to the gas manifold was 316 S.S. Copper was used for \( \text{H}_2 \) and CO. Stainless steel needle valves (NUPRO "S" Series Fine Metering Valves) with inlet filters (NUPRO "F" Series Inline Filters) were used with the capillary flowmeters. The system diluent, He or \( N_2 \), was metered in with a glass-ball rotometer (Manostat Corp. No. 36-541-12). The control on the water feed rate was the water bath temperature. The pressure tap lines from the manometers to the capillaries were Tygon tubing. Catch pots were built in the lines to prevent manometer fluid from contaminating other equipment if a system upset occurred. The gas manifold was a 25-mm X 25-mm X 127-mm block of 316 stainless steel. Hoke valves, attached directly to the manifold, were connected with each flowmeter line. The system diluent entered through the 6.4-mm center bore. All of the tubing in the remainder of the system was 316 S.S. except a short Tygon section connecting the outlet condenser with the outlet system line. The main gas stream tubing 6.4-mm I.D. The sample lines were 3.2-mm I.D. and the tubing around the switch and gas sample valves in the G.C. system was 1.6-mm I.D.
Table ii - 1. Gas-Cylinder Specifications.

<table>
<thead>
<tr>
<th>GAS</th>
<th>PURITY &amp; SPECIFICATIONS</th>
<th>SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>99.99% Min.</td>
<td>Univ. of Calif., Berk., gas.</td>
</tr>
<tr>
<td>N₂</td>
<td>99.99% Min.</td>
<td>Univ. of Calif., Berk., gas.</td>
</tr>
<tr>
<td>NO</td>
<td>99.0 % Min.</td>
<td>Liquid Carbonics Co.</td>
</tr>
<tr>
<td>N₂O</td>
<td>98.0 % Min.</td>
<td>Matheson Gas Co.</td>
</tr>
<tr>
<td>NO₂</td>
<td>99.5 % Min.</td>
<td>Baker Chemical Co.</td>
</tr>
<tr>
<td>NH₃</td>
<td>98.37% NH₃, 1.00% H₂, 0.57% N₂, 0.06% O₂</td>
<td>Matheson Gas Co.</td>
</tr>
<tr>
<td>SO₂</td>
<td>99.98% Min.</td>
<td>Matheson Gas Co.</td>
</tr>
<tr>
<td>H₂S</td>
<td>99.6 % Min.</td>
<td>Matheson Gas Co.</td>
</tr>
<tr>
<td>COS</td>
<td>99.4 % Min.</td>
<td>K &amp; K Laboratories, Inc.</td>
</tr>
<tr>
<td>CO₂</td>
<td>99.5 % Min.</td>
<td>Matheson Gas Co.</td>
</tr>
<tr>
<td>CO</td>
<td>99.5 % Min.</td>
<td>Matheson Gas Co.</td>
</tr>
<tr>
<td>H₂</td>
<td>99.9 % Min.</td>
<td>Matheson Gas Co.</td>
</tr>
<tr>
<td>O₂</td>
<td>99.99% Min.</td>
<td>Univ. of Calif., Berk., gas.</td>
</tr>
</tbody>
</table>


a. Removal/regeneration condenser.

A 9.5-mm X 98-mm section 316 S.S. tubing was connected to the 6.4-mm reactor outlet line. Air was blown over this section during the runs. The ammonium salts precipitated primarily in this unit. Also trace amounts of sulfur and water precipitated from the gas stream if they were high in concentration. This unit was installed after Run 15. Prior to this run a section of Tygon tubing served the same function.
b. Water-collection condenser.

At the start of each run after Run 13, the catalyst was dried for 3 hours. The desorbed water was collected in a U-tube emersed in a dry ice-acetone bath. The U-tube was Pyrex glass. It was connected to the reactor outlet line and system outlet line with Tygon tubing. Typically, the glass tube was removed and weighed three times during the drying period to determine the initial catalyst water content.

7. Outlet-line apparatus.

a. Capillary flow restriction.

In order to divert a sample flow from the inlet and outlet gas lines, capillary restrictors were placed in the main flow stream and the sample loop bypass stream. The position of each is shown in Figure ii-1. This produced a system pressure drop of 25-mm Hg for the 32-mm reactor and 100-mm Hg for the smaller reactors. This provided a split of 2.3/100 for the inlet sample flow/total inlet flow and of 1.8/100 for the outlet sample flow/total outlet flow.

b. Gas scrubber.

After exiting the flow restriction capillary the gases then passed to a 250-ml catch pot and then into a 250-ml fritted-glass bubbler. The bubbler was used to remove either NH₃ or HCl. This apparatus is discussed in more detail in Chapter III.
CHAPTER III

Analytical Systems

A. Gas Analysis.

A large number of reactive gases were present simultaneously in samples which had to be analyzed in this experimental study. The presence of the following gases was possible: \( \text{H}_2, \text{H}_2\text{O}, \text{N}_2, \text{NH}_3, \text{N}_2\text{O}, \text{NO}, \text{H}_2\text{S}, \text{COS}, \text{SO}_2, \text{CO}, \text{CO}_2, \) and \( \text{O}_2 \). One approach was to provide a selective analyzer for each species. Although reliable instruments for this purpose can be purchased, their cost was prohibitive for this work. A second approach was to use instruments which detect and quantify all of the gases. Two such instruments are the Mass Spectrometer and the Gas Chromatograph. Gas chromatography was selected for gas analysis because of its simplicity and availability.

1. Detector selection.

Gas chromatographs can be tailored to a wide range of applications. The types of detector and column packing vary with the specific application. The combination of gases listed above can be analyzed best with a thermal conductivity cell (Katharometer), an electron capture detector, or a gas density detector. The gas density detector, although good for corrosive gas analysis, is not recommended for use with helium, the system diluent in this work. The electron capture detector is recommended for gas concentrations less than 10 ppm. It can be modified to work in the range of 10 to \( 10^4 \) ppm. With this modification its sensitivity decreases to that obtained with the thermal conductivity cell (Mitchell, 1972). Two available
gas chromatographs with thermal conductivity cells were used in this study.

A major deficiency of thermal conductivity detectors is that they react in varying degrees with certain gases. Oxygen and sulfur compounds are especially reactive. Rhenium-tungsten and nickel filaments were used because of their low reactivity toward oxygen and sulfur compounds and their corrosion resistance (Gow-Mac). The rhenium-tungsten filament has the added advantage of a relatively high sensitivity.

2. Column selection.

A literature review and private conversations with technical representatives of Varian Aerograph revealed that no one column packing would produce all of the desired gas separation. Therefore, two packed columns connected in series were required. Polymer packing which has a small degree of polarization is effective for the separation of $\text{H}_2$, $\text{CO}_2$, $\text{N}_2\text{O}$, $\text{NH}_3$, $\text{H}_2\text{S}$, $\text{COS}$, $\text{SO}_2$, and $\text{H}_2\text{O}$, Group I. Molecular Sieve packing effects the separation of $\text{H}_2$, $\text{O}_2$, $\text{N}_2$, NO, and CO, Group II.

In the first third of this work, Runs 1 through 16, Chromosorb 104, a cross-linked polystyrene matrix with no coating, was used for separating the Group I gases. The major reason for selecting Chromosorb 104 was that it reportedly separated $\text{NO}_2$ from $\text{CO}_2$, $\text{H}_2\text{S}$, COS, and $\text{SO}_2$. However, it irreversibly adsorbs $\text{NH}_3$ and $\text{H}_2\text{O}$. Since the analysis of these two gases was important in the later part of the experimental work, after Run 16, Porapak R packing was substituted for the Chromosorb 104. Porapak R is a porous cross-linked polymer...
bead packing made with a small amount of polar monomer. This packing separates all of the gases in Group I, but does not pass NO₂. As expected, NO₂ was not found in the first part of this work, so this was not a major limitation.

Porapak R was selected after screening seven different columns. The hardest criterion to meet was to find a column which gave the desired peak separations with a minimum amount of tailing. The H₂O, SO₂, and NH₃ peaks generally had tailing, NH₃ being the worst in this regard. A qualitative comparison of NH₃ peaks on these columns is given in Table iii-1.

Table iii-1 Qualitative evaluation of low concentration NH₃ peaks on several columns.*

<table>
<thead>
<tr>
<th>Column</th>
<th>Dimensions cm x cm</th>
<th>Temperature (°C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromosorb 104</td>
<td>0.635 x 305</td>
<td>120</td>
<td>Tail continued for over 5 min.</td>
</tr>
<tr>
<td>Porapak Q</td>
<td>0.318 x 214</td>
<td>110</td>
<td>Tail ended after 5 min.</td>
</tr>
<tr>
<td>Porapak R</td>
<td>0.318 x 92</td>
<td>92</td>
<td>Almost no tail after 5 min.</td>
</tr>
<tr>
<td>Porapak T</td>
<td>0.318 x 92</td>
<td>120</td>
<td>Significant tail after 4 min.</td>
</tr>
<tr>
<td>Porapak Q +</td>
<td>0.318 x 214</td>
<td>130</td>
<td>Almost no tail after 4 min.</td>
</tr>
<tr>
<td>Porapak R</td>
<td>0.318 x 92</td>
<td>130</td>
<td>Almost no tail after 4 min.</td>
</tr>
<tr>
<td>Carbowax</td>
<td>0.635 x 305</td>
<td>155</td>
<td>Tail continued for over 5 min.</td>
</tr>
<tr>
<td>Carbowax on</td>
<td>0.635 x 153</td>
<td>156</td>
<td>Tail continued for over 5 min.</td>
</tr>
<tr>
<td>Firebrick</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* NH₃ concentrations ranged from 1-4% in this study.
Only the Porapak R column gave a reasonable peak for NH₃ at these low levels. Although quantification was possible at the 1 to 4% level, lower concentrations produced peaks which were primarily of qualitative value. Wilhite (1968) also reports that tailing of NH₃ occurs at low temperature programming. Landau (1973) reports tailing of NH₃ at low concentrations on a combined Porapak R and polyethyleneimine-coated Porapak R. From the referenced and present work it is obvious that the quantitative analysis of low NH₃ concentrations with a gas chromatograph has not yet been achieved. The NH₃ peaks were primarily used to confirm the presence of NH₃ qualitatively. A bubbler containing an HCl solution collected the NH₃ to give a cumulative quantitative sample. This procedure will be described in section B.1.

Molecular Sieve 5A packing, a synthetic zeolite, separated Group II gases. It was selected for its ability to separate O₂, N₂, NO and CO without giving excessively long tailing patterns for NO. Prior to Run 17, H₂ was also separated with this packing. In the later part of this work, the H₂ peak on the Porapak R column was monitored since this column was connected to the more sensitive rhenium tungsten detector.


Gas chromatograms of the two G.C. systems, Chromosorb 104 in series with Molecular Sieve 5A and Porapak R in series with Molecular Sieve 5A, are given in Figures iii-1 and 2.

Since all of the gases were never present in any one chromatogram in either system, these figures are a composite of several samples. A two-pen recorder allowed simultaneous detection of peaks from both
Fig. iii-1. Gas chromatographic trace: Chromosorb 104-molecular Sieve 5A.

<table>
<thead>
<tr>
<th>Gas</th>
<th>%</th>
<th>Attn.</th>
<th>Span (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromosorb-104</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. CO₂</td>
<td>1.0</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>b. N₂O</td>
<td>0.80</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>c. COS</td>
<td>0.34</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>d. H₂S</td>
<td>2.0</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>e. SΟ₂</td>
<td>0.53</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>f. NO₂</td>
<td>3.1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>g. H₂, O₂, N₂, NO, CO</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Molecular Sieve 5A

<table>
<thead>
<tr>
<th>Gas</th>
<th>%</th>
<th>Attn.</th>
<th>Span (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>h. H₂</td>
<td>3.6</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>i. O₂</td>
<td>1.0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>j. N₂</td>
<td>0.05</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>k. NΟ</td>
<td>0.32</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>l. CO</td>
<td>0.37</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>m. H₂, O₂, N₂, NO, CO</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. iii-2. Gas chromatographic trace
Porapak R - molecular sieve 5A.

<table>
<thead>
<tr>
<th>Porapak R</th>
<th>Molecular Sieve 5A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>%</td>
</tr>
<tr>
<td>H₂</td>
<td>2.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.58</td>
</tr>
<tr>
<td>N₂O</td>
<td>2.0</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.24</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.92</td>
</tr>
<tr>
<td>COS</td>
<td>0.34</td>
</tr>
<tr>
<td>H₃O</td>
<td>1.3</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.71</td>
</tr>
<tr>
<td>O₂, N₂, CO, NO</td>
<td></td>
</tr>
</tbody>
</table>
chromatographs. Since the recorder had only one integrator, which could be switched to either pen, it was advantageous to have the peaks eluting at different times. In the first system, Figure iii-1, all peaks except N₂ from the Molecular Sieve, and H₂S from the Chromosorb 104 elute at different times. In this case the N₂ peak area was manually calculated while the H₂S peak area was counted by the integrator. The excessive tailing of NO and CO is both a reflection of noise at the 0.20mv span and some tailing. The tailing of NO₂ even at high concentrations permitted only qualitative analysis. In the second system, Figure iii-2, the NH₃ peak area was either manually calculated or only used for confirming the presence of NH₃. Either the CO or H₂S peak area was manually calculated while the other was counted by the disc integrator. The detailed description of the sampling techniques and equipment arrangement is given in section 5.


The 305-cm x 6.4-mm Chromosorb 104 column, mesh size 60 to 80 (250-177 μm), 316 stainless steel (S.S.) wall, was purchased directly from Varian Aerograph. The packed column was pretreated by heating to 230°C under a helium atmosphere for 12 hours.

The 305-cm x 6.4-mm Porapak R column, mesh size 80 to 100 (177-149 μm) 316, S.S. wall, was made in this laboratory. The steel column was cleaned with the following sequence of solvents:

Table iii-2. Sequence of solvents for cleaning column casing.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Volume ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>300</td>
</tr>
<tr>
<td>Chloroform</td>
<td>300</td>
</tr>
<tr>
<td>Toluene</td>
<td>375</td>
</tr>
<tr>
<td>Methanol</td>
<td>175</td>
</tr>
<tr>
<td>Acetone</td>
<td>100</td>
</tr>
</tbody>
</table>
The tubing was dried in a helium atmosphere before it was packed. Then while the tubing was still straight, the packing was added. Constant rapping insured even filling. Glass wool plugs held the packing in the column. The column was pretreated by heating to 245°C in a helium atmosphere for 12 hours.

The 305-cm x 6.4-cm Molecular Sieve 5A column, mesh size 30 to 50 (500-250 μm), S.S. wall, was made in this laboratory. The same cleaning and packing procedures described for the Porapak R column were used. The initial column pretreatment was that reported by Dietz (1968). In addition to desorbing all gases, Dietz found that the column must be treated to prevent excessive tailing at low NO concentrations.

Dietz describes his technique as one which first adsorbs NO on very active sieve sites. This adsorbed NO is permanently fixed to these sites by reacting it with O₂ to form NO₂ in situ. This procedure eliminates later adsorption of NO by active adsorbing sites, thereby greatly reducing NO tailing.

The summarized pretreatment described by Dietz is listed below.

1. Activate the sieve by heating to 300°C under vacuum for 20 hours to desorb all gases.
2. Break the vacuum at 300°C with NO, maintaining a low NO flow for 1 hour to saturate the column.
3. Cool the column to 20°C continuing to saturate with NO for another hour.
4. Flush the column with Helium for ½ hour to remove all nonadsorbed NO. Add a stream of O₂ at 25°C to form NO₂ on the active sites.
5. Raise the temperature to 100°C with the O₂ atmosphere and hold for ½ hour to insure that O₂ and NO react.
With this technique Dietz reported NO detection limits of 12 ppm.

The same pretreatment in the present study did little to decrease the NO tailing. Figure iii-3 shows a 7.6%[NO] peak with excessive tailing. A more detailed look at Dietz's work revealed that the column was subjected to temperature programming up to 250°C. In contrast, the operating column temperature in this work was 120°C. Joithe (1972) found that the presence of NO₂ on adsorbed Molecular Sieve 13X aids in the adsorption of NO at 25°C. Similar behavior may occur on the Molecular Sieve 5A if the adsorbed NO₂ is not strongly held. By heating the column to 250°C, Dietz desorbed the majority of the loosely held NO₂. Since the maximum column temperature in this study was only 130°C, the loosely held NO₂ is thought to have been present and partially reactive toward the NO in the sample. Higher temperatures were tested to find the point where loosely held NO₂ would be desorbed and tightly held NO₂ would be retained. The temperature of 250°C gave the best NO peaks.

Figure iii-4 is a trace of an NO peak. This peak is 1.17% and uses the 0.5 mv span yet still has a smaller degree of tailing than the 7.6%[NO] shown in Figure iii-3. The pretreatment for the Molecular Sieve 5A column is therefore that reported by Dietz plus:

6. Heat the column to 250°C under a helium atmosphere for 8 hours.

During Run 14, the NO peaks began to tail and large discrepancies developed between the inlet NO concentrations obtained by G.C. analyses and those obtained from flowmeter reading. The column was
Fig. iii-3. NO peak from Molecular Sieve 5A column treated with Dietz method.

[NO] 7.6%
Span 2 mV
Attn. 2
System: Chromosorb 104-
Molecular Sieve 5A
Fig. iii-4. NO peak from Molecular Sieve 5A column treated with 6-step pretreatment.

- [NO] 1.17%
- Span 0.50 mV
- Attn. 1

System: Chromosorb 104-Molecular Sieve 5A
regenerated following the six-step pretreatment described above, but this did not lead to complete NO sample elution or sharp peaks. Several variations of this procedure failed to regenerate the Molecular Sieve 5A column successfully.

A second, identical column was made. After the six-step pretreatment this column produced good quality NO peaks. This same column-poisoning phenomenon occurred following Run 30. As before a new, identical Molecular Sieve column, pretreated as described, produced good quality NO peaks.

Before Run 14 all of the sulfur compounds were sent directly to Molecular Sieve 5A column where they were irreversibly adsorbed. These adsorbed compounds are suspected of poisoning the Sieve. After Run 16, a bypass valve was installed after the Porapak R column to dump these compounds and water before they entered the second column. This is described in section 5. Several times after installation this valve was not switched at the proper time, allowing the sulfur gases and water to pass into the Sieve causing a poisoning similar to the first case.

5. Chromatographic, recording and integration equipment.

The columns and detectors discussed above were housed in the following specific chromatographs.

Table III-3. Gas chromatographic equipment.

<table>
<thead>
<tr>
<th>Position in Sequence</th>
<th>Column 1</th>
<th>Column 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Varian Aerograph</td>
<td>Varian Aerograph</td>
</tr>
<tr>
<td>Model No.</td>
<td>90-P</td>
<td>A-90-P</td>
</tr>
<tr>
<td>Column</td>
<td>Chrom.104</td>
<td>Por R. Molecular Sieve 5A</td>
</tr>
<tr>
<td>Detector</td>
<td>Re/W</td>
<td>Re/W</td>
</tr>
<tr>
<td>Column Temp. (°C)</td>
<td>100</td>
<td>85</td>
</tr>
<tr>
<td>Detector Temp. (°C)</td>
<td>120</td>
<td>165</td>
</tr>
<tr>
<td>Filament current (ma)</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Helium Carrier (ml/min)</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Helium Reference (ml/min)</td>
<td>7.1</td>
<td>7.1</td>
</tr>
</tbody>
</table>
In the first third of the study, through Run 16, the two machines were connected in series. The entire effluent from the Chromosorb 104 column was fed into the Molecular Sieve 5A column. In the last part of the work the two machines were interconnected to allow both series and parallel operation. The columns were operated in the series mode until the wave of Group I gases had left the first column and entered the Molecular Sieve 5A column. A switch valve arrangement, shown in Figure iii-5 then allowed the other gases which separated on the first column to be discarded before they passed into the Molecular Sieve 5A column. It also provided a separate and parallel helium carrier for the Molecular Sieve 5A column after the gases to be separated on it had eluted from the first column. The 6-port Varian Quad-ring valve was switched at 2 minutes after sample injection, Figure iii-2. The resulting pressure surges in both columns rapidly decayed.

A Leeds and Northrup Speedomax XL Recorder 600 Series with a Series 2000 Disc Integrator was used to record the peaks and their areas. The recorder has two channels one of which is connected to the integrator. A switching arrangement shown in Figure iii-6. enabled the integrated channel to be used on either column. In this way, the output signals from both columns could be monitored simultaneously and the peaks from both columns could be integrated as long as they had different retention times. The channel without
Fig. iii-5. Valve system for chromatographs.
Fig. iii-6. Switch diagram for two-pen recorder.
the integrator was also used for monitoring the voltage output from various thermocouples around the system.


The gas samples were injected into the column with a 6-port Varian Aerograph Quad-ring valve. Prior to Run 8, all samples were collected in nominal 2-ml pyrex gas sample loops with teflon valves and transferred to the G.C. Prior to purging these loops with the carrier, the connecting lines between the valve and the loops were evacuated and filled with helium. After Run 8, a continuous sample purge was maintained in a 2-ml, 316 stainless steel sample loop. This could be either the inlet or outlet sample. The 6-port valve was again used for the sample injection.

7. Calibration and detection limits for G.C. analyses.

The response of the G.C. columns to gases was determined by passing a stream of a particular gas at atmospheric pressure through the 2-ml sample loop and then to a bubbler. After at least 5 minutes of purging, the response for that gas was recorded several times. In all cases except H₂ and H₂O, 100% gas concentration was used. The number of integrator counts is multiplied by the product of the span and attenuation to give the relative area. The standard areas and their relative standard deviations are given in Table iii-4. The columns were not recalibrated on a regular basis but rather when system changes were made or when large discrepancies developed between the concentrations calculated from the flowmeter readings and the G.C. values for inlet gas samples. The large standard deviation for SO₂ in Table iii-4, 11.6%, represents the difference
between two calibrations 5 months apart.

The calibrations presented in Table iii-4, are for a sample loop temperature of 21.1°C. When the outlet lines and sample loop were heat traced, after Run 26, the temperature was 58.9°C. At this point, the calibrations were adjusted down by the factor 1.128, the ratio of absolute temperatures. A check was made with 0.195% \( \text{O}_2 \) when the temperatures were 22.8°C & 57.8°C. The predicted ratio was 1.12 and the experimental ratio was 1.17, within 5%.

Table iii-4. Percent standard deviation in gas chromatographic standards.

<table>
<thead>
<tr>
<th>GAS</th>
<th>COLUMN</th>
<th>PERCENT STANDARD DEVIATION</th>
<th>RELATIVE AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 )</td>
<td>Porapak R</td>
<td>0.41</td>
<td>142,933</td>
</tr>
<tr>
<td></td>
<td>Chromosorb 104</td>
<td>0.88</td>
<td>148,838</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} )</td>
<td>Chromosorb 104</td>
<td>0.14</td>
<td>129,408</td>
</tr>
<tr>
<td>( \text{COS} )</td>
<td>Porapak R</td>
<td>0.45</td>
<td>161,152</td>
</tr>
<tr>
<td></td>
<td>Chromosorb 104</td>
<td>0.39</td>
<td>185,940</td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>Porapak R</td>
<td>12.0</td>
<td>148,304</td>
</tr>
<tr>
<td></td>
<td>Chromosorb 104</td>
<td>2.0</td>
<td>177,152</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>Porapak R</td>
<td>1.1</td>
<td>133,424</td>
</tr>
<tr>
<td></td>
<td>Chromosorb 104</td>
<td>0.60</td>
<td>112,384</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}(1%) )</td>
<td>Porapak R</td>
<td>7.9</td>
<td>2,695.3</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td>Porapak R</td>
<td>0.53</td>
<td>88,062</td>
</tr>
<tr>
<td>( \text{H}_2(1%) )</td>
<td>Porapak R</td>
<td>4.4</td>
<td>24.74</td>
</tr>
<tr>
<td></td>
<td>Mol. Sieve 5A</td>
<td>12.0</td>
<td>6.94</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>Mol. Sieve 5A</td>
<td>0.34</td>
<td>31,725</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>Mol. Sieve 5A</td>
<td>0.34</td>
<td>28,592</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>Mol. Sieve 5A</td>
<td>0.22</td>
<td>30,387</td>
</tr>
<tr>
<td>( \text{NO} )</td>
<td>Mol. Sieve 5A</td>
<td>0.74</td>
<td>28,592</td>
</tr>
<tr>
<td>( \text{NO}_2 )</td>
<td>Chromosorb 104</td>
<td>(Only qualitative value)</td>
<td></td>
</tr>
</tbody>
</table>
In addition to the calibration values, the detectable limits of the most important gases were determined. The detection limits of the remaining gases were estimated. In the context of this work, the detection limit is the lowest concentration which can be determined within an accuracy of about 25%. Table iii-5 lists the detection limits and the elution times of the gases. The Molecular Sieve 5A times are for the Porapak R-Molecular Sieve 5A system. The high detection limit for H\textsubscript{2} is a result of the close thermal conductivity of He and H\textsubscript{2}. The high limits for NH\textsubscript{3}, H\textsubscript{2}O and SO\textsubscript{2} on the Porapak R and NO\textsubscript{2} on Chromosorb 104 columns result from the tailing of each gas.

8. Interactions of gases in chromatographic columns.

The discussion in this chapter so far has centered on analysis of individual gases with no mention of samples containing multiple reactive gases. Unavoidable gas interactions were found when multiple gases were analyzed. These interactions resulted in lower concentrations being reported for some gases. This section discusses the interactions and the techniques used to estimate gas concentrations correctly.

In the initial stages of this work multiple gas streams were metered into a helium diluent. This mixture was then sampled and used to determine the conditions necessary for peak separation. During this work it was noted that the gas concentrations calculated from the flowmeter readings did not always correspond to the chromatographic values. This was noticed especially when there was a combination of H\textsubscript{2}S and SO\textsubscript{2} or NO and O\textsubscript{2}. These proved to be the two...
major interactions. A secondary interaction was the effect of 
H$_2$O on the H$_2$S/SO$_2$ interactions.

Table iii-5. Detection limits of gases.

<table>
<thead>
<tr>
<th>GAS</th>
<th>ELUTION*</th>
<th>COLUMN</th>
<th>DETENTION LIMIT (ppm)</th>
<th>ESTIMATION TECHNIQUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>2.0</td>
<td>Molecular Sieve 5A</td>
<td>6,000</td>
<td>Direct (2/14/73)</td>
</tr>
<tr>
<td></td>
<td>1.15</td>
<td>Porapak R</td>
<td>2,000</td>
<td>Direct (Run 42)</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.2</td>
<td>Chromosorb 104</td>
<td>100</td>
<td>Direct (Run 13)</td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>Porapak R</td>
<td>100</td>
<td>Direct (Run 28)</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>1.4</td>
<td>Chromosorb 104</td>
<td>100</td>
<td>Estimate from CO$_2$</td>
</tr>
<tr>
<td></td>
<td>2.70</td>
<td>Porapak R</td>
<td>100</td>
<td>Estimate from CO$_2$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>4.7</td>
<td>Porapak R</td>
<td>2,000</td>
<td>Direct (4/10/73)</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>3.2</td>
<td>Chromosorb 104</td>
<td>150</td>
<td>Estimate</td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>Porapak R</td>
<td>150</td>
<td>Direct (Run 39)</td>
</tr>
<tr>
<td>COS</td>
<td>2.1</td>
<td>Chromosorb 104</td>
<td>100</td>
<td>Direct (Run 13)</td>
</tr>
<tr>
<td></td>
<td>9.7</td>
<td>Porapak R</td>
<td>200</td>
<td>Direct (Run 30)</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>18.8-19.8</td>
<td>Porapak R</td>
<td>2,500</td>
<td>Direct (Run 29)</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>7.7</td>
<td>Chromosorb 104</td>
<td>250</td>
<td>Direct (Run 13)</td>
</tr>
<tr>
<td></td>
<td>27-29</td>
<td>Porapak R</td>
<td>800</td>
<td>Direct (Run 29)</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>17.5</td>
<td>Chromosorb 104</td>
<td>10,000</td>
<td>Estimate (5/5/72)</td>
</tr>
<tr>
<td>O$_2$</td>
<td>3.3</td>
<td>Molecular Sieve 5A</td>
<td>40</td>
<td>Direct (8/18/72)</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.9</td>
<td>Molecular Sieve 5A</td>
<td>40</td>
<td>Direct (8/18/72)</td>
</tr>
<tr>
<td>NO</td>
<td>4.9</td>
<td>Molecular Sieve 5A</td>
<td>200</td>
<td>Direct (8/14/72)</td>
</tr>
<tr>
<td>CO</td>
<td>6.2</td>
<td>Molecular Sieve 5A</td>
<td>200</td>
<td>Direct (Run 13)</td>
</tr>
</tbody>
</table>

*Elution time for low-concentration samples. Actual values at 100% level are slightly greater.

In view of the sulfur-formation reaction between H$_2$S and SO$_2$, these gases were never used together in the inlet stream. In two of the later runs, 37 and 38, there were outlet samples in which both
were present. In this case, however, one was much greater in concentration than the other and there was no noticeable interaction.

There was approximately a 10% loss in the SO$_2$ peak area when water was in the same sample. This was caused by a definite broadening of the peak which increased the SO$_2$ detection limit. The formation of sulfurous or sulfuric acid in the column may have been the cause for the slower desorption. When H$_2$O and SO$_2$ were present in the inlet, the SO$_2$ flowmeter value was used to determine the inlet SO$_2$. The outlet samples only had SO$_2$ and H$_2$O present in those runs in which the catalyst/absorbent was deactivated.

Since the highly detectable H$_2$S and COS breakthroughs must precede that of SO$_2$ (Chapter IV, Section E.1.b.), low SO$_2$ concentrations did not exist in the outlet during the removal steps. After the SO$_2$ breakthrough, its measured concentration was increased by 10% to compensate for the analytical loss.

Prior to Run 25, NO and O$_2$ were never present together in either an inlet or an outlet gas stream. In the majority of the following runs, both were present in the inlet gas stream in concentrations of NO from 0.3% to 0.5% and of O$_2$ from 0.5% to 1.0%. In these runs, the flowmeter readings for each gas were used to obtain their inlet concentrations. Typically the outlet streams from these reactions contained neither NO nor O$_2$. In some of the runs where the catalyst/absorbent became deactivated, however, the run was continued until both O$_2$ and NO eluted. In order to determine the extent of interaction of NO and O$_2$ on the G.C. column a separate study was made.

After Run 30, O$_2$ (0.22%) and NO (0.56%) were simultaneously
analyzed on what was found later to be a poisoned Molecular Sieve 5A column. Three samples reported an average of only 73% of the $O_2$ flowmeter level and only 54% of the NO flowmeter level. When the $O_2$ was cut off, the average NO level in three samples was still only 54%. In this case, the apparent loss of sample was due to the NO$_2$, H$_2$O, and sulfur compounds adsorbed to the sieve.

When the new Molecular Sieve 5A column was made and pretreated as described in section 4, simultaneous sampling was still not quantitative. Four separate samples of [NO] from the Molecular Sieve averaged 0.48% for an NO flowmeter level of 0.50%. This 4% loss is within experimental error and confirmed that NO could be analyzed separately. Three inlet samples with both NO and $O_2$ present in Run 31, the first run following the new column installation, reported losses of both NO and $O_2$. The ratio of the G.C. to flowmeter concentrations for NO averaged 0.88 and the G.C. to flowmeter concentration for $O_2$ averaged 0.77. The ratio of the NO concentrations for two inlet samples in Run 33 averaged 0.58, while that for $O_2$ averaged 0.65. The NO and $O_2$ concentrations were the same in both runs. Subsequent runs with NO and $O_2$ in the inlet gas showed the same trend. As with the study on the poisoned column it appears that some NO$_2$ is formed which is subsequently reactive with later NO samples. An estimate of the final NO and $O_2$ in the outlet samples was made using the factors of 0.54 for NO, and 0.73 for $O_2$ mentioned earlier. Since a constant correction factor was not found, the NO and $O_2$ removals for the runs which resulted in deactivated catalyst are at best only estimates of the actual value. The important runs with active catalysts were not affected. Inlet NO and $O_2$ values from
all runs were obtained from the flowmeters as discussed earlier.

Joithe (1972) has shown that Molecular Sieve 13X can catalyze the oxidation of NO to NO₂, and that NO₂ can also aid in the adsorption of additional NO. Similar, if not the same, reactions are undoubtedly occurring on the 5A sieve used in this work. Since the NO₂ is irreversibly adsorbed, there is a net loss of nitrogen oxides and O₂ in the column when O₂ is present. Fortunately, this interaction was not significant when both O₂ and NO were present at very low concentration, less than 1000 ppm. The lack of interaction was evidenced by the detection of low NO and O₂ concentration in the effluent streams from the deactivated catalyst/absorbent.

B. **Wet-Chemical Gas Analysis.**

In addition to the chromatographic gas analyses discussed in section A, a fritted-glass bubbler was used to absorb NH₃ in the removal runs and SO₂ in the regeneration runs. Ammonia collection was necessary since the G.C. was not able to determine accurately the low concentration present. Sulfur dioxide collection was necessary during regeneration, especially in the runs with short residence times. In these runs, the SO₂ eluted from the entire bed more rapidly than the G.C. sampling could follow.

1. **Ammonia collection.**

Beginning with Run 19, the effluent gas from all runs in which NH₃ could be formed was passed into a fine fritted-glass bubbler. The solutions in the bubbler ranged from 0.02747 N to 0.05382 N HCl. The liquid height above the bubbler base was 90-mm with 150-ml of
acid and 115 mm with 225 ml of acid. The concentration of acid depended on the total amount of NH₃ expected during a run. At least 150 ml of acid was used. The scrubber efficiency with 225-ml solutions and 3.6% inlet NH₃ was 93%. This was determined from both G.C. and flowmeter NH₃ measurements. After the run, a 25-ml aliquot of the scrubber solution was titrated with NaOH solution to determine the NH₃ pick-up. The NaOH and HCl solutions were standardized against potassium acid phthalate (KHC₈H₄O₄) solutions.

2. Sulfur dioxide collection.

An NaOH solution was used to scrub the regeneration gases in the same way in which the NH₃ was removed. The concentration ranged from 0.08024 to 0.9885 N NaOH. This solution was titrated with HCl and the endpoint determined with a pH meter. The efficiency of the scrubber was 93%. This efficiency was determined by using 3 fritted-glass bubblers in series to remove all of the 0.54% SO₂ from the inlet gas stream.

C. Catalyst/absorbent analysis.

After each run, the catalyst was qualitatively tested for its magnetic properties and color. Intermittent tests were run to determine the presence of iron sulfide. Quantitative tests were made at the end of the experimental series to determine the amount of sulfur in the catalysts.

1. Qualitative tests.

A magnet was passed over the catalyst after the run to detect the presence of Fe₃O₄. Typically all of the catalyst material after
reduction, removal reactions, or regeneration reactions exhibited some Fe$_3$O$_4$.

The fresh Fe$_2$O$_3$ catalyst was bright red. After either reduction or removal reactions in which no deactivation occurred, the catalyst was black. The Chemical Handbook gives black as the color for FeS, FeO, and Fe$_3$O$_4$. When deactivation occurred the catalyst became a dull orange color. In the short-residence-time runs, after Run 36, the black particles were slightly more magnetic than the red.

The presence of FeS was determined by the evolution of H$_2$S when the catalyst was acidified with HCl.

2. Quantitative tests.

An oxidation reaction similar to the regeneration runs was used to determine the amount of sulfur in the catalyst. All of the catalyst from each run was ground up and thoroughly mixed. A small sample, about 1 gram, was placed in the 0.95-cm reactor and heated to 677°C. A 1% O$_2$ stream oxidized the sulfur to SO$_2$ for 1 hour. The SO$_2$ was collected in an NaOH scrubber.

Table III-6 gives a listing of the S to Fe ratio found with this technique. The value of S/Fe from the gas analysis is based on the net loss of sulfur from the gas stream less any sulfur which precipitated. Large discrepancies exist between these two estimates of the sulfur on the solid. The solid analysis reported in this work is that based on the calculated values. This method had less room for error than the stripping technique.
Table iii-6 Comparison of S/Fe ratios

<table>
<thead>
<tr>
<th>Run</th>
<th>Calculated from Net SO₂ Absorption</th>
<th>Calculated from SO₂ Evolution at 676°C²</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>0.51</td>
<td>0.28</td>
</tr>
<tr>
<td>29</td>
<td>0.30</td>
<td>0.52</td>
</tr>
<tr>
<td>30</td>
<td>0.20</td>
<td>0.29</td>
</tr>
<tr>
<td>31, 32</td>
<td>0.57</td>
<td>0.58</td>
</tr>
<tr>
<td>35</td>
<td>0.57</td>
<td>0.76</td>
</tr>
<tr>
<td>36</td>
<td>0.94</td>
<td>0.76</td>
</tr>
<tr>
<td>37</td>
<td>1.01</td>
<td>1.06</td>
</tr>
<tr>
<td>38</td>
<td>0.25</td>
<td>--</td>
</tr>
<tr>
<td>39</td>
<td>0.96</td>
<td>0.64</td>
</tr>
<tr>
<td>40b, 40c</td>
<td>0.91</td>
<td>0.87</td>
</tr>
<tr>
<td>40d, 40e</td>
<td>1.00</td>
<td>0.75</td>
</tr>
<tr>
<td>41b, 41c</td>
<td>0.48</td>
<td>--</td>
</tr>
<tr>
<td>41d, 41e</td>
<td>0.65</td>
<td>--</td>
</tr>
<tr>
<td>42</td>
<td>1.30</td>
<td>1.12</td>
</tr>
</tbody>
</table>

D. Precipitate Analysis.

There were two basic types of precipitate which formed in the outlet line, sulfur and ammonia-sulfur salts.

These were first tested for their water solubility. The sulfur was insoluble and the salts were soluble. Some of the sulfur samples were heated to confirm that only a sulfur smell developed. When the salts were heated, an NH₃ smell developed. When an H₂S smell developed in conjunction with the NH₃, the solid was NH₄HS. When an SO₂ smell developed the solid was (NH₄)₂SO₃. In some cases, an NH₃ smell developed when the precipitate was dissolved in an NaOH solution, but no sulfur gases eluted upon either heating or acidification. This eliminated NH₄HS or (NH₄)₂SO₃ as the precipitate. Precipitation in a BaCl₂ solution of the salt confirmed the presence of SO₄²⁻. As much of the precipitate as possible was collected, but because of H₂O adsorption as well as precipitation after the condenser, a quantitative measure of the precipitate was not always possible.
E. Experimental Error.

The experimental error can be separated into six independent areas:

1. Gas chromatographic analysis
2. Integration of effluent gas profiles
3. Catalyst weight measurements
4. Capillary gas flowmeters
5. Condensate and/or precipitate in system lines
6. Effluent gas scrubbing with either HCl or NaOH solutions

1. Gas chromatographic analysis.

The error in the G.C. determinations vary with the gas and the column used. In the first part of this study, through Run 16, a Chromosorb 104 column was used to determine CO₂ and sulfur compounds. In the last part of this work, it was replaced with a Porapak R column which also separated H₂, NH₃ and H₂O. A molecular sieve 5A column was used to analyze the remaining gases. The relative percent error in the standard for each gas was given previously in Table iii-4. Except for H₂ and H₂O all gases were standardized at 100%. The large error in SO₂ and H₂O standardizations on the Porapak R column was due to erratic tailing patterns. The large error in H₂ on the molecular sieve column results because the signal is quite small and is therefore difficult to quantify accurately. The error was significantly lowered when H₂ was separated on the Porapak R column. The remainder of the gases had errors of less than 3%. The assumption of a linear scaling factor of these standards to lower concentration was used. To the extent that this assumption
does not hold, the actual errors will be greater than those presented.

2. Integration of effluent gas peak profiles.

Manual plotting and integration of peak profiles with time gave the total change in concentration of each gas for the run. The trapezoidal curve approximation technique was used for the integration. The greatest error in this part was associated with curve estimation, especially in short residence time runs where rapid breakthrough occurred. It is not possible to quantify this error.

3. Catalyst weight measurement

A Mettler balance, accurate to within 0.0001 g., gave negligible error in the actual weighing process. The loss of catalyst in the reactor and or the water content of the catalyst contributed greatly to sample weight error. When 3.2-mm pellets were used there was essentially no sample loss. With 1/4mm to 1/2mm sized particles some material was embedded in the glass wool plugs. Since glass wool looses binder when heated and frays quite readily when removed from the smaller reactors, the exact amount of material lost could not be determined. An estimate of this would be less than 0.5%.

Not until Run 19 was the catalyst dried for 3 hours at 370°C before use. These conditions were necessary to completely remove all of the adsorbed water. Before this run, the drying conditions varied from a vacuum oven at 115°C to drying at 370°C for 1 hour in the reactor. Typical water contents of the catalyst were around 2.5%. The first technique reported values from 1.8% to 2.1%. This would mean that the weight loss in runs before Run 19 were at least 0.5% in error.
Even though these two errors are very small it is of the order of the calculated weight changes from the reactions. This means that greater than 100% error may exist because of the uncertainty in water lost from the catalyst. After Run 19, the error was smaller in the water determination but when the smaller particles were used, the effect of weight loss again became important.

4. Capillary flowmeters.

All gases were metered into the helium diluent with capillary tube flowmeters. Helium was metered with a rotameter.

Maximum and minimum percent deviation of data points from the average straight line approximation for the flow characteristics are given in Table iii-7.

Table iii-7. Percent standard deviation in gas flowmeters.

<table>
<thead>
<tr>
<th>GAS</th>
<th>Percent Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum</td>
</tr>
<tr>
<td>CO</td>
<td>10.00</td>
</tr>
<tr>
<td>SO₂</td>
<td>5.50</td>
</tr>
<tr>
<td>H₂</td>
<td>4.10</td>
</tr>
<tr>
<td>H₂S</td>
<td>6.10</td>
</tr>
<tr>
<td>O₂</td>
<td>5.20</td>
</tr>
<tr>
<td>NO</td>
<td>7.30</td>
</tr>
<tr>
<td>NH₃</td>
<td>8.20</td>
</tr>
<tr>
<td>He</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Maximum deviations reflect lower flows, while minimum deviations reflect higher flows. The lowest flows used in these calculation corresponded to the lowest percentages of each gas used in the study. The large CO error is present only in the first few runs where CO was below 0.5%. In the simultaneous removal runs, the
error would be less than 2%. NH₃ was fed only to check one reaction. The other maximum errors correspond to gas concentrations typically used in the simultaneous runs. Therefore, flowmeters reflect errors ranging from 2 to 7%.

5. Condensation and/or precipitation in system lines.

Appreciable errors in effluent gas concentrations resulted from condensation and/or precipitation in outlet lines. Sulfur precipitate was first noted in the outlet line in Run 1. Between Runs 1 and 12 only trace amounts were noticed. After Run 13, a large build-up of sulfur halfway between the reactor outlet and end of the outlet line was found. Reactions made in Runs 9-12 could have deposited some of this precipitate. Distribution of sulfur between these runs is at best a guess. A secondary heater was added to prevent sulfur condensation deep within the reactor tube. It maintained temperatures between 157°C and 270°C. In later runs, sulfur precipitated in a removable air cooled stainless steel condenser which could be cleaned and weighed. Sulfur-determination errors after Run 13 were about 5%. A second type of precipitate which developed was ammonia-sulfur salts, NH₄HS, (NH₄)₂SO₃, and (NH₄)₂SO₄. These precipitates were first noticed after Run 22. Collection of these in the air-cooled condenser was not as efficient as sulfur, since their condensation temperatures are lower. These salts sometimes condensed in the outlet sample line and sample loop of the G.C. Outlet lines were heat traced after Run 26. Still some precipi-
tate collected at the switch valve in the G.C. Quantitatively this was a small percentage of the total precipitate. Its effect on the H₂O, SO₂ and NH₃ levels was more pronounced. These gases adsorbed or reacted to form the precipitate.


The HCl and NaOH scrubbers used to collect the SO₂ and NH₃, respectively, were only 93% efficient. A series of 3 bubblers was used to determine the efficiency for both NH₃ and SO₂. Standard solutions and titrations used to determine the amount of gas scrubber were within 5% experimental error.

7. Summary of experimental error analysis.

The main error in these experiments is associated with the measurement of the weight change of the catalyst over the run. In view of this, material balances to estimate the sulfur gained and the oxygen lost from the catalyst were done with the changes in gas composition. Since only an accurate measure of relative gas concentrations was required to calculate the percent removal this value has less than 5% error.
CHAPTER IV

Experimental Results

A. Initial Process Studies.

The initial studies confirmed that the proposed process chemistry was feasible. The 32-mm reactor and 3.2-mm Fe/Al₂O₃ catalyst/absorbent pellets were used in these studies.

1. Reduction of NO with CO over Iron Oxide.

The reduction of NO with CO over iron oxide was studied in seven different runs. N₂ was the only N-product measured. No N₂O was detected. The data are presented in Figure iv-1.

The main influence on the NO removal was the CO/NO ratio. The values of x listed for FeOₓ are the arithmetic average of x at the beginning and end of each run. In all cases reported in the figure, except Runs 1a and 4, the catalyst was pre-reduced with CO. Fast (1965) presents equilibrium calculations for the Fe₂O₃, Fe₃O₄, FeₓOₓ, and Fe systems. Fe₂O₃-Fe₃O₄, Fe₃O₄-FeₓOₓ, and Fe₃O₄-Fe equilibria are possible. Below 550°C., only the Fe₂O₃-Fe₃O₄ and Fe₃O₄-Fe equilibria are present. Fe₃O₄ is a mixed Fe²⁺-Fe³⁺ oxide which has an inverse spinel structure (Cotton, 1972). Therefore, under the above experimental conditions, the iron is a mixture of Fe³⁺, Fe²⁺, and Fe⁰. The actual net valence state appears to have little effect on NO reduction. Similarly, there was no correlation between NO concentration, reactor temperature, or gas residence time and the NO removal within the ranges studied.
Fig. iv-1. Percent NO removal versus CO/NO over FeO$_x$.

<table>
<thead>
<tr>
<th>Run</th>
<th>1a</th>
<th>1b</th>
<th>2b</th>
<th>4</th>
<th>5</th>
<th>6b</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NO] (%)</td>
<td>4.1</td>
<td>3.7</td>
<td>1.7</td>
<td>2.6</td>
<td>2.0</td>
<td>0.29</td>
<td>0.30</td>
</tr>
<tr>
<td>[CO] (%)</td>
<td>6.6</td>
<td>4.4</td>
<td>1.0</td>
<td>1.8</td>
<td>3.4</td>
<td>0.37</td>
<td>0.35</td>
</tr>
<tr>
<td>FeO$_x$, x =</td>
<td>1.38</td>
<td>1.01</td>
<td>1.19</td>
<td>1.46</td>
<td>0.92</td>
<td>0.31</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>345</td>
<td>347</td>
<td>365</td>
<td>390</td>
<td>390</td>
<td>380</td>
<td>370</td>
</tr>
<tr>
<td>Res. time (sec)</td>
<td>0.88</td>
<td>0.88</td>
<td>0.37</td>
<td>0.40</td>
<td>0.40</td>
<td>0.39</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Fe-301-T 1/8 (3.2mmX3.2mm)
2. Simultaneous removal of NO and H$_2$S with CO.

The reduced catalyst/absorbent produced after Run 1b was used to test the potential for simultaneous H$_2$S and NO removal with CO. During the first 120 minutes no H$_2$S or NO were detected in the effluent gas. Traces of light yellow and white precipitates were noticed close to the bubbler 85 minutes after starting the run. In the last 150 minutes of the run no H$_2$S or NO were detected. The run was terminated after 270 minutes because sulfur precipitated, plugging the outlet line. The amount of H$_2$S removed at this point corresponded to 109% of the calculated bed sulfur capacity. Sulfur compounds eluted from the bed because its sulfur capacity had been exceeded. Formation of sulfur is thought to have been by the following reaction:

$$\Delta H_{25^\circ C} \quad \Delta F_{227^\circ C}$$

(kcal) \quad (kcal)

$$2 \text{H}_2\text{S} + \text{SO}_2 \rightarrow 2 \text{H}_2\text{O} + 3 \text{S(s)}$$

\[-35.0 \quad -13.61\]

Failure of a copper gasket permitted air to leak in, which oxidized some sulfur to SO$_2$. Had the leak not been present, all of the sulfur would have eluted as H$_2$S. In subsequent runs either a stainless steel or an aluminum gasket was used. The early traces of light yellow and white precipitates were ignored. Later experiments showed that these were ammonium sulfides and sulfates. The system diluent for this run was N$_2$, which prevented an accurate closing of the nitrogen material balance. Despite problems in this run, it demonstrated that FeO$_x$ can simultaneously remove H$_2$S and NO when CO is present.
3. Reduction of NO with CO over Iron Sulfide.

Since the bed capacity for sulfur (as FeS) in Run 1b had been exceeded while maintaining no detectable NO elutions, it was concluded that iron sulfide must also be catalytic for NO reduction. Runs 2d and 32 demonstrated this fact. Figure iv-2 compares these results with those from the FeO\textsubscript{x} data. For both low and high CO/NO ratios, FeO\textsubscript{x}s\textsubscript{y} data are close to the correlation for FeO\textsubscript{x}. Run 32 had a slight amount of water present, hence both N\textsubscript{2} and NH\textsubscript{3} were generated. Since NH\textsubscript{3} was only 13% of the nitrogen products, the water effect was small. The conclusion from these runs is that iron sulfide has activity comparable to iron oxide for NO reduction by CO.

4. Oxidation of CO and H\textsubscript{2} with Iron Oxide.

Oxidation of CO and H\textsubscript{2} by reduction of Fe\textsubscript{2}O\textsubscript{3} was checked in Runs 8a and 9a. Prior to these runs, reduced iron oxide was produced with net reducing CO and NO streams. Maximum removal of CO in Run 8a was 46% while that for H\textsubscript{2} in Run 9a was only 21% at 370°C in 0.67 seconds. A detailed discussion of these oxidation reactions is given in section H. This cursory look confirmed that both CO and H\textsubscript{2} can be oxidized by Fe\textsubscript{2}O\textsubscript{3}, CO reacting more readily than H\textsubscript{2}.

5. Oxidation of FeS to Iron Oxide and SO\textsubscript{2}.

The final process stage to check was the catalyst/absorbent regeneration. Runs 2e and 10b confirmed the regeneration reactions. In Run 2e at 444°C the initial concentration of SO\textsubscript{2} was 0.066%
Fig. iv-2. Percent NO removal versus CO/NO. Comparison of FeO\textsubscript{x} data to FeO\textsubscript{S\textsubscript{y}} data.

<table>
<thead>
<tr>
<th>Run</th>
<th>[NO]</th>
<th>[CO]</th>
<th>FeO\textsubscript{S\textsubscript{y}}(avg)</th>
<th>temp. (°C)</th>
<th>res. time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2d</td>
<td>1.8%</td>
<td>0.80%</td>
<td>x=10, y=1.1</td>
<td>356</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>x=63, y=63</td>
<td>379</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Fe-301-T 1/8
(3.2mm x 3.2mm)
over FeS when \([O_2]\) was 0.75%. At 518°C the maximum \([SO_2]\) was 1.4% when \([O_2]\) was 0.78%. A quantitative sulfur balance was not obtained. However, the relative product distribution, based on gas chromatograph (G.C.) and precipitate analyses, showed that approximately 95% of the product was \(SO_2\) and 5% was sulfur.

In Run 10b, \(SO_2\) began to evolve rapidly from \(FeSO_4\) at a temperature around 670°C. The iron sulfate gave an \(SO_2\) concentration of 0.47% at 560°C. This increased dramatically to 16% at 670°C. Lowell (1971) reports decomposition of \(FeSO_4\) between 603-810°C and of \(Fe_2(SO_4)_3\) between 781-810°C. The National Bureau of Standards (1966) reported slightly lower temperature levels of 550°C and 680°C, respectively. NBS also state that in the range of 680°C to 730°C, the decomposition pressure of \(FeSO_4\) is greater than that of \(Fe_2(SO_4)_3\). Yost and Russell (1944) support the lower decomposition temperatures. They report an \(SO_3\) concentration at one atmosphere of 26% over \(Fe_2(SO_4)_3\) at 670°C. Since the run continued until the \(SO_2\) concentration was 0.86%, most of the sulfates had already decomposed. The pellets from both Runs 2e and 10b were visually similar to fresh pellets. A sulfur balance was not possible.

6. Summary of initial studies.

The initial process studies confirmed the following:

a. NO can be reduced to \(N_2\) by CO over either iron oxide or iron sulfide at 370°C.

b. NO and \(H_2S\) can be simultaneously removed by reactions with reduced iron and CO at 370°C.
c. Both CO and H₂ can be oxidized by Fe₂O₃ at 370°C.
d. Catalyst regeneration can be accomplished at temperatures around 670°C to yield iron oxide and SO₂.

B. Removal of Sulfur Compounds.

Normal power plants emit sulfur in the form of either SO₂ or SO₃. SO₂ accounts for more than 98% of the total sulfur (Levy, 1970). The proposed removal process requires that a net reducing flue gas be generated. This means that in addition to SO₂, other potential sulfur compounds will be produced – H₂S, COS and S₂. Under reducing conditions, essentially no SO₃ will be present (Reese, 1965).

1. Removal of H₂S with Iron Oxide.

The following reaction was studied in five different runs.

\[
\text{FeO + H}_2\text{S} \rightarrow \text{FeS + H}_2\text{O}
\]

<table>
<thead>
<tr>
<th></th>
<th>ΔH₂₅°C</th>
<th>ΔF₃₇₀°C</th>
<th>ΔF₅₃₈°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal</td>
<td>kcal</td>
<td>kcal</td>
</tr>
<tr>
<td>FeO + H₂S</td>
<td>-11.9</td>
<td>-9.25</td>
<td>-9.57</td>
</tr>
</tbody>
</table>

These runs had approximate conditions of 2% H₂S, 370°C, and a gas residence time of 0.50 seconds. Figure iv-3 is a plot of the percent H₂S removal as a function of run time. All runs gave essentially complete H₂S removal during the first 3 minutes. The rate of departure from 100% removal appears to be a function of the initial amount of FeO in the solid. Run 16b, with FeO₁.₃₅, departs at 3 minutes. Runs 19c and 24c, with FeO₁.₂₇ and FeO₁.₂₆, depart at about 18 minutes. Run 2c, with FeO₁.₁₉, deviates from this trend due to a lower residence time and reaction temperature. Surprisingly Run 24e, with FeO₁.₂₃, gives the longest time until departure, 30 minutes. The oxidation state of the iron would predict that the
Fig. iv-3. Removal of $\text{H}_2\text{S}$ by reduced iron oxide.

<table>
<thead>
<tr>
<th>Run</th>
<th>T(°C)</th>
<th>$\theta$ (sec)</th>
<th>$[\text{H}_2\text{S}]$%</th>
<th>Solid(I)</th>
<th>Solid(F)</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>2c</td>
<td>360</td>
<td>0.37</td>
<td>1.9</td>
<td>FeO$1.19$</td>
<td>FeO$0.10$</td>
<td>O</td>
</tr>
<tr>
<td>16b</td>
<td>381</td>
<td>0.50</td>
<td>2.1</td>
<td>FeO$1.35$</td>
<td>FeO$0.57$</td>
<td>$\triangle$</td>
</tr>
<tr>
<td>19c</td>
<td>376</td>
<td>0.47</td>
<td>1.85</td>
<td>FeO$1.27$</td>
<td>FeO$0.50$</td>
<td>□</td>
</tr>
<tr>
<td>24c</td>
<td>376</td>
<td>0.45</td>
<td>2.1</td>
<td>FeO$1.26$</td>
<td>FeO$0.50$</td>
<td>●</td>
</tr>
<tr>
<td>24e</td>
<td>376</td>
<td>0.45</td>
<td>2.0</td>
<td>FeO$1.23$</td>
<td>FeO$0.71$</td>
<td>▼</td>
</tr>
</tbody>
</table>

Fe-301-T1/8
(3.2mm×3.2mm)
breakthrough time for Run 24c should be similar to that for Run 16b. No explanation has been found for this discrepancy. Based on equation iv-2, the hydrogen material balance in Run 16b closed to within 8.5%, supporting the contention that one sulfur is exchanged for one oxygen. The qualitative lead acetate test for the presence of sulfide was positive for the catalyst/absorbent from Run 1c.

2. Removal of COS with Iron Oxide.

Similar results were obtained for the reaction:

\[
\text{FeO} + \text{COS} \rightarrow \text{FeS} + \text{CO}_2
\]

Percent removal of COS as a function of run time for Run 9b is shown in Figure iv-4. Departure from 100% removal occurs at 5 minutes, somewhat sooner than expected based on the \( \text{H}_2\text{S} \) work. Fifty percent removal of COS occurs after 65 minutes for COS, while for Run 24c with comparable initial \( \text{FeO}_x \), 50% removal of \( \text{H}_2\text{S} \) occurs after 80 minutes. It appears from these two comparisons that \( \text{H}_2\text{S} \) is the more reactive species.

The overall carbon balance on Run 9b closed within 7.3%. \( \text{CO}_2 \) was the primary product of the reaction. It decreased with time as the COS removal decreased. \( \text{CO} \) was the other product. After the first 20 minutes, \( \text{CO} \) eluted at a constant concentration of 0.20%. This concentration corresponds to 5.3% of the inlet COS which is far greater than could be expected from the 0.32% \( \text{CO} \) in the COS feed cylinder. The constant elution rate for \( \text{CO} \) implies that it is generated independent of the extent of the main reaction.
Fig. iv-4. Removal of COS with reduced iron oxide.

Run                  96                  Fe-301-T 1/8
T(°C)               370                  (3.2mmX3.2mm)
θ (sec)              0.60
[ COS]              3.75%
Solid(I)           FeO_{1.25}
Solid(F)         FeO_{0.765}.49
The following decomposition reactions are thermodynamically unfavorable:

\[
\begin{array}{ccc}
\Delta H_{25^\circ C} & \Delta F_{370^\circ C} & \Delta F_{538^\circ C} \\
\text{COS} & \rightarrow & \text{CO} + \frac{1}{2} \text{S}_2(g) \\
& & +21.8 & +9.46 & +6.27 \\
\text{COS} & \rightarrow & \text{CO} + \text{S}(s) \\
& & +6.38 & +5.75(227^\circ C) \\
\end{array}
\]

This next reaction is thermodynamically favorable.

\[
\begin{array}{ccc}
\Delta H_{25^\circ C} & \Delta F_{370^\circ C} \\
\text{FeS} + \text{COS} & \rightarrow & \text{FeS}_2 + \text{CO} \\
& & -13.42 & -6.50 \\
\end{array}
\]

Haas (1973) has confirmed the presence of both FeS and FeS\(_2\) by x-ray diffraction analysis under similar conditions. He studied the following reaction at a temperature of 400°C over an iron/alumina catalyst.

\[
\begin{array}{ccc}
\Delta H_{25^\circ C} & \Delta F_{370^\circ C} & \Delta F_{538^\circ C} \\
\text{SO}_2 + 2 \text{CO} & \rightarrow & 2 \text{CO}_2 + \frac{1}{2} \text{S}_2 \\
& & -48.9 & -33.4 & -29.3 \\
\end{array}
\]

COS was identified as the reaction intermediate.

Since CO was formed and the presence of FeS\(_2\) was implied, reactions iv-3 and iv-5 undoubtedly have occurred in Run 9b. With this interpretation, 8.8% of the sulfided iron was FeS\(_2\) and 91.2% was FeS. No independent determination of FeS\(_2\) was made in this work.


If sulfur is present in the flue gas it should be decreased to a very low value over the catalyst/absorbent in view of the following equilibria:
Querido (1973) reported that above 327°C, reaction iv-7 proceeded to a significant extent in less than 0.20 seconds over a CuS/Al₂O₃ catalyst. Haas (1971) reported that reaction iv-7 occurs above 300°C over an FeS/Al₂O₃ catalyst. In these investigations COS was the final product. In the present work COS and H₂S would subsequently react with FeO to form FeS, resulting in a lower potential S₂ level than in either of the cited references. In view of these facts, no experimental work was done specifically with S₂.


a. Removal with Iron Oxide.

The final sulfur compound considered was SO₂. Direct contact of SO₂ with either oxidized or reduced iron oxide resulted in negligible SO₂ removal. Figure iv-5 shows that SO₂ removal is greatest for reduced iron oxide. Even with reduced oxide, however, only 7% of the potential sulfur absorption was realized.

b. Removal with CO or H₂ over Iron Oxide.

In the presence of either CO or H₂, SO₂ was substantially removed over the Fe/Al₂O₃ catalyst/absorbent. Figure iv-6 presents results of these studies. The major reactions included the following:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH₂5°C (kcal)</th>
<th>ΔF³⁷₀°C (kcal)</th>
<th>ΔF₅₃₈°C (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + ½ S₂(g) → COS</td>
<td>-21.8</td>
<td>-9.46</td>
<td>-6.27</td>
</tr>
<tr>
<td>H₂ + ½ S₂(g) → H₂S</td>
<td>-20.2</td>
<td>-13.7</td>
<td>-11.7</td>
</tr>
</tbody>
</table>

Querido (1973) reported that above 327°C, reaction iv-7 proceeded to a significant extent in less than 0.20 seconds over a CuS/Al₂O₃ catalyst. Haas (1971) reported that reaction iv-7 occurs above 300°C over an FeS/Al₂O₃ catalyst. In these investigations COS was the final product. In the present work COS and H₂S would subsequently react with FeO to form FeS, resulting in a lower potential S₂ level than in either of the cited references. In view of these facts, no experimental work was done specifically with S₂.


a. Removal with Iron Oxide.

The final sulfur compound considered was SO₂. Direct contact of SO₂ with either oxidized or reduced iron oxide resulted in negligible SO₂ removal. Figure iv-5 shows that SO₂ removal is greatest for reduced iron oxide. Even with reduced oxide, however, only 7% of the potential sulfur absorption was realized.

b. Removal with CO or H₂ over Iron Oxide.

In the presence of either CO or H₂, SO₂ was substantially removed over the Fe/Al₂O₃ catalyst/absorbent. Figure iv-6 presents results of these studies. The major reactions included the following:
Fig. iv-5. Removal of SO$_2$ with oxidized and reduced iron oxide.

**Run**
- 13c
- 11d

**T (°C)**
- 377
- 382

**$\theta$ (sec)**
- 0.56
- 0.54

**[SO$_2$] in**
- 1.46%
- 1.40%

**Solid (F)**
- FeO$_{1.5}$
- FeO$_{1.26}$

**Solid (F)**
- FeO$_{1.5}$(SO$_2$)$_{0.03}$
- FeO$_{1.26}$(SO$_2$)$_{0.07}$

Fe-301-T 1/8
(3.2mmX3.2mm)
Fig. iv-6.

Sulfur removal with time as a function of solid and gas compositions.

\[ T = 370-379^\circ C, \ \theta = 0.5-0.7 \text{ sec} \]

Fe-301-T 1/8 (3.2mmX3.2mm)

<table>
<thead>
<tr>
<th>Run</th>
<th>[CO]</th>
<th>[H2]</th>
<th>[SO2]</th>
<th>[H2]</th>
<th>[SO2]</th>
<th>[CO2]</th>
<th>[SO2]</th>
<th>Solid Initial</th>
<th>Solid Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>11e</td>
<td>0</td>
<td>3.5</td>
<td>2.8</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td>FeO_{1.3S.074}</td>
<td>FeO_{0.6S.40}</td>
</tr>
<tr>
<td>12d</td>
<td>1.9</td>
<td>0</td>
<td>0</td>
<td>-2.8</td>
<td></td>
<td>-2.8</td>
<td></td>
<td>FeO_{1.5S.018}</td>
<td>FeO_{1.5S.50}</td>
</tr>
<tr>
<td>12e</td>
<td>3.1</td>
<td>0</td>
<td>0</td>
<td>-2.5</td>
<td></td>
<td>-2.5</td>
<td></td>
<td>FeO_{1.5S.50}</td>
<td>FeO_{1.4S.68}</td>
</tr>
<tr>
<td>13e</td>
<td>2.1-2.6</td>
<td>0</td>
<td>0</td>
<td>-2.8</td>
<td></td>
<td>-2.8</td>
<td></td>
<td>FeO_{1.5S.023}</td>
<td>FeO_{1.2S.43}</td>
</tr>
</tbody>
</table>
$\frac{1}{2} \text{Fe}_2\text{O}_3 + \frac{7}{2} \text{CO} + \text{SO}_2 \rightarrow \text{FeS} + 7/2 \text{CO}_2$

FeO + 3 CO + SO$_2$ $\rightarrow$ FeS + 3 CO$_2$

2 CO + SO$_2$ $\rightarrow$ 2 CO$_2$ + $\frac{3}{2}$ S$_2$

$\frac{1}{2} \text{Fe}_2\text{O}_3 + \frac{7}{2} \text{H}_2 + \text{SO}_2 \rightarrow \text{FeS} + 7/2 \text{H}_2\text{O}$

FeO + 3 H$_2$ + SO$_2$ $\rightarrow$ FeS + 3 H$_2$O

2 H$_2$ + SO$_2$ $\rightarrow$ 2 H$_2$O + $\frac{3}{2}$ S$_2$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ _25^\circ$C (kcal)</th>
<th>$\Delta F$ _370^\circ$C (kcal)</th>
<th>$\Delta F$ _538^\circ$C (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iv-9</td>
<td>-90.1</td>
<td>-64.5</td>
<td>-57.9</td>
</tr>
<tr>
<td>iv-10</td>
<td>-90.8</td>
<td>-60.2</td>
<td>-53.1</td>
</tr>
<tr>
<td>iv-11</td>
<td>-48.9</td>
<td>-33.4</td>
<td>-29.3</td>
</tr>
<tr>
<td>iv-12</td>
<td>-55.7</td>
<td>-50.3</td>
<td>-48.4</td>
</tr>
<tr>
<td>iv-13</td>
<td>-61.4</td>
<td>-48.7</td>
<td>-45.8</td>
</tr>
<tr>
<td>iv-14</td>
<td>-29.2</td>
<td>-25.7</td>
<td>-24.4</td>
</tr>
</tbody>
</table>

In Run 11e reduced iron oxide was contacted with a net reducing gas stream. The gradual increase of SO$_2$ removal with time is a result of continual surface reduction as well as sulfidation. The overall ratio of the change of [H$_2$] to the change of [SO$_2$] ($\Delta$[H$_2$]/$\Delta$[SO$_2$]) was 2.8. This would imply that all three reactions iv-12, 13, and 14 could be important, based on reaction stoichiometry.

Oxidized iron and a reducing atmosphere relative to reaction iv-11 were used in Runs 12d and 13e. A significantly longer time was required for these runs to achieve the same SO$_2$ removal as in Run 11e. In both cases, the overall change of product CO$_2$ to reactant SO$_2$ ($\Delta$[CO$_2$]/$\Delta$[SO$_2$]) was -2.8, even through the inlet reactant ratio ([CO]/[SO$_2$]) only ranged from 1.9 to 2.6. SO$_2$ removals up to 100% were achieved in the later part of Run 13e. The negative signs only reflect product/reactant ratio changes. This apparent anomaly is explained by realizing that at the beginning of these runs, the majority of the reducing agent was consumed in reducing Fe$_2$O$_3$. As more reduced iron became available, the CO + SO$_2$ reaction became dominant. Therefore, the initial ($\Delta$[CO$_2$]/$\Delta$[SO$_2$]) will be greater...
than 3.5 and the final absolute ratio will be between 2.0 and 3.5. Figure iv-7 illustrates this point. The initial $\Delta [CO_2]/\Delta [SO_2]$ is much greater for Runs 12d and 13e than for Runs 12e of 11e. After sufficient time, Runs 11e, 12e, and 13e approach a $\Delta [CO_2]/\Delta [SO_2]$ of between -2.5 and -2.7. Run 12d, with a lower inlet $[CO]/[SO_2]$ ratio, drops to about 2.0. These limiting values, plus sulfur precipitate in the lines, verify that reactions iv-11 and iv-14 do proceed to some extent.

Because sulfur precipitate was not anticipated, only a combined measure of sulfur from Runs 9b, 11e, 12d, and 12e was obtained. Measured precipitate accounted for 15% of the total sulfur removed in these runs. In Run 13e sulfur precipitate was anticipated but it accounted for only 4.8% of the total change in $SO_2$. A weighted average of $\Delta [CO]/\Delta [SO_2]$ calculated according to equation iv-10 and iv-11 to give the experimentally found value of 2.5 would predict that 50% of the total change of $SO_2$ could be accounted for by the sulfur precipitate. This value predicts a much greater amount of sulfur than was found. In keeping with earlier findings that $FeS_2$ may form, the following overall reactions should be considered:

$\Delta H_{25^\circ C}$ $\Delta F_{370^\circ C}$ $\Delta F_{538^\circ C}$

(kcal) (kcal) (kcal)

$\frac{4}{3} FeO + 6 CO + \frac{7}{3} SO_2 \rightarrow$ $FeS_2 + \frac{1}{3} FeS + 6 CO_2$ $-205$ $-130$ $-111$ iv-15

$\frac{4}{3} FeO + 6 H_2 + \frac{7}{3} SO_2 \rightarrow$ $FeS_2 + \frac{1}{3} FeS + 6 H_2O$ $-146$ $-107$ $-95.8$ iv-16
Fig. iv-7. Variation of reaction stoichiometry with time for both $H_2$ and CO reduction of $SO_2$.

<table>
<thead>
<tr>
<th>Run</th>
<th>$T$</th>
<th>$\theta$</th>
<th>[SO$_2$]</th>
<th>[H$_2$]</th>
<th>[CO]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>382</td>
<td>0.54</td>
<td>1.35</td>
<td>4.8</td>
<td>0</td>
</tr>
<tr>
<td>△</td>
<td>370</td>
<td>0.59</td>
<td>1.1</td>
<td>0</td>
<td>2.1</td>
</tr>
<tr>
<td>□</td>
<td>370</td>
<td>0.59</td>
<td>1.08</td>
<td>0</td>
<td>3.4</td>
</tr>
<tr>
<td>▼</td>
<td>377</td>
<td>0.56</td>
<td>0.72→0.77</td>
<td>1.5→1.8</td>
<td></td>
</tr>
</tbody>
</table>

Fe-301-T 1/8
(3.2mm×3.2mm)
For these reactions, the $\Delta[\text{CO}]/\Delta[\text{SO}_2] = \Delta[\text{H}_2]/\Delta[\text{SO}_2] = 2.57$, which is within the experimentally determined range. Since sulfur precipitate alone cannot account for deviation from a stoichiometric ratio below 3.0, some FeS$_2$ may have formed.

In addition to $S_2$ which eluted from the bed, small amounts of $\text{H}_2\text{S}$ (Run 11e) and COS (Runs 12d, 12e, and 13) were detected. $\text{H}_2\text{S}$ eluted in Run 11e during the entire sulfidation. It increased from 2.8% to 14% of the inlet SO$_2$ value as the bed became sulfided.

In Runs 12d-12e and 13e, COS was detected during the majority of each run. The highest COS measured was 10% of the inlet SO$_2$. COS formation is in agreement with the theory proposed by Haas (1973) that COS is the reaction intermediate in the reduction of SO$_2$ to sulfur by CO. By analogy H$_2$S may also serve this function in the SO$_2$ + H$_2$ reaction.

c. Removal with CO and H$_2$ over Iron Oxide.

A comparison of the simultaneous reaction kinetics of CO and H$_2$ with SO$_2$ was made in Run 27d. In the first 110 minutes a stream of CO and H$_2$ passed over reduced and partially sulfided catalyst. Figure iv-8 shows only 15% H$_2$ removal and 2% CO removal. Introduction of SO$_2$ resulted in 100% SO$_2$ removal and increased the CO removal to 33%. No change in H$_2$ removal was noted. Both the CO and H$_2$ removals gradually dropped off with time, H$_2$ removal decreasing more rapidly. Measured $\Delta[\text{CO}]/\Delta[\text{SO}_2]$ was 2.70, which is what would be expected with an excess of reducing agent, based on Figure iv-7. Thus, the sulfided catalyst promotes reduction of SO$_2$ with CO in preference to reduction of SO$_2$ with H$_2$. 
Fig. iv-8. Reduction of SO₂ in a combined CO and H₂ stream.

Run 27d
T(°C) 374
θ (sec) 0.43
[H₂] 3.7%
[CO] 4.0%
[SO₂] 0.45%
Solid(I) FeO₁.₁₅S₀.₁₅
Solid(F) FeO₀.₈₅S₀.₂₆
Fe-301-T 1/8
(3.2mm×3.2mm)
5. Reduced catalytic activity.

Absence of a reducing agent for SO$_2$ not only results in the incomplete removal of SO$_2$ but also inhibits the catalyst with respect to reduction reactions. In Figure iv-9, the upper line, Run 13a, represents CO removal over fresh Fe$_2$O$_3$, while the middle line, Run 13d, shows CO removal over Fe$_2$O$_3$ which had been exposed to a stream of 1.46% [SO$_2$]. The fresh catalyst exhibits a rate roughly 3.3 times that of the inhibited catalyst. This rate decrease is more than can be explained by the CO concentration difference. The catalyst was inhibited for surface reduction in Run 13d by adsorbed SO$_2$. Introduction of SO$_2$ into the inlet gas line resulted in an immediate increase in CO$_2$ formation and an equivalent SO$_2$ reduction. In this case, the catalyst was still active for the CO + SO$_2$ reaction. The lower line, Run 12b, is CO removal from a system containing both absorbed and gas-phase SO$_2$. In this case, neither Fe$_2$O$_3$ nor SO$_2$ reacted with CO for over one hour. The CO removal rate is nearly 35 times slower than that over the fresh catalyst in Run 13a. The only significant differences between the bottom two lines was the SO$_2$ present in Run 12b. After treating this catalyst in Run 12b with CO at 370°C for 38 minutes, introduction of SO$_2$ resulted in stoichiometric conversion of CO to CO$_2$ and SO$_2$ reduction as noted above following Run 13d.


This work confirms that both H$_2$S and COS react with reduced iron oxide to give, primarily, FeS. Rapid decline of both H$_2$S and
Fig. iv-9. The effect of absorbed SO$_2$ on Fe$_2$O$_3$ and SO$_2$ reaction by CO.

<table>
<thead>
<tr>
<th>Run</th>
<th>T(°C)</th>
<th>$\theta$ (sec)</th>
<th>[CO]%</th>
<th>$[$SO$_2$]%</th>
<th>Solid(I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12b</td>
<td>371</td>
<td>0.59</td>
<td>2.2</td>
<td>1.2</td>
<td>FeO$_{1.5}$(SO$<em>2$)$</em>{0.28}$</td>
</tr>
<tr>
<td>13a</td>
<td>377</td>
<td>0.51</td>
<td>1.94</td>
<td>1.28</td>
<td>FeO$_{1.5}$</td>
</tr>
<tr>
<td>13d</td>
<td>377</td>
<td>0.51</td>
<td>1.28</td>
<td>1.28</td>
<td>FeO$_{1.5}$(SO$<em>2$)$</em>{0.23}$</td>
</tr>
<tr>
<td>12b</td>
<td>377</td>
<td>0.51</td>
<td>1.28</td>
<td>1.28</td>
<td>FeO$_{1.5}$(SO$<em>2$)$</em>{0.23}$</td>
</tr>
</tbody>
</table>

Fe-301-T 1/8 (3.2mm X 3.2mm)
COS percent removals could be slowed by higher temperatures and smaller catalyst/absorbent pellets. These changes should also increase the total amount of sulfur absorbed per mole of iron.

Almost complete removal of SO$_2$ with CO or H$_2$ is possible at 370°C and a residence time of approximately 0.6 seconds over the 3.2-mm Fe/Al$_2$O$_3$ catalyst/absorbent. The problem of sulfur elution before complete bed sulfidation requires further study. Higher temperature and small particles should help solve this problem. For effective SO$_2$ removal, the gas stream needs to contain a reducing agent. Exposure of the catalyst/absorbent at 370°C to SO$_2$ without reducing agent results in partial deactivation for both SO$_2$ and Fe$_2$O$_3$ reduction. The original activity can be restored by treating the catalyst at this temperature with CO. Experimental results of Run 11b indicated that H$_2$ is also effective for this reactivation.

7. Sulfur compound distribution in a net reducing flue gas.

The form in which sulfur will be present in reduced flue gas is a function of the equilibrium conditions at the temperature where reaction kinetics essentially freeze. Initially, sulfur will be completely oxidized to SO$_2$ with excess oxygen. At the point of addition of the rich CO and H$_2$ stream, SO$_2$ could be reduced to H$_2$S COS, or S$_2$ depending upon conditions in the flue gas. Thermodynamic calculations show that these reduced sulfur species predominate at lower temperatures. Since no useful information was located on the homogeneous kinetics of SO$_2$ reduction, runs were made to determine
an approximate lower temperature limit.

a. Thermodynamic equilibria of sulfur compounds in reduced flue gas.

Thermodynamic equilibrium calculations for a typical oil-fired power plant flue gas under reducing conditions indicate that as the temperature decreases, $\text{H}_2\text{S}$, COS, and $\text{S}_2$ increase while $\text{SO}_2$ decreases. Table iv-1 lists flue gas compositions and the corresponding reactions considered. Results are shown in Figure iv-10.

Table iv-1. Gas composition and reactions for plant equilibrium calculations.

<table>
<thead>
<tr>
<th>Flue Gas Composition (before reaction):</th>
<th>Reactions Considered:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{N}_2]$</td>
<td>2 COS + $\text{SO}_2$ $\rightarrow$ 2 $\text{CO}_2$ + $3/2$ $\text{S}_2$</td>
</tr>
<tr>
<td>$[\text{CO}_2]$</td>
<td>2 $\text{H}_2\text{S}$ + $\text{SO}_2$ $\rightarrow$ 2 $\text{H}_2\text{O}$ + $3/2$ $\text{S}_2$</td>
</tr>
<tr>
<td>$[\text{H}_2\text{O}]$</td>
<td>$\text{CO}$ + $\text{H}_2\text{O}$ $\rightarrow$ $\text{CO}_2$ + $\text{H}_2$</td>
</tr>
<tr>
<td>$[\text{CO}]$</td>
<td>3 $\text{H}_2$ + $\text{SO}_2$ $\rightarrow$ $\text{H}_2\text{S}$ + 2 $\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$[\text{H}_2]$</td>
<td>3 $\text{CO}$ + $\text{SO}_2$ $\rightarrow$ COS + 2 $\text{CO}_2$</td>
</tr>
<tr>
<td>$[\text{O}_2]$</td>
<td>$\text{H}_2$ + $\frac{1}{2}$ $\text{S}_2$ $\rightarrow$ $\text{H}_2\text{S}$</td>
</tr>
<tr>
<td>$[\text{SO}_2]$</td>
<td>$\text{CO}$ + $\frac{1}{2}$ $\text{S}_2$ $\rightarrow$ COS</td>
</tr>
</tbody>
</table>

Oxidizing Equivalents $= \frac{2[\text{O}_2] + 3[\text{SO}_2]}{[\text{CO}] + [\text{H}_2]} = 0.521$

Reducing Equivalents $= \frac{[\text{CO}_2]}{[\text{H}_2\text{O}]} = 1.37$

At temperatures below 800°C, $\text{H}_2\text{S}$ is the primary equilibrium sulfur species when the $\text{CO}_2$ to $\text{H}_2\text{O}$ ratio is 1.37, which is typical
Fig. iv-10. Equilibrium distribution of sulfur compounds in a typical power plant flue gas. (See Table iv-1 for data.)
of oil-fired power plant conditions. Coal-fired plants have a higher $[\text{CO}_2]/[\text{H}_2\text{O}]$, typically around 2. As long as reaction kinetics are rapid at $800^\circ\text{C}$ or below, neither $\text{SO}_2$, $\text{S}_2$, nor COS will be present to a significant extent. The next section will discuss a case where the $\text{CO}_2$ to $\text{H}_2\text{O}$ ratio is much less than one. Under these conditions, sulfur is the main reduced product at lower temperatures.

b. Homogeneous kinetics of $\text{SO}_2$ reduction.

A non-catalytic experiment, Run 28, was made to determine the lowest temperature at which these reactions would proceed. The inlet gas was 0.5% $\text{SO}_2$, 1.6% $\text{CO}$, 1.6% $\text{H}_2$, and 1.7% $\text{H}_2\text{O}$ in a helium diluent. The stream was fed directly into the 44.4-mm ID Mullite furnace tube. This substantially increased the gas residence time in the reactor to a value about 10 times that found in normal coal-fired furnaces above $1090^\circ\text{C}$, 2.4 sec. compared to 0.24 sec.

Results of this work are shown in Figure iv-11 and indicate that reaction did not occur at a significant rate at temperatures up to $950^\circ\text{C}$. In tests run above $1093^\circ\text{C}$, reaction took place. When reaction occurred, large amounts of sulfur precipitated, preventing any quantitative estimation of the gas composition at high temperatures after reaction. Qualitatively, there must have been some COS or $\text{H}_2\text{S}$ present which, cooled, reacted with $\text{SO}_2$ to form sulfur.

The equilibrium calculations of Figure iv-9 are based on a $[\text{CO}_2]/[\text{H}_2\text{O}]$ ratio of 1.37. Run 28 had $[\text{CO}_2]/[\text{H}_2\text{O}]$ equal to 0.088 for $1094^\circ\text{C}$ and 0.37 for $1260^\circ\text{C}$. The low $\text{CO}_2$ level allowed small changes
Fig. iv-11. Equilibrium distribution of sulfur compounds under Run No. 28 conditions. Experimental SO₂ distribution.

Expt. | [H₂O]  | 1.95%  |
     | [CO]   | 1.5%   |
     | [H₂]   | 1.6%   |
     | [SO₂]  | 0.5%   |
in CO₂, indicative of reaction progress, to be detected. From an equilibrium point of view, this lower value favors the reduction reactions over that in the actual flue gas.

The effect of this lower [CO₂]/[H₂O] ratio on the experimental system equilibria is to make S₂ the predominant species at lower temperatures. Figure iv-11 is a plot of the calculated equilibria and the experimental SO₂. Only at temperatures above 1094°C does the experimental SO₂ value begin to approach equilibrium value.

These results show that reaction kinetics should freeze at around 1094°C or higher in normal flue gases. Figure iv-10 illustrates a typical sulfur compound distribution at 1094°C:

- SO₂ -- 95.3%
- H₂S -- 3.8%
- S₂ -- 0.63%
- COS -- 0.29%

Freezing the equilibria at a higher temperature would result in a higher SO₂ level. Therefore, the primary sulfur species in flue gas will be SO₂ even though it contains an excess of CO and/or H₂.

Okay and Short (1973) report equilibrium calculations for a net reducing flue gas with [CO₂]/[H₂O] = 1.17. As in the present study they report H₂S as the predominant sulfur species at low temperatures. In their kinetic studies, as in the present work, no effort was made to maintain CO₂ in the inlet feed or [CO₂]/[H₂O] in the outlet. At their highest SO₂ removal and lowest water concentration the CO₂ formed from reaction would yield only a [CO₂]/[H₂O] ratio of about 0.2. The previous discussion of Figures iv-10 and
iv-11 has shown that at high \([\text{CO}_2]/[\text{H}_2\text{O}]\) \(\text{H}_2\text{S}\) is the prime lower temperature sulfur species while at low \([\text{CO}_2]/[\text{H}_2\text{O}]\) \(\text{S}_2\) is the prime species. Therefore, even though \(\text{S}_2\) was the primary reduced sulfur species in the experimental system it will not necessarily be so under power plant conditions. A catalyst promoting these reactions at lower temperatures (below 800°C) with a typical flue gas ratio of \([\text{CO}_2]/[\text{H}_2\text{O}]\) under reducing conditions will form primarily \(\text{H}_2\text{S}\).

C. Removal of Nitric Oxide.

Nitric oxide forms in the primary combustion zone of the furnace. A small amount of the NO is oxidized during flue gas cooling. This results in the effluent \(\text{NO}_x\) being 90 – 95% NO and 5 – 10% \(\text{NO}_2\). (Bartok, 1969). Rosser, (1956) reports homogeneous thermal decomposition rates for \(\text{NO}_2\) above 540°C, which imply negligible \(\text{NO}_2\) in the flue gas above this temperature. Since the flue gas entering the contact zone will not only be at 540°C but also reducing, essentially all the \(\text{NO}_x\) will be NO. The experimental work studied only the reduction of NO.

1. Reduction of NO with Iron Oxide.

Removal of NO by catalytic reduction with a reducing agent over iron oxide and iron sulfide was reported in part A. At that time, no attempt was made to understand the removal mechanism. Klimisch (1972) has proposed an oxidation-reduction mechanism for the iron oxide system. Experiments were run to confirm this mechanism by demonstrating that NO could be reduced by reaction with either reduced iron oxide or iron sulfide. Figure iv-12 shows the percent
Fig. iv-12. Oxidation of reduced iron oxide with NO.

<table>
<thead>
<tr>
<th>Run</th>
<th>14b</th>
<th>15b</th>
<th>18b</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(°C)</td>
<td>374</td>
<td>377</td>
<td>377</td>
</tr>
<tr>
<td>θ (sec)</td>
<td>0.55</td>
<td>0.51</td>
<td>0.48</td>
</tr>
<tr>
<td>[NO]%</td>
<td>2.17</td>
<td>0.98</td>
<td>1.34</td>
</tr>
<tr>
<td>Solid(I)</td>
<td>FeO$_{1.34}$</td>
<td>FeO$_{1.19}$</td>
<td>FeO$_{1.42}$</td>
</tr>
</tbody>
</table>

Fe-301-T 1/8
(3.2mmX3.2mm)
\[
\begin{array}{c|c|c|c}
 & \Delta H_{250^\circ C} \text{(kcal)} & \Delta F_{370^\circ C} \text{(kcal)} & \Delta F_{538^\circ C} \text{(kcal)} \\
7 \text{ NO} + 2 \text{ FeS} & & & \\
\rightarrow & \text{Fe}_2\text{O}_3 + \frac{7}{2} \text{N}_2 + 2 \text{SO}_2 & -444 & -392 & -377 \text{ iv-19} \\
3 \text{ NO} + \text{FeS} & & & \\
\rightarrow & \text{FeO} + \frac{3}{2} \text{N}_2 + \text{SO}_2 & -177 & -162 & -157 \text{ iv-20} \\
\end{array}
\]

The overall \(\Delta [\text{N}_2]/\Delta [\text{SO}_2]\) was 2.42 for this run. The ratio of \(\Delta [\text{N}_2]/\Delta [\text{SO}_2]\) for individual samples ranged from 3.85 for the first sample to 1.84 for the last sample. If the mechanism of oxidation required \(\text{FeSO}_3\) first to form and subsequently to decompose, initially [\(\text{N}_2\)] would be greater than \(1.5 [\text{SO}_2]\). Figure iv-13 shows that this is what occurred experimentally. Since Lowell (1971) reports \(\text{FeSO}_3\) decomposition at \(382^\circ \text{C}\) to form \(\text{SO}_2\) and \(\text{FeO}\), this mechanism is probably what occurred. The \(\Delta [\text{N}_2]/\Delta [\text{SO}_2]\) for reactions iv-19 and iv-20 are 1.75 and 1.50 respectively. Based on these reactions, the surface is still undergoing oxidation at 160 minutes. Quantitative sampling for NO on the Molecular Sieve 5A column was not possible in the first 65 minutes. However, the Chromosorb 104 column, indicated qualitatively that large NO concentrations were present. Absence of \(\text{N}_2\) on the Molecular Sieve 5A column in the first 65 minutes also concurred with this fact. Gradual increase of NO removal with time is opposite to the effect noticed for reduced iron oxide in Figure iv-12. This suggests that the oxidation of \(\text{FeO}\) by NO proceeds more rapidly than that of \(\text{FeS}\). As fresh \(\text{FeO}\) is formed from \(\text{FeS}\) the overall rate of NO removal gradually increases for the bed. Initially
NO removal by reduced iron oxide as a function of run time for three different runs. The following reactions may occur:

\[
\begin{array}{c|c|c|c}
 & \Delta H_{25^\circ C} & \Delta F_{370^\circ C} & \Delta F_{538^\circ C} \\
& \text{(kcal)} & \text{(kcal)} & \text{(kcal)} \\
2 \text{Fe}_3\text{O}_4 + \text{NO} & -76.4 & -53.6 & -46.8 \\
3 \text{Fe}_2\text{O}_3 + \frac{1}{2} \text{N}_2 & -90.8 & -67.1 & -62.2 \\
2 \text{FeO} + \text{NO} & & & \\
\text{Fe}_2\text{O}_3 + \frac{1}{2} \text{N}_2 & & & \\
\end{array}
\]

Run 15b exhibits a higher removal of NO because the solid was more strongly reduced and the NO concentration was lower than in other runs. The gradual decrease with time is caused by depletion of reduced iron on the outer surface of the catalyst pellets.

In Runs 14b and 15b, the catalyst had been initially reduced with CO to levels reported in Figure iv-12. In Run 18, H\textsubscript{2} was used. Oxidation of FeO in Run 15b produced not only N\textsubscript{2} but also CO\textsubscript{2}. This result was probably caused by desorption of CO\textsubscript{2} or oxidation of adsorbed CO remaining after reduction. The N\textsubscript{2} generated from reaction with CO was 18% of the total. In Run 14b, CO\textsubscript{2} was not monitored, but it must also have been present since reduction conditions for 14a and 15a were similar. The analytical system, at this time, was not set up to monitor water, so adsorption of H\textsubscript{2} was not checked.

2. Reduction of NO with Iron Sulfide.

Oxidation of iron sulfide not only produces N\textsubscript{2} but also liberates SO\textsubscript{2}. Figure iv-13 presents the results from Run 16c. Possible overall reactions include the following:
Fig. iv-13. Oxidation of iron sulfide with NO.
Run 16c
T(°C) 373
θ (sec) 0.50
[NO] 1.44%
Solid(I) FeO.57S.80
Fe-301-T1/8 (3.2mm×3.2mm)
the decomposition of FeSO₃ prevents major pore blocking that may
have caused the rapid decrease in NO removal over Fe₂O₃. Fresh FeO
formed from decomposition of FeSO₃ may also be a very active reduc-
ing agent for NO. When a reducing gas is present, reduction of FeSO₃
back to FeS, will occur instead of its decomposition, preventing SO₂
evolution.

3. Reduction of NO with H₂ over Iron Oxide.

In addition to CO, H₂ is also an active reducing agent for NO
over both reduced iron oxide and iron sulfide. In Runs 18c and 19a,
fresh catalyst was reduced to FeO₁.₄₁ and FeO₁.₂₇ and then used to
catalyze the following reactions:

\[
\begin{align*}
\text{NO} + H₂ & \rightarrow \frac{1}{2} N₂ + H₂O & \Delta H_{25°C} & -79.4 \\
\text{NO} + \frac{5}{2} H₂ & \rightarrow NH₃ + H₂O & \Delta H_{370°C} & -90.4 \\
\end{align*}
\]

\[
\begin{align*}
\text{NH₃ selectivity} &= \frac{[NH₃]}{2[N₂]+[NH₃]} \times 100 \\
\end{align*}
\]

Figure iv-14 shows results of those runs in which there was
complete NO removal. The final value of the NH₃ selectivity was 23%
and 30%, respectively. NH₃ selectivity is the percent reduced N
formed from NO in the form of NH₃. Determinations of instantaneous
NH₃ selectivities were based on N₂ gas chromatographic (G.C.) peaks.
The material balances for H₂ and N₂ had 18% and 22% error in run 18d;
8% and 12% in Run 19b. The large error in Run 18d was cause by H₂O
and NH₃ adsorbing to an appreciable extent on catalyst pellets at
370°C. This adsorption produced a chromatographing effect of H₂O
Fig. iv-14. Reduction of NO with H₂ over reduced iron oxide and sulfide. Percent NH₃ selectivity and percent removal.

Run  | 18d | 19b | 21c
--- | --- | --- | ---
T (°C) | 379 | 377 | 372
θ (sec) | 0.49 | 0.47 | 0.51
[NO]% | 0.50 | 0.42 | 0.33
[H₂]% | 2.44 | 2.3 | 0.43
Solid(I) | FeO₁.41 | FeO₁.27 | FeO₁.4₅S₆₀
Symbol | O | □ | △

Fe-301-T 1/8 (3.2mm×3.2mm)
and NH$_3$ through the bed. In Run 18d, sampling and material balances were terminated when inlet gases were cutoff, while in Run 19b, sampling and material balances continued until NH$_3$ and H$_2$O peaks were negligible. This procedure required an additional sampling time of 30 minutes.

4. Reduction of NO with H$_2$ over Iron Sulfide.

Run 21c was conducted after the reduced oxide had been sulfided. These results are presented in Figure iv-14. As before, complete NO removal was obtained. NH$_3$ selectivity was noticeably higher even though there was a lower stoichiometric ratio between H$_2$ and NO. The 54% NH$_3$ selectivity measured corresponds to all the H$_2$ forming NH$_3$. The N$_2$ formed was probably from excess NO oxidizing the surface. Had more H$_2$ been present, a higher NH$_3$ selectivity might have resulted.

5. Reaction of NO and H$_2$O with Iron Oxide or Iron Sulfide.

Since both reduced iron oxide and iron sulfide were found to be capable of reducing NO to N$_2$ without any other reducing agent, their ability to form NH$_3$ from a stream of NO and H$_2$O was tested in Run 24. Both substances were capable of forming NH$_3$. Figure iv-15 shows the percent removal NO and the NH$_3$ selectivity for each trial. Higher NO removals and higher NH$_3$ selectivity obtained in Run 24d implies that regardless of the reducing agent present in the gas phase, iron sulfide will reduce most of the NO to NH$_3$ if H$_2$O is present. The decrease in sulfur content of the solid in Run 24d was determined from the quantity of the precipitate, NH$_4$HS, in the outlet line. NH$_3$ and H$_2$S were not detected in the G.C. sample. NH$_3$ and H$_2$S elutions were close to the same values since no NH$_3$
Fig. iv-15. Reaction of NO+\text{H}_2\text{O} with either iron oxide or iron sulfide.

Run \hspace{1em} 24b \hspace{1em} 24d

$T(°C)$ \hspace{1em} 372 \hspace{1em} 372

$\theta$ (sec) \hspace{1em} 0.45 \hspace{1em} 0.45

$[\text{NO}]$ \hspace{1em} 0.45\% \hspace{1em} 0.47\%

$[\text{H}_2\text{O}]$ \hspace{1em} 1.3\% \hspace{1em} 1.5-2.5\%

Solid(I) \hspace{1em} FeO$_{1.13}$ \hspace{1em} FeO$_{0.5}$S$_{0.76}$

Solid(F) \hspace{1em} FeO$_{1.26}$ \hspace{1em} FeO$_{1.23}$S$_{0.14}$

Symbol \hspace{1em} $\Delta$ \hspace{1em} O

$\Delta^S$ = NH$_3$ selectivity \hspace{1em} Fe-301-T 1/8

Fe-301-T 1/8 \hspace{1em} (3.2mm$\times$3.2mm)
collected in the HCl scrubber and no H$_2$S was detected in the G.C. samples.

NH$_4$HS is formed by reaction of equivalent amounts of NH$_3$ and H$_2$S. The decomposition temperature of NH$_4$HS is 118°C (Handbook Chemistry & Physics). Ammonium sulfide, (NH$_4$)$_2$S, is formed in an excess of NH$_3$. It is stable only below -18°C (Kirk, 1963). At ambient conditions, it loses NH$_3$ and changes to NH$_4$HS. There are also a number of ammonium polysulfides possible but their definite compositions are rather uncertain.

6. Reduction of NO with CO and H$_2$O over Iron Sulfide.

The presence of CO in the NO-H$_2$O-FeS system gave NH$_3$ selectivities over 90%. Figure iv-16 shows data from two runs with a sulfided catalyst. In both cases complete NO removal was achieved. Because N$_2$ evolutions were very small in both cases, there is no real difference between the apparent 91% and 96% NH$_3$ selectivities. At 204 minutes into Run 24f, the H$_2$O feed was terminated. Immediately, N$_2$ was generated as seen by the decreased NH$_3$ selectivity. A significant difference between these two runs is that no sulfur was removed from the catalyst in Run 22d while a significant amount was stripped off in Run 24f. Removal was evident by the absence of NH$_3$ in the gas sample and precipitation of ammonium salts in the lines.

An important parameter in these runs was the reducing or oxidizing character of the gas stream. Reduction of 1 mole of NO to form 1 mole of N$_2$ requires either 1 mole of H$_2$ or CO. To form NH$_3$ from NO requires 2.5 moles of H$_2$ or CO per mole of NO. Formation of a
Fig. iv-16. Reduction of NO with CO+H₂O over iron sulfide.

<table>
<thead>
<tr>
<th>Run</th>
<th>22d</th>
<th>24f</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(°C)</td>
<td>374</td>
<td>373</td>
</tr>
<tr>
<td>θ (sec)</td>
<td>0.49</td>
<td>0.44</td>
</tr>
<tr>
<td>[NO]</td>
<td>0.58%</td>
<td>0.46%</td>
</tr>
<tr>
<td>[CO]</td>
<td>1.1%</td>
<td>0.40%</td>
</tr>
<tr>
<td>H₂O%</td>
<td>3.4</td>
<td>2.2-2.8</td>
</tr>
<tr>
<td>Solid(I)</td>
<td>FeO.27S.97</td>
<td>FeO.71S.65</td>
</tr>
<tr>
<td>Solid(F)</td>
<td>FeO.17S.97</td>
<td>FeO.68S.46</td>
</tr>
</tbody>
</table>

Fe-301-T 1/8 (3.2mm×3.2mm)
sulfide from $SO_2$ requires 3 moles of $H_2$ or $CO$ per mole of $SO_2$.

Reduction of $O_2$ requires 2 moles of $H_2$ or $CO$ per mole of $O_2$. The following definitions are used in the remainder of the text:

\[
\frac{\text{oxidizing equivalents}}{\text{reducing equivalents}} = R
\]

\[
(O/R)N_2 = (\{NO\} + 3\{SO_2\} + 2\{O_2\})/([H_2] + [CO])
\]

\[
(O/R)NH_3 = (2.5[NO] + 3[SO_2] + 2[O_2])/([H_2] + [CO])
\]

Run 24f was made under oxidizing conditions, $(O/R)NH_3 = 2.88$, which could have enabled $SO_2$ to escape and form $(NH_4)_2SO_3$ with effluent $NH_3$. After the $H_2O$ was cut off there was no $H_2$ source for $NH_3$ formation. The system was then close enough to stoichiometric with respect to $N_2$ formation, $(O/R)N_2 = 1.15$, so that no $SO_2$ eluted and no precipitate formed.

7. Summary NO removal reactions.

This series of studies showed that $H_2$, $CO$, $FeO$, and $FeS$ can act either in combination or independently as reducing agents for NO. When either $H_2$ or $H_2O$ is present, both $N_2$ and $NH_3$ will be the products of NO reduction. $NH_3$ selectivity is greatest for a sulfided catalyst under reducing conditions with either $H_2$ or $CO$ and $H_2O$ as the reducing agents. When a source of hydrogen is available, the system must be net reducing with respect to $NH_3$ formation to prevent sulfur compounds from being stripped from the catalyst/absorbent.

D. Simultaneous Removal of Sulfur Compounds and Nitric Oxide at Low Temperatures.
The last section studied removal of NO over sulfided catalysts. In this section, the simultaneous removal of NO and the sulfiding of the catalyst/absorbent are discussed.

1. Reduction of NO with $H_2$S over Iron Sulfide.

The potential for the catalytic reduction of NO by $H_2$S over iron sulfide was studied first. Sulfur formation and sulfide formation reactions which are possible include the following:

\[
\begin{align*}
\text{NO} + H_2S & \rightarrow \\
\frac{1}{4}N_2 + H_2O + \frac{1}{4}S_2 & \rightarrow -59.2 \quad -56.7 \quad -56.0 \quad \text{iv-23} \\
FeO + H_2S & \rightarrow \\
FeS + H_2O & \rightarrow -11.9 \quad -9.25 \quad -9.57 \quad \text{iv-2} \\
\text{NO} + \frac{5}{2} H_2S & \rightarrow \\
NH_3 + \frac{5}{4} S_2 + H_2O & \rightarrow -39.8 \quad -31.1 \quad -28.6 \quad \text{iv-24} \\
\text{NO} + 3/2 H_2O + 5 \text{FeO} & \rightarrow \\
NH_3 + \frac{5}{4} \text{Fe}_2O_3 & \rightarrow -119 \quad -57.0 \quad -44.3 \quad \text{iv-25} \\
\frac{1}{2} S_2 + 2 \text{NO} & \rightarrow \\
SO_2 + N_2 & \rightarrow -130 \quad -115 \quad -111.0 \quad \text{iv-26} \\
FeO + \text{NO} + 2 H_2S & \rightarrow \\
\frac{1}{4} N_2 + 2 H_2O + FeS_2 & \rightarrow -106.3 \quad -81.8 \quad -76.0 \quad \text{iv-27}
\end{align*}
\]

In Run 22c, 1.1% $H_2S$ and 0.55% NO were passed over iron sulfide. Complete NO and $H_2S$ removal resulted. \(NH_3, N_2, H_2O,\) and precipitate
were present in the outlet line. The precipitate indicated that some \( \text{H}_2\text{S} \) possibly eluted from the bed. The precipitate was yellowish-white in color with a crystalline appearance suggesting a mixture of ammonium salts and sulfur. Data for this run are given in Figure iv-17. Since the catalyst was almost completely sulfided at the start of the run, reactions iv-2 and iv-27, (surface sulfiding) probably did not occur to any significant extent. The reported loss of \( \text{S} \) from the surface is within the experimental error. Reactions generating \( \text{N}_2 \) and \( \text{NH}_3 \) occur at the start of the run with reactions generating \( \text{NH}_3 \) predominating after the first hour. All of the collected precipitate was water soluble and had a significant partial pressure of \( \text{NH}_3 \). As noted earlier, \( \text{NH}_4\text{HS} \) has a high \( \text{NH}_3 \) partial pressure. If reaction iv-26 occurred, another possibility would be \((\text{NH}_4)_2\text{SO}_3\), which also decomposes giving \( \text{NH}_3 \). Since essentially 100\% \( \text{H}_2\text{S} \) removal was found there must have either been some sulfur which precipitated upstream of the condenser or ammonium polysulfides formed in the low temperature precipitates.

As noted in the change of solid composition in Figure iv-17, the surface was oxidized, possibly by a reaction such as iv-25. Net surface oxidization implies that even with sulfur present as \( \text{H}_2\text{S} \), a reducing agent will be needed to maintain an active reduced catalyst.

2. Removal of \( \text{NO} \) and \( \text{H}_2\text{S} \) with \( \text{H}_2 \) over Iron Oxide.

In Run 21a, \( \text{H}_2 \) was used as the reducing agent to remove \( \text{H}_2\text{S} \) and \( \text{NO} \) over fresh \( \text{Fe}_2\text{O}_3 \). Figure iv-18 presents the results. In this
Fig. iv-17. Reduction of NO with H₂S.

Run 22c
T(°C) 366
[NO] 0.55%
[H₂S] 1.1%
Solid(I) Fe₅₀S₁₀
Solid(F) FeO₅₇S₉₇

O H₂S removal
□ NO removal
△ NH₃ selectivity

Fe-301-T 1/8
(3.2mmx3.2mm)
Fig. iv-18. Simultaneous removal of NO and \( \text{H}_2\text{S} \) with \( \text{H}_2 \). Part a, 0-428 minutes. Part b, 428-495 minutes.

- **Run**: 21a, 21b
- **T (°C)**: 372, 372
- **\( \theta \) (sec)**: 0.49, 0.50
- **[NO]**: 0.33%, 0.33%
- **[\( \text{H}_2 \)]**: 3.1%, 0.43%
- **[\( \text{H}_2\text{S} \)]**: 1.97%, 1.97%
- **Solid(I)**: FeO\(_{1.5}\), FeO\(_{2.3}\text{S}_{0.76}\)
- **Solid(F)**: FeO\(_{2.2}\text{S}_{0.96}\), FeO\(_{2.3}\text{S}_{1.2}\)

Fe-301-T 1/8
(3.22 mm \times 3.2 mm)
run there was a large excess of $H_2$, 3.8 times the stoichiometric amount for $NH_3$ formation. This large $H_2$ excess and the presence of $H_2S$ resulted in 100% $NH_3$ selectivity over the entire run. The solid was not only sulfided but also reduced. In Run 21b, $H_2$ was decreased to 0.52 times the stoichiometric amount for $NH_3$ formation. The reactivity of $H_2S$ with NO was seen immediately by the large increase in $H_2S$ removal. Although $H_2$ removal increased, the absolute amount of $H_2$ reacting in the system decreased.

3. Removal of NO and $H_2S$ with both CO and $H_2$ over Iron Oxide.

Run 22a used both CO and $H_2$ to remove $H_2S$ and NO. Figure iv-19 reports the data. In this run the NO removal was 100% and the $NH_3$ selectivity was 100%. CO reacts to a greater extent in the system than $H_2$, reporting about 90% removal while the $H_2$ removal was about 30%.

4. Removal of NO and $H_2S$ with CO over Iron Sulfide.

After Run 22a $H_2O$ and $H_2$ were cut off and the [CO] increased. Figure iv-20 shows the data for Run 22b. As before, all NO was converted to $NH_3$. The H source in this run was $H_2S$ causing the initial increase in $H_2S$ removal. As the bed is sulfided $H_2S$ removal decreases back to the level in Run 22a. Excess CO with respect to the $NH_3$ reaction slightly reduced the solid. Figures iv-18 and 19 show 50% $H_2S$ removal at 193 and 115 minutes, respectively. These times are within those reported in Figure iv-3 for sulfidation of reduced iron in the absence of NO and reducing agents. The longer time above 50% $H_2S$ removal in Figure iv-18 is probably due to the
Fig. iv-19. Simultaneous removal of NO and H₂S with CO and H₂.

Fig. iv-20. Simultaneous removal of NO and H₂S with CO.

Run 22a 22b
T(°C) 371 371
θ (sec) 0.48 0.48
[NO] 0.52% 0.50%
[H₂] 1.2% 0%
[CO] 0.96% 2.0%
[H₂S] 2.0% 2.0%
[H₂O] 6.3% 0%
Solid(I) FeO₄.5 FeO₉₂S₆₁
Solid(F) FeO₉₂S₆₁ FeO₄₀S₁₄₁
Fe-301-T 1/8 (3.2mmX3.2mm)
stronger reducing atmosphere, i.e. Figure iv-18 \((O/R)N_2 = 0.106\) and Figure iv-19 \((O/R)N_2 = 0.238\).

5. Removal of NO and COS over Iron Sulfide.

The second sulfur compound tested for removal with NO was COS. A short test confirmed that this system also removed all of the NO as \(NH_3\). The potential reactions in this system would be:

\[
3 \text{H}_2\text{O} + 5 \text{COS} + 2 \text{NO} \rightarrow 5 \text{CO}_2 + 5/2 \text{S}_2 + 2 \text{NH}_3
\]

\[
\Delta H_{25°C} \quad \Delta F_{370°C} \quad \Delta F_{538°C} \\
\text{(kcal)} \quad \text{(kcal)} \quad \text{(kcal)}
\]

\[
-121.0 \quad -102 \quad -97.0 \quad \text{iv-28}
\]

\[
\text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2
\]

\[
-8.27 \quad -8.05 \quad -7.95 \quad \text{iv-29}
\]

Since both \(S_2\) and \(H_2S\) can form, reactions iv-24 and iv-26 could also occur. In Run 22e \([\text{COS}]\) was 0.23%; \([\text{NO}]\), 0.56%; \([\text{H}_2\text{O}]\), 4.0%. Complete removal of NO and COS resulted. The \(NH_3\) selectivity was 100%. The same type of precipitate developed in this run as in the \(H_2S + \text{NO}\) reactions, Section D.1. Final catalyst/absorbent analysis could not be calculated because the COS feed to the system was erratic. Since there was more NO than COS, the surface of the catalyst/absorbent was probably oxidized.

6. Removal of NO and \(SO_2\) with CO and \(H_2\) over Iron Oxide.

Simultaneous removal of NO and \(SO_2\) with CO and \(H_2\) over iron sulfide was studied in Runs 27e and 27f. Data from these runs are plotted in Figure iv-21 with the last 35 minutes from Run 27d, removal of \(SO_2\) with CO and \(H_2\). Introduction of 0.53% NO caused an increase in both CO and \(H_2\) removals. \(NH_3\) selectivity is about 80%. Complete
Fig. iv-21. Simultaneous removal of NO and SO$_2$ with H$_2$ and CO over iron sulfide. (Part f, 35-131 minutes; part g, 131-320 minutes.)

<table>
<thead>
<tr>
<th>Run</th>
<th>T(°C)</th>
<th>θ (sec)</th>
<th>[NO]</th>
<th>[SO$_2$]</th>
<th>[CO]</th>
<th>[H$_2$]</th>
<th>[H$_2$O]</th>
<th>Solid(I)</th>
<th>Solid(F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>f</td>
<td>374</td>
<td>0.43</td>
<td>0.53%</td>
<td>0.45%</td>
<td>3.9%</td>
<td>3.7%</td>
<td>0%</td>
<td>FeO.85S.26</td>
<td>FeO.92S.26</td>
</tr>
<tr>
<td>g</td>
<td>374</td>
<td>0.43</td>
<td>0.58%</td>
<td>0.44%</td>
<td>3.8%</td>
<td>3.7%</td>
<td>1.0%</td>
<td>FeO.72S.26</td>
<td>FeO.106S.26</td>
</tr>
</tbody>
</table>

Fe-301-T 1/8
(3.2mmX3.2mm)
NO and SO removal were obtained. SO did not sulfide the catalyst but was converted to COS and H2S which eluted from the bed. H2S reacted with eluted NH3 to precipitate as NH4HS. In Run 27f, H2O was added to the inlet gases. There was no immediate effect on the effluent gas. Toward the end of the run, though, the NH3 selectivity had increased to 95%. This suggests that H produced from the water-gas shift reaction may be more reactive than molecular H2 in NH3 formation. Klimisch (1972) reported this result for the Cu-Cr oxide system. COS and H2S eluted in this run. There was slight oxidation of the catalyst surface when H2O was present.

7. Removal of NO, H2S, and O2 with CO and H2 over Iron Oxide.

Experimental work reported to this point was done in the absence of O2. Since there may be some O2 present in the flue gas, experiments were run to determine its effect on NO and sulfur-compound removal. Runs 25a and 25b studied the effect of O2 on the removal of H2S and NO. Figure iv-22 reports the results. Almost immediately after starting the run, precipitate deposited in the outlet lines. The precipitate was NH4HS and S2. This was a much quicker breakthrough of H2S and COS than had previously occurred. Because some of the effluent H2S reacted to form the precipitate, actual H2S removal is only about 75% of that shown in the figure. At 160 minutes, H2S in the inlet gas was cut down, resulting in a higher percent removal of H2S and a lower percent removal for H2. The [COS] eluted was roughly constant at 0.08%. At 288 minutes both [CO] and [H2] were increased. This increase produced higher removals of H2 and lower removals of H2S. CO removal remained
Fig. iv-22. Simultaneous removal of NO, H$_2$S, O$_2$ with H$_2$ and CO.

Run  | 25a | 25b
---|---|---
T(°C) | 368 | 374
θ (sec) | 0.45 | 0.45
[NO] | 0.51% | 0.56%
[CO] | 1.1% | 1.4%
[O$_2$] | 0.55% | 0.62%
[H$_2$S] | 2.0-4.0% | 2.1%
[H$_2$O] | 1.7% | 1.4%
[H$_2$] | 1.1% | 1.3%
Solid(I) | FeO$_{1.5}$ | FeO$_{6.87}$
Solid(F) | FeO$_{6.87}$ | FeO$_{0.4S1.3}$

CO removal
H$_2$ removal
O$_2$ removal
NO removal
H$_2$S removal

Fe-301-T 1/8
(3.2mm×3.2mm)
constant. The NH$_3$ collected in both the HCl scrubber and in the precipitate corresponded to a selectivity of 80%. This is only slightly less than the 100% selectivity reported in the absence of O$_2$, over iron sulfide in Run 22a. Throughout this run, the catalyst remained active for reduction of NO and O$_2$. The early elution of sulfur compounds suggests that oxygen inhibits sulfidation. The ratio, (O/R)NH$_3$, was 1.08 and 0.98 for Runs 25a and 25b, respectively. This proximity to the stoichiometric ratio in the gas stream and the initially unreduced catalyst both contributed to the system oxygen.

8. Removal of NO, SO$_2$, and O$_2$ with CO and H$_2$ over Iron Oxide.

When SO$_2$ and higher O$_2$ levels were tested, Run 26a, the catalyst became inactive for reduction of NO and SO$_2$. The only reactions which continued were O$_2$ and Fe$_2$O$_3$ reduction. Figure iv-23 shows the deactivation with respect to all reactions followed by reactivation of all but the NO and SO$_2$ reduction. In this run, (O/R)N$_2$ was 1.02, oxidizing with respect to even the N$_2$ formation reactions. Since no NH$_3$ was formed, there was no precipitate in this run. A significant difference in this run is that H$_2$ removal is substantially greater than CO removal, even though both have the same concentration. When O$_2$ was absent, the reverse was noted.

A final system variable which was studied under these conditions was particle size. Simultaneous removal of NO, O$_2$, and SO$_2$ with CO was tested with 3.2-mm pellets and with particles .50-mm to .25-mm in size. In both cases, catalyst deactivation was noted. In Run 29b, the catalyst initially removed all the NO, SO$_2$, and O$_2$. After 80
Fig. iv-23. Simultaneous removal of NO, SO\(_2\), O\(_2\) with H\(_2\) and CO.

Run 26a
T(°C) 368
θ (sec) 0.45
[C\(_{\text{CO}}\)] 2.2%
[C\(_{\text{H}_2}\)] 2.2%
[C\(_{\text{O}_2}\)] 2.0%
[C\(_{\text{NO}}\)] 0.5%
[C\(_{\text{SO}_2}\)] 0.37%
Solid(I) FeO\(_{1.5}\)
Solid(F) FeO\(_{1.3}\)S\(_{0.1}\)

Fe-301-T 1/8
(3.2mm×3.2mm)
minutes on stream, it was eluting 6% and 12% of inlet NO and SO₂, respectively. O₂ was removed over the entire run. These data are presented in Figure iv-24. The NH₃ selectivity was about 30%, much lower than previously noted. In Run 29b (O/R)NH₃ was 1.10, slightly oxidizing with respect to total NH₃ product. If the 30% NH₃ selectivity is accounted for, the ratio is 0.98, slightly reducing. The outer layer of the catalyst near the bed exit was reduced. Had the run continued, the oxidation front would undoubtedly have passed through the entire bed.

In Run 30c there was a net oxidizing atmosphere and the entire bed of particles was oxidized. The 0.50-mm to 0.25-mm particles were exposed to a stream with (O/R)N₂ = 1.16, net oxidizing with respect to N₂ formation. As Figure iv-25 shows, all removals rapidly drop to zero. The order of decrease is the same as in Run 29b, SO₂ first, NO second, and O₂ third. This suggests a relative order of oxidizing power, O₂ being the most powerful. The specific effect of the smaller particle size at this temperature was masked by the deactivation. At the end of this run, the entire bed was oxidized. The particles were completely oxidized, exhibiting no reducing inner core as was seen in Run 29b.

9. Summary of simultaneous removal of NO and sulfur compounds.

Simultaneous removal of NO and sulfur compounds at 370°C is best accomplished with reduced iron oxide in a net reducing atmosphere which has no O₂ present. If O₂ is present, rapid catalyst deactivation will occur when the gas is net oxidizing. Even under net reducing conditions, slow catalyst oxidization will occur when O₂ is present in the gas stream. Smaller particles do not appear to slow or
Fig. iv-24. Simultaneous removal NO, O₂, SO₂ with CO.

Run 29b  [CO] 4.2-4.6%  [SO₂] 0.51%  Solid(I)  Fe₃O₄.23

T(°C) 374  [NO] 0.53%  [H₂O] 1.14%  Solid(F)  FeO₂.55.43

θ (sec) 0.44  [O₂] 1.0%  Fe-301-T 1/8 (3.2mm×3.2mm)
Fig. iv-25. Simultaneous removal of NO, O₂, SO₂ with CO.
Fe-301-T 1/8 (0.50mm-0.25mm)

<table>
<thead>
<tr>
<th>Run</th>
<th>T(°C)</th>
<th>θ (sec)</th>
<th>[CO]</th>
<th>[NO]</th>
<th>[O₂]</th>
<th>[SO₂]</th>
<th>[H₂O]</th>
<th>Solid(I)</th>
<th>Solid(F)</th>
<th>NH₃ selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30c</td>
<td>0.28</td>
<td>4.95%</td>
<td>0.61%</td>
<td>1.1%</td>
<td>0.98%</td>
<td>0.7-1.2%</td>
<td>Fe₂O₄.18</td>
<td>Fe₂O₄.25.29</td>
<td></td>
</tr>
</tbody>
</table>

XBL 745-3250
prevent catalyst deactivation.

The capability of NO to oxidize FeS forming SO\textsubscript{2} was shown. Since O\textsubscript{2} is a stronger oxidizer, it is capable of oxidizing FeS at least to the same extent and probably continuing to form sulfate. If FeSO\textsubscript{4} forms, as is expected thermodynamically, it can be reduced as follows:

\[
\begin{align*}
\Delta H_{25^\circ C} & \quad \Delta F_{370^\circ C} & \quad \Delta F_{538^\circ C} \\
(kcal) & \quad (kcal) & \quad (kcal) \\
FeSO_4 + 4 \text{ CO} & \rightarrow FeS + 4 \text{ CO}_2 & -72.7 & -74.1 & -76.4 & \text{ iv-30} \\
FeSO_4 + 4 \text{ H}_2 & \rightarrow FeS + 4 \text{ H}_2\text{O} & -33.4 & -58.7 & -66.5 & \text{ iv-31}
\end{align*}
\]

Kinetic limitations at 370°C may inhibit these reactions even under net reducing conditions. The upper temperature of 538°C may allow these reactions to proceed.

E. Simultaneous Removal of SO\textsubscript{2} and NO at High Temperatures.

Experiments reported in all previous sections are run at temperatures close to 370°C. In power plants this corresponds to the temperature of the flue gas at the inlet of the air preheater. The upper limit on the reaction zone is the inlet to the economizer. Temperatures here are about 540°C. Runs discussed in this section were at this temperature level.

1. Removal of NO, SO\textsubscript{2}, and O\textsubscript{2} with CO and H\textsubscript{2}O over Iron Oxide.

a. Long residence time runs.

Simultaneous removal of NO, SO\textsubscript{2}, and O\textsubscript{2} with CO and H\textsubscript{2}O over reduced iron oxide was studied in Runs 31b and 35b. The catalyst/
absorbent size was 3.2-mm pellets. The data are presented in Figures iv-26 and iv-27. Both runs maintained complete removal of NO and O₂ over the entire run. SO₂ was not completely removed. Estimation of SO₂ removal with time was not possible because eluted sulfur compounds formed ammonia salts. The average SO₂ removal is plotted starting when precipitate was first seen. The precipitate which formed was white and released NH₃ when heated. Tests confirmed that is was (NH₄)₂SO₃. NH₃ was also collected in the HCl scrubbers. These two sources gave average NH₃ selectivities for the runs of 64% and 69%, respectively. The precipitate formed most heavily toward the end of the run in both cases. The NH₃ selectivity increased with time in both runs. In Run 31b and 35b (O/R)NH₃ was 0.956 and 1.00. Both runs were thus net reducing, with Run 35b being slightly less so. The pellets at the end of each run were solid black and reflected no tendency to poison. The high removals achieved for all compounds over the entire bed suggest that the actual reaction time is less than the gas residence time in the bed. The CO removal begins to drop off only after 75% of the iron has been sulfided. This behavior suggests reaction times of the order of 0.10 second or less, 36,000 hr⁻¹ space time.

b. Short residence time runs

Runs 36b and 37b confirmed that reaction does occur in less than 0.10 second. A 6.4-mm ID. 316 stainless steel reactor gave residence times about 0.04 to 0.02 seconds, depending on the catalyst charge. In this smaller reactor 2 grams of catalyst corresponded to
Fig. iv-26. Simultaneous removal of NO, O₂, SO₂ with CO and H₂O.

Run 31b
θ (sec) 0.33
T(°C) 538
[NO] 0.58%
[O₂] 0.50%
[SO₂] 0.65%
[CO] 4.6%
[H₂O] 1.6%
Solid(I) FeO\(_{1.18}\)
Solid(F) FeS\(_{0.78}\)
○ CO removal
△ NO removal
● O₂ removal
— SO₂ avg. removal
◇ NH₃ selectivity

Solid(I) FeO\(_{1.18}\)
Solid(F) FeS\(_{0.78}\)

Fe-301-T 1/8
(3.2mm\times3.2mm)
Fig. iv-27. Simultaneous removal of NO, O₂, SO₂ with CO and H₂O.

<table>
<thead>
<tr>
<th>Run</th>
<th>35b</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ (sec)</td>
<td>0.34</td>
</tr>
<tr>
<td>[NO]</td>
<td>0.50%</td>
</tr>
<tr>
<td>[O₂]</td>
<td>0.49%</td>
</tr>
<tr>
<td>[SO₂]</td>
<td>0.48%</td>
</tr>
<tr>
<td>[CO]</td>
<td>3.7%</td>
</tr>
<tr>
<td>[H₂O]</td>
<td>1.8%</td>
</tr>
</tbody>
</table>

Solid(I) FeO₁₁.₁₇
Solid(F) FeS₀.₉₆

- O CO removal
- Δ NO removal
- O₂ removal
- SO₂ avg. removal Fe₃₀₁-T₁/₈
- NH₃ selectivity (3.2mm×3.2mm)
a residence time of about 0.034 seconds. This smaller volume cuts the sulfur breakthrough time 10-fold from that in the 3.2-mm reactor. With the SO₂ feed rates in Runs 36b and 37b, the calculated sulfur breakthrough times were 78 and 56 minutes, respectively. Figures iv-28 and 29 report the actual breakthrough times close to these values. Exact determination of the breakthrough curve was not possible with the existing analytical system.

In Figure iv-28, Run 36b, sulfur eluted in the form of H₂S and COS. Ammonia was collected both as precipitate and in the HCl scrubber. The average NH₃ selectivity for Run 36b was 48%. The oxidation level for this run was (O/R)N₂ = 0.81 and (O/R)NH₃ = 1.01. If 100% NH₃ selectivity had occurred anywhere in the bed, the atmosphere would have been net oxidizing. Although the bed remained reactive for the entire run, the catalyst at the end of the run was oxidized in the first half of the bed; both Fe₂O₃ and FeSO₄ were found to be present.

In Run 37b, Figure iv-29, the average NH₃ selectivity was 68%. The oxidation levels at the start were (O/R)N₂ = 0.84 and (O/R)NH₃ = 1.05. Producing 100% NH₃ locally would result in a net oxidizing atmosphere. This apparently occurred after 80 minutes, since all removals went below 10%. At 160 minutes the O₂ level was decreased to make (O/R)NH₃ = 0.85. Removals immediately increased. The O₂ was cycled again, and the same results occurred. When the system had a net reducing atmosphere with respect to NH₃ generation, the catalyst was active. It is significant to note that even though the catalyst was substantially sulfided in the first cycle, sulfur compounds
Fig. iv-28. Simultaneous removal of NO, O₂, sulfur compounds and CO.

Run 36b
T(°C) 370
[NO] (sec) 0.34
[NO] 0.50%
[O₂] 0.45%
[SO₂] 0.50% Fe-301-T 1/8
[CO] 3.6% (0.50mm-0.25mm)
[H₂O] 1.4%
Solid(I) FeO1.34
Solid(F) FeSO0.76
Fig. iv-29. Simultaneous removal of NO, O₂, sulfur compounds and CO.

<table>
<thead>
<tr>
<th>Run</th>
<th>37b</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(°C)</td>
<td>378</td>
</tr>
<tr>
<td>θ (sec)</td>
<td>0.031</td>
</tr>
<tr>
<td>[NO]</td>
<td>0.49%</td>
</tr>
<tr>
<td>[O₂]</td>
<td>Varied</td>
</tr>
<tr>
<td>[SO₂]</td>
<td>0.50%</td>
</tr>
<tr>
<td>[CO]</td>
<td>3.5%</td>
</tr>
<tr>
<td>[H₂O]</td>
<td>1.3%</td>
</tr>
<tr>
<td>Solid(I)</td>
<td>FeO₁.₃₀</td>
</tr>
<tr>
<td>Solid(F)</td>
<td>FeO₀.₆₃S₁.₀₆</td>
</tr>
</tbody>
</table>

Fe-301-T 1/8
(0.50mm-0.25mm)
stopped eluting immediately after the $O_2$ level was decreased. As in Run 36b, when the run was complete, the last half of the bed had remained active while the entrance had been oxidized during the run.

The sulfur compound elution pattern is shown in Figure iv-30. $H_2S$ initially breaks through followed by COS then $SO_2$. NO elutes at about the same time as $SO_2$, followed by $O_2$. This pattern was repeated twice. The third pattern appears to be the same, only slower. This suggests that the level of $O_2$ or the O/R ratio has a direct influence on the bed capacity.

In normal operating conditions, the catalyst/absorbent would not be used after complete sulfidization. Run 37b continued after complete sulfidization. Another extended run was made, Run 38, in which the CO level was varied at a constant $O_2$ level of 0.98%. Even under net reducing conditions, the sulfided catalyst rapidly deactivated. Reactivation only occurred when $O_2$ was removed from the inlet gases. This emphasizes the importance of maintaining reduced iron oxide in the catalyst/absorbent. Ferrous oxide is required both for the absorption of sulfur compounds and to prevent rapid catalyst deactivation.

2. Removal-Regeneration Cycles for NO, $SO_2$, and $O_2$ with CO over Iron Oxide.

In Runs 39 and 40, a cyclic removal/regeneration procedure was used to provide a high level of FeO when testing the catalyst activity. A larger, 9.5-mm reactor was used in this study to give longer breakthrough times for sulfur compounds. The charge of 2.6 grams of
Fig. iv-30. Distribution of sulfur compounds eluted in Run 37b.

- H$_2$S
- COS
- SO$_2$

(Detailed data, see Fig. iv-29.)
catalyst gave a residence time of 0.040 seconds. Calculated break-through times for sulfur compounds for Runs 39 and 40 were 69 minutes and 75 minutes, respectively. This longer time enabled at least two samples to be taken prior to breakthrough.

In Run 39 the actual breakthrough of $H_2S$ below 90% removal occurred between 50 and 70 minutes for the four trials. The data are presented in Figure iv-31. Complete $O_2$ and NO removal were achieved for all trials. The average $NH_3$ selectivity for these trials ranged between 53 and 64%. The $(O/R)N_2$ was 0.758 and $(O/R)NH_3$ was 0.896, reducing with respect to both $NH_3$ and $N_2$ formation.

The catalyst was regenerated in situ between each trial. The temperature was first raised to 670°C. The [$O_2$] in the regeneration gas stream in Run 39 was varied from 2% to 21%. The regeneration conditions are given in Figure iv-31. Air regeneration gave the catalyst with the highest sulfur capacity. All removal steps, however, appear comparable to the first.

Run 40 had removal conditions, parts b and e, similar to Run 39. The data are presented in Figure iv-32. The regeneration conditions, parts c,d and f,g were altered to determine sulfate levels in each half of the bed. Run 40b was with fresh catalyst and Run 40e was with the regenerated catalyst from Run 40d. After the removal steps, the black particles (reactor exit) were separated from the red (reactor entrance). Each half was heated to 693°C for one hour under stream of a He. Any $FeSO_4$ would decompose under these conditions. A stream with 1% $O_2$ was then introduced for one hour to oxidize the sulfide to $SO_2$. The $SO_2$ generated in steps c,d and f,g was collected in
Fig. iv-31. Percent removal of S-compounds, NO, CO versus run time with four successive removals. Run No. 39.

Removal conditions

\[
\begin{align*}
[\text{NO}] &= 0.50\% \\
[\text{CO}] &= 5.5\% \\
[\text{SO}_2] &= 0.56\% \\
[\text{O}_2] &= 1.0\% \\
[H_2O] &= 1.7.
\end{align*}
\]

Removal at:

\( T = 560^\circ\text{C} \)

\( \theta = 0.04 \text{ sec} \)

Fe-301-T1/8 (0.50mm-0.25mm)

Regeneration conditions

\[
\begin{align*}
1\text{st} & \quad 4\% [\text{O}_2] \text{ for 66 min.} \\
2\text{nd} & \quad 2\% [\text{O}_2] \text{ for 129 min.} \\
3\text{rd} & \quad 21\% [\text{O}_2] \text{ for 63 min.}
\end{align*}
\]

Regeneration at:

\( T = 670^\circ\text{C} \)

\( \theta = 0.038 \text{ sec} \)
Fig. iv-32. Removal of S-compounds, NO, CO versus run time.

Removals:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>0.53%</td>
</tr>
<tr>
<td>O₂</td>
<td>1.0%</td>
</tr>
<tr>
<td>CO</td>
<td>5.55%</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.53%</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.7%</td>
</tr>
</tbody>
</table>

Renewals:

- Fe-301-T 1/8 (0.50mm-0.25mm)
- [O₂] 0.53% T = 693°C 1%[O₂] for 65 minutes
- [H₂O] 1.7% T = 675°C 0%[O₂] for 60 minutes
- θ = 0.038 sec
- T = 599°C
NaOH scrubber solutions. Sulfate was found in both reduced and oxidized particles. The two bed sections were then combined and recharged to the reactor for the second removal step. The results are summarized below:

Table iv-2. Sulfate level in reacted catalyst/absorbent.

<table>
<thead>
<tr>
<th>Run</th>
<th>Reduced, Black (Bed Exit)</th>
<th>Oxidized, Red (Bed Entrance)</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
<td>40b-c,d 40e-f,g</td>
<td>40b-c,d 40e-f,g</td>
<td>40b-c,d 40e-f,g</td>
</tr>
<tr>
<td>S as SO₄²⁻ (%)</td>
<td>11.6 13.3 64 48.1 23.0 18.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S as S (%)</td>
<td>88.4 86.7 36 52.9 77.0 81.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The O₂ in the sulfate corresponded to only 17 and 21% of the total O₂ in the feed for Runs 40b and 40e, respectively. Removal of the remaining O₂ was by reaction with CO. Integration of the curve area and solid analysis from the second regeneration show about the same capacity. Both trials had an NH₃ selectivity of 45%. In Run 40 the (O/R)N₂ was 0.80 and (O/R)NH₃ was 0.94, both net reducing.

In Run 39, each trial resulted in an S/Fe ratio of around 0.60 to 0.70. In Run 40, the S/Fe ratio was between 0.90 and 1.0. Comparison of the O/R ratios would suggest that Run 39 should have been more strongly sulfided. The increased temperature of Run 40, 39°C higher than Run 39, may account for the higher sulfidation level.

These two runs have demonstrated the activity and regenerability of the catalyst even when 1% O₂ is present in the inlet stream. This oxygen level results in between 15 to 25% of the sulfur forming sulfate. The oxygen consumed in this sulfate formation is only 15 to 20% of the inlet O₂ feed.
F. Ammonia Generation

Numerous runs have been discussed in which either NH$_3$ or ammonia-sulfur salts were formed. Jones (1971) and Klimisch (1972) have shown that the presence of oxygen will decrease ammonia selectivity during NO reduction. A correlation between both this effect and the effect of the oxidizing or reducing nature of the catalyst/absorbent on NH$_3$ selectivity was found. Figure iv-33 shows the effect on the NH$_3$ selectivity of the product of the ratio of the moles of oxide to moles of sulfide in the solid with the ratio of oxidation to reduction equivalents in the inlet gas. The ratio for the oxide to sulfide is an average of initial and final conditions. This procedure is not strictly correct since initially no sulfide is present and at the end there is a large amount of sulfide. The qualitative trend on this graph is important: the greater the reducing equivalents in the gas or the more sulfide on the solid, the greater will be the NH$_3$ selectivity. This correlation is for runs between 370° and 590°C. NH$_3$ is unstable relative to N$_2$ and H$_2$ at and above 370°C for the concentrations used in this experiment. Shelef (1972) reports NH$_3$ decomposition at the upper temperature limit with an iron oxide catalyst. There is no apparent decomposition in these runs since all runs have about the same dependence on the combined factor. Runs with copper and nickel, reported in the next two sections, were made to test the potential of these metals to produce lower NH$_3$ selectivities.

G. Simultaneous Removal of SO$_2$, NO and O$_2$ with Copper Oxide and Nickel Oxide.
Fig. iv-33. NH₃ selectivity as a function of solid and gas composition.

<table>
<thead>
<tr>
<th>Run</th>
<th>[NO]</th>
<th>[SO₂]</th>
<th>[CO]</th>
<th>[H₂]</th>
<th>[O₂]</th>
<th>[H₂O]</th>
</tr>
</thead>
<tbody>
<tr>
<td>19d</td>
<td>0.38</td>
<td>0</td>
<td>0</td>
<td>2.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22d</td>
<td>0.58</td>
<td>0</td>
<td>1.1</td>
<td>0</td>
<td>0</td>
<td>3.4</td>
</tr>
<tr>
<td>26c</td>
<td>0.50</td>
<td>0.95</td>
<td>3.7</td>
<td>3.6</td>
<td>2.0</td>
<td>4.9</td>
</tr>
<tr>
<td>27a</td>
<td>0.50</td>
<td>0.41</td>
<td>3.6</td>
<td>3.6</td>
<td>2.0</td>
<td>1.4</td>
</tr>
<tr>
<td>27e</td>
<td>0.53</td>
<td>0.44</td>
<td>3.9</td>
<td>3.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>27f</td>
<td>0.55</td>
<td>0.44</td>
<td>3.8</td>
<td>3.7</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>27g</td>
<td>0.53</td>
<td>0.45</td>
<td>3.7</td>
<td>3.6</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>29c</td>
<td>0.53</td>
<td>0.50</td>
<td>4.6</td>
<td>0</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>30c</td>
<td>0.61</td>
<td>0.98</td>
<td>4.9</td>
<td>0</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>35b</td>
<td>0.50</td>
<td>0.48</td>
<td>3.7</td>
<td>0</td>
<td>0.49</td>
<td>1.8</td>
</tr>
<tr>
<td>36b</td>
<td>0.50</td>
<td>0.50</td>
<td>3.6</td>
<td>0</td>
<td>0.45</td>
<td>1.3</td>
</tr>
<tr>
<td>37b</td>
<td>0.49</td>
<td>0.50</td>
<td>3.5</td>
<td>0</td>
<td>0.48</td>
<td>1.3</td>
</tr>
<tr>
<td>39d</td>
<td>0.49</td>
<td>0.56</td>
<td>5.5</td>
<td>0</td>
<td>1.0</td>
<td>1.7</td>
</tr>
<tr>
<td>40b</td>
<td>0.53</td>
<td>0.53</td>
<td>5.6</td>
<td>0</td>
<td>1.0</td>
<td>1.7</td>
</tr>
</tbody>
</table>

O T = 370-380°C, \( \theta = 0.5-0.7 \) sec
△ T = 538-590°C, \( \theta = 0.02-0.04 \) sec
(Fe-301-T1/8)
1. Removal with Copper Oxide.

Copper Oxide was reported to accomplish simultaneous SO$_2$ and NO removal by forming S$_2$ and N$_2$ (Quinlan, 1973 and Ryason, 1967). A similar copper catalyst was tested for its ability to remove SO$_2$ as a sulfide and NO as N$_2$ and NH$_3$. The catalyst was Harshaw Cu-0803T1/8 which has 10% CuO deposited on activated Al$_2$O$_3$. The 3.2-mm pellet size was used. The catalyst was first reduced with CO to CuO$_{0.15}$. Calculated breakthrough time for the sulfur compounds is 129 minutes assuming Cu$_2$S formation. Figure iv-34 presents the data. NO, O$_2$, and SO$_2$ were completely removed. CO removal dropped at first then increased to about 100% toward the end of the run. Sulfur compound removal reflects elution of COS during the first 150 minutes. The large breakthrough after 150 minute is H$_2$S. NH$_3$ selectivity constantly increased over the run. The average value from the HCl scrubber and precipitate was 73%. In this run (O/R)N$_2$ was 0.714 and (O/R)NH$_3$ was 0.95, net reducing. If all NO had been converted locally to NH$_3$, a condition close to stoichiometric, within experimental error, may have occurred. Quinlan (1973) assumed that the water-gas shift reaction did not proceed and hence no NH$_3$ could be formed. They could have missed generated NH$_3$ since they did not analyze for it. At the start of Run 33b, when O was being removed from the catalyst, the system may have gone slightly oxidizing, causing elution of CO and COS. With iron oxide in Runs 31b and 35b, SO$_2$ eluted throughout the runs instead of COS. This fact implies that copper has higher catalytic activity for SO$_2$ reduction but that iron is more reactive with the H$_2$S or COS which are produced.
Simultaneous removal of $SO_2$, NO, CO, and $O_2$ over copper oxide catalyst.

Run 33b

$T$ (°C) 538

$\theta$ (sec) 0.33

$[NO]$ 0.50%

$[O_2]$ 0.50%

$[SO_2]$ 0.50%

$[CO]$ 4.2%

$[H_2O]$ 1.9%

Solid (I) CuO, 15

Solid (F) CuS, 59

△ NO removal

● $O_2$ removal

□ Sulfur compounds

○ CO removal

◊ NH₃ selectivity

Cu-0803-T 1/8

(3.2mmX3.2mm)
2. Removal with Nickel Oxide.

A combination of nickel and iron oxides was tested to see if the amount of $\text{NH}_3$ produced could be decreased. Klimisch (1973) has demonstrated the ability of Ni to decompose $\text{NH}_3$ on a Pt-Ni-Al catalyst at 500°C. The iron was to function as it had in previous runs while the nickel was to decompose the $\text{NH}_3$ which formed.

Run 41 was identical with Run 40 except that the first half of the bed was Fe-0301 and the second half was Ni-301 catalyst. Both catalysts were ground to 0.50-0.25-mm in size, $\text{NH}_3$ selectivities for the two parts were 27% and 41%, respectively. These values are only slightly lower than for the iron oxide runs. The data are presented in Figure iv-35. Calculated breakthrough times for parts a and c are 65 minutes and 75 minutes, respectively. The two-step regeneration was used separately on the iron and nickel portions after each trial. The reported S/Ni values were 1.29 and 1.26 while the S/Fe values were 0.48 and 0.65. The overall sulfate level was 26%, most of which was in the iron. Contamination of the nickel portion of the catalyst bed with some of the iron probably caused the high S/Ni ratio.

3. Summary of Copper and Nickel Runs

These runs show that although both nickel and copper catalysts are active for the proposed removal reactions neither significantly lowers the $\text{NH}_3$ selectivity or inhibits the formation of sulfate. The reactions forming the copper and nickel sulfides and sulfates are:
Fig. iv-35. Removal of sulfur compounds, NO, O₂ and CO.
Two successive cycles. Run No. 41.

Removals:
- [NO] 0.53%
- [O₂] 1.0%
- [CO] 5.6%
- [SO₂] 0.58%
- [H₂O] 1.7%
- $\theta = 0.043 \text{ sec}$
- $T = 600°C$

Regeneration:
- $T = 671°C$  $[O₂] = 0\%$
- $T = 695°C$  $[O₂] = 1\%$
\[
\begin{array}{l}
\text{2 CuO + CO} \rightarrow \\
\text{Cu}_2\text{O} + \text{CO}_2 \\
\Delta H_{25^\circ\text{C}} = -32.8 \text{ (kcal)} \\
\Delta F_{25^\circ\text{C}} = -36.2 \text{ (kcal)} \\
\Delta F_{370^\circ\text{C}} = -36.9 \text{ (kcal)} \\
\Delta F_{676^\circ\text{C}} = \text{iv-32}
\end{array}
\]

\[
\begin{array}{l}
\text{Cu}_2\text{O} + \text{SO}_2 + 3 \text{ CO} \rightarrow \\
\text{Cu}_2\text{S} + 3 \text{ CO}_2 \\
\Delta F_{25^\circ\text{C}} = -110.5 \text{ (kcal)} \\
\Delta F_{370^\circ\text{C}} = -87.1 \text{ (kcal)} \\
\Delta F_{676^\circ\text{C}} = -81.1 \text{ (kcal)} \\
\text{iv-33}
\end{array}
\]

\[
\begin{array}{l}
\text{NiO + SO}_2 + 3 \text{ CO} \rightarrow \\
\text{NiS} + 3 \text{ CO}_2 \\
\Delta F_{25^\circ\text{C}} = -92.1 \text{ (kcal)} \\
\Delta F_{370^\circ\text{C}} = \text{(Not Known)} \\
\Delta F_{676^\circ\text{C}} = \text{iv-34}
\end{array}
\]

\[
\begin{array}{l}
\text{CuSO}_4 \rightarrow \\
\text{CuO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \\
\Delta F_{25^\circ\text{C}} = +75.64 \text{ (kcal)} \\
\Delta F_{370^\circ\text{C}} = +54.72 \text{ (kcal)} \\
\Delta F_{676^\circ\text{C}} = +13.37 \text{ (kcal)} \\
\text{iv-35}
\end{array}
\]

\[
\begin{array}{l}
\text{NiSO}_4 \rightarrow \\
\text{NiO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \\
\Delta F_{25^\circ\text{C}} = +84.74 \text{ (kcal)} \\
\Delta F_{370^\circ\text{C}} = +61.52 \text{ (kcal)} \\
\Delta F_{676^\circ\text{C}} = \text{iv-36}
\end{array}
\]

Lowell (1971) lists the decomposition temperatures of CuSO\textsubscript{4} and NiSO\textsubscript{4} as 840-935°C and 730-890°C, respectively. In the regeneration runs, 1% O\textsubscript{2} was used at 675°C. These conditions only partially regenerated copper oxide. A comparison of SO\textsubscript{2} collected in the scrubber with that on the solid showed that CuO was only 50% regenerated. The dark greenish color present is characteristic of CuSO\textsubscript{4}. The same comparison for nickel showed that it was almost completely regenerated. The catalyst was a faint green color which is the characteristic color of NiO.

H. Oxidation of CO and H\textsubscript{2}.

One of the process requirements is that the flue gas have a net
reducing atmosphere. Excess CO or $H_2$ needs to be removed by oxidation with oxidized catalyst to prevent discharge into the atmosphere.

Reactions for the iron oxide system include the following:

$$\begin{align*}
\text{Fe}_2O_3 + CO & \rightarrow 2 \text{FeO} + CO_2 \\
2 \text{FeO} + CO_2 & \rightarrow \Delta H_{25°C} = +1.57 \quad \Delta F_{370°C} = -6.96 \quad \Delta F_{538°C} = -7.77 \\
3 \text{Fe}_2O_3 + CO & \rightarrow 2 \text{Fe}_3O_4 + CO_2 \\
2 \text{Fe}_3O_4 + CO_2 & \rightarrow \Delta H_{25°C} = -12.83 \quad \Delta F_{370°C} = -20.42 \quad \Delta F_{538°C} = -23.28 \\
\text{Fe}_2O_3 + H_2 & \rightarrow 2 \text{FeO} + H_2O \\
2 \text{FeO} + H_2O & \rightarrow \Delta H_{25°C} = +11.4 \quad \Delta F_{370°C} = -3.28 \quad \Delta F_{538°C} = -5.50 \\
3 \text{Fe}_2O_3 + H_2 & \rightarrow 2 \text{Fe}_3O_4 + H_2 \\
2 \text{Fe}_3O_4 + H_2 & \rightarrow \Delta H_{25°C} = -3.0 \quad \Delta F_{370°C} = -16.8 \quad \Delta F_{538°C} = -20.9
\end{align*}$$

1. CO Oxidation.

Oxidation of CO was studied in more detail than that of $H_2$, since a greater percentage of the reducing agent will be CO, see Chapter V.

The data are presented in Figure iv-36. A 60% maximum CO removal was achieved with the 3.2-mm pellets of $\text{Fe/Al}_2O_3$ in Runs 14a, 15a, and 24a. When the CO level was decreased and the particles were sized 0.50-0.25-mm, close to 100% CO removal was initially achieved. As in other runs, CO removal drops off rapidly. Higher removals with smaller particles suggests that diffusion limits the extent of reaction in the larger particles. Raising the temperature to 538°C with the larger pellets also produced removals close to 100%. In all runs
Fig. iv-36. Oxidation of CO with iron oxide. Long residence time.

<table>
<thead>
<tr>
<th>Run</th>
<th>14a</th>
<th>15a</th>
<th>24a</th>
<th>30a</th>
<th>31a</th>
<th>35a</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(°C)</td>
<td>378</td>
<td>368</td>
<td>407</td>
<td>370</td>
<td>538</td>
<td>538</td>
</tr>
<tr>
<td>θ (sec)</td>
<td>0.55</td>
<td>0.52</td>
<td>0.43</td>
<td>0.29</td>
<td>0.33</td>
<td>0.34</td>
</tr>
<tr>
<td>[CO] (%)</td>
<td>1.7</td>
<td>1.6</td>
<td>2.0</td>
<td>0.50</td>
<td>2.9</td>
<td>3.0</td>
</tr>
<tr>
<td>Solid(I)</td>
<td>FeO1.5</td>
<td>FeO1.5</td>
<td>FeO1.5</td>
<td>FeO1.5</td>
<td>FeO1.5</td>
<td>FeO1.5</td>
</tr>
<tr>
<td>Solid(F)</td>
<td>FeO1.34</td>
<td>FeO1.25</td>
<td>FeO1.13</td>
<td>FeO1.18</td>
<td>FeO1.18</td>
<td>FeO1.19</td>
</tr>
<tr>
<td>Symbol</td>
<td>O</td>
<td>△</td>
<td>□</td>
<td>▽</td>
<td>◊</td>
<td>●</td>
</tr>
<tr>
<td>Size(mm)</td>
<td>3.2</td>
<td>3.2</td>
<td>0.5-0.25</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Fe-301-T 1/8
where CO removal was 100% in the first sample, the outlet CO\textsubscript{2} did not equal inlet CO flow. As the run progressed, the total CO\textsubscript{2} + CO did equal the inlet CO within the experimental error. It is suspected that adsorption of CO or CO\textsubscript{2} occurs. This phenomenon was briefly discussed in connection with Run 15, Section C.1. The initial high removal for the low CO is in part due to CO adsorption.

Another set of runs with a much shorter residence time is illustrated in Figure iv-37. These runs were with 0.50-0.25-mm sized particles. A rapid drop-off of CO removal is shown for the 1% CO runs. Run 38a with CO 0.38% shows a much slower drop-off with time.

CO removals in both Runs 30a and 38a remained high since the time required to reduce the surface is longer with the low CO concentration. If diffusion or first-order kinetic limitations predominated, the percent removal should be unaffected by the CO concentration. The variation can be explained by an initially active surface followed by a progressively less active surface species. This fact would suggest that, in order of decreasing activity toward CO, the iron oxides would rank Fe\textsubscript{2}O\textsubscript{3} > Fe\textsubscript{3}O\textsubscript{4} > FeO.

Some of the excess CO may also be oxidized by unreacted O\textsubscript{2} in the gas stream. In Run 8 the CO + O\textsubscript{2} reaction was studied over both reduced and oxidized iron. The data are present in Figure iv-38. O\textsubscript{2} removal was 100% in the two cases. In the net reducing system, the solid was reduced in both cases. After 100 minutes, both Runs 8b and 8d had CO removals which corresponded to only the O\textsubscript{2} oxidation, demonstrating the catalytic ability of iron oxide.
Fig. iv-37. Oxidation of CO with iron oxide. Short residence time.

<table>
<thead>
<tr>
<th>Run</th>
<th>T(°C)</th>
<th>θ (sec)</th>
<th>[CO] (%)</th>
<th>Solid(I)</th>
<th>Solid(F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>38a</td>
<td>538</td>
<td>0.022</td>
<td>0.38</td>
<td>FeO_{1.5}</td>
<td>FeO_{1.20}</td>
</tr>
<tr>
<td>39a</td>
<td>560</td>
<td>0.040</td>
<td>0.94</td>
<td>FeO_{1.5}</td>
<td>FeO_{1.16}</td>
</tr>
<tr>
<td>40a</td>
<td>566</td>
<td>0.040</td>
<td>1.0</td>
<td>FeO_{1.5}</td>
<td>FeO_{1.13}</td>
</tr>
<tr>
<td>42a</td>
<td>571</td>
<td>0.045</td>
<td>1.0</td>
<td>FeO_{1.5}</td>
<td>FeO_{0.99}</td>
</tr>
</tbody>
</table>

Fe-301-T 1/8
(0.50mm-0.25mm)
Fig. iv-38. Oxidation of CO with O₂ over oxidized and reduced iron oxide.

<table>
<thead>
<tr>
<th>Run</th>
<th>T(°C)</th>
<th>θ (sec)</th>
<th>[CO]</th>
<th>[O₂]</th>
<th>Solid(I)</th>
<th>Solid(F)</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>8b</td>
<td>436-377</td>
<td>0.61-0.66</td>
<td>3.0%</td>
<td>0.87%</td>
<td>FeO₁.14</td>
<td>FeO₁.09</td>
<td>O</td>
</tr>
<tr>
<td>8d</td>
<td>377</td>
<td>0.67</td>
<td>3.1%</td>
<td>0.78%</td>
<td>FeO₁.50</td>
<td>FeO₁.35</td>
<td>△</td>
</tr>
</tbody>
</table>

Fe-301-T 7/8
(3.2mmx3.2mm)
2. H₂ oxidation.

The H₂ oxidation study was conducted only with the large, 3.2-mm pellets. The data are presented in Figure iv-39. The highest H₂ removal for these tests was about 25%. This result is some 35 percent units lower than the CO removal under comparable conditions. The rise in the curve for Run 9a is a result of the temperature increase to 453°C. If diffusion limitations within the pellets were the rate-determining step, H₂ oxidation should proceed faster than CO oxidation. The reverse is the actual case, implying that H₂ oxidation kinetics are slower than combined CO oxidation diffusion and kinetic rates.

I. Other Reactions Studied.

1. Water-gas shift reaction.

In experiments on NO reduction, NH₃ was formed when H₂O and CO were the reducing agents. This fact suggested that the water-gas shift reaction proceeds in the presence of either iron oxide or iron sulfide. Run 42 showed that both H₂ and CO₂ were produced, confirming this prediction. The data are presented in Figure iv-40. The H₂O removal was determined by the H₂ produced. The percent water removal is much lower than that of CO because it is in excess. The discrepancy between the [CO₂] and [H₂] produced is due to error in the H₂ measurement and oxidation of the surface by CO. There is very little significant difference between the two catalysts. Since the water-gas shift reaction does proceed, H₂ may be an important intermediate not only for the NH₃, but also for the H₂S seen in runs containing SO₂, H₂O and CO. Okay (1973) reports that with a CuS
Fig. iv-39. Oxidation of H₂ with iron oxide.

<table>
<thead>
<tr>
<th>Run</th>
<th>9a</th>
<th>18a</th>
<th>19a</th>
</tr>
</thead>
<tbody>
<tr>
<td>T(°C)</td>
<td>378-453</td>
<td>385</td>
<td>374</td>
</tr>
<tr>
<td>θ (sec)</td>
<td>0.60-0.53</td>
<td>0.49</td>
<td>0.49</td>
</tr>
<tr>
<td>[H₂]%</td>
<td>4.45</td>
<td>1.40</td>
<td>3.1</td>
</tr>
<tr>
<td>Solid(I)</td>
<td>FeO₁.5</td>
<td>FeO₁.50</td>
<td>FeO₁.36</td>
</tr>
<tr>
<td>Solid(F)</td>
<td>FeO₁.25</td>
<td>FeO₁.42</td>
<td>FeO₁.29</td>
</tr>
</tbody>
</table>

Fe-301-T 1/8
(3.2mm×3.2mm)
Fig. iv-40. Progress of water-gas shift reaction over iron oxide and iron sulfide.

Run   T(°C)  θ (sec)  [CO]  [H₂O]  Solid(I)  Solid(F)  Fe-301-T 1/8
42b   571    0.045  0.50%  1.7%  FeO.77       FeO.55     (0.50-0.25mm)
42d   571    0.045  0.50%  1.7%  FeS₁₁       FeS₁₁

XBL 745-3241
catalyst the water-gas shift reaction does not occur. He based this claim on the fact that neither H₂ nor H₂S were produced when H₂O was added to a system of CO and SO₂. This is not an adequate test for the water-gas shift reaction.

2. High temperature, short residence time sulfidation.

The discussion in part B on sulfidation of iron oxide presented data collected at 370°C. The sulfidation step in Run 42c was carried out at 570°C with a gas residence time in the bed of 0.045 seconds. This run showed that COS did not break through until 85% to 98% of the bed was sulfided. This fact implies that the actual reaction time was much less than 0.045 seconds. The data are presented in Figure iv-41. The COS breakthrough curve is extrapolated from one point. Breakthrough occurred too rapidly to obtain more intermediate samples.

The calculated COS breakthrough, assuming only FeS formation, is 82 minutes, somewhat less than the actual. Under similar conditions, except that O₂ and NO were present, breakthrough was in 60 to 65 minutes, Run 39 (Figure iv-31). These results suggest that some FeS₂ may have formed in this run and that NO and O₂ may inhibit sulfidization.

3. NH₃ oxidation.

The potential of Fe₂O₃ to oxidize NH₃ at 368°C was studied in Run 23 over 3.2-mm pellets. No reaction which produced N₂ occurred. A slight adsorption of NH₃ resulted in some NH₃ loss from the 2.1% NH₃ inlet stream. When O₂ (1.4%) was added, 20% of the NH₃ was
Fig. iv-41. Sulfidation of iron oxide. High temperature, short residence time.

<table>
<thead>
<tr>
<th>Run</th>
<th>T(°C)</th>
<th>θ (sec)</th>
<th>[SO₂]</th>
<th>Solid(I)</th>
<th>Solid(F)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>42c</td>
<td>0.045</td>
<td>0.53%</td>
<td>FeO 55</td>
<td>FeS₁.₃</td>
</tr>
</tbody>
</table>

Fe-301-T 1/8
(0.50mm-0.25mm)
initially oxidized. After 10 minutes the amount of NH$_3$ oxidized dropped to 5%. The oxidization was short-lived. Therefore, if NH$_3$ forms at 368°C, it will not decompose or oxidize to N$_2$ over iron oxide. Following this run, H$_2$ and H$_2$S were successively passed over the catalyst. Neither H$_2$ nor H$_2$S reacted, which indicated that adsorbed NH$_3$ deactivated the catalyst for reductions at 368°C. Peri (1965) reports a 5% monolayer coverage of NH$_3$ on activated alumina at 400°C.

4. Activity of Activated Alumina.

Run 34 tested the activity of activated alumina for the proposed reactions. Activated Alumina No. LA-6173 from the Norton Company was tested. The alumina was 3.2-mm extruded pellets with a surface area of 250 m$^2$/gm. Adsorbed water on the alumina reacted with CO at 538°C to produce some CO$_2$. The reaction rapidly decreased. Similarly, when a gas mixture of 4% CO, 0.48% NO, 0.54% SO$_2$, 0.48% O$_2$ and 1.7% H$_2$O was passed over the catalyst at 538°C only a small amount of the gases reacted. The solid composition corresponded to Al$_2$O$_3$$^0.09S_{0.08}$. This run showed that the Al$_2$O$_3$ matrix is relatively inactive. Lowell (1971) reports that Al$_2$(SO$_4$)$_3$ decomposes to the oxide at 650°C. Thus, if any does form, it will decompose in the regeneration step, 677°C.

J. Iron Sulfide Oxidation.

Oxidation of FeS to form Fe$_2$O$_3$ and to liberate SO$_2$ or S$_2$ is required to regenerate the spent catalyst/absorbent. The desired sulfur product will depend on the specific plant location. In general, sulfur would be preferable to sulfuric acid. The initial
regeneration work discussed in section A yielded almost exclusively SO₂. The regeneration process was studied in more detail to determine if S₂ could be generated. The important reactions include the following:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH₂⁰°C (kcal)</th>
<th>ΔF₂⁰°C (kcal)</th>
<th>ΔF₆⁰°C (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 FeS + 7/2 O₂ →</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃ + 2 SO₂</td>
<td>-293.3</td>
<td>-262.2</td>
<td>-232</td>
</tr>
<tr>
<td>2 FeS + 3/2 O₂ →</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃ + S₂(g)</td>
<td>-120.5</td>
<td>-106</td>
<td>-91.9</td>
</tr>
<tr>
<td>2 FeS + 3/2 SO₂ →</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃ + 7/4 S₂(g)</td>
<td>+ 9.05</td>
<td>+10.2</td>
<td>+12.8</td>
</tr>
<tr>
<td>2 FeS + 3/2 SO₂ →</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃ + 7/2 S(s)</td>
<td>-44.92</td>
<td>-10.3</td>
<td></td>
</tr>
<tr>
<td>2 FeSO₄ →</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃ + 2 SO₂ + 1/2 O₂</td>
<td>+102.2</td>
<td>+49.9</td>
<td>-6.8</td>
</tr>
</tbody>
</table>

Thermodynamics shows that sulfur is favored at low temperatures and SO₂ is favored at high temperatures. Reaction kinetic limits may prevent low temperature formation of sulfur, while S₂ oxidation may prevent S₂ production.

1. High temperature, low O₂ concentration.

a. Large pellets.

Runs 11f and 12 were conducted at temperatures between 538°C
and 720°C to see if sulfur could form at low O₂ levels. O₂ ranged from 1.5% to 2.8% with residence times between 0.36 and 1.0 seconds. The 3.2-mm pellets were used. Trace amounts of sulfur collected in outlet lines, but by far the majority of sulfur from these runs eluted as SO₂. In Run 12 a mixture of 1.7% SO₂ and 0.5% O₂ was fed to see if SO₂ formation reactions could be inhibited. The same results were noted: only trace amounts of sulfur formed.

b. Small particles.

Low O₂ levels and high temperatures were used in Runs 39 and 42 with the 0.50-0.25-mm sized particles to check on the sulfur product. In these runs, only SO₂ eluted. No traces of sulfur were detected even though the O₂ level ranged from 0 to 1.9% and residence times varied from 0.02 to 0.04 seconds.

The initial regeneration period (677°C and 1% O₂) in Run 42 lasted for 65 minutes. A second regeneration period (677°C and 1% O₂) of 210 minutes for this same catalyst showed that only 84% of the bound sulfur had been evolved in the initial period. A closer look at the three different O₂ regeneration steps in Run 39 is shown in Table iv-3.

<table>
<thead>
<tr>
<th>Run 39 (677°C)</th>
<th>2%O₂</th>
<th>4%O₂</th>
<th>21%O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>% SO₂ after t(min.)</td>
<td>t=37</td>
<td>t=69</td>
<td>t=35</td>
</tr>
<tr>
<td>% O₂ after t(min.)</td>
<td>0.88</td>
<td>1.2</td>
<td>0</td>
</tr>
<tr>
<td>Regeneration time (min.)</td>
<td>129</td>
<td>66</td>
<td>63</td>
</tr>
<tr>
<td>SO₂ collected in scrubber (ml)</td>
<td>89</td>
<td>86</td>
<td>93</td>
</tr>
</tbody>
</table>
Even after 129 minutes with 2% \( \text{O}_2 \) and 66 minutes with 4% \( \text{O}_2 \), there was still a substantial \( \text{O}_2 \) removal over the bed. With air, there was no detectable \( \text{O}_2 \) removal after 34 minutes. In both the 4% and 21% \( \text{O}_2 \) case \( \text{SO}_2 \) elution ceased after 5 to 35 minutes. In the 2% \( \text{O}_2 \) case some \( \text{SO}_2 \) still eluted. The \( \text{SO}_2 \) collected by the NaOH scrubbers for each step differ by only 7.8%. This is within the experimental error. The \( \text{O}_2 \) breaks through only after most of the \( \text{SO}_2 \) has eluted in the low concentration cases. The remaining \( \text{O}_2 \) removal is caused by iron oxide oxidation.

Additional regeneration tests at 677°C and 1% \( \text{O}_2 \) were conducted on samples from selected runs. The particles tested were ground to less than 0.25-mm. The comparison of the S/Fe ratio determined by the sulfur picked up in the removal step to that determined by \( \text{SO}_2 \) evolution in the regeneration step for each run is given in Table iii-6. There is no consistent pattern in the reported deviation. The major error is caused by the inability to predict the extent of oxidation of the surface with the 1% \( \text{O}_2 \).

From this study it was concluded that air is the best regeneration gas at 677°C. Actual residence times for the 0.50-0.25-mm particles should be between 5 and 35 minutes. The 100 micron particles used in a power plant with air as the regeneration gas should require the lower limit, 5 minutes.

2. Low temperature-low \( \text{O}_2 \) concentration.

Low-temperature regeneration runs were made with 3.2-mm pellets. In Runs 13f, 16d, and 21d, temperatures were 260-288°C, and the \( \text{O}_2 \) level was 1.5-1.3%. Run 21d also had 1.9% \( \text{H}_2\text{O} \). In both Runs, 13f
and 16d, there was an initial large SO$_2$ elution which decreased rapidly to zero. No O$_2$ reacted after this step. When the catalyst was heated to 374°C more SO$_2$ eluted. The catalyst bed showed that only a few of the pellets at the bed entrance had been oxidized. The remainder of the bed was not oxidized. No S$_2$ was collected. SO$_2$ evolution may have been from FeSO$_3$ decomposition. Evolved SO$_2$ may have poisoned the remaining pellets for oxidation, explaining why only partial bed oxidation resulted. No SO$_2$ or S$_2$ eluted from Run 21d. Lower temperatures were used in Run 19e, 71°C, and Run 24g, 104°C. H$_2$O was present in the air mixture used in Run 24g. Oxygen at 1.3% was used in Run 19. Neither run produced any S$_2$ or SO$_2$, either at these temperatures or when the catalyst was heated to 370°C.

3. Summary of regeneration results.

Regeneration of iron sulfide with oxygen to give iron oxide and sulfur directly does not appear possible. High temperature (677°C) regeneration to give iron oxide and SO$_2$ is a practical reaction.
CHAPTER V. Process Design

A. Overall Rate Analysis.

1. Removal process.

a. Defining equation for reactors.

In order to translate the experimental results obtained in a small, fixed-bed contactor to an operating system with a large, dispersed-phase contactor, a model describing the system behavior must be developed. The general expression which governs NO and SO$_2$ removal in both fixed and dispersed contactors is the following:

$$\frac{C_{ag}}{C_{ag0}} = \exp \left( -K_1 \Gamma \rho_B \right)$$

where:
- $C_{ag}$ = gas concentration after residence time $\Theta$.
- $C_{ag0}$ = gas concentration at inlet conditions.
- $K_1$ = overall reaction coefficient.
- $\Theta$ = residence time of gas in the contactor.
- $\rho_B$ = solid density within the contactor.

The development and assumptions of this equation are given in Appendix A - 2. $K_1$ is a composite function involving both mass transfer and kinetics. The value of $K_1$ will be calculated for both fixed-bed and dispersed contactors in section B.b.1. The variables $\Theta$ and $\rho_B$ are set by experimental conditions in the fixed-bed work. In the dispersed contactor design $\Theta$ and $\rho_B$ will be adjusted to give the required $C_{ag}/C_{ag0}$.

As will be discussed in section B.1.b.ii., although $C_{ag}/C_{ag0}$ is the same for both contactors, the absolute values of $C_{ag}$ and $C_{ag0}$ for the experimental work were slightly higher than the concentrations found in practice.
b. Key process variables.

The important process variables identified in the experimental study are listed below.

1. Reaction temperature.
2. Gas residence time.
3. Particle size.
4. Gas concentration.
5. Gas composition.

From the design equation, \( v - 1 \), two additional variables when scaling up will include:

7. Mass-transfer effects.

These variables are discussed in section B.1. of this chapter in a slightly different order.

2. Regeneration process.

a. Defining equations for regenerator.

The experimental study showed that high-temperature regeneration of the sulfide was needed to produce an active catalyst. The model will therefore be similar to that developed by Guha (1972) for the oxidation of FeS\(_2\). Expressing the extent of regeneration as the percent of FeS reacted to give Fe\(_2\)O\(_3\) and SO\(_2\), the model becomes

\[
\text{% Solid reacted} = 100 - \frac{\frac{K_2}{r^{7/4}(1-\epsilon')p_{SM}C_{ag\,t}}}{r^3} 100
\]

\( v - 2 \)
where: \( r \) = radius of particles.
\( C_{agO} \) = \( O_2 \) concentration.
\( K_0 \) = overall reaction coefficient.
\( t \) = time of solids reaction.
\( 1 - \varepsilon' \) = volume fraction of particle which is FeS
\( \rho_{sm} \) = molar density of FeS.

The development and assumptions of this equation are given in Appendix A-3. \( K_2 \) is a composite function involving both mass transfer and kinetics.

b. Key process variables.

The important regeneration variables found in the experimental study include the following:

1. Regeneration temperature.
2. \( O_2 \) concentration.
3. Particle size.
5. Solid composition.

From equation v-2, the mass transfer effects, as they influence \( K_2 \), will also be a variable of the process. These variables will be discussed in Section B.2. of this chapter.

B. Discussion of the Variables.

1. Removal reactions.

a. Reaction temperature.

All of the removal reactions occurred in the desired temperature region of 370°C - 540°C. The upper level (540°C) is the recommended temperature of operation. At this temperature, catalyst deactivation due to sulfate formation is inhibited, reaction kinetics are more rapid, and large differences between the temperature for removal and that for regeneration are avoided.
b. Kinetic and mass transfer effects.

The overall reaction coefficient, $K_1$, is a function which includes both kinetic and mass transfer effects. This is shown in the following relationship:

$$K_1 = \frac{1}{V_p k_m \eta} + \frac{1}{S_{ex} k_m}$$

where:
- $k_m =$ overall mass transfer coefficient.
- $k_r =$ overall kinetic rate coefficient.
- $S_{ex} =$ specific external surface area of particles.
- $V_p =$ specific volume of particles.
- $\eta =$ kinetic effectiveness factor.

(See Appendix A-2 for development.)

This expression, like equation v-1, assumes first-order dependence of the gas concentration on both the kinetic and mass-transfer rates. In order to estimate the required density of solids in the dispersed contactor as well as the gas residence time in the contactor, $K_1$ must be evaluated for both the fixed and dispersed contactor.

i. Fixed-bed contactor.

(a.) Required residence time.

Sulfur dioxide removal in a fixed-bed contactor proceeds until the bed has been almost completely sulfided. During sulfidation there is an oxide/sulfide reaction zone which moves through the bed. Since breakthrough of sulfur compounds in the runs at 540°C did not occur until the bed was almost completely sulfided, this reaction zone is much smaller than the bed length. The
sulfidation of iron oxide with SO₂ and CO in Run 42, Figure iv-41, resulted in sulfur compound elution only after 85% to 98% of the bed had been sulfided. Since the nominal gas residence time in the bed was 0.045 seconds, the gas phase removal process went to completion in the fixed bed in 0.0068 to 0.001 seconds.

Nitric oxide removal is catalytic and will proceed until the bed becomes deactivated. The deactivation of catalyst/absorbent results when the catalyst is partially oxidized by O₂. Runs 36b and 37b reported simultaneous removal of SO₂ and NO when the gas residence time was 0.030 - 0.034 seconds. Examination of the catalyst from both of these runs showed that only the last half of the bed was active. This meant that the reactive residence time for NO removal was less than 0.015 seconds in the fixed-bed reactor. A more definitive residence time can be obtained from Figure iv-30 with the gas concentration profiles of Run 37b. In this run, the catalyst was poisoned, first eluting H₂S then COS, SO₂, NO, and O₂. If it is assumed that the bed was poisoned for NO removal when the first outlet NO was measured, at 110 minutes, then the extrapolated NO breakthrough, between 80 - 90 minutes, occurs after 73 - 82% of the bed is inactive. Therefore the residence time in the reaction zone is estimated at 0.005 - 0.008 seconds.

These results confirm that in the experimental fixed-bed reactor the maximum required residence time for simultaneous NO and SO₂ removal is about 0.008 seconds. This is with at least 99%
removal of both NO and SO₂. The minimum residence time for 99% removal was not obtained in this study. The reason for this apparent lack of data is given in the next few paragraphs. Data extrapolation, which was discussed in the previous paragraphs, suggests that times as fast as 0.001 seconds may be the minimum.

(b) External mass transfer rate estimation.

The reaction residence times measured in the fixed-bed are for processes in which both kinetic and mass transfer rates are important. The gas phase mass transfer rates in the fixed-bed can be estimated from empirical correlations and then used to calculate the kinetic contribution to $K_1$.

Sherwood (1974) presents an empirical correlation for external mass transfer in fixed-beds when the particle Reynolds Number ($Re_p$) is greater than 1.0.

$$J_D = 1.17 \left(Re_p\right)^{-0.415}$$

Since the experimental $Re_p$ in the present work is less than 1.0, this expression, representing an upper bound, and the correlation based on one experimenter's data, (Sherwood, 1974) representing the lower bound, were used for obtaining the value of $J_D$, the mass transfer j-factor. The mass transfer coefficient is related to $J_D$ by the following equation:

$$k_m = \left[ \frac{J_D}{\left(S_c \right)^{2/3}} \right] U_{AVE}$$
where:  
\[ J_D = \text{mass-transfer j factor.} \]
\[ k_m = \text{external mass transfer coefficient.} \]
\[ S_c = \text{Schmidt Number} \]
\[ U_{AVE} = \text{Interstitial velocity past particles.} \]
(Sherwood, 1974)

In addition to \( k_m \), the Sherwood Number for mass transfer, \( Sh \), is also calculated. Table v-1 presents the calculated \( k_m \) and \( Sh \) for the listed conditions.

Table v-1  Calculated \( k_m \) and \( Sh \) for the fixed-bed contactor.

<table>
<thead>
<tr>
<th>Diameter, ( d_p ) (mm)</th>
<th>0.250</th>
<th>0.500</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Re_p )</td>
<td>0.304</td>
<td>0.608</td>
</tr>
<tr>
<td>( J_D )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>high</td>
<td>1.92</td>
<td>1.44</td>
</tr>
<tr>
<td>low</td>
<td>0.22</td>
<td>0.60</td>
</tr>
<tr>
<td>( k_m ) (cm/sec)</td>
<td>225</td>
<td>169</td>
</tr>
<tr>
<td>high</td>
<td>25.8</td>
<td>70.3</td>
</tr>
<tr>
<td>low</td>
<td>25.8</td>
<td>70.3</td>
</tr>
<tr>
<td>( Sh = \frac{k_m d_p}{D} )</td>
<td>1.63</td>
<td>2.44</td>
</tr>
<tr>
<td>high</td>
<td>0.187</td>
<td>1.02</td>
</tr>
<tr>
<td>low</td>
<td>0.187</td>
<td>1.02</td>
</tr>
</tbody>
</table>

The expected range for \( k_m \) for the 0.250-mm particles is 25 - 255 cm/sec and for the 0.500-mm particles is 70 - 169 cm/sec.

The lack of more experimental data below a \( Re_p \) of 1.0 prevents the narrowing of these ranges.

The reaction kinetics, to be discussed in section B.1.b.i.(c), were significantly influenced by the external mass transfer limitations. The NO and \( \text{SO}_2 \) removal reactions rates were so rapid that it was impractical to design an experimental unit which would
be free of external mass transfer limitations. In order to have such a system, the feed velocity would have to be substantially increased. This would mean, at a constant SO₂ concentration and bed volume, that bed sulfidation would occur much more rapidly, hence limiting the amount of sampling before sulfur compound breakthrough. As it was, in the runs with the shortest residence time and with the lowest possible inlet SO₂ (about 0.5%), only two samples could be taken before breakthrough. Increasing the bed volume would not help since the total feed of SO₂ to the bed would have to be increased proportionately to maintain the same residence time. Continuous gas monitors with a higher sensitivity would have allowed operation of a small scale system which was free of external mass transfer limitations.

(c.) Reaction rate estimation.

Equation v-3 has presented the model for the overall reaction coefficient $K_1$. The values of $S_k$ can be estimated based on the previous section. The value for $K_1$ can be calculated from equation v-1 using the experimental data obtained in this work. Given these two parameters, the value of the solids rate constant, $V_{pr,n}$, can be estimated in equation v-3. These values are given in Table v-2.
Table v - 2. Estimation of solids rate constants for removal reactions in the fixed-bed contactor.

(Run 42. Discussed section i.(a.) & Figure iv - 41)

Bed Density = 1.172 g/cm³
Diluent, Helium 400 cm³/min @ 23°C, 1 Atmosphere.
Temperature = 538°C
Cₐg/Cₐgo = 0.010
Residence time = 0.008 sec (max); 0.001 sec (min)

<table>
<thead>
<tr>
<th>Particle Size (mm)</th>
<th>0.250</th>
<th>0.500</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>kₘₑₓ (cm³/g-sec)</td>
<td>30,150</td>
<td>3,457</td>
</tr>
<tr>
<td></td>
<td>(max)</td>
<td>(min)</td>
</tr>
<tr>
<td>K₁ (cm³/g-sec)</td>
<td>3,929</td>
<td>491</td>
</tr>
<tr>
<td>Vₚkₙ (cm³/g-sec)</td>
<td>4,518</td>
<td>499</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* K₁ & kₘₑₓ combination not possible.
A range for $V_{k,n}$ is reported instead of one number for each particle size since neither $K_{m,ex}$ nor $k_1$ could be determined accurately. For all cases except one, the particle rate appears to be the rate controlling step.

ii. Dispersed-bed contactor.
(a.) External mass transfer rate estimation.

Dispersed-bed contactors can range from a fluidized bed with void fractions close to 0.60 up to highly dispersed systems with void fractions very close to 1.0 (Reh, 1971). Separate mass transfer correlations have been developed for dense-phase and dilute-phase contactors. Kunii and Levenspiel (1969) present correlations for fluidized beds:

\[
\begin{align*}
Sh &= 0.374 \frac{Re}{lB_{p}}^{1.18} \quad 0.1 < \frac{Re}{lB_{p}} < 15 \quad v-6 \\
Sh &= 2.01 \frac{Re}{p}^{0.5} \quad 15 < \frac{Re}{p} < 250 \quad v-7
\end{align*}
\]

and for a single sphere,

\[
Sh = 2.0 + 0.6 \left( \frac{Sc}{c} \right)^{1/3} \frac{Re}{p}^{1/2} \quad v-8
\]

At a $\frac{Re}{p}$ of 1.0 the Sh for a fluidized bed would be lower than that for a single sphere. The theoretical value for Sh for a single sphere in an infinite stagnant medium is 2.0. Since equation v-6 would predict lower values, the validity of equation v-6 is questionable when studying anything but dense-phase fluid beds. In dense fluid beds, as in fixed beds, the interaction of concentration gradients may result in the Sh being less than 2.0. However, the proposed type of contactor is a dilute dispersed-
phase system. As a conservative estimate of the mass transfer under these conditions the last terms in equation v-8 will be deleted. Therefore,

$$Sh = 2.0$$  \hspace{1cm} v-9

will be used to estimate the mass transfer coefficients. Since the value of $k_{m_{ex}}$ is used in the rate equations, Table v-3 lists the values of both $k_m$ and $k_{m_{ex}}$ for several candidate particle sizes.

**Table v-3. Estimation of mass transfer coefficients for a dispersed-phase contactor.**

<table>
<thead>
<tr>
<th>Diameter, $d_p$ (mm)</th>
<th>0.050</th>
<th>0.075</th>
<th>0.100</th>
<th>0.150</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_m$ (cm/sec)</td>
<td>459</td>
<td>306</td>
<td>229</td>
<td>153</td>
</tr>
<tr>
<td>$k_{m_{ex}}$ (cm$^3$/g·sec) x $10^5$</td>
<td>3.18</td>
<td>1.37</td>
<td>.792</td>
<td>0.325</td>
</tr>
</tbody>
</table>

Section B.1.b.ii.(c.) will give a discussion of the reason for selection of these particle sizes.

(b.) Reaction rate estimation.

In the discussion of the fixed-bed data above, an estimate of the solids rate parameter was made for the catalyst tested. The catalyst used in the dispersed contactor will be slightly different than the one on the fixed-bed case. It will still have 20% ferric oxide but will have an alumina-silica matrix instead of only alumina. The latest commercial alumina-silica matrix cracking catalysts have surface areas ($S_v$) around 200 m$^2$/g (Gussow, 1972).
The experimental catalyst had an $S_v$ of 41 $m^2/g$. This means that an increase in the specific volume can be expected in going from the fixed-bed unit to the dispersed phase contactor with the newer catalyst. The increase in $V_p$ will not be proportional to the increase in $S_v$. A comparison of two commercial Harshaw catalysts was used to estimate the new $V_p$. Table v-4 presents the data.

Table v-4. Estimation of specific pore volume of high surface area catalyst (Harshaw, 1973).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_v (m^2/g)$</th>
<th>$V_p (cm^3/g)$</th>
<th>$x = \frac{\ln \left( \frac{V_{p1}}{V_{p2}} \right)}{\ln \left( \frac{S_{v1}}{S_{v2}} \right)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Fe-0301T 1/8</td>
<td>41</td>
<td>0.31</td>
<td>0.4878</td>
</tr>
<tr>
<td>2. Fe-0303P</td>
<td>105</td>
<td>0.49</td>
<td></td>
</tr>
</tbody>
</table>

The logarithmic proportionality constant, $x$, is used to calculate the new $V_p$ of 0.67 cc/g. The ratio $V_{p2}/V_{p1}$ is then 2.16, where 1 denotes experimental catalyst and 2 denotes new catalyst.

Predicting the effectiveness factor for the reactions with the solid in a dispersed phase is somewhat more difficult. Petersen (1965) presents an equation for the effectiveness factor for a first-order reaction developed for a spherical pellet:

$$\eta = \frac{3}{h_s} \left[ \frac{1}{\tan h_s} - \frac{1}{h_s} \right]$$  \hspace{1cm} (v-10)

where: $h_s = \text{thiele modulus} = \frac{1}{3} \left[ \frac{\rho_p S_v k_f}{D_e} \right]^{1/2}$.

$\rho_p = \text{particle density.}$

$S_v = \text{specific surface area.}$
De = effective diffusivity = \( \frac{1}{D_{ke}} + \frac{1}{D_{12,e}} \)^{-1}

\( k_r \) = reaction rate coefficient.
\( r \) = particle radius.

When intraparticle diffusion is controlling, the asymptotic solution to equation v-10 becomes:

\[ \eta = \frac{3}{h_s} \]

for \( \eta = \frac{h_s}{3} > 3 \)

The effectiveness factor is a ratio of the average rate of reaction or adsorption in the pellet to the maximum rate if intraparticle diffusion were absent. Since the maximum rate is unknown, one way to determine whether intraparticle diffusion is rate controlling is to calculate the ratio of the rate predicted by intraparticle diffusion and compare that with the overall rate measured. This ratio is simply the effectiveness factor using the rate coefficient determined from experiments instead of the actual kinetic rate coefficient. The values of \( K_1 \) (Table v-2), divided by the catalyst specific surface area (41 x 10^4 cm^2/g) give the pseudo \( k_r \) for the conditions of that run. At 538°C in He with a calculated De of 0.0293 cm^2/sec (see eqn. v-10), the ratio of the calculated diffusion rate to the overall rate is 0.95. Since this value is close to 1.0, the overall particle rate is strongly diffusion controlled. This implies that the variation of \( \eta \) will be represented by the following equation:

\[ \eta \propto \frac{1}{h_s} = \frac{3}{r} \left[ \frac{De}{\rho S k_r} \right]^{1/2} \]
The largest contribution to $D_e$ was the Knudsen diffusion coefficient which varies with $\varepsilon^2/(S_v\rho_p)$ (Satterfield, 1963). The apparent density can be expressed as

$$\rho_p = \rho_s (1-\varepsilon)$$  \hspace{1cm} \text{(v-14)}

where: \(\rho_s\) = absolute solid density.
\(\varepsilon\) = particle porosity.

With the above proportionalities for \(n\), \(D_e\), and \(\rho_p\) and with \(\varepsilon_2 = 0.74\) and \(\varepsilon_1 = 0.567\), the new effectiveness factor for the 200 $m^2/g$ catalyst can be expressed as a function of the original.

$$\eta_2 = 0.44\eta_1 (r_1/r_2)$$  \hspace{1cm} \text{(v-15)}

where: subscript 1 denotes experimental conditions.
subscript 2 denotes dispersed conditions.

The new product \(k_r V_p \eta\) will be

$$\left(V_p \eta_k\right)_2 = \left(V_p \eta_k\right)_1 (2.16) (0.44)^{r_1/r_2} = 0.957 \left(\frac{d_1}{d_2}\right) \left(V_p \eta\right)_1$$  \hspace{1cm} \text{(v-16)}

The factor 0.957 in equation v-16 shows that the reaction rate will be essentially the same for both the experimental and the new catalyst matrix. The calculated values for \(\left(V_p \eta_k\right)_2\) are given in Table v-5 for various particle sizes. Table v-2 is used to obtain conditions for case 1. An average particle size, \(d_1 = 0.375\) mm is used. Two values for \(\left(V_p \eta_k\right)_1\) are used, 4518 and 533 cm$^3$/g-sec. These are the values of the lowest maximum value of \(\left(V_p \eta_k\right)_1\) and the average of the minimum \(\left(V_p \eta_k\right)_1\) values. This analysis assumes that $n$ will be much less than 1 at the new conditions.
Table v-5. Estimation of dispersed phase solids rate coefficient.

<table>
<thead>
<tr>
<th>(d_2) (mm)</th>
<th>0.050</th>
<th>0.075</th>
<th>0.100</th>
<th>0.150</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{(cm/g-sec)} \times 10^3)</td>
<td>max</td>
<td>min</td>
<td>max</td>
<td>min</td>
</tr>
<tr>
<td>(V_p\eta_k_r)</td>
<td>32.4</td>
<td>3.83</td>
<td>21.6</td>
<td>2.55</td>
</tr>
</tbody>
</table>

(c.) Solids concentration.

The estimates of the mass-transfer and solids rate coefficients for the dispersed phase are combined by way of equation v-3 into a value for \(K_1\). \(K_1\) can then be used in equation v-1 to determine the required dispersed phase concentration as a function of particle size and residence time. Table v-6 summarizes these results.
Table v-6. Required dispersed-phase density as a function of residence time and particle diameter.

Temperature = 538°C
\( C_{ag} / C_{ag_0} = 0.10 \)

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>( k_m S_{ex} ) (cm(^3)/g·sec) ( \times 10^5 )</th>
<th>( V_p n_k ) (cm(^3)/g·sec) ( \times 10^3 )</th>
<th>( K_1 ) (cm(^3)/g·sec) ( \times 10^3 )</th>
<th>( \theta ) (sec)</th>
<th>( \rho_B ) (g/cm(^3)) ( \times 10^{-3} )</th>
<th>( \rho_B ) (g/cm(^3)) ( \times 10^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>3.18</td>
<td>32.4</td>
<td>29.4</td>
<td>0.500</td>
<td>0.157</td>
<td>0.0785</td>
</tr>
<tr>
<td>0.75</td>
<td>1.37</td>
<td>21.6</td>
<td>18.6</td>
<td>0.500</td>
<td>0.248</td>
<td>0.610</td>
</tr>
<tr>
<td>0.100</td>
<td>0.792</td>
<td>16.2</td>
<td>13.4</td>
<td>0.500</td>
<td>0.344</td>
<td>0.124</td>
</tr>
<tr>
<td>0.150</td>
<td>0.325</td>
<td>10.8</td>
<td>8.11</td>
<td>0.500</td>
<td>0.568</td>
<td>0.072</td>
</tr>
</tbody>
</table>

\( e \) (sec) | 0.500 \( \times 10^6 \) | 0.500 \( \times 10^6 \) | 0.500 \( \times 10^6 \) | 1.00  | 1.00            | 2.00             |
| \( \rho_B \) (g/cm\(^3\)) \( \times 10^{-3} \) | 2.00            | 2.00            | 2.00            | 2.00  | 2.00            | 2.00             |
| \( \rho_B \) (g/cm\(^3\)) \( \times 10^{-3} \) | 0.0393          | 0.305           | 0.062           | 0.460 | 0.086           | 0.142            |
With a catalyst/absorbent size distribution between 0.050 - 0.150 mm and a 0.5-second residence time, the required bed density will be between $0.16 \times 10^{-3}$ and $3.7 \times 10^{-3}$ g/cm$^3$. With a 1.0-second residence time for this same size distribution, the range of the bed density would be between $0.079 \times 10^{-3}$ and $1.87 \times 10^{-3}$ g/cm$^3$. Existing power plant duct work allows for about 0.5-second residence time. Duct modifications could increase this time to 1.0 seconds if necessary. The 1-second residence time is chosen for the design basis. This criterion will be discussed in the next section. Therefore, the required bed density will be between $0.079 \times 10^{-3}$ and $1.87 \times 10^{-3}$ g/cm$^3$. With a catalyst particle density of 1.79 g/cm$^3$, the void fraction, $\varepsilon$, ranges between 0.99996 and 0.99895. Since the $\varepsilon$ for normal fluid bed operation is less than 0.70, the contactor required for the entire range of void fractions would have the solids highly dispersed (Reh, 1971).

The specific design presented in Section D.4. of this chapter has a catalyst/absorbent loading of $0.185 \times 10^{-3}$ g/cm$^3$ (1.14 x $10^{-3}$ lbs/ft$^3$), which is 2.3 times as concentrated as the minimum and 0.10 times as concentrated as the maximum. This concentration lies within the acceptable, experimentally determined range.

The MnO$_2$ dry absorption process for SO$_2$ removal (Uno, 1971) uses a dispersed phase of MnO$_2$ at 100 to 180°C to absorb and remove SO$_2$ from oil-fired power plant stack gases. The concentration of solids in this process has a range, $0.15 \times 10^{-3}$ g/cm$^3$ to $0.20 \times 10^{-3}$ g/cm$^3$, roughly the same as that used in the proposed process.
An SO₂ removal of 90% is claimed. Since the proposed process will operate at 540°C, mass transfer and kinetic rates should increase substantially over the MnO₂ process. In view only of these considerations, the proposed solids concentration should be quite adequate.

(d.) Residence time in contactor.

The initial discussion of residence time was the time that it took the flue gas to pass from the economizer inlet (540°C) to the air preheater inlet (370°C). The experimental studies showed that the best operation would be obtained at 540°C. The residence time normally available at 540°C will vary with the unit. Heil (1972) reports that the flue gas velocity in this region varies from 22.9 m/sec (75 ft/sec) for high volatile eastern coals to 13.7 m/sec (45 ft/sec) for coals with highly abrasive tendencies. An average value of 15.2 m/sec (50 ft/sec) is selected for design purposes. Typical distances in coal-fired units at 540°C correspond to residence times around 0.20 seconds (Stevens, 1974). Table v-6 shows that to achieve nearly complete reaction at low solid densities, higher residence times are needed. The reaction constants presented in this table show that 90% removal can be achieved in 1 second with low solids density. Typical velocities in this region would require then that about 15.2 m (50 ft) of ducting be added. This would be a reasonable addition to a unit. Additional residence time may also be obtained. First, the gas and solids must pass
through a solids separator at this temperature. Second, the 15.2 m/sec velocity is typically that within the economizer section. In the free duct it would be reduced to about 13.4 m/sec. This additional residence time (possibly 0.20 seconds) provides some margin of safety.

Equation v-1 showed that the residence time and bed density can be adjusted to give a constant removal, i.e., increasing the bed density by a factor of 2 would enable the residence time to be cut by one half. Therefore, the actual amount of removal for a given residence time can be controlled by the solids density, i.e., the recycle solids rate, within the contractor.

(e.) Particle size.

Mass transfer and kinetic effects were shown to require a catalyst/absorbent size distribution between 0.050 - 0.150 mm. Sizes smaller than this range would tend to enhance the reaction rates and hence the overall rate, since the particle rates are the rate-limiting step. The difficulty with smaller particles is that they would be more difficult to collect in either cyclones or electrostatic precipitators and they would also be more difficult to separate from the flyash in pulverized coal-fired units.

A typical flyash size distribution for pulverized coal-fired furnaces is given in Table v-7. The average size is 20 microns. Table V-7 also lists the size distribution for a typical commercial fluid-bed cracking catalyst to illustrate the range of particle
sizes when the average size is 58 microns.

Table v-7. Particle size distribution of P.C. flyash and Si - Al cracking catalyst.

<table>
<thead>
<tr>
<th>Size (microns)</th>
<th>Wgt % less than</th>
<th>Size (microns)</th>
<th>Wgt % less than</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flyash (USDHGW, 1969)</td>
<td></td>
<td>Catalyst (Gussow, 1972)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>20</td>
<td>&lt;2</td>
</tr>
<tr>
<td>20</td>
<td>50</td>
<td>40</td>
<td>13 - 20</td>
</tr>
<tr>
<td>40</td>
<td>70</td>
<td>80</td>
<td>78 - 85</td>
</tr>
<tr>
<td>60</td>
<td>80</td>
<td>105</td>
<td>93 - 97</td>
</tr>
<tr>
<td>80</td>
<td>85</td>
<td>149</td>
<td>99+</td>
</tr>
<tr>
<td>100</td>
<td>90</td>
<td>200</td>
<td>96</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

With a catalyst/absorbent of this size distribution, there is definitely significant overlap. If an average size of 75 microns is used, a better separation of catalyst/absorbent and flyash will be possible without significantly effecting the mass transfer and kinetic rates. Table v-8 presents a size distribution for such a catalyst.

Table v-8. Size distribution for catalyst/absorbent with average size 75 microns.

<table>
<thead>
<tr>
<th>Size (microns)</th>
<th>Wgt % less than</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>20</td>
<td>0.9</td>
</tr>
<tr>
<td>40</td>
<td>6</td>
</tr>
<tr>
<td>60</td>
<td>28</td>
</tr>
<tr>
<td>80</td>
<td>56</td>
</tr>
<tr>
<td>100</td>
<td>77</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
</tr>
</tbody>
</table>

This distribution was obtained by extrapolating the data of Gussow
(1972) on a log/probability plot of particle size versus cumulative percent. Although there is still some overlap between this distribution and normal flyash, it is not as significant. That is, flyash has 70% less than 40μ while the catalyst/absorbent has 6% less than 40μ.

In addition to the kinetic and mass transfer limits on larger sized particles, the influence of particle size on catalyst attrition is also important. Zenz (1971, 1974) reports that catalyst attrition results primarily from high velocity impact. He found that attrition occurred mainly from breakdown of coarse particles: fines (less than 44 microns) do not get finer. In fluid-bed catalytic cracking units he found that essentially all of the attrition occurred in the cyclones. Thermal cycling (between 500°C and 650°C) as well as attrition in the dense phase fluid beds contributed little to the overall attrition rate of Si/Al catalysts. In laboratory experiments, Tanaka (1968), found that below a critical particle size, the rate of particle breakup drops essentially to zero. The critical particle size decreased with impact velocity and increased with material strength. However, in all cases the critical size was in the vicinity of 50 microns. Therefore attrition considerations would require particles with an average diameter around 50 microns.

Flanders (1974) has reported that a commercially operating SiO₂/Al₂O₃ cracking catalyst with an average particle size of 60 microns has an attrition loss of about 0.004% of the material sent into the cyclones. High-velocity, 22.3 m/sec (75 ft/sec), cyclones
are used in the proposed process. The catalyst has a Moh hardness of 6. Forsythe (1949), Gwyn (1969), and Gussow (1972) all discuss relative rates of attrition between various catalysts tested but do not give any absolute value for the attrition rates.

Since an average particle size of 75 microns is desired from the standpoint of particle separation and collection, an estimate of the expected attrition rate needs to be made. The data of Flanders (1974) is used as the starting point and the relationship between particle-size distribution and attrition rate found by Gwyn (1969) is used to predict the rate with an average size of 75 microns. Unlike previously quoted investigators, who found that in this size range the attrition rate increased with increasing particle size, Gwyn's correlations indicate a 14% decrease in the rate. This would predict an attrition loss of 0.0034%. Since there appears to be some uncertainty as to the validity of this decrease, the attrition rate is taken as 0.004% of the material entering all the cyclones in the process.

(f.) Gas concentrations.

The removal rates presented in section A.1.a. assumed first-order kinetics for all reactions. Equation v-1 shows that with this assumption the level of concentration of the reactants does not effect the percent removal. Therefore, if this assumption holds, even though most of the experiments were carried out at NO and SO₂ concentrations 10 times and 2 times, respectively, those encountered in practice, the results will still be applicable.
Shelef (1972) found that when the NO concentration was decreased from 4000 ppm to 250 ppm, NO conversion actually increased from 80% to 100%. Copper chromite catalyst at 305°C with 1.4% H₂ was used. With this large excess H₂, the NH₃ selectivity increased from 20% to 95% when the inlet NO was decreased. The major effect of a lower NO concentration would possibly be an increase in the NH₃ formed. The extrapolation of the SO₂ data over a factor of 2 is reasonable and should present no difficulties.

(g.) Gas and solid composition.

Experiments summarized in Figure iv-33 have shown that the solid and gas composition are both important variables in determining NH₃ selectivity. Increasing the sulfide content of the solid or the amount of CO + H₂ in the gas stream increases the NH₃ selectivity. Increasing the oxide content of the solid or the amount of O₂ in the gas stream decreases the NH₃ selectivity. To have a low NH₃ selectivity would require high oxygen levels in both the solid and the gas. These trends go counter to the requirements for effective NO and SO₂ removal. The balance of these variables is such that the minimum NH₃ selectivity is about 50%. This results in acceptable sulfur loadings on the solid and reducing agents in the gas to allow self-sustained regeneration and effective removal reactions. Solid and gas compositions cannot practically be selected to minimize NH₃. Ammonia emitted from this process is well below current allowable levels, and is not
considered an environmental detriment. This is discussed in more detail in Chapter VI. The important consideration for the gas composition is that it be at least net reducing. This means that the ratio

\[
\frac{0}{R} = \frac{2[O_2] + [NO] + 3[SO_2]}{[CO] + [H_2]}
\]

should be equal to or less than 1. Values greater than 1 may result in eventual catalyst deactivation.

The allowable solid composition will be determined by both the removal and regeneration processes. In the fixed-bed experiments only an averaged solids composition, at the end of the run, could be estimated. The range of compositions within the bed varied from highly sulfided at the bed entrance to slightly sulfided at the bed exit. In tests with the smaller particles the reaction rates, discussed in section B.1.b.i., were so rapid that apparently the percent sulfidation of the solid had no significant effect on the removal rate of sulfur compounds, as long as the solid was less than about 85% sulfided. The biggest influence of the solid composition on NO removal was the level of sulfate. The experimental work showed that for active catalyst/absorbent the sulfate level could reach 15% of the total sulfur reacted.

Excess Fe$_2$O$_3$ will also be needed in the catalyst/absorbent
to remove the excess CO and H₂. The amount required is arbitrarily set at 110% of the stoichiometric requirement for reduction of the excess CO and H₂.

The level of sulfide in the solid is also important from the standpoint of regeneration. In the regenerator a net exothermic reaction is desired to maintain the high temperature. Exothermic reactions are the oxidation of FeS to SO₂ and Fe₂O₃ and the oxidation of FeO to Fe₂O₃. The decomposition of any FeSO₄ formed in the removal process and heating requirements for the solids and air are endothermic loads. Given the limits for FeSO₄ and Fe₂O₃ in the removal step, the minimum amount of FeS necessary can be calculated from an energy balance. From an operational standpoint, the amount of FeS should be substantially higher than this minimum to allow for system fluctuations. Any excess heat generated will be removed and used in another part of the process or in the power plant.

2. Regeneration reactions.

a. Regeneration temperature.

High temperature regeneration, producing SO₂ and Fe₂O₃, was found in the experimental work to produce an active catalyst. The lowest temperature suitable was 680°C. The upper temperature limit will depend on catalyst sintering effects and materials of construction. Harnsberger (1974) reported sintering of SiO₂/Al₂O₃ catalytic cracking catalysts around 760°C. The upper limit for
castable-lined stainless steel is also about 760°C. Therefore, acceptable regeneration temperatures range between 680 - 760°C. The temperature level attained will be a function of the solid composition and the heat either removed or added to the system.

b. Kinetic and mass transfer effects.

i. Fixed-bed regenerator.

(a.) Required residence time.

In the experimental study the required regeneration time for the 0.250 - 0.500 mm particles was between 300 - 2100 seconds when air was used as the regeneration gas.

(b.) Mass transfer and reaction rate estimation.

In section B.1.b.i. the gas phase mass transfer in the removal study was found in all practical cases to be more rapid than the estimate of the particle reaction kinetics. Since higher gas reaction temperatures were used in the regeneration study than in the removal study, the gas phase mass transfer was probably not rate-limiting in the former case. Higher temperatures will also increase the reaction kinetics to a greater extent than intraparticle diffusion. This means that, as in the removal step, the regeneration step will probably be controlled by the intraparticle diffusion rate.

Equation v-2 expresses the extent of regeneration as a function of particle kinetics, residence time, and particle radius. The overall rate coefficient, $K_2$, can be estimated from experimental
data. This is shown in Table v-9. The range of $K_2$ presented results from the uncertainty in the % solid reacted and in the time required. The maximum range of $K_2$ is expected to be between 0.0669 and 0.00326 cm/sec.

Table v-9. Overall coefficient for fixed-bed regeneration.

<table>
<thead>
<tr>
<th>Diameter (cm)</th>
<th>0.0250</th>
<th>0.0500</th>
</tr>
</thead>
<tbody>
<tr>
<td>% solid reacted</td>
<td>90</td>
<td>99</td>
</tr>
<tr>
<td>time (sec)</td>
<td>300</td>
<td>2100</td>
</tr>
<tr>
<td>$K_2 \times 10^{-2}$ (cm/sec)</td>
<td>2.29</td>
<td>.326</td>
</tr>
</tbody>
</table>

ii. Fluidized bed regenerator.

The regenerator will be a fluidized bed which will function as a reactor to oxidize the solid to $Fe_2O_3$ and as a classifier to separate the flyash and the catalyst/absorbent. The catalyst/absorbent size distribution will range between 50 - 100 microns. The reasons for this range are given in section B.1. The main design parameters to be determined are the residence time at temperature necessary to regenerate the catalyst/absorbent and the air velocity in the bed.

The entrance velocity of small particles in a continuous fluid bed is reported to be higher than the terminal velocity of an isolated particle. Lewis (1949) found this effect for particles less
than 0.25 mm. Table v-10 presents entrmt. velocities for both flyash and catalyst/absorbent at regeneration conditions.

Table v-10. Entrmt. velocities of flyash and catalyst/absorbent under conditions of continuous fluidization. (Correlation of Lewis, 1949).

<table>
<thead>
<tr>
<th>Diameter (mm)</th>
<th>.020</th>
<th>.100</th>
<th>.020</th>
<th>.040</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terminal velocity (mm/sec)</td>
<td>5.08</td>
<td>127</td>
<td>10.8</td>
<td>43.3</td>
</tr>
<tr>
<td>Entrmt. velocity (mm/sec)</td>
<td>66</td>
<td>293</td>
<td>140</td>
<td>333</td>
</tr>
</tbody>
</table>

Based on the flyash distribution in Table v-7, and the catalyst/absorbent distribution in Table v-8, a bed velocity of 333 mm/sec (1.09 ft/sec) would result in eluting at least 90% of the flyash and only 6.0% of the catalyst/absorbent. The cyclone banks would be arranged so that the primary cyclones collect the majority of the catalyst/absorbent and the secondary cyclones collect the flyash. The solids stream from the primary cyclones is sent back into the system. The solids stream from the secondary cyclones is discarded.

The necessary residence time for the catalyst in the regenerator can be estimated from equation v-2. The values for \( \rho_{sm} \), \( 1-e \) and \( C_{ago} \) used in these calculations are typical of an actual design case. Since a range for \( K_2 \) was found experimentally, (Table v-9), a corresponding range for \( t \) will be given with each particle size.
Table v-11. Estimated catalyst/absorbent regeneration time under continuous fluidization conditions.

\[
p_{sm} = 1.414 \times 10^{-3} \text{ gmoles FeS/cm}^3 \text{ Cat.}
\]

\[
l - e' = 0.9863
\]

\[
C_{ag0} = 2.69 \times 10^{-6} \text{ gmoles/cm}^3
\]

<table>
<thead>
<tr>
<th>Diameter (cm)</th>
<th>.0050</th>
<th>.0100</th>
<th>.0150</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_2) (cm/sec)</td>
<td>.00326</td>
<td>.0669</td>
<td>.00326</td>
</tr>
<tr>
<td>(t_{99%}) (sec)</td>
<td>367</td>
<td>17.9</td>
<td>732</td>
</tr>
<tr>
<td>(t_{99.9%}) (sec)</td>
<td>421</td>
<td>20.5</td>
<td>840</td>
</tr>
</tbody>
</table>

The ranges of acceptable residence times for 99.9% regeneration from Table v-11 for the catalyst/absorbent is 20 - 421 seconds and 61 - 1260 seconds depending on the particle size. The upper limit in both of these ranges is high only because rapid gas sampling during experimentation was not possible. One would expect that the regeneration time and sulfidation time would be at least similar in magnitude since both are controlled by intraparticle diffusion.

The regeneration rate could be higher than the sulfidation rate since the \(O_2\) concentration during regeneration will be about 80 times the \(SO_2\) concentration used in the experiments.

In Run 42, Figure iv-41, the sulfidation of the solid was reported to occur very rapidly. The elution of sulfur compounds in Run 42 occurred only after 85 - 98% of the bed had been sulfided. Since the calculated COS breakthrough (assuming FeS formed) was 4920 seconds, the sulfidation time of the solid was 100 - 740 seconds. With a higher concentration of reactant in the gas, 21% instead of...
0.53%, the time would be between 2.5-18.7 seconds. This discussion shows that the lower range of residence times for regeneration presented in Table v-11 correspond more closely to the actual case than the upper range. For design considerations a solids hold-up time of 300 seconds will be provided to ensure complete regeneration.

C. CO and H$_2$ Generator.

1. Practical considerations.

   The discussion in Chapter I showed that an excess of CO and H$_2$ can be produced when fossil fuels are burned in an O$_2$-deficient environment. The first requirement is that the fuel used to produce the CO/H$_2$ mixture be the same as the fuel used in the plant. This minimizes fuel, storage, handling and conveying equipment. The second requirement is that the heat of the gasification be recovered in the boiler cycle. The third requirement is that carbon and soot formation be minimized in the gasifier.

2. Type of generator.

   Recent restrictions on the use of natural gas have essentially eliminated the construction of new natural gas-fired power plants. New fossil-fueled power plants will burn almost exclusively oil or coal. The generator for CO + H$_2$ must also be designed to be fueled by oil or coal. A fluidized bed of limestone (EPA, 1971) could be used in the case of oil and a coal-fired stoker unit could be used in the case of coal. In either case the unit should operate
adiabatically, the heat of reaction being recovered in the boiler convection pass.

Under reducing conditions, both oil and coal have the potential to form soot. In the detailed design, the considerable experience in the production of producer gas will be drawn upon to minimize soot formation in the gasifier. Once the carbon has been oxidized, equation v-18 shows that the CO combination reaction to give C and CO₂ is unfavorable at operating conditions.

\[
\begin{align*}
\text{2 CO} & \rightarrow \text{CO}_2 + \text{C} \\
\Delta H_{25^\circ C} & = -41.2 \text{ kcal} \\
\Delta F_{727^\circ C} & = -0.81 \text{ kcal} \\
\Delta F_{1093^\circ C} & = +14.2 \text{ kcal}
\end{align*}
\]

In order to minimize the amount of carbon formation in the main flue gas when coal or oil is burned, the main combustion zone of the furnace will be operated under oxidizing conditions. At roughly 1100°C, a rich stream of CO/H₂ produced in a fuel gasifier will be added to convert the flue gas to net reducing stoichiometry. This pre-gasification of a portion of the fuel will prevent carbon formation in the main flue gas stream. The amount of fuel gasified will depend on the CO/H₂ requirements to accomplish the removal reactions. Since the design presented in section D is for a coal-fired plant, only the chain grate stoker design will be discussed in detail.

The gasifier will operate with an amount of air just sufficient to convert the carbon to CO and the sulfur to SO₂. In actual practice, with high CO levels, the sulfur will probably be in the form of H₂S. Designing for SO₂ formation provides for a conservative
design since this requires more CO and H\textsubscript{2}. The conversion of fuel N to NO was assumed to be 20%. Under the actual reducing conditions in the gasifier this value may be much lower. The H\textsubscript{2} content of the gasifier streams is taken as the amount of H\textsubscript{2} in the fuel. The actual amount of H\textsubscript{2} present after the gasifier stream has mixed with the flue gas will be a function of the equilibrium established by the water-gas shift reaction. Figure v-1 shows the H\textsubscript{2}/CO established when this gasifier stream is mixed with a typical coal flue gas, where CO\textsubscript{2}/H\textsubscript{2}O is 2.14. Above 1100°C, the H\textsubscript{2}/CO ratio is around 0.20. Therefore, the major reducing agent will be CO. With oil-fired units there will be slightly more H\textsubscript{2} present but still the major reducing agent will be CO.

D. Design Bases.


To obtain an evaluation of the merit of the proposed process, the conceptual design discussed in Chapter I is combined with the experimental results of Chapter IV to produce the detailed design of a system to remove SO\textsubscript{x} and NO\textsubscript{x} from a 1000-Mw coal-fired power plant. The flow sheet for this design is presented in Figure v-2. The stream flows and temperatures are presented in Table v-12. This version of the process uses a sulfuric acid plant for sulfur recovery.

In the discussion of the experimental work in Chapters II, III, and IV, the metric system of units has been used. In the discussion
Fig. v-1. Equilibrium $\frac{H_2}{CO}$ ratio in flue gas for oil and coal units.

Oil: $(CO_2/H_2O)_{avg.} = 1.38, \frac{H_2+CO}{H_2O+CO_2} = 0.0004082$

Coal: $(CO_2/H_2O)_{avg.} = 2.14, \frac{H_2+CO}{H_2O+CO_2} = 0.0004545$
Fig. v-2. Simultaneous NO and SO$_2$ removal process.
TABLE V-12.

PROCESS FLOWS.

SOLID STREAMS
C,OAL (TPHI

.10

11

0

0

13

14

15

17

18

19

20

21

23

0

0

0

0

0

0

0

0

0

.001320 .6640

.6400

0

.2134

14.32

.004354 .000218 14.32

10.74

19.23

.00585

.00029

~4.42

14.42

0

4.81-

~5.29

.01377

.00069

33.97

33.97,

0

9

10 2

2.736

.6129

FLY ASH (Tphl x 102

0

0

.8798

.02639

CAT./ABS. ITph). x 10 2
FeS (lbmphl x 10 2

0

0

0

0

0

0

. FeO (lbmph)

X

X

1o2

102
FeS04 (lbmphl x 10 2
2
. Al 2 o3 ~lbmph) x 10
Fe

o (lbmph) x
2 3

Temp ( F)

12

0

3.583

.2150

0

.004136 .004136 .2149

o·

0

4.816.

0

0

.005 558

.005558

0

0

0

11:32

0

0

0

0

11.33

0

0

.01308

.01308

0

0

a·

.4713

0

8.975

7.906

0

.4718

0

.000542 .000542 1 .040

.8483

0

0

0

0

.8493

0

0

.000978 .000978

56.17
1000

0

52.65
1250

0·

77
0

56.18
1000
.1567

.77 45

3.578
1250
1.093

0
1250

0

56.23
890
.04829

0

762.1

83464

0

2471

0

11907

39411

5.07

.277

.0461

164

6.557
6.54

.0196

33829

20

22

.00057

.000029 10.38

1.414

.co 103

.00005

2.545

2.545

0

0

224.7

.068J
1000
42.02

.0034
300
21.87

224.7
1000
.1567

168.5
0

0

0

.00345
.0209

.000332 3046
.00201
141

79347

79347

84075

2.23

2.23

1000
42.02
11.36'
.697

1000

0
.02039.

3.368

1.885

77

36

0

3.393

250

0

3.583

0

Den. CAT./ABS.~ x 10· 3
Den. F.A.HJ · x 10·3_

35

0
o

0

0

Gas Flow (acfml x 10 5

34

0
.D2S07

0

0

.01127
77.

33

0
.o2sa1

.02384

0

0

32

.02384

.000716 3.579

.001791

.00832

26

0

.001073 .2384

750

.2146

1.0403

.02146

1.093

.06489
300
0

0

:1931
.000143

.000336
0

.06489
150

3.576
1250

.00224
125.0

.02182

0

0

6.31

84075

.622

38.3

0

39120

0

0
0
0
750

0
0
39410

LIQUID
GAS STREAM FLOWS
4·
N2 (lbmph) X 10
0 (lbmph)
2
co 2 (lbmph) x 1o4 ·
H2 0 llbmph) x 10 2
CO (lbmphl x 10 2

2

16.12
42.850

6

1.347·
3,579

8

9
17.48

10

11

1.354

16.11

17.48

17.48

0

194.8

0

17.48
0

3.796

4.030

4.030

0
4.030

17.48

16
.4554
1,211

.4650
123

0

0

.01502

.06513

26
.4650

27

31

FLOWS

24

25

29

.00699

Feed H2 o (gpm) 2.488

·sao·

Temp (°F)

2.488
365

123

.1998
199.2

0

0

0
.00161

.7959

0

0

.08546

0

0

0

0
4.81

0

0

0
4.81

.154

0

0

0

0

0

0

0

0

0

0

3.895
3.292

194.8
·3.796

43.35

3.621

5.963

183.8

·213.7

213.7

213.6

213.6

213.6

1.225

0

0

0

0

23.56

23.56

.1955

.1955

0

0

0
5.13
. 1.455

5.348

5.348

.4335

.1955
.4335

.4335

0

6.283
1.717

6.283
1.717

.6283
.1717

.6283
.1717

.6283
.1717

0

0

0

0

0

0
0

0

73.75
29.17
1.149

0

.2607

0
20.84

0
1.741

0
23.80

0
23.80

77.26
23.67

77.26
23.67

77.26
23.67

0
5888

0
.5255

0

2.455

0
21.70

0

Total Gas (lbmph) x 10

.0882

.5255

0
.2i13

0
.0294

Temp tFJ

300

300

2000

2780

2300

1000

·1000

1000

300

300

750

300

1250

180

7.7

H (lbmph) x 102
2
so2 Obmph) x 10 2
2
NO llbmph) x 10
NH (lbmph)
3

acfm

4

6

H so 4 ITpd)
2

280

280

30
500
365

28
210

0

,._ actual cubic feet per minute.

Ibm ph= pound moles per hour.

Tph

= Tons per hour.

N
0
00

..


of the plant design and throughout the remainder of this chapter, the English system of units will be used because of its greater ease of interpretation by most engineers. The removal reactions reported between 370 - 538°C are between 700 - 1000°F. The regeneration reaction at 677°C is at 1250°F. Equipment dimensions are given in inches and feet. Flow rates are given in pound moles per hour (lbm/hr) or tons per hour (Tph). Densities and concentrations are given in pounds per cubic foot (lbs/ft³).


The bases for the design are presented in Appendix A - 4. Table V-13 gives a listing of the calculations used to develop this design. The gas compositions at key points in the process are given in Table V-14.
### Table v-13. Calculation flowsheet.

<table>
<thead>
<tr>
<th>Select</th>
<th>Calculate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Furnace</td>
<td></td>
</tr>
</tbody>
</table>
- Coal composition.  
- Excess air level  
- Inlet air humidity.  
- Power plant efficiency.  
- % fuel N to NO  
- % thermal NO of total NO  
- Ash split between flyash and bottoms. |  
- Thermal value of coal.  
- Total coal rate  
- Furnace flue gas composition.  
- Rate of flue gas and required CO/H₂ flow per wgt.  
- furnace-fired-coal. |
| 2. Gasifier | Adiabatic operating temperature.  
- Coal composition.  
- Excess air level  
- Inlet air humidity.  
- % fuel N to NO.  
- % thermal NO of total NO.  
- Ash split between flyash and bottoms. |  
- Gasifier gas composition.  
- Thermal value of coal.  
- Rate of flue gas per wgt.  
- gasifier-fired coal.  
- Coal split between gasifier and furnace. |
| 3. Total flue gas |  
- % O₂ removed in flue gas when CO/H₂ added.  
- Maximum temperature of superheater inlet. |  
- Temperature when CO/H₂ added  
- Flue gas' composition.  
- Flue gas rate. |
| 4. Contactor |  
- % Removal (CO + H₂), SO₂, NO.  
- % SO₂ removed as S⁻².  
- % SO₂ removed as SO₄⁻².  
- Temperature.  
- Fraction of solids sent to regenerator.  
- Amount of excess Fe₂O₃.  
- Composition of original solid. |  
- Flow of FeS, FeO, Fe₂O₃, FeSO₄.  
- Flow of catalyst in contactor.  
- Flue gas composition after contactor.  
- Exit gas from regenerator. |
| 5. Regenerator |  
- % Inlet solid regenerated.  
- Temperature.  
- Stoichiometric air requirement. |  
- Catalyst/absorbent exit composition.  
- Solids exit flow rate.  
- Exit gas rate.  
- Exit gas composition. |
Table v-14. Gas compositions in the process.

<table>
<thead>
<tr>
<th></th>
<th>Contactor Entrance</th>
<th>Contactor Exit</th>
<th>Regenerator Exit</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2} (%)</td>
<td>73.44</td>
<td>73.86</td>
<td>88.5</td>
</tr>
<tr>
<td>CO\textsubscript{2} (%)</td>
<td>15.95</td>
<td>17.02</td>
<td>0</td>
</tr>
<tr>
<td>H\textsubscript{2}O (%)</td>
<td>8.98</td>
<td>9.02</td>
<td>0</td>
</tr>
<tr>
<td>O\textsubscript{2} (ppm)</td>
<td>819</td>
<td>0</td>
<td>2.35</td>
</tr>
<tr>
<td>NO (ppm)</td>
<td>721</td>
<td>72.5</td>
<td>0</td>
</tr>
<tr>
<td>SO\textsubscript{2} (ppm)</td>
<td>2247</td>
<td>265</td>
<td>91,450</td>
</tr>
<tr>
<td>CO (ppm)</td>
<td>9900</td>
<td>82.6</td>
<td>0</td>
</tr>
<tr>
<td>H\textsubscript{2} (ppm)</td>
<td>2247</td>
<td>183</td>
<td>0</td>
</tr>
<tr>
<td>NH\textsubscript{3} (ppm)</td>
<td>0</td>
<td>326</td>
<td>0</td>
</tr>
<tr>
<td>(O/R)\textsubscript{NH\textsubscript{3}}</td>
<td>0.93</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>


The process has been designed to minimize heat losses. The heat generated in the gasifier is recovered in the boiler convection pass. The exit flue gas contains no excess air, which minimizes sensible heat losses. The excess heat produced by the exothermic regeneration reactions is recovered in heating coils containing boiler feedwater. The regeneration exit gas is cooled with a heat exchanger containing boiler feedwater. In both cases the boiler feedwater transfers the heat back into the steam boiler cycle. The solids, exiting from the regenerator, also transfer sensible heat back to the flue gas where it can be recovered in either the
economizer or the air preheater. The combustion potential of CO, H₂, and NH₃ and the sensible heat of the regenerator gas and disposed flyash represent process heat losses. The next paragraphs will give the details of the energy balance.

The heat liberated during combustion of coal in the furnace was estimated from the following formula (Steam, 1963):

\[
\text{BTU/1b Coal} = 14,544 \, C + 62,028 \left( H_2 - \frac{0.2}{8} \right) + 4,050 \, S. \tag{v-19}
\]

where: C, H₂, O₂, and S are the weight fractions of each element in coal.

The heat liberated from the partial combustion of coal in the gasifier unit was first calculated from the \( \Delta H_f \) for CO and SO₂ formation. This value was increased slightly (2.4%) to be consistent with the bases of equation v-19.

The heat liberated when the CO/H₂ stream reduces 95% of the excess O₂ was calculated from \( \Delta H_f \) data for CO₂ and H₂O. The final value for H₂/CO in the flue gas stream was taken as the equilibrium value from the water-gas shift reaction at 2200°F. With this assumption the amount of CO₂ and H₂O formed and the amount of heat released can be calculated. Table v-15 summarizes the heat generated during combustion.
Table v-15. Heat released in combustion reactions.

(1000-MW coal-fired unit.)
334.92 Tons coal/hr.

<table>
<thead>
<tr>
<th>% of Coal</th>
<th>BTU/hr (x 10⁹)</th>
<th>% of heat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidizing furnace</td>
<td>81.70</td>
<td>7.168</td>
</tr>
<tr>
<td>Gasifier</td>
<td>18.30</td>
<td>0.374</td>
</tr>
<tr>
<td>O₂ Removal reaction</td>
<td>---</td>
<td>0.859</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>8.401</td>
</tr>
</tbody>
</table>

If the same amount of coal were burned in an oxidizing furnace to CO₂, H₂O, and SO₂, the heat liberated would be 8.774 x 10⁹ BTU/hr. This implies a potential heat loss of around 4%. A more accurate estimate of the loss is obtained by calculating the amount of heat liberated if the excess CO and H₂ were reacted to CO₂ and H₂O. This calculation shows a potential loss of 0.342 x 10⁹ BTU/hr, which is 3.9% of the total heat liberated.

Some of the apparent loss in this step of the process is offset by the fact that instead of the usual 20% excess air there is essentially 0% excess air in the effluent gas from the plant. Heating this excess air from 77°F, an average inlet temperature, to 300°F, an average stack-gas temperature, requires approximately 0.072 x 10⁹ BTU/hr, which is 0.82% of the total energy.

The removal reactions in the contactor are also exothermic. Appendix A - 5 lists the reactions considered and their ΔH₂⁵°C values. Table v-16 lists the heat evolved during the removal reactions. This heat is recovered in the economizer and air preheater.
Table v-16. Energy released in removal reactions.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Assumptions</th>
<th>$\Delta H$ BTU/hr ($x 10^9$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>50% NH$_3$ selectivity</td>
<td>0.0204</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>15% sulfur removed as SO$_4^{2-}$</td>
<td>0.0776</td>
</tr>
<tr>
<td></td>
<td>95% sulfur as SO$_2$ in gas</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5% sulfur as H$_2$S</td>
<td></td>
</tr>
<tr>
<td>CO + H$_2$</td>
<td>% Red H$_2$/% Red CO = 0.776</td>
<td>-0.00598</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Iron reduced to FeO for FeS formation reaction</td>
<td>-0.00332</td>
</tr>
<tr>
<td>O$_2$</td>
<td>97.6% O$_2$ formed SO$_4^{2-}$</td>
<td>0.00000478</td>
</tr>
<tr>
<td></td>
<td>(Amount to give required SO$_4$ = level)</td>
<td></td>
</tr>
<tr>
<td>Total Release</td>
<td></td>
<td>0.0887</td>
</tr>
</tbody>
</table>

All of the reactions except the reduction of Fe$_2$O$_3$ and the oxidation of CO and H$_2$ are exothermic. The selected split of the reduction between CO and H$_2$ was based on an average of the H$_2$/CO ratios between 1000°F and 2200°F. If more of the reduction were by CO, the reactions would all be more exothermic. The role of H$_2$ in the reduction is not expected to increase above the assumed value.

Heat is also produced in the process external to the furnace. The two main reactions occurring in the regenerator, which are the last three reactions in Appendix A - 5, are exothermic.

As stated earlier, the amount of heat liberated in the regeneration will depend upon the solids composition and inlet temperature, the inlet air flow rate and its temperature, and the temperature level required for regeneration. In order to operate the regenerator at
a constant temperature, this heat must be removed by cooling coils (using boiler feedwater) immersed in the fluidized bed. The heat release for this design is given in Table v-17.

Table v-17. Energy generation in regeneration reactions.

(1000-Mw coal-fired unit)

<table>
<thead>
<tr>
<th>Conditions:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid:</td>
<td></td>
</tr>
<tr>
<td>0.05899 lbs FeS/lb Catalyst</td>
<td></td>
</tr>
<tr>
<td>0.1136 lbs FeO/&quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>0.01799 lbs FeSO_4/lb &quot;</td>
<td></td>
</tr>
<tr>
<td>0.01051 lbs Fe_2O_3/&quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>0.7989 lbs Al_2O_3/&quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>1000°F Inlet Temperature</td>
<td></td>
</tr>
<tr>
<td>Regenerator: 1250°F; Contactor: 1000°F</td>
<td></td>
</tr>
</tbody>
</table>

Air: 110% of stoichiometric for complete oxidation to Fe_2O_3 and SO_2, 300°F Inlet Temperature

H_2O: Inlet 280°F, Outlet 365°F

Sensible heat recovered in regenerator coils: 0.1057 x 10^9 BTU/hr.
Sensible heat transferred by solids to contactor: 0.0258 x 10^9 BTU/hr.
Heat recovered in regenerator gas cooler: 0.0212 x 10^9 BTU/hr.

Adding both of the heat sources from the process reactions and the heat recovered from the solids and gas gives a total of 0.2684 x 10^9 BTU/hr. With the potential loss of 0.342 x 10^9 BTU/hr from the excess CO + H_2 and the gain of 0.2684 x 10^9 BTU/hr the percentage heat loss as a result of the process is 0.839% of the total liberated in the power plant. This loss is approximately the same as that calculated for the savings gained by the decreased amount of excess air used. Reducing the excess air effectively to zero would result in a significant reduction in the loss of sensible heat in the stack gas.
If this is in fact found operationally possible, there would be a definite incentive for the process from the standpoint of energy conservation. In the operating cost section it is assumed that there will be a 0.839% energy loss. This gives a conservative design estimate.

4. Equipment description.

a. Contactor.

The contactor is basically an extension of the duct between the primary superheater and the economizer sections. It is to be fabricated of 3/16-in carbon steel lined with 3 inches of 85% MgO/CaSiO₃ castable insulation. The duct length of 50 feet provides the required residence time. The contactor cross section is 32.6 ft x 83.6 ft. The catalyst/absorbent is sprayed into the contactor entrance by pneumatic conveying lines. The solids and the flue gas are in concurrent flow. Within the contactor, the catalyst/absorbent concentration for this design is $1.14 \times 10^{-2}$ lb/ft³. This concentration corresponds to a dilute-phase contactor and is within the experimental range required. Flyash will also be present in the contactor at a concentration of $0.070 \times 10^{-2}$ lb/ft³. This gives a flyash to catalyst/absorbent ratio of 0.061. The concentration of flyash used in this design is expected to be a maximum. The large amount is a result of overlap in catalyst/absorbent and flyash distribution. Either smaller flyash or larger catalyst/absorbent particles would result in a better separation, decreasing the amount of flyash recycled.
b. Regenerator.

The regenerator is a series of ten fluidized beds stacked vertically. The inlet solids are pneumatically conveyed to the top of the regenerator and pass through the series of beds, exiting at the regenerator base. Solids pass between beds in downcomers. The basis for ten fluid beds instead of one is to conserve construction area. If plant space were available, a single fluidized bed could be constructed. In the 10-unit design the regeneration air enters a manifold on one side of the tower. One-tenth of the inlet air passes to each fluid bed. The effluent gas and solids are collected in a manifold on the opposite side of the regenerator and pass to the high efficiency cyclones. Sectional views of the regenerator are shown in Figure v-3. The interior cross section is 13.7 ft x 13.7 ft. The plates are 6 feet apart, with a bed height of about 1 foot. The beds were designed with a void fraction of 0.60. Given the feed of both catalyst/absorbent and flyash, the bed density ranges from 43.3 lb/ft$^3$ at the top to 44.6 lb/ft$^3$ at the bottom.

The interior of the regenerator and the exit manifold are 1/4-inch 316 SS. The entrance air manifold is 3/8-inch carbon steel. The outside area is insulated with 3 inches of 85% MgO/CaSiO$_3$. The gas distributor plates and the bed separation plates are 1/8-inch 316 SS. A 3/8-inch, 8-ft carbon steel skirt is provided.

The inlet air temperature to the bed is 300°F. The beds are kept at 1250°F by cooling coils in which boiler feedwater is circulated. These coils are 1.66-inch Sch 40 316 SS pipe having 0.25-inch fins with 10 fins/inch. A total of 165.3 ft$^2$ of surface area per bed is
Fig. v-3. Regenerator schematic.
A. Solids flow.
B. Gas flow.
C. Plan view.
provided. Ten control values in the lines remove heat as needed from each bed.

c. Gasifier.

The design of the gasifier is based on the design of a continuous feed, rectangular construction incineration system. The fuel is burned on a moving chain grate. Niessen (1970) reports that a 250-Tpd municipal incinerator generates about $1.7 \times 10^5$ acfm of flue gas at $1600^\circ F$. The required gasifier gas rate at $1600^\circ F$ is $6.51 \times 10^5$ acfm. With linear extrapolation of the gas volumes this implies that a municipal incinerator capable of handling 957 Tpd would be roughly the size of the gasifier. The furnace would have refractory walls with no heat-transfer surface provided. All of the heat generated would be removed in the convection zone of the boiler. The air supplied to the gasifier will come from the normal F.D. fan system for the inlet air. The coal burned in this unit will typically be between 1/8-inch and 1-inch in size (Steam, 1963). The larger size allows about 85% of the ash to be collected in the bottoms.

d. Cyclones and electrostatic precipitators.

The main cyclone bank which collects the solids immediately after the contactor are medium-efficiency cyclones found on normal coal-fired units. EPA (August, 1973) and Benson (1974) report that such cyclones are 85% efficient on flyash. The typical pressure drop is 3 inches of H$_2$O. The material of construction is carbon steel. Popper (1970) reports the collection efficiency as a function of particle size from 2.5 up to 150 microns for this type cyclone
bank on coal flyash. With the catalyst/absorbent size distribution given in Table v-8 these cyclones would be expected to give an overall efficiency of 98.876%. Even though this is relatively high it still would allow a large loss of catalyst/absorbent. A second similar bank of cyclones was therefore added to the design. This gives a total pressure drop across the cyclones of 6.0 inches. The second bank of cyclones will be 80% efficient for flyash removal and 97.293% for catalyst/absorbent. The overall efficiency of the cyclone banks will thus be 97% for the flyash and 99.9696% for the catalyst/absorbent.

The electrostatic precipitator (ESP) for the main flue gas is not considered a part of this design since most plants either have one or will have to have one regardless of the installation of this process. The ESP will provide an efficiency of 95% for both the flyash and catalyst/absorbent. The large amount of iron on the catalyst should give resistivities similar to the flyash. With the ESP in the system the overall efficiencies become 99.85% for the flyash and 99.998% for the catalyst/absorbent.

The cyclones on the regenerator are operated at 1250°F. These are high efficiency cyclones made of 316 SS and lined with castable insulation to prevent high erosion rates. Flanders (1974) discussed cyclones of this design which had removal efficiencies of 99.996% on Si/Al catalyst/absorbent with an average size of 60 microns. The units discussed had primary and secondary cyclones which developed a pressure drop of 30 inches of H₂O. The units handled a gas flow
from a fluid bed catalytic cracking regenerator, which was 2.93 times the rate required in the present regenerator. The specifications for the cyclone bank required for the regenerator will be similar to these. The catalyst/absorbent removal efficiency is taken as 99.933%. The flyash removal efficiency is taken at 90%. The catalyst/absorbent will primarily be collected in the first bank of cyclones while the second bank will collect the flyash and the remainder of the catalyst/absorbent.

An electrostatic precipitator is added before the H$_2$SO$_4$ plant to remove 95% of the flyash remaining after the cyclones. This unit is sized by scaling up from the TVA data reported by Benson (1974). Since the precipitator operates at 750°F, it is classed as a "hot" precipitator. The material of construction to be used is 316 SS.

e. Blowers and motors.

The centrifugal blowers used for the regenerator air supply and the pneumatic conveying lines are capable of moving gas up to pressure differentials greater than 1000 inches H$_2$O but are operated at the required level. (See Table v-18). This high pressure capability is obviously more than is required under normal conditions but may be needed if solids plug up in any part of the system.

The motors used were all 3-phase, enclosed-fan-cooled electric motors operating at a nominal 1,800 rpm.

f. Catalyst storage tank.

A carbon-steel storage tank with manholes and ladders is provided
for storage for the catalyst/absorbent. The size is 1100 gallons, 8257 ft³. This would give a 90-day supply at a net consumption of 143 lbs/hr.

g. Regenerator gas cooler.
   After the regenerator cyclones a SS-U-tube exchanger is used to cool the flue gas from 1250°F to 752°F. The 1-inch tubes had boiler feedwater flowing in them; the total surface area provided was 3225 ft². An overall U of 10 BTU/hr ft² °F was used for the design. This is a conservative design since finned tubes could be used to decrease the tubing length.

h. Pumps and motors.
   The pumps required to circulate the regenerator bed coolant and the regenerator gas coolant will be the same as those used to circulate water to and from the economizer. Control valves will be used to regulate the flow to each bed. Only the control valves are considered as a process cost.

i. Piping and Ductwork.
   Solids conveyance in the process is by means of fluidized transport. The gas used to accomplish the fluidization is taken from a gas stream at approximately the same temperature as the solids. The fluid density in the transport lines ranges from 3.05 to 0.0063 lb/ft³. The piping and ductwork required are designed for a transport velocity of 50 ft/sec. This velocity was selected to achieve the smallest cross-section possible without having excessive erosion
(Flanders, 1974). All bends should be 90° to minimize solids attrition (Flanders, 1974). The lengths of piping selected were estimated to be reasonable for the design presented. The details are given in the Cost Summary, Table v-18. The transport reference was Zenz (1960).

j. \( \text{H}_2\text{SO}_4 \) plant.

The sulfuric acid plant design was taken from Sittig (1971). The plant is an integrated contact plant with 3-stage contacting. The overall conversion efficiency for the unit was 96.8%. The product can range from 93% \( \text{H}_2\text{SO}_4 \) to various grades of oleum. Total production from this plant is 210 Tpd as 100% \( \text{H}_2\text{SO}_4 \). The regenerator exit gas, the feed to the \( \text{H}_2\text{SO}_4 \) plant, has 9.1% \( \text{SO}_2 \) in it. The tail gas from the \( \text{H}_2\text{SO}_4 \) plant can be mixed with the air to the furnace so that the remaining \( \text{SO}_2 \) can be recovered. Facilities are provided for 30 days storage and for shipping of the acid.

E. **Economic Analysis.**

1. **General discussion.**

In order to estimate the economic feasibility of the proposed process a cost model was developed for both the fixed capital investment (FCI) and the operating cost (OC). This model includes all of the added equipment required by the removal process. The FCI and OC for the \( \text{H}_2\text{SO}_4 \) plant were obtained directly from Sittig (1971).

The basic reference for constructing the cost model was Peters (1968). The FCI was separated into direct costs and indirect costs. Table v-19 shows the breakdown of the items within each group. The
<table>
<thead>
<tr>
<th>EQUIPMENT</th>
<th>DESCRIPTION</th>
<th>SIZE UNIT</th>
<th>COST UNIT</th>
<th>DATED COST $</th>
<th>OCTOBER 1973 PURCHASE COST $</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Contactor</td>
<td>Steel (carbon) 2 @ 3/16 in x 32.6 ft x 50 ft</td>
<td>88,935 lbs</td>
<td>0.13 $/lb</td>
<td>11,562 (I) 1/67</td>
<td>10,877</td>
<td>Peters, 1968, p. 654</td>
</tr>
<tr>
<td></td>
<td>Insulation (MgO/CaSiO₃) 3 in x 11,620 ft²</td>
<td>11,620 ft²</td>
<td>.961 $/ft² (cost) .335 $/ft² (labor)</td>
<td>15,234 11/62</td>
<td>21,994</td>
<td>Dinning, 1963, p. 186</td>
</tr>
<tr>
<td>2. Regenerator</td>
<td>Steel (stainless, 316) Shell 1/4 in x 13.65 ft x 17.1 ft x 66 ft</td>
<td>69,789 lbs</td>
<td>1.196 $/lb</td>
<td>106,525 (II) 1/67</td>
<td>105,615</td>
<td>Peters, 1968, p. 654</td>
</tr>
<tr>
<td></td>
<td>Plates 1/8 in x 13.65 ft x 14.3 ft x 19 ft</td>
<td>19,278 lbs</td>
<td>0.23 $/lb</td>
<td>5,734 (I) 1/67</td>
<td>5,951</td>
<td>Peters, 1968, p. 654</td>
</tr>
<tr>
<td></td>
<td>Steel (carbon) 3/8 in x 8 ft x 17.1 ft</td>
<td>24,930 lbs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/8 in x 13.65 ft x 66 ft</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Insulation 3 in MgO/CaSiO₃</td>
<td>4,539 ft²</td>
<td>.961 $/ft² (cost) .33 $/ft² (labor)</td>
<td>5,951</td>
<td>1962</td>
<td>8,591</td>
</tr>
<tr>
<td>3. Gasifier</td>
<td>7.772 x 10⁵ cfm @ 2000 °F</td>
<td>957 TPD equi Incinerator</td>
<td>1,900 $/TPD</td>
<td>2.218 x 10⁶ (I) 1969</td>
<td>1,584,000</td>
<td>Niessen, 1970, p. VII, 93-111</td>
</tr>
<tr>
<td>4. Cyclone (contactor)</td>
<td>(scale factor 0.80) 2 Cyclone Banks identical</td>
<td>606,919 cfm @ 1000°F</td>
<td>$112,000</td>
<td>752,760</td>
<td>1970</td>
<td>866,760</td>
</tr>
<tr>
<td></td>
<td>Insulation + Struct. Estimated at 15%</td>
<td></td>
<td></td>
<td>130,014</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Cyclone (regenerator) (ss)</td>
<td>(scale factor 0.80) High Efficiency @ 1250 °F</td>
<td>358,700 cfm</td>
<td>$407,000</td>
<td>172,107</td>
<td>1973</td>
<td>172,107</td>
</tr>
<tr>
<td>6. ESP (regenerator) (ss)</td>
<td>(ss construction) (scale factor 0.80) 95% Efficient @ 750 °F</td>
<td>606,919 cfm</td>
<td>$1,231,000</td>
<td>536,610</td>
<td>1972</td>
<td>562,032</td>
</tr>
<tr>
<td>8. Fans and Blowers</td>
<td>Reg. Air Blower #3 Centrifugal @ 300 °F</td>
<td>$4.4 x 10⁶ cfm</td>
<td></td>
<td>70,000 1/67</td>
<td>92,196</td>
<td>Peters, 1968, p. 470</td>
</tr>
<tr>
<td></td>
<td>Reg. Solids Blower #2 Centrifugal @ 77 °F</td>
<td>$1.92 x 10⁶ cfm</td>
<td></td>
<td>9,000 1/67</td>
<td>11,854</td>
<td>Peters, 1968, p. 470</td>
</tr>
<tr>
<td>EQUIPMENT</td>
<td>DESCRIPTION</td>
<td>SIZE UNI I</td>
<td>COST UNIT</td>
<td>DATED COST $</td>
<td>OCTOBER 1973 PURCHASE COST $</td>
<td>REFERENCE</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
<td>------------</td>
<td>-----------</td>
<td>--------------</td>
<td>-----------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Cont. Solids Blower 1</td>
<td>Centrifugal @ 300 °F</td>
<td>$8.156 \times 10^3$ cfm</td>
<td>----</td>
<td>21,000 1/67</td>
<td>27,659</td>
<td>Peters, 1968, p. 470</td>
</tr>
<tr>
<td>8. Motors for Fans and Blowers</td>
<td>(3-phased, enclosed fan cooled)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reg. Air Blower Motor</td>
<td>$\Delta p = 1.50$ psi, $E_f = 70$, $E_m = 94.5$</td>
<td>538 bhp</td>
<td>----</td>
<td>30,000 1/67</td>
<td>52,225</td>
<td>Peters, 1968, p. 474,460</td>
</tr>
<tr>
<td>Reg. Solids Blower Motor</td>
<td>$\Delta p = 1.49$ psi, $E_f = 70$, $E_m = .86$</td>
<td>21 bhp</td>
<td>----</td>
<td>650 1/67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cont. Solids Blower Motor</td>
<td>$\Delta p = 4.64$ psi, $E_f = 70$, $E_m = .92$</td>
<td>256 bhp</td>
<td>----</td>
<td>9,000 1/67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. Flue Gas Cooler from Reg.</td>
<td>$3225$ ft$^2$ (1250 °F $\rightarrow$ 752 °F) (ss)</td>
<td>----</td>
<td>550,000 1/67</td>
<td>65,857</td>
<td>Peters, 1968, p. 569</td>
<td></td>
</tr>
<tr>
<td>11. Catalyst Storage Tank</td>
<td>Carbon Steel, 90 day</td>
<td>8257 ft$^3$</td>
<td>----</td>
<td>1,440 1/67</td>
<td>1,097</td>
<td>Peters, 1968, p. 477</td>
</tr>
<tr>
<td>12. Piping and Duct</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duct Work</td>
<td>2.28 ft x 2.28 ft x 1/8 in x 400 ft</td>
<td>$18,718$ lbs</td>
<td>$5.18$/lb</td>
<td>$3,369$ 1/67</td>
<td>22,601</td>
<td>Peters, 1968, p. 654</td>
</tr>
<tr>
<td>Duct work</td>
<td>4.26 ft x 4.26 ft x 1/8 in x 100 ft</td>
<td>$8,820$ lbs</td>
<td>$5.23$/lb</td>
<td></td>
<td>2.029 1/67</td>
<td></td>
</tr>
<tr>
<td>Remainder</td>
<td>(Estimated at 50% other)</td>
<td></td>
<td></td>
<td></td>
<td>11,300</td>
<td></td>
</tr>
<tr>
<td>TOTAL:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insulation</td>
<td>= $160,599$ (I)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piping</td>
<td>= $34,449$ (P)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Major Equip.</td>
<td>= $3,580,081$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pur. Eq.</td>
<td>= $33,775,129$ (E)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TABLE V-19. PROCESS FIXED CAPITAL INVESTMENT (FCI).</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>DIRECT COSTS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>METHOD CALCULATED</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>OCTOBER 1973 COST</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Purchased Equipment (E)</strong> Itemized Equipment Costs</td>
<td>$3,775,129</td>
<td>Total ($)</td>
<td>Percent of Total</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Installation (Labor, Found., Const.) 40% (E)</td>
<td>1,510,052</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Instrumentation 13% (E)</td>
<td>490,767</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Instrumentation Installation and Accessories 8% (E)</td>
<td>302,010</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pipe Costs (P) Itemized Pipe Costs</td>
<td>34,449</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pipe Labor Installation 46% (P)</td>
<td>15,846</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pipe Insulation Material and Labor 25% (P)</td>
<td>8,612</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical Installation 7.5% (FCI)</td>
<td>1,265,603</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Building and Service 5% (FCI)</td>
<td>843,735</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insulation Major Equipment (I) Itemized Insulation Costs</td>
<td>160,599</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Startup Expense 8% (FCI)</td>
<td>1,349,977</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>INDIRECT COSTS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Engineering and Supervision 35% (E)</td>
<td>1,321,295</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Construction Expenses 34% (E)</td>
<td>1,283,544</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contractor's Fee 3.75% (FCI)</td>
<td>632,802</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contingencies 8% (FCI)</td>
<td>1,349,977</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Working Capital 15% (FCI)</td>
<td>2,531,206</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SUMMARY</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$16.87 \times 10^6 H_2SO_4 FC1 = 1.67 \times 10^6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$18.54 \times 10^6 Total FC1 = $18.54 \times 10^6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
items were estimated as a function of the total purchased equipment cost (E), piping and duct costs (P), insulation costs (I), and FCI. The piping and insulations costs were calculated from the amount required instead of as a percentage of E. The cost model used for the removal process is

\[ FCI = 4.36(E) + 3.24(P) + 1.89(I) \]  

The operating costs were divided into direct costs and fixed costs. Table v-20 shows the breakdown of the items for each group. Only the maintenance and fixed costs are estimated as a percentage of FCI. The royalties are calculated as a percentage of the total operating cost. The fixed operating costs are taken as 14.67% of FCI. This assumes depreciation over a 15 year period as suggested by Buchard (1972). It is assumed that all of the capital will be borrowed for the removal process at an average interest of 5% over the 15 years.

2. Cost Basis.

The costs required for the model are non-installed equipment costs. In some cases only the installed equipment costs were available. The equipment cost was estimated by dividing these costs by 1.4, which assumes a 40% installation charge. Those costs which were treated this way have a superscript I in the dated cost column of Table v-18. The equipment cost sources are given in this table. In order to standardize all costs the Chemical Engineering plant cost index was used. All costs were updated to October 1973. The CE plant index for the pertinent years is given in Table v-21.
<table>
<thead>
<tr>
<th>TABLE V-20. REMOVAL PROCESS OPERATING COSTS.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DIRECT COSTS</strong></td>
</tr>
<tr>
<td>Energy Loss Charge</td>
</tr>
<tr>
<td>Catalyst Make-up</td>
</tr>
<tr>
<td>Operating Labor and Supervision</td>
</tr>
<tr>
<td>Utilities</td>
</tr>
<tr>
<td>Maintenance</td>
</tr>
<tr>
<td>Royalties</td>
</tr>
<tr>
<td>Laboratory Charges</td>
</tr>
<tr>
<td>Plant Overhead</td>
</tr>
</tbody>
</table>

**FIXED COSTS**

<table>
<thead>
<tr>
<th></th>
<th><strong>METHOD CALCULATED</strong></th>
<th><strong>OCTOBER 1973 COSTS</strong></th>
<th><strong>TOTAL COSTS</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Depreciation (15 years)</td>
<td>6.67% FCI</td>
<td>1,125,543</td>
<td></td>
</tr>
<tr>
<td>Taxes and Property</td>
<td>2% FCI</td>
<td>337,494</td>
<td></td>
</tr>
<tr>
<td>Insurance</td>
<td>1% FCI</td>
<td>168,747</td>
<td></td>
</tr>
<tr>
<td>Interest</td>
<td>5% FCI</td>
<td>843,735</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>2,475,519 $/yr.</strong></td>
<td><strong>2,476 x 10^6</strong></td>
<td><strong>0.322</strong></td>
</tr>
</tbody>
</table>

**Mills/kwhr**

<table>
<thead>
<tr>
<th></th>
<th><strong>INCREASING cat. make-up by factor of 10 gives total cost of 1.23 mills/kwhr</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$5.949 x 10^6/yr.</td>
</tr>
</tbody>
</table>

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Table v-21. CE Plant cost index.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Index</td>
<td>100</td>
<td>101.5</td>
<td>109.1</td>
<td>113.7</td>
<td>119.0</td>
</tr>
</tbody>
</table>

Index | 125.7| 132.2| 137.2| 143.7|

The items costed from Peters (1968) were generally obtained from correlations of equipment cost versus size. The items obtained elsewhere were generally only listed in one size. The scaling factors for specific equipment types suggested by Popper (1970) were used to obtain the cost of specific size equipment.


The total purchase equipment cost for the process comes to $3.78 \times 10^6. The three most costly items are the gasifier, the contactor cyclones, and the electrostatic precipitator on the regenerator effluent gas stream. These items account for $3.14 \times 10^6 or 83% of the total. The gasifier alone represents 42% of the cost. The gasifier cost, stated above, is based on a 957 Tpd municipal incinerator plant.

The cost data presented by Niessen (1970) for the municipal incinerator furnace includes the costs for a crane, primary chamber, secondary chamber, FD fans, associated ducting, ash removal system, gas cooling by water spray, stack, piping, instrumentation and controls. The gasifier unit obviously does not require all of this equipment, but since a further breakdown of furnace costs was not found this cost was used, giving a conservative value. Niessen (1970) reports that above 300 Tpd the furnace cost will average around $1,900/Tpd. More accurate cost data on the gasifier would probably result in a lower
The total FCI for the removal process is $16.87 \times 10^6$. Direct costs represent 57.8% of the total. The two largest costs are the purchased equipment, $3.78 \times 10^6$, and the working capital, $2.53 \times 10^6$. Since in equation \( v-20 \) \( E \) is multiplied by 4.36 to give its contribution to FCI, it is by far the most sensitive item in the analysis.

The operating costs listed in Table \( v-20 \) show 58.4% as direct process costs. The energy loss is that due to the net heat lost by the process and the energy needed to overcome the added 3-inch pressure drop in the second bank of cyclones. The fuel charge for the heat requirement is \( 38\frac{¢}{10^6} \) BTU. The electrical charge for the power is \( 1\frac{¢}{kwh} \).

Catalyst costs are about \( 30\frac{¢}{lb} \), Harnsberger (1974). The high charge for maintenance (8% FCI) is used since there may be material erosion problems in the solid transport lines. The overall operating cost is 0.774 mills/kwh. With a catalyst attrition rate of 10 times that used in Table \( v-20 \) the operating cost would be 1.23 mills/kwh.

The process costs for the \( H_2SO_4 \) plant were taken directly from Sittig (1971). This report gives both FCI and operating costs for the \( H_2SO_4 \) plant. For a 210 Tpd plant the FCI is $1.55 \times 10^6$. Storage and shipping facilities were estimated from EPA (May, 1973) to be $1.23 \times 10^5$. This gives the total investment of $1.67 \times 10^6$. The operating cost for the plant is $101/hr. With a 20% increase for distribution and marketing costs the \( H_2SO_4 \) cost would be $121/hr (0.138 mills/kwh). If the \( H_2SO_4 \) were sold at $25/Ton, a credit of
$219/hr would be realized. This credit corresponds to about 0.25 mills/kwh.

The total process costs with and without $H_2SO_4$ credit are given in Table v-21.

Table v-21. Process costs for 1000-Mw coal-fired power plant.

<table>
<thead>
<tr>
<th></th>
<th>Removal Process</th>
<th>$H_2SO_4$ Plant</th>
<th>Credit</th>
<th>Total Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCI ($/Kw)</td>
<td>16.87</td>
<td>1.67</td>
<td>----</td>
<td>18.54</td>
</tr>
<tr>
<td>OC (mills/ kwh)</td>
<td>0.77</td>
<td>0.14</td>
<td>-0.25</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Even if the acid were not sold the operating cost would be only around 0.90 mills/kwh.
CHAPTER VI
Discussion and Recommendations

A. Process Evaluation.

1. Description of the process.

A dry process operating at relatively high temperatures (1000°F) has been developed for the simultaneous removal of NO and SO₂ from power plant stack gases. A catalyst/absorbent consisting of 20% ferric oxide supported on alumina contacts the flue gas under reducing conditions in a dispersed-phase reactor. Reactions occur which effect the absorption of SO₂ as either ferrous sulfide or sulfate and the reduction of NO to either N₂ or NH₃ (Section IV.E.). In the high temperature (1250°F) fluidized bed regenerator, the catalyst/absorbent is reoxidized by air to ferric oxide and produces an effluent gas containing about 9% SO₂, which is a suitable feed for a H₂SO₄ plant. The flow sheet for the process is shown in Figure v-2.

The removal reactions for both SO₂ and NO require a net reducing flue gas. A coal gasification unit produces the required amount of CO and H₂ (Section V.C.), while most (81%) of the coal is burned under oxidizing conditions in the furnace. Since the rich CO/H₂ stream is added prior to the superheater section, the heat generated in the coal gasifier is recovered in the convection pass of the boiler. The CO/H₂ concentration in the effluent stack gas is controlled by maintaining an excess of ferric oxide in the catalyst/
absorbent recycle stream.

A process flow sheet applicable to a 1000-Mw coal-fired power plant and designed to remove 90% of the NO and SO₂ in the flue gas is presented in Chapter V. Since the process equipment and reactant transport techniques are similar in scale and throughput to those in fluidized bed catalytic cracking units, the technology required for implementing this process is considered to be established. The economic analysis of the process is based on October 1973 dollars. The process requires a fixed capital investment of $18.5/kw and has operating costs of 0.91 mills/kw-hr. The investment cost includes $1.67/kw for the H₂SO₄ plant. With a $25/Ton credit for the concentrated H₂SO₄, the operating cost would be reduced to 0.66 mills/kw-hr.

2. Comparison with other processes.

Princiotta (1974) has evaluated the six leading processes for SO₂ removal. All of these processes, except the low-sulfur fuel alternative, involve cooling the flue gas and contacting it with an aqueous stream. The investment and operating costs for these processes are presented in Table vi-1. The costs for the proposed process are reported at 100% load factor and fixed operating charges at 14.67% of the capital costs per year, whereas the basis in Table iv-1 is an 80% load factor and an 18% rate for fixed charges. The operating cost for the proposed process on this basis is still 0.91 mills/kw-hr. The decrease in direct charges is almost compensated for by the increase in fixed costs. The capital investment charge
<table>
<thead>
<tr>
<th>Process System</th>
<th>Reactant Input Requirements</th>
<th>Thowaway or Recovery</th>
<th>Approx. Invest. Costs (a) for Coal-Fired Boilers $/kw</th>
<th>Approx. (Annual) Costs (b) mills/kw-hr</th>
<th>SO₂ Removal Efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-fired power plant</td>
<td>N. A.</td>
<td>N. A.</td>
<td>200</td>
<td>8.9 (c)</td>
<td>N. A.</td>
</tr>
<tr>
<td>Low-sulfur fuel increment (coal and oil)</td>
<td>N. A.</td>
<td>N. A.</td>
<td>N. A.</td>
<td>2.0 - 4.0</td>
<td>N. A.</td>
</tr>
<tr>
<td>Wet lime/limestone/ Ca(OH)₂ slurry scrubbing</td>
<td>Lime (100-120% Stoich.); limestone (120-150% Stoich.)</td>
<td>Throwaway CaSO₃/ CaSO₄</td>
<td>35 - 52</td>
<td>1.5 - 2.4</td>
<td>N. A.</td>
</tr>
<tr>
<td>Magnesium oxide scrubbing</td>
<td>MgO alkali; carbon and fuel for regeneration and drying</td>
<td>Recovery of conc. H₂SO₄ or elem. sulfur</td>
<td>36 - 66</td>
<td>1.6 - 3.0</td>
<td>1.4 - 2.8</td>
</tr>
<tr>
<td>Monsanto catalytic oxidation (add-on)</td>
<td>Catalyst V₂O₅ (periodic replacement) and fuel for heat</td>
<td>Recovery of dilute H₂SO₄</td>
<td>43 - 67</td>
<td>1.6 - 2.7</td>
<td>1.5 - 2.6</td>
</tr>
<tr>
<td>Wellman-Lord process (soluble sodium scrubbing with regeneration)</td>
<td>Sodium make-up and heat for regeneration</td>
<td>Recovery of conc. H₂SO₄ or sulfur</td>
<td>40 - 68</td>
<td>1.5 - 3.2</td>
<td>1.2 - 2.8</td>
</tr>
<tr>
<td>Double alkali process</td>
<td>Sodium make-up plus lime/limestone (100-150% Stoich.)</td>
<td>Throwaway CaSO₃/ CaSO₄</td>
<td>26 - 47</td>
<td>1.2 - 2.2</td>
<td>N. A.</td>
</tr>
</tbody>
</table>

(a) Generally, where a cost range is indicated, the lower end refers to a new unit (1000 Mw); the high end refers to a 200 Mw retrofit unit. Costs include particulate removal and are in 1973 dollars.
(b) Assumptions: Costs calculated at 80% load factor, fixed charges per year ~18% of capital costs.
(c) Includes environmental controls to minimize land and water pollution.
remains unchanged.

If the maximum retrofit factor of 1.25 is applied to the capital charge cost, as suggested by Burchard (1972) for existing installations, the cost would be $23.1/kw including the $2,500 plant. Based on both efficient removal of pollutants and on the process economics, the process definitely shows potential for practical application.

3. Reasons for economy.

The strikingly lower costs predicted for this process are due to several advantages inherent to the design which has been developed. These are enumerated below.

a. Equipment size and complexity.

The contacting zone in the proposed process is at 1000°F and has a gas velocity around 50 ft/sec. A residence time around 1 second is required. The wet scrubbing processes cited by Princiotta (1974) operate around 130°F with maximum gas velocities of 8 - 13 ft/sec (Nannen, 1974; EPA, 1973). The flue gas residence time in the scrubbers is around 1.5 - 2.5 seconds. In spite of the high temperature, and the resulting high specific volume of the flue gas, the shorter residence time results in similar volumes for the high temperature contactor and scrubbers for a given flow rate. More explicitly, the higher contactor temperature results in a specific gas volume increase of 2.47. Therefore, the contactor volume needs to be increased by this amount over the scrubber volume to achieve
the same residence time. Since the required gas residence time in the scrubber is between 1.5 to 2.5 times that in the contactor, the contactor volume needs to be increased by only 1 to 1.6 times that of the scrubber. The faster allowable gas velocities in the contactor result in its cross-section being between 3.8 to 6.3 times smaller than that in a scrubber for the same gas volume. This means less duct expansion and gas distribution equipment at the contactor entrance. It also allows for a more compact design since at power plant sites vertical distance in one unit is less expensive than horizontal area in several units. The higher temperatures also result in more rapid diffusion and kinetic rates in the contactor than in the scrubbers. The faster rates are reflected in shorter required residence times.

Other considerations which combine with a smaller required cross-section to give a relatively low capital investment for the process are related to the process simplicity. In this process no large holding tanks are required for reaction or settling of reactants. All of the blowers are operated at 300°F or below with negligible solids in the gas streams passing through them. The contactor has no complicated internal structure. The contactor can be made of carbon steel. The regenerator and the solids recycle line temperatures are within the service range for normal stainless steels.

b. Improved thermal efficiency.
With the flue gas exiting the power plant stack very close to stoichiometric composition, the thermal efficiency of the plant will be improved by about 0.82% relative to operation with 20% excess air. The fuel requirements for removing the SO₂ and NO are estimated to be roughly this same amount (Section V.D.3.). If there are no thermal losses in the process, there are indications that a slight increase in thermal output over normal operating conditions may actually result. Finally, the fuel required for reheating the stack gas, necessary for plume buoyancy in wet-scrubbing processes, is of course avoided in this case.

c. Make-up cost.

The size distribution of the catalyst/absorbent (average size 75 microns) has been selected to allow highly efficient (99.998%) collection in a series of low-pressure-drop cyclones and an electrostatic precipitator in the main gas stream. The high-efficiency cyclones in the regenerator collect 99.933% of the inlet solids. The net result is first, a low catalyst/absorbent make-up requirement. Second, no solids disposal problem is created since the catalyst/absorbent is regenerated and almost totally recycled.

B. Potential Process Problems.

1. Ammonia emissions.

The catalytic reduction of NO forms both N₂ and NH₃, although it would be desirable to produce only N₂. Since the latter was not found possible, the process is expected to emit 300 - 400 ppm NH₃.
NH₃ is not reactive in the photochemical smog cycle. However, it will react with H₂SO₄ or HNO₃ present in the air to form ammonium salts. These will be in the form of aerosols which limit visibility. NH₃ emissions will not increase the aerosol problem, however, since the H₂SO₄ or HNO₃ would already be present as aerosols. In fact, the addition of NH₃ to the atmosphere will tend to neutralize the acid aerosols present, making them less objectionable.

The only NH₃ emissions standard which has been established is that for the San Francisco Bay Area. For large industrial stacks the limit is 2500 ppm (BAAPCD, 1972). Since the proposed emissions are only 13% of this standard, the ammonia emission is considered acceptable at present.

2. Accuracy of process design.

The prediction of dispersed-phase behavior from fixed-bed data is based on a model correlating the gas phase mass transfer rates for the two cases. As discussed in section V.B.1.ii., the prediction of these rates at low Reynolds numbers is not well established. At worst, the rates might be about one-tenth of those used in the design (Kunni, 1969). The dispersed-phase kinetics were estimated from the fixed-bed data. Due to the uncertainties in the experimental work, a range was given for the reaction rate constant. If the minimum reaction time required were 0.01 second, instead of 0.001 second as stated in section V.B.1.b., the reaction rate in the dispersed-phase contactor would be one-tenth of that discussed. A decrease in both the mass transfer rate and the reaction rate by a
factor of 10 would still result in the reaction rate controlling. Hence, the overall rate would be decreased by 10. The effect on the design would be to require 10 times the solids density within the contactor to effect the same removal. Streams to and from the regenerator would not be affected. If the solids density in the contactor were increased by 10 and the amount of solids lost from the process were increased by 10, then the operating costs would increase to about 1.31 mills/kw-hr. If the size of the solids blower, motor, and ductwork were increased to provide the same solids density with this added load, the capital investment would increase to a maximum of $20.5/Kw. Thus, the uncertainty in the experimental data has little potential effect on the process economics.

3. Flyash separation from catalyst/absorbent.

The separation of flyash from the catalyst/absorbent is important for the process. In the design the following collection efficiencies were used:

<table>
<thead>
<tr>
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<th>Flyash</th>
<th>Cat/Abs</th>
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<tbody>
<tr>
<td>Contactor cyclone</td>
<td>97%</td>
<td>99.9696%</td>
</tr>
<tr>
<td>Main flue gas ESP</td>
<td>95%</td>
<td>95%</td>
</tr>
<tr>
<td>Regenerator (by elution)</td>
<td>10%</td>
<td>94%</td>
</tr>
<tr>
<td>Regenerator cyclones</td>
<td>90%</td>
<td>99.933%</td>
</tr>
<tr>
<td>Regenerator ESP</td>
<td>95%</td>
<td>95%</td>
</tr>
</tbody>
</table>

The difference in these efficiencies will provide adequate separation of the flyash and catalyst/absorbent. This assumes that the flyash particles will break up while cycling around the process. If this does not occur, large particles of flyash will build up in the system until the attrition rate equals the rate of flyash collection. Un-
fortunately there are no available data to predict the attrition characteristics of flyash. If the flyash built up to 10 times the present level assumed for the contactor, the ratio of flyash to catalyst/absorbent would rise to about 0.60. The effect on the economics would probably be something less than the effect of increasing the recycle of catalyst/absorbent by a factor of 10. The latter effect was shown earlier to be quite small in comparison with other process economics.

C. Recommendations.

The next step in the process development would be to determine the reaction kinetics in a dispersed-phase contactor. This contactor would probably be a fluidized bed at first, moving later to a unit with highly dispersed solids. The dispersed-phase contactors will not only give some idea of the gas phase mass transfer limitations expected, but also will allow the reactions to proceed in a bed with a more uniform solids composition. The experimental data showed qualitative evidence that under this uniform condition less ferrous sulfate and ammonia would form.

At several points in the experimental work, the number of samples taken was limited by the batch gas sampling technique used. In the dispersed contactor tests, continuous monitors on at least SO₂ and NO should be used. Sensitivity should also be improved in the gas monitoring system to allow analysis of all reactant gases at levels below 100 ppm.
The addition of silica to the alumina matrix has been suggested to decrease catalyst attrition. Tests are needed to confirm that this does not decrease the solids activity for NO and SO₂ removal. Any new catalyst matrix developed should also be tested for attrition. The most reasonable way would be to compare the new catalyst's attrition rate with that of a known commercial catalyst whose plant-scale attrition rate is known. Zenz (1974) discusses the technique for such tests. Samples of flyash tested in such an apparatus may give an estimate of flyash attrition relative to catalyst/absorbent attrition which could be used to establish better the level of flyash in the contactor.

The activity of the catalyst/absorbent as a function of time needs also to be tested. In these tests the solids should be cycled between removal and regeneration steps. The effect of flyash on the catalyst activity needs to be determined.

These suggested studies should produce sufficient data to obtain design values with substantially narrower ranges for the process variables. The process effectiveness and costs could then be stated with more certainty.
**NOMENCLATURE**

- $a$: radius of $\text{FeS/Fe}_2\text{O}_3$ interface in particle during regeneration.

- $C_{ag}$: bulk gas concentration at a particular time.

- $C_{ago}$: bulk gas concentration at inlet conditions.

- $C_{as}$: gas concentration at external surface of particle.

- $d_p$: particle diameter.

- $D$: gas phase diffusivity.

- $D_e$: effective diffusivity in particles.

- $D_{ke}$: effective Knudsen diffusivity in particles.

- $D_{12e}$: effective gas phase bulk diffusivity.

- $E$: total equipment cost.

- $F_{ao}$: reactant flowrate.

- $FCI$: fixed capital investment.

- $\Delta F_T$: thermodynamic free energy of reaction at temperature $T$.

- $h_s$: Thiele modulus for a sphere.

- $\Delta H_T$: thermodynamic heat of reaction at temperature $T$.

- $I$: insulation costs.

- $j_D$: mass transfer $j$-factor.

- $k_m$: overall mass transfer coefficient.

- $k_r$: overall kinetic rate coefficient.

- $K_1$: overall reaction coefficient for removal reactions.

- $K_2$: overall reaction coefficient for regeneration reactions.

- $\text{lbmph}$: pound moles per hour.

- $N_a$: moles of reactant.

- $\text{NH}_3$ selectivity ($\%$): percent reduced nitrogen compounds formed from NO in the form of $\text{NH}_3$. 
OC = process operating costs.

\[(O/R)_{NH3} = (2.5[NO] + 3[SO_2] + 2[O_2])/([H_2] + [CO])\]

\[(O/R)_{N_2} = ([NO] + 3[SO_2] + 2[O_2])/([H_2] + [CO])\]

P = piping costs.

r = catalyst/absorbent radius.

r_a = reaction rate.

R_ep = particle Reynolds number.

Sc = Schmidt number.

S_{ex} = specific external surface area of particles.

S_v = total specific surface area of particles.

t = residence time of solid in regenerator.

T = temperature.

Tph = tons per hour.

u_{ave} = average interstitial velocity past particles.

V = reactor volume

V_p = specific volume of particles.

W_m = molar amount of FeS in particles.

X_a = fractional conversion of reactant a.

z = amount of solid in contactor.

\(\epsilon\) = particle porosity.

\(1-\epsilon\) = volume fraction of particle which is FeS.

\(\eta\) = kinetic effectiveness factor.

\(\theta\) = residence time of gas in contactor.

\(\rho_B\) = bulk solids density.

\(\rho_p\) = particle density.
\( \rho_{sm} \) = molar density of FeS in solids.

[ ] = gas concentrations.
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APPENDIX
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<td>Fe₂O₃</td>
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<td>1b</td>
<td>205 110 33 44 Fe₂O₃</td>
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<td>100 0.95 Fe₅₆</td>
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<td>342 440 CO = 0.59 N₂</td>
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<td>41 168 Fe₂O₃</td>
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<td>582 360 H₂S + H₂O</td>
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<td>2e</td>
<td>103 454 NO + CO</td>
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### Experimental Summary

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<th>CONDITIONS FOR RUN</th>
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<tr>
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*H₂S leak*
## Experimental Summary

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<th>Date</th>
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<th>Conditions for Run</th>
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<th>Ovrl. Mat. Balance</th>
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### Table Notes:
- **Date:** Date of the experiment.
- **Run:** Identification number for the experiment.
- **Reaction:** Chemical reaction performed.
- **Conditions for Run:** Details of the conditions under which the reaction was carried out.
- **Solid:** Solid phase materials involved.
- **Ovrl. Mat. Balance:** Overall material balance data.
- **Particulate:** Particulate matter data.
- **Comments:** Additional notes or comments related to the experiment.
## Experimental Summary

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<tr>
<th>Day</th>
<th>Run</th>
<th>Reaction</th>
<th>Conditions for Run</th>
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<td>25b</td>
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<td>26b</td>
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<td>38a</td>
<td>Fe₂O₃+CO → Fe₃O₄, FeO</td>
<td></td>
<td>Fe₃O₄</td>
<td>— X X X 25-50</td>
<td>6.4 mm reactor</td>
<td></td>
</tr>
<tr>
<td>12/5</td>
<td>38b</td>
<td>Fe₂O₃+CO+NO+SO₂+H₂O</td>
<td>0.04</td>
<td>Fe₀₃₀₄</td>
<td>— X X X 25-50</td>
<td>6.4 mm reactor</td>
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<td>12/5</td>
<td>39a</td>
<td>Fe₂O₃+CO → Fe₃O₄, FeO</td>
<td></td>
<td>Fe₃O₄</td>
<td>— X X X 25-50</td>
<td>9.5 mm reactor</td>
<td></td>
</tr>
<tr>
<td>12/5</td>
<td>39b</td>
<td>Fe₂O₃+CO+NO+SO₂+H₂O</td>
<td></td>
<td>Fe₀₃₀₄</td>
<td>— X X X 25-50</td>
<td>9.5 mm reactor</td>
<td></td>
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<tr>
<td>12/5</td>
<td>39c</td>
<td>Fe₂O₃+CO → Fe₃O₄, FeO</td>
<td></td>
<td>Fe₃O₄</td>
<td>— X X X 25-50</td>
<td>9.5 mm reactor</td>
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<tr>
<td>12/5</td>
<td>39d</td>
<td>Fe₂O₃+CO+NO+SO₂+H₂O</td>
<td></td>
<td>Fe₀₃₀₄</td>
<td>— X X X 25-50</td>
<td>9.5 mm reactor</td>
<td></td>
</tr>
<tr>
<td>12/5</td>
<td>39e</td>
<td>Fe₂O₃+CO → Fe₃O₄, FeO</td>
<td></td>
<td>Fe₃O₄</td>
<td>— X X X 25-50</td>
<td>9.5 mm reactor</td>
<td></td>
</tr>
<tr>
<td>12/5</td>
<td>39f</td>
<td>Fe₂O₃+CO+NO+SO₂+H₂O</td>
<td></td>
<td>Fe₀₃₀₄</td>
<td>— X X X 25-50</td>
<td>9.5 mm reactor</td>
<td></td>
</tr>
<tr>
<td>12/5</td>
<td>40a</td>
<td>Fe₂O₃+CO → Fe₃O₄, FeO</td>
<td></td>
<td>Fe₃O₄</td>
<td>— X X X 25-50</td>
<td>9.5 mm reactor</td>
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<tr>
<td>12/5</td>
<td>40b</td>
<td>Fe₂O₃+CO+NO+SO₂+H₂O</td>
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<td>Fe₀₃₀₄</td>
<td>— X X X 25-50</td>
<td>9.5 mm reactor</td>
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</tr>
<tr>
<td>12/5</td>
<td>40c</td>
<td>Fe₂O₃+CO → Fe₃O₄, FeO</td>
<td></td>
<td>Fe₃O₄</td>
<td>— X X X 25-50</td>
<td>9.5 mm reactor</td>
<td></td>
</tr>
<tr>
<td>12/5</td>
<td>40d</td>
<td>Fe₂O₃+CO+NO+SO₂+H₂O</td>
<td></td>
<td>Fe₀₃₀₄</td>
<td>— X X X 25-50</td>
<td>9.5 mm reactor</td>
<td></td>
</tr>
<tr>
<td>RUN</td>
<td>REACTION</td>
<td>CONDITIONS FOR RUN</td>
<td>SOLID</td>
<td>OVEN</td>
<td>MET. BALANCE</td>
<td>PARTICLE SIZE (μm)</td>
<td>COMMENTS</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
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<td>-------</td>
<td>------</td>
<td>--------------</td>
<td>-------------------</td>
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</tr>
<tr>
<td>1/6/74</td>
<td>40e.</td>
<td>FeO+CO+O₂+NO+SO₂+H₂O</td>
<td>6.00</td>
<td>0.038</td>
<td>He</td>
<td>O₂ NO CO SO₂ NO</td>
<td>FeO₄</td>
</tr>
<tr>
<td></td>
<td>40f.</td>
<td>Fe₂SO₄ + Fe₂O₃ + SO₂</td>
<td>6.70</td>
<td>0.012</td>
<td>He</td>
<td>O₂ NO CO SO₂ NO</td>
<td>FeO₄</td>
</tr>
<tr>
<td></td>
<td>40g.</td>
<td>Fe₂O₃ + O₂ + Fe₂O₃</td>
<td>6.95</td>
<td>0.020</td>
<td>He</td>
<td>O₂ NO CO SO₂ NO</td>
<td>FeO₄</td>
</tr>
<tr>
<td>1/8/74</td>
<td>41a.</td>
<td>NiO + Fe₂O₃ + CO</td>
<td>5.60</td>
<td>0.043</td>
<td>He</td>
<td>CO</td>
<td>FeO₄</td>
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<tr>
<td></td>
<td>41b.</td>
<td>Ni + Fe₂O₃ + H₂O + SO₂ + NO</td>
<td>6.00</td>
<td>0.015</td>
<td>He</td>
<td>O₂ NO CO SO₂ NO</td>
<td>FeO₄</td>
</tr>
<tr>
<td></td>
<td>41c.</td>
<td>NiSO₄ + Fe₂O₃ + Fe₂O₃ + NO</td>
<td>6.70</td>
<td>0.015</td>
<td>He</td>
<td>O₂ NO CO SO₂ NO</td>
<td>FeO₄</td>
</tr>
<tr>
<td></td>
<td>41d.</td>
<td>NiSO₄ + Fe₂O₃ + Fe₂O₃ + NO</td>
<td>6.70</td>
<td>0.015</td>
<td>He</td>
<td>O₂ NO CO SO₂ NO</td>
<td>FeO₄</td>
</tr>
<tr>
<td></td>
<td>41e.</td>
<td>NiO + Fe₂O₃ + H₂O + SO₂ + NO</td>
<td>6.00</td>
<td>0.015</td>
<td>He</td>
<td>O₂ NO CO SO₂ NO</td>
<td>FeO₄</td>
</tr>
<tr>
<td></td>
<td>41f.</td>
<td>NiSO₄ + Fe₂O₃ + Fe₂O₃ + NO</td>
<td>6.70</td>
<td>0.015</td>
<td>He</td>
<td>O₂ NO CO SO₂ NO</td>
<td>FeO₄</td>
</tr>
<tr>
<td></td>
<td>41g.</td>
<td>NiSO₄ + Fe₂O₃ + Fe₂O₃ + NO</td>
<td>6.70</td>
<td>0.015</td>
<td>He</td>
<td>O₂ NO CO SO₂ NO</td>
<td>FeO₄</td>
</tr>
<tr>
<td>1/14/74</td>
<td>42a.</td>
<td>Fe₂O₃ + CO → Fe₂O₃ + FeO</td>
<td>5.90</td>
<td>0.045</td>
<td>He</td>
<td>CO</td>
<td>FeO₄</td>
</tr>
<tr>
<td></td>
<td>42b.</td>
<td>H₂O + CO → H₂ + CO₂</td>
<td>8.4</td>
<td>0.045</td>
<td>He</td>
<td>CO</td>
<td>FeO₄</td>
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<tr>
<td></td>
<td>42c.</td>
<td>Fe₂O₃ + SO₂ → Fe₂O₃ + CO₂</td>
<td>16.3</td>
<td>0.045</td>
<td>He</td>
<td>CO</td>
<td>FeO₄</td>
</tr>
<tr>
<td></td>
<td>42d.</td>
<td>H₂O + CO → H₂ + CO₂</td>
<td>6.9</td>
<td>0.045</td>
<td>He</td>
<td>CO</td>
<td>FeO₄</td>
</tr>
</tbody>
</table>

**EXPERIMENTAL SUMMARY**
APPENDIX A-2

Overall Reaction Rate Analysis

A. Kinetic Rate:
(Levenspiel, 1962)

1. Assumptions: First-order reaction kinetics.
   
   Effectiveness factor can account for effect of intraparticle diffusion.

2. Rate per unit volume of catalyst/absorbent (p. 446):

   \[
   \frac{1}{V_p z} \frac{dN_a}{dt} = - k_r \eta C_{as}
   \]

   where:
   
   \( V_p \) = specific volume (cm³/g).
   
   \( z \) = amount of catalyst (g).
   
   \( N_a \) = moles of reactant A (g moles).
   
   \( t \) = time (sec).
   
   \( k_r \) = reaction rate constant (sec⁻¹).
   
   \( \eta \) = effectiveness factor (dimensionless).
   
   \( C_{as} \) = gas concentration at exterior surface of solid (g moles/cm³).

3. Since the reactor volume is a more useful quantification than the amount of catalyst, \( z \), the relationship: \( V = z/\rho_B \) is used to eliminate \( z \). Where: \( V \) = reactor volume (cm³).

   \( \rho_B \) = solids density in the contactor (g/cm³).

   Therefore:

   \[
   \frac{1}{V} \frac{dN_a}{dt} = - \rho_B V_p k_r \eta C_{as}
   \]  \hspace{1cm} (A2-1)

B. External Mass Transfer:
(Levenspiel, 1962)

   The value of \( C_{as} \) in the above equation may differ from \( C_{ag} \), bulk concentration since there may be gas-film resistance. The relationship given on p. 445 (Levenspiel):

   \[
   \frac{-1}{S_{ex}} \frac{dN_a}{dt} = k_m (C_{ag} - C_{as})
   \]  \hspace{1cm} (A2-2)
assumes: Linear concentration gradients.
No interaction of diffusing species.

In this expression: \( S_{\text{ex}} \) = external particle surface area (cm\(^2\)/g).
\( k_m \) = mass transfer coefficient (cm/sec).

C. Overall Rate:
(Levenspiel, 1962)

Since the kinetics and mass transfer rates are in series they can be combined as follows:

kinetic: \[ \frac{1}{(V \rho B k)} \frac{dN_a}{dt} = - C_{as} \]
mass transfer: \[ \frac{1}{(S k z)} \frac{dN_a}{dt} = - (C_{ag} - C_{as}) \]
overall: \[ \frac{dN_a}{dt} \left( \frac{1}{(V \rho B k)} + \frac{1}{(S k z)} \right) = - C_{ag} \]

where: \( r_a \) = overall rate (g moles/cm\(^3\)-sec).

Substituting the relationship for \( V \) to eliminate \( z \), the expression becomes:

\[ r_a = \frac{1}{V} \frac{dN_a}{dt} \left[ \frac{1}{(V \rho B k)} + \frac{1}{(S k z)} \right] = - C_{ag} \]

Substituting this expression into the overall rate equation:

\[ r_a = \frac{1}{V} \frac{dN_a}{dt} = - (1/V k + 1/S k) C_{ag} \rho B \]

Then:

\[ r_a = \frac{1}{V} \frac{dN_a}{dt} = - K_1 \rho B C_{ag} \]  \( \text{(A2-3)} \)

D. Packed-Bed Reactor Equation:
(Levenspiel, 1962)

1. Levenspiel presents the analysis of a differential section of a packed-bed reactor as:

\[ F_{ao} \text{d}X_a = (-r_a) \text{d}V \]

Where: \( F_{ao} \) = inlet rate of reactant (g moles/sec).
\( X_a \) = fractional conversion of reactant (dimensionless).

\( C_{ag} \) can be eliminated in equation \( \text{(A2-4)} \) by the relationship:

\[ C_{ag} = C_{ago} (1-X_a) \]

where: \( C_{ago} \) = inlet gas concentration (g moles/cm\(^3\)).
Then: $F_{ao} \, dX_a = K_1 C_{ago} (1-X_a) \rho_B \, dV$. \hspace{1cm} (A2-5)

2. The above equation is now integrated over the entire reactor volume.

\[
\int_0^{X_a} \frac{dX_a}{(1-X_a)} = \int_0^V \frac{\rho_B K_1 C_{ago}}{F_{ao}} \, dV
\]

\[
1 - X_a = \exp\left[-\frac{C_{ago} V}{F_{ao}} K_1 \rho_B\right]
\]

Since the residence time $\theta = C_{ago} V / F_{ao}$

\[
\frac{C_{ag}}{C_{ago}} = \exp[-K_1 \theta \rho_B]
\]
APPENDIX A-3

Regeneration-Rate Analysis

A. The main regeneration reaction is:

\[
\text{FeS} + \frac{7}{4} \text{O}_2 \rightarrow \frac{1}{2} \text{Fe}_2\text{O}_3 + \text{SO}_2
\]

Guha (1972) presented an equation representing the oxidation of FeS₂.

The development here is analogous to his work.

1. Assumptions: First-order reaction.

Mass transfer resistance in bulk fluid is negligible.

2. Rate of particle oxidation can be given as:

\[
\left(-\frac{1}{4\pi a^2}\right) \frac{dW_m}{dt} = \frac{7}{4} (1-\epsilon') K_2 C_{ago}
\]

where:

- \(a\) = radius of particle at FeS/Fe₂O₃ interface, (cm).
- \(W_m\) = molal amount of FeS, (g moles FeS)
- \(t\) = time (sec).
- \(1-\epsilon'\) = volume FeS/volume particle (cm³ FeS/cm³ particle).
- \(K_2\) = overall reaction coefficient (cm/sec).
- \(C_{ago}\) = \(\text{O}_2\) bulk concentration (g moles/cm³).

The factor \(7/4\) is the stoichiometric coefficient. With a redefinition of \(K_2\) this could be incorporated into \(K_2\).

3. The molal amount of FeS, \(W_m\), can be expressed as a volume times a density:

\[
\frac{dW_m}{dt} = \frac{d(4/3\pi a^3 \rho_{sm})}{dt} = 4\pi a^2 \rho_{sm} \frac{da}{dt}
\]

where:

- \(\rho_{sm}\) = molal density of FeS (g moles/cm³).

Equation (A3-1) can thus be expanded as:
\[-\rho_{sm} \frac{da}{dt} = \frac{7}{4} (1-\epsilon') K_2 C_{ago}.\]

Separating variables:
\[da = -\frac{7}{4} (1-\epsilon') \left(\frac{1}{\rho_{sm}}\right) K_2 C_{ago} \, dt.\]

Integrating from the outer surface \(a = r, t = 0\) to the center \(a = 0\),
\[t = t, \text{ where } r \text{ is the particle radius.}\]

\[a - r = \left(-\frac{7}{4}\right) (1-\epsilon') \left(\frac{K_2}{\rho_{sm}}\right) C_{ago} t. \quad \text{(A3-2)}\]

4. The percent solid reacted is
\[100\left[\frac{(r^3 - a^3)}{r^3}\right] = 100\left[1 - \left(\frac{a}{r}\right)^3\right].\]

Combining with (A3-2);
\[
\text{% solid reacted} = 100\left\{1 - \frac{r}{7/4(1-\epsilon')(K_2/\rho_{sm})C_{ago}} t^3/r^3\right\}.
\]
\[
\quad \text{(A3-3)}
\]

5. The required time for a given % solid reacted is then:
\[
t = r \left[1 - \left(\frac{1 - \text{% solid reacted}}{100}\right)^{1/3}\right] / \left[7/4(1-\epsilon')(K_2/\rho_{cm})C_{ago}\right].
\]
\[
\quad \text{(A3-4)}
\]
APPENDIX A-4
Design Bases - 1000-Mw Power Plant

1. Furnace- Pulverized coal, tangentially fired.
   a. Coal Analysis: wgt fraction
      Carbon (C) 0.7220
      Hydrogen (H) 0.0476
      Oxygen (O) 0.0615
      Nitrogen (N) 0.0149
      Sulfur (S) 0.0300
      Water $\text{H}_2\text{O}$ 0.0347
      Ash 0.0893 (Steam, 1963)
   b. Ten percent excess air at 60% relative humidity.
   c. Power plant efficiency 38.9% (Robinson, 1970).
   d. Twenty percent fuel N converted to NO.
   e. Thermally formed NO is 20% of total NO.
   f. Ash - 15% bottoms and 85% flyash.

2. Gasifier- chain grate stoker.
   a. Coal analysis: same as in furnace.
   b. Stoichiometric air for conversion of all carbon to CO and sulfur to $\text{SO}_2$; 60% relative humidity in inlet air.
   c. Twenty percent fuel N converted to NO.
   d. No NO is formed thermally.
   e. Ash - 85% bottoms and 15% flyash.

3. Total flue gas.
   a. Ninety-five percent of the excess $\text{O}_2$ removed when CO/$\text{H}_2$ added.
   b. Inlet temperature to superheaters 1260°C (2300°F).
   a. Ninety percent removal of excess (CO + H₂), SO₂, NO.
   b. Eighty-five percent of SO₂ removed as S⁻².
   c. Fifteen percent of SO₂ removed as SO₄⁻².
   d. Removal reactions occur at 1000°F.
   e. Twenty-five percent of solids stream leaving contact sent to regenerator; 75% is recycled.
   f. Ten percent excess Fe₂O₃ in solids feed to contactor from regenerator.
   g. Composition and properties of catalyst/absorbent:
      \[ 20\% \text{ Fe}_2\text{O}_3, 80\% (\text{Al}_2\text{O}_3 + \text{SiO}_2), S_v = 200 \text{ m}^2/\text{g}, V_p = 0.67 \text{cm}^3/\text{g}. \]

5. Regenerator.
   a. All inlet iron converted to Fe₂O₃.
   b. Regeneration reactions occur at 1250°F.

   a. Contactor Cyclones and Electrostatic Precipitator for main flue gas.

<table>
<thead>
<tr>
<th>Collection Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclones</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>Flyash</td>
</tr>
<tr>
<td>Cat./Abs.</td>
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</table>

   (Solids collected in ESP are sent to the regenerator while those collected in the cyclones are sent to the contactor (75%) or to the regenerator (25%).)
b. Regenerator Cyclones.

<table>
<thead>
<tr>
<th>Collection Efficiency (%)</th>
<th>Primary</th>
<th>Secondary</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flyash</td>
<td>0</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Cat./Abs.</td>
<td>99.933</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

(Solids collected in the primary cyclones are sent to the contactor while those collected in the secondary cyclones are sent to ash disposal)

c. Regenerator ESP. This unit collects 95% of the inlet flyash.
### APPENDIX A-5

Heat effects in the removal and regeneration reactions.

<table>
<thead>
<tr>
<th>REACTIONS</th>
<th>$\Delta H_{25^\circ C}$ (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2$</td>
<td>-89.23</td>
</tr>
<tr>
<td>2. $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$</td>
<td>-79.40</td>
</tr>
<tr>
<td>3. $2\text{NO} + 3\text{H}_2\text{O} + 5\text{CO} \rightarrow 2\text{NH}_3 + 5\text{CO}_2$</td>
<td>-230.10</td>
</tr>
<tr>
<td>4. $\text{NO} + 5/2\text{H}_2 \rightarrow \text{NH}_3 + \text{H}_2\text{O}$</td>
<td>-90.40</td>
</tr>
<tr>
<td>5. $\text{FeO} + \text{SO}_2 + 3\text{CO} \rightarrow \text{FeS} + 3\text{CO}_2$</td>
<td>-90.90</td>
</tr>
<tr>
<td>6. $\text{FeO} + \text{SO}_2 + 3\text{H}_2 \rightarrow \text{FeS} + 3\text{H}_2\text{O}$</td>
<td>-61.36</td>
</tr>
<tr>
<td>7. $\text{FeO} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2\text{O}$</td>
<td>-11.91</td>
</tr>
<tr>
<td>8. $\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{FeO} + \text{CO}_2$</td>
<td>+ 1.57</td>
</tr>
<tr>
<td>9. $\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{FeO} + \text{H}_2\text{O}$</td>
<td>+11.40</td>
</tr>
<tr>
<td>10. $\text{FeO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{FeSO}_4$</td>
<td>-85.40</td>
</tr>
<tr>
<td>11. $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$</td>
<td>- 9.83</td>
</tr>
<tr>
<td>12. $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$</td>
<td>-67.64</td>
</tr>
<tr>
<td>13. $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$</td>
<td>-57.80</td>
</tr>
<tr>
<td>14. $2\text{FeS} + 7/2\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2\text{SO}_2$</td>
<td>-293.30</td>
</tr>
<tr>
<td>15. $2\text{FeO} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$</td>
<td>-69.21</td>
</tr>
<tr>
<td>16. $2\text{FeSO}_4 \rightarrow \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$</td>
<td>+78.8</td>
</tr>
</tbody>
</table>
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