Reduction of nitric oxide using metal sulfide promoter mixtures and metal sulfides
by Kent Moroni Hodgson

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University

Abstract:
One of the most difficult problems in air pollution control is that of reducing nitric oxide emmissions. Nitric oxide is emitted into the atmosphere where it is then oxidized to NO2. The reduction of NO with NH3 over a catalyst is a process which is beginning to be used in some industrial applications. However, the use of NH3 is undesirable because of the many other industrial applications for it.

This research was concerned with using the metal sulfides BaS,CaS, SrS and FeS mixed with the chemical promoters NaF, FeCl2, NiCl2, CoCl2 and Fe203 to reduce NO in an oxidizing atmosphere.

To determine if the chemical promoters reacted with NO, they were placed on the weighing pan of a Cahn R-100 continuous recording electrobalance.

The weight change was then recorded when the promoter was exposed to a gas stream containing 2.5% NO and 97.5% He. The only promoters showing a weight change were: CoCl2 and Fe203 gained weight at 300°C and CoCl2 lost weight at 400°C.

The reaction rates of the metal sulfide mixtures were determined using the electrobalance at 400°C and 300°C. These were determined with a gas having a composition of 2.5% NO and 97.5% He. At 400°C the fastest reaction rate was 3.155 x 10-6 moles of NO reacted per minute per gram of mixture for the BaS/FeCl2 mixture. The FeS/FeCl2 and BaS/CoCl2 mixtures showed weight losses at 400&;C. At 300°C the fastest rate was 4.69 x 10-6 moles of NO reacted per minute per gram of FeS/FeClg mixture.

The metal sulfide promoter mixtures and metal sulfides were tested in a fixed packed bed reactor to determine how well they would remove NO from a simulated flue gas. The simulated flue gas composition was 1000 ppm NO, 1% O2, 18% CO2 and the balance N2. The effluent gas was analyzed for NO using a Thermo Electron Corp. Chemiluminescent N0-N0 Analyzer. A simulated flue gas flow rate of 100 ml/minute was used.

The capacities at 400°C ranged from 0 grams of NO/gram of CaS for unpromoted CaS to .0372 grams of NO/gram of FeS for the FeS/FeClg mixture. The four largest capacities were FeS/FeCl2, .0372 grams of NO/gram FeS; SrS/NaF, .0317 grams of NO/gram SrS; CaS/NaF, .0186 grams of NO/gram CaS and BaS/FeCl2, .0l68 grams of NO/gram of BaS. The capacity for FeS/FeClg mixture at 300°C was .0020 grams of NO/gram of FeS.

It was determined that the presence of CO2, SO2 and H2O in the simulated flue gas had no effect on the amount of NO removed by CaS at 500, 600 and 700°C. The presence of CO2 and SO2 in the simulated flue gas did not effect the removal of NO by the CaS/NaF mixture at 400°C. The presence of H2O in the simulated flue gas was shown to reduce the amount of NO removed by the CaS/NaF, SrS/NaF and FeS/FeClg mixtures at 400°C. The higher the concentration of O2 the lower the NO removal capacity.

REDUCTION OF NITRIC OXIDE USING METAL SULFIDE PROMOTER MIXTURES AND METAL SULFIDES

by

KENT MORONI HODGSON

A thesis submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Chemical Engineering

Approved:

J P McCauley
Chairperson, Examining Committee

Lloyd Berg
Head, Major Department

Henry L Parsons
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

May, 1978

ACKNOWLEDGMENTS

The author wishes to thank the faculty and staff of the Department of Chemical Engineering for their suggestions and assistance.

The author is grateful to Dr. F.P. McCandless for his advice and encouragement throughout the course of this project.

The author gratefully acknowledges the financial support provided by the Environmental Protection Agency and by the Department of Chemical Engineering at Montana State University.

The author also wishes to thank his wife and daughter for their support, and his wife for her help in preparing this thesis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

One of the most difficult problems in air pollution control is that of reducing nitric oxide emmissions. Nitric oxide is emitted into the atmosphere where it is then oxidized to NO_2. The reduction of NO with NH_3 over a catalyst is a process which is beginning to be used in some industrial applications. However, the use of NH_3 is undesirable because of the many other industrial applications for it.

This research was concerned with using the metal sulfides BaS, CaS, SrS and FeS mixed with the chemical promoters NaF, $FeCl_2$, $NiCl_2$, $CoCl_2$ and Fe_2O_3 to reduce NO in an oxidizing atmosphere.

To determine if the chemical promoters reacted with NO, they were placed on the weighing pan of a Cahn R-100 continuous recording electrobalance. The weight change was then recorded when the promoter was exposed to a gas stream containing 2.5% NO and 97.5% He. The only promoters showing a weight change were: $CoCl_2$ and Fe_2O_3 gained weight at 300°C and $CoCl_2$ lost weight at 400°C.

The reaction rates of the metal sulfide mixtures were determined using the electrobalance at 400°C and 300°C. These were determined with a gas having a composition of 2.5% NO and 97.5% He. At 400°C the fastest reaction rate was 3.155×10^{-6} moles of NO reacted per minute per gram of mixture for the $BaS/FeCl_2$ mixture. The $FeS/FeCl_2$ and $BaS/CoCl_2$ mixtures showed weight losses at 400°C. At 300°C the fastest rate was 4.69×10^{-6} moles of NO reacted per minute per gram of $FeS/FeCl_2$ mixture.

The metal sulfide promoter mixtures and metal sulfides were tested in a fixed packed bed reactor to determine how well they would remove NO from a simulated flue gas. The simulated flue gas composition was 1000 ppm NO, 1% O_2, 18% CO_2 and the balance N_2. The effluent gas was analyzed for NO using a Thermo Electron Corp. Chemiluminescent NO-NO_x Analyzer. A simulated flue gas flow rate of 100 ml/minute was used. The capacities at 400°C ranged from 0 grams of NO/gram of CaS for unpromoted CaS to .0372 grams of NO/gram of FeS for the $FeS/FeCl_2$ mixture. The four largest capacities were $FeS/FeCl_2$, .0372 grams of NO/gram FeS; SrS/NaF, .0317 grams of NO/gram SrS; CaS/NaF, .0186 grams of NO/gram CaS and $BaS/FeCl_2$, .0168 grams of NO/gram of BaS. The capacity for $FeS/FeCl_2$ mixture at 300°C was .0020 grams of NO/gram of FeS.

It was determined that the presence of CO_2, SO_2 and H_2O in the simulated flue gas had no effect on the amount of NO removed by CaS at 500, 600 and 700°C. The presence of CO_2 and SO_2 in the simulated flue gas did not effect the removal of NO by the CaS/NaF mixture at 400°C. The presence of H_2O in the simulated flue gas was shown to reduce the amount of NO removed by the CaS/NaF, SrS/NaF and $FeS/FeCl_2$ mixtures at 400°C. The higher the concentration of O_2 the lower the NO removal capacity.

INTRODUCTION

NO_x may be the most vexing single pollutant in terms of finding an effective and cost efficient method of controlling its release. Several decades of scientists have been challenged by the difficulty of finding either a way to prevent the formation of NO or a way to render it a non-pollutant after its formation. The most common oxides of nitrogen are NO (nitric oxide), NO_2 (nitrogen dioxide) and N_2O (nitrous oxide). N_2O is an anesthetic, NO is not considered an irritant, but NO is slowly oxidized in the atmosphere to NO_2 and NO_2 is considered to be poisonous.

Nitric oxide is formed in several ways. It has been found that the NO formed in the combustion of fuels can occur by two principal mechanisms: high temperature oxidation of molecular nitrogen in the combustion air to yield thermal NO, and conversion of chemically bound nitrogen in the fuel to yield fuel nitric oxide (Lachapelle et al., 1976). The equilibrium concentration of NO with N_2 and O_2 is about 25,000 ppm at 4400°F but the equilibrium concentration is only .001 ppm at 70°F (Peters, 1971).

NO_2 is formed in a somewhat different manner. At 4400°F the kinetics of the N_2, O_2, NO_2 and NO reactions are such that only 5 to 10% of the NO_x formed is NO_2 with most of the rest being NO (Bartok et al., 1971). At 70°F the equilibrium between NO_2, O_2, and NO highly favors NO_2. Thus, in exhaust gases most of the NO_x is NO while at equilibrium most of the NO is converted to NO_2.

At 4400°F the formation of NO from N_2 and O_2 is very fast, while at 70°F the decomposition of NO to N_2 and O_2 is very slow. In 1917 an experiment was begun in which several containers of NO were sealed with various catalysts at ordinary temperatures. When the containers were opened in 1958 the decomposition of NO to N_2 and O_2 had proceeded so slowly that there was no N_2 detected (Shelef and Kummer, 1971). There is no thermodynamic hinderance to the thermal decomposition of nitric oxide, which is virtually complete to nitrogen and oxygen at temperatures below 1000°K. In the case of most reduction reactions the thermodynamic relations are even more favorable than for the thermal decomposition. Therefore, kinetics must be important in NO reduction and decomposition because experimentation has shown the reduction and decomposition of NO to be very slow at temperatures below 1000°K (Shelef and Kummer, 1971).

NO_2 is the most toxic of the oxides of nitrogen. Low levels of NO_2 have been shown to cause damage to plants, animals and humans. A concentration of 100 ppm for a few minutes can be very damaging to a persons health. A six month study in Chattanooga, Tenn. showed that concentrations of NO_2 of .06 to .11 ppm caused increased respiratory illnesses. Plants begin to show leaf damage at concentrations of 10-15 ppm in one hour and at concentrations of 1 ppm in 48 hours. Also, continuous exposure to concentrations of .25 ppm NO have been shown to reduce citrus crop yields (Pollution Control Technology, 1973).

NO_2 is not only dangerous in itself, it has been shown that NO_2 tends to promote the formation of such compounds as formaldehyde, acrolein and a group of plant poisons (peroxyacyl nitrates) (LaMantia and Field, 1969). Visually, NO_2 pollution may be identified by the reddish brown hue it gives to the atmosphere.

In 1976 it was estimated that 20 million tons of NO_x/year would be released into the atmosphere (Bartok et al., 1971). Stationary sources generally account for 60% of the amount of NO_x released. Some of these sources are: power plants using coal, oil and gas; industrial boiling incinerators; home heating systems and home applicances. Chemical plants where NO is produced or used and where metallurgical or high temperature processes are used are also stationary sources (LaMantia and Field, 1969). The NO_x emitted in the United States from stationary sources in 1972 is listed as follows (Mason and Shimizu, 1974):

SOURCE	ESTIMATED NO_x EMISSIONS tons/year
Utility Boiler	5,670,000
Reciprocating I.C. Engine	2,189,000
Industrial Boilers	2,108,000
Commercial/Residential Heating	826,000
Industrial Process Heating	390,000
Gas Turbines	291,000
Noncombustion	149,000
Incineration	41,000
TOTAL	11,665,000

The average United States urban concentration of NO_x in the air

is 20-25 times the natural atmospheric condition (Hopper and Yaws, 1974). The EPA has set the emission standard for coal fired steam generators at .70 lb/10^6 Btu of heat input. This is approximately 600 ppm (Walter and Goodwin, 1974).

Oxides of nitrogen are second only to SO_2 emissions in amount of pollutants released every year. Given the large amounts of NO_x being released each year and the toxic effect of NO_2 on humans, animals and plants it is important that effective and economical means of controlling NO_x emissions be developed. The present methods of controlling NO_x emissions fall into two categories: (1) chemical reduction, decomposition or physical removal and (2) combustion modification to minimize the formation of nitric oxides (LaMantia and Field, 1969). Current research is directed toward improving these methods, to make them more efficient and more economical.

II. REVIEW OF CURRENT NO_x CONTROL METHODS

A. Combustion Modification

There are many ways in which combustion modification can be used to reduce nitrogen oxide emissions. Low excess air is one of the most promising and widely applicable combustion modification techniques for reducing nitrogen oxide emissions. By reducing oxygen availability at the burners both thermal and fuel nitric oxide can be reduced. When the technique is employed, the lowest practical excess air levels are generally dictated by a need to limit products of incomplete combustion or to prevent operating problems such as boiler vibration, slugging and fireside corrosion (Lachapell et al., 1976). Low excess air can reduce nitric oxide emissions from 30 to 50% (Pershing et al., 1975); (Crawford et al., 1975).

Flue gas recirculation is also a combustion modification technique employed. Its effect in reducing nitrogen oxide is two fold; the flame zone temperature is reduced by the recirculating flue gases, and the concentration of oxygen available for nitric oxide production is reduced. This modification can be expensive due to the need for a high temperature fan and additional duct work (Lachapelle et al., 1976). Flue gas recirculation can reduce nitric oxide emissions as much as 30% (Pershing et al., 1975) (Henry et al., 1975).

Water or steam injection reduces thermal nitric oxide because it reduces the flame temperature. Installation costs are low; however, water injection will impose an efficiency penalty (Lachapelle et al.,

1976);(Blakeslee and Burbach, 1975). Staged combustion has also been shown to reduce nitric oxide emission (Armento and Sage, 1975). In staged combustion the burners may be staggered fuel rich and either fuel lean or air only. This modification is applicable to all fuels, especially coal. However, load reduction can result and there may be fireside corrosion problems (Lachapelle et al., 1976).

Reduced air preheat temperature lowers combustion zone peak temperatures and reduces thermal nitric oxide emissions (Pershing et al., 1975) (Armento and Sage, 1975).

Load reduction causes a decrease in combustion intensity and peak temperatures which causes a reduction in the amount of thermal nitric oxide produced (Armento and Sage, 1975)(Blakeslee and Burbach, 1975). This modification is not consistent with today's energy needs. Progress has been made in reducing nitric oxide emission through improved burner design. Several promising low nitric oxide (150 to 300 ppm) burner configurations for use in wall fired pulverized coal boilers have been identified. Scale-up criteria must still be developed (Lachapelle et al., 1976). Rocketdyne Division of Rockwell International is developing an optimum distillate oil burner for residential and commercial applications. The design has reduced NO levels from 50 to 65% of those from conventional burners and is capable of smoke free operation in 10% excess air (Dickerson and Okuda, 1974).

Stack gases from oil and coal-fired power plants are known to be major sources of NO_x (Bartok et al., 1969). A significant fraction of the NO derives from the reaction of nitrogen with oxygen at high temperatures. This NO production can be greatly reduced by combustion modification (Bartok et al., 1969). It has been shown, however, (Pershing et al., 1975; Turner et al., 1972) that the NO deriving from the nitrogen content of the fuel is still well above desirable limits in spite of combustion modification. The high nitrogen content of coal makes its use undesirable in this respect. The need to develop processes to control NO_x emissions is thus clearly established.

B. Chemical Reduction, Decomposition or Physical Removal

TRW Systems has conducted a technical and economic assessment of various catalytic schemes for nitrogen oxide control for stationary power plants (Lachapelle et al., 1976). On a laboratory scale with simulated flue gas, catalytic reduction of nitric oxide was studied over a range of space velocities from 5000 hr^{-1} to 20,000 hr^{-1} (standard temperature and pressure) and temperatures from 200°C to 450°C. Approximately forty-five catalysts were screened to determine nonselective nitric oxide reduction with hydrogen and carbon monoxide and selective reduction with ammonia, hydrogen and carbon monoxide. Identified as being the most promising for selective reduction with ammonia are iron-chromium, vanadium, copper-lead, molybdenum and platinum catalysts. Parametric studies have obtained nitric oxide conversion of about 60 to

90% with ammonia stoichiometry about 1.0, temperature 400°C, space velocities of 5,000 to 20,000 hr^{-1}, and inlet nitric oxide concentrations of 250 to 1000 ppm (Lachapelle et al., 1976). Ammonia has been the only reductant purported to show true selectivity for the heterogeneous reduction of nitric oxide to nitrogen in the presence of excess oxygen. Mitsubishi Petrochemical Co., Ltd. and Hitachi Ltd. (Toyko, Japan) have developed a metal oxide catalyst which when used with ammonia can reduce nitric oxide emissions from industrial plants. The nitric oxide is changed with the ammonia to water and nitrogen. This process works efficiently at 250-300°C and removes over 90% of the nitric oxide. This process meets Japan's NO_x standards which are much stiffer than those of the United States (Environ. Sci. & Tech., 1975). Hitachi Ltd. has also developed a catalyst which can decompose NO_x in stack gases at temperatures of about 100°C. This decomposition is done with a catalyst of activated carbon pellets treated with ammonium chloride, bromide or iodide and packed in a column. Ammonium bromide is the most effective of the three halides, and gave 80% NO_x removal at 100°C and 97% removal at 130°C. Over several months of tests, no change in NO_x removal or release of bromine was observed. The output gas is nitrogen and water vapor. The same catalyst removes SO_2 at a high rate, with ammonium sulfate as a product. High oxygen and low water vapor concentrations increase the reaction rate (Environ. Sci. & Tech., 1975).

Iron oxide supported on alumina is a promising catalyst/absorbent

for use in the simultaneous removal of NO_x and SO_x from power plant stack gases. A dry-contacting process is under development which would operate under net reducing conditions at temperatures of 370°C to 540°C. Iron oxide is converted to the ferrous state, NO is reduced to N_2 or NH_3, and SO_2 is removed as ferrous sulfide or sulfate. Regeneration with air produces SO_2 and reforms Fe_2O_3 (Clay and Lynn, 1975).

A dual bed catalyst system for the simultaneous reduction of SO_2 and NO has been developed by Sood and Kettrell (1974). The reactions:

$$CO + NO \longrightarrow CO_2 + 1/2\ N_2$$

$$2CO + SO_2 \longrightarrow 2CO_2 + 1/2\ S_2$$

$$CO + 1/2\ S_2 \longrightarrow COS$$

$$2COS + SO_2 \longrightarrow 3/2\ S_2 + 2CO_2$$

are considered to take place in this system. To get 90% removal stoichiometric quantities are necessary and the catalyst bed temperature must be controlled very carefully.

At Montana State University, Evoniuk (1978) has developed a process using mixtures of alkalai carbonates and transition metal oxides to absorb dilute concentrations of NO (800 ppm to 10,000 ppm). The NO is then desorbed in a concentrated stream.

Shell Oil Company has developed a flue gas desulfurization process using a fixed bed reactor of unusual design. This design eliminates

high pressure drops, plugging and acceptor contamination by the fly ash. The acceptor is copper supported on alumina, and contamination of the acceptor with particulate is avoided by causing the flue gas to flow alongside the acceptor mass rather than through it. In this arrangement, the gas passes through open channels with the result that the pressure drop is low and particulate does not accumulate in the acceptor. The acceptor is contained by gauze in a large number of flat, thin layers with passages in between for the flue gas; the sulfur dioxide in the flue gas reaches the acceptor by diffusion (Groenendaal et al., 1976). This reactor design may be of use with metal sulfides in controlling NO_x emissions.

Earlier in this section several processes were discussed for reducing NO_x emissions. Most of these have not passed the laboratory scale of development. Some of these processes appear to be nearing industrial application. Those reducing the NO using NH_3 over a catalyst appear to be promising. The major disadvantage of NH_3 reduction processes is that if some of the NH_3 is not reacted and is released, it becomes an air pollutant. Reduction using NH_3 is used quite a bit in Japan on an industrial scale; however, NH_3 is an expensive reactant. In 1972 it was estimated that 11,665,000 tons of NO_x were emitted from stationary sources (Mason and Shimizu, 1974). If this were all reduced using NH_3, 2,874,000 tons of NH_3 would be required. This represents 18.9% of the 1972 production of NH_3 (U.S. Bureau of the Census, 1974).

NH_3 is in great demand as a raw material for many industries. Therefore, if an alternate method of reducing NO could be developed it would probably be economically advantageous. A new and better method is needed for NO_x control. The reduction of NO using metal sulfides may provide this method.

C. Reduction With Metal Sulfides

It was shown by White (1973) initially that metal sulfides will reduce nitric oxide. Complete reduction was attained over a temperature range of 400°C to 800°C. The metal sulfides used were aluminum sulfide, antimony trisulfide, barium sulfide, cadmium sulfide, calcium sulfide, cupric sulfide, cuprous sulfide, ferric sulfide, lead sulfide, molybdenum disulfide, strontium sulfide, sulfurated potash, tungsten disulfide and zinc sulfide. Of these, White recommended barium sulfide, bismuth sulfide, cadmium sulfide, calcium sulfide, cuprous sulfide, ferric sulfide, molybdenum disulfide, strontium sulfide and zinc sulfide for further study. White also successfully lowered the temperature for the reduction of NO by the addition of various chemicals; the temperature range was lowered to 400°C to 500°C. The most promising additives were K_3FeF_6, K_3FeF_6/NaCl and NaF. It was also shown that NO would be reduced in the presence of O_2 and that the presence of water vapor did not appear to deter the reduction of NO. White also determined that in the reduction of NO with calcium sulfide, the solid product was at least

80 weight percent calcium sulfate.

Erickson (1974) studied the reduction of NO using CaS impregnated on high surface area supports. The results of the support material tests showed that Harshaw 1602 1/8 inch pellets of alumina and silica gave good reduction of NO without forming any undesirable products such as H_2S or SO_2. Nalco 2910-B 1/8 inch pellets of mostly alumina gave good reduction of NO, but caused the formation of some H_2S. Alcoa T-71 1/4 inch to 8 mesh tabular alumina gave very poor reduction of NO, but no H_2S or SO_2 was formed. Linde TM-0-1114 1/8 inch molecular sieves, which are synthetic crystalline metal alumina-silicates with Na as the metal in this case, gave good reduction of NO, but it caused the formation of SO_2.

In testing NiS as a reducing agent, Erickson found that SO_2 was produced along with the reduction of NO. In working with contaminants in the NO gas stream, it was found by Erickson that H_2O produced small amounts of H_2S and decreased the reduction of NO. The presence of H_2 seemed to increase the reductions of NO by CaS but caused the formation of H_2S. Natural gas also produced H_2S but did not seem to effect the reduction of CaS. He also found that O_2 and CO_2 did not effect the reduction of CaS.

McIntyre (1974) used a continuous recording electrobalance in studying the reaction

$$CaS(s) + 4NO(g) \longrightarrow CaSO_4(s) + 2N_2(g)$$

and found that the global rates for the reaction of CaS on high alumina Harshaw pellets increased from .25 x 10^{-4} at 390°C to .45 x 10^{-4} moles of $CaSO_4$ formed per hour per gram of pellet at 493°C. Linde molecular sieves gave greater average rates. Rates varied between .32 x 10^{-4} and .64 x 10^{-4} moles $CaSO_4$ formed per hour per gram of pellet for three temperatures between 392° and 438°C. The pellets impregnated with CaS were approximately 5 wt.% CaS. McIntyre also determined that at 440°C and with a flow rate ranging from .12 std. cm^3 per second to 3.8 std. cm^3 per second external film diffusion was not important for the reaction using Harshaw pellets. It was also shown by McIntyre that the rate of reaction of CaS with O_2 is greater than the rate of reaction of CaS with NO. The reaction rates of the two following reactions:

$$MeS + 4NO \longrightarrow MeSO_4 + 2N_2$$

$$MeS + 2O_2 \longrightarrow MeSO_4$$

were determined by Hodgson (1975) using a Cahn R-100 continuous recording electrobalance. The rates of reaction of NO with metal sulfides were determined using a gas with a composition of 2.5% NO and 97.5% He. The rate of reaction of O_2 with metal sulfides was determined using a gas mixture with a composition of 2.5% O_2 and 97.5% He. In general, the rate of reaction of the metal sulfide with oxygen was faster that with NO for all temperatures tested. Over the temperature range of 300°C to 500°C the reaction rates with NO ranged from no reaction for ZnS at 400°C

and 500°C and no reaction for Cu_2S at 500°C to 5.48×10^{-6} moles of NO reacted per minute per gram of FeS at 500°C. The reaction rates of O_2 ranged from no reaction with CaS and BaS at 300°C to 7.49×10^{-6} moles of O_2 reacted per minute per gram of BaS at 500°C. Based on this study, it was recommended that BaS, FeS, SrS and CaS be studied further to see if they might provide a method to reduce NO_x emissions.

III. PURPOSE OF RESEARCH

The purpose of this research is to further investigate the possibility that metal sulfides, in this case BaS, CaS, SrS and FeS, with various chemical promoters may provide an economical and efficient solution to the NO_x emissions problem.

Specifically this study is concerned with:

(1) The ability of powdered metal sulfides (BaS, CaS, SrS, and FeS) mixed with various chemical promoters (NaF, $NiCl_2$, $CoCl_2$, $FeCl_2$ and Fe_2O_3) and placed in a fixed packed bed to remove NO from a simulated flue gas.

(2) The effect of temperature on the ability of these mixtures to remove NO_x.

(3) The effect the presence of CO_2, SO_2 and H_2O in the simulated flue gas will have on the amount of NO removed.

(4) The possibility of using a metal sulfide impregnated on a high surface area support to remove NO.

IV. APPARATUS

Figure 1 shows a schematic diagram of the apparatus used with the tubular reactor. Four rotameters were used to mix the feed gas stream. A typical coal fired steam generating plant flue gas stream composition was used. The feed gas was usually 1000 ppm NO, 1% O_2, 18% CO_2 and the remainder was N_2. A reactor bypass was included so that the feed stream NO_x composition could be determined directly with the analyzer. The feed gas was fed into the top of a 5/8 inch diameter stainless steel pipe reactor. The reactor is shown in Figure 2. The reactor consisted of two sections; the top 8 inches were packed with stainless steel rings and functioned as a gas preheat section. It was connected to the bottom section by a 1 1/2 inch piece of 1/2 inch inside diameter stainless steel pipe. The bottom section was 11 1/2 inches long and contained a porous stainless steel disk about one inch from the top of the bottom section. The packed bed was placed on this disk. Directly under the disk was a 1/4 inch outside diameter stainless steel thermowell into which an iron-constantan thermocouple was placed. The gas entered the top of the reactor and left the bottom. A glass wool filter and a heat exchanger were placed directly after the reactor to prevent any of the powdered sulfide from escaping and to cool the gas stream. The gas stream then passed to the analyzer which was a Thermo Electron Corporation Model 10A Self Contained Chemiluminescent NO-NO_x Analyzer.

A rotameter was also provided that would bleed air or N_2 directly into the analyzer. This was to dilute the NO_x if its concentration was

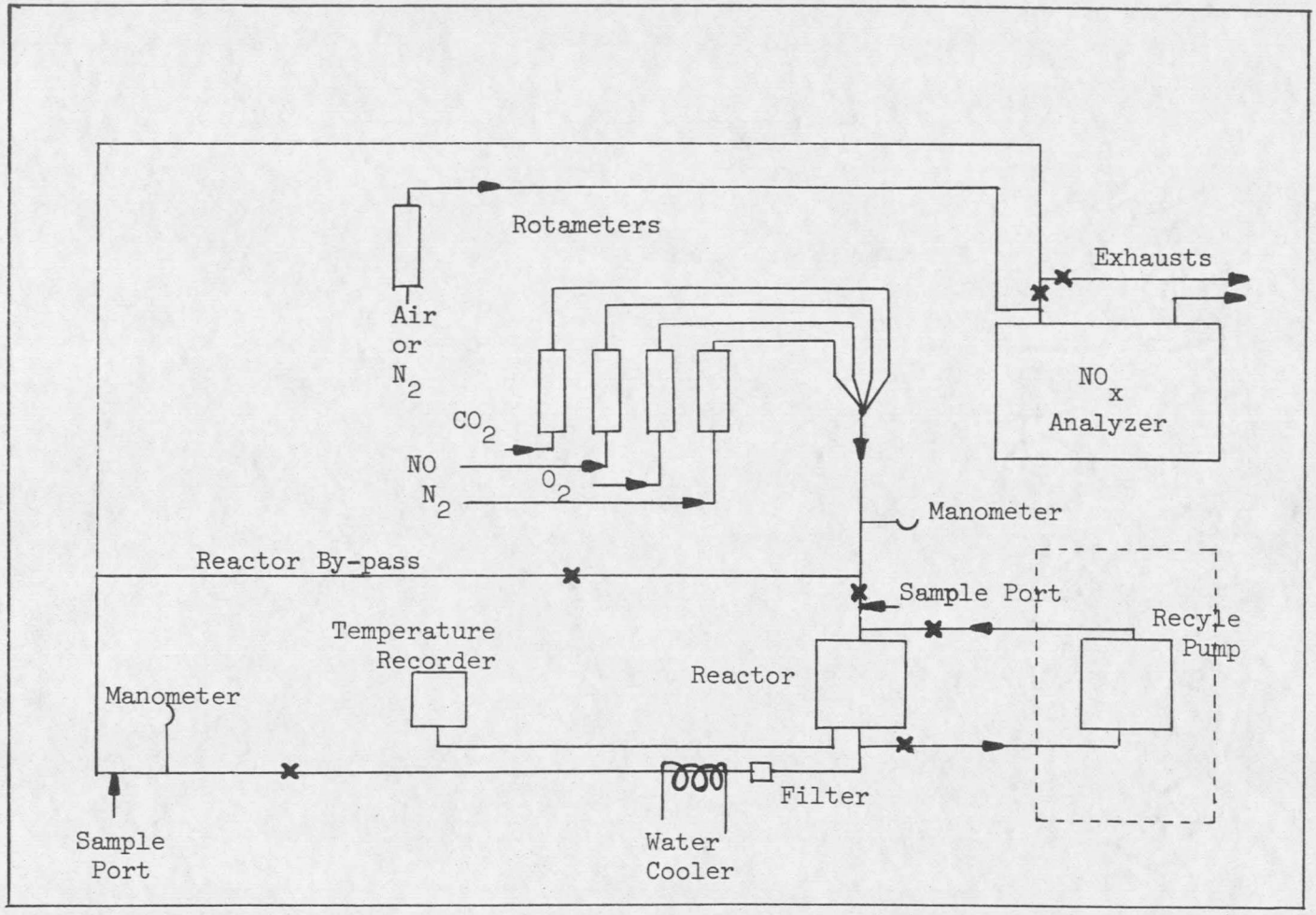

FIGURE 1. A SCHEMATIC OF THE APPARATUS USED WITH THE TUBULAR FIXED BED REACTOR

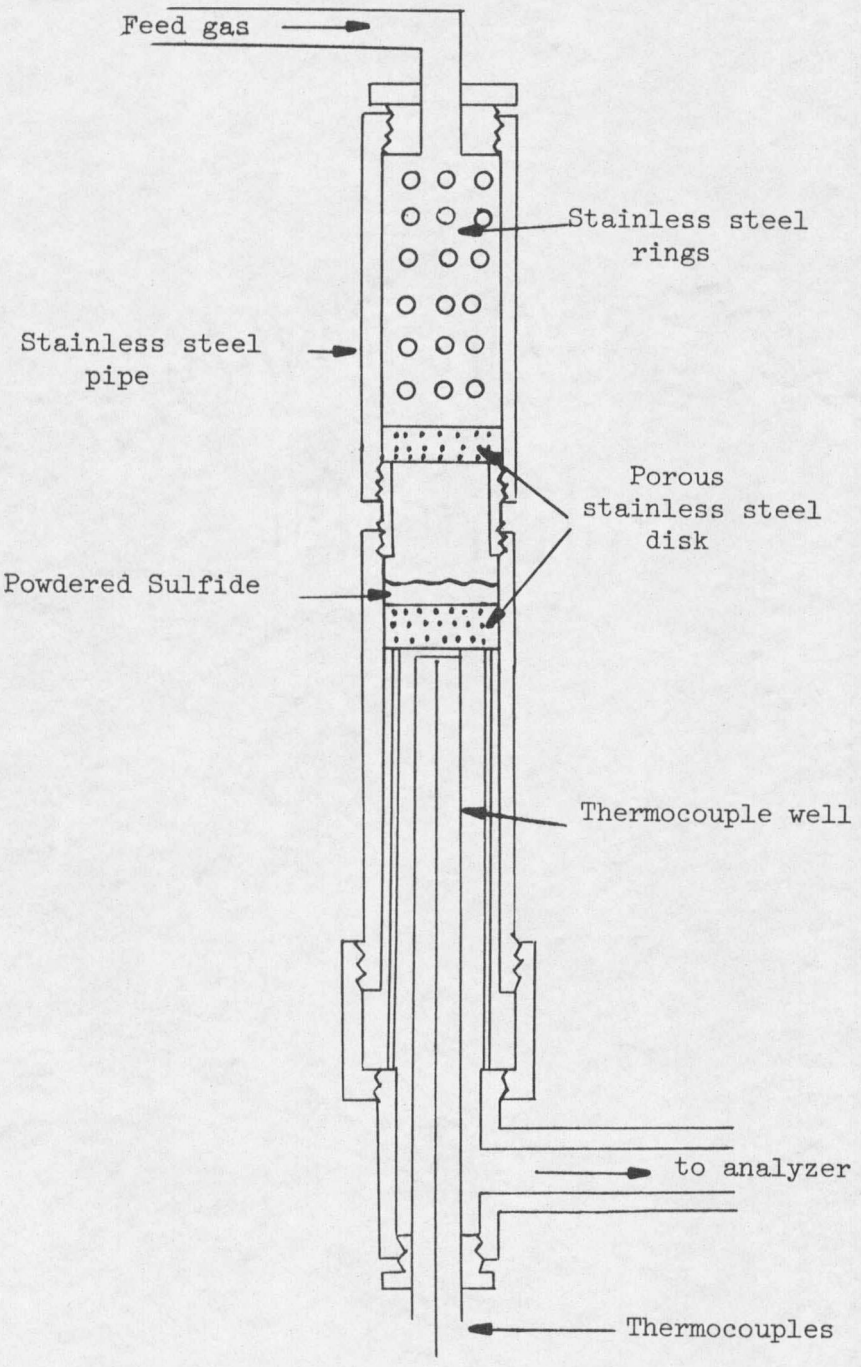

FIGURE 2. TUBULAR FIXED BED REACTOR CROSS-SECTION

greater than 10,000 ppm or to provide sufficient flow through the analyzer to allow it to function properly. Septum ports were provided before and after the reactor so that the O_2 and CO_2 concentrations could be determined using a gas chromatograph with a thermal conductivity detector (Aerograph 200). A 1/8 inch o.d. stainless steel column at 100°C packed with 13X molecular sieve packing was used to analyze for the O_2 and a 1/8 inch o.d. stainless steel column packed with Waters Associates Por Pak Q-S packing was used to determine the CO_2 concentration.

The reactor was heated by a cylindrical stainless steel block which was 18 inches long and had a 3 inch outside diameter and a 15/16 inch inside diameter. The block was wrapped by two 6 foot segments of ceramic beaded nichrome wire (1 ohm/foot resistance).

When flat plates were used in the reactor a metal bellows pump was placed in a recycle line between the outlet and inlet of the reactor. The recycle rate used was 130:1.

Figure 3 is a schematic diagram of the apparatus used to study the reaction rates. The balance mechanism is a Cahn R-100 continuous recording electrobalance. This device is used to measure the weight of a sample continuously as it hangs suspended from one arm of the balance in the reactor. The R-100 electrobalance has a 100 gram capacity for sample container and weight. Tare capacity is 100 grams mechanically and 50 milligrams with the coarse zero. The electro-

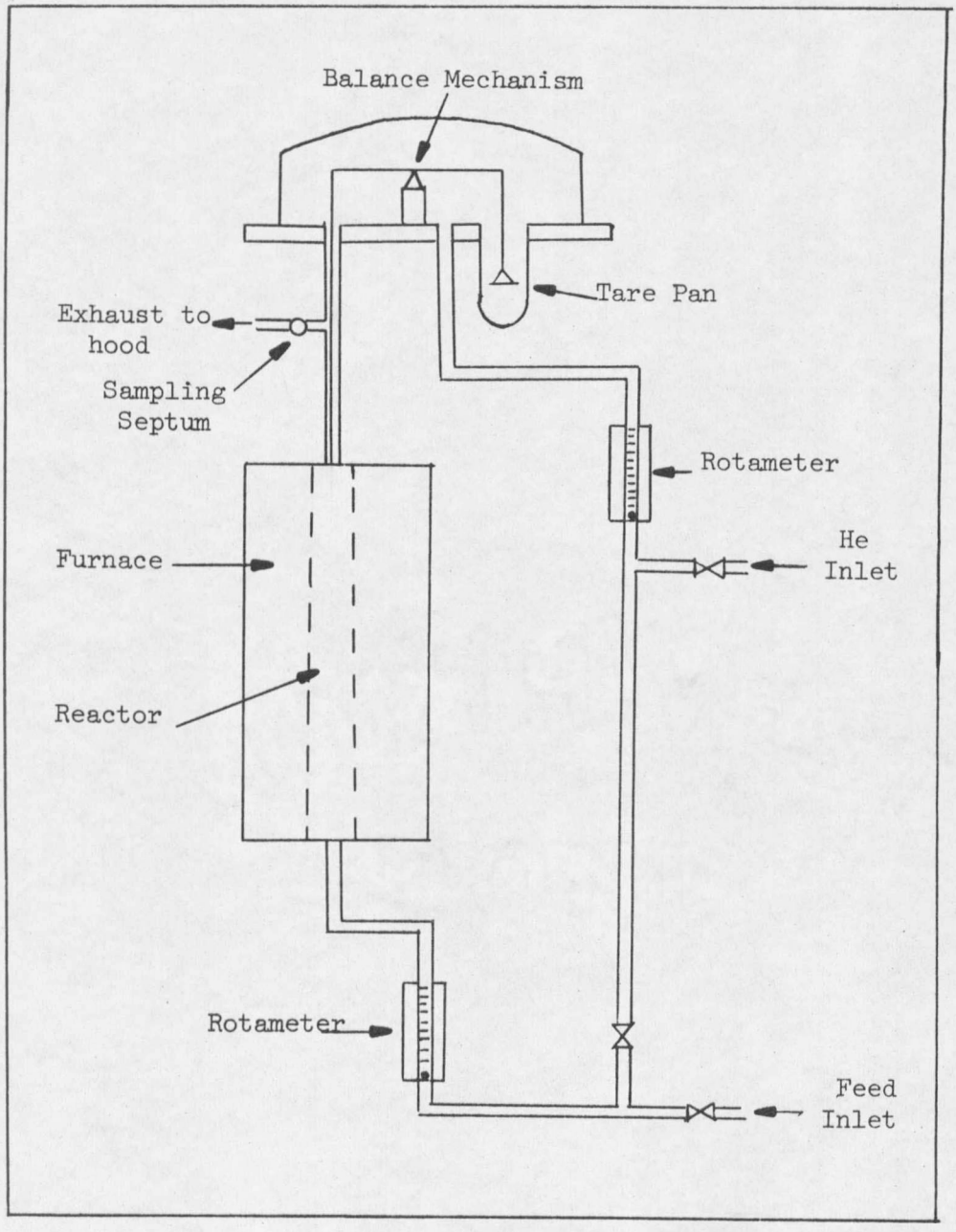

FIGURE 3. FLOW DIAGRAM OF APPARATUS FOR MEASURING RATE OF REDUCTION OF NO

balance has three electrical weight suppression ranges capable of electronically taring as little as 10 micrograms or as much as 10 grams.

The readability of the electrobalance is .5 micrograms and it has six weight ranges: 10 grams, 1 gram, 100 milligrams, 1 milligram and 100 micrograms full chart scale. An automatic range expander automatically brings the chart pen back to zero up to ten times when a weight change takes the weight outside of the recorder weight range. The precision of the instrument is $\pm 10^{-3}$ of the meter and recorder range and $\pm 10^{-6}$ of load and the accuracy is $\pm 5 \times 10^{-4}$ of mass suppression range for absolute weighings. The maximum weight change is 10 grams increase or decrease.

The system shown in Figure 3 normally operates with feed gas passing through a rotameter and entering the bottom of the reactor. Exhaust gases leave just above the reactor and are vented to hood. A helium line is run into the glass bell housing the balance mechanism to keep the bell purged of exhaust gases. During startup the valve arrangement makes it possible to pass helium through the reactor as well as over the balance mechanism.

The reactor is enclosed in a Lindberg 54331 hinged tube furnace during normal operation. It can be removed to allow access to the reactor tube before and after a run. It is controlled by a Teco TC-1000 proportional temperature controller (not shown).

The reactor cross-section is shown in Figure 4. The powdered

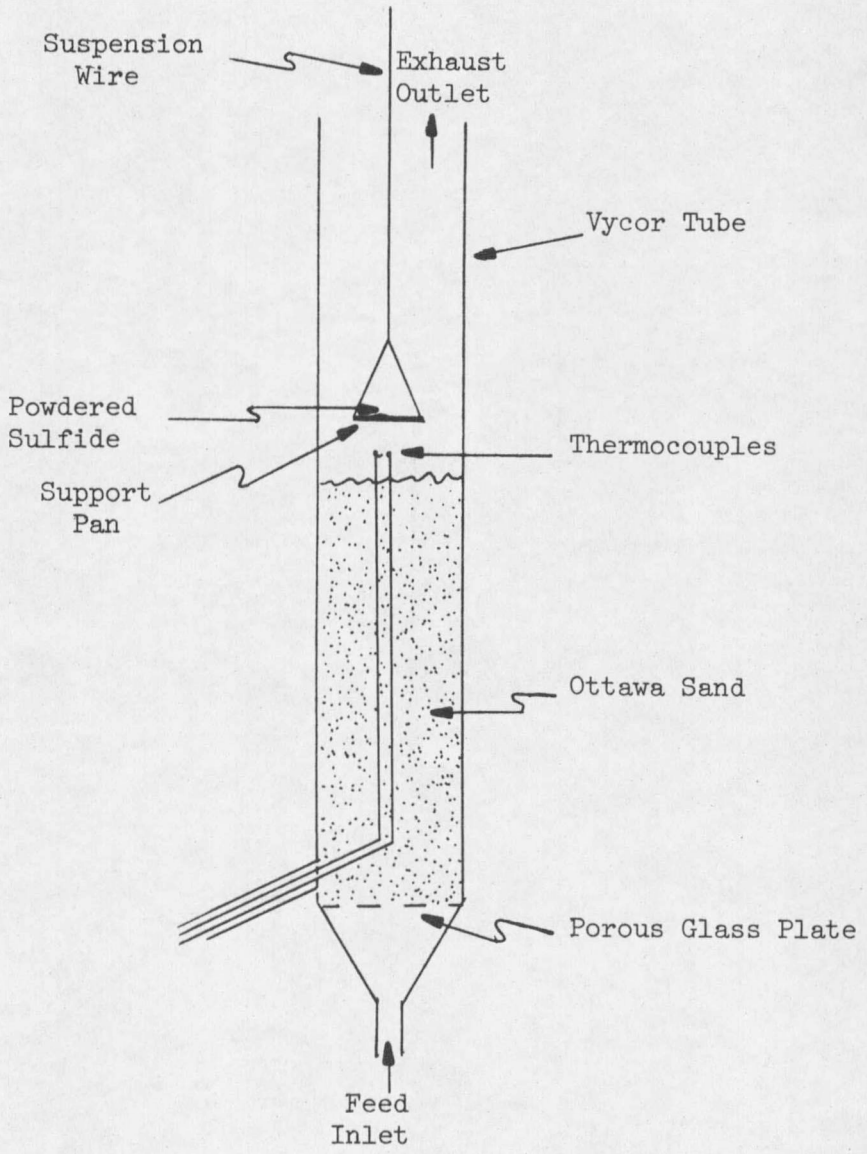

FIGURE 4. REACTOR CROSS-SECTION

metal sulfide promoter mixture rests on a 39mm diameter circular stainless steel pan suspended by a .1mm nickel wire from the balance arm. The reactor is a 57mm diameter, 840mm long Flothru Vycor tube with a ground glass joint at the bottom and a ground glass ball joint at the top.

Attached to the bottom joint of the reactor is a glass connector, and in this connector is mounted a porous glass plate. Two thermocouples are cemented with epoxy into a hole in the side of the glass connector and extend up the Vycor tube to a point just below the support pan. One thermocouple wire is attached to a proportional controller and the other is attached to a temperature recorder. The tube is filled with 40 mesh Ottawa sand to preheat the feed gas. The gas is fed into the bottom of the reactor, passes over the powdered mixture and is exhausted out the top.

V. PROCEDURE

The feed stream was made by mixing .05% NO in N_2, with pure O_2, CO_2 and N_2. The flow rates of these gases were determined by four rotameters. At the start of each run this mixture was by-passed past the reactor and fed directly into the analyzer until a steady feed NO_x concentration was recorded. To determine if any NO was being converted to NO_x in the feed line, the NO and NO_x analyzer readings for the feed gas were compared. The fact that there was no difference in the readings showed that NO was not being converted to NO_2 before it entered the reactor.

In order to place or replace the packed bed in the reactor the top section was removed from the bottom section. Then 2 ml of 40 mesh Ottawa sand was placed on the porous disk. On top of the Ottawa sand was placed the powdered sulfide or the powdered sulfide promoter mixture. The reactor was gently tapped to settle the bed, then the top portion was attached and the reactor was placed in the heater. For runs made at a constant temperature the reactor was heated to the desired temperature and after a steady temperature had been reached the feed gas was fed through the reactor and then to the analyzer. The NO_x exit concentration was continuously recorded on a Sargent-Welch (model SRG) chart recorder. Immediately at the beginning of each run the reactor inlet and outlet O_2 and CO_2 concentrations were determined using the gas chromatograph. At various times during the run the reactor inlet and outlet O_2 and CO_2 concentrations were again determined. When the

outlet NO_x concentration reached a level nearly equal to that of the beginning feed NO_x concentration, the reactor was again by-passed and the gas stream was fed directly to the analyzer. At this time the final NO_x feed concentration was determined. The reactor was then removed from the heater, the product removed and new material was placed in the reactor. Some of the products were kept for sulfate ion analysis using the barium sulfate test (Walton, 1963).

Because the flow rate through the reactor (100 ml/minute) was not sufficient to allow the analyzer to function properly, air was fed into the analyzer at the point at which the sample gas entered the analyzer. The flow rate of this air stream was 425 ml/minute. Of course this caused the exit concentration to be recorded as less than it actually was; however by analyzing the feed stream in the chemiluminescent analyzer the analyzer reading corresponding to a NO_x concentration of 1000 ppm could be determined. This reading was used as the basis for determining the reactor exit NO_x concentration during a run. By multiplying 1000 ppm times the ratio of the exit NO_x analyzer reading to the 1000 ppm analyzer reading the actual reactor exit NO_x concentration was determined. Not only was the analyzer accuracy increased because the sample flow rate was 525 ml/minute; but, the chart recorder was able to be read with greater accuracy. A full scale setting of 250 ppm was used instead of a setting of 1000 ppm. For the 250 ppm full scale setting each division on the chart paper was 2.5 ppm whereas for a full scale

setting of 1000 ppm each division was 10 ppm. The principal inaccuracy is that the feed concentration is determined by the flow rates of the individual gas constituents. These flow rates are determined using rotameters which were accurate to ± 10%. The rotameters were calibrated using a bubble tube and a stop watch. A feed composition of 1000 ppm NO was obtained by using a flow rate of 20 ml/minute of 0.5% NO, 99.5% N_2 gas and a total flow rate for the other gas constituents of 80 ml/minute. This gave a total simulated flue gas flow rate of 100 ml/minute and a NO concentration of 1000 ppm.

Water runs were made by bubbling the N_2 stream through water before it was mixed with the other constituents of the simulated flue gas.

For testing the high surface area support materials, an amount of the support material was put into a muffle oven at 400°C for 24 hours, then placed in a desiccator to cool. This drove off any adsorbed gases or H_2O that may have been picked up by the support. A few pellets were weighed and soaked in water overnight to determine the amount of solution that could be absorbed. Then a solution of calcium nitrate (as $Ca(NO_3) \cdot 4H_2O$) and H_2O was prepared so that the pellets would be 5% CaS by weight. The support material was then soaked in this solution for 24 hours. The excess solution was stripped off and the support material was placed into the muffle oven at 400°C for 24 hours. This evaporated the water and converted the $CaNO_3$ to CaO. For each run, two milliliters of pellets were placed in the reactor and a stream of pure

H_2S was fed through the reactor for 24 hours at 400°C to convert the CaO to CaS. Then the simulated flue gas was fed into the reactor and the amount of NO removed was recorded.

For measuring the rates of reactions of the various metal sulfide promoter mixtures, each mixture was prepared by intimately mixing 20% by weight promoter together with the metal sulfide using a mortar and pestle. Eight tenths of a gram of the powdered mixture was evenly distributed on the weighing pan and placed in the reactor and attached to the Cahn Electrobalance. After the weighing pan had been placed in the reactor, the reactor was heated to the operating temperature. A stream of pure helium was passed through the purge line in the bell and another stream of pure helium was passed through the reactor while heating the reactor and until no further weight change was recorded.

Next, the feed gas mixture was fed into the reactor at a rate of .2125 std. cm^3 per second. The feed gas composition was 2.5% NO and 97.5% He. The reaction was then allowed to proceed for at least one hour or until it was possible to determine the rate of reaction from the continuously recorded weight increase.

VI. EXPERIMENTAL RESULTS AND DISCUSSION

A. Reaction Rates

The reaction rates of calcium sulfide, barium sulfide, strontium sulfide and ferric sulfide mixed with various promoters were determined using the R-100 Cahn continuously recording electrobalance. First the promoters, which were NaF, $NiCl_2$, $FeCl_2$, $CoCl_2$ and Fe_2O_3, were tested for reactivity on the electrobalance at 300 and 400°C. Table I shows the weight changes that occurred when the various promoter materials were contacted with the 2.5% NO gas stream. In general, these materials showed no weight changes at 300 or 400°C. The exceptions were $CoCl_2$ at 300 and 400°C and Fe_2O_3 at 300°C. Table II gives the reaction rates of the metal sulfides mixed with the promoters at 400°C. All mixtures were 20 wt.% promoter. The reaction rates that were the fastest were those of the FeS/NaF, BaS/$FeCl_2$ and CaS/Fe_2O_3 mixtures. Table III gives the reaction rates of the metal sulfide promoter mixtures at 300°C. The fastest rate was the FeS/$FeCl_2$ mixtures. This was a dramatic change from the 400°C rate. At 400°C the FeS/$FeCl_2$ mixture lost weight when contacted with the NO. Reisz et al. (1957) showed that NO would rapidly oxidize FeS giving N_2 and SO_2. It may be that this takes place at 400°C giving a negative weight change. White (1974) has also documented the formation of SO_2 when FeS is reacted with NO. The other difference between the reaction rates at 300°C and 400°C is seen with the BaS/$FeCl_2$ mixture. The weight change of the BaS/$FeCl_2$ mixture goes from a negative weight change at 300°C to a very positive weight change

TABLE I

A SUMMARY OF THE WEIGHT CHANGE FOR THE VARIOUS CHEMICAL PROMOTERS REACTING WITH NO

Chemical	Grams of Weight Change / Minute 300°C	400°C
$NiCl_2$	0	0
$FeCl_2$	0	0
$CoCl_2$	.0015	-.01295
Fe_2O_3	.0029	0
NaF	0	0

TABLE II

THE RATES AT WHICH NO REACTS WITH THE

VARIOUS METAL SULFIDE CHEMICAL PROMOTER MIXTURES AT 400°C

	RATE x 10^7 $\frac{\text{Moles of NO Reacted}}{\text{Minute Initial Gram of Mixture}}$					
Metal Sulfide	Pure Metal Sulfide	NaF	$NiCl_2$	$FeCl_2$	$CoCl_2$	Fe_2O_3
FeS	.89	15.89	21.09*	—	1.35	3.35
BaS	3.19	5.89	25.4	31.55	—	0
SrS	2.14	.8014	0	0	0	5.58
CaS	1.64	5.99	4.29	1.56	1.79	25.60

* The rate was rapid for a short time then became zero and finally a weight loss was recorded.

TABLE III

THE RATE AT WHICH NO REACTS WITH THE

VARIOUS METAL SULFIDE CHEMICAL PROMOTER MIXTURES AT 300°C

RATE x 10^7 $\frac{\text{Moles NO Reacted}}{\text{Minute Initial Gram of Mixture}}$

Metal Sulfide	Pure Metal Sulfide	NaF	$NiCl_2$	$FeCl_2$	$CoCl_2$	Fe_2O_3
FeS	0	1.31	0	46.9	1.06	0
BaS	0	2.16	2.17	—	.46	1.75
SrS	1.73	2.28	.84	0	0	1.74
CaS	0	1.93	0	1.05	.698	.80

at 400°C. A reasonable explanation of this phenomena has not been found. The negative signs in Tables II and III indicate that there was a weight loss and no rate was calculated.

The results in Tables II and III indicate that the mixtures of FeS/NaF, BaS/$FeCl_2$ and CaS/Fe_2O_3 show the most promise at 400°C. At 300°C the mixture of FeS and $FeCl_2$ shows the most promise. If the results in Tables I, II and III are compared it seems that some of these chemical promoters do act as catalysts. The promoters mixed with the metal sulfides seemed to catalyze the reaction between the metal sulfide and NO in the following cases: at 400°C FeS/NaF, FeS/$NiCl_2$, FeS/Fe_2O_3, BaS/NaF, BaS/$NiCl_2$, BaS/$FeCl_2$, CaS/NaF, CaS/$NiCl_2$, CaS/Fe_2O_3 and SrS/Fe_2O_3; at 300°C FeS/NaF, BaS/NaF, CaS/NaF, SrS/NaF, BaS/$NiCl_2$, FeS/$FeCl_2$ and CaS/$FeCl_2$. In each case where a promoter seemed to act as a catalyst, in looking at Table I, it can be seen that alone the promoters did not react with NO. This indicates that in these cases the effect of mixing the promoters with the metal sulfides may have been a catalytic effect.

B. NO_x Removal With A Tubular Reactor, Using Simulated Flue Gas

Figures 5 through 24 show the percent NO_x and O_2 removed versus time for the metal sulfides CaS, SrS, BaS and FeS mixed with the promoters NaF, $NiCl_2$, $CoCl_2$, $FeCl_2$ and Fe_2O_3. The composition of each mixture was 20 weight percent promoter and 80 percent metal sulfide. Each run was done at 400°C using 2 grams of the mixture and a simulated flue gas

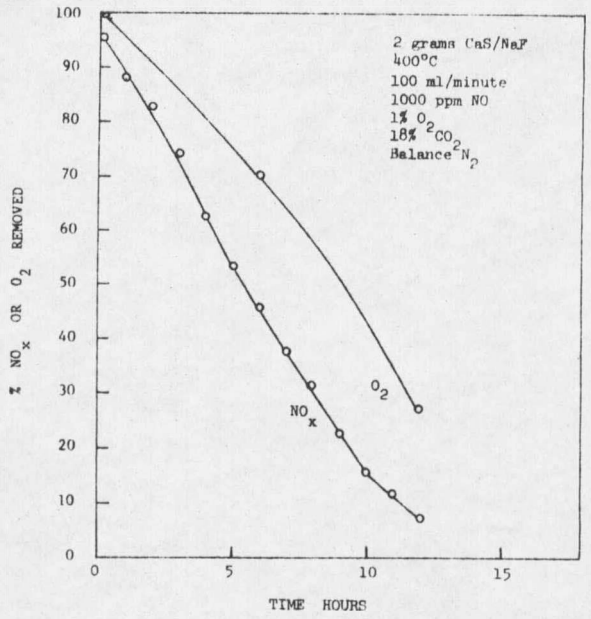

FIGURE 5. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF CaS/NaF AT 400°C

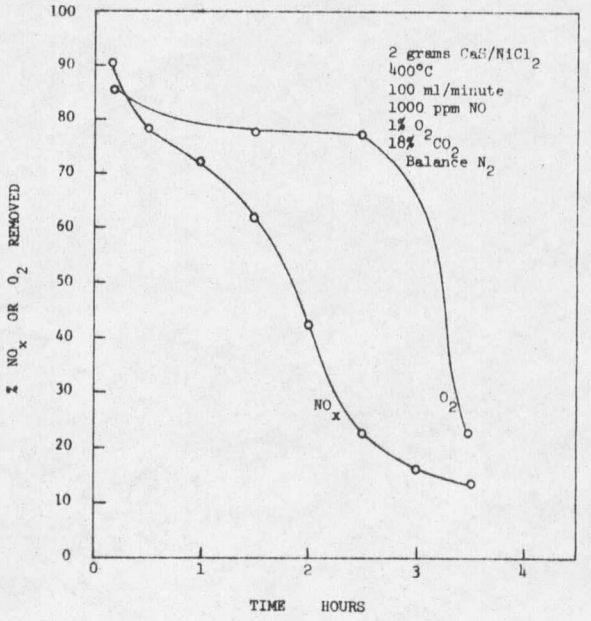

FIGURE 6. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF CaS/$NiCl_2$ AT 400°C

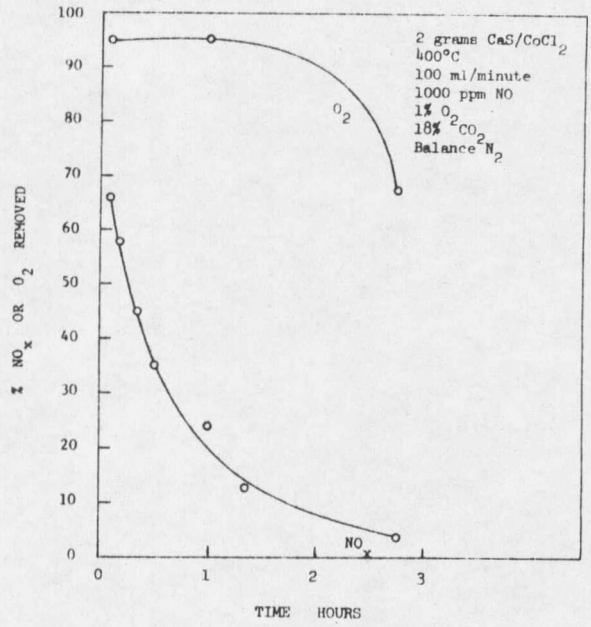

FIGURE 7. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF $CaS/CoCl_2$ AT 400°C

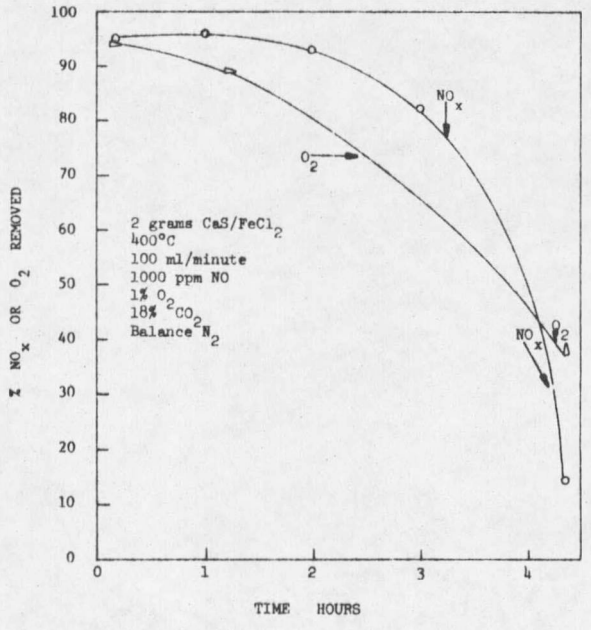

FIGURE 8. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF $CaS/FeCl_2$ AT 400°C

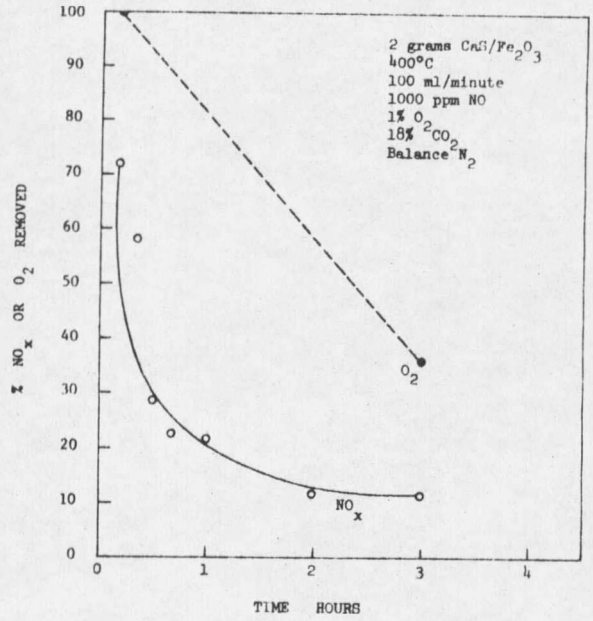

FIGURE 9. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF CaS/Fe_2O_3 AT 400°C

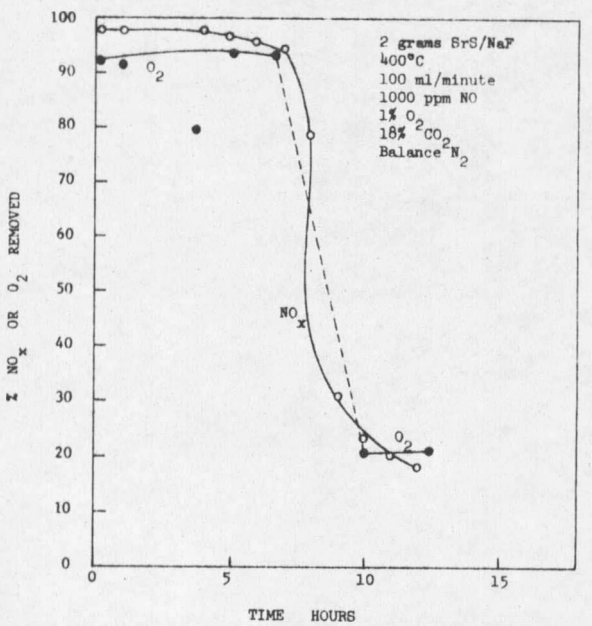

FIGURE 10. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF SrS/NaF AT 400°C

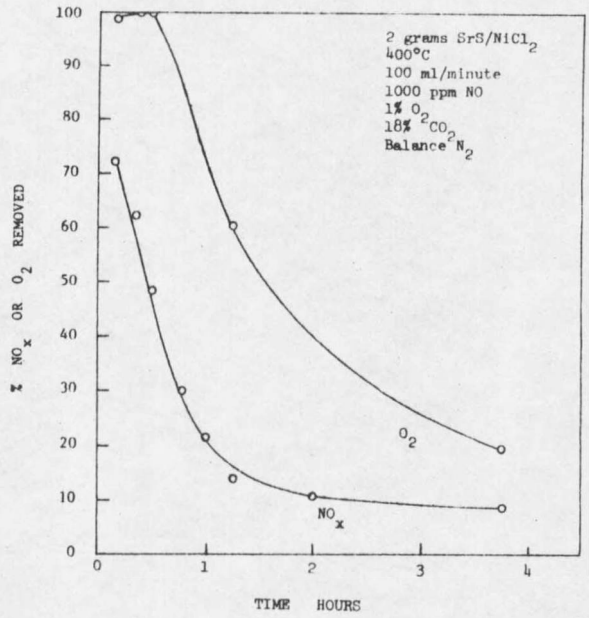

FIGURE 11. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF $SrS/NiCl_2$ AT 400°C

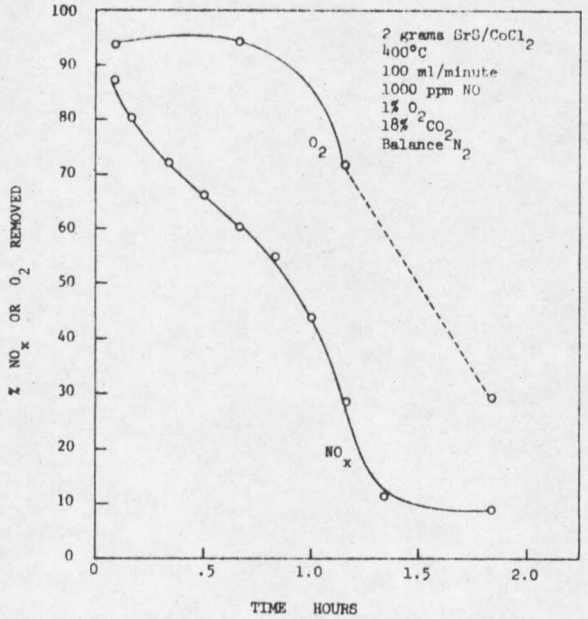

FIGURE 12. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF $SrS/CoCl_2$ AT 400°C

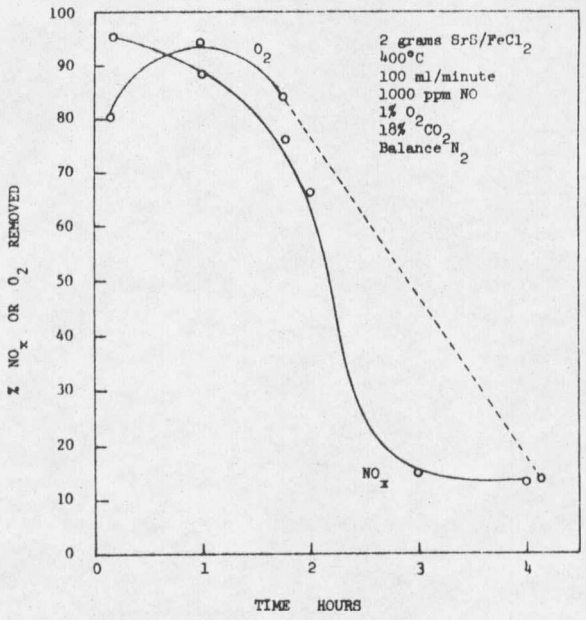

FIGURE 13. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF $SrS/FeCl_2$ AT 400°C

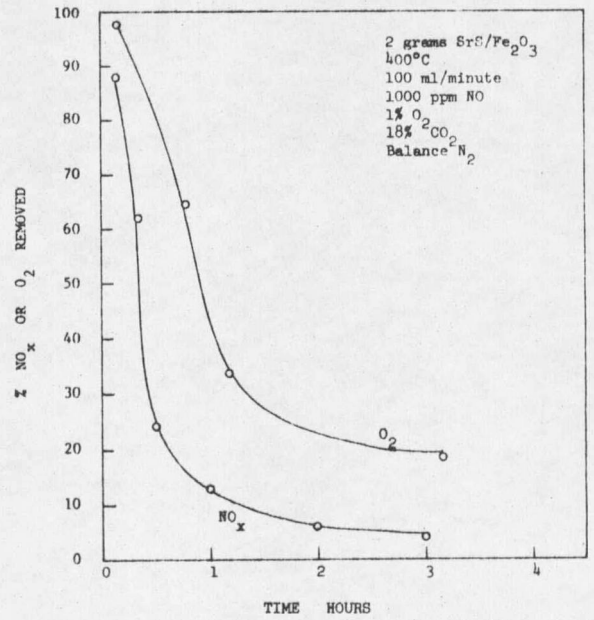

FIGURE 14. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF SrS/Fe_2O_3 AT 400°C

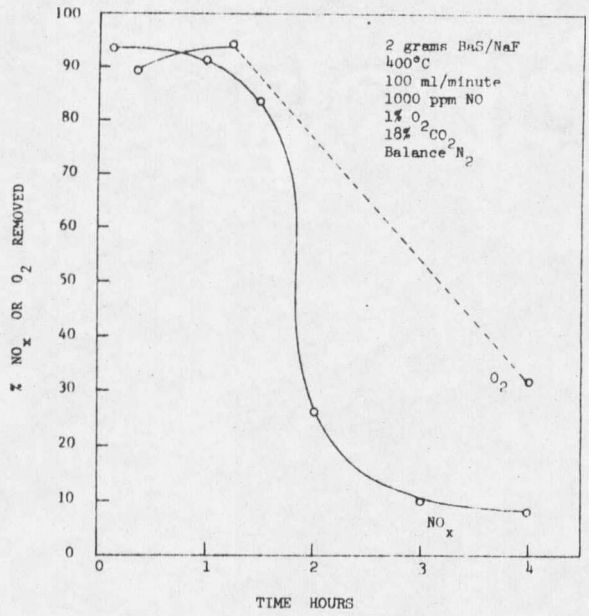

FIGURE 15. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF BaS/NaF AT 400°C

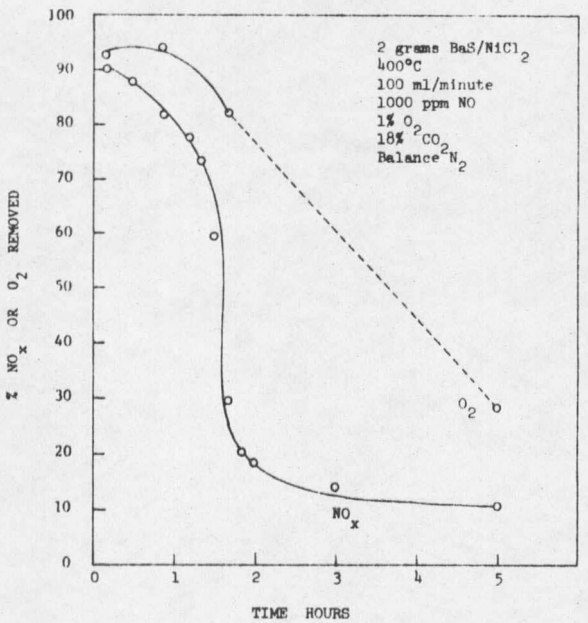

FIGURE 16. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF BaS/$NiCl_2$ AT 400°C

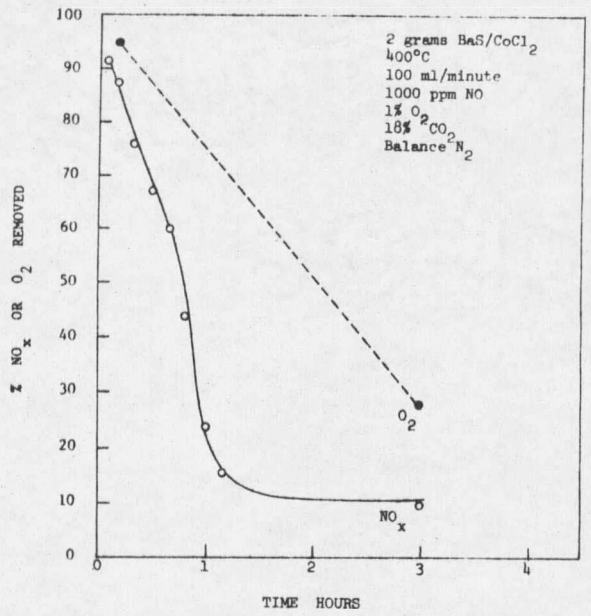

FIGURE 17. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF $BaS/CoCl_2$ AT 400°C

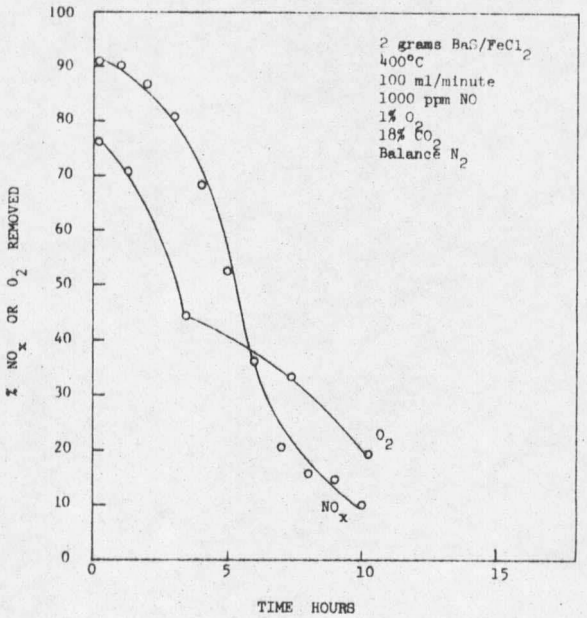

FIGURE 18. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF $BaS/FeCl_2$ AT 400°C

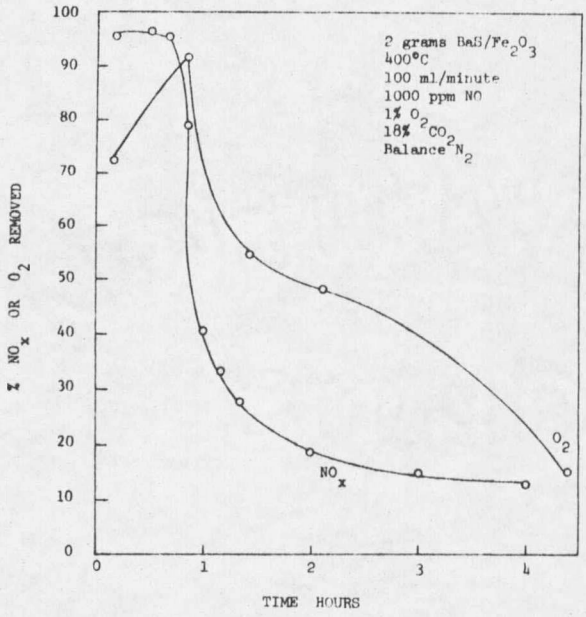

FIGURE 19. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF BaS/Fe_2O_3 AT 400°C

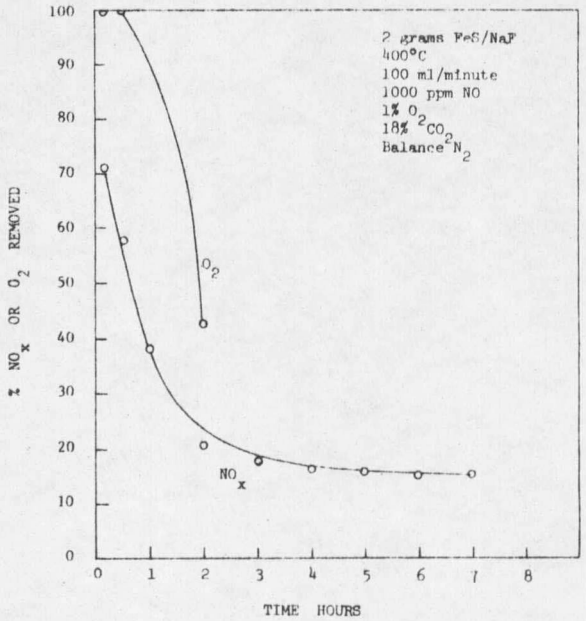

FIGURE 20. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF FeS/NaF AT 400°C

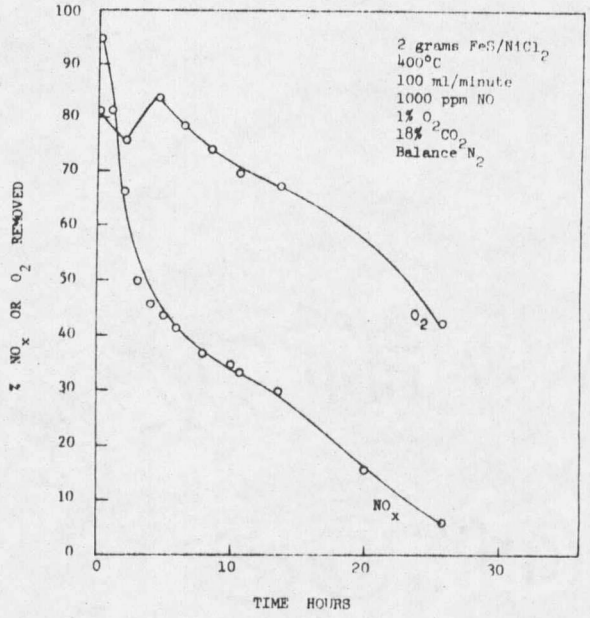

FIGURE 21. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF $FeS/NiCl_2$ AT 400°C

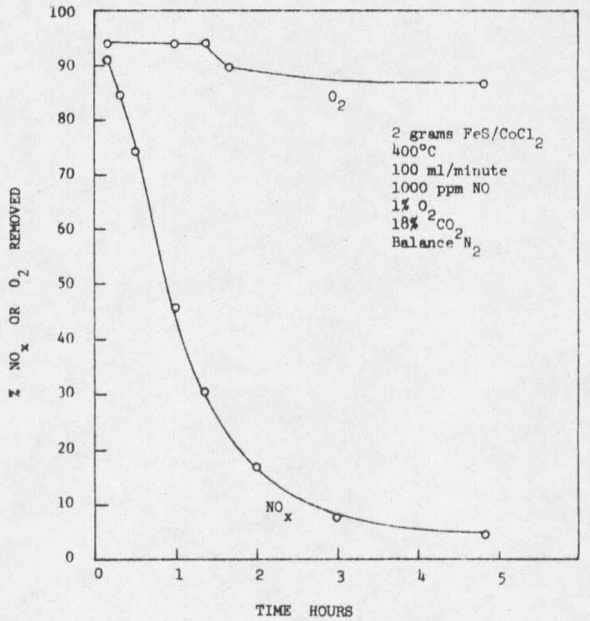

FIGURE 22. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF $FeS/CoCl_2$ AT 400°C

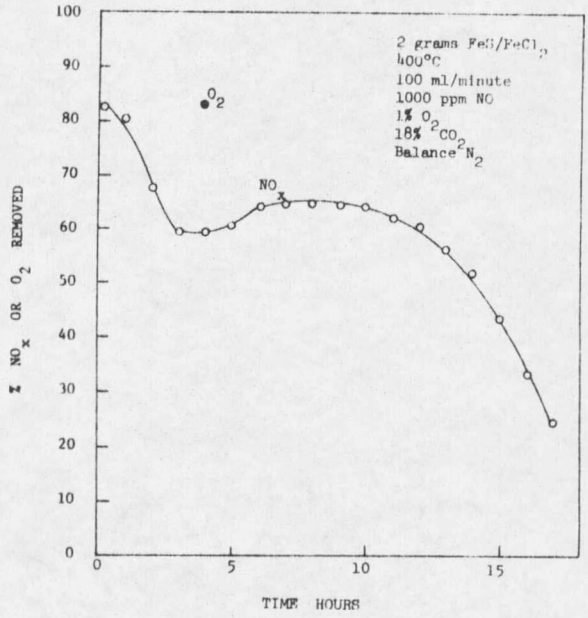

FIGURE 23. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF $FeS/FeCl_2$ AT 400°C

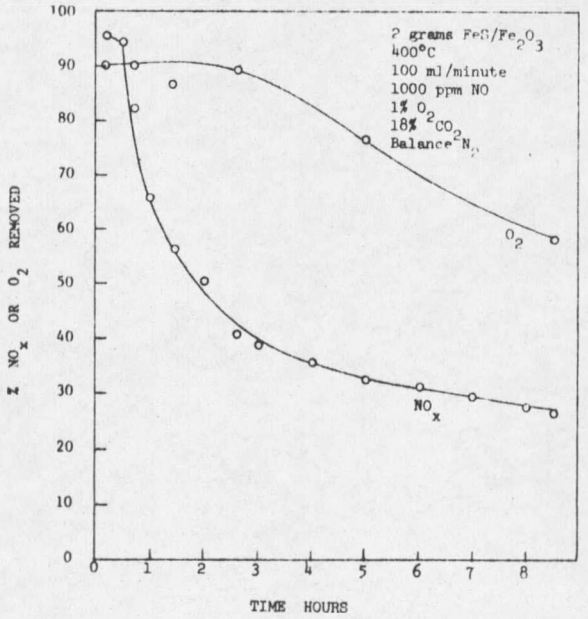

FIGURE 24. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF FeS/Fe_2O_3 AT 400°C

having an approximate composition of 1000 ppm NO, 1% O_2, 18% CO_2 and the balance was N_2. The solids were mixed using a mortar and pestal to insure good contact between the two solids. Two important facts can immediately be seen from these figures. First, the oxygen in almost every case, with the exception of the BaS/$FeCl_2$ and CaS/$FeCl_2$ mixtures, is removed to a greater extent than the nitric oxide. Second, and very important, is the fact that in every case some nitric oxide was removed by the metal sulfide promoter mixtures. The capacities (grams of NO/gram MeS) were calculated for the metal sulfide catalyst mixtures using this data.

The capacity of a mixture is the number of grams of NO reduced per gram of the MeS initially present from the start of the run until the exit concentration exceeds 600 ppm. The current standard for coal-fired power plants is 600 ppm (Walters and Goodwin, 1974). For an example of how the capacity of a metal sulfide promoter mixture is calculated, see Appendix A. These capacities are listed in Table IV. The six best metal sulfide promoter mixtures are: FeS/$FeCl_2$, SrS/NaF, CaS/NaF, BaS/$FeCl_2$, FeS/$NiCl_2$ and CaS/$FeCl_2$. The capacities in this sequence decrease from FeS/$FeCl_2$ to CaS/$FeCl_2$. These results generally agree with those obtained on the electrobalance at 400°C; the main exception is the FeS/$FeCl_2$ mixture. As noted previously, the FeS/$FeCl_2$ mixture registered a weight loss on the electrobalance. If it is assumed that the NO is reacting with the FeS to give SO_2 and N_2 this would agree

TABLE IV

THE CAPACITIES OF THE METAL SULFIDE PROMOTER MIXTURES AND OF THE METAL SULFIDES

Grams of NO / Gram MeS

Metal Sulfide	NaF	$NiCl_2$	$CoCl_2$	$FeCl_2$	Fe_2O_3	Unpromoted Metal Sulfide
CaS	.0186	.0055	.0009	.0134	.0010	0
SrS	.0317	.0014	.0021	.0072	.0011	0
BaS	.0063	.0048	.0020	.0168	.0034	.0023
FeS	.0019	.0136	.0022	.0372	.0073	.0005

both with the high capacity for NO removal shown by the $FeS/FeCl_2$ mixture and with the weight loss recorded on the electrobalance. This reaction was observed by Reisz et al. (1975). White (1974) also observed that in certain conditions with certain promoters, when NO was reacted with FeS, some SO_2 was formed, thus the $FeS/FeCl_2$ system probably would not be viable for NO_x control in processes in which SO_2 is not already present.

Attempts were made to analyze for SO_2 using the gas chromatograph. However, the conditions required to analyze for O_2 and CO_2 did not result in the gas chromatograph being able to detect SO_2.

The results seen in Table III for metal sulfide mixtures at 300°C seem to agree with the results from the tubular reactor at 400°C. The major difference between the results in Table III and those from the tubular reactor is that a negative weight change was recorded for the $BaS/FeCl_2$ mixture on the electrobalance. Figures 25 and 26 show the removal of NO_x and O_2 using FeS and BaS. The capacity of BaS is .0023 grams of NO/gram BaS and the capacity of FeS is .0005 grams of NO/gram of FeS. These show that in the case of $FeS/NiCl_2$, $FeS/FeCl_2$ and $BaS/FeCl_2$ the promoters seem to have some catalytic effect. There is no capacity for CaS given because at 400°C CaS will remove no NO. Because of the high capacity of the $FeS/FeCl_2$ mixture it was reacted at 300°C with the simulated flue gas. Figure 27 shows the percent NO_x removed. The CaS/NaF mixture was also run at 300°C but it did not remove any NO_x.

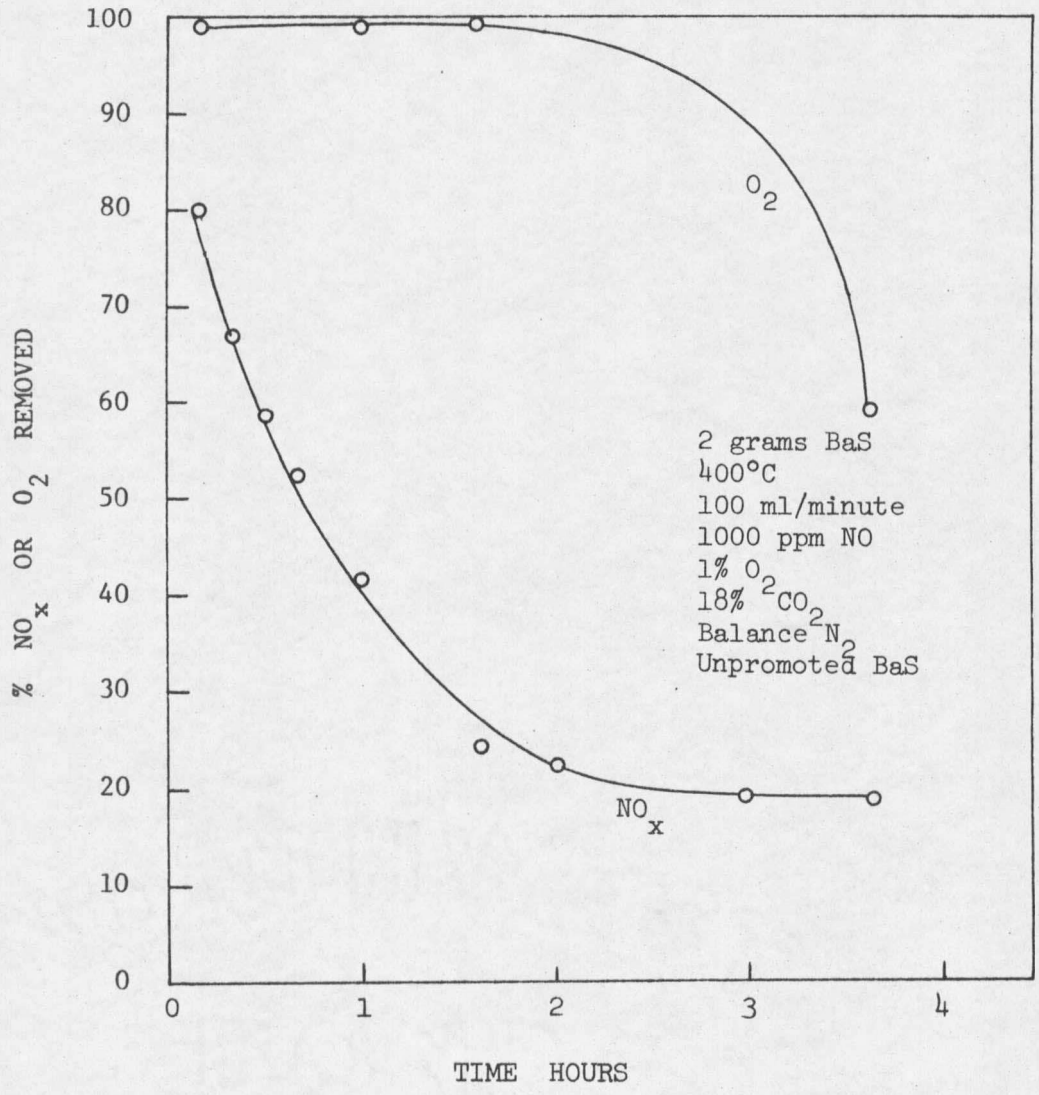

FIGURE 25. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF BaS AT 400°C

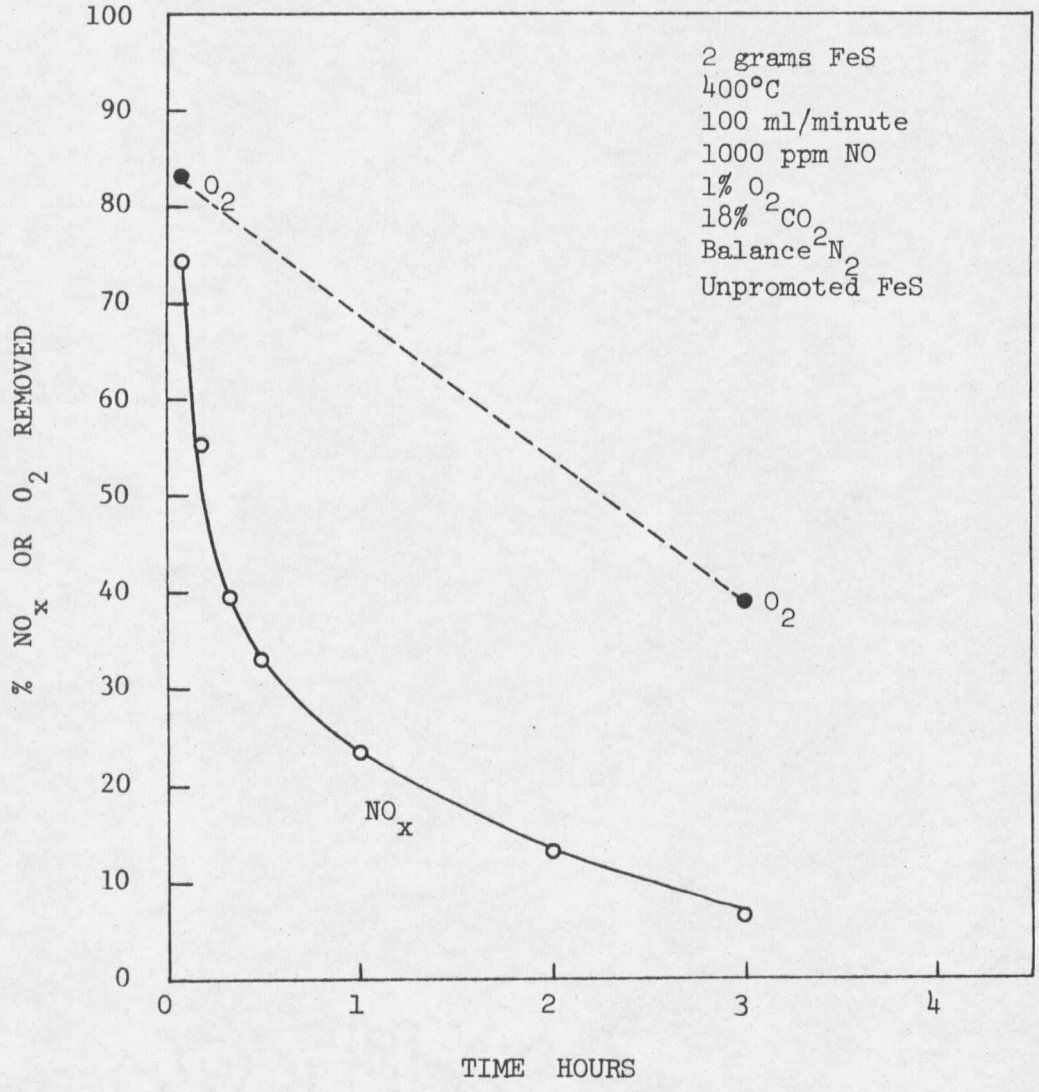

FIGURE 26. THE PERCENT NO_x AND O_2 REMOVED BY 2 GRAMS OF FeS AT 400°C

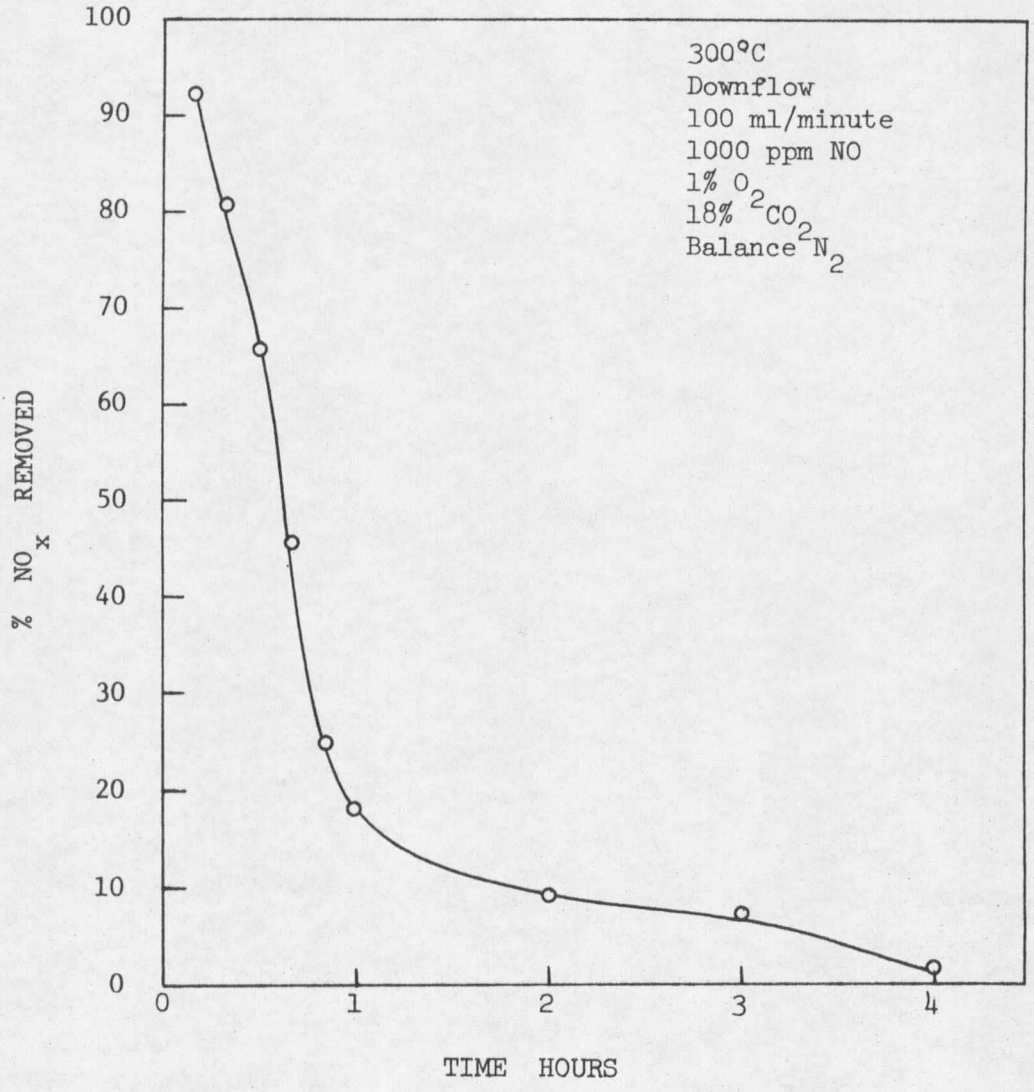

FIGURE 27. THE PERCENT NO_x REMOVED BY 2 GRAMS OF $FeS/FeCl_2$ AT 300°C

The effect of temperature and the reproducibility of the data were studied using the CaS/NaF mixture. Figure 28 shows the results of three runs at 400°C with the CaS/NaF mixture. The reproducibility is generally good, each run gives results fairly close to the others. Figure 29 gives the results for the CaS/NaF mixture at 500°C. About the same amount of NO_x was removed as at 400°C. Again the trends are generally consistent, although there is some difference especially near the end of the run. Attempts were made to determine at what temperature CaS alone would significantly remove NO_x. In Figure 30 it can be seen that at 600°C CaS has a low capacity to remove NO_x. The results are very reproducible early in the runs, but diverge slightly later in the runs. In Figure 31 the results for 2 grams of CaS reacted at 700°C are shown. For a number of runs the results varied greatly. The ability to remove NO_x was greater than at 600°C in all cases and even in the worst case was comparable to the ability of the CaS/NaF mixture at 400°C. The variability in this data is believed to be due to variation in the flow characteristics of the packed bed from one run to another. The flow characteristics through the fixed packed bed are not understood. That is, it is not known if the gas flows primarily between the edge of the bed and the reactor wall or if it flows fairly uniformly through the bed. It is not known if the flow characteristics are identical from run to run. If the bed was to pack more solidly in one run, more of the flue gas may be forced to flow between the edge of the bed and the

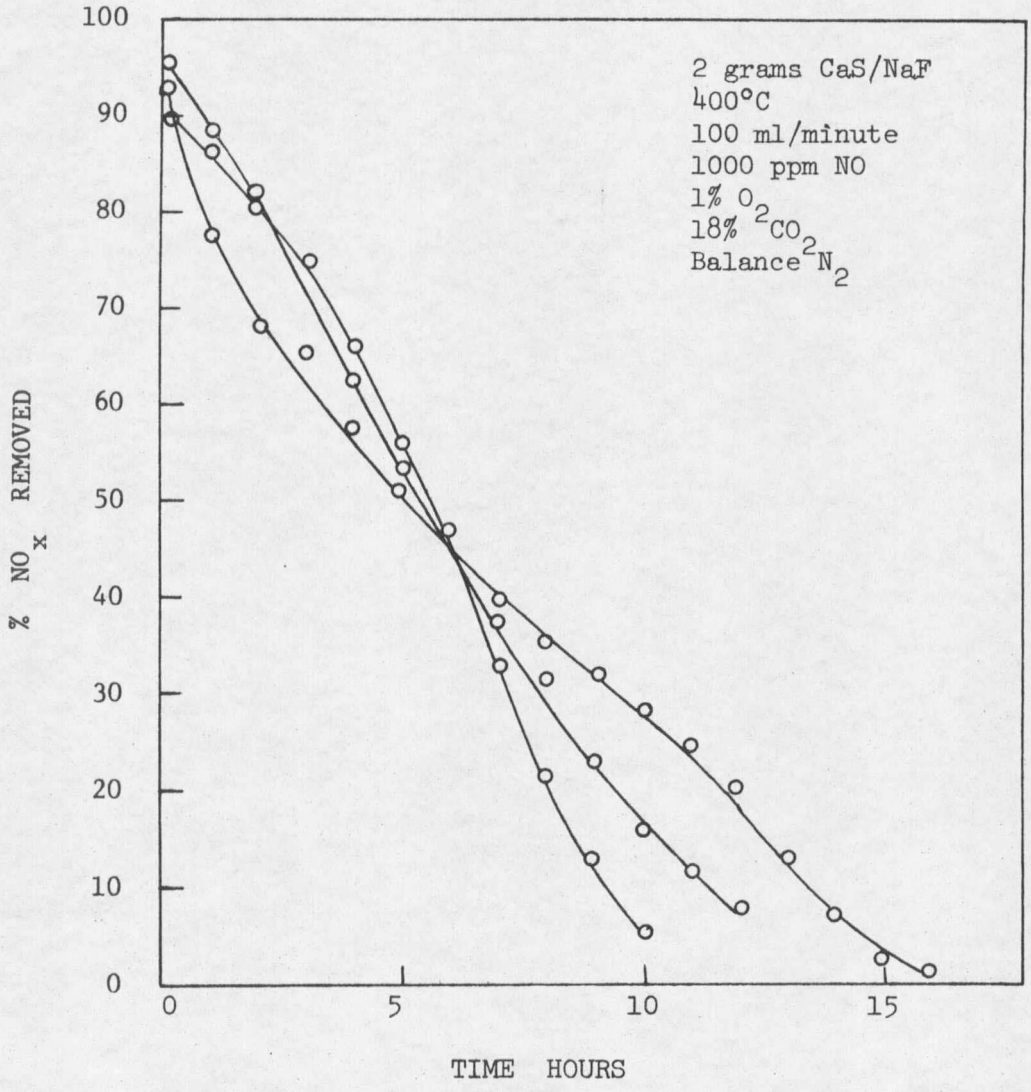

FIGURE 28. THE PERCENT NO_x REMOVED BY 2 GRAMS OF CaS/NaF AT 400°C

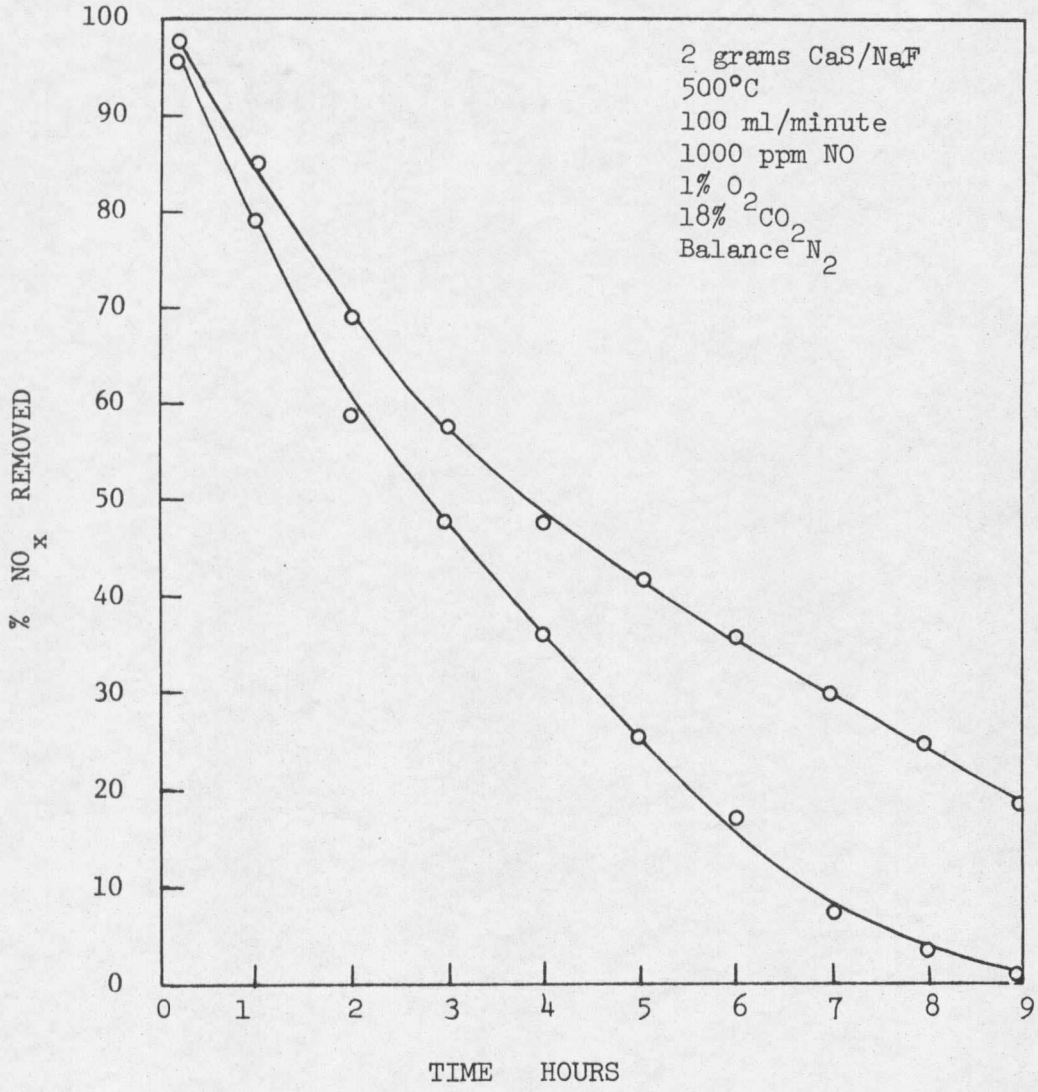

FIGURE 29. THE PERCENT NO_x REMOVED BY 2 GRAMS OF CaS/NaF AT 500°C

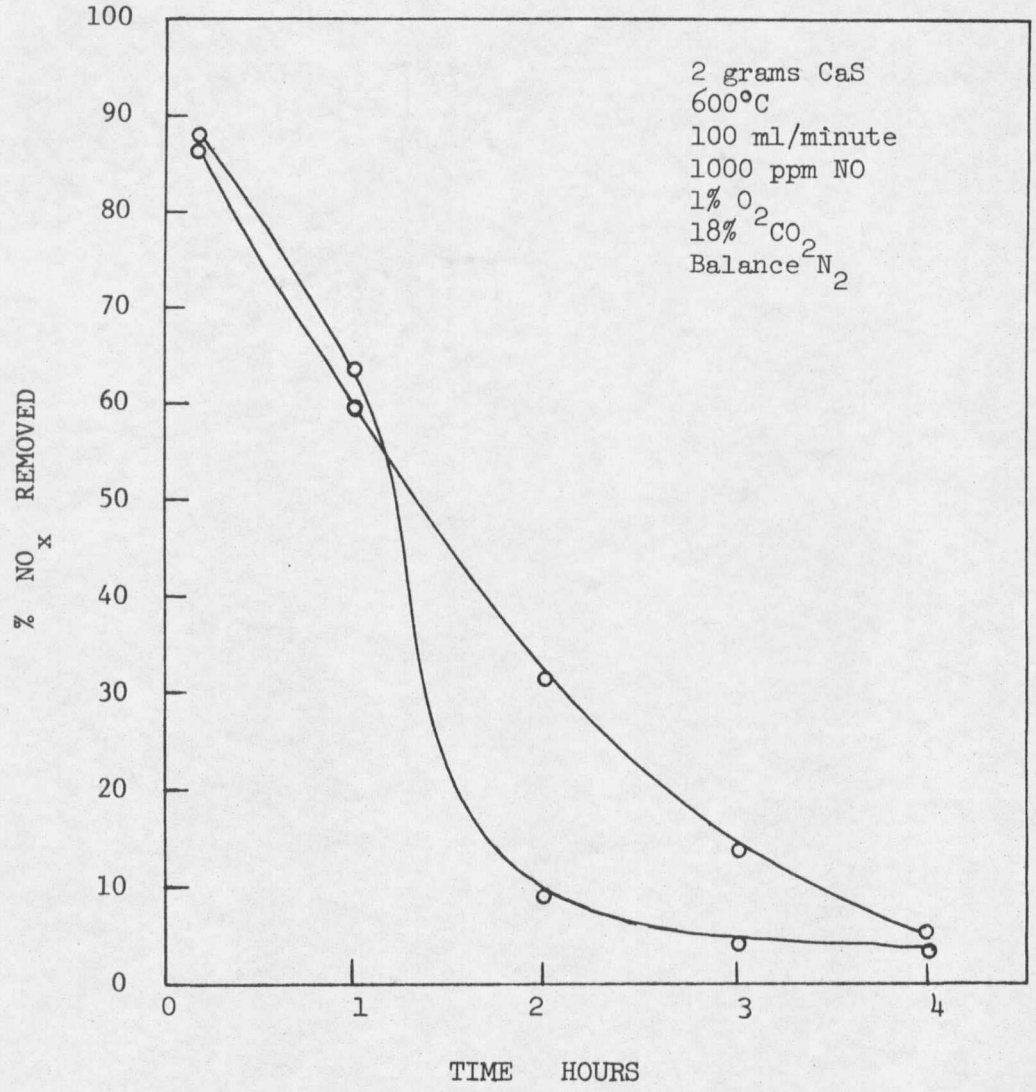

FIGURE 30. THE PERCENT NO_x REMOVED BY 2 GRAMS OF CaS AT 600°C

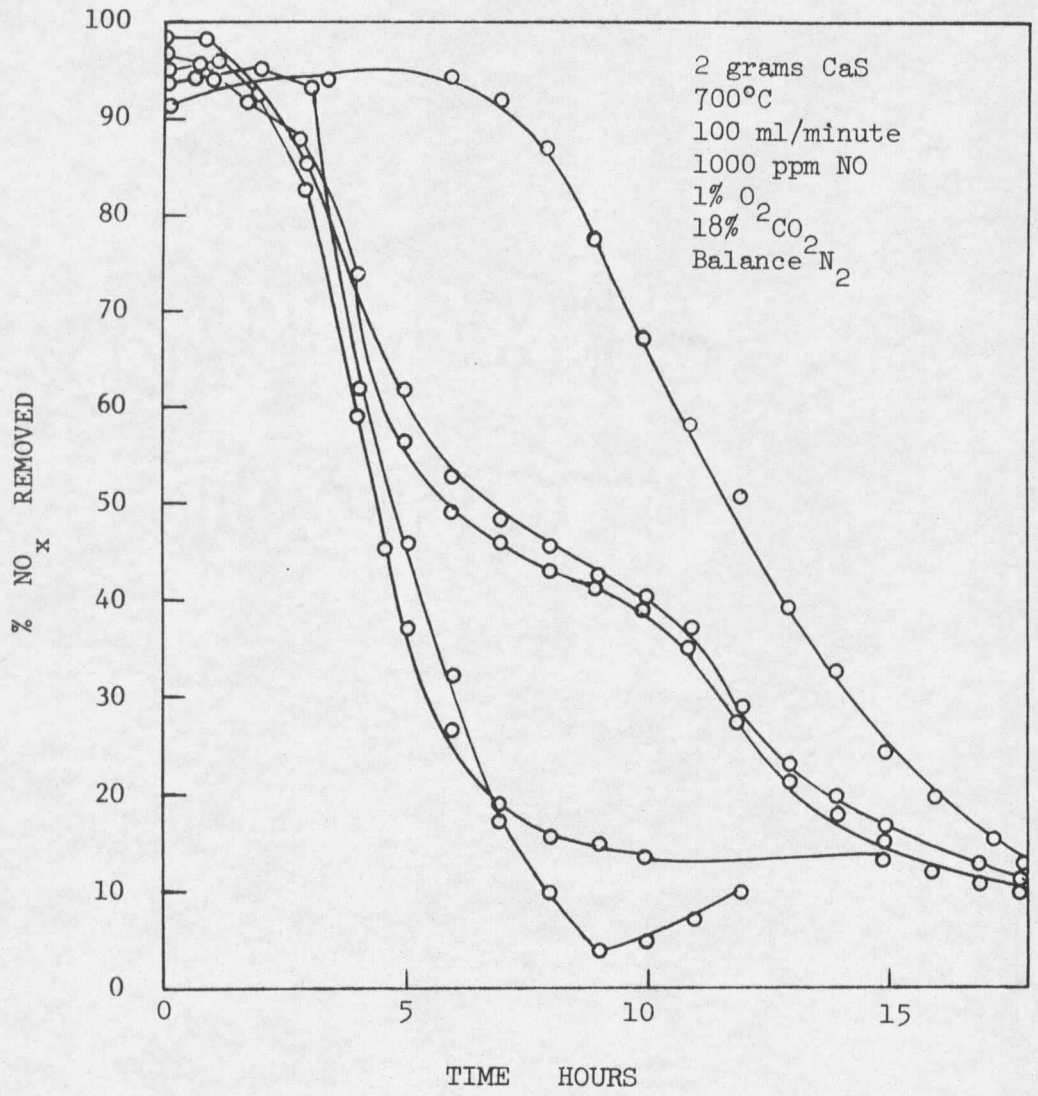

FIGURE 31. THE PERCENT NO_x REMOVED BY 2 GRAMS OF CaS AT 700°C

reactor wall or large channels may form in one run and not in another. In an attempt to remove the effect of packing, one gram samples of CaS and the CaS/NaF mixture were pressed onto 3 inch by 1/2 inch stainless steel plates. A very fine mesh stainless steel screen was placed in the bottom of the plate to support the CaS and CaS/NaF. The CaS and CaS/NaF mixtures were pressed into the plates using a 2 ton hydraulic jack. The plates were placed vertically in the reactor and a metal bellows recycle pump was used to develop a recycle rate of 130:1. The same simulated flue gas was used. Figures 32 through 35 show the results of runs at 400 and 500°C for the CaS/NaF mixture and at 600 and 700°C for the CaS. The trends in ability to remove NO_x agree with those seen in the fixed packed bed data. There is also better reproducibility indicating that the variation in the fixed packed bed data was probably caused by differences in packing and thus differences in flow characteristics.

By experiment one can determine whether film diffusion plays a role by using varying flow rates of identical feed. Where gas film resistance is important, conversion will vary significantly with changing gas flow rate. Where gas film resistance does not influence the rate of reaction, conversion should remain approximately the same for various flow rates. To determine if external film diffusion played an important role in this fixed bed reactor system, runs were made using 1 gram of the CaS/NaF mixture at a flow rate of 50 ml/minute and 4 grams of

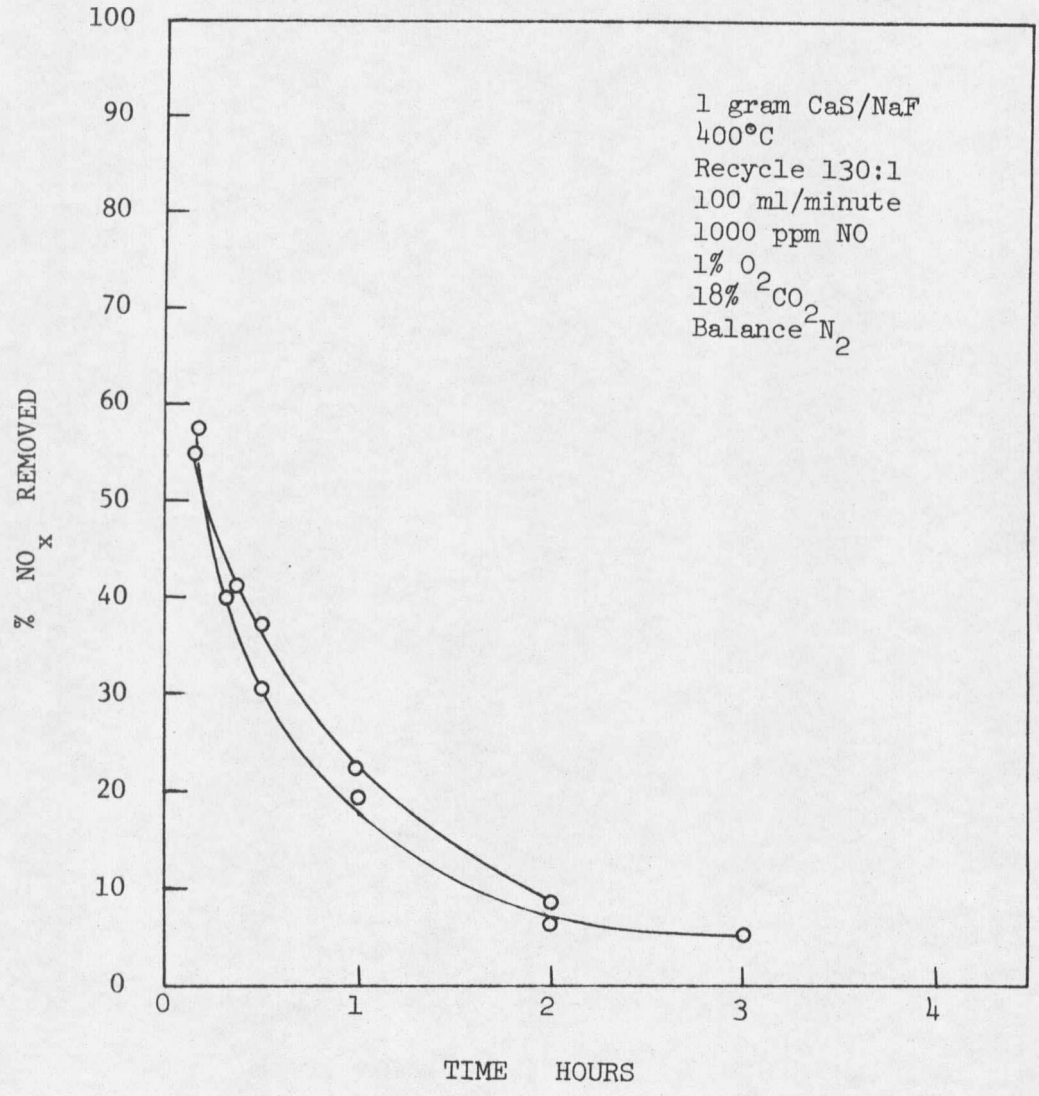

FIGURE 32. THE PERCENT NO_x REMOVED BY 1 GRAM OF CaS/NaF AT 400°C ON A THREE INCH PLATE

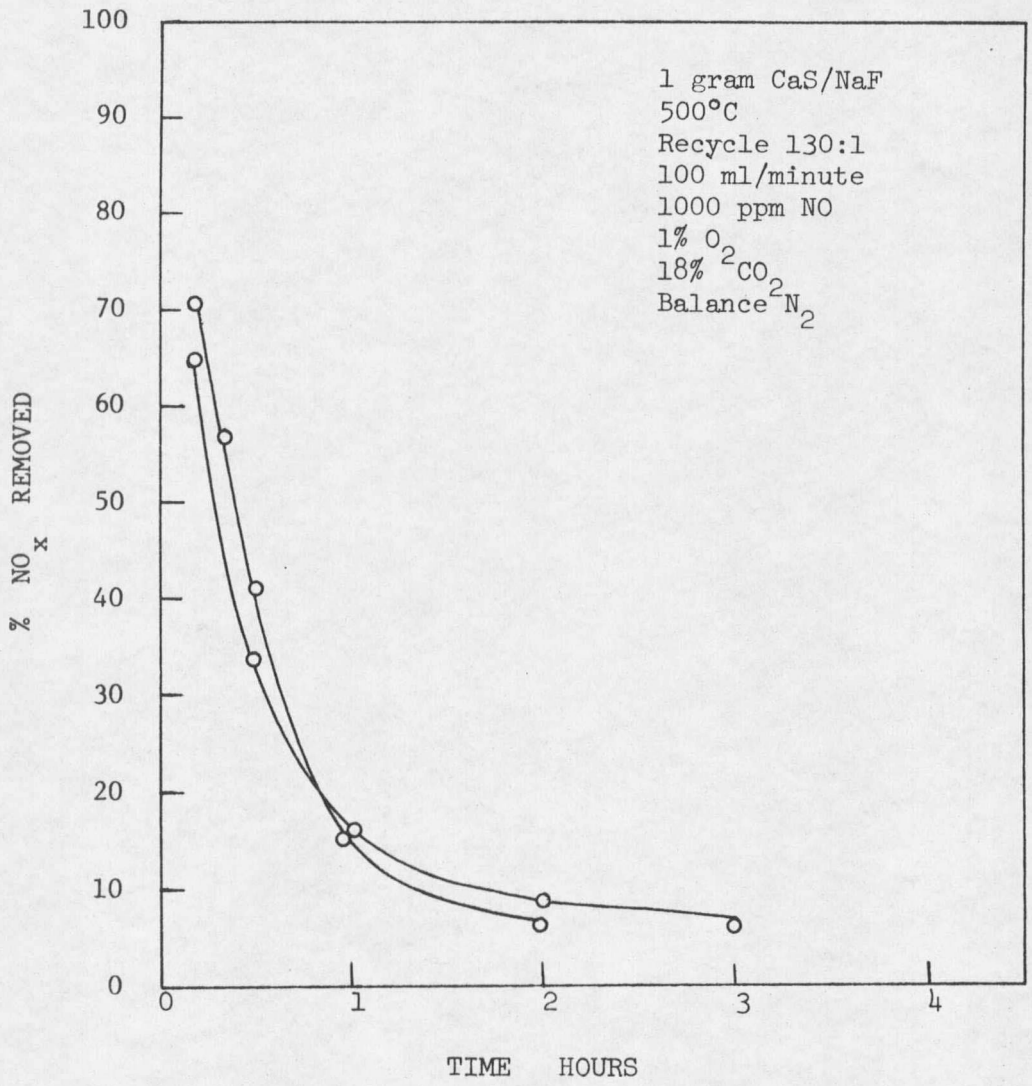

FIGURE 33. THE PERCENT NO_x REMOVED BY 1 GRAM OF CaS/NaF AT 500°C ON A THREE INCH PLATE

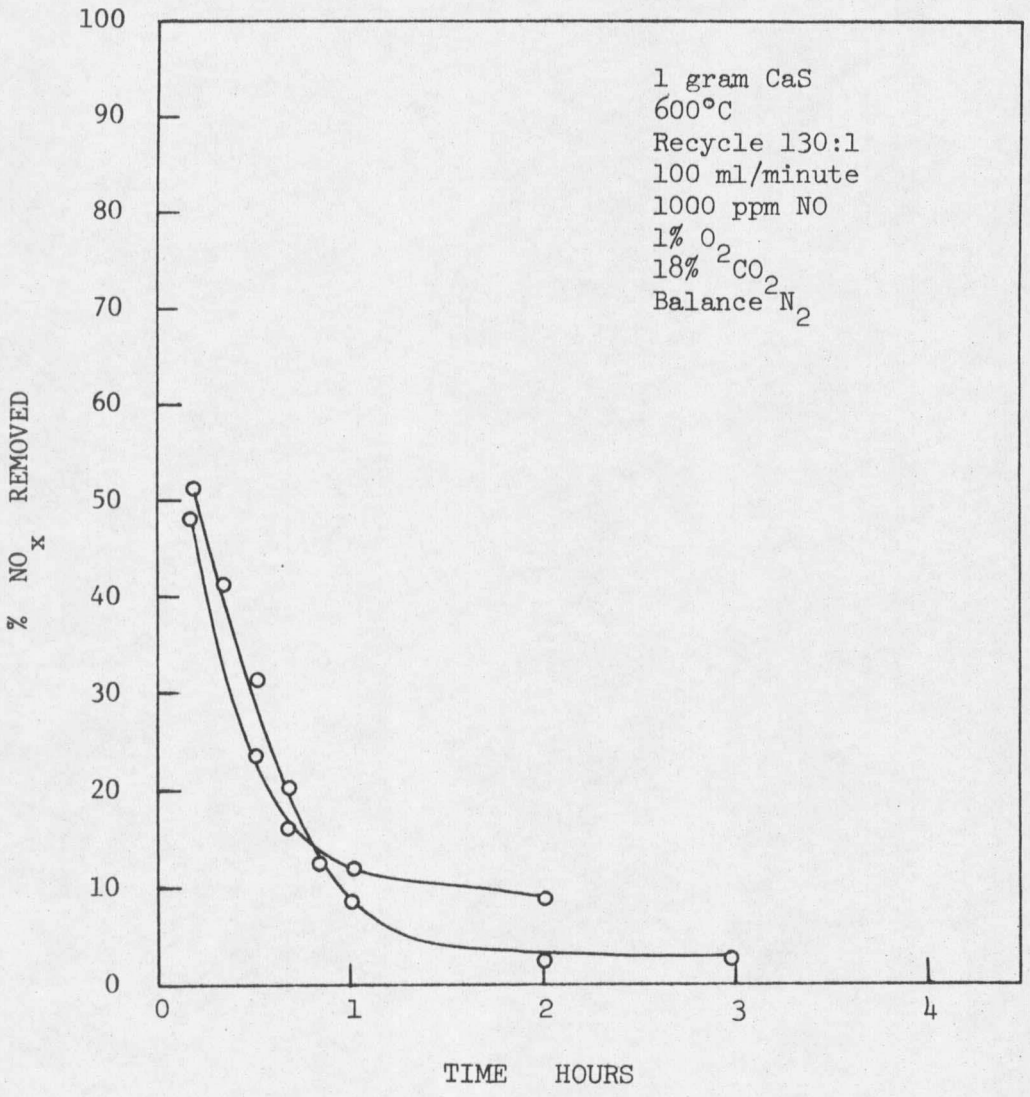

FIGURE 34. THE PERCENT NO_x REMOVED BY 1 GRAM OF CaS AT 600°C ON A THREE INCH PLATE

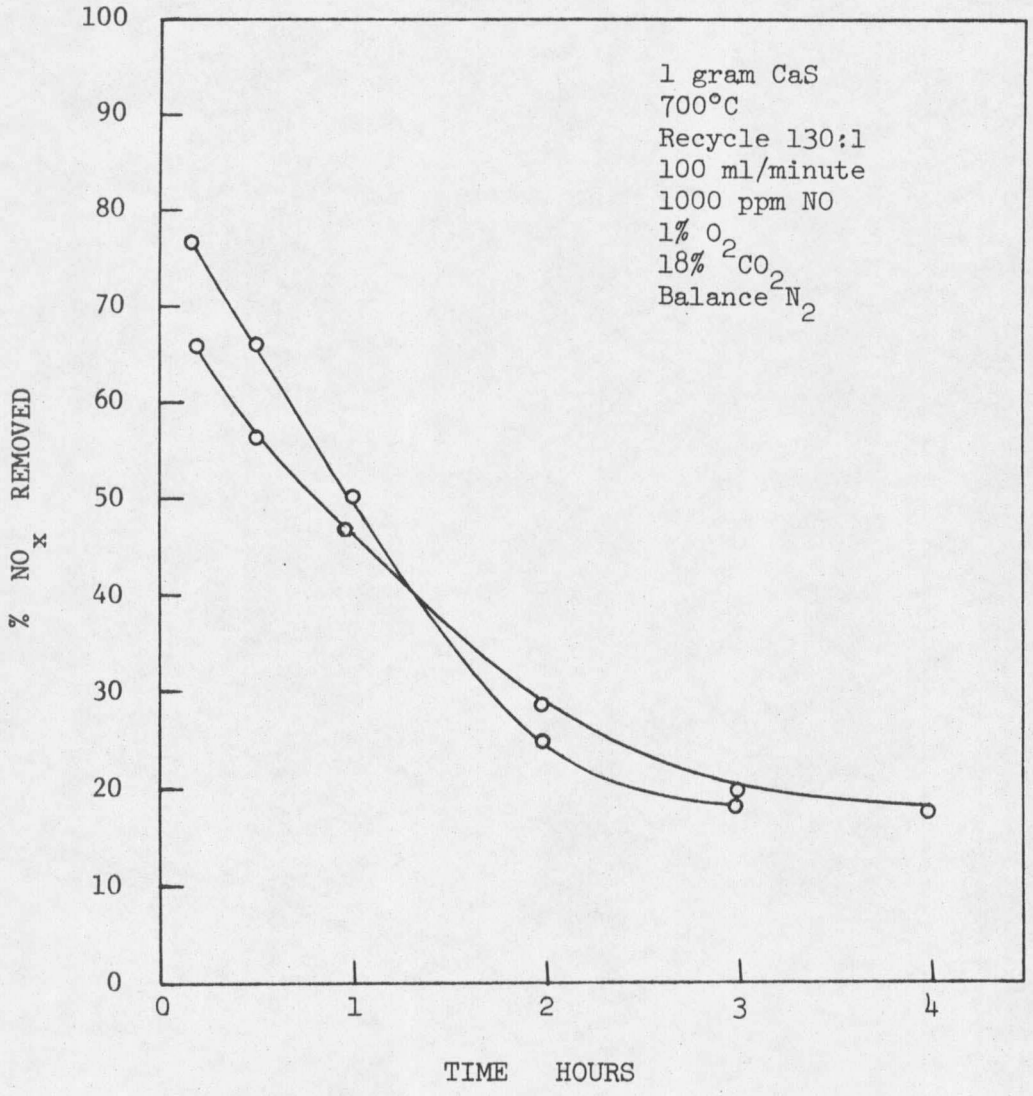

FIGURE 35. THE PERCENT NO_x REMOVED BY 1 GRAM OF CaS AT 700°C ON A THREE INCH PLATE

CaS/NaF at a flow rate of 200 ml/minute. This changed the flow rate but kept the space velocity the same. The simulated flue gas was used at a temperature of 400°C.

The results of Figure 36 indicated that the simulated flue gas flow rate exhibited little effect on the reduction of NO. In general, the conversions were reasonably close for each flow rate. Therefore, film diffusion can be eliminated as a controlling mechanism.

The effect of pore diffusion was not studied. In order to investigate the effect of pore diffusion on this reaction, particles of various known sizes are required. This would mean that the reactants would have to be screened. The reactants used in this study were finely ground reagent grade particles and were not suitable for sizing.

The effect of the O_2 to NO ratio in the simulated flue gas was also studied. The concentration of the NO was kept constant while the O_2 concentration was varied. Ratios of O_2:NO of 0:1, 10:1 and 100:1 were tried. Figure 37 shows that the amount of O_2 in the feed gas is very important. The 0:1 ratio run had a much greater capacity than the 10:1 and the 100:1 ratio run had almost no ability to remove NO_x. This is in agreement with electrobalance data which showed the rate of reaction of the CaS/NaF mixture with O_2 was 3 times as fast as the rate of reaction with NO.

The simulated flue gas contained 18% CO_2. In order to determine if the presence of CO_2 effected the removal of NO the removal of NO

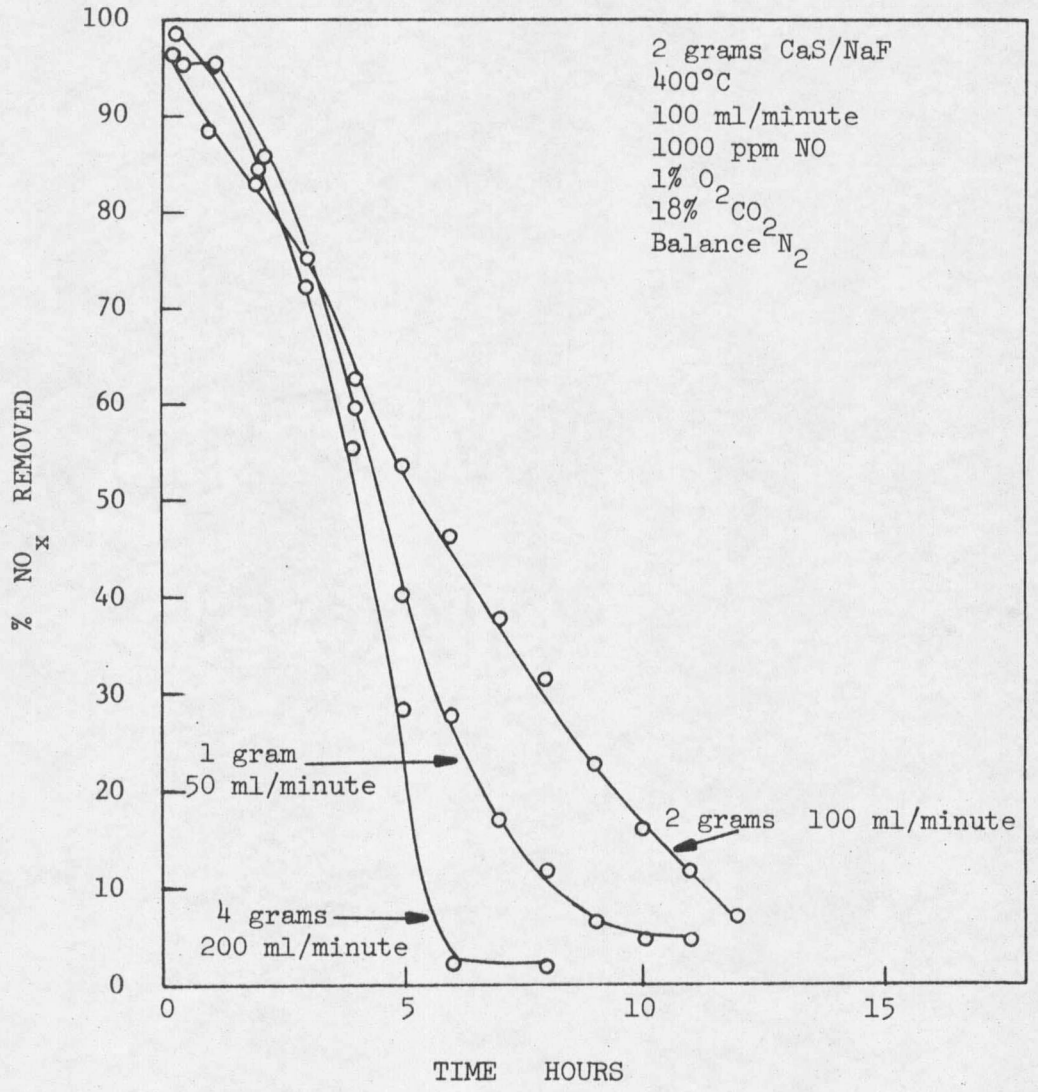

FIGURE 36. THE EFFECT OF EXTERNAL FILM DIFFUSION ON THE AMOUNT OF NO_x REMOVED

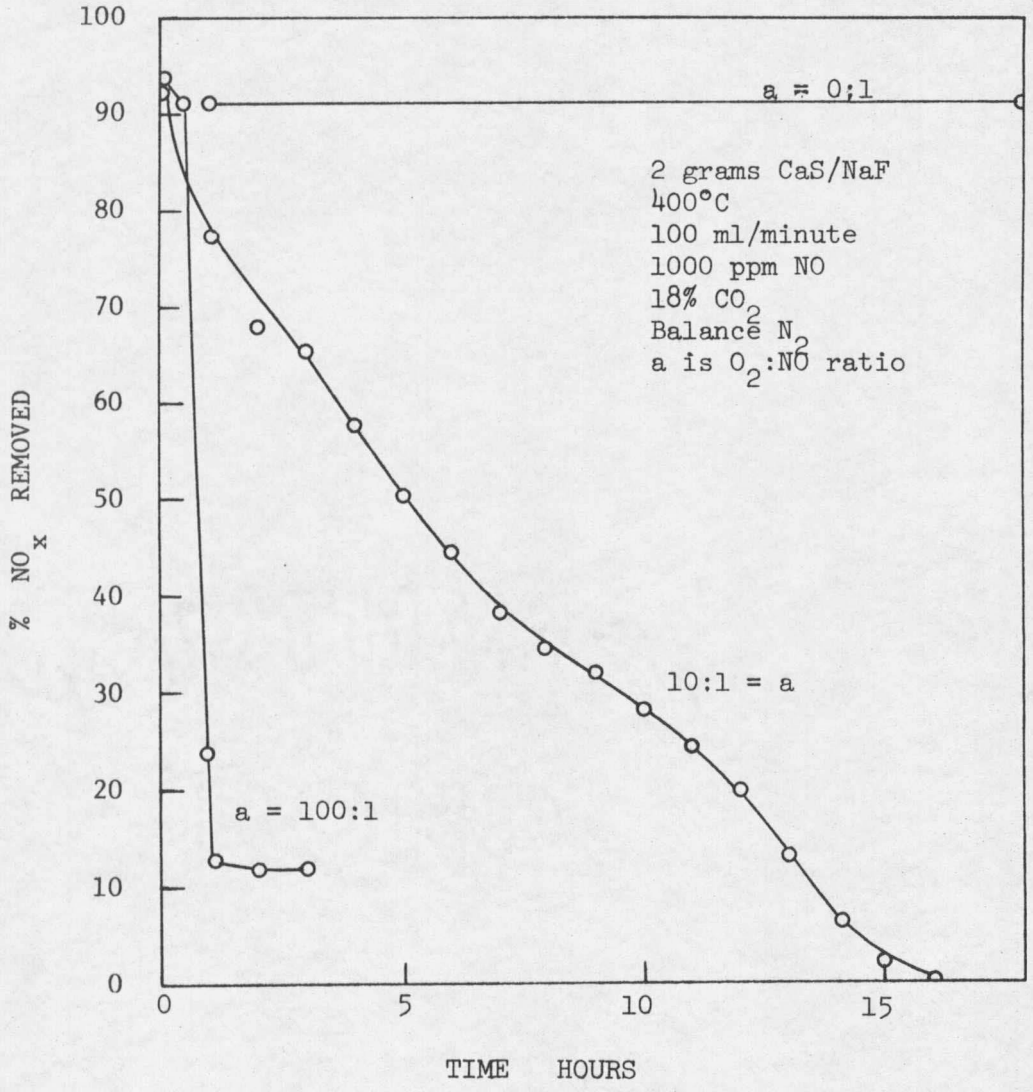

FIGURE 37. THE EFFECT OF O_2:NO RATIO ON NO_x REMOVAL

from a gas stream containing CO_2 was compared to the removal of NO from a gas stream in which no CO_2 was present. This was done over a temperature range of 200°C to 700°C. Figure 38 shows that CO_2 concentrations probably do not effect the removal of NO since the two runs are probably within experimental variability. The presence of SO_2 in the simulated flue gas was also shown not to effect the removal of NO. Figure 39 shows that runs at 400°C with the CaS/NaF for a simulated flue gas containing SO_2 and for a simulated flue gas in which no SO_2 was present were almost identical. Figure 40 shows that within the experimental variability the presence of SO_2 in the simulated flue gas does not seem to effect the removal of NO by CaS at 700°C.

Figures 41 and 42 show the effect on NO removal by CaS at 500°C and 600°C when water is introduced into the feed stream. Prior to mixing the simulated flue gas the nitrogen was bubbled through water. This resulted in a simulated flue gas that was 2.0 mole percent H_2O. At 700°C with CaS, reproducibility was again difficult to obtain. Figure 43 shows the removal of NO by CaS at 700°C with H_2O in the simulated flue gas. A wide variation in results was obtained. In comparing Figure 43 to Figure 31 it does not appear as if the H_2O had an effect on the NO removal. However, at 400°C the H_2O apparently caused a decrease in the NO removed by the CaS/NaF mixture. Figure 44 shows the extent to which the NO_x removal was decreased. Figures 45 and 46 show that the presence of H_2O in the simulated flue gas also reduced the NO_x

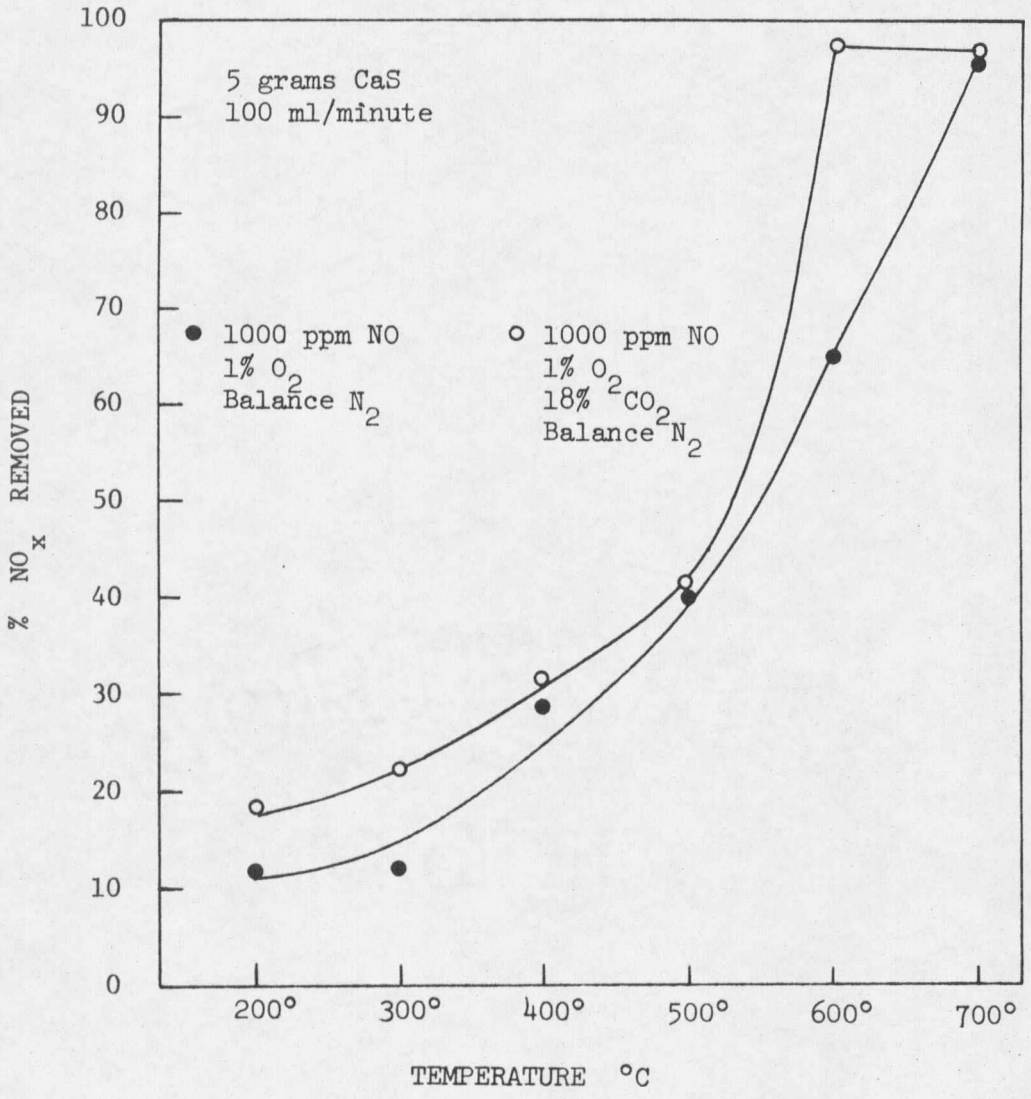

FIGURE 38. THE EFFECT OF FEED STREAM CONSTITUENTS ON NO_x REMOVAL

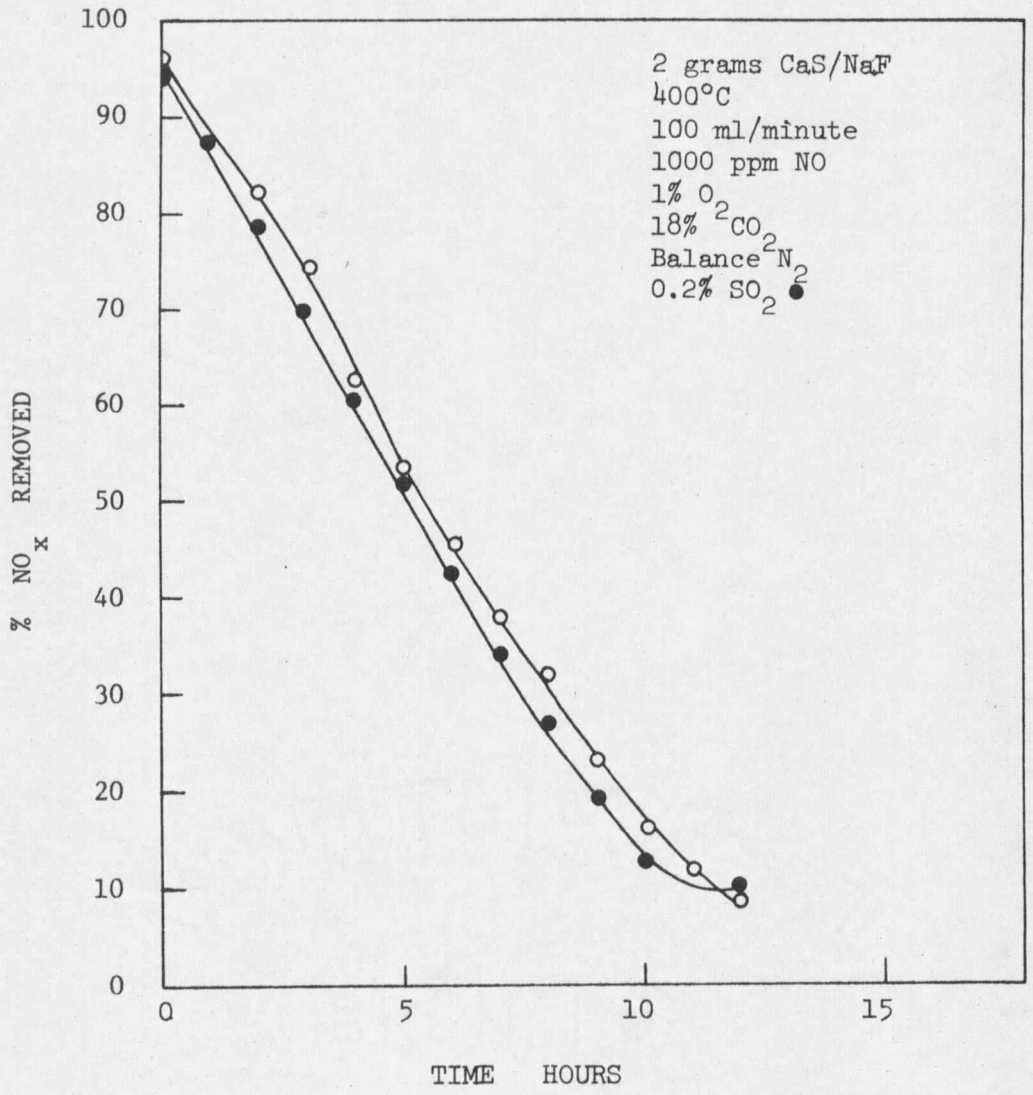

FIGURE 39. THE EFFECT OF SO_2 IN THE FEED GAS STREAM ON NO_x REMOVAL AT 400°C WITH CaS/NaF

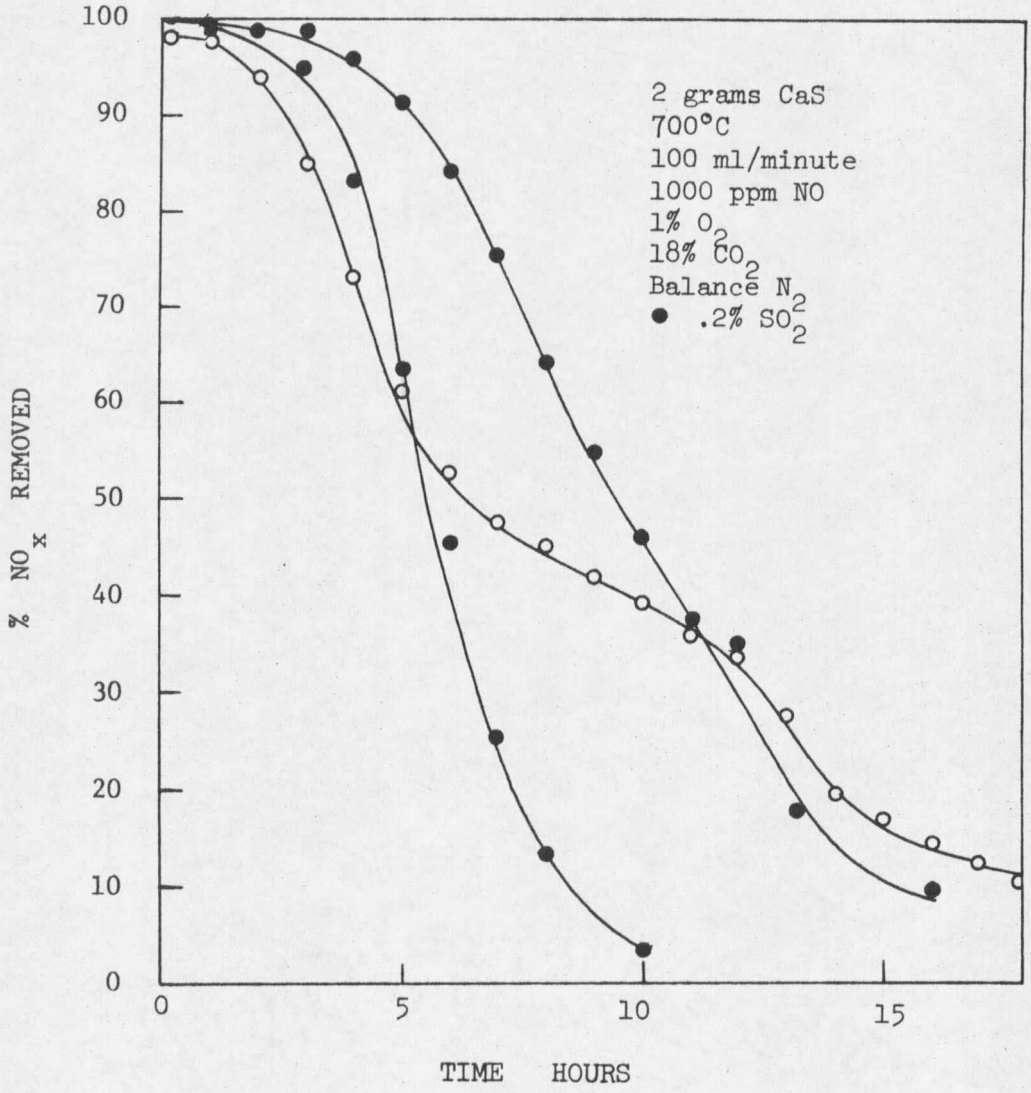

FIGURE 40. THE EFFECT OF SO_2 IN THE FEED GAS STREAM ON NO_x REMOVAL AT 700°C WITH CaS

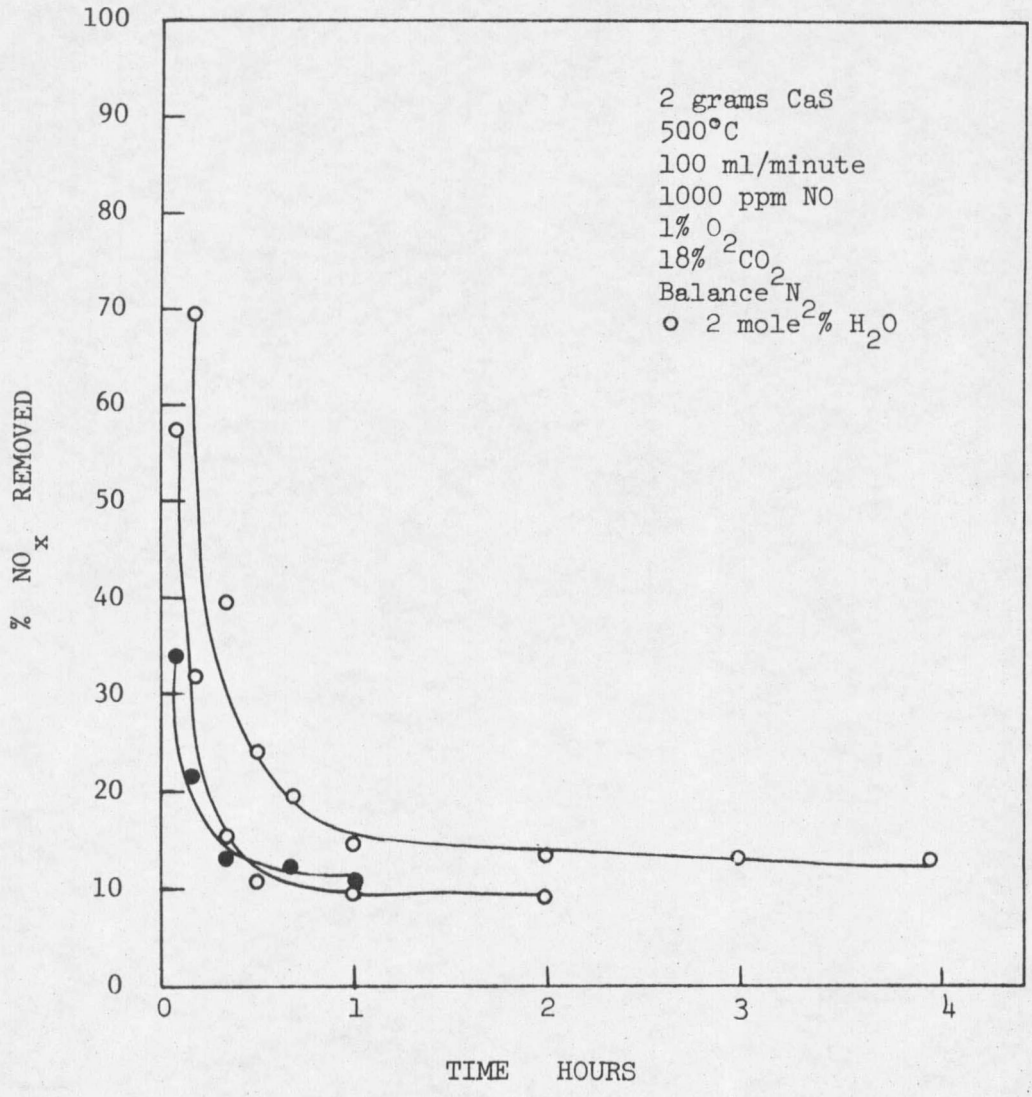

FIGURE 41. THE EFFECT OF H_2O IN THE FEED GAS STREAM ON NO_x REMOVAL AT 500°C WITH CaS

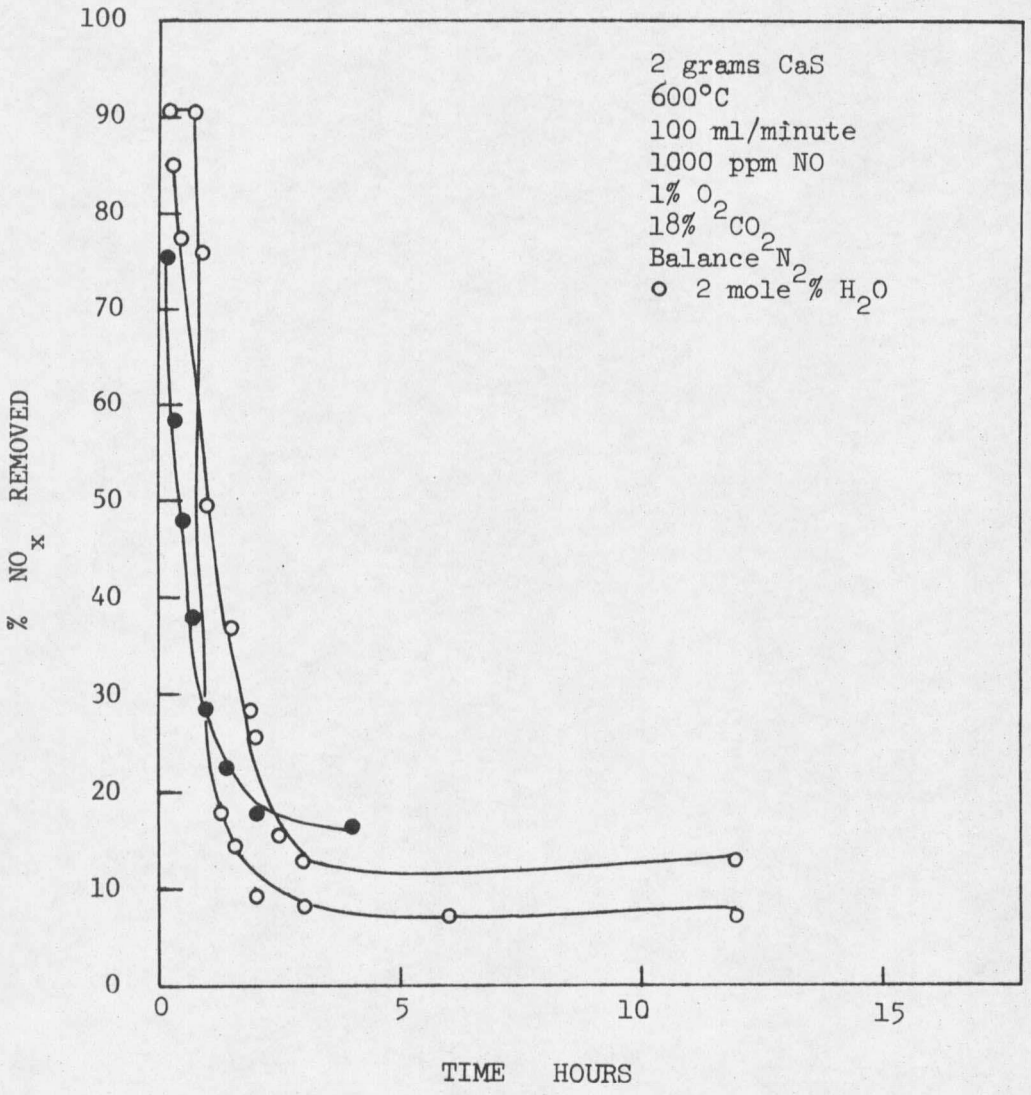

FIGURE 42. THE EFFECT OF H_2O IN THE FEED GAS STREAM ON NO_x REMOVAL AT 600°C WITH CaS

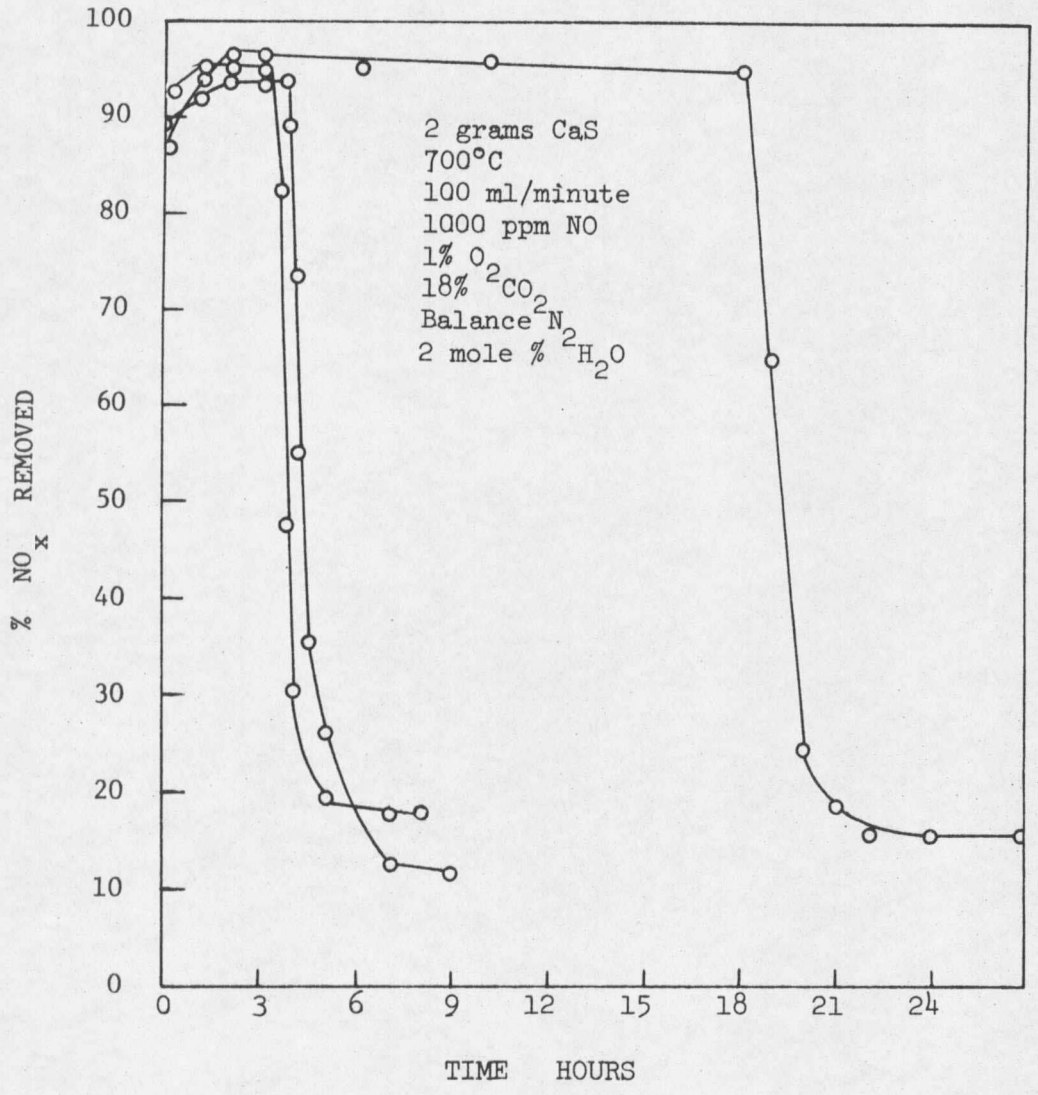

FIGURE 43. THE EFFECT OF H_2O IN THE FEED GAS STREAM ON NO_x REMOVAL AT 700°C WITH CaS

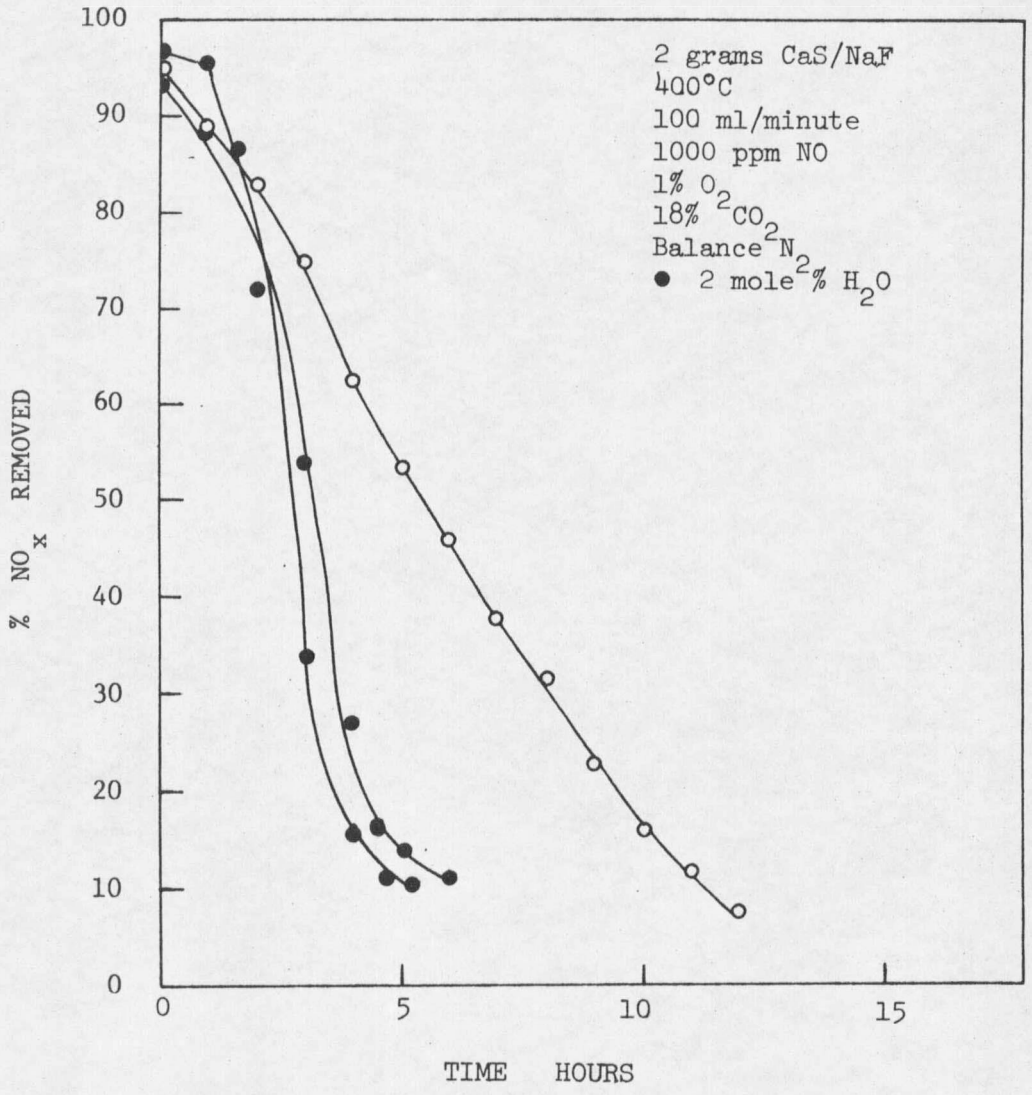

FIGURE 44. THE EFFECT OF H_2O ON NO_x REMOVAL BY CaS/NaF AT 400°C

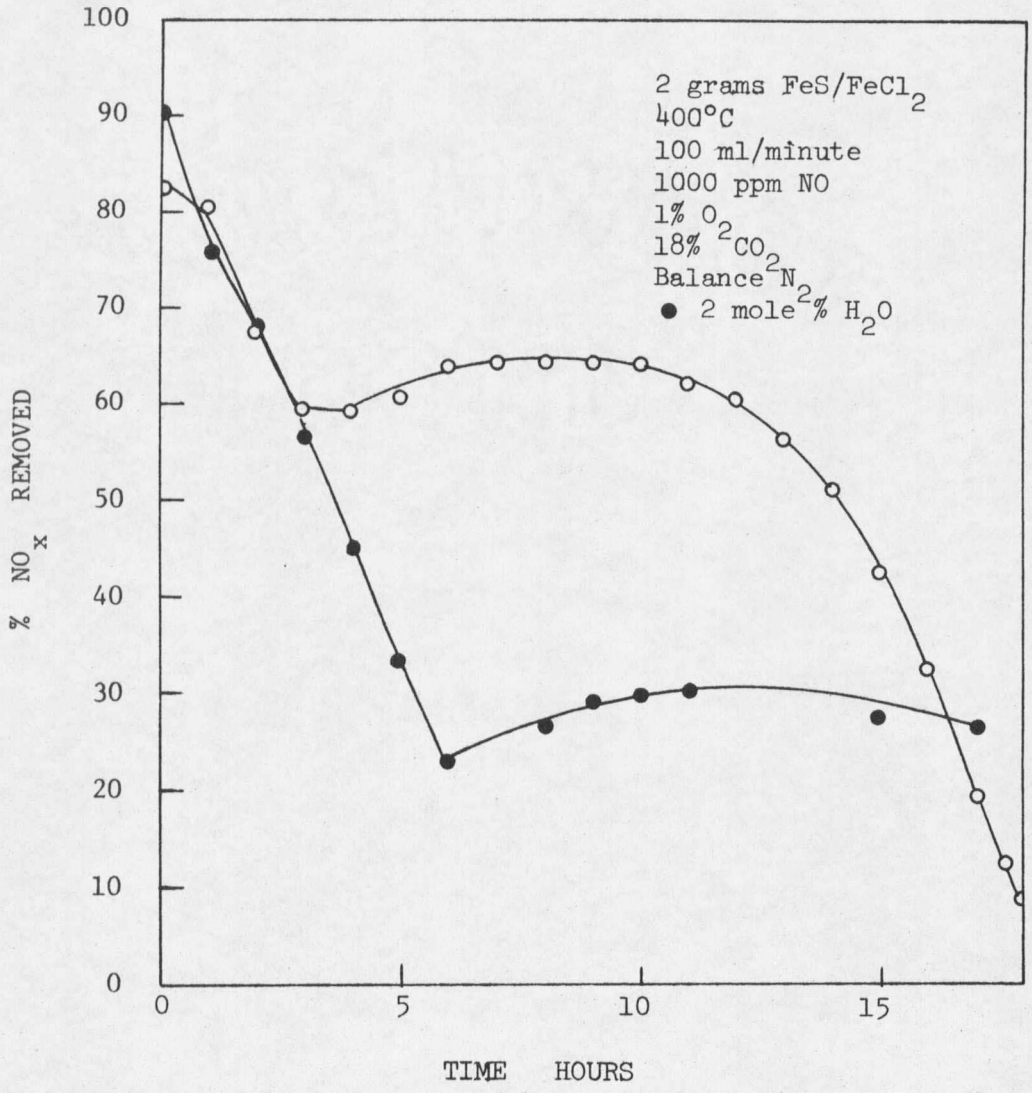

FIGURE 45. THE EFFECT OF H_2O ON NO_x REMOVAL BY 2 GRAMS OF $FeS/FeCl_2$ AT 400°C

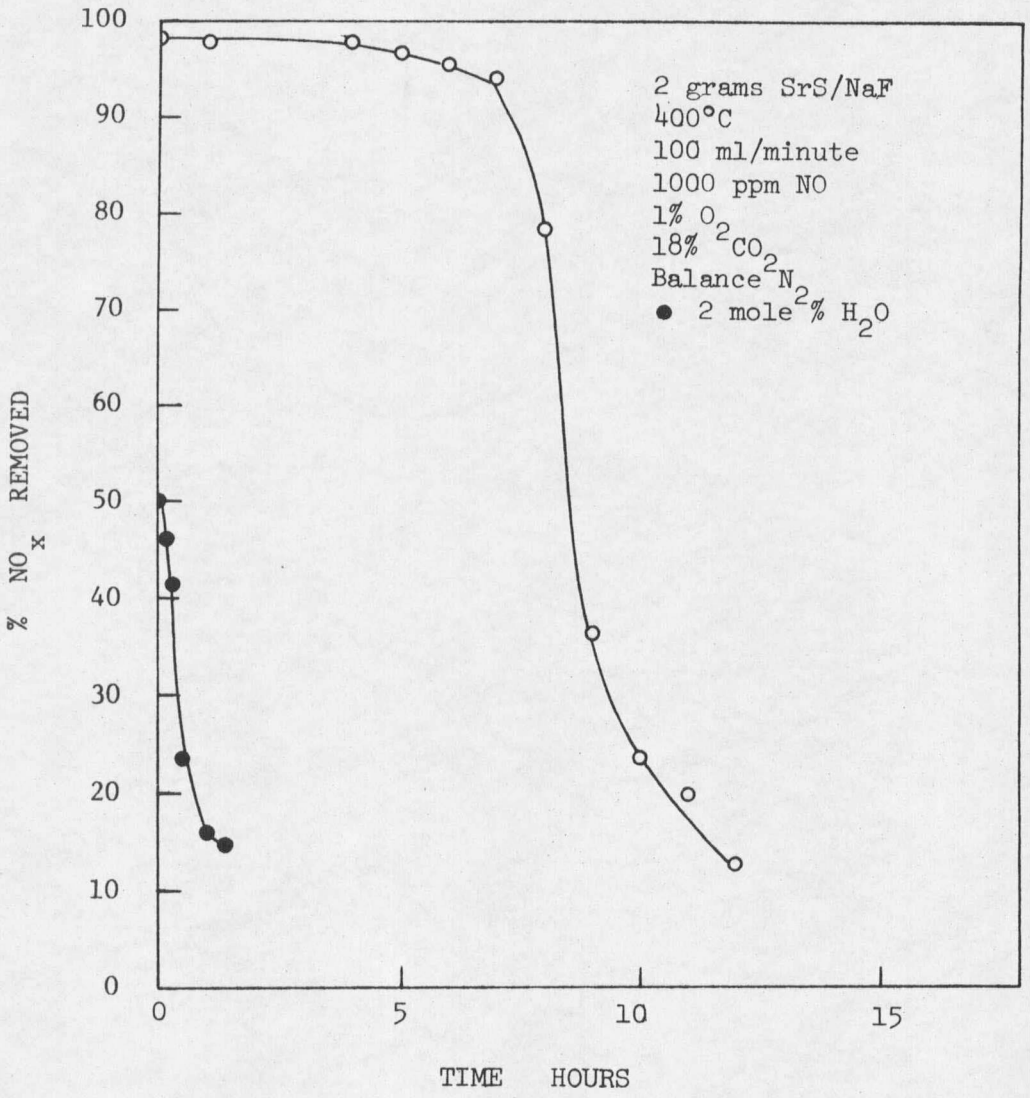

FIGURE 46. THE EFFECT OF H_2O ON THE REMOVAL OF NO_x BY 2 GRAMS OF SrS/NaF AT 400°C

removed by the $FeS/FeCl_2$ mixture and the SrS/NaF mixture.

The product from a run with CaS/NaF at 400°C and the product from a run with CaS/NaF at 400°C with H_2O in the gas were analyzed for sulfate. The product of the run without H_2O was 18.01% sulfate and the run with H_2O was 7.91% sulfate. This indicates that the H_2O was not reacting with the CaS to form $CaSO_4$. The H_2O may have either been interfering with the removal of the NO_x by interfering with the catalytic action involved or it may have been reacting with the CaS to form H_2S and/or SO_2. The runs with CaS and H_2O indicate that the H_2O is not reacting with the CaS, because if the H_2O were reacting with the CaS this should reduce the sites available to react with the NO and this would reduce the amount of NO removed.

Since the chemical reaction involved here is heterogeneous, involving a gas and a solid phase, it was thought that the chemical mechanism of the catalytic effect may involve some type of gas-solid contacting. In order to see if this was reasonable, a run was made in which the NaF catalyst was not mixed with the CaS. The CaS was placed in the reactor first and the reactor tapped to settle the bed, then the NaF was placed on top of the CaS and the reactor tapped to settle the NaF. 1.6 grams of CaS were used and .4 grams of NaF were used. Figure 47 shows that the removal of NO_x was much less than when the CaS and NaF were intimately mixed. If the catalytic effect of the NaF was assumed to be due to some type of gas-solid contacting, that the reacting

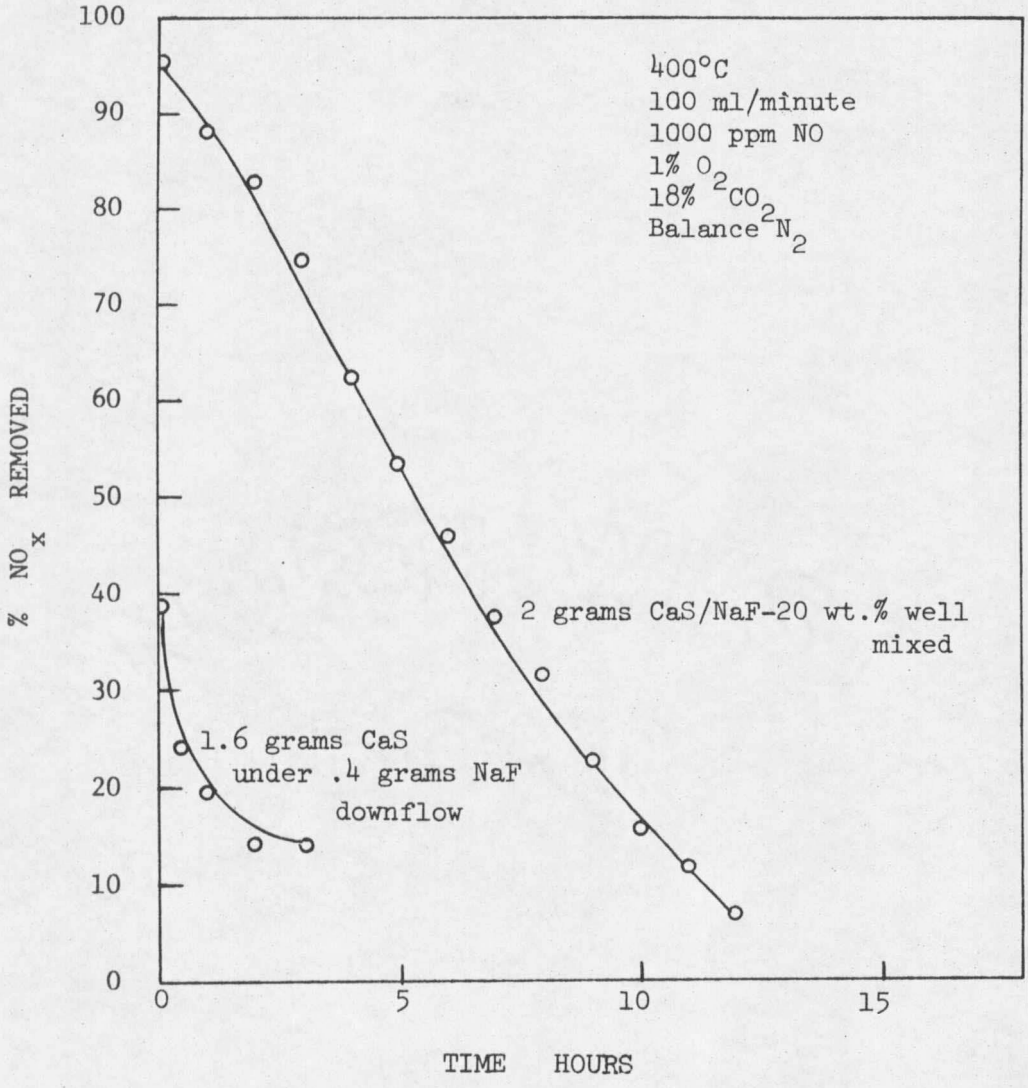

FIGURE 47. THE EFFECT OF MIXING THE NaF INTIMATELY WITH THE CaS

gas is activated by the promoter or by an activating atmosphere close to the surface of the promoter, then the calcium sulfide would have to be close to the catalytic surface in order to be reacted by the activated gas. This would explain the lower amount of NO removed by the separated catalyst run.

Zadick (1971) showed that $CaSO_4$ could be reduced to CaS according to the following reaction.

$$CaSO_4 + 4CO \xrightarrow[700°C]{Fe_2O_3} CaS + 4CO_2$$

It was thought that an attempt should be made to regenerate the CaS used in this research. In attempting to see what effect the CO would have on the stainless steel reactor, the results in Figure 48 were obtained. These results indicated that remarkable amounts of NO_x were being removed at 400°C to 700°C using a stainless steel reactor that had been exposed to a 100% CO gas stream for four hours at the temperature at which the NO_x was removed. Possible reaction may be:

$$FeO + CO \longrightarrow Fe + CO_2$$

$$Fe + NO \longrightarrow FeO + 1/2\ N_2$$

The FeO is probably found on the inner surface of the stainless steel pipe and on the surface of the stainless steel rings which were used to pack the preheat section of the reactor.

The effluent gas from the reactor when the feed was 100% CO initially contained 50% CO_2; this decreased to 15% CO_2 in the four hours

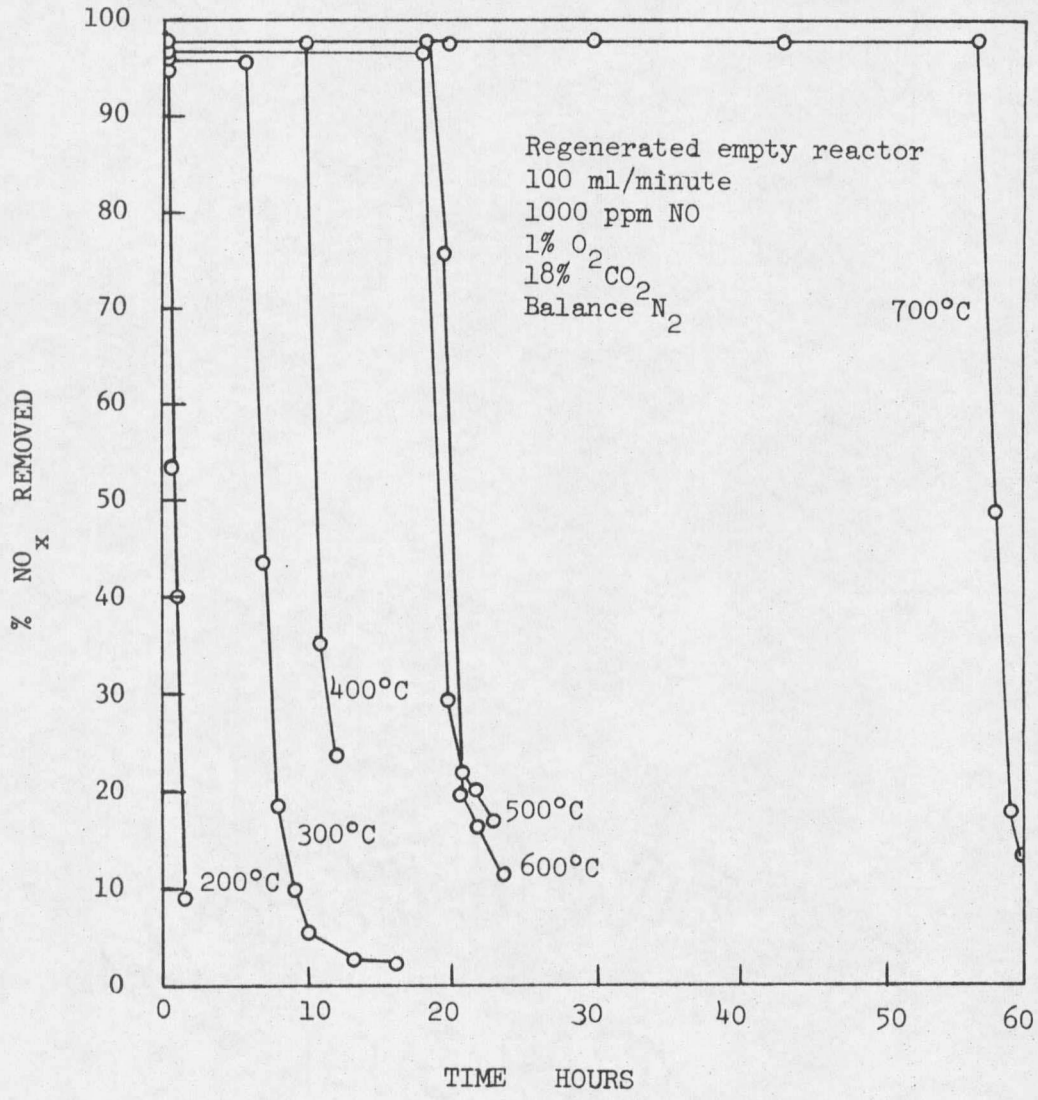

FIGURE 48. THE EFFECT OF AN EMPTY REGENERATED REACTOR ON NO_x REMOVAL

that CO was fed through the reactor. When a gas of composition 2.5% NO and 97.5% He was fed through the reactor, that had been exposed to the CO, substantial amounts of N_2 were detected in the effluent gas. These results support the possibility that these two chemical reactions are taking place.

An attempt was made to react 2 grams of CaS/NaF at 400°C in one reactor and then regenerate it in another reactor at 700°C using 100% CO. The purpose of using the two reactors was so that when the regenerated material was again exposed to the simulated flue gas the amount of NO removed could be attributed to the mixture and not the reactor. Quite a bit of the mixture was lost in transfering from one reactor to the other and no conclusive evidence was obtained.

To determine the performance of high surface area support materials in this reactor, some 1/8 inch Harshaw 1602-T pellets of alumina and silica and some 1/16 inch Linde TM-0-1114 molecular sieve pellets (synthetic crystalline metal alumino-silicates with Na as the metal) were impregnated with CaS. Figure 49 shows the results of these runs. These runs were done at 400°C with 2 ml of support material. Both supports removed NO_x quite well; the Linde molecular sieves were slightly better, but this might have been due to better contacting because of their smaller size.

To determine if the sulfate was indeed being formed, the product from a run with the CaS/NaF mixture at 400°C and the product from a run

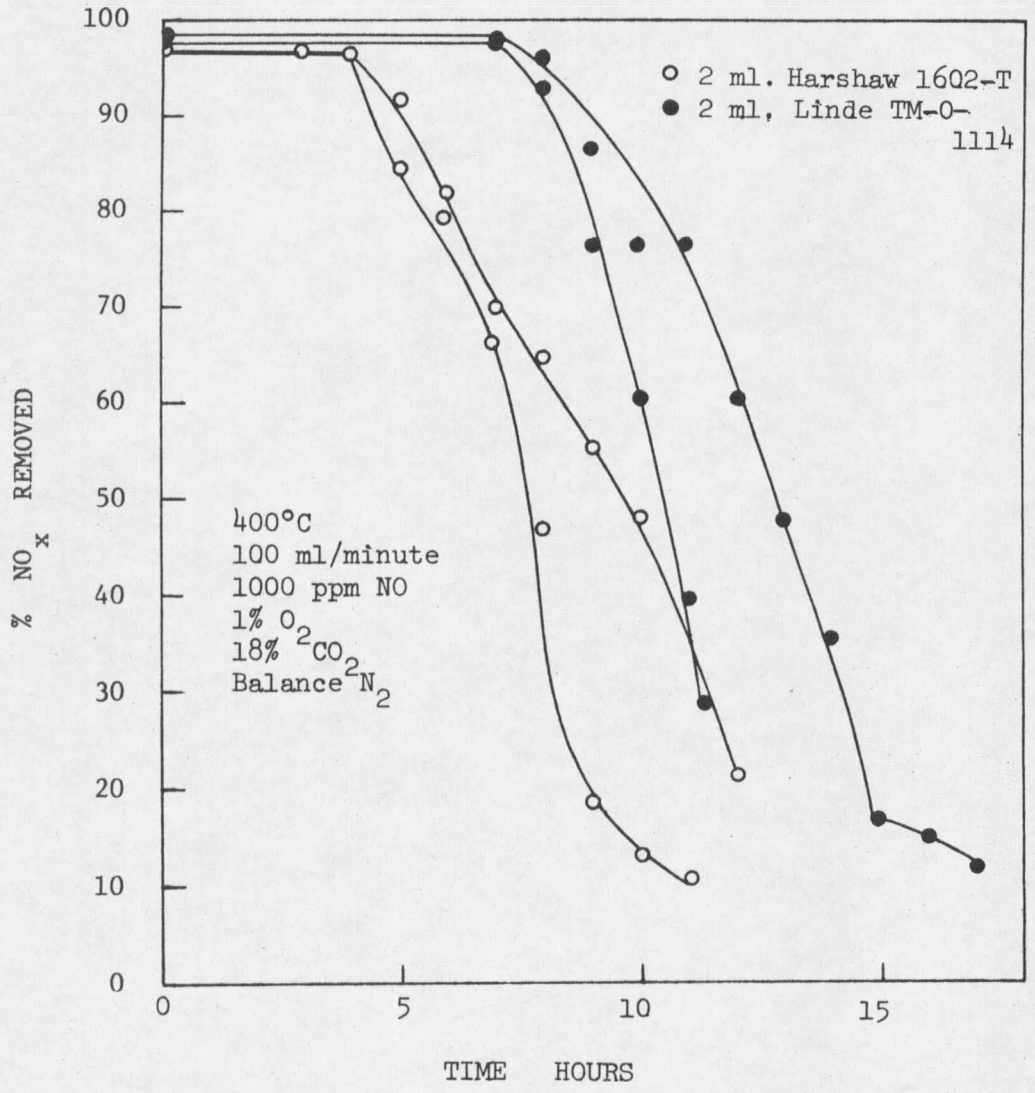

FIGURE 49. THE REMOVAL OF NO_x BY HARSHAW PELLETS AND LINDE MOLECULAR SIEVES IMPREGNATED WITH CaS

with CaS at 700°C were analyzed for sulfate ion using the barium sulfate analysis described by Walton (1963). The CaS/NaF product was determined to be 18.01% sulfate. The CaS product was determined to be 19.97% sulfate. White (1973) showed that if the CaS was exposed to NO for an extended period of time at temperatures between 400°C and 700°C the solid product would be at least 80% sulfate.

VII. GENERAL DISCUSSION

The rates determined on the electrobalance indicated that the most promising mixtures were FeS/NaF, BaS/$FeCl_2$, CaS/Fe_2O_3 at 400°C and FeS/$FeCl_2$ at 300°C. The electrobalance data also indicated that, in general, the chemical promoters do not react with NO at 300 and 400°C. Results from the fixed packed bed reactor gave the mixtures of FeS/$FeCl_2$, SrS/NaF, CaS/NaF and BaS/$FeCl_2$ as those with the greatest capacities. Even though the fastest rates determined on the electrobalance did not correspond to the greatest capacities recorded in the fixed packed bed, both sets of data indicate that NO can be reduced.

The chemical promoters seemed to show a catalytic effect in some cases, both by increasing the rate measured on the electrobalance and by increasing the capacities of the metal sulfides to remove NO in the fixed packed bed. All of the mixtures were shown to have some ability to remove NO from a simulated flue gas at 400°C. The mixtures also removed oxygen, which of course is an undesirable effect. However, the presence of SO_2 and CO_2 in the simulated flue gas did not effect the amount of NO removed. This means in a flue gas containing SO_2, the SO_2 could be removed after the NO without effecting the NO removal. It was disappointing to learn that the presence of H_2O in the simulated flue gas caused a reduction in the amount of NO removed by the CaS/NaF, FeS/$FeCl_2$ and SrS/NaF mixtures at 400°C. The H_2O may interfere with the catalytic action of the promoters or it may react with the MeS, thus

making it more difficult for the NO to react with the MeS. If the catalytic effect is assumed to be due to some type of gas-solid contacting, in that the reacting gas is activated by the promoter or by an activating atmosphere close to the surface of the promoter, the chemical mechanism could be represented by the following reactions:

$$NO \xrightarrow{\text{promoter}} NO^*$$

$$MeS + 4NO^* \longrightarrow MeSO_4 + 2N_2$$

The run in which the MeS (CaS) and the promoter (NaF) were separated shows that the CaS must be close to the promoter surface in order to get good NO removal. The H_2O could either prevent the gas from being activated or deactivate it before it could react with the metal sulfide. The runs with water in the flue gas at 500, 600 and 700°C with CaS indicate that the H_2O does not react with the CaS since in these conditions the H_2O did not effect the amount of NO removed. If the H_2O were reacting with the CaS in the CaS/NaF mixture at 400°C to from $CaSO_4$, it would be expected that at least as much sulfate would be found in the product from a run with H_2O as without. The product from a run at 400°C with H_2O in the flue gas and with CaS/NaF was analyzed for sulfate ion and was found to contain quite a bit less sulfate than was found in the product of a run with CaS/NaF at 400°C with no H_2O in the simulated flue gas. Even though the run with H_2O and CaS at 500, 600 and 700°C indicates that the H_2O does not react with the CaS, the possibility that the

H_2O may be reacting with the CaS/NaF mixture at 400°C to from H_2S or SO_2 cannot be eliminated.

The results of this work show that NO can be reduced using metal sulfide promoter mixtures in an oxidizing atmosphere. This fact is very important in that in this method of reducing NO it is not necessary to introduce an expensive reducing gas, such as NH_3, into the flue gas in order to reduce the NO. Almost all current industrial methods for reducing NO use NH_3.

At 400°C when the $FeS/FeCl_2$ mixture was exposed to a gas containing 2.5% NO on the electrobalance, a weight decrease was observed. But, when placed in the fixed packed bed reactor, the $FeS/FeCl_2$ mixture had the highest capacity to remove NO at 400°C. These two facts may not seem to agree, however, other investigators have shown that under certain conditions NO reacts with FeS to give N_2 and SO_2. The question is, if it is assumed that this is the reaction taking place, does this eliminate the $FeS/FeCl_2$ mixture as a possible method for NO_x pollution control? In many combustion processes, particularly those in which coal is the primary fuel, some SO_2 is formed and processes are available to remove the SO_2. Therefore, the $FeS/FeCl_2$ mixture could be used in processes where there is already SO_2 in the flue gas and where an SO_2 removal process is provided. It would also be necessary for the economics of the situation to allow the spent $FeS/FeCl_2$ mixture to be discarded since the FeS is consumed.

It is significant, and should be mentioned again, that in the cases tested the presence of SO_2 in the simulated flue gas did not interfere with the removal of NO. Therefore, if a liquid system is to be used to remove the SO_2 from the gas stream, the gas stream will not have to be cooled to remove the SO_2 and then reheated to remove the NO. The NO could be removed and then the gas cooled and the SO_2 removed.

It is important to note that the mixtures $BaS/FeCl_2$ and $CaS/FeCl_2$ removed more NO than oxygen. These two mixtures were also among the top six mixtures in terms of maximum capacities.

The fact that when CaS was impregnated on high surface area supports good removal of NO was obtained is important. If the interference of the H_2O with the removal of NO by CaS/NaF or other metal sulfide mixtures was to prove insurmountable; good removal could possibly be obtained by using these high surface area supports with CaS impregnated on them.

VIII. CONCLUSIONS

1. NO can be reduced in an oxidizing atmosphere at 400°C using the metal sulfides: CaS, SrS, FeS and BaS mixed with the chemical promoters; NaF, $NiCl_2$, $CoCl_2$, $FeCl_2$ and Fe_2O_3.

2. At 400°C the reaction between FeS and NO is promoted by NaF, $NiCl_2$ and Fe_2O_3. Also, the reaction of BaS with NO is promoted by NaF, $NiCl_2$ and Fe_2O_3. NaF, $NiCl_2$ and Fe_2O_3 promote the reaction of NO with CaS and Fe_2O_3 acts as a promoter when mixed with SrS.

3. In all cases at 300°C, NaF acts as a promoter in the reaction of FeS, BaS, CaS and SrS with NO. $NiCl_2$ promotes the reaction of BaS with NO and $FeCl_2$ promotes the reaction of NO with FeS and CaS.

4. The four metal sulfide promoter mixtures with the greatest capacities to remove NO from the simulated flue gas containing 1% O_2 were: $FeS/FeCl_2$, .0372 grams of NO per gram of FeS; SrS/NaF, .0317 grams of NO per gram of SrS; CaS/NaF, .0186 grams of NO per gram of CaS; and $BaS/FeCl_2$, .0168 grams of NO per gram of BaS.

5. .2% SO_2 in the simulated flue gas does not effect the removal of NO by the CaS/NaF mixture or by CaS.

6. 18% CO_2 in the simulated flue gas does not effect the removal of NO by CaS/NaF mixture or by CaS.

7. The presence of H_2O in the simulated flue gas reduces the capacity of these metal sulfide mixtures to remove NO at 400°C, but does not effect the capacity of CaS to remove NO at 500, 600 and 700°C.

8. The O_2 concentration in the simulated flue gas has a strong effect on the capacity to remove NO. The higher the concentration of O_2 the lower the NO removal capacity and the lower the O_2 concentration the higher the NO removal capacity.

9. The CaS impregnated on high surface area supports removed more NO than the fixed packed bed of CaS at 400°C.

10. External film diffusion was not found to be the controlling mechanism.

IX. RECOMMENDATIONS

1. The flow characteristics of this reactor were not known. It would be very informative to continue this work using a reactor in which the flow characteristics are well understood.

2. The manner in which the solid reactant is presented in NO removal needs much more investigation. A fixed packed bed is not suitable for removing NO from flue gas streams containing fly ash. The Shell Process (Groenendaal et al., 1976) for removing SO_2 may provide a gas-solid contacting system that could be used. Commercial supports also offer some possibility and should be studied further.

3. A study should also be done to study the reactions of:

$$FeO + CO \longrightarrow Fe + CO_2$$

$$Fe + NO \longrightarrow FeO + 1/2\ N_2$$

These reactions should be studied in a reactor packed with small stainless steel rings. These reactions may provide a method for controlling NO_x emissions.

APPENDIX

APPENDIX A

This appendix describes the method used to calculate the capacities of the metal sulfide promoter mixtures and of the metal sulfides. The calculation of the capacity of the CaS/NaF mixture at 400°C will be used for this example.

Step 1. The maximum amount of NO that could be removed was calculated.

NO_m — Maximum amount of NO that could be removed

CO — Concentration of NO in the simulated flue gas

Q — Volumetric flow rate of the simulated flue gas

t — Time in the actual case for the percent NO_x removed to fall below 40%

When the percent NO_x removed is below 40%, this means the exit concentration of NO exceeds 600 ppm and therefore exceeds the EPA standard for coal-fired steam generators.

$C_0 = 3.654 \times 10^{-8}$ moles NO/ml

Q = 100 ml/minute

t was determined from Figure A-1

t = 390 minutes

$NO_m = C_0 Q t$

$NO_m = (3.654 \times 10^{-8})(100)(390)$

$NO_m = .001425$ moles NO

Step 2. The area in Figure A-1 which represented the amount of NO_x actually removed until less than 40% NO_x was being removed was calculated. This was done by determining the area under the curve in Figure A-1.

A_{40} — Area under the curve from time zero until the time when the % NO_x removed became less than 40%

A_{40} = 27,186 minutes

Step 3. The area in Figure A-1 which represented 100% removal of NO_x was calculated.

A_{100} — Area representing 100% removal of NO

A_{100} = (100)(390 min.) = 39,000 minutes

Step 4. The capacity of the mixture was calculated. This was done by multiplying the fraction $(\frac{A_{40}}{A_{100}})$ by the maximum amount of NO that could be removed.

NO_{40} — Capacity of the mixture or metal sulfide

$$NO_{40} = (\frac{A_{40}}{A_{100}})NO_m$$

$$NO_{40} = \frac{27,186}{39,000}(.001425 \text{ moles NO})$$

$$NO_{40} = .000993 \text{ moles NO}$$

$$NO_{40} = .000993 \text{ moles } NO_x \frac{30 \text{ grams NO}}{1 \text{ mole NO}} \times \frac{1}{1.6 \text{ grams CaS}}$$

$$NO_{40} = .0186 \frac{\text{grams NO}}{\text{gram CaS}}$$

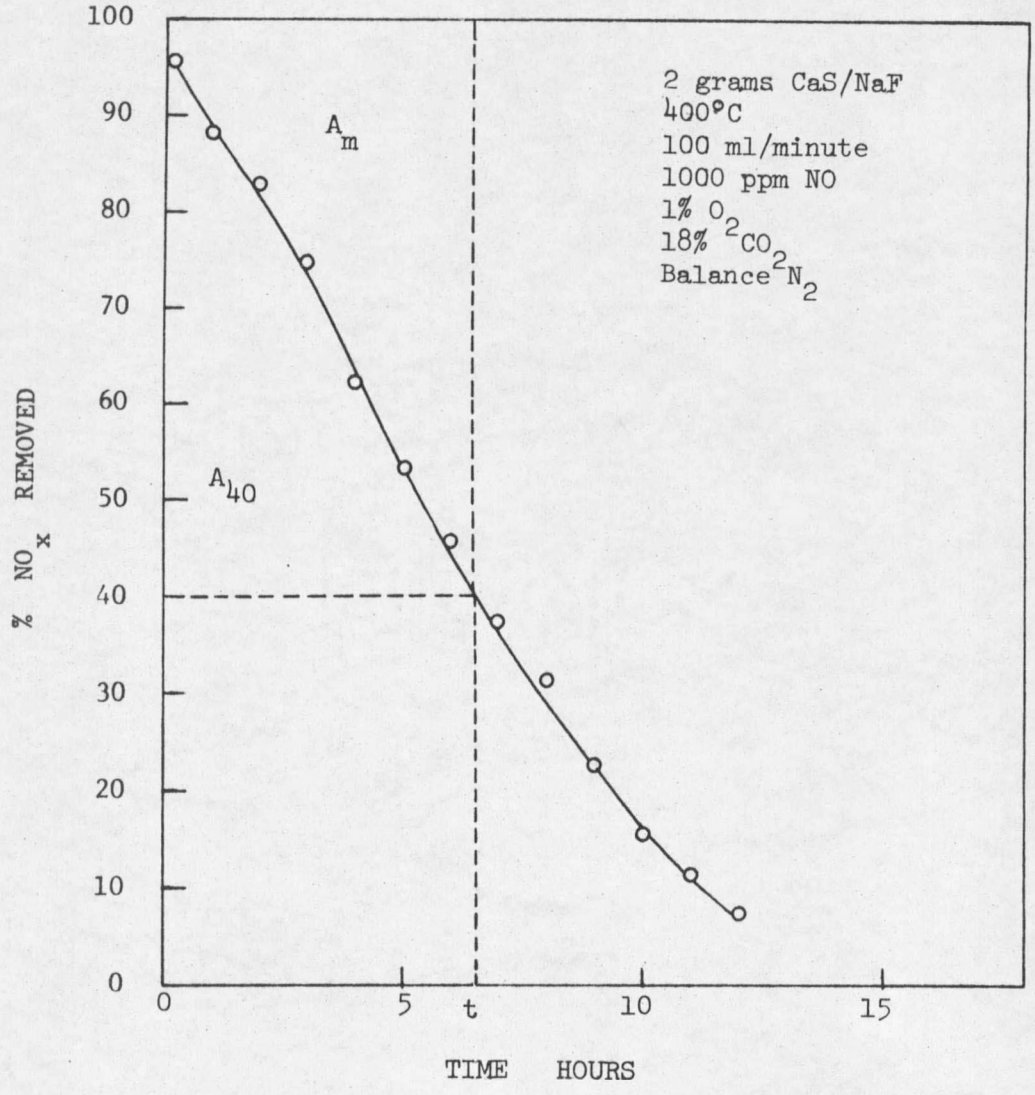

FIGURE A-1. A SAMPLE CALCULATION OF THE CAPACITY OF A METAL SULFIDE PROMOTER MIXTURE

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Armento, W.J., and W.L. Sage, "Effect of Design and Operational Variables on NO_x Formation in Coal Fired Furnaces: Status Report," AICHE Symposium Series, 148 (71), pp. 63-70, 1975.

2. Bartok, A.R. Crawford, A.R. Cunningham, H.J. Hall, E.H. Manny and A. Skopp, "Systems Study of Nitrogen Oxide Control Methods for Stationary Sources-Volume II," National Air Pollution Control Association, (1969).

3. Bartok, W., A.R. Crawford, and A. Skopp, "Control of NO_x Emissions from Stationary Sources," Chemical Engineering Progress, 67 (2), pp. 64-72, February, 1971.

4. Blakeslee, C.E., and H.E. Burdach, "NO_x Emissions from Tangentially-Fired Utility Boilers: Part II Practice," AICHE Symposium Series, 148 (71), pp. 94-102, 1975.

5. Clay, D.T., and S. Lynn, "Reduction and Removal of SO_2 and NO_x from Simulated Flue Gas Using Iron Oxide as Catalyst/Absorbent," AICHE Journal, 21 (3), pp. 466-473, May, 1975.

6. Crawford, A.R., E.H. Manny, W. Bartok, and R.E. Hall, "NO_x Emission Control for Coal-Fired Utility Boilers," AICHE Symposium Series, 148 (71), pp. 75-84, 1975.

7. Dickerson, R.A., and A.S. Okuda, "Design of an Optimum Distillate Oil Burner for Control of Pollutant Emissions," EPA-650/-2-74-047, June, 1974.

8. Erickson, R.J., "Reduction of Nitric Oxide by Calcium Sulfide and Nickel Sulfide," Master of Science Thesis, Department of Chemical Engineering, Montana State University, 1974.

9. Environmental Science & Technology, "Currents," 9 (5), p. 400, May, 1975.

10. Environmental Science & Technology, "Currents," 9 (10), p. 902, October, 1975.

11. Evoniuk, C.J., "Kinetic Studies on Absorption of NO_x by Alkali Carbonate-Metal Oxide Sorbents," PhD. Thesis, Department of Chemical Engineering, Montana State University, 1978.

12. Gidaspow, D, D. Dharia, and L. Leung, "Gas Purification by Porous Solids with Structural Changes: Breakthrough Curve Analysis for Reaction Controlled Isothermal Sorption with Diffusion into Spherical Particles," Chemical Engineering Science, 31, pp. 337-344, 1976.

13. Groenendaal, W., J.E. Naber, and J.B. Pohlenz, "The Shell Flue Gas Desulfurization Process: Demonstration on Oil and Coal Fired Boilers," AICHE Symposium Series, 156 (72), pp. 12-22, 1976.

14. Henry, J.M., C.R. McCann, J.J. Demeter, and D. Bienstock, "NO_x Control by Flue Gas Recirculation in Pulverized-Fuel Combustion," AICHE Symposium Series, 148 (71), pp. 71-74, 1975.

15. Hodgson, K.M., "Rate of Reaction of Nitric Oxide and Oxygen by Metal Sulfides," Master of Science Thesis, Department of Chemical Engineering, Montana State University, 1975.

16. Hooper, J.R., and C.L. Yaws, "Oxides of Nitrogen N_2O, NO, NO_2," Chemical Engineering, 81 (17), pp. 99-106, August 19, 1974.

17. Lachapelle, O.G., J.S. Bowen, and R.D. Stern, "Overview of Environmental Protection Agency's Nitrogen Oxide Control Technology For Stationary Combustion Sources," AICHE Symposium Series, 156 (72), pp. 263-290, 1976.

18. LaMantia, C.R., and E.L. Field, "Tackling the Problems of Nitrogen Oxides," Power, pp. 63-69, April, 1969.

19. Mason, H.B., and A.B. Shimizu, "Definition of the Maximum Stationary Source Technology Systems Program for NO_x Control," Draft of Final Report, October, 1974.

20. McIntyre, J.C., "Rate of Reaction of Nitric Oxide by Calcium Sulfide on High Surface Area Supports," Master of Science Thesis, Department of Chemical Engineering, Montana State University, 1974.

21. Pershing, D.W., G.B. Martin, and E.E. Berkau, "Influence of Design Variables on the Production of Thermal and Fuel NO From Residual Oil and Coal Combustion," AICHE Symposium Series, 148 (71), pp. 19-29, 1975.

22. Peters, M.S., "Summary of Present Knowledge of the Chemistry of Air Pollution," Chemical Engineering Progress (Symposium Series), 67 (115), pp. 1-6, 1971.

23. Pollution Control Technology, Research and Education Association, p. 94, 1973.

24. Riesz, C.H., F.L. Morritz, and K.D. Franson, "Catalytic Decomposition of Nitric Oxide," Air Pollution Foundation of Los Angeles Report No. 20, 1957.

25. Sood, A., and J.R. Kittrell, "Dual Bed Catalyst for Simultaneous Reduction of SO_2 and NO with CO," Industrial and Engineering Chemistry Product Research and Development, 13 (3), pp. 180-185, September, 1974.

26. Turner, D.W., R.L. Andrews and C.W. Siegmund, "Influence of Combustion Modification and Fuel Nitrogen Content on Nitrogen Oxide Emissions from Fuel Oil Combustion," AICHE Symposium Series, 126 (68), p. 55, 1972.

27. U.S. Bureau of the Census, "Statistical Abstract of the United States:1974," Washington, D.C., p. 738, 1974.

28. Walter and Goodwin, "Federal Emission Standard for Stationary Sources," AICHE Symposium Series, 137 (70), p. 3, 1974.

29. Walton, H.F., Elementary Quantitative Analysis, Prentice-Hall Inc., New Jersey, pp. 68-77, 1963.

30. White, R.H., "Reduction of Nitric Oxide Using Metal Sulfides," Master of Science Thesis, Department of Chemical Engineering, Montana State University, 1973.

31. Zadick, T.W., "Catalytic Reduction of Calcoim Sulfate," Master of Science Thesis, Department of Chemical Engineering, Montana State University, 1971.

Hodgson, Kent M

Reduction of nitric oxide using metal sulfide promoter mixtures ...

DATE	ISSUED TO