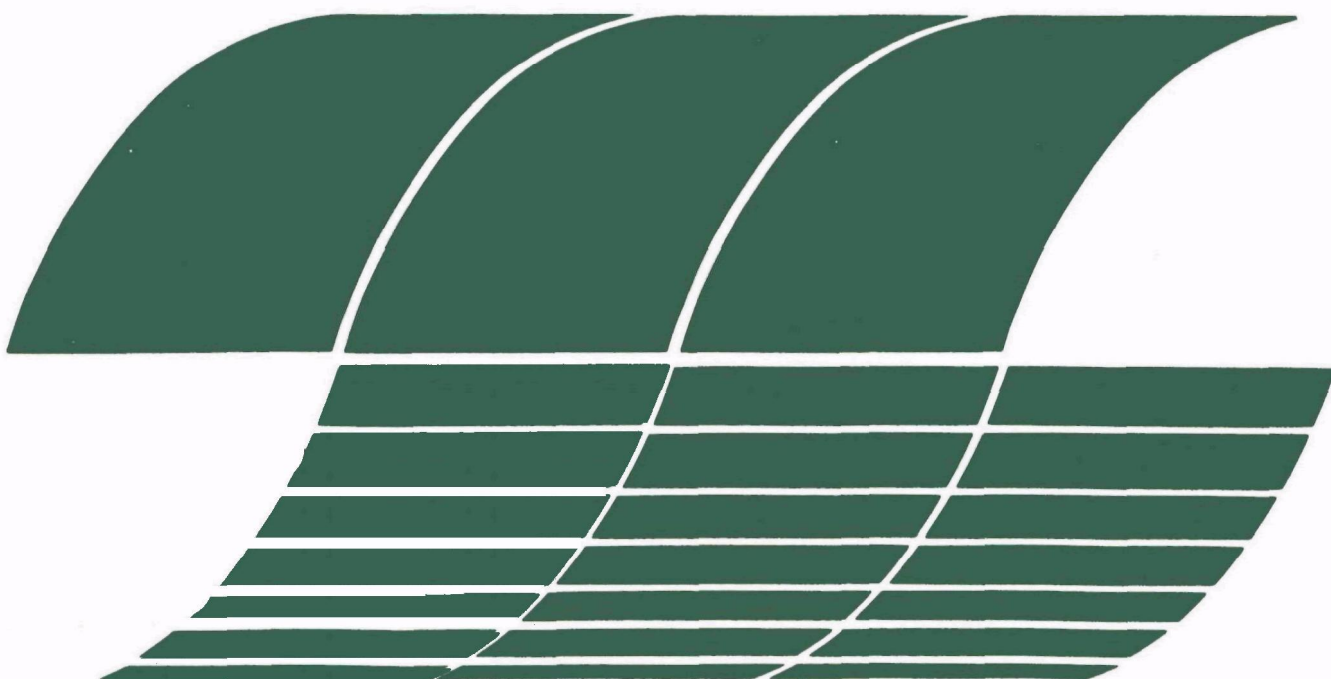**&EPA**

Reduction of Nitric Oxide with Metal Sulfides

Interagency Energy/Environment R&D Program Report

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EPA REVIEW NOTICE

Reduction of Nitric Oxide with Metal Sulfides

by

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Abstract

This research program was initiated to determine the technical feasibility of using metal sulfides for the chemical reduction of NO_x to N_2.

Nineteen different metal sulfides were investigated for this use in an initial screening using a test gas of pure NO. Although most sulfides investigated resulted in some NO reduction, BaS, CaS, SrS, and FeS were judged to be the most promising. Several catalysts were found which reduced the temperature at which the reduction reaction proceeds by as much as 200°C. A further temperature reduction was obtained by impregnating the sulfide and catalyst on high surface area supports of activated alumina or molecular sieves. The most promising catalysts were NaF, $NiCl_2$, and $FeCl_2$.

Continuous electrobalance studies showed that O_2 reacted with the sulfides at rates higher than with NO at higher temperatures but at 300°C CaS mixed with NaF reacted with NO and not O_2. However, a test of this mixture in a tubular reactor at 300°C resulted in no reduction of NO from a synthetic flue gas stream.

All combinations of the most promising sulfides and catalyst were tested for NO reduction in a tubular reactor using a synthetic flue gas containing 1000 ppm NO and 1 percent O_2. The capacities of the six best were $FeS-FeCl_2$ > $SrS-NaF$ > $CaS-NaF$ > $BaS-FeCl_2$ > $FeS-NiCl_2$ > $CaS-FeCl_2$ and ranged from 0.0372 to 0.0134 grams NO reduced per gram of initial sulfide present. Capacities of 0.91 and 0.76 were obtained when using 5% CaS (only) impregnated on alumina and molecular sieves, respectively. It was concluded that these sulfides can reduce NO in the presence of O_2 but more research is required to establish the economic feasibility.

This report was submitted in fulfillment of Grant No. R800682 by Montana State University under the (partial) sponsorship of the Environmental Protection Agency. Work was completed as of May, 1978.

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LIST OF ABBREVIATIONS AND SYMBOLS

AgF_2	argentic fluoride		K_2S	ferrous sulfate
Ag_2S	argentic sulfide		MeS	metal sulfide
Ag_2SO_4	argentic sulfate		$MeSO_4$	metal sulfate
Al_2O_3	alumina		MnS	manganous sulfide
Al_2S_3	aluminum sulfide		$MnSO_4$	manganous sulfate
$Al_2(SO_4)_3$	aluminum sulfate		MoS_2	molybdenum disulfide
BaS	barium sulfide		N_2	nitrogen
BiS	bismuth monosulfide		NO	nitric oxide
$CaCl_2$	calcium chloride		NO_2	nitrogen oxide
$Ca(NO_3)_2$	calcium nitrate		N_2O	nitrous oxide
CaO	calcium oxide		N_2O_3	nitrogen trioxide
CaS	calcium sulfide		N_2O_4	nitrogen tetroxide
$CaSO_3$	calcium sulfite		N_2O_5	nitrogen pentoxide
$CaSO_4$	calcium sulfate		$NaCl_2$	sodium chloride
$CaSiO_3$	calcium metasilicate		NaF	sodium fluoride
CdS	cadmium sulfide		NaI	sodium iodide
$CdSO_4$	cadmium sulfate		Na_2O	sodium oxide
CO	carbon monoxide		NH_3	ammonia
CO_2	carbon dioxide		NH_4OH	ammonium hydroxide
$CoCl_2$	cobaltous chloride		$NiCl_2$	nickelous chloride
$CuCl$	cuprous chloride		NiS	nickel monosulfide
$CuCl_2$	cupric chloride		O_2	oxygen
CuS	cupric sulfide		$PdCl_2$	palladium chloride
Cu_2S	cuprous sulfide		PbS	lead sulfide
$CuSO_4$	cuprous sulfate		$PbSO_4$	lead sulfate
$FeCl_2$	ferrous chloride		$PtCl_2$	platinum dichloride
Fe_2O_3	ferric oxide		S_2	sulfur
FeS	ferrous sulfide		Sb_2S_3	antimony trisulfide
$FeSO_4$	ferrous sulfate		SiO_2	silica
H_2	hydrogen		SO_2	sulfur dioxide
H_2O	water		SrS	strontium sulfide
H_2S	hydrogen sulfide		$SrSO_4$	strongium sulfate
Hg_2S	mercurous sulfide		ThS_2	thorium sulfide
K_3CrFi	potassium chromium fluoride		Tl_2S	thallium sulfide
K_3FeFi	potassium iron fluoride		WS_2	tungsten disulfide
K_3ZrFi	potassium zirconium fluoride		ZnS	zinc sulfide
			$ZnSO_4$	zinc sulfate
cm^3	cubic centimeters		ml	milliliters
g	grams		ppm	parts per million
hr	hours		SCR	selective catalytic reduction
mg	milligrams			
min	minutes		sec	seconds

ACKNOWLEDGMENT

EXECUTIVE SUMMARY

This report presents the results of a preliminary investigation of the novel use of metal sulfides for the chemical reduction of NO_x to N_2 with the objective of determining the technical feasibility of using metal sulfides to control NO_x pollutants from stationary sources.

In an initial screening, nineteen different metal sulfides were investigated for this use. In tests of the bulk powdered sulfides, using pure NO, all but one reduced NO to N_2 at temperatures varying between 90 and 650°C. However, there was a weight loss using many of the sulfides indicating an undesirable side reaction was occurring, probably the formation of SO_2. Most of the tests also showed that at least some metal sulfate was formed. BaS, CdS, CaS, Cu_2S, PbS, SrS, ZnS and NiS all gained weight but the alkaline earth sulfides were judged to be the most promising because of the stability of the sulfides and sulfates and because previous research has shown that the sulfate can easily be reduced to the sulfide. Due to its availability, most of the subsequent tests used CaS.

The temperature at which the reduction reaction proceeds was significantly reduced (by as much as 200°C) by intimately mixing the powdered sulfide with suitable catalysts. Of the materials tested, NaF and the transition metal chlorides appeared to be the most active. The temperature was also greatly reduced by impregnating the sulfide on a high surface area solid support. Activated alumina appeared to be the best support since side reactions producing SO_2 were observed with silica, silica alumina, and molecular sieve supports. The temperature for reaction was further reduced by impregnating both the sulfide and catalyst on the pellets. Kinetic studies using a recording electrobalance showed that the rate of reaction of the sulfides with O_2 was generally greater than that with NO but that certain catalysts selectively increase the rate of reaction with NO and indicate that some sulfide-catalyst combinations will react with NO and not O_2 at temperatures below 300°C.

Finally, initial tests using a synthetic flue gas containing 1,000 ppm NO, 1% O_2, and 18% CO_2 (balance N_2), showed that NO was rapidly reduced by CaS at temperatures above 600°C. The reaction temperature was reduced to about 400°C by mixing the metal sulfides with a catalyst.

All combinations of BaS, CaS, SrS and FeS with NaF, $NiCl_2$, $CoCl_2$, $FeCl_2$ and Fe_2O_3 were tested at 400°C using the synthetic flue gas and the capacity for NO_x reduction calculated. Capacity is defined as the weight of NO reduced per unit weight of sulfide initially present from the start of the run until the exit concentration exceeds 600 ppm. Of the combinations tested, the six best were: $FeS-FeCl_2$ > $SrS-NaF$ > $CaS-NaF$ > $BaS-FeCl_2$ > $FeS-NiCl_2$ > $CaS-FeCl_2$. For these combinations capacities varied from 0.0372 to 0.0134 grams NO reduced per gram of metal sulfide intially present when tested in a packed bed tubular reactor. Using the same test conditions 5 percent CaS (only) impregnated on a Harshaw activated alumina and a Linde Molecular sieve

had capacities of 0.76 and 0.91 grams of NO reduced per gram of metal sulfide initially present. This indicates that capacity can be greatly increased by making the sulfide more available for reaction. For comparison, assuming the reaction:

$$CaS + 4NO \rightarrow CaSO_4 + 2N_2$$
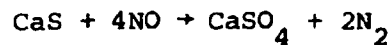
the maximum capacity for CaS would be 1.66 grams NO/gram CaS. Capacity was greatly reduced by increasing the O_2 concentration to 10 percent.

At 400°C the presence of 2 percent water vapor reduced the rate of reaction, probably by interfering with the action of the catalyst. At higher temperatures, where the reaction probably is not catalytic, there was no effect. SO_2 and CO_2 had no effect on the reduction reaction.

It is concluded that calcium sulfide is capable of reducing NO_x even in the presence of O_2. However, more research is required to better define an optimum system and to establish the economic feasibility of using this process to control NO_x emissions.

OBJECTIVES AND SCOPE OF WORK

The objective of this research program was to investigate the use of metal sulfides for the reduction of nitrogen oxides with the aim of controlling emissions of these pollutants from stationary sources. The study included an extensive laboratory investigation of various metal sulfides both in bulk powdered form and sulfides impregnated on high surface area supports for the reduction of NO; an investigation of the use of various materials to catalyze the reduction reaction; and continuous recording electrobalance studies so that rates of reaction could be measured.

BACKGROUND

Oxides of nitrogen are one of the most prevalent air pollutants with present (1975) total annual emissions estimated at about 20 million tons per year in the U.S. alone. They are major reactants in the formation of photochemical smog and their emissions must be controlled because of their adverse effects on human health and plant life (1).

Emission levels of nitrogen oxides will probably rapidly increase in the future, even with the application of the best control technology currently available because of the very rapid growth rate of combustion sources as energy demands continue to rise. This is in contrast to emissions of SO_2 and particulate matter which are also produced in the combustion of fossil fuels. Unlike NO_x, both SO_2 and particulate emissions can probably be maintained at present levels, or reduced, using present technology (2).

Of the current U.S. NO_x emission, about 55 percent originate from stationary sources and 93 percent of all stationary NO_x emissions are from the combustion of fossil fuels for steam and/or electricity generation, or space heating (3).

Emission levels from stationary sources are most frequently in the 50 to 1000 ppm range (8), but at the very high temperatures that will be present in the combustor of an MHD generator the equilibrium NO concentration may be as high as 3.25 percent (32,500 ppm)(4). Organically bound nitrogen in the fuel may set a lower limit on the formation of nitric oxide, particularly if a high nitrogen containing fuel such as coal is used (5,6).

Nitric oxide (NO) is generated in all high temperature processes including air by the direct combination of nitrogen and oxygen:

$$N_2 + O_2 \rightleftarrows 2NO$$
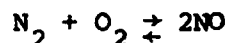
The kinetics of the N_2, O_2, NO reaction system is such that an equilibrium composition is rapidly established at temperatures above 2000°K. NO becomes unreactive at lower temperatures even though its decomposition is thermodynamically favored by low temperatures. The decomposition reaction is very slow at temperatures below 2000°K and after temperatures of about 1800°K and below are reached very rapidly the NO concentration is essentially "frozen" at the high temperature equilibrium value. Surfaces may exhibit a catalytic effect for the decomposition reaction. Thus, the concentration of NO appearing in an effluent gas from a combustion process depends on the combustion process, the fuel-oxidizer mixture, and the time-temperature-surface contact history of the gas as it goes through a particular combustor system.

Nitric oxide (NO) is the species formed in the high temperature combustion but it is quite unreactive at lower temperatures. At ambient temperatures, it is oxidized slowly to the more reactive and irritant nitrogen dioxide (NO_2) by oxidizing agents (ozone, O_2) in the atmosphere. NO_2 is the main cause of the highly visible red-brown color of smog. The relative amounts of NO and NO_2 in a gas containing oxygen vary widely depending on temperature and O_2 concentration and the combination (NO + NO_2) is usually referred to as combined NO_x.

Nitric oxide (NO) and nitrogen dioxide (NO_2) are the major pollutants but the unstable NO_3, N_2O_3, N_2O_4, and N_2O_5 forms also exist. Nitrous oxide (N_2O) is a stable oxide which is formed by the decomposition of nitrogen compounds in the soil by bacterial action and the atmosphere contains about 0.5 ppm of this compound from natural sources. N_2O is also an intermediate in the catalytic reduction of NO, and in some cases it may be a substantial portion of nitrogen oxides emitted from chemical processes with nitric acid. N_2O is innocuous and considered non-polluting.

There are (at least) two general routes available for controlling NO_x emissions from stationary combustion sources; combustion modification and flue gas treatment.

The release of NO_x in combustion gases can be minimized by several combustion modification techniques, but not entirely eliminated. The most promising combustion modification methods include: load reduction, low excess air firing, two stage combustion, off-stoichiometric firing, flue gas recirculation, water and steam injection, or a combination of these techniques (7). However, many of these less costly control methods can easily produce undesirable results such as reduced efficiency, heat transfer surface corrosion and increased CO and hydrocarbons emissions (2,8). Additionally, as noted above, organic nitrogen compounds in the fuel may put a lower limit on NO_x production from coal, and to a lesser degree with some other fuels (2,5, 6,8). For example, when an oil containing about 0.2% nitrogen is burned, the amount of NO_x produced from the fuel is about equal to that of thermal NO_x (5).

Although there is no thermodynamic hindrance to the decomposition of NO to N_2 and O_2 at temperatures below 1000°K, apparently the energy of activation of the NO molecule is very high and this results in the decomposition reaction being kinetically limited. Heterogeneous catalysts are available that reduce this activation energy considerably, but reaction rates are still too low to be practical for NO_x emission control, apparently because of an unusually small pre-exponential term in the reaction rate constant (9).

Since the decomposition of NO to N_2 and O_2 is too slow to be practical at moderate temperature even with the best catalysts available, the heterogeneous catalytic reduction of NO to form N_2 has been studied using a wide variety of reducing agents (hydrocarbons, activated carbon, hydrogen, carbon monoxide, ammonia) and catalysts with the aim of the chemical destruction of NO in gas streams. In particular, reduction with ammonia shows promise since it can reduce NO and NO_2 without simultaneously reacting with oxygen between the limits of 210 to 270°C. Above 270°C, ammonia will react with O_2 to form NO, below 210°C, it apparently forms ammonium nitrate (10).

Since 1973 selective catalytic reduction (SCR) with ammonia has been used in Japan in many industrial plants for NO_x control (Ando et al., 1977). These plants apparently use reaction temperatures of 300 to 450°C. Under these conditions the presence of oxygen promotes the reactions and the reduction reactions can be represented by the following equations:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O$$
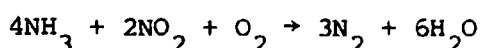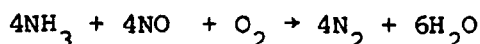
A large number of proprietary base-metal catalysts have been developed to promote the reduction reaction with claims of over 90% NO_x reduction being obtained using NH_3:NO_x ratios of about 0.8 to 1.4:1 with less than 10 ppm NH_3 in the treated flue gas.

Other technically feasible methods for NO_x control from stationary sources include absorption or adsorption. However, since NO itself is quite unreactive, absorption or adsorption usually requires a two stage process to first oxidize the NO to either N_2O_3 or NO_2 followed by treatment of the oxidized gas for NO_x removal. This greatly complicates the process because the oxidation of NO to NO_2 is a relatively slow reaction with the rate decreasing with increasing temperature. To date, performance tests of the sorption methods have ranged from unsatisfactory to partially successfull (10,11,12).

In considering the various methods for NO_x minimization and/or flue gas denitrification that are available or in the development stage, certainly the combustion modification techniques are the simplest and in most cases more economical to use. However, usually this is only helpful in reducing NO_x emission from new facilities. In most cases a modification of combustor design is necessary to provide significant NO_x reduction. This is difficult in existing plants but good results are obtained when the design modifications are incorporated into new plants. However, many of these less costly modification techniques can produce such undesirable results as lower fuel efficiency and increasing hydrocarbon and CO emissions. In addition, stricter standards are likely to require flue gas denitrification to reduce NO_x levels below what can be obtained by combustion modifications in some cases (2). This is particularly true of coal fired plants because it is difficult to reduce the NO_x in the flue gases from coal burning below 400 ppm by combustion modifications alone (5).

Of the flue gas denitrification techniques being used in Japan (where strict emission standards require low emission levels), several modifications of selective catalytic reduction with ammonia are the processes most widely used. The major problem with this process is plugging of the catalyst with dirt, catalyst poisoning by dust components, SO_2 and SO_3, and the

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formation of ammonium bisulfate which is very corrosive. In addition, since ammonia injection ratios typically are $NH_3:NO=1.1\sim1.4$, large amounts of ammonia are required. Indeed, in Japan it is estimated that about 400,000 tons of ammonia per year would have to be consumed to attain ambient air standards using the SCR method and this is equivalent to about 1/2 the total annual consumption of nitrogen fertilizers in that country! This would appear to be a socially unacceptable use of a valuable fixed nitrogen fertilizer when the world food production is being limited by fertilizer shortages (12).

In any case, however, it is necessary and desirable to develop alternative flue gas denitrification processes as well as better combustion modification techniques as long as the consumption of fossil fuels continues to increase (2,5,12).

The literature of 60 years ago (13,14) discusses the "Thiogen" processes for the recovery of sulfur from SO_2 according to the reactions

$$CaS + 2SO_2 \rightarrow CaSO_4 + S_2$$

$$4CaS + 6SO_2 \rightarrow CaSO_3 + 3S_2$$
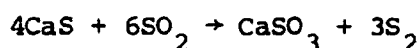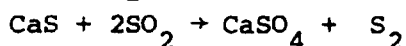
Preliminary research by the authors indicated that the reaction

$$CaS + 4NO \rightarrow CaSO_4 + 2N_2$$
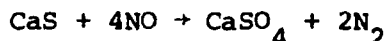
proceeds rapidly at temperatures above 450°C when pure NO is passed through a reactor containing powdered calcium sulfide. Based on the promise of this type of reaction for NO_x emissions control, a research program was initiated. This report presents the results of a preliminary investigation of various metal sulfides for reducing NO together with tests of various materials to catalytically enhance the reaction.

THERMODYNAMIC STUDY

Thermodynamics gives a good indication of the potential of metal sulfides for NO_x reduction and so a brief study was made to compare the reduction reactions using various metal sulfides. Several possible side reactions of CaS were also considered together with the thermodynamics of reducing NO with hydrogen. Possible side reactions with other gaseous compounds which may be present in flue gases were not considered. The study was limited to systems for which data on both the sulfide and corresponding sulfate were available. Approximate methods were used to calculate the effects of temperature on the free energy of reaction where heat capacity data were not available. The results are summarized in Table 1.

Several interesting and important conclusions can be drawn from these data. First, the reduction reaction of NO_x using metal sulfides are very favorable at all temperatures of practical interest and in particular at temperatures below 1000°K. In addition, from a standpoint of free energy driving force, the use of metal sulfides compares favorably with reduction using a conventional reducing agent such as hydrogen. This includes the reduction of both NO and NO_2 with the formation of either N_2 and/or N_2O. In addition, from a thermodynamic standpoint it appears that the reduction of NO or NO_2 is favored over the oxidation of the sulfide with free oxygen and indicates that the formation of the sulfate is favored over the formation of SO_2 and

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CaO. However, the same data also show that these undesired side reactions are also very possible (and indeed probable). Unfortunately, thermodynamics only indicates which reactions are theoretically possible and gives no indication as to how fast the reactions will proceed or the relative rates of the various reactions. The kinetics of the reactions must be determined from experimental data. Thus, experimental data are required to determine if practical use of these reactions can be made to control NO_x emissions.

TABLE 1. CALCULATED FREE ENERGY CHANGE AND HEAT OF REACTION FOR THE REDUCTION OF NO WITH VARIOUS METAL SULFIDES

Reaction	ΔF_R KCal/Mole Sulfide				ΔH_R KCal/ Mole Sulfide
	298°K	500°K	1000°K	1500°K	298°K
$CaS+4NO \rightarrow CaSO_4+2N_2$	-284.3	-264.3	-215.7	-166.7	-313.5
$MnS+4NO \rightarrow MnSO_4+2N_2$	-261.4	-241.0	-190.0	-139.2	-291.8
$PbS+4NO \rightarrow PbSO_4+2N_2$	-253.6	-234.2	-186.1	-138.0	-282.3
$ZnS+4NO \rightarrow ZnSO_4+2N_2$	-243.7	-224.5	-177.0	-129.5	-273.1
$CdS+4NO \rightarrow CdSO_4+2N_2$	-242.0	-222.8	-174.8	-116.8	-270.8
$CuS+4NO \rightarrow CuSO_4+2N_2$	-229.3	-209.5	-160.2	-110.8	-258.8
$Ag_2S+2NO \rightarrow Ag_2SO_4+2N_2$	-220.3	-200.9	-152.4	-104.0	-249.3
$1/3\ Al_2S_3+4NO \rightarrow 1/3\ Al_2(SO_4)_3+2N_2$	-289.9	-270.3	-221.1	-171.8	-319.5
$4H_2+4NO \rightarrow 4H_2O+2N_2$	-301.3	-290.4	-263.2	-236.1	-317.5
$CaS+1.5O_2 \rightarrow CaO+SO_2$	-102.0	-98.3	-89.1	-79.8	-107.6
$CaS+2O_2 \rightarrow CaSO_4$	-201.5	-184.1	-141.1	-98.1	-227.5
$CaS+3NO \rightarrow CaO+SO_2+1.5N_2$	-164.32	-158.88	-145.39	-131.91	-172.36
$CaS+2NO_2 \rightarrow CaSO_4+N_2$	-226.24	-219.60	-195.91	-172.21	-243.30
$CaS+8NO \rightarrow CaSO_4+4N_2O$	-268.18	-231.80	-141.60	-51.40	-322.00

SECTION II

CONCLUSIONS

The novel use of metal sulfides to chemically reduce nitrogen oxides to elemental nitrogen was investiged in a comprehensive screening program. The following important conclusions were made based on the preliminary experimental investigation.

THERMODYNAMIC STUDY

(a) A thermodynamic study showed that there are no thermodynamic limitations on reactions of the type:

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

$$2NO_2 + MeS \rightarrow MeSO_4 + N_2$$
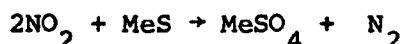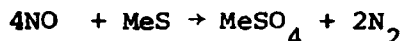
where "Me" represents the various metal sulfides studied.

These reactions have very high negative free energy changes indicating they are very favorable at all temperatures of practical interest. Conversion to nitrogen would be virtually complete at equilibrium.

(b) The free energy changes for the sulfide reduction of NO_x compares favorably with reduction using conventional reducing agents such as H_2 or carbon.

(c) However, the oxidation of the sulfides with oxygen is also thermodynamically possible as well as other undesirable side reactions which result in the formation of gaseous sulfur compounds.

(d) The reduction reactions using sulfides are highly exothermic.

PRELIMINARY SCREENING OF BULK POWDERED SULFIDES

(a) Nineteen sulfides were tested for NO reduction using pure NO as the test gas. All but one resulted in the reduction of NO to N_2 and/or N_2O and in most cases at least some sulfate was formed. The temperature at which N_2 and/or N_2O was formed varied with the different sulfides between 90 and 650°C.

(b) Al_2S_3, Sb_2S_3, BiS, CuS, FeS, MnS, HgS, MoS_2, K_2S, WS_2, and TlS, all lost weight during the reaction with NO indicating undesirable side reactions were occurring.

(c) BaS, CdS, CaS, Cu_2S, PbS, SrS, ZnS, and NiS all gained weight during reaction with pure NO. Of these, the alkaline earth sulfides, BaS,

CaS and SrS, were judged to show the most promise, particularly CaS because of the abundance of $CaSO_4$ which can be reduced to the sulfide.

PRELIMINARY PROMOTER STUDIES

(a) Several materials were found to increase the rate of the reduction reaction including K_3FeF_6, CuCl, $CaCl_2$, $NiCl_2$, NaF, NaI, $CoCl_2$, and $FeCl_2$ when physically mixed with some of the sulfides. This resulted in the reaction occurring at temperatures about 200°C lower than with the sulfide alone. The investigation of possible catalysts was limited to materials on hand and was by no means exhaustive.

(b) K_3ZrF_6, K_3CrF_6, $FeSO_4$, Fe_2O_3, and Cr_2O_3 were less active or did not enhance the reduction reaction.

(c) Some of the catalysts appeared to result in the formation of SO_2 at higher temperatures.

PRELIMINARY STUDIES OF DISPERSED SULFIDES ON HIGH SURFACE SUPPORTS

(a) A very active form of CaS can be obtained by impregnating $Ca(NO_3)_2$ on the high surface area solid such as activated alumina, silica or molecular sieves; conversion of the nitrate to the oxide, and conversion of the oxide to the sulfide with H_2S. This results in the NO reduction reaction occurring at temperatures below 100°C.

(b) Impregnation of a catalyst on the support along with the sulfide further lowers the reaction temperature so that reduction occurs at room temperature.

(c) Oxygen also reacts with the high surface area sulfide pellets, even at room temperature.

(d) The high silica and molecular sieve supports resulted in the formation of SO_2 at higher reaction temperatures.

KINETIC STUDIES

The following conclusions were made from kinetic studies of the rate of reaction of the sulfides using a continuous recording electrobalance: (a) The rate of reaction of 8.6% CaS impregnated on activated alumina varied from 1×10^{-4} to 1.8×10^{-4} mole NO removed/(hr)(gram pellet) at temperatures of 390 and 493°C respectively when tested with a gas mixture containing 2.5% NO in helium. In most cases, the rate rapidly declined with time indicating significant diffusional resistance to reaction as the sulfide in the pellet is consumed.

(b) Reaction rate measurement with powdered sulfides alone showed that the rate of reaction of O_2 with the sulfides is more rapid than with NO in most cases. The ratio of the rates O_2/NO varied between 3 and 8 for CaS at a temperature between 400 and 500°C.

(c) CaS mixed with NaF or NaCl as catalysts reacts only with NO at lower temperatures. However, in a tubular reactor using a test gas containing both

NO and O_2 the rate was too low to detect a change in the NO concentration.[2]

(d)   In tests of pure promoters, K_2FeF_6 reacted with NO at all temperatures investigated and with O_2 at 500°C. NaF and NaCl did not react with either NO or O_2 at temperatures of 400°C and below. $NiCl_2$ and $FeCl_2$ did not react with NO or O_2 at 300 or 400°C.

PRELIMINARY TESTS USING A SYNTHETIC FLUE GAS

(a)   A 5 gram bed of unpromoted CaS reduced about 98% of the NO_x in a gas stream containing 1000 PPM NO_x and 1% O_2 at temperatures between 600°and 700°C at a gas flow rate of 100 cc/min.

(b)   The capacities at 400°C of all combinations of BaS, CaS, SrS and FeS mixed with NaF, $NiCl_2$, $CoCl_2$, $FeCl_2$ and Fe_2O_3 for NO reduction was determined using a synthetic flue gas. The gas contained 1000 ppm NO, 1 percent O_2, 18 percent CO_2, with the balance N_2. The capacity is defined as the weight of NO reduced per unit weight of metal sulfide initially present from the start of the run until the exit combination exceeds 600 ppm. Of the combinations tested the six best were $FeS-FeCl_2$ > $SrS-NaF$ > $CaS-NaF$ > $BaS-FeCl_2$ > $FeS-NiCl_2$ > $CaS-FeCl_2$. For these combinations, capacities varied from 0.037 to 0.013 grams NO reduced per gram of initial sulfide present.

(c)   Using the same test conditions as in (b), 5 percent CaS (only) impregated on a Linde Molecular Sieve and on a Harshaw activated alumina had capacities of 0.91 and 0.76 grams of NO reduced per gram of CaS initially present.

(d)   The presence of 10 percent O_2 in the gas stream greatly decreased to capacity of CaS-NaF to reduce NO at 400°C.

(e)   The presence of 2 mole percent of water vapor in the gas stream greatly decreased the capacity for CaS-NaF and SrS-NaF at 400°C.

(f) SO_2 and CO_2 had no effect on the capacity of CaS for NO reduction.

(g)   NO can be reduced with CaS, BaS, SrS, or FeS in the presence of 1 percent O_2.

SECTION III

RECOMMENDATIONS

The preliminary results with CaS mixed with certain catalysts indicates that NO_x is rapidly reduced at temperatures above 400°C in the presence of O_2 although the sulfide also reacts rapidly with O_2 under these conditions. However, the kinetic studies indicate that certain catalysts are selective for NO; that is, the rate of reaction of NO with the sulfide is increased while with O_2 it is not. In these tests, CaS reacted with NO and not O_2 at temperatures below 300°C when promoted with NaF. Further, only CaS has been tested extensively although the kinetic studies indicated that BaS or SrS may be better in the presence of O_2. As a result, it may be possible to find a sulfide-catalyst combination which will rapidly react with NO but not O_2 under certain conditions and thus minimize the consumption of the sulfide with O_2. This may also be true for a metal sulfide-catalyst mixture impregnated on high surface area pellets.

Also, the effects of gas composition, in particular O_2 and H_2O, have not been adequately investigated. In addition, the side reaction in which gaseous sulfur compounds are produced have not been investigated in any detail. Only the formation of SO_2 and H_2S have been observed under certain conditions. The reaction mechanism for these reactions must be determined and the conditions under which the reactions occur must be better defined. Thus, there are many critical factors which must be investigated further before both the technical and economic feasibility of using this process for pollution control can be established. As a result, it is recommended that further work be carried out including the following:

1) Further kinetic studies should be carried out to determine the relative rate of reaction of NO and O_2 with promoted BaS, CaS, SrS, FeS, and possibly ZnS and CdS. An extensive screening of possible catalysts should be carried out in connection with this study. This would further indicate which systems and conditions might result in the reduction of NO_x in the presence of O_2 with a minimum of oxidation of the sulfide with O_2. The use of a gradientless reactor of the Berty or Carberry type (17,18) would be ideal for this study.

2) Further tests in a bench scale flow reactor should be made using the most promising sulfide-catalyst combinations and a synthetic test gas with a composition more typical of power plant effluent gas streams. The effects of temperature, sulfide-catalyst composition, space time, gas composition, etc., on NO_x reduction and the reaction of O_2 should be determined.

3) Studies similar to that outlined in (2) should be made where the sulfide-catalyst is impregnated on high surface area supports.

4) A study whould be made of the regeneration of the spent sulfide-catalyst.

The results of these studies would permit a preliminary economic evaluation of NO_x pollution control using sulfides.

SECTION IV

EXPERIMENTAL APPROACH

APPARATUS AND PROCEDURE

A simple semi-batch reactor system (continuous flow of the test gas to the reactor but batch-wise sulfide reactant addition) was used for many of the tests including initial screening of various metal sulfides, catalyst tests, and more detailed preliminary tests of the most promising sulfides. A schematic diagram of this reactor system is shown in Figure 1. The test gas mixture (previously blended) from a high pressure cylinder was fed to the reactor through a calibrated rotameter. For some tests the gas mixture was first saturated with water vapor by sending the gas through a gas washing bottle before it was sent to the reactor. The details of the reactor are shown in Figure 2. Several size reactors were used at various times in the research but all had the same basic design. The reactors were constructed from 14 to 18 inch lengths of schedule 40 type 304 stainless steel pipe with diameters of 1.5, 0.75 and 0.5 inch with appropriate inlet and outlet fittings. The bottom half of the pipe was packed with stainless steel wire rings to increase heat transfer and ensure that the gas entering the reaction chamber was at the desired temperature. The top half constitutes the reaction chamber and is contained between two porous stainless steel plates. A thermowell made from 1/4" stainless steel tubing was mounted axially in the pipe where thermocouples were mounted at three locations in the reaction chamber. In operation the reactor was mounted in a 3 or 4 inch diameter metal block with a slightly oversize hole through it. This block was wrapped with three nichrome heating coils in ceramic beads and controlled by variable transformers. This heater-block assembly was mounted in an outer container which was filled with vermiculite insulating material. Both bronze and stainless steel heating blocks were used but the bronze block proved to be less satisfactory due to oxidation corrosion at higher temperatures. The metal block insured near isothermal operation throughout the reactor length and helped to eliminate both radial and longitudinal temperature gradients. The gas outlet passed through a small water cooler and then through a tee containing a silicone rubber sampling septum and thence to either a continuous analyzer or a vent hood. Stainless steel fittings and stainless steel tubing were used throughout the reactor system. A typical test was made as follows: 2 to 20 grams of the powdered sulfide or sulfide-catalyst mixture, or sulfide impregnated on high surface area support, was placed in the reactor and the test gas fed to the reactor at a constant rate while the reactor was heated. Samples of the exit gas were taken periodically in a gas tight syringe and analyzed by gas chromatography.

Relative rates of reaction were determined with a Cahn R-100 continuous recording electrobalance in the apparatus shown schematically in Figure 3. The balance has a 100 gram capacity for sample weight plus container. Mechanical tare capacity is 100 grams and the balance has three electrical weight

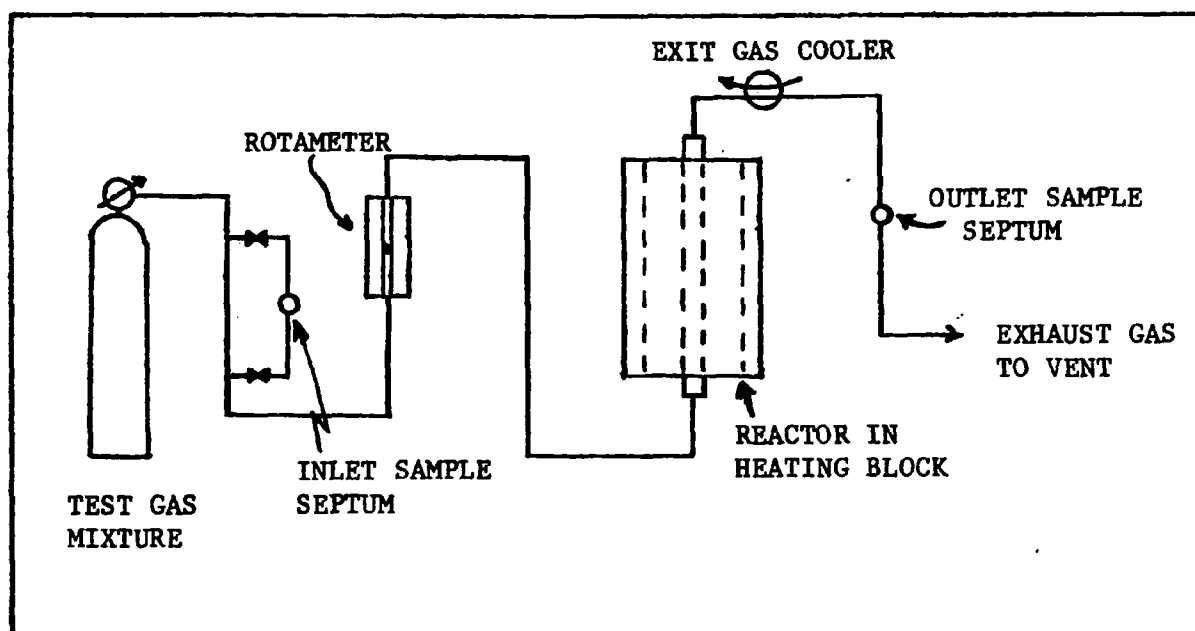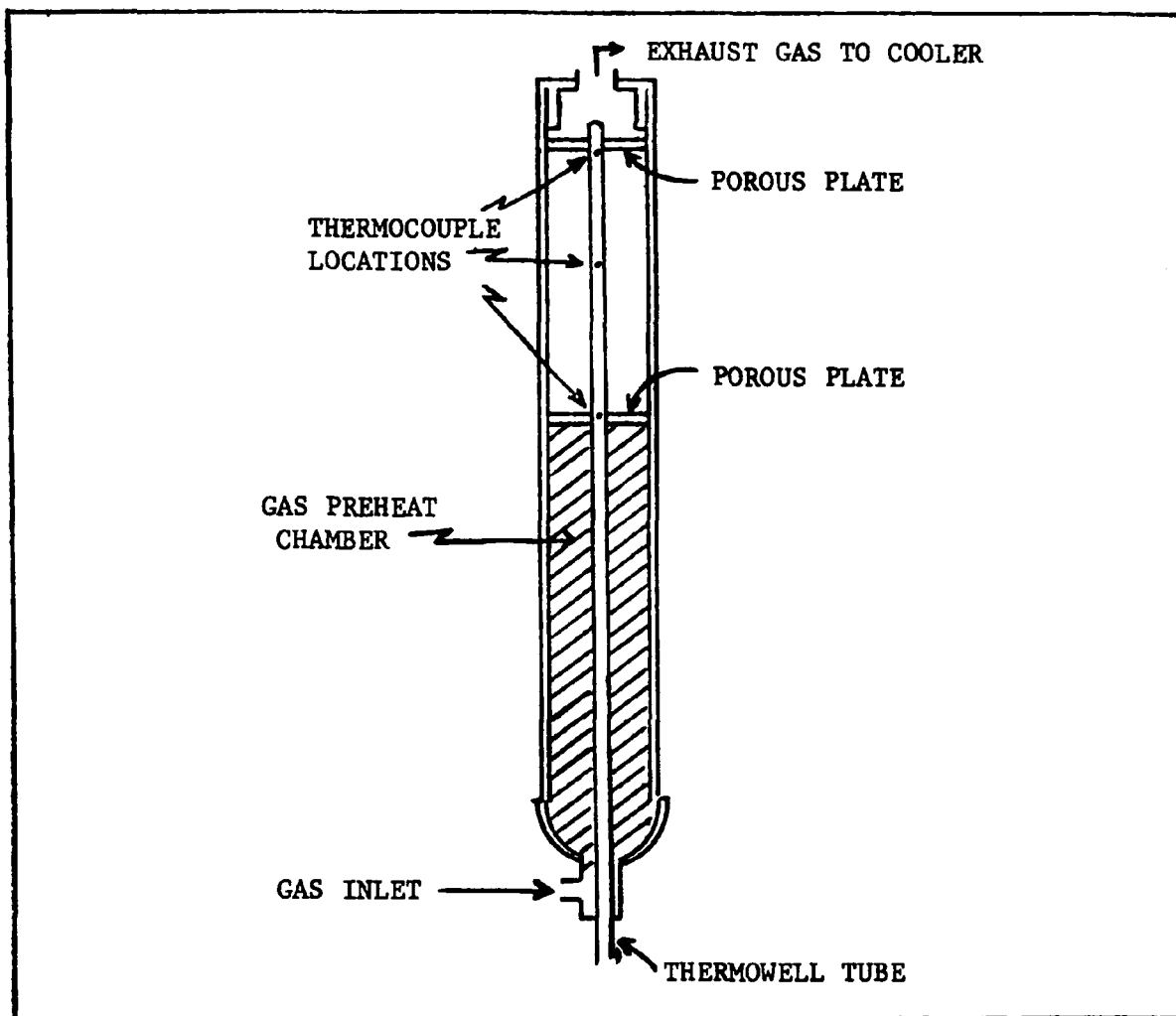FIGURE 1 — Flow Diagram of Reactor System

EXHAUST GAS TO COOLER

POROUS PLATE

THERMOCOUPLE
LOCATIONS

POROUS PLATE

GAS PREHEAT
CHAMBER

GAS INLET

THERMOWELL TUBE

FIGURE 2 – Details of Flow Reactor

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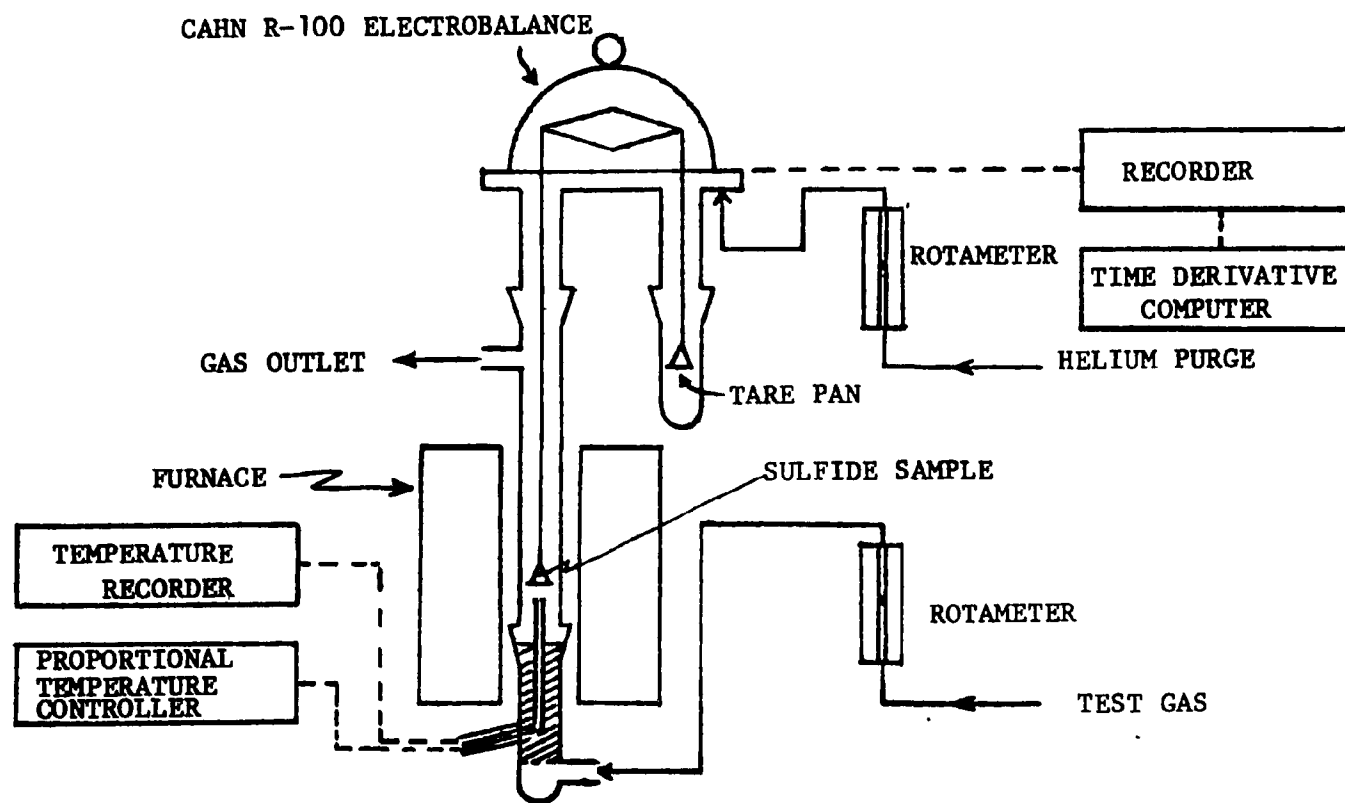
FIGURE 3 - Diagram of Electrobalance Reactor System

suppression ranges capable of electronically taring from 10 micrograms to 10 grams. The readibility of the balance is 0.5 micrograms with five weight ranges: 10 grams, 1 gram, 100 milligrams, 1 milligram, and 100 micrograms full chart scale. The precision of the instrument is $\pm 10^{-3}$ of the meter (or recorder) range and $\pm 10^{-6}$ of load while the accuracy is $\pm 5 \times 10^{-4}$ of mass suppression range for absolute weighings. The maximum weight change is 10 grams, either increase or decrease.

The system shown in Figure 3 operates with the feed gas passing through a rotometer to the bottom part of the reactor. Exhaust gases leave the reactor below the glass bell housing which contains the weighing mechanism. A continuous helium purge is run through the bell housing to keep the balance mechanism free of the corrosive feed gases. Although most of the weighing mechanism is gold plated to resist corrosion, some parts are subject to attack by NO_2. The reactor hang down tube was enclosed in a vertically mounted tube furnace which could easily be opened to allow access to the reactor tube before and after a run. It was controlled by a Teco TC-1000 proportional temperature controller.

The cross section of the reactor hang down tube is shown in Figure 4. In powdered sulfide tests, the reactant rested on a circular stainless steel pan suspended by a 0.1 mm nickel wire from one side of the balance arm. An identical pan suspended from the other side of the balance arm was used for the tare weights. Some of the tests using sulfides impregnated on high surface area support pellets were carried out using a 200 mesh stainless steel screen suspended from the balance arm. During the course of the investigation two reactor hang down tubes were used, one 16 mm diameter, 780 mm long ATM Flothru mullite with ground glass joints top and bottom, and the other a 57 mm diameter, 840 mm long ATM Flothru Vycor tube with the same joints. In operation a pyrex glass connector containing a porous glass plate was attached to the bottom joint. Two chromel-alumel thermocouples were cemented with epoxy into a hole in the side of the connector and extended up into the hang down tube to a point just below the support pan. One thermocouple was attached to a proportional controller, the other to a temperature recorder. The hang down tube-connector assembly was filled with 40 mesh Ottawa sand to a point just below the end of the thermocouples to aid in preheating the feed gas. The gas was fed into the bottom of the reactor and flowed past the sulfide being tested before being exhausted out the top.

To measure the rate of reaction, the particular sulfide, either in powder or pellet form, was placed on the weighing pan (or wire mesh pan) and the reactor heated to the desired temperature while continuously purging the system with helium. This was done until the weight of the sample remained constant since there was usually some weight loss due to the removal of moisture in the sample. After a constant sample weight was reached, the test gas was introduced into the reaction tube through a rotameter and the weight change continuously recorded as the gas-solid reaction proceeded.

The slope of the weight versus time curve represents the rate of reaction and can be calculated graphically, or by use of the time derivative computer which is also part of the system. Since the rate of reaction gradually decreases with time because of diffusional resistance through the outer reacted layer of solid, the weight change during the first hour was usually used to determine the reaction rate for comparison purposes. This simple
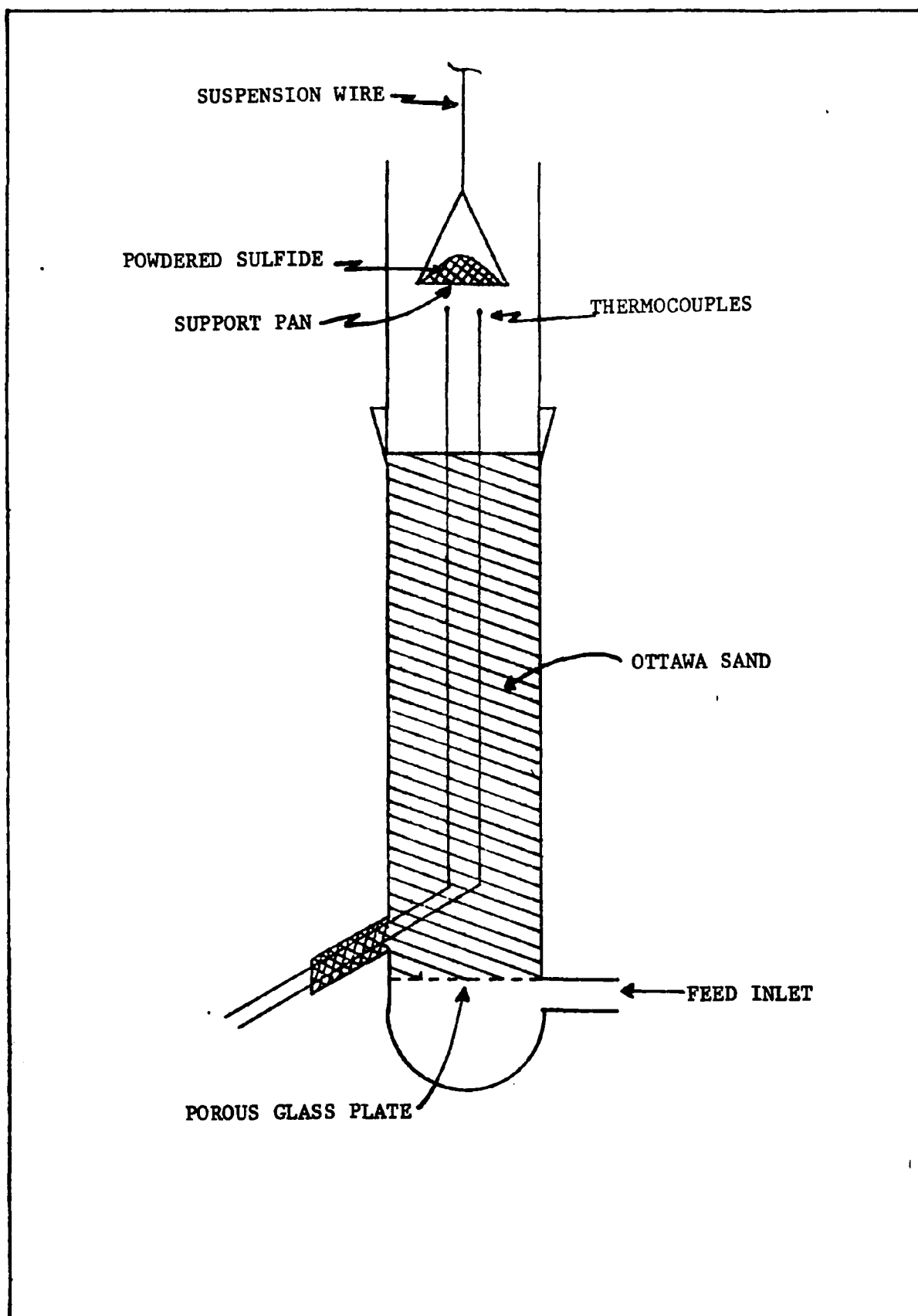
FIGURE 4 - Electrobalance Reactor Details

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procedure was not satisfactory for comparison of the ratio of reaction for CaS impregnated on high surface area pellets because of the large variation of rate with time. Integrated average rates calculated for the entire run time were used for these comparisons.

During the late stages of this research, a chemiluminescent analyzer became available which permitted the analysis of NO_x down to the 10 parts per million range. With this addition, the testing of the metal sulfide for NO_x reduction using a synthetic flue gas became feasible.

For the tests using the synthetic flue gas, a reactor very similar to those previously discussed was used, except that flow was down through powdered sulfide rather than up. Better reproducibility was obtained with this arrangement, probably because it eliminated some of the channeling which was evident in the up-flow reactor. Figure 5 is a schematic flow diagram of the apparatus used for these tests. The synthetic flue gas was made by mixing the various gases with a gas containing 0.5 percent NO in N_2 using calibrated rotameters. Since the NO_x analyzer requires a minimum continuous flow of sample gas to it, under the conditions of some tests, dilution was required to provide sufficient flow to the analyzer. This was accomplished by mixing pure N_2 with the gas stream before it entered the analyzer. A metal bellows pump was available in the system to provide a high gas recycle rate through the reactor. At high enough recycle rates, the reactor performance approaches that of a perfect mixed reactor and permits the simple determination of reaction rates under conditions in the flow reactor.

ANALYSES

Depending on the test gas and the reaction conditions, the exit gas could contain varying amounts of O_2, N_2, NO, NO_2, N_2O, SO_2 and CO_2 and thus the analytical problem is quite complex. For much of the preliminary work, only a gas chromatograph was available for analysis and this put limitations on the specific combinations of compounds that could be quantitatively determined. Thus, for much of the work reported in this report, a test gas containing NO in helium was used, and the reacted gas stream was analyzed for N_2 to determine reduction of the NO. A two column system was used for most of the gas analysis in a Varian Aerograph Model 1420 low volume thermal conductivity chromatograph. This instrument is capable of detection in the 1-10 ppm range. The following columns and conditions were used:

	Internal Column	External Column
Packing	12' x 1/8" Stainless Steel Porapak Q-S	25' x 1/8" Stainless Steel Porapak Q
Column Temp	130°C	0°C
Dector Temp	130°C	130°C
He Flow	10 cc/min	10 cc/min

In the first (internal) column, N_2 and NO emerge as one peak while N_2O and SO_2 are eluted separately. N_2 and NO are separated in the low temperature (external) column which was enclosed in a Dewar flask containing ice. Equal gas volumes are injected into each column using a gas tight syringe and the chromatograph polarity switched manually at the proper time to obtain both sets of peaks.
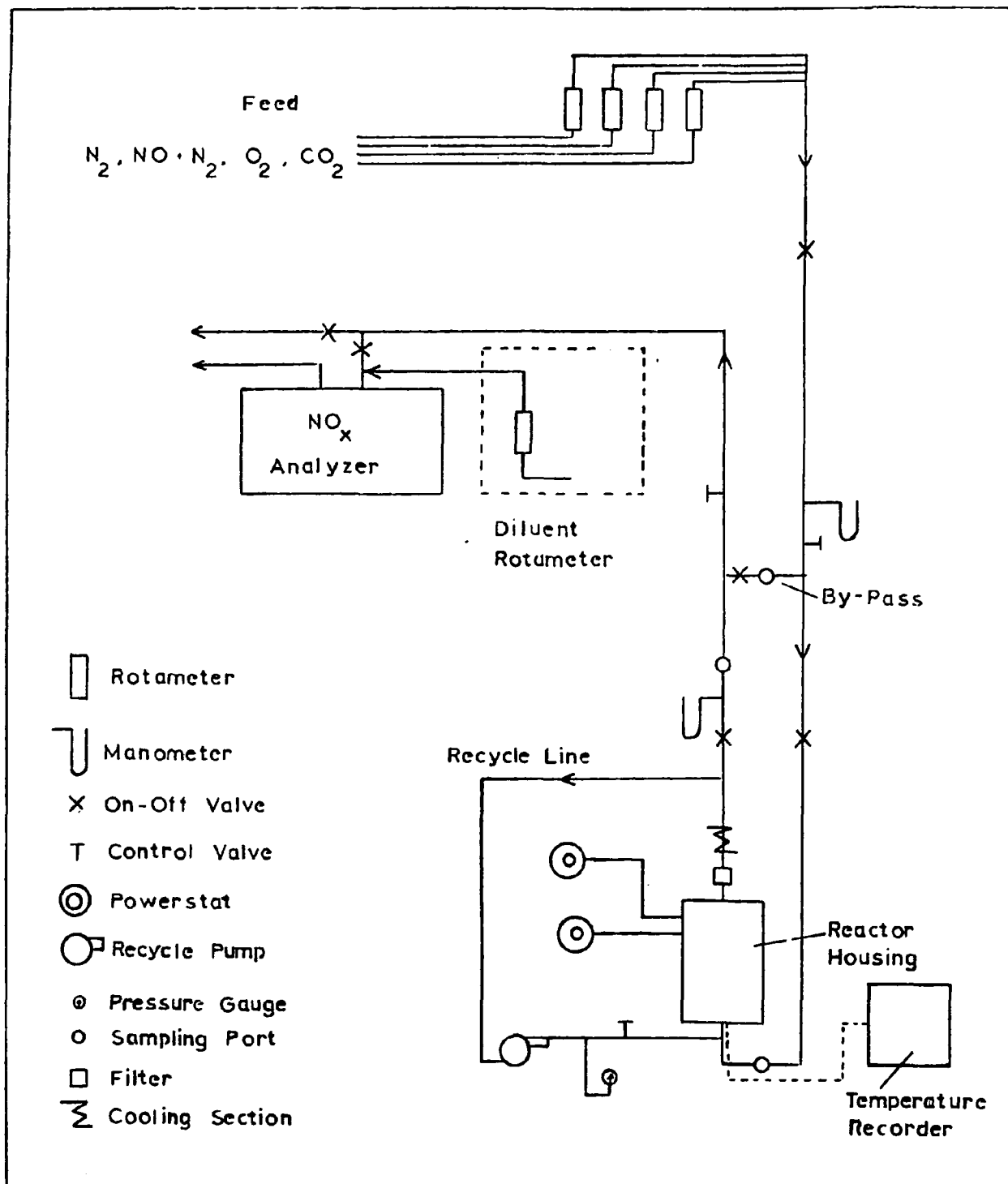
FIGURE 5. Schematic of the Apparatus used with the Tubular Reactor for Synthetic Flue Gas Tests

During the late stages of the project a Thermo-Electron Model 10A Chemi-luminescent analyzer became available and this was used to determine NO and NO_x concentrations, especially when working with NO_x concentrations below 1,000 PPM when O_2 was also present. N_2 and O_2 concentrations were determined using a molecular sieve 13X column in the chromatograph.

Reacted solids were analyzed for sulfate using simple barium precipitation techniques.

SECTION V

EXPERIMENTAL RESULTS

PRELIMINARY SCREENING

For the preliminary tests, approximately 20 grams of the sulfide were placed in the reactor and then pure NO was injected at a rate of about 0.3 liters/hour while the reaction zone was being heated. Samples of the exit gas were taken periodically and analyzed by the gas-chromatograph for NO, N_2O and N_2. The temperature at which N_2O or N_2 was first detected was noted and the heating was continued until complete conversion (within the sensitivity of the chromatograph) of the NO to N_2 was obtained. The reactor was then purged with helium while cooling and then the reacted sulfide was weighed and when positive weight gains were noted tested for sulfate by the barium precipitation method. The results of these preliminary tests are presented in Table 2. As can be seen from the data presented in Table 2, virtually all of the metal sulfides tested resulted in the reduction of pure NO to N_2 but the temperature range in which the reaction proceeds varies widely. Actually, the temperature at which the reaction will proceed also probably depends on a number of uncontrolled variables such as particle size (surface area), bed packing, and fluid-particle dynamics. But these data give an indication of overall reactivity of the various sulfides and was sufficient for the preliminary tests.

Many of the sulfides reacted with pure NO to form at least some sulfate but analysis for other possible reaction products was not carried out and other oxidation products are also possible. Al_2S_3, Sb_2S_3, BiS, CuS, FeS, MnS, HgS, MoS_2, K_2S, WS_2, and Tl_2S all lost weight during reaction. Visual inspection showed that considerable elemental mercury was formed when HgS was tested, but the final form of the other materials was not determined and most of them were not considered further. Al_2S_3 is unstable and reacts with atmospheric water to form H_2S and, as a result, probably would not be practical for use under any conditions.

Based on the success of the initial tests, several of the sulfides which appeared to have promise were tested further to see if the reduction reaction could be catalytically promoted. The first candidate catalysts tested were Fe_2O_3 and Cr_2O_3 since these have been reported to increase the rate of reduction of NO with carbon monoxide (3) but the catalytic effects of these materials were negligible. However, the addition of about 5 Wt. % $CoCl_2$ or $FeCl_2$ to CaS resulted in a pronounced (about 200°C) decrease in the temperature at which the reduction reaction proceeded although they appeared to exhibit this effect only in the temperature range between 250 to 300°C. The reaction rate declined at temperatures above 350°C and the mixtures were relatively inactive until a temperature of about 450°C was again reached. Based on the success of these tests, other compounds were tried on a trial and error basis with the tests being limited to materials on hand.

TABLE 2. PRELIMINARY TESTS OF VARIOUS METAL SULFIDES FOR NO REDUCTION

Reducing Agent	Temperature of Reaction Initiation, °C	Temperature for 100% Conversion	Weight Change	Sulfate Test
Al_2S_3	250	400	loss	
Sb_2S_3	200	550	loss	
BaS	475	650	gain	?
BiS	350	600	loss	
CdS	650	800	gain	+
CaS	450	650	gain	+
CuS	250	500	loss	
Cu_2S	450	700	gain	+
FeS	300	525	loss	
PbS	250	550	gain	+
MnS	475	550	loss	+
HgS	450	650	loss	+
MoS_2	400	500	loss	
SrS	400	650	gain	+
K_2S (sulfurated potash)	100	450	loss	
WS_2	250	500	loss	
ZnS	550	800	gain	+
NiS	90	360	gain	
Tl_2S	--	--	loss	

For these tests 20 grams of powdered sulfide were physically mixed with 20 Wt. % of the candidate catalyst using a mortar and pestle. Again, the test gas was pure NO at a rate of 0.3 liters per hour. The results of these tests are presented in Table 3.

As can be seen from Table 3, the addition of $CoCl_2$, $NiCl_2$, $FeCl_2$, and K_3CrF_6 to CaS significantly reduced the temperature at which the reduction reaction proceeded while Fe_2O_3, Cr_2O_3, $CaCl_2$, $CuCl_2$, $FeSO_4$, K_3ZrF_6, $PdCl_2$, and $PtCl_2$ had little or no effect on the reaction. K_3FeF_6 and $NiCl_2$ also reduce the reaction temperature with BaS, SrS, ZnS, MoS_2, and FeS_2. NaCl and $CaCl_2$ both appear to enhance the reaction with BaS while CuCl appears to exhibit a catalytic effect with Cu_2S, MoS_2 and FeS_2.

A violent, highly exothermic reaction occurred when argentic (silver) fluoride, AgF_2, was mixed with CaS, and so this material was not tested further.

These tests showed that at higher temperatures when using some of the promoters another peak showed up in the gas analysis using the internal Q-S

TABLE 3. CATALYST STUDIES FOR NO REDUCTION USING VARIOUS SULFIDES
TEST GAS PURE NO

| Catalyst | Sulfide | Temp. for Initial Reduction with Unpromoted Sulfide, °C | Temperature at Which Reaction Product Observed, °C | | | |
			N_2O	N_2	100% NO Conversion	Weight Change
K_3FeF_6	BaS	475	200	350	700	gain
	BiS	350	450	350	--	loss
	CdS	650	350	350	--	loss
	CaS	450	--	250	400	gain
	CuS	250	350	250	550	gain
	FeS	300	250	200	600	gain
	MoS_2	400	300	300	450	loss
	SrS	400	200	200	500	gain
	ZnS	550	500	500	700	loss
$CuCl_2$	CdS	650	300	300	--	loss
	CaS	450	--	--	450	gain
	Cu_2S	450	--	350	--	--
	CuS	250	350	350	--	loss
	FeS	300	100	100	--	loss
	MoS_2	400	350	350	550	gain
$CaCl_2$	BaS	475	200	300	600	gain
	CaS	450	250	400	650	gain
	FeS	300	150	250	550	no change
$NiCl_2$	BaS	475	100	300	--	gain
	CdS	650	100	250	--	no change
	CaS	450	100	325	450	gain
	CuS	250	100	400	--	loss
	FeS	300	50	200	550	loss
NaCl	BaS	475	400	450	650	gain
	CdS	650	--	600	--	no change
	CaS	450	300	450	700	gain
NaF	BaS	475	250	300	450	gain
	CdS	650	350	450	--	gain
	CaS	450	250	400	--	gain

TABLE 3 (continued)

Catalyst	Sulfide	Temp. for Initial Reduction With Unpromoted Sulfide, °C	N_2O	N_2	100% NO Conversion	Weight Change
NaI	BaS	475	250	400	--	gain
	CdS	650	500	500	--	gain
	CaS	450	250	400	650	gain
K_3FeF_6+ NaCl	BaS	475	250	350	450	gain
	CdS	650	150	450	--	no change
	CaS	450	250	300	550	gain
Fe_2O_3	CaS	450	--	450	--	--
Cr_2O_3	CaS	450	--	450	--	--
$CoCl_2$	CaS	450	--	250	--	--
$FeCl_2$	CaS	450	--	255	--	--
$FeSO_4$	CaS	450	--	390	--	--
K_3ZrF_6	CaS	450	--	400	--	--
K_3CrF_6	CaS	450	--	300	--	--
$PdCl_2$	CaS	450	--	450	--	--
$PtCl_2$	CaS	450	--	450	--	--
AgF_2	CaS	--	--	--	--	--

Porapak column. This was identified as SO_2. Further tests were carried out to better define the conditions for SO_2 formation. These data are presented in Table 4. The same conditions as used in the catalyst tests were used in this study.

Significantly, the reduction reaction proceeds at temperatures below the temperature at which SO_2 is produced and SO_2 was not formed from BaS or CaS under these conditions. Several preliminary runs also investigated the reduction using a dilute NO feed stream. Helium was chosen as the diluent for these tests because of its inertness and because it did not interfere with the chromatographic analysis. Table 5 presents the tests using a gas stream containing 2.5% NO in He using the same run conditions and procedures as before.

These data are somewhat different from the results presented when 100% NO was used as the test gas using the same catalysts. The temperature at which N_2O and N_2 were first observed is generally lower and the temperature required for 100% conversion of the NO is somewhat higher. This is a result of using a lower attenuation on the chromatograph for the more dilute samples. At the higher sensitivity the NO, N_2O, and N_2 were more readily detected.

TABLE 4. PRELIMINARY TESTS FOR SO_2 FORMATION

System	Temperature at Which Reaction Product First Observed, °C		
	SO_2	N_2O	N_2
$Cu_2S-NiCl_2$	550	100	400
FeS_2-NiCl_2	450	50	200
$CdS-NiCl_2$	450	100	250
$BaS-NiCl_2$	--	100	300
$CaS-NiCl_2$	--	100	325
$BaS-NaCl$	--	250	150
$CaS-NaCl$	--	250	50
$CdS-NaCl$	--	--	300
$BaS-CaCl_2$	--	200	300

To further simulate what might be present in an actual effluent gas stream, further runs were made with gas stream containing both O_2 and O_2 plus H_2O using the $CaS-K_3FeF_6$ system. Test gas compositions were: 2.5% NO, 5.0% O_2 and 92.5% He and 2.4% NO, 4.9% O_2, 2.7% H_2O and 90% He. Test results were nearly identical to the tests of the dilute gas stream without O_2 or H_2O although with H_2O present there appeared to be some H_2S formed.

The analysis of the gas mixture containing both NO and O_2 presented some problems since they react to form NO_2 and this appeared to be irreversibly absorbed in the chromatograph column. However, the complete disappearance of an NO peak together with the appearance of a larger N_2+O_2 peak and a N_2O peak indicated that the reduction reaction was occurring. In addition, there was a consistent weight gain of the sulfide-catalyst mixture.

TABLE 5. REDUCTION USING 2.5% NO IN He

System	Temperature for 100% NO Conversion	Temperature at Which Reaction Product First Observed		Weight Change
		N_2O	N_2	
	°C	°C		
$CaS-K_3FeF_6$	600	50	150	gain
$CaS-K_3FeF_6+NaCl$	600	100	200	gain
$BaS-NaF$	550	100	150	gain
$BaS-K_3FeF_6+NaCl$	600	100	200	gain

To further characterize the solid product of reaction, a run lasting nine days was made using calcium sulfide. Pure NO was passed through the reactor

while it was maintained at temperatures between 450 and 700°C. After nine days, N_2 was still being produced but at a very low rate thought to be limited by diffusion through the outer reacted layer. The solid reaction product analyzed 87.2% $CaSO_4$.

DISCUSSION OF PRELIMINARY RESULTS

The preliminary results were very interesting and encouraging. Nineteen sulfides were tested for NO reduction and all gave positive results. Of these, BaS, CaS, CdS, Cu_2S, NiS, PbS, SrS, and ZnS all gained weight during reaction indicating that undesirable side reactions producing gaseous sulfur compounds may not be occurring. The alkaline earth sulfides BaS, CaS and SrS looked particularly attractive. Of these, CaS probably would be preferable because of availability and cost. In addition, CaS can easily be regenerated from the sulfate by reduction with CO, H_2 or Coke (6.7).

The temperature required for the reduction reaction to proceed was lowered considerably by mixing certain materials with the powdered sulfide. This effect may or may not be catalytic in nature and the mechanism is not known. It is possible that the promoter takes part in the reaction and is chemically altered and thus not a true catalyst. The most active materials found were metal chlorides and fluorides with K_3FeF_6, $NiCl_2$, NaF, $CoCl_2$, and $FeCl_2$ being the most active. It is interesting to note that certain metal chlorides form metal complexes ($FeNOCl_2$, for example) with NO.

The nine day run with CaS indicated that diffusion through the outer layer probably controls the rate of reaction after the sulfide on the outer surface has reacted. This indicates that a fluidized bed of very fine particles or sulfide impregnated on a high surface area support may be necessary to obtain high rates of reaction and efficient use of the reactant.

Oxidation by free oxygen may also present problems. In the preliminary runs, only one test was made using a gas stream containing free oxygen. Under this condition it appeared that the reduction of NO_x was occurring but it could not be determined whether or not O_2 was also contributing to the oxidation of the sulfide.

Hence, subsequent tests were made of sulfides impregnated on high surface area carriers and an investigation was made of the relative rates of reaction of NO and O_2.

PRELIMINARY TESTS OF CaS IMPREGNATED ON SUPPORTS

Because of the apparent diffusional limitations through the outer reacted sulfate layer, a study was made of the use of sulfide dispersed on high surface area solid supports to see if this problem could be reduced. The properties of the support materials that were tested are shown in Table 6. These included a high surface area silica-alumina, a molecular sieve developed for SO_2 adsorption, and two aluminas, one with 6% silica and the other with low impurity levels. These were impregnated with calcium sulfide in the following manner: The support material was first dried in a muffle furnace at about 400°C for 24 hours and allowed to cool in a desiccator and weighed. The dry pellets were then impregnated with $Ca(NO_3)_2$ by dissolving appropriate amounts of the salt in distilled water and pouring this solution over the dry

pellets. The pellets were left in the solution for about 24 hours to insure saturation before the excess solution was filtered from the pellets. They were then dried in air and calcined at about 400°C for 24 hours to convert the nitrate to the oxide, CaO. The pellets were cooled and weighed again to determine the amount of CaO that had been deposited on the pellets. The oxide was then converted to the sulfide by placing the pellets in the reactor and passing a mixture of 20% H_2S in H_2 over them while the reactor was heated to 500°C. The course of the reaction was followed by periodically analyzing the exit gas stream for H_2S and H_2O. Although in most cases it appeared that conversion was complete at about 400°C, the sulfiding reaction was continued up to 500°C to insure complete conversion of the oxide to the sulfide. This procedure is commonly used for forming the sulfide in hydrotreating catalysts which are normally made via an oxide intermediate. In some cases, a catalyst was also dissolved in the $Ca(NO_3)_2$ solution.

TABLE 6. PHYSICAL PROPERTIES OF SUPPORT MATERIAL

Material	Nalco 1290-A	Harshaw AL-1602-T	Alcoa H-51	Linde MS-TM-0-1114
Density (gr/cc)	0.35	.83	.95	--
Surface Area (M^2/gr)	270	210-240	350	--
Pore Volume (cc/gr)	1.22	0.48	0.50	0.53
Pore Diameter (A)	180	91-80	60	Synthetic crystalline metal aluminum silicate containing sodium.
SiO_2 (%)	74.7	6.0	--	
Al_2O_3 (%)	23.0	91.0	--	Material developed for SO_2 adsorption
Na_2O (%)	0.05	--	--	
Physical form	1/8" extrusions	1/8" pellets	8-14 mesh	1/16" extrusions

The NO reduction tests were carried out without removing the pellets from the reactor for weighing. Pellet sulfide compositions were assumed to be a result of complete conversion of the CaO to CaS.

The following summarizes the results of the preliminary runs using pellets impregnated with calcium sulfide.

Run 1

7.2 wt. % CaS (only) on Harshaw Al-1602-T. Test gas: Pure NO, 0.3 standard liters per hour.

Remarks--
Some N_2O was formed at room temperature and the amount increased up to about 180°C. At 150°C the exit gas analyzed about 10% N_2O, 10% N_2, and 80% NO. Some N_2 was formed at the lower temperature and the amount of N_2 in exit gas increased at temperatures above 300°C but conversion was not complete

until a temperature of about 400°C was reached. At 400°C there was no N_2O present in the exit gas. At constant temperature, the rate of reaction decreased rapidly with time indicating diffusional limitations.

Run 2

7.2 wt. % CaS+2.5% $NiCl_2$ on Harshaw Al-1602T. Test gas: Pure NO, 0.3 standard liters per hour.

Remarks--

At 60°C there was nearly complete conversion of the NO to N_2O. The main product was N_2O up to about 250°C where the reaction shifted, giving lesser amounts of N_2O and larger amounts of N_2. At 300°C the exit gas was 100% N_2. The run was continued holding the reactor constant at 375°C and there was complete conversion of the NO to N_2 for about 7 hours. After NO breakthrough the proportion of NO in the exit gas steadily increased.

Pellet weights: 50.00 grams original pellets
                    52.53 grams after impregnation/calcination
                    53.90 grams at end of run

Qualitative analysis of the spent pellets showed that considerable sulfate had been formed and that chloride was still present in the pellets indicating that the nickel was still in the chloride form.

Run 3

4.5 wt. % CaS+1.5% $NiCl_2$ on Alcoa H-51. Test gas: Pure NO, 0.3 standard liters per hour.

Remarks--

Using this material the reaction started at about 65°C when the exit gas analyzed about 35% N_2O, 65% N_2. The proportion of N_2O increased up to about 100°C when the exit gas was about 85% N_2O, 15% N_2 with no detectable NO. At 270°C the composition was 40% N_2O, 45% N_2 and 15% NO. At 380°C it was 95% N_2 and 5% NO. The proportion of NO steadily increased as the temperature was held constant at about 390°C for the remainder of the 8-hour run even though the gas feed rate was dropped from 0.3 to .07 standard liters per hour.

Pellet weights: 50.0 grams original pellets
                    51.8 grams after impregnation/calcination
                    53.6 grams at end of run

Run 4

5.3 wt. % CaS+1.8% $NiCl_2$ on Linde TM-0-1114. Test gas: Pure NO, 0.3 standard liters per hour.

Remarks--

Using this material it appeared that a large amount of NO was physically adsorbed by the pellets at room temperature when the NO feed was first introduced since the analysis showed mostly He (purge) in the exit gas for the first 1/2 to 3/4 hour. After about one hour of operation (during which

time the reactor was heated to 100°C) the exit gas appeared to be 100% N_2 but as the reactor was further heated, N_2O appeared and the amount increased with increasing temperature. At 190°C the exit gas analyzed 26% N_2O, 74% N_2; at 250°C, 50% N_2O and 50% N_2, and at 285°C, about 3% N_2O and 97% N_2. The temperature was then held constant at about 300°C as the test was continued and the exit gas analyzed 100% N_2 for the next four hours. Then, over the next hour period, the composition changed to about 10% N_2O, 45% N_2, and 45% NO. The temperature was then increased to 500°C where conversion was again to 100% N_2 at an NO feed rate of 0.07 standard liters per hour.

Pellet weights: 50.00 grams original pellets
                   52.18 grams after impregnation/calcination
                   54.10 grams after NO reaction

Run 5

8.1 wt. % CaS+2.7% $NiCl_2$ on Nalco 2910-A. Test gas: Pure NO, 0.15 standard liters per hour.

Remarks--
     For this run only 30.9 grams of pellets could be loaded in the reactor because of their low bulk density. Using these pellets there was little reaction at the lower temperatures. At 110°C the exit gas analyzed 17% N_2O, 3% N_2, and 80% NO. At 280°C it was 56% N_2O, 27% N_2, and 17% NO. Complete conversion to N_2 was attained at 475°C. A temperature of 510°C was then maintained for the next three hours of the run. Analysis of the exit gas showed that there was complete conversion to N_2 at this high temperature but it also showed that a large mount of SO_2 was also being evolved. The temperature was then reduced to about 425°C where the exit gas contained no SO_2, but there was about 30% NO in the exit gas at this temperature.

Pellet weights: 29.8 grams original pellets
                   30.9 grams after impregnation/calcination
                   31.2 grams after NO reaction

Subsequent tests were made using a test gas containing 2.5% NO in helium to determine the effects of space velocity on the reduction of NO.

Run 6

7.2 wt. % CaS+2.5% $NiCl_2$ on Al-1602-T.

Remarks--
     For this test the reactor was purged with He as it was heated to 230°C and the reactor was held at this temperature and the pellets tested with the 2.5% NO - Helium test gas with the following results:

°C Temp.	Time on Stream Hours	Gas rate - Standard liter/hr.	Exit Gas Composition (He free)
230	0-5	2.2	100% N_2
	5-6	6.5	100% N_2
	6-7	12.2	35% N_2, 65% NO, trace N_2O
	7-8	22.7	20% N_2, 80% NO, trace N_2O
	8-10	2.2	40% N_2, 40% NO, 20% N_2O
325	10-12	2.2	100% N_2
	12-13	6.5	81% N_2, 9% NO, 10% N_2O
	13-15	13.2	SO_2 in exit gas
440	15-17	13.2	large amounts of SO_2 in exit gas - rest 100% N_2

Run 7

12% MoS_2 on Al-1602-T

Remarks--

These pellets were made by impregnating the pellets with MoO_3 dissolved in NH_4OH solution, drying, calcining and converting the oxide to the sulfide in the usual manner. They were treated with the 2.5% NO in helium gas with the following results:

°C Temp.	Time on Stream Hours	Gas rate - Standard liter/hr.	Exit Gas Composition (He free)
167	0-4	2.2	65% N_2, 35% N_2O
200-325	4-13	2.2	100% N_2
325	13-16	6.5	large SO_2 peak, otherwise 100% N_2
325	16-20	2.2	large SO_2 peak, otherwise 100% N_2

Pellet weights: 50.00 grams original pellets
                    56.16 grams after impregnation/calcination
                    57.85 grams after NO reaction

Run 8

7.3% ThS_2 on Al-1602-T

Remarks--

These pellets were made by impregnating the alumina with a solution of thorium nitrate, drying, calcining and converting the oxide to the sulfide

in the usual manner. They were tested using the test gas containing 2.5% NO with the following results:

°C Temp.	Time on Stream Hours	Gas Rate - Standard liter/hr.	Exit Gas Composition (He free)
90-510	0-14	2.2	100% N_2, all temperatures
510	14-17	22.7	100% N_2, trace N_2O, large SO_2 peak
			(An SO_2 peak appeared the last 3 hours of the run.)

Pellet weights: 50.00 grams original pellets
53.26 grams after impregnation/calcination
53.45 grams after NO reaction

Several important conclusions can be made from these tests. First, it appears that a very active form of the sulfide can be made by dispersing it and a catalyst on a high surface area support. If it were desirable to develop a process based on sulfide pellets, the selection of the support material would be very important since the four materials evaluated behaved very differently in the testing. The performance of the two aluminas and the molecular sieve pellets were satisfactory from a standpoint of initial activity but there appeared to be significant diffusional resistance after only a few hours of operation, especially with the molecular sieve and H-51 alumina pellets. The performance of the high-silica pellets was unsatisfactory because of a low activity and because of the side reaction which consumed sulfur. The 6% SiO_2 pellets (Al-1602-T) also produced SO_2 during the latter part of the runs.

The mechanism of the SO_2 formation is not known but there are several possibilities, among them:

$$CaSO_4 + SiO_2 \rightarrow SO_2 + CaSiO_3 + 0.5O_2 \qquad (1)$$

$$CaS + SiO_2 + 3NO \rightarrow SO_2 + CaSiO_3 + 1.5N_2 \qquad (2)$$

Reaction (1) has been studied as a means of desulfuring gypsum but apparently the reaction requires temperatures on the order of 1250°C when using bulk quantities of gypsum and silica sand (8). Since there is considerable silica in both the Al-1602-T and 1290-A pellets, both reactions are distinct possibilities. This follows since SO_2 was only observed after a run had proceeded for some time when there was considerable $CaSO_4$ present and at higher temperatures.

The tests made with MoS_2 and ThS_2 dispersed on alumina pellets were interesting because of their high activity and because analysis showed that very little sulfate was formed. However, with these materials there was also a large amount of SO_2 formed late in the run and so these materials were not investigated further.

At temperatures below about 250°C and at higher space velocities, there was considerably N_2O formation. This may be acceptable, however, because N_2O is less of a concern than NO and NO_2.

The low capacity of the impregnated pellets is disturbing and thought to be due to diffusional limitations. There are at least two possible mechanisms for the rapid decline in activity with use. If the reactions proceed throughout the pellet, there still may be diffusional limitation caused by diffusion limitations through the $CaSO_4$ layer dispersed throughout the pellet. On the other hand, if the reaction proceeds inwardly from the outside of the pellet, severe pore diffusion limitations may result.

Figure 6 presents the results of a series of 3 runs to show typical break-through curves. In each of the 3 runs, 13 grams of pellets from the same batch (7.2% CaS+2.5% $NiCl_2$ on AL-1602-T) were evaluated using a test gas containing 2.5% NO in He with a gas flow of 5 liters/hour. As can be seen at 300°C there is NO in the exit gas from the beginning of the run while about 4.5 hours were required for break-through at 400°C.

The upper curve in Figure 6 presents results of a run using material from the same batch but crushed and screened to 14 mesh. This was done in an attempt to test for pore diffusion; however, the results of this run are poorer than with the whole pellets. This may have been due to poor contact because of channeling in the bed of smaller particles or, a more likely possibility is that there was air oxidation of the pellets during crushing and screening. In comparing the results of these tests with Run #6 that was previously described, it can be seen that the performance was not as good as in Run #6. This further indicates air oxidation of the sulfide since these pellets were exposed to air while those in Run #6 were not.

Subsequent tests were aimed at determining the rate of reaction of CaS impregnated on the different supports and comparing the rate of reaction of some of the sulfides with NO and O_2. The electrobalance was used for these studies.

ELECTROBALANCE STUDIES

The pellets for this study were prepared as previously described and the pellets were stored under a nitrogen blanket until needed. For these tests, only CaS was impregnated on the pellets since it appeared that the addition of a catalyst such as $NiCl_2$ also resulted in SO_2 being formed.

A prepared pellet was tested by placing it on the weighing pan of the electrobalance and the hang down tube was purged with pure helium while the tube was heated to the desired temperature. The purge was continued until the weight remained constant (there was usually a weight loss due to moisture loss). Then a 2.5% NO, 97.5% He mixture was passed through the tube at a rate of about 11 cc/min. For all of the tests except one only, one pellet was placed on the weighing tray for testing. In the other test, 5 pellets were used. Table 7 gives the reaction conditions for the various tests.

The results of the reaction rate determination are conveniently shown on plots which indicates both the pellet weight and the rate of reaction as a function of time. The rates of reaction (which is the slope of the weight
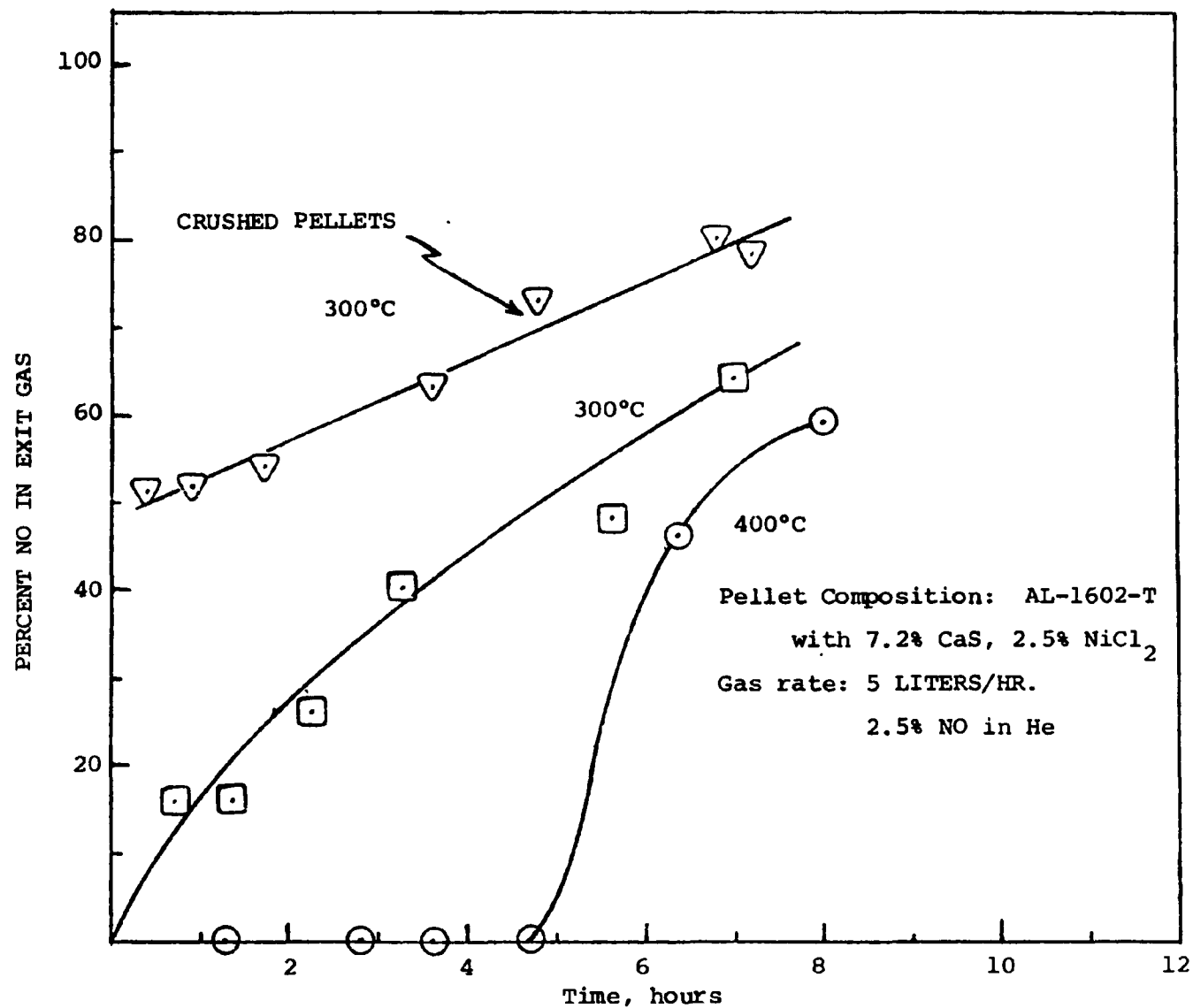
FIGURE 6 - Break Through Curves for CaS Pellets Promoted with $NiCl_2$

versus time curve at any point) were determined by evaluating the slopes of the weight curve by a least squares technique over small intervals.

TABLE 7. REACTION CONDITIONS

Run No.	Type of Support	Temp. °C	CaS (Wt. %)	Test Gas Flow Rate (Std.cm^3/ sec.)	Helium Purge Thru Bell Jar (Std.cm^3/ sec.)	Total Run Time (hr)	No. of Pellets
1	Harshaw 1602-T	390	8.6	.18	.046	7	1
2	Harshaw	410	8.6	.15	.045	9-1/2	1
3	Harshaw	437	8.6	.16	.045	8	1
4	Harshaw	438	8.6	.18	.045	9	1
5	Harshaw	468	8.6	.20	.032	5	1
6	Harshaw	493	8.6	.18	.045	4	5
7	Harshaw	442	8.6	.16	.045	18	5
8	Harshaw	440	.9*	3.48	.052	4	1
9	Harshaw	444	.9*	.12	.052	3-1/2	1
10**	Harshaw	444	.9*	.12	.063	4-1/2	1
11	Linde TM-0-1114	392	6.6	.14	.043	12	1
12	Linde	410	11.4	.14	.043	4	1
13	Linde	438	6.6	.17	.043	18-1/2	1

* Pellets were pre-oxidized by contact with air
**Feed gas composition was 2.5% O_2, 97.5% He

The time derivatives are shown on the plots only as points rather than curves because of the scatter in the data. This scatter is typical of derivative data.

The results of the runs are presented in Figures 7 through 18. Some of the data exhibit periods of increasing rate of reaction several hours into the run after a period of steadily decreasing rate. These are all thought to be due to changing controlling resistances and non-isothermal effects caused by the highly exothermic reaction. The two lower temperature runs, Figures 7 and 8, are examples of this.

Figures 9 and 10 show the results of runs carried out at nearly the same temperature to determine reproducibility. The results of these two runs are in fair agreement as can be seen by comparing the rates at any given time. For the first three hours the rates are approximately constant at about 0.45×10^{-4} moles/hour per gram and then the rate gradually drops to zero after about nine hours. There are many mechanism that can explain this behavior.
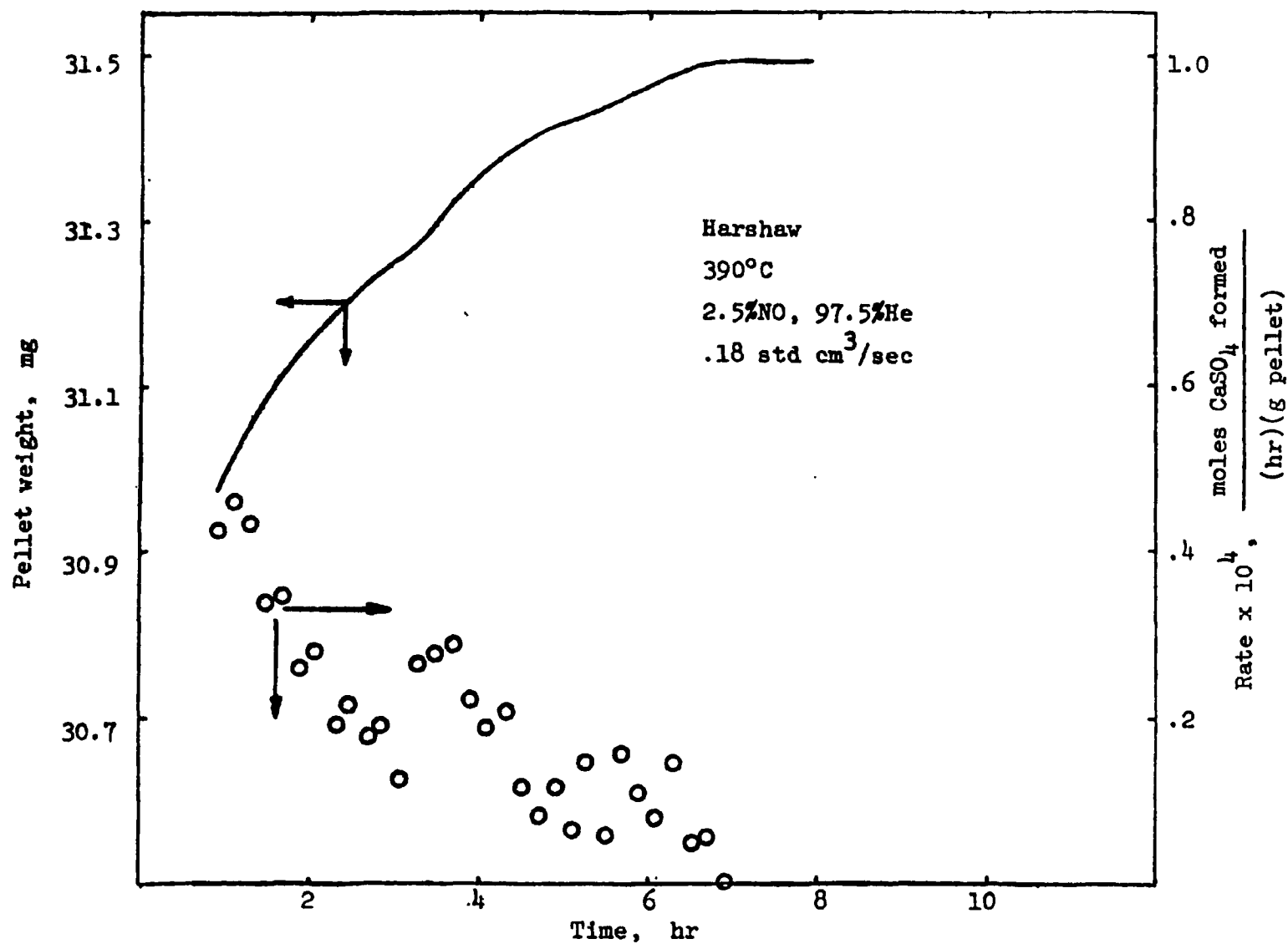
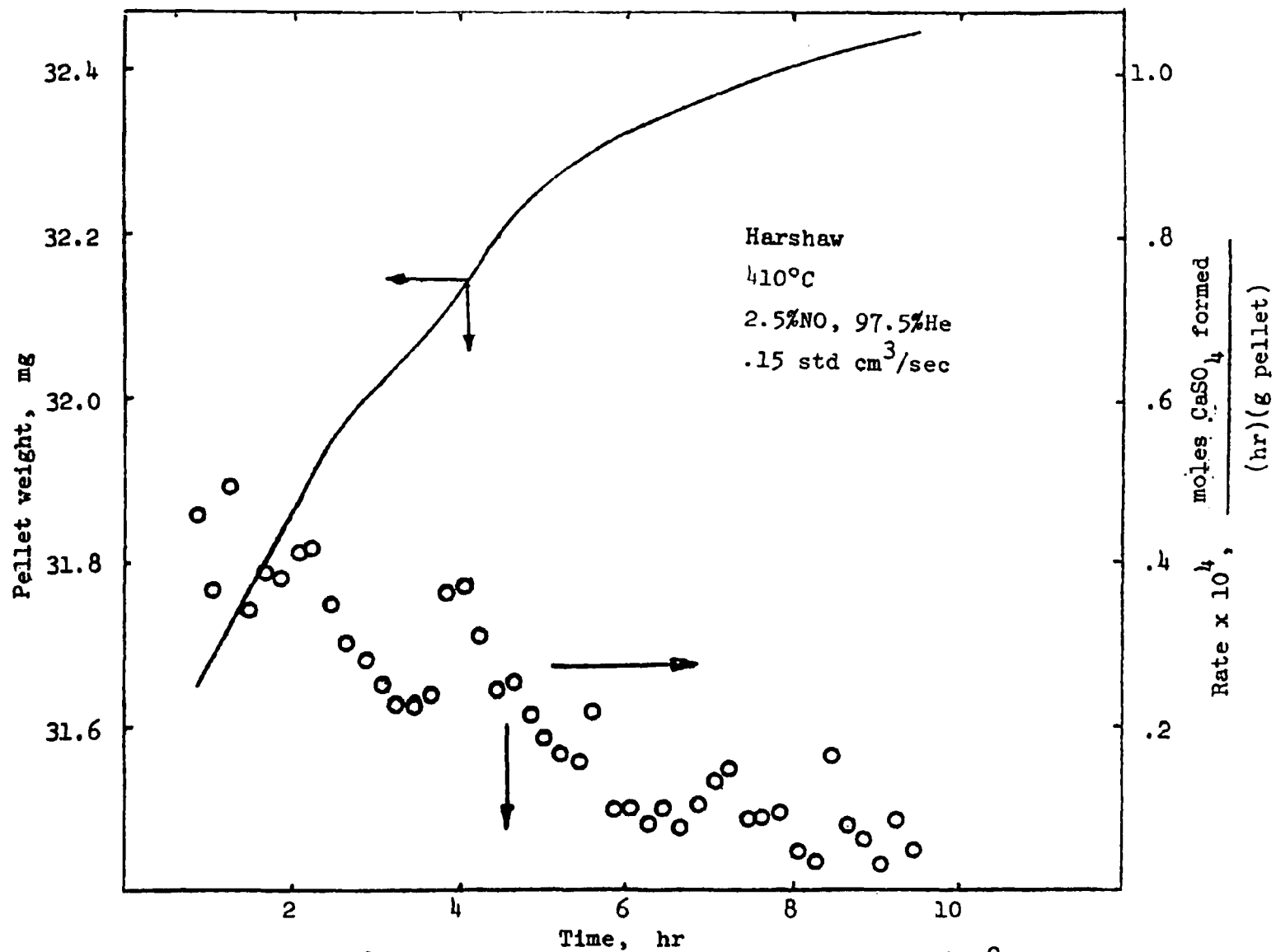Figure 7. Reaction data for a Harshaw pellet at 390°C
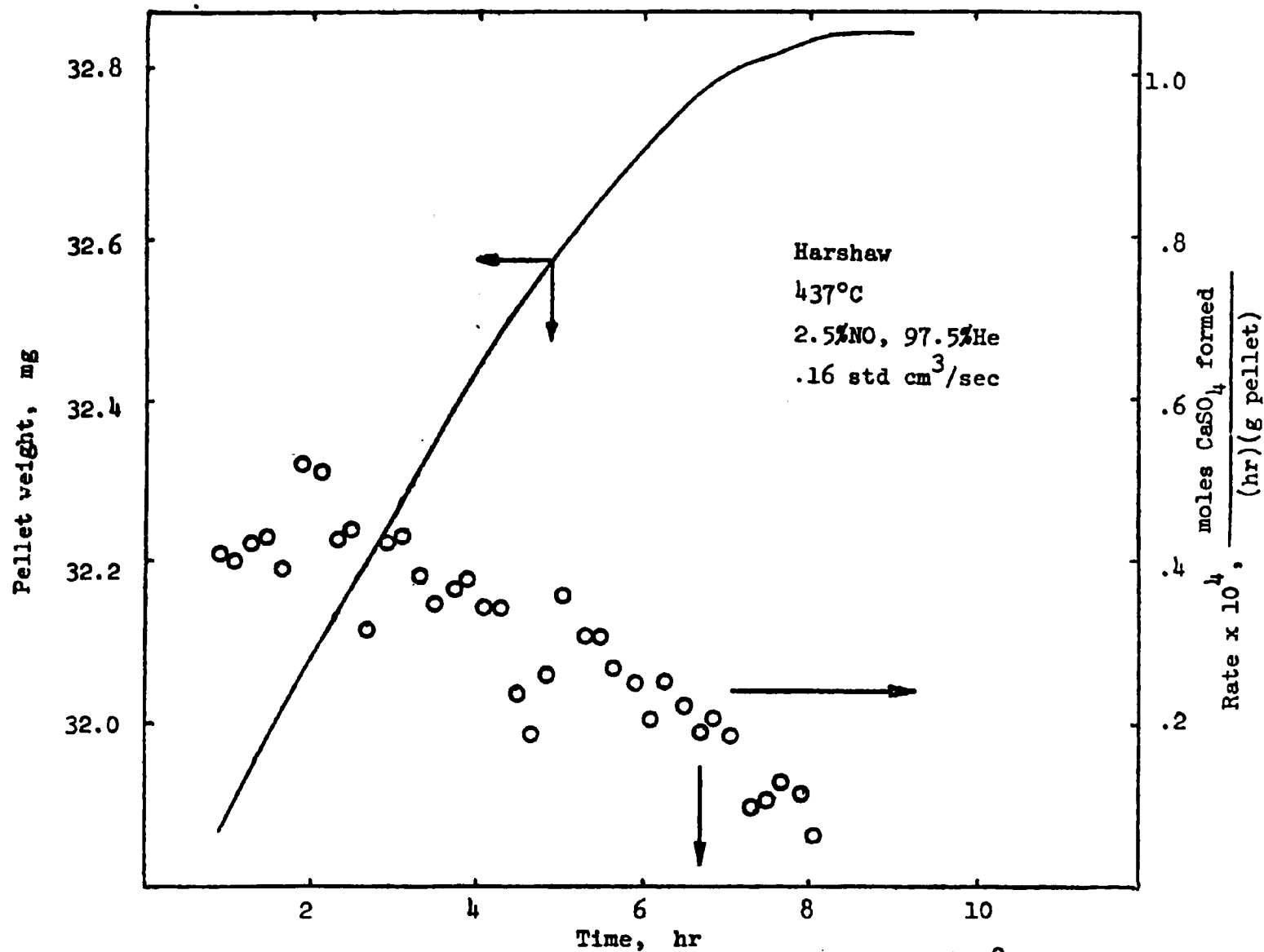
Figure 8. Reaction data for a Harshaw pellet at $410°C$
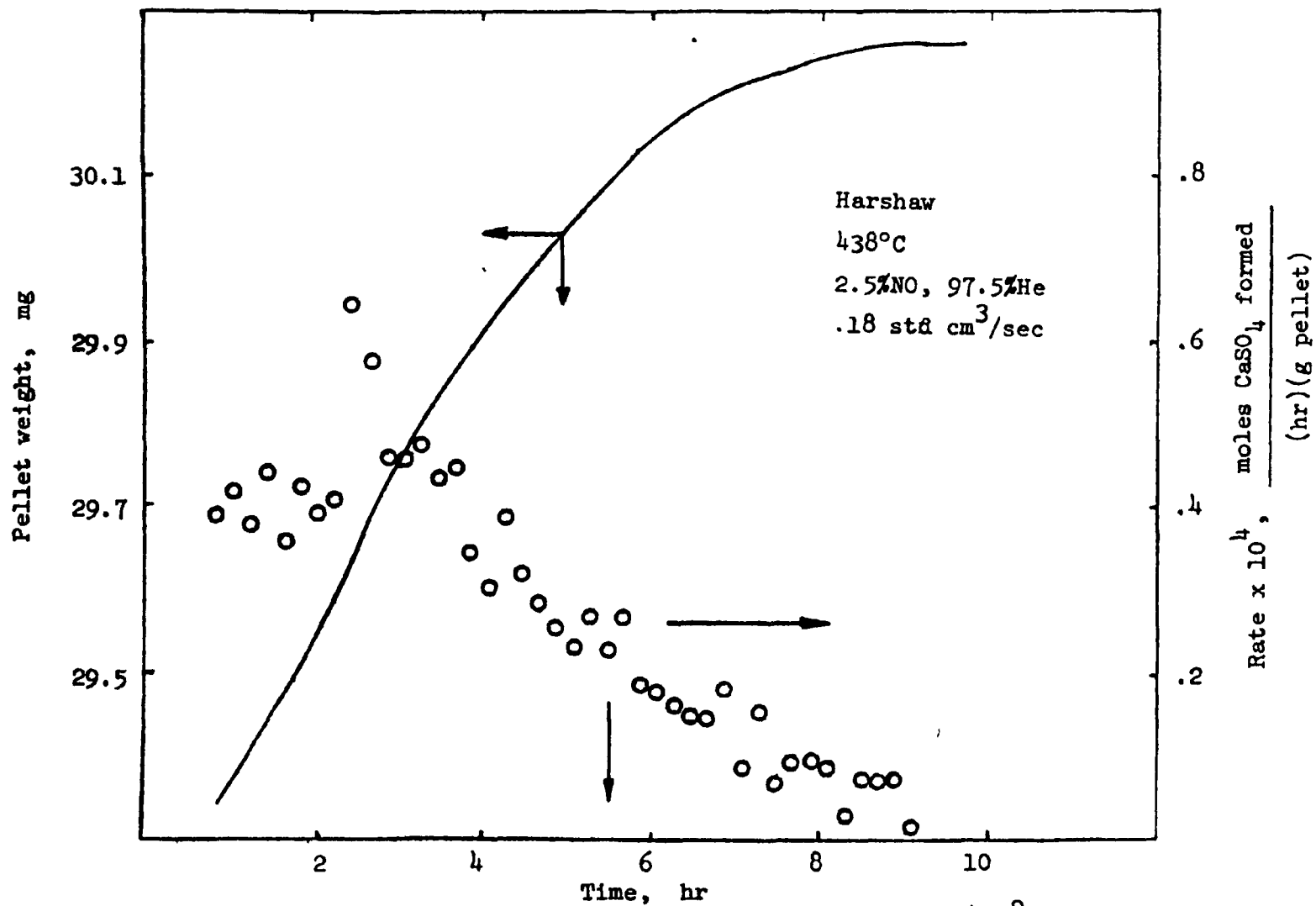
Figure 9. Reaction data for a Harshaw pellet at 437°C

Figure 10. Reaction data for a Harshaw pellet at 438°C

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However, it may be an indication that the reaction is occurring throughout the pellet and the rate remains high as long as easily accessible CaS remains on the surface. When the CaS on the surface is reacted, the reaction may be controlled by a slower diffusion of the NO through reacted layers of sulfate. If pore diffusion were controlling for this situation, there would be a very rapid decline in activity as the material near the outer surface was consumed.

At the higher temperatures investigated (468 and 493°C), shown in Figures 11 and 12, pore diffusion may be the controlling resistance since for these runs there is a period of nearly constant reaction rate followed by a very rapid decline in activity over a two hour period.

Figure 13 presents the results of a run made at 442°C with 5 pellets on the pan in a pile (some on top of others) in a random manner. The weight versus time curve exhibits a classical sigmoid shape for this case. This is thought to be due to non-isothermal temperature effects in the pile caused by the highly exothermic reaction. The average rate of reaction for this case was about an order of magnitude less than for the single pellet runs. This is probably due to stagnant gas pockets within the pile since gas flow was around the pan rather than through the pile. The single pellet data are probably more representative of the rate that would be obtained in a packed bed reactor where gas flow would be through a bed of pellets.

Figures 14 and 15 are a comparison of the rate of reaction of the Harshaw pellets with NO and O_2. As can be seen, the initial rate of reaction with O_2 was very high (about 2.4×10^{-4} moles/hr. gram) being about 6 times the rate observed for NO. However, the reaction quickly slowed and after the first hour was at a rate comparable to that with NO.

The last three pellet tests on the microbalance used Linde Molecular Sieves TM-0-1114. These data are presented in Figures 16 through 18 for temperatures of 392, 410, and 438°C respectively. All of the runs made with the molecular sieve pellets exhibited a very high initial rate of reaction (up to 3 times the rate observed with the Harshaw pellets) but there was a very rapid decline in rate. As previously discussed, this is typical of a system in which pore diffusion is important and activity rapidly declines as the CaS near the outer surface reacts.

Because of difficulties in comparing the runs made at different temperatures, average rates for each run were computed. Table 8 presents the integrated average rates for each run. Though instantaneous rates vary without much pattern, the average rates consistently increase with temperature as would be expected.

For the single Harshaw pellets the rate increased with temperatures from 0.25×10^{-4} to 0.45×10^{-4} moles of $CaSO_4$ formed per hour per gram of initial pellet weight for a temperature increase from 390 to 493°C. Kinetically, this probably means that the overall rate of reaction is being controlled by diffusion since, if the reaction were controlling, the rate should roughly double for a 10°C temperature increase.

The average rate of reaction for the run with the test gas containing 2.5% O_2 instead of NO was about twice that for NO on a $CaSO_4$ basis; however,
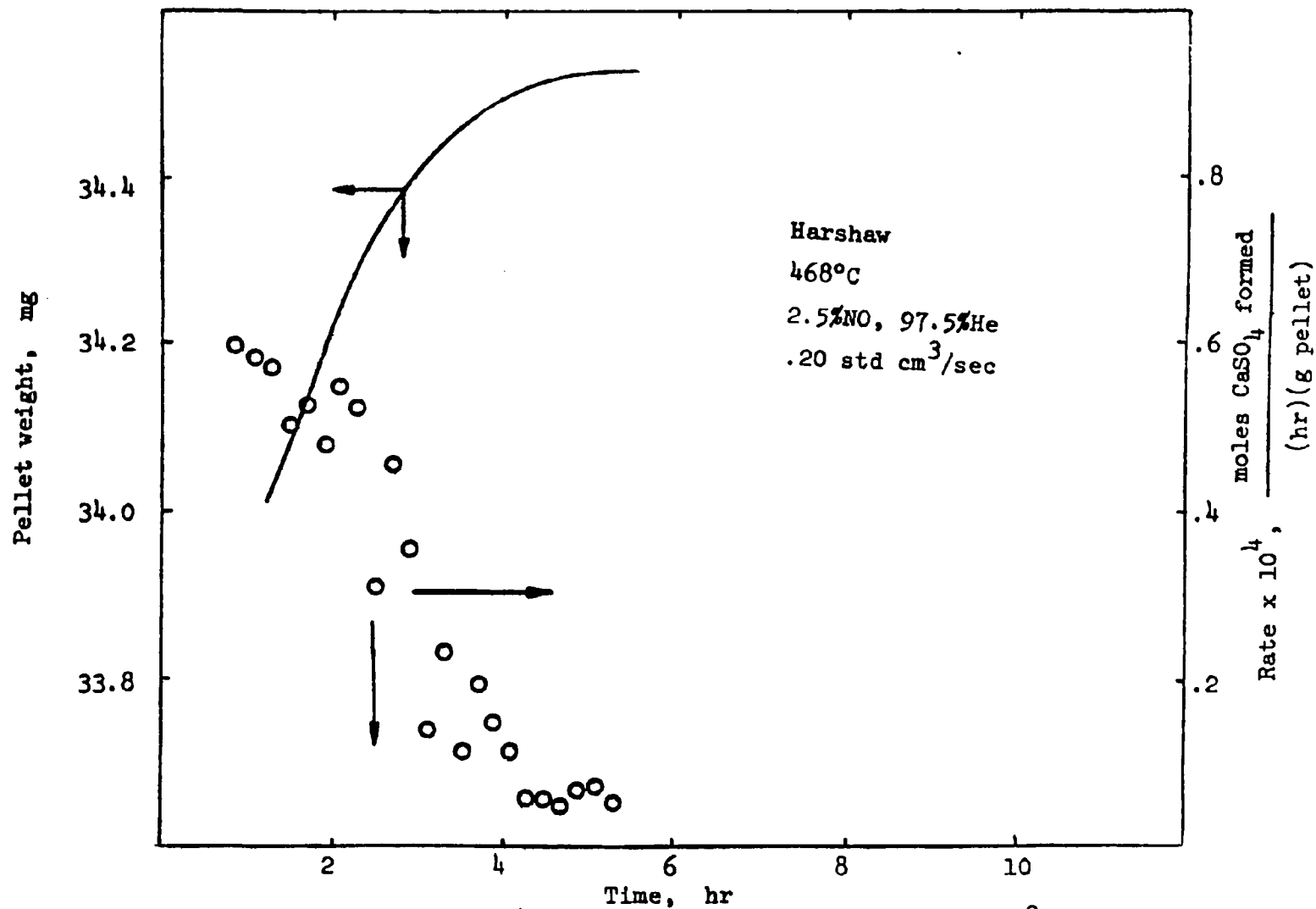
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Figure 11. Reaction data for a Harshaw pellet at 468°C

Harshaw
468°C
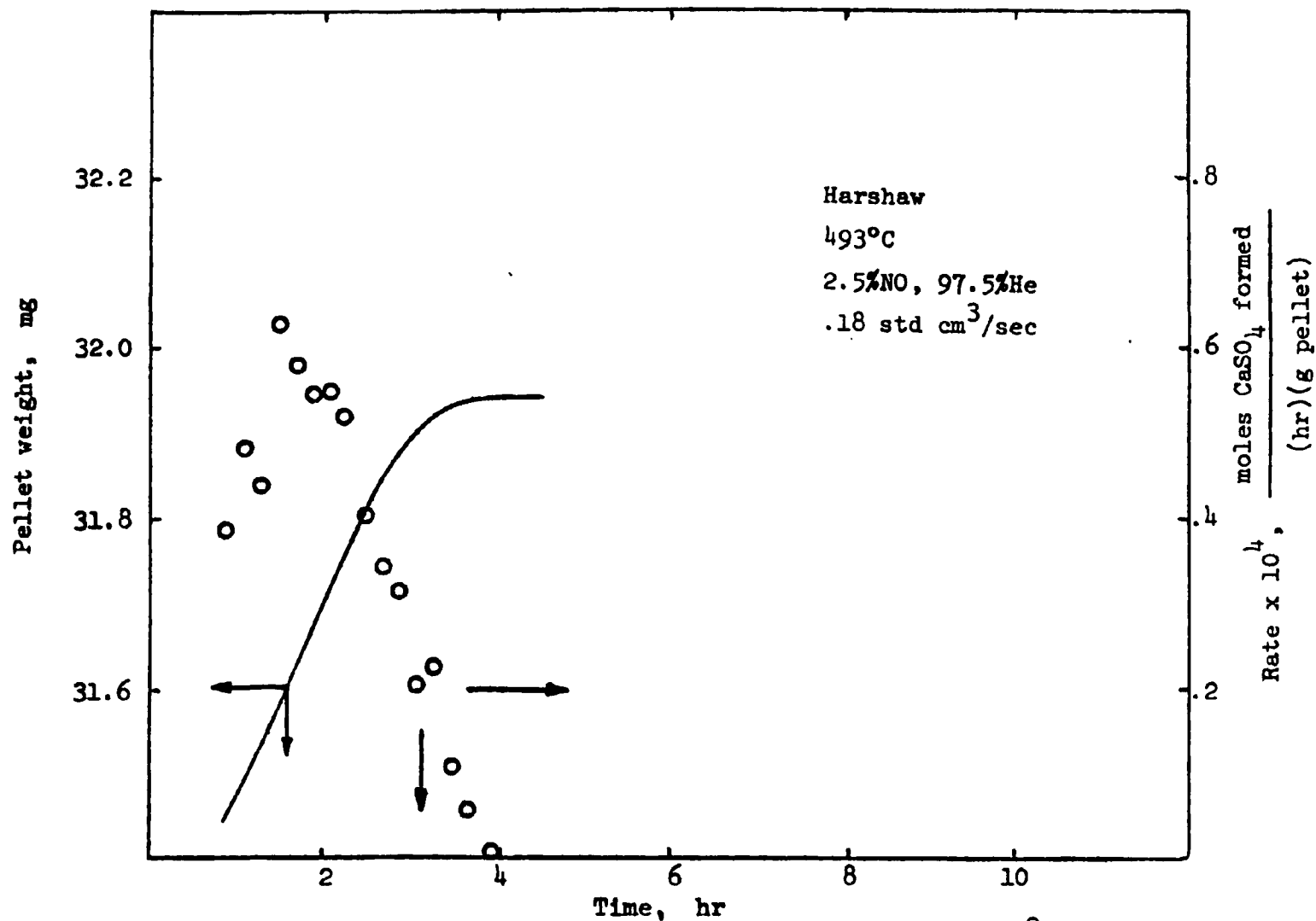2.5%NO, 97.5%He
.20 std cm³/sec

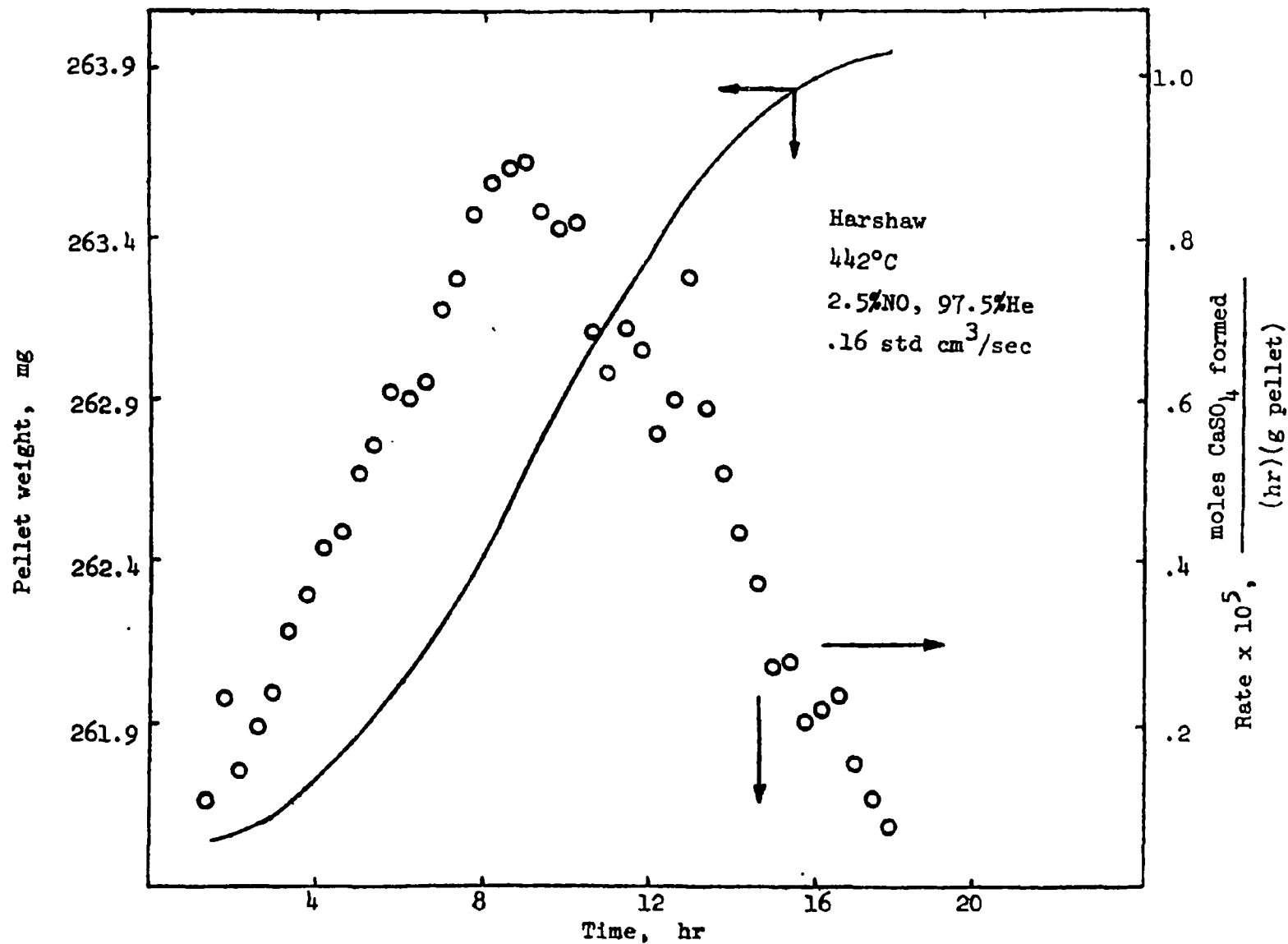Figure 12. Reaction data for a Harshaw pellet at 493°C

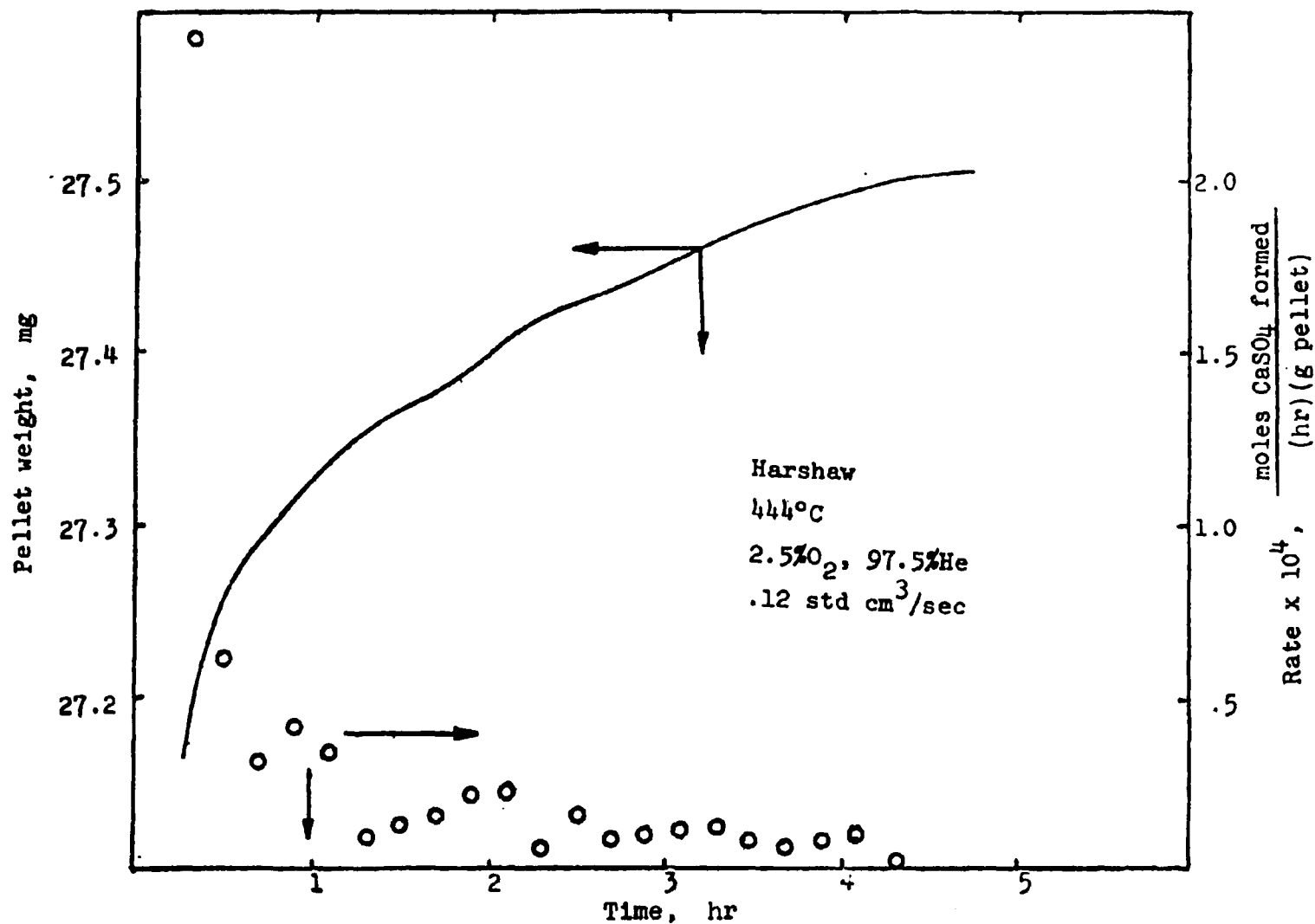Figure 13. Reaction data for five Harshaw pellets at 442°C

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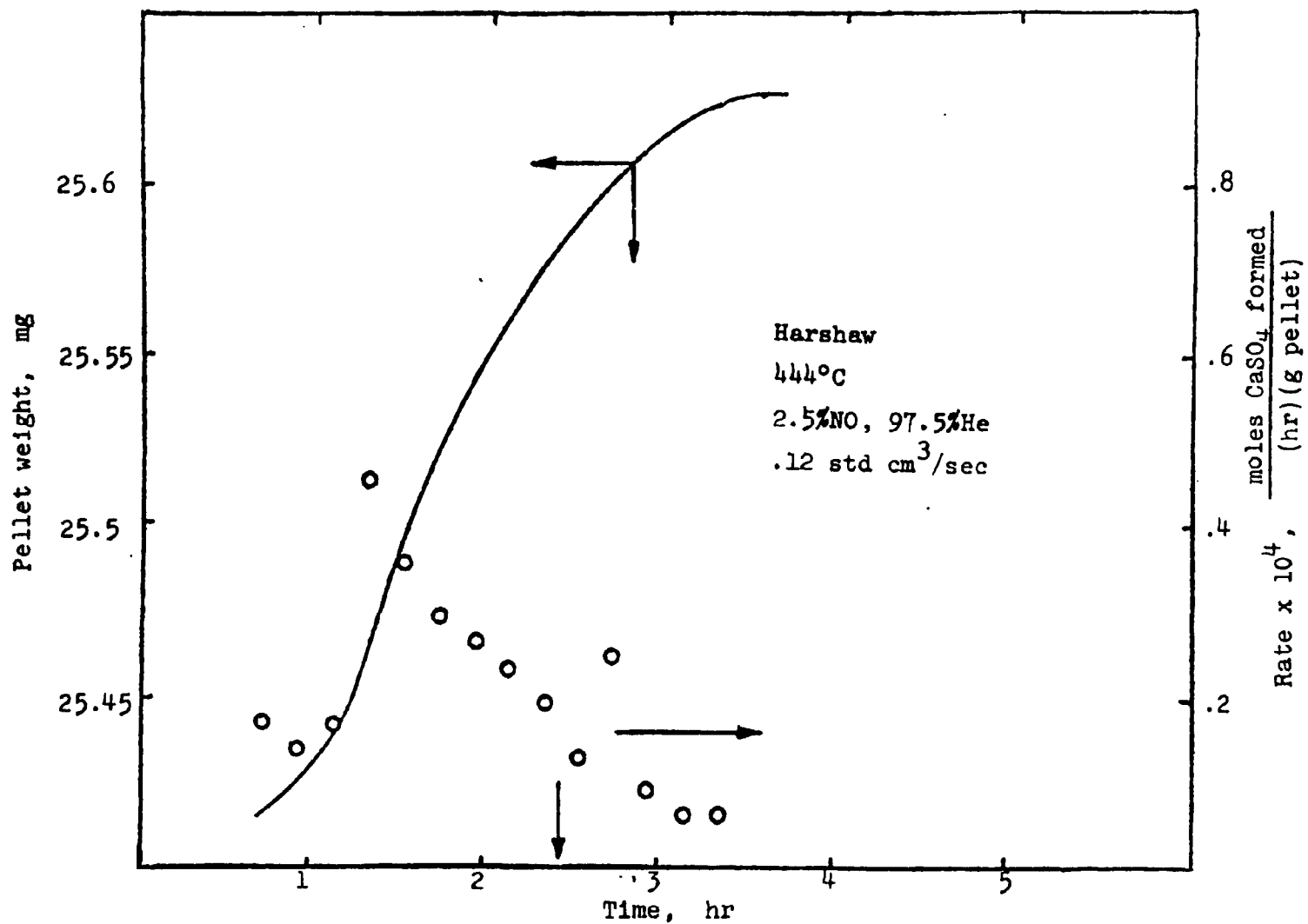Figure 14. Reaction data for a Harshaw pellet using oxygen

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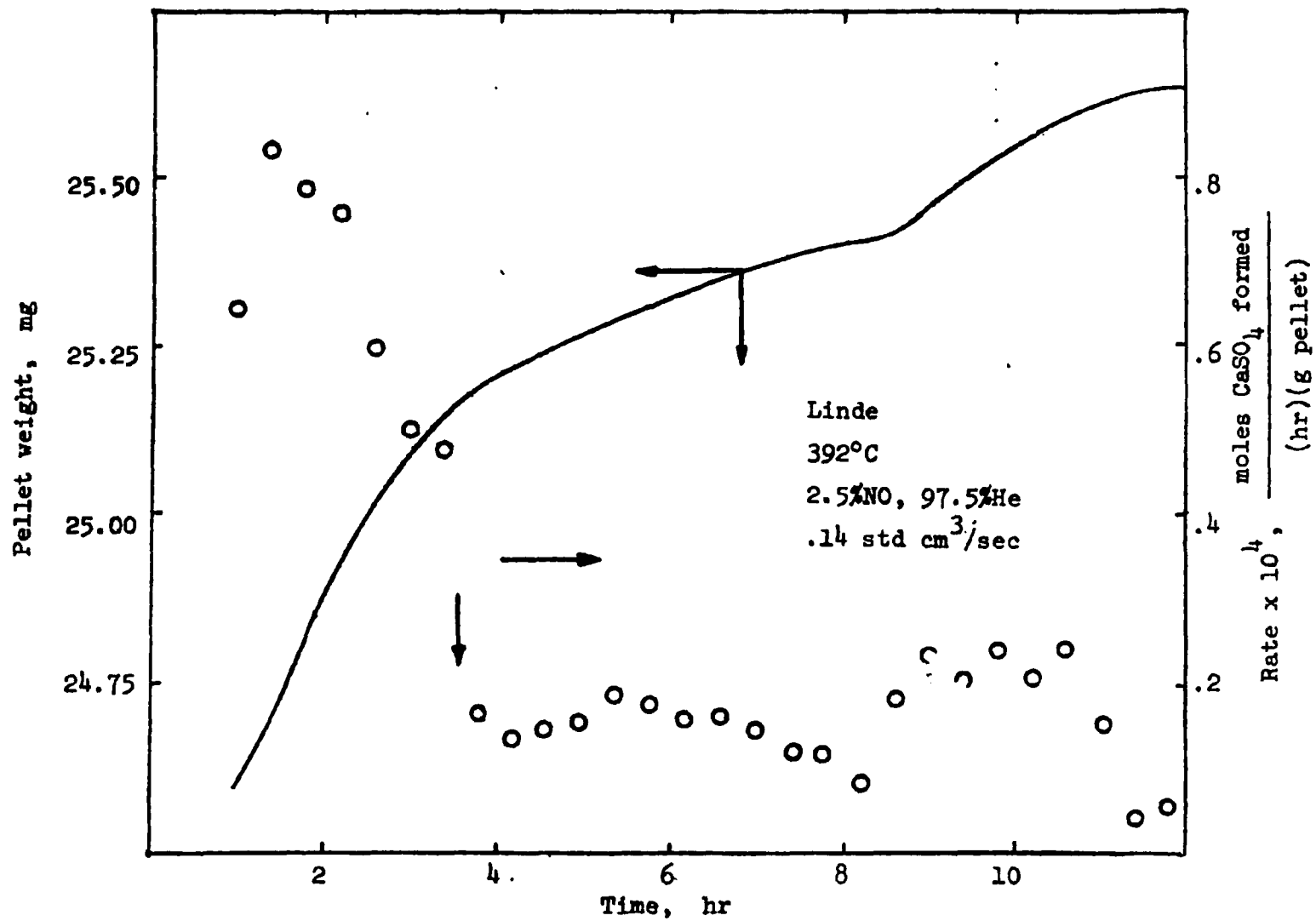Figure 15. Reaction data for a Harshaw pellet at low flow rates

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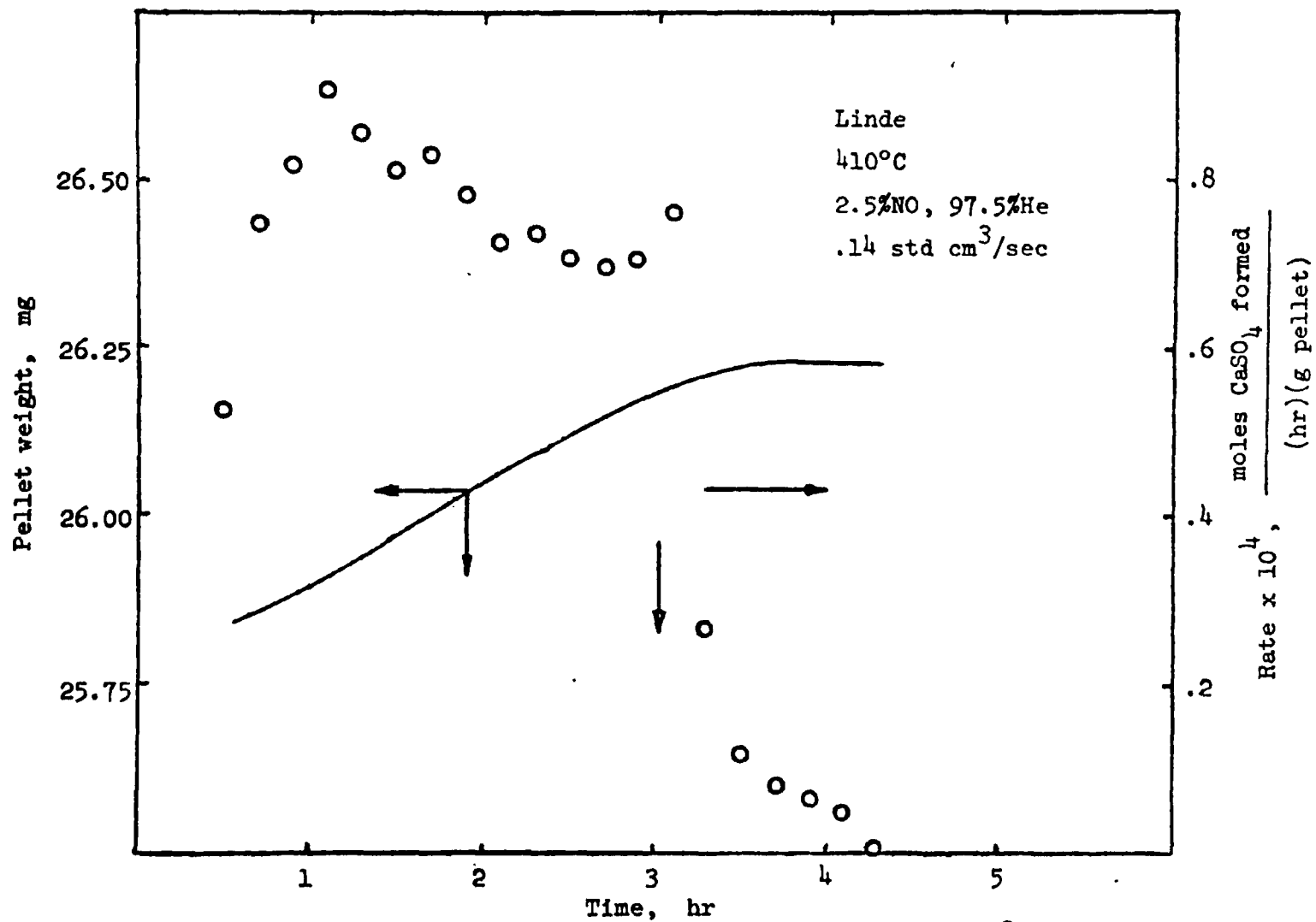Figure 16. Reaction data for a Linde sieve at 392°C

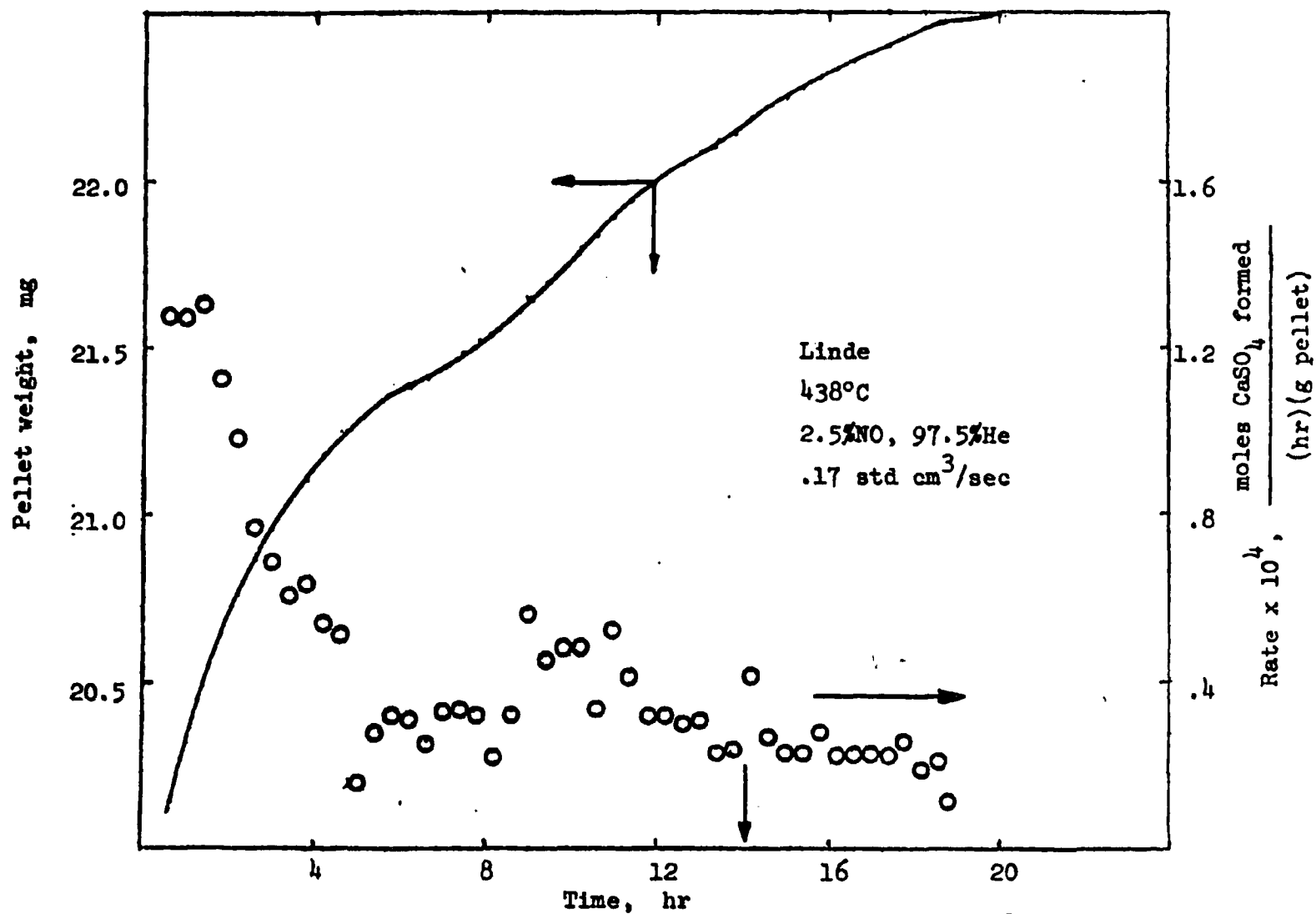Figure 17. Reaction data for a Linde sieve at 410°C

Figure 18.   Reaction data for a Linde sieve at 438°C

on a per mole of O_2 basis, the rates are comparable since the rate of reaction is twice that for O_2 per mole of $CaSO_4$.

TABLE 8.   AVERAGE RATES OF REACTION VS. TEMPERATURE

Run No.	Type of Support	Temp. °C	Rate x 10^4 mol $CaSO_4$ formed (hr)(g pellet)	mol NO removed (hr)(g pellet)	Time Range Time
1	Harshaw	390	.25	1.00	.9 to 6.9
2	Harshaw	410	.25	1.00	.9 to 9.5
3	Harshaw	437	.34	1.36	.9 to 8.1
4	Harshaw	438	.31	1.24	.9 to 9.1
5	Harshaw	468	.40	1.60	.9 to 5.3
6	Harshaw	493	.45	1.80	.9 to 3.9
7*	Harshaw	442	.05	.20	1.4 to 17.8
8	Harshaw	444	.22	.90	.7 to 3.3
9**	Harshaw	444	.41	.92***	.3 to 4.3
10	Linde	392	.32	1.28	1.0 to 12.2
11	Linde	410	.64	2.56	.5 to 4.3
12	Linde	438	.47	1.88	.6 to 18.6

*   5 pellets
** pellets partially oxidized before run for runs 9 and 10 2.5% O_2, 97.5% He feed
***Rate based on moles of O_2 removed

The average rate of reaction for the Linde Molecular Sieve was higher than for the Harshaw pellets at comparable temperatures with the maximum average rate being 0.64×10^{-4} moles $CaSO_4$ formed per hour per gram of initial pellet weight at 410°C. This rate was higher than the rate obtained at 438°C. This inconsistency probably resulted due to deactivation of the molecular sieve pellets because of oxidation in air. If the pellets were exposed to air for even short periods of time, they became very hot and analysis showed almost complete oxidation to $CaSO_4$.

Placing pellet on the balance pan required a finite but variable time exposure to air. For comparison, the Harshaw Pellets became about 50% oxidized after being exposed to air for about 17 days at room temperature.

All of the pellets underwent a color change upon reaction. The Harshaw pellets were initially light blue and became light brown or beige when impregnated with CaS. Upon reaction with NO they became bright white. The molecular sieve pellets were initially brown and turned black when impregnated with CaS. After reaction they again became brown.

The discovery that the CaS impregnated on high surface area pellets are rapidly oxidized by atmospheric air at ambient temperatures was disturbing.

It had been assumed that this would not be a problem, especially at lower temperatures. This assumption was based on a study by the U.S. Bureau of Mines of the reduction of $CaSO_4$ to CaS using gypsum-coke pellets in a rotary kiln which showed that CaS was not appreciably oxidized when the pellets were discharged from the kiln at 700-800°C (9).

Subsequent tests were carried out to compare the relative rate of reaction of various sulfide-catalyst combinations with NO and O_2. The electrobalance was also used for these studies.

RATE OF REACTION OF METAL SULFIDES WITH NO AND O_2

For these tests, 0.8 grams of the powdered sulfide were distributed evenly on the weighing pan of the balance, and the weight change noted when a test gas mixture of either 2.5% NO or O_2 in helium was passed through the hang down tube at a rate of about 13 cc/min. Temperatures of 300, 400 and 500°C were investigated with a fresh sample of sulfide being used for each temperature and each gas mixture. The reactor was purged with pure helium while heating the reactor to the desired temperature and until the weight remained constant (due to moisture being removed from the sample). Table 9 is a summary of the rate of weight gain or loss for the various sulfides listed. These same data converted to rate of formation of sulfate per minute per initial weight of the sulfide are shown in Table 10. In these tables, the negative sign indicates a weight loss when the test gas containing NO or O_2 is passed through the reactor tube while the "d" indicates a weight loss while purging with pure He at that temperature indicating a decomposition.

As can be seen from the data, the metal sulfides react faster with oxygen in every case except one. At 300°C the rate of reaction of SrS was slightly faster with NO than with O_2. BaS, FeS and CaS all lost weight when NO was passed through the reactor at 300°C indicating the possibility of undesirable side reactions taking place. Analysis of the dilute exit gas stream from these runs was impossible so these possible side reactions were not investigated further. BaS, FeS, SrS, CdS, CaS and sulfurated potash (K_2S) all reacted both with NO and O_2. MnS, TlS, CuS, and MoS_2 all decomposed in the helium purge. WS_2 lost weight when reacting with both O_2 and NO. ZnS did not react with NO at 400 and 500°C but did react with O_2. This is in line with the preliminary tests which showed that NO does not react with ZnS at temperatures below about 550°C.

The sulfurated potash (K_2S plus higher sulfides) exhibited a very rapid weight gain but the rate of formation of the sulfate could not be calculated because the exact composition of the sulfurated potash was not known. During the test of the sulfurated potash at 500°C with NO, there was a large (0.3 gram) loss in weight of the stainless steel weighing pan and so a 500°C run using O_2 was not made.

The fact that the rate of weight changes when the sulfides react with O_2 is faster than with NO is slightly misleading since it takes twice as much NO as O_2 on a molar basis (assuming sulfate is formed) to produce the same weight change. Table 11 presents the same data based on the moles of NO or O_2 reacting, assuming the metal sulfide is the reaction product. As can be seen from Table 11, on this basis, the rate of reaction of NO is greater than O_2 for SrS at 300 and 400°C and BaS and CdS at 400°C. Also,

significantly, there is little difference between the rates of reaction for NO and O_2 for SrS at all temperatures.

TABLE 9. A SUMMARY OF THE RATE OF WEIGHT GAIN OR LOSS FOR THE VARIOUS SULFIDES REACTING WITH NO AND O_2

| Sulfides | Rate x 10^3, $\dfrac{\text{grams of weight change}}{\text{minute}}$ | | | | | |
| | 300°C | | 400°C | | 500°C | |
	NO	O_2	NO	O_2	NO	O_2
BaS	-2.08	0	4.09	5.3	7.22	182.00
FeS	-2.27	-20.80	1.172	27.58	70.9	144.0
ZnS	1.50	1.77	0	4.53	0	7.97
SrS	2.22	2.15	2.73	5.29	3.68	7.81
CuS	d	d	d	d	d	d
CdS	.98	3.80	3.62	5.50	2.43	27.6
Cu_2S					0	8.07
PbS	2.53	8.26	3.52	31.70	1.59	108.00
WS_2	0	-3.08	-8.33	-22.90	-6.54	-25.20
MoS_2	0		d		d	
K_2S (Sulfurated Potash)	38.8	185.00	79.8	88.70	127.00	
TlS	d		d		d	
CaS	- .49	0	2.08	6.50	3.85	32.40
MnS	d		d		d	

NOTES: - represents a weight loss
d indicates weight loss while purging the reactor tube with pure He

The next series of experiments investigated the relative rates and reactions of CaS with NO and O_2 when it was mixed with various promoters and tests of the promoters alone. The results of the tests of NaF, NaCl, K_3FeF_6 and K_3FeF_6+NaCl mixed with CaS are shown in Table 12. For these tests 20 wt % promoter was mixed with CaS and runs conducted as in the previous runs using test gases containing 2.5% NO or O_2.

As can be seen from Table 12, the presence of NaF or K_3FeF_6 has a pronounced effect on the rate of reaction of CaS with both NO and O_2 but there is a greater increase in the rate of reaction of NO, especially at the lower temperature of 200 and 300°C. This is very significant because it indicates that there is a possibility that the sulfide can be used to reduce NO in a gas stream also containing O_2, without excessive consumption of the solid by reaction with O_2. It also probably indicates that the mechanism of the reaction of NO with the sulfide is different than the mechanism for the reaction with O_2.

TABLE 10.   REACTION RATES OF NO AND O_2 WITH VARIOUS METAL SULFIDES

Sulfides	Rate x 10^6 $\dfrac{\text{(wt. of MeSO}_4 \text{ formed)}}{\text{(minute)(initial wt. of MeS)}}$					
	300°C		400°C		500°C	
	NO	O_2	NO	O_2	NO	O_2
BaS	--	0.00	18.60	24.00	32.60	874.00
FeS	--	--	3.38	85.00	207.60	428.00
ZnS	4.80	5.90	0.00	14.00	0.00	25.10
SrS	7.92	7.65	9.81	18.70	13.20	27.70
CuS	d	d	d	d	d	d
CdS	3.98	15.50	14.70	22.80	9.79	116.00
Cu_2S					0.00	37.00
PbS	14.80	50.30	20.50	191.00	9.18	648.00
WS_2	0.00	--	--	--	--	--
MoS_2	0.00	--	d	d	d	d
K_2S (Sulfurated Potash)	+	+	+	+	d	d
TlS	d	d	d	d	d	d
CaS	--	0.00	5.58	17.70	10.90	86.50
MnS	d	d	d	d	d	d

TABLE 11.   THE RELATIVE RATES AT WHICH NO AND O_2 REACT WITH THE VARIOUS SULFIDES

Sulfides	Rate x 10^7 $\dfrac{\text{moles of NO reacted}}{\text{(minute)(initial grams of MeS)}}$ or $\dfrac{\text{moles of } O_2 \text{ reacted}}{\text{(minute)(initial grams of MeS)}}$					
	300°C		400°C		500°C	
	NO	O_2	NO	O_2	NO	O_2
BaS	--	0	3.19	2.06	5.59	74.90
FeS	--	--	.89	11.20	54.80	56.40
ZnS	1.19	.73	0	1.73	0	3.11
SrS	1.73	.83	2.14	2.04	2.88	3.02
CdS	.76	1.49	2.82	2.19	1.88	11.10
Cu_2S					0	3.32
PbS	1.95	3.32	2.70	12.60	1.21	42.70
CaS	--	0	1.64	2.56	3.20	5.71

TABLE 12. RATE OF REACTION OF CaS AT VARIOUS TEMPERATURES
USING DIFFERENT PROMOTERS

Promoter	Rate x 10^7 $\frac{\text{gram moles of gas reacted}}{\text{(minute)(gram initial CaS)}}$							
	200°C		300°C		400°C		500°C	
	NO	O_2	NO	O_2	NO	O_2	NO	O_2
NaF	3.35	0	1.93	1.02	5.99	18.5	43.5	73.9
NaCl	0	0	2.67	0	1.00	2.39	2.69	21.0
K_3FeF_6	2.99	0	3.73	1.39	10.80	21.60	25.9	24.2
K_3FeF_6 + NaCl	2.68	0	3.58	1.66	5.99	47.3	4.63	56.7
no promoter	--	--	--	--	1.64	2.56	3.20	5.71

To further test these promoters, runs were made using the pure material on the electrobalance to see if they reacted with either NO or O_2. The results of these experiments are shown in Table 13. As can be seen, the NO reacts with K_3FeF_6 at all temperatures investigated while it does not react with O_2 except at 500°C. NaF does not react with NO and only reacts with O_2 at 500°C. NaCl does not react with either gas at temperatures of 400°C or below. There appears to be synergetic effect on the reaction of NO with K_3FeF_6 and NaCl mixtures at 500°C.

TABLE 13. THE WEIGHT CHANGE WITH TIME OF VARIOUS PROMOTERS REACTING
WITH NO OR O_2

Promoter	Reaction rate, (Milligrams of Weight Change/Min) x 10^3							
	200°C		300°C		400°C		500°C	
	NO	O_2	NO	O_2	NO	O_2	NO	O_2
NaF	0	0	0	0	0	0	0	11.0
NaCl	0	0	0	0	0	0	7.3	113.9
K_3FeF_6	3.4	0	22.9	0	3.0	0	42.2	45.5
K_3FeF_6 + NaCl	3.0	0	1.0	0	1.8	0	606.8	29.4
$NiCl_2$			0	0	0	0		
$FeCl_2$			0	0	0	0		
$CoCl_2$			1.5	0	-12.9	0		
Fe_2O_3			2.9	0	0	0		

From these tests the K_3FeF_6 should probably be eliminated from further consideration for use as a promoter. Not only does it react with both NO and O_2 but it undergoes a color change from white to reddish brown as it is heated in helium indicating that it is unstable at higher temperatures.

Another series of tests (Table 14) investigated NaF, NiCl, $FeCl_2$, $CoCl_2$ and Fe_2O_3 mixed with FeS, BaS, SrS and CaS in the reduction of 2.5% NO in helium at 300 and 400°C. As can be seen the combinations giving the highest reaction rates were $FeS-FeCl_2$ at 300°C, $BaS-FeCl_2$ at 400°C and $CaS-Fe_2O_3$ at 400°C. All combinations were investigated further using a synthetic flue gas in the flow reactor system.

TABLE 14.   THE RATE AT WHICH NO REACTS WITH THE VARIOUS METAL
SULFIDE CHEMICAL PROMOTER MIXTURES

Metal Sulfide	Rate x 10^7 $\dfrac{\text{Moles NO Reacted}}{\text{(Minute)(Initial) Gram Sulfide)}}$					
	Pure Metal Sulfide	Promoter				
		NaF	$NiCl_2$	$FeCl_2$	$CoCl_2$	Fe_2O_3
300°C						
FeS	0	1.64	0	58.63	1.33	0
BaS	0	2.70	2.71	--	.58	2.19
SrS	2.16	2.85	1.05	0	0	2.18
CaS	0	2.41	0	1.31	.87	1.00
400°C						
FeS	1.11	19.86	26.36	--	1.69	4.19
BaS	3.99	7.36	31.75	39.44	--	0
SrS	2.68	1.00	0	0	0	6.98
CaS	2.05	7.49	5.36	1.95	2.24	32.00

Reduction of NO_x In a Synthetic Flue Gas

The reduction of NO_x in a synthetic flue gas was investigated in the down flow reactor previously described. Two grams of the sulfide-catalyst-material was added to the reactor and the test gas mixture passed through the sulfide bed at a rate of 100 ml/min. The test gas contained 1000 ppm NO_x, 1 percent O_2, 18 percent CO_2 and the balance N_2. A concentration of this magnitude would be expected in a flue gas from the burning of coal using about 10 percent excess air. Although most flue gases probably would contain more O_2 then this, 1 percent was chosen because it represented the lower limit likely to be encountered and reasonable run times could be obtained. Sulfide-catalyst combinations that looked to be the most promising in the electro-balance studies were investigated at 400°C. Mixtures of BaS, CaS, SrS and FeS with NaF, $NiCl_2$, $CoCl_2$, $FeCl_2$, and Fe_2O_3 were investigated

using 20 wt. percent promoter mixed with the sulfide. NO_x analysis was accomplished using the chemiluminescent analyzer and O_2 was analyzed using the molecular sieve column in the chromatograph.

The results of these tests are shown in Figures 19 through 38. As can be seen by comparing these figures, the various sulfide-promoter mixtures behaved quite differently under the test conditions but most important in certain cases NO_x removal was at a high level for significant periods of time even in the presence of O_2. Of the mixtures tested, $CaS-FeCl_2$, $SrS-NaF$, $SrS-FeCl_2$, $FeS-NiCl_2$, $BaS-FeCl_2$, and $FeS-FeCl_2$, appeared to be the best.

The capacity (defined as the weight of NO_x reduced per unit weight of sulfide initially present from the start of the run until the concentration exceed 600 ppm) was calculated for each combination from the data presented in Figures 19 through 38. This gives a quantitative indication of how good the mixtures are for NO_x reduction. These are listed in Table 15.

TABLE 15.   THE CAPACITIES OF THE METAL SULFIDE-CATALYST MIXTURES
AND OF THE METAL SULFIDES

Metal Sulfide	$\dfrac{\text{Total wt. of NO reduced to 600 ppm}}{\text{Wt. MeS initially present}} \times 10^3$							
	400°C					Unpromoted Metal Sulfide	300°C	
	NaF	$NiCl_2$	$CoCl_2$	$FeCl_2$	Fe_2O_3		NaF	$FeCl_2$
CaS	18.6	5.5	0.9	13.9	1.0	0	0.1	
SrS	31.7	1.4	2.1	7.2	1.1	0		
BaS	6.3	4.8	2.0	16.8	3.4	2.3		
FeS	1.9	13.6	2.2	37.2	7.3	0.5		2.0

As can be seen from Table 15, the capacities varied from 0 to 37.2×10^{-3} grams NO_x reduced/gram of sulfide initially present. The six best were $FeS-FeCl_2 > SrS-NaF > CaS-NaF > BaS-FeCl_2 > FeS-NiCl_2 > CaS-FeCl_2$. These results generally agree with the data obtained on the electrobalance. The $FeS-FeCl_2$ and $CaS-NaF$ mixtures were also tested at 300°C but both showed a low capacity so lower temperatures were not investigated further.

A very limited study also investigated the effect of CO_2, SO_2, H_2O and the O_2 concentration on NO_x removal. Preliminary runs using unpromoted CaS at various temperatures with 18% CO_2 and no CO_2 in the test gas indicated
negligible effects and so the effects of CO_2 were not investigated further. The effect of adding 0.2% SO_2 to the feed gas when a CaS-NaF mixture was tested is shown in Figure 39. As can be seen, at least for this mixture, SO_2 appears not to effect the reduction reaction. However, the presence of 0.2 mole % water vapor dramatically decreases the capacity of CaS-NaF and SrS-NaF mixtures for NO_x reduction at 400°C, as shown in Figures 40 and 41. Figure 42 shows the effect of the amount of O_2 in the gas stream on NO_x reduction. As can be seen, increasing the amount of O_2 also dramatically decreases the capacity of the CaS-NaF mixture for NO_x reduction.
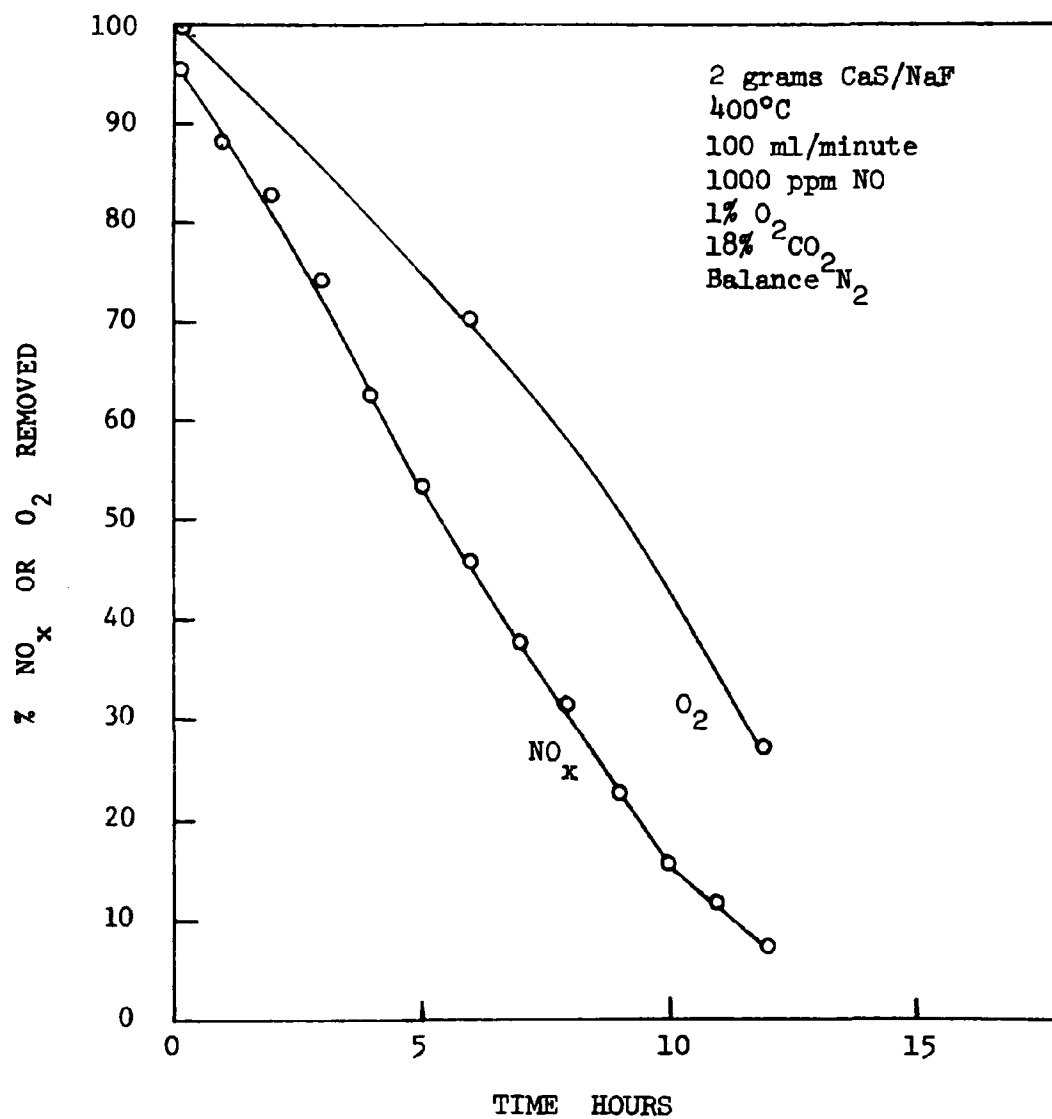
FIGURE 19. THE PERCENT NO_x AND O_2 REMOVED
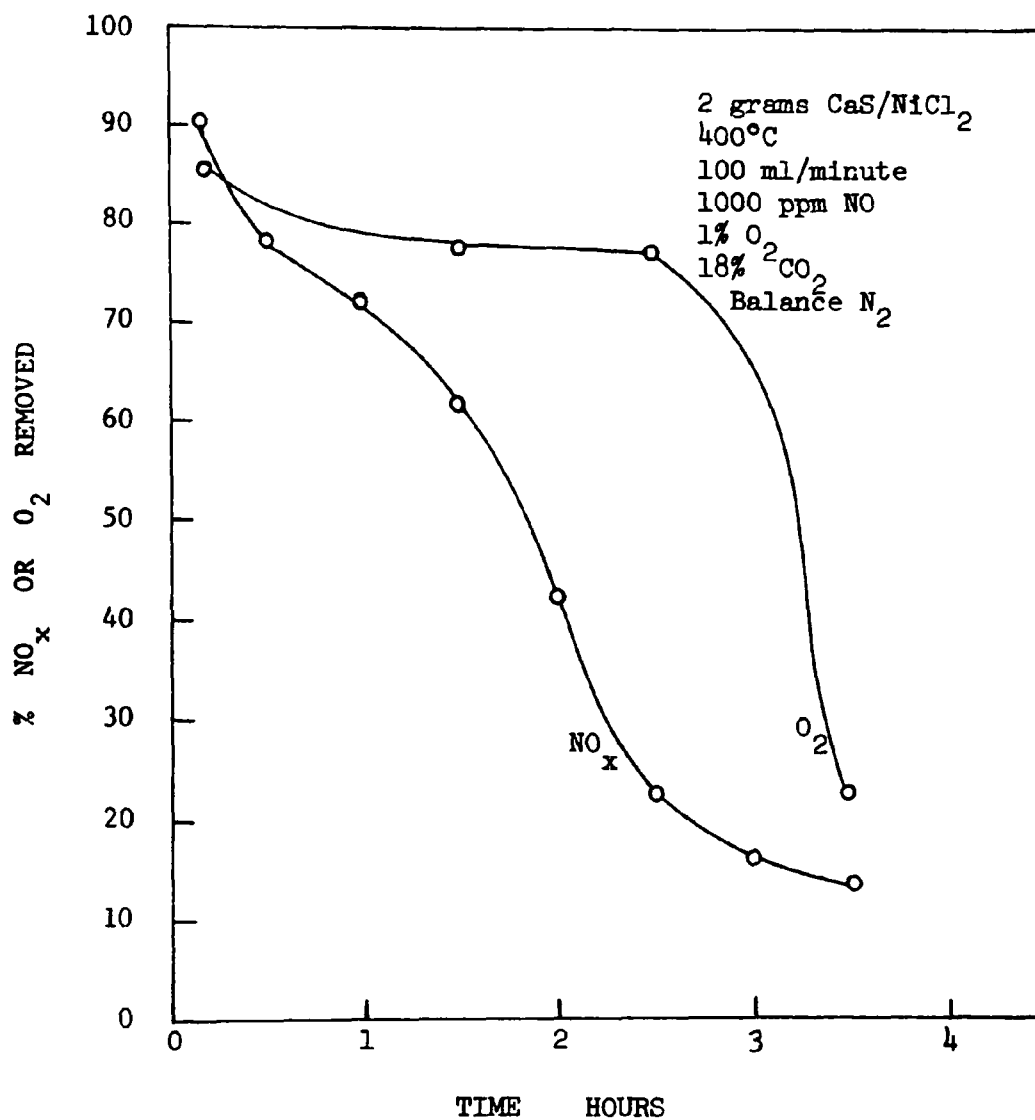
BY 2 GRAMS OF CaS/NaF AT 400°C

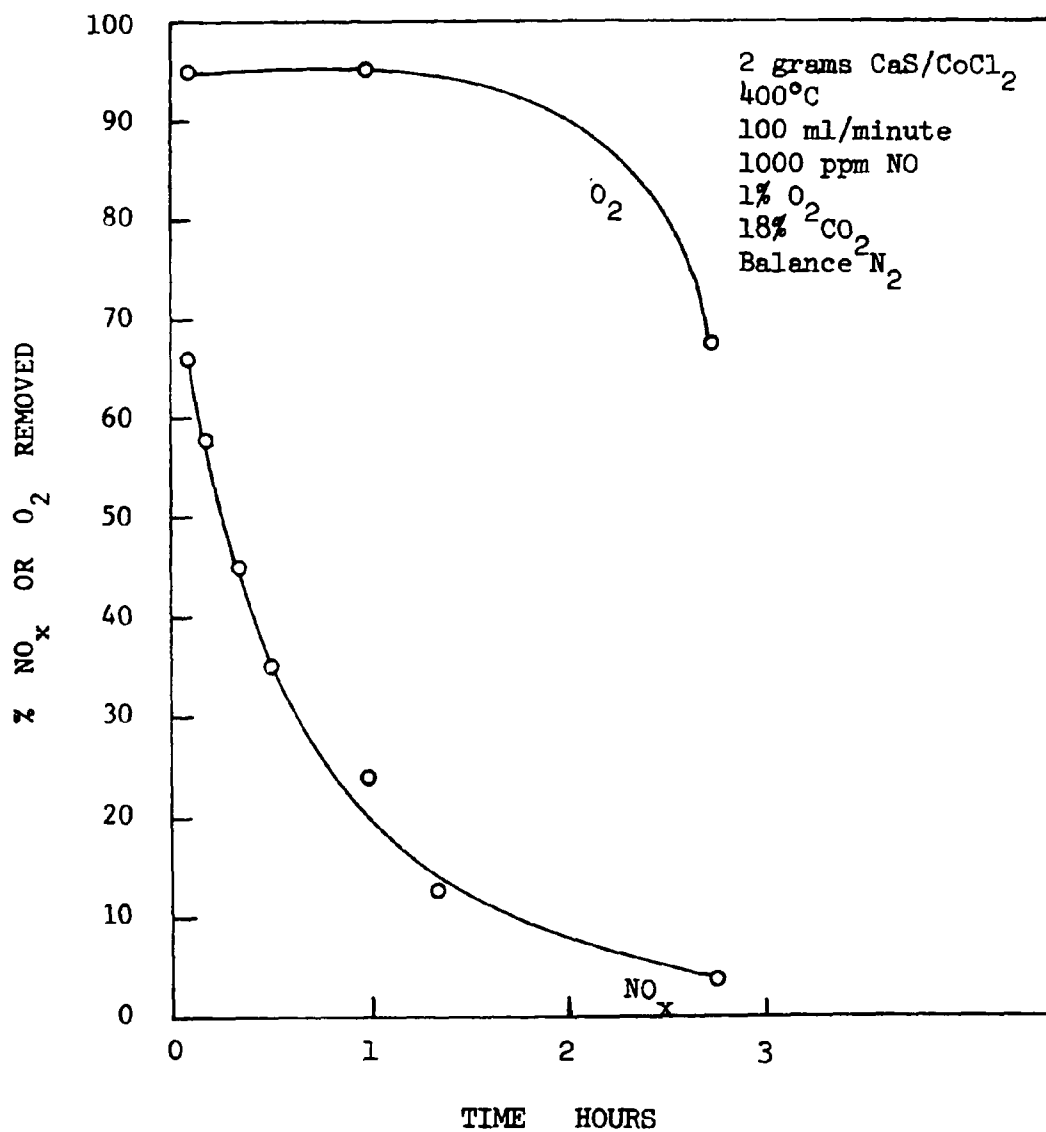FIGURE 20. THE PERCENT NO_x AND O_2 REMOVED

BY 2 GRAMS OF CaS/NiCl$_2$ AT 400°C

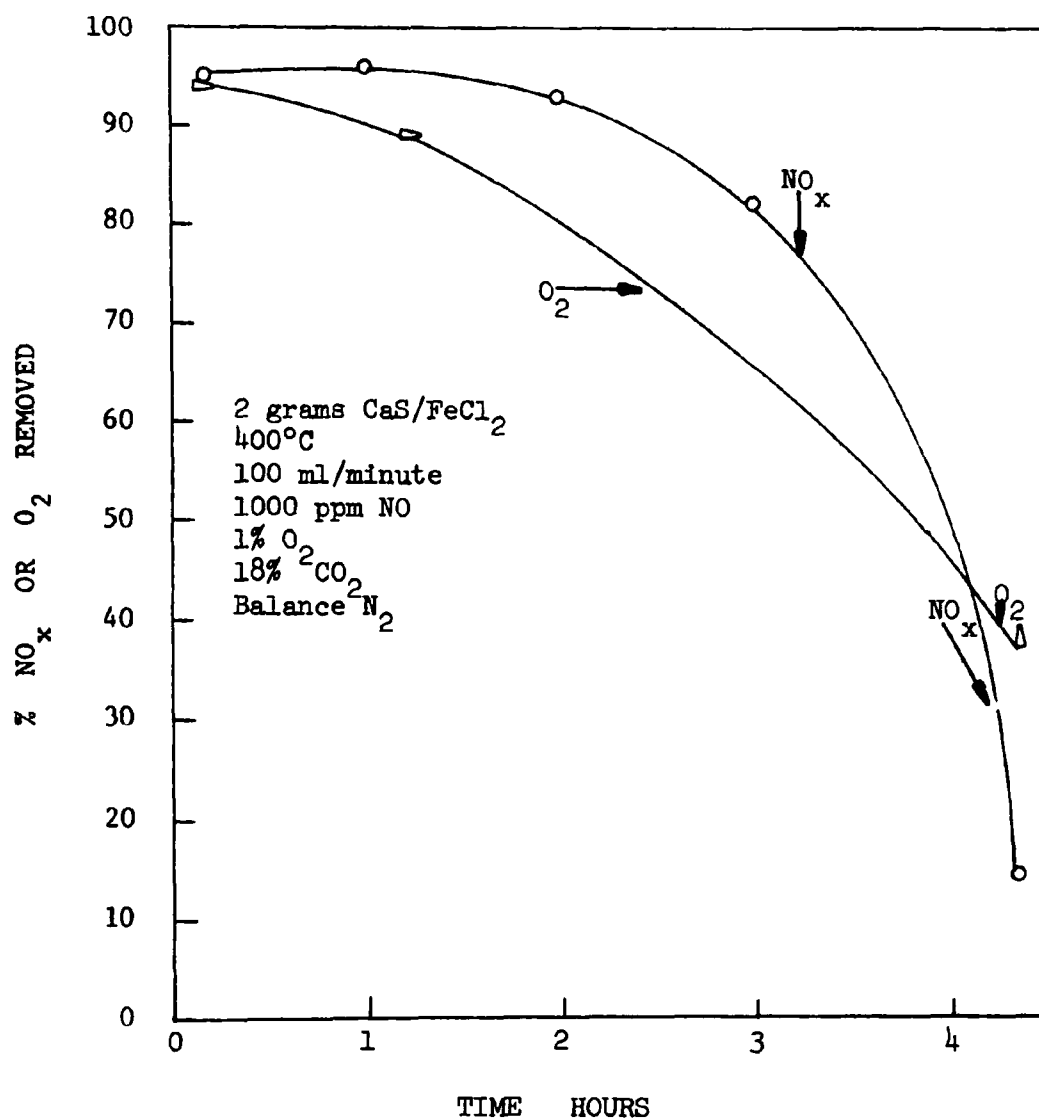FIGURE 21. THE PERCENT NO_x AND O_2 REMOVED

BY 2 GRAMS OF $CaS/CoCl_2$ AT 400°C

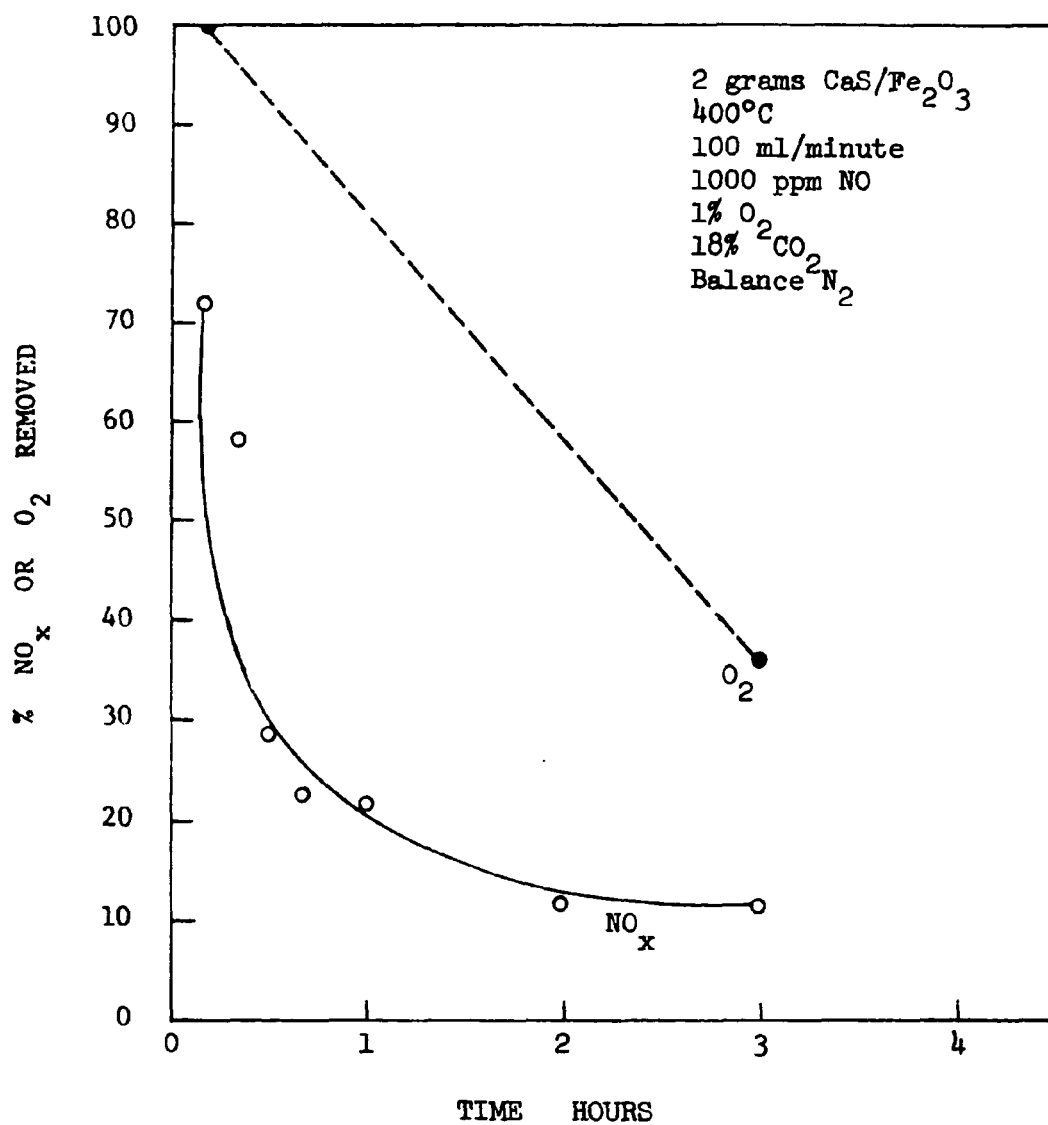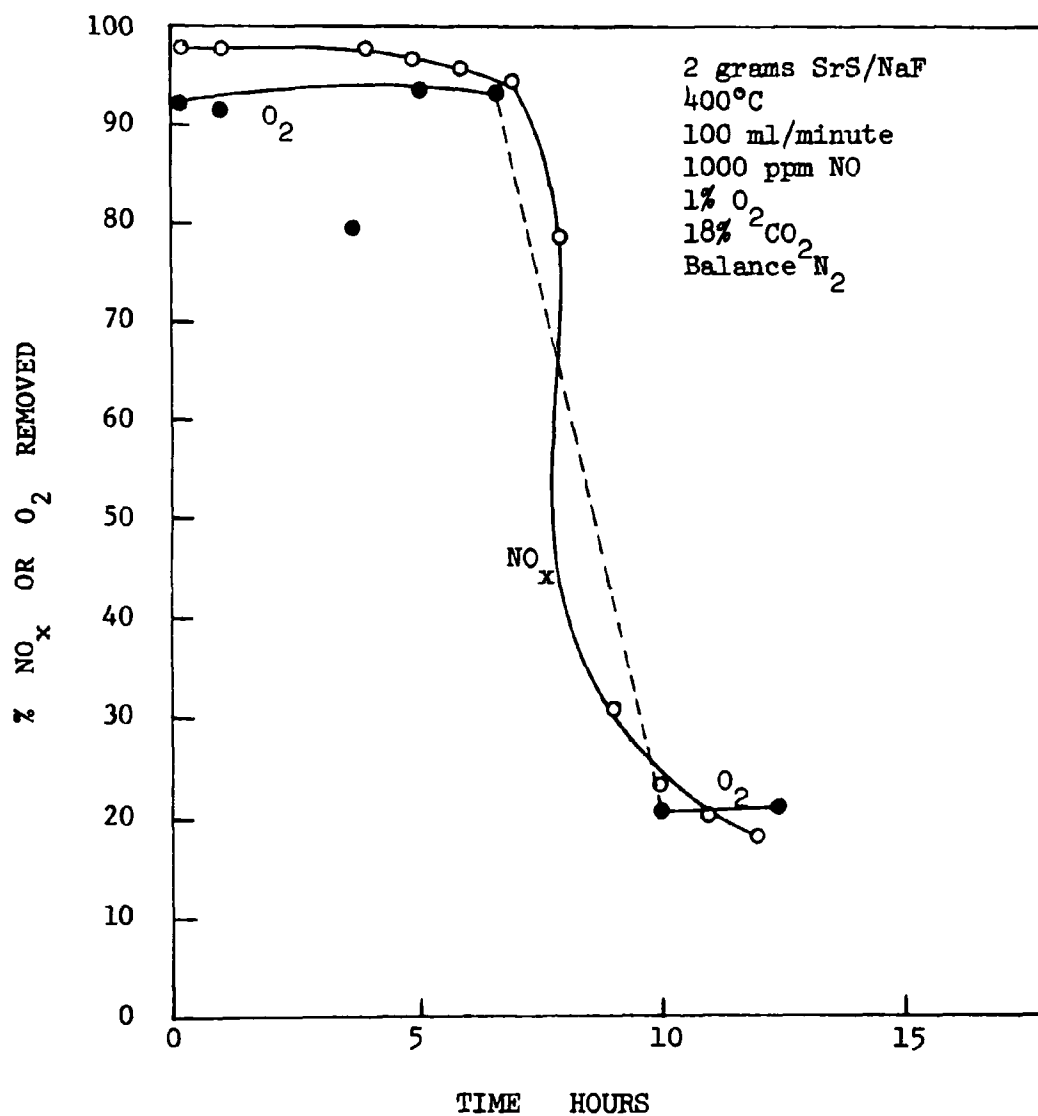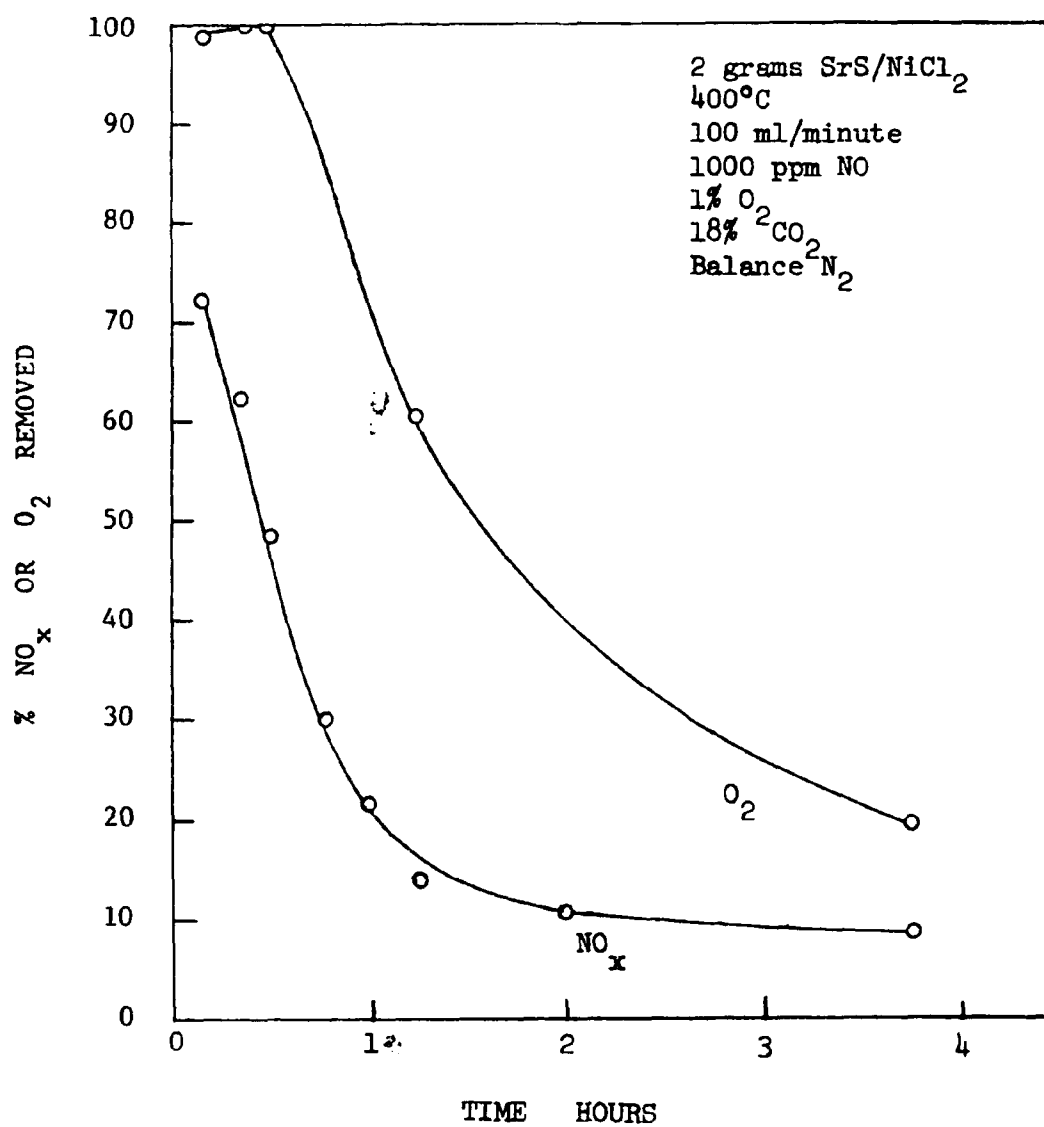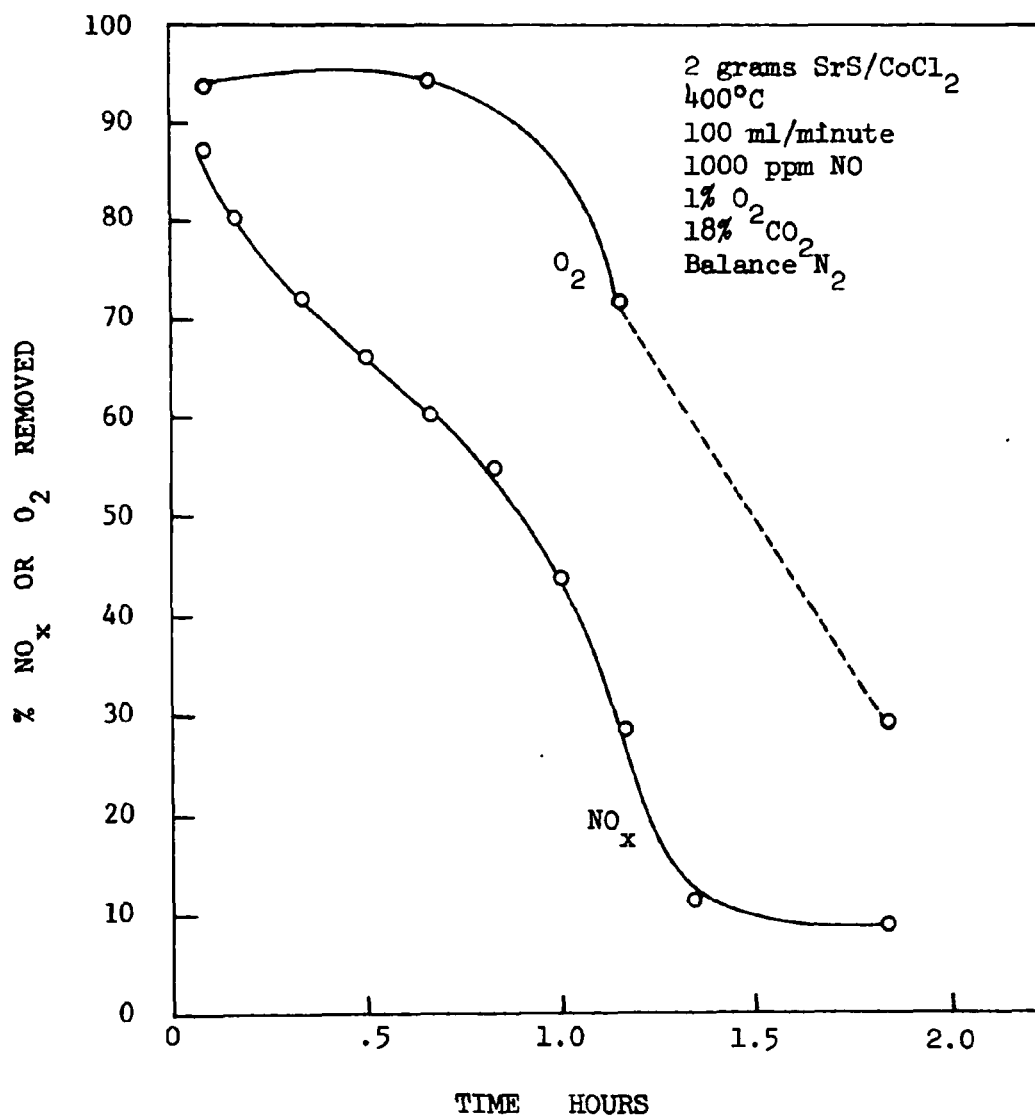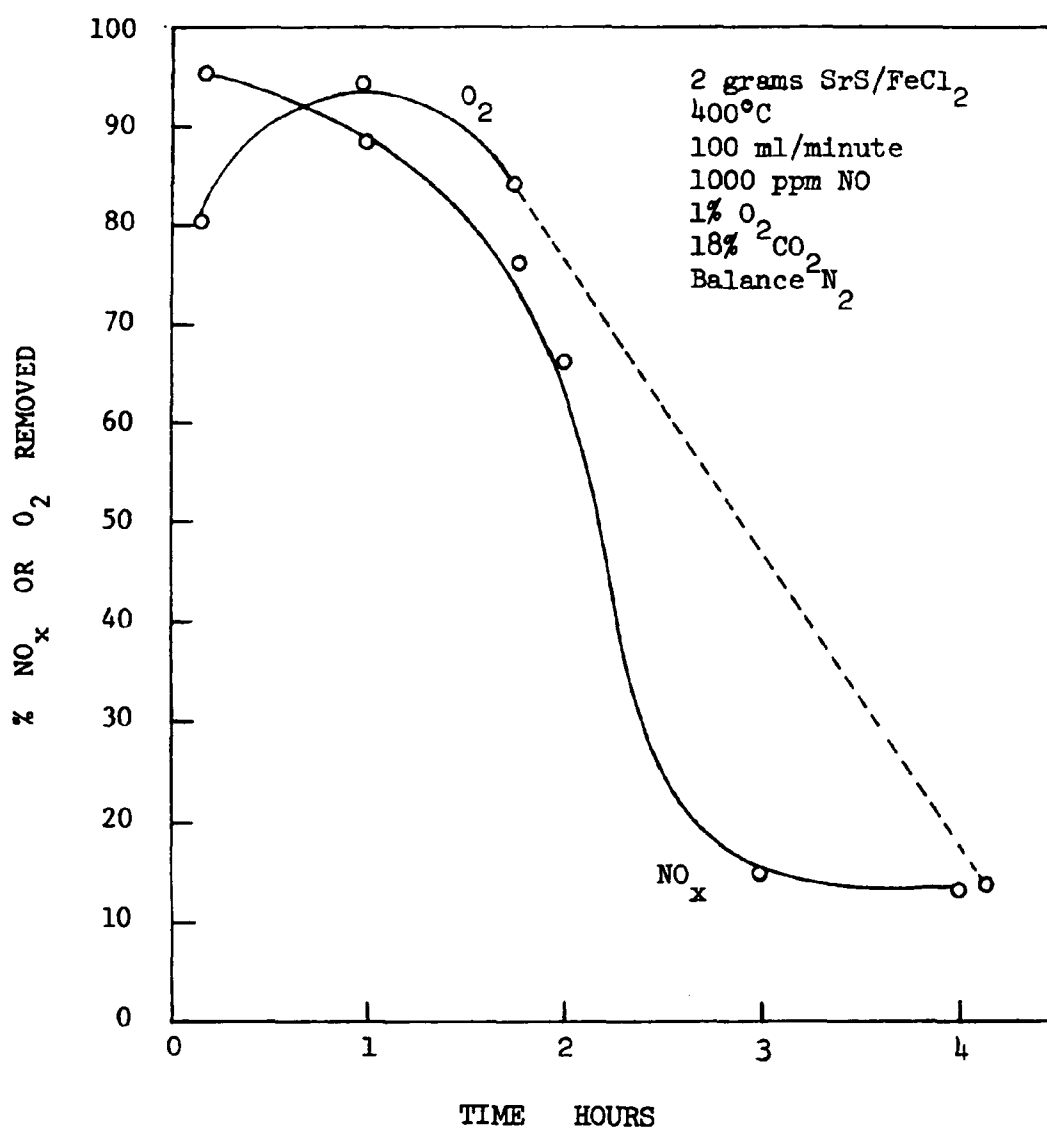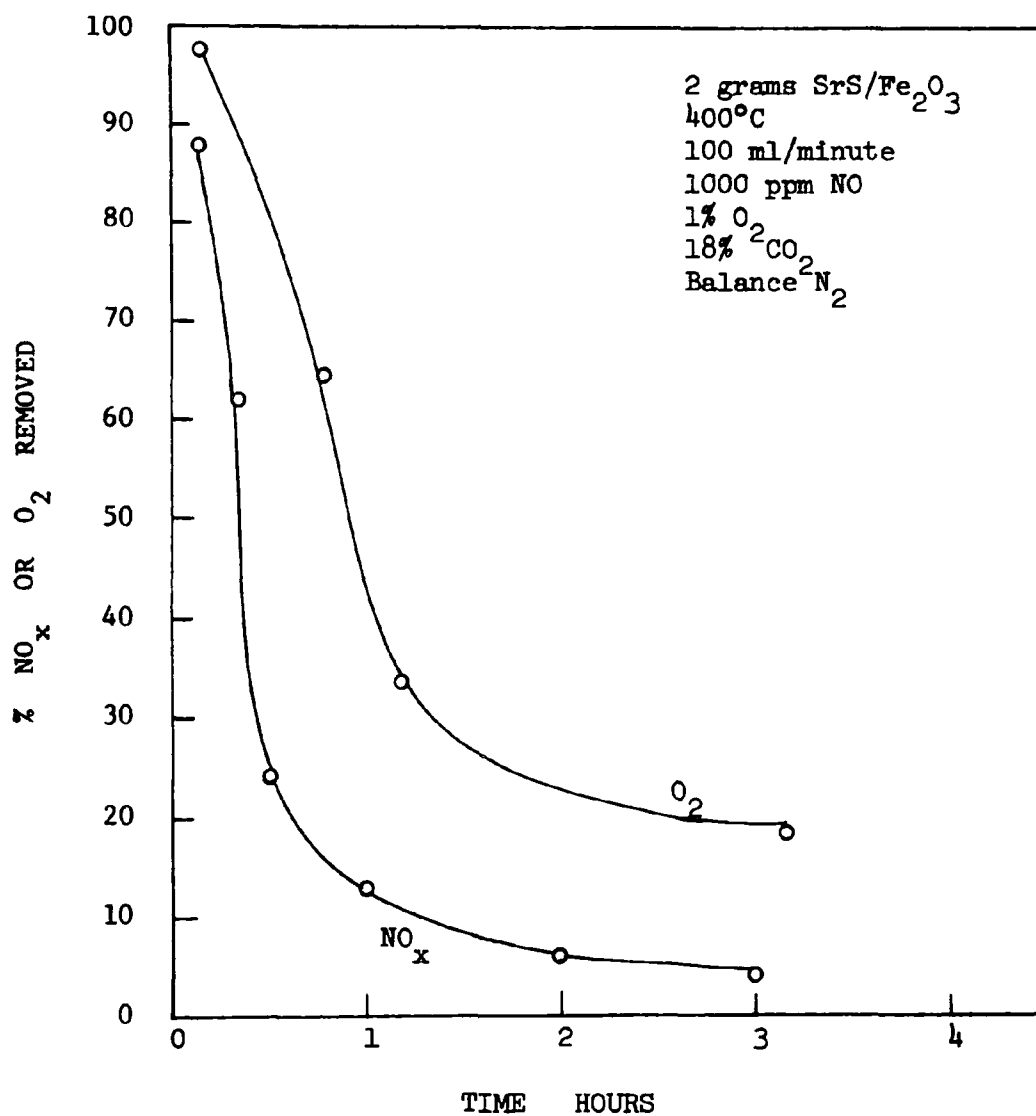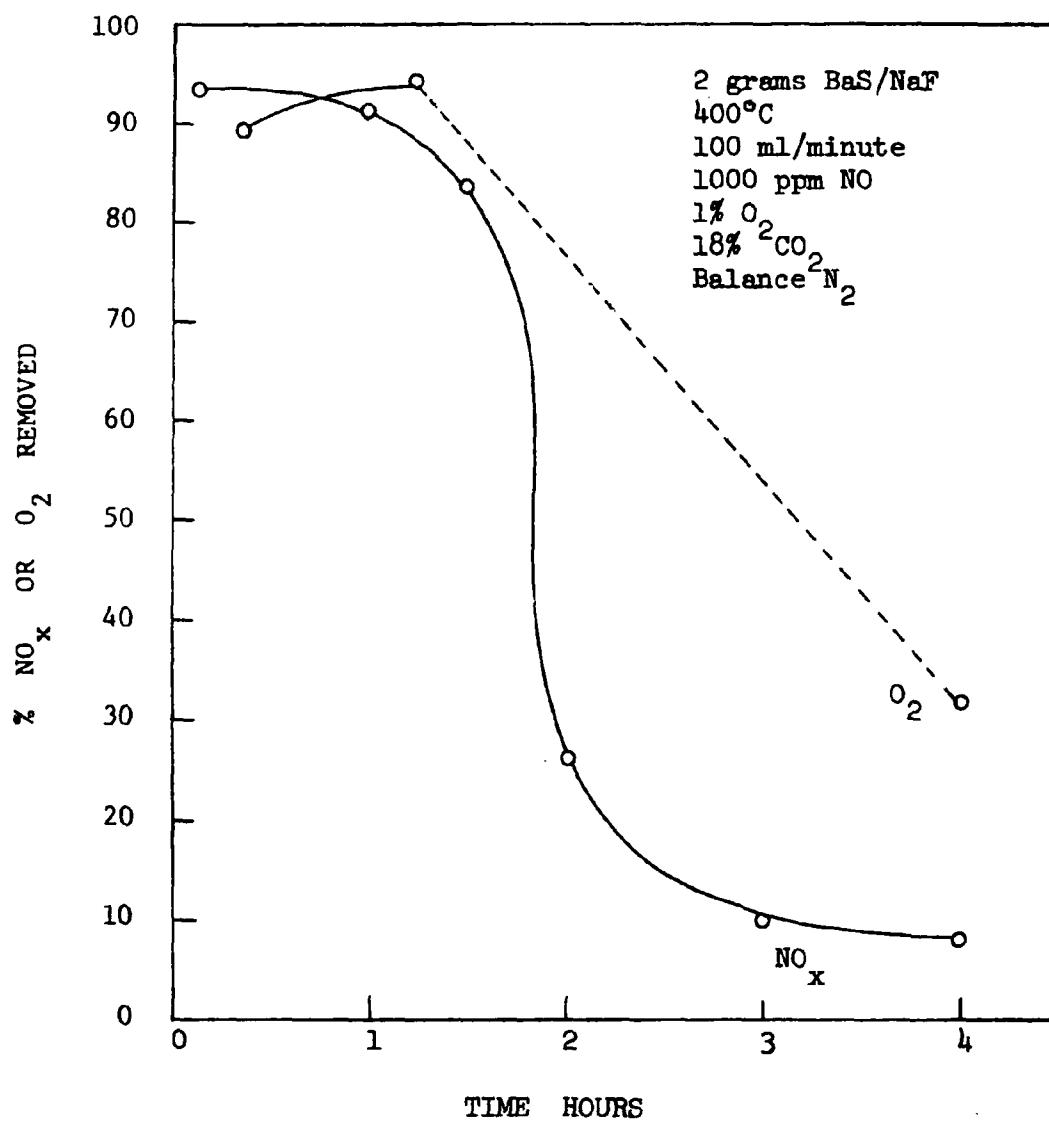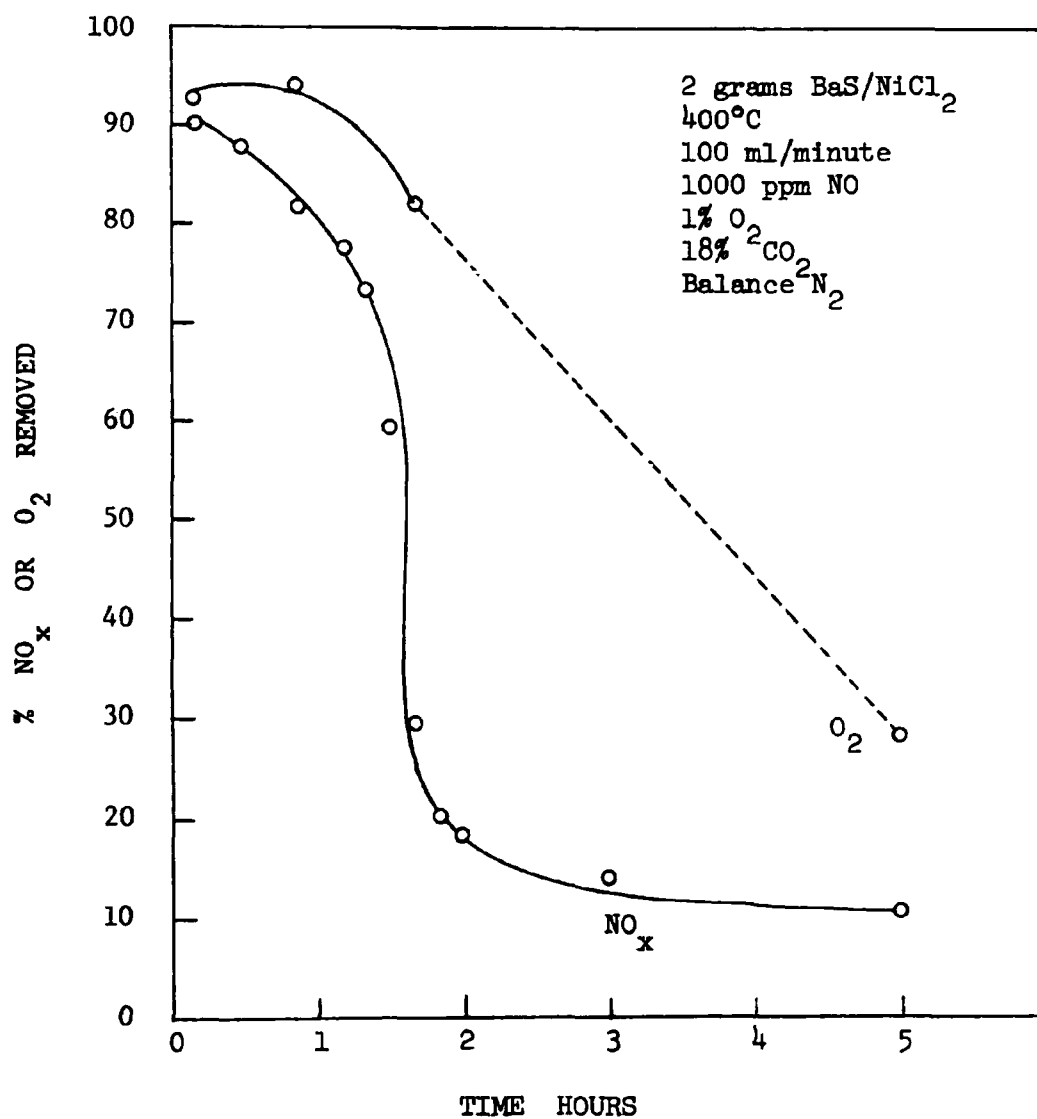FIGURE 22. THE PERCENT NO_x AND O_2 REMOVED

BY 2 GRAMS OF CaS/FeCl$_2$ AT 400°C

The figure shows a graph with the following axis labels and annotations:

Y-axis: % NO_x OR O_2 REMOVED (0 to 100)

X-axis: TIME HOURS (0 to 4)

Conditions listed:
2 grams CaS/FeCl$_2$
400°C
100 ml/minute
1000 ppm NO
1% O$_2$
18% CO$_2$
Balance N$_2$

FIGURE 23. THE PERCENT NO_x AND O_2 REMOVED
BY 2 GRAMS OF CaS/Fe_2O_3 AT 400°C

FIGURE 24. THE PERCENT NO_x AND O_2 REMOVED

BY 2 GRAMS OF SrS/NaF AT 400°C

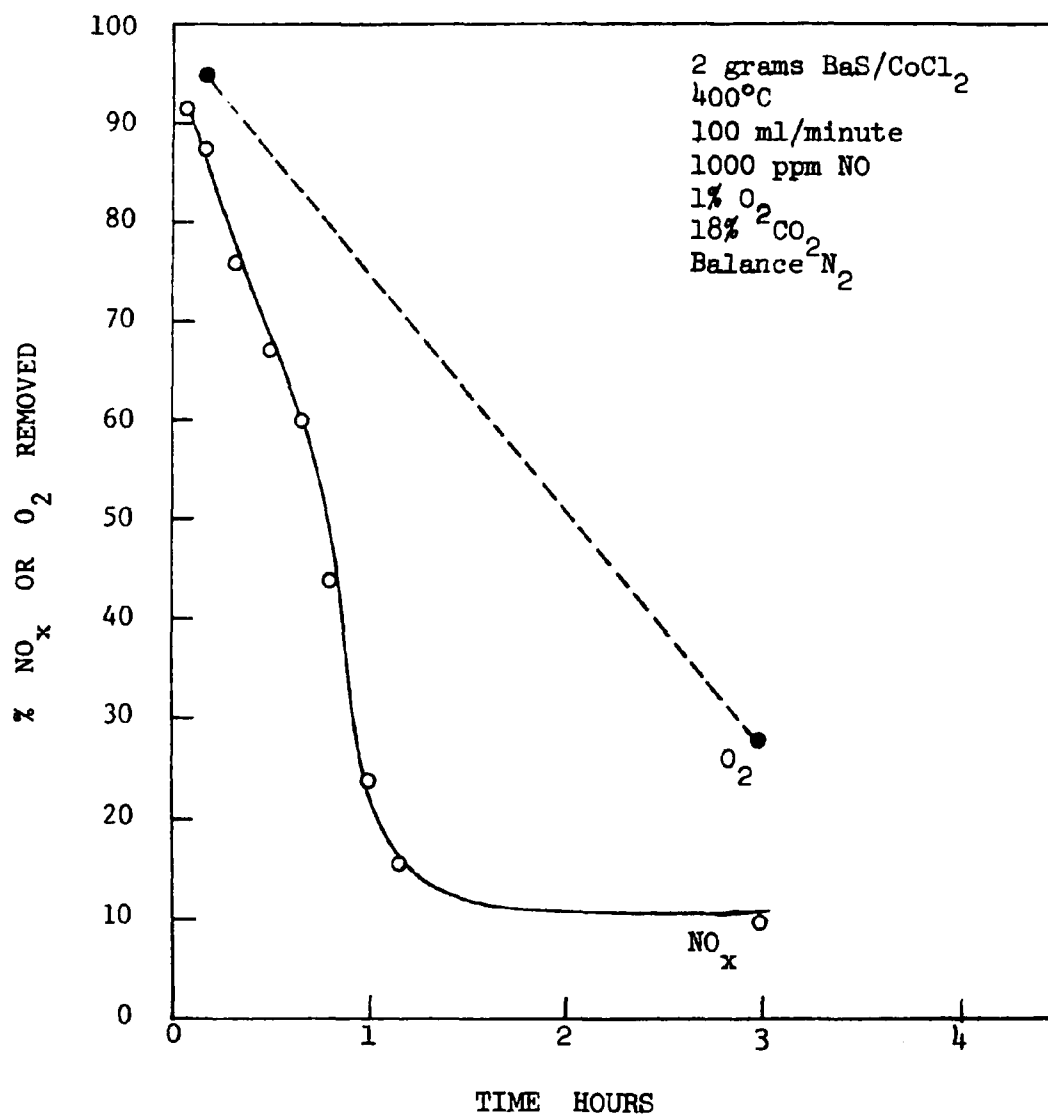FIGURE 25.   THE PERCENT NO$_x$ AND O$_2$ REMOVED

BY 2 GRAMS OF SrS/NiCl$_2$ AT 400°C

FIGURE 26.   THE PERCENT NO$_x$ AND O$_2$ REMOVED

BY 2 GRAMS OF SrS/CoCl$_2$ AT 400°C

FIGURE 27.   THE PERCENT NO_x AND O_2 REMOVED

BY 2 GRAMS OF SrS/$FeCl_2$ AT 400°C

FIGURE 28. THE PERCENT NO_x AND O_2 REMOVED
BY 2 GRAMS OF SrS/Fe_2O_3 AT 400°C

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FIGURE 29. THE PERCENT NO_x AND O_2 REMOVED
BY 2 GRAMS OF BaS/NaF AT 400°C

FIGURE 39.   THE PERCENT NO$_x$ AND O$_2$ REMOVED

BY 2 GRAMS OF BaS/NiCl$_2$ AT 400°C

FIGURE 31. THE PERCENT NO_x AND O_2 REMOVED
BY 2 GRAMS OF $BaS/CoCl_2$ AT 400°C
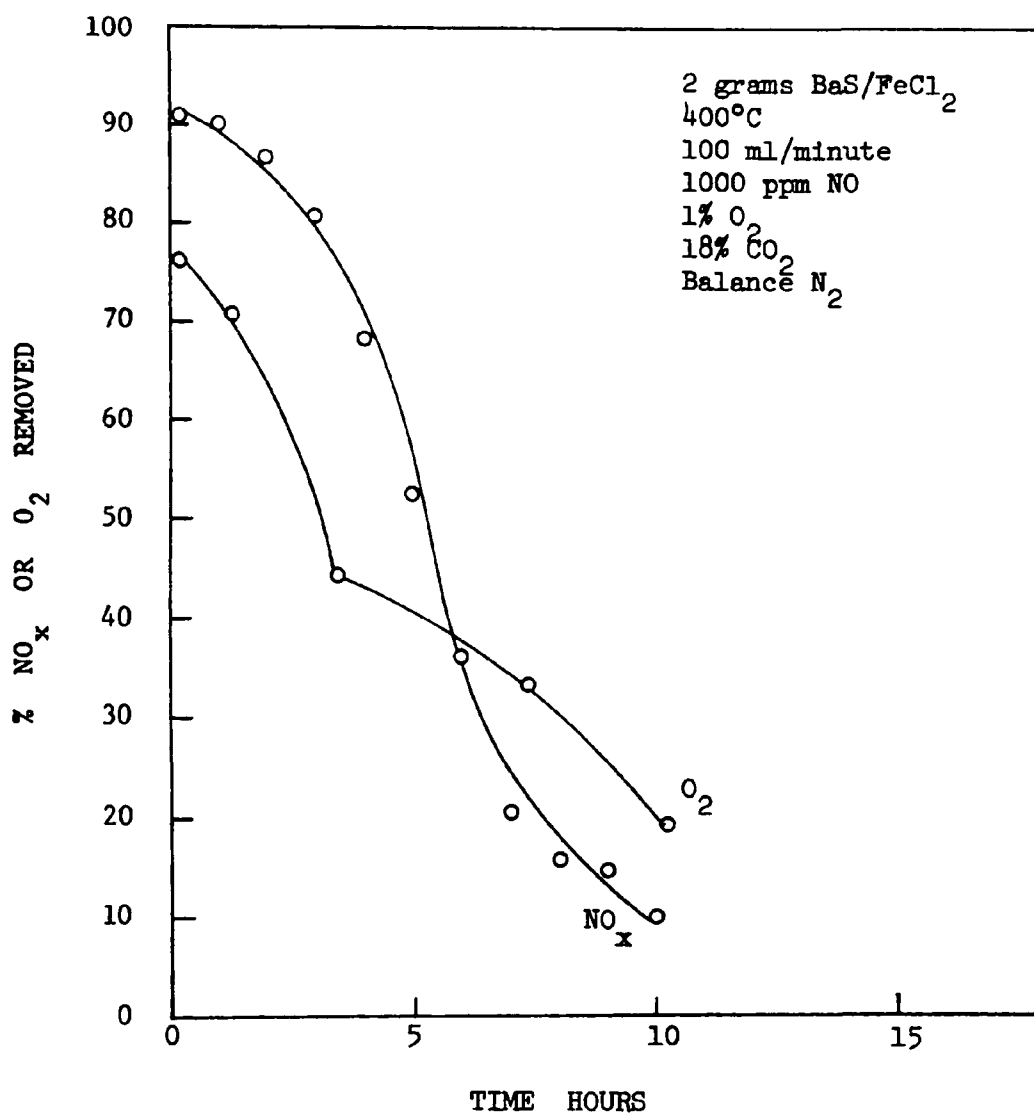
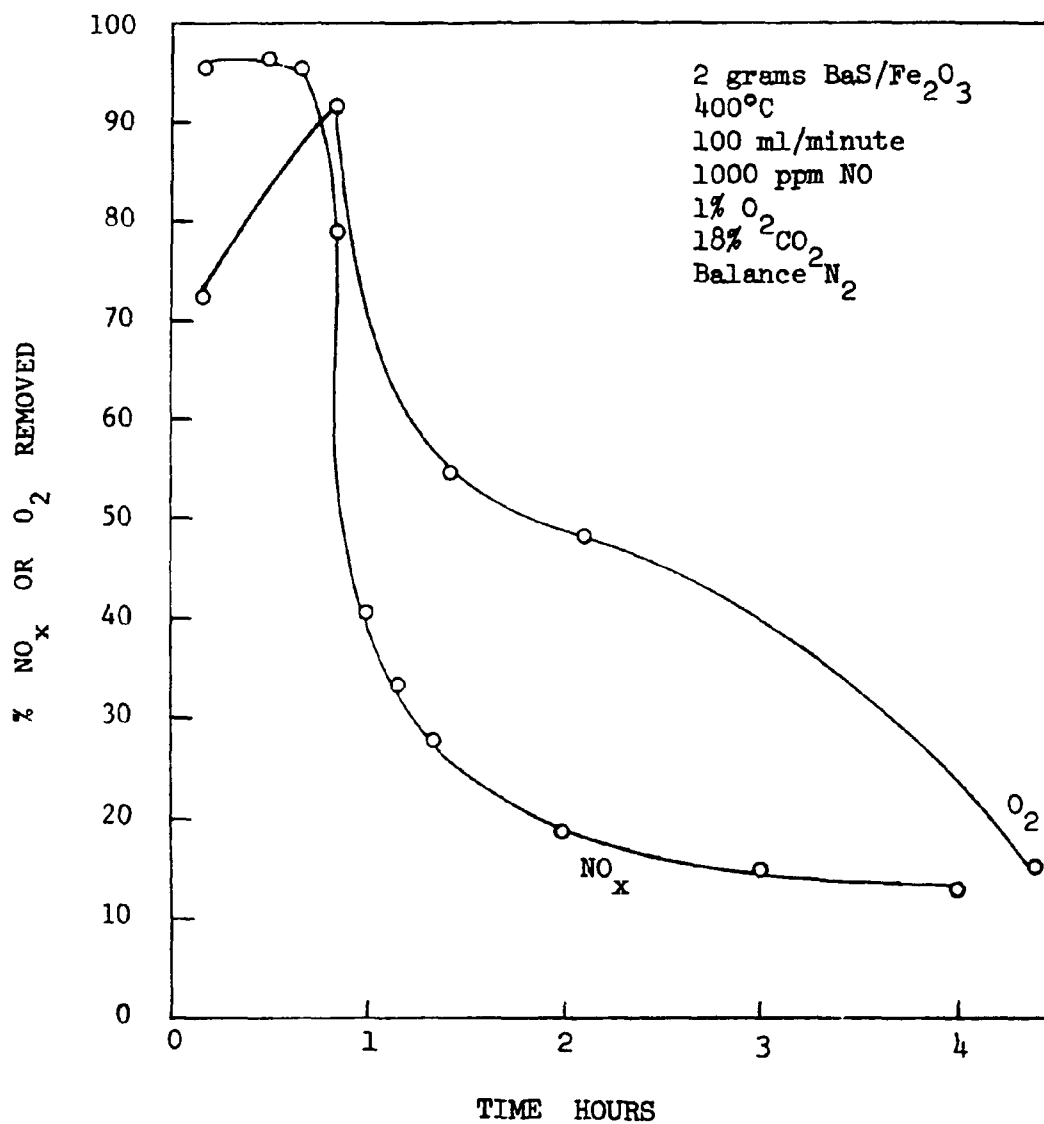FIGURE 32. THE PERCENT NO_x AND O_2 REMOVED
BY 2 GRAMS OF BaS/FeCl$_2$ AT 400°C

FIGURE 33. THE PERCENT NO$_x$ AND O$_2$ REMOVED
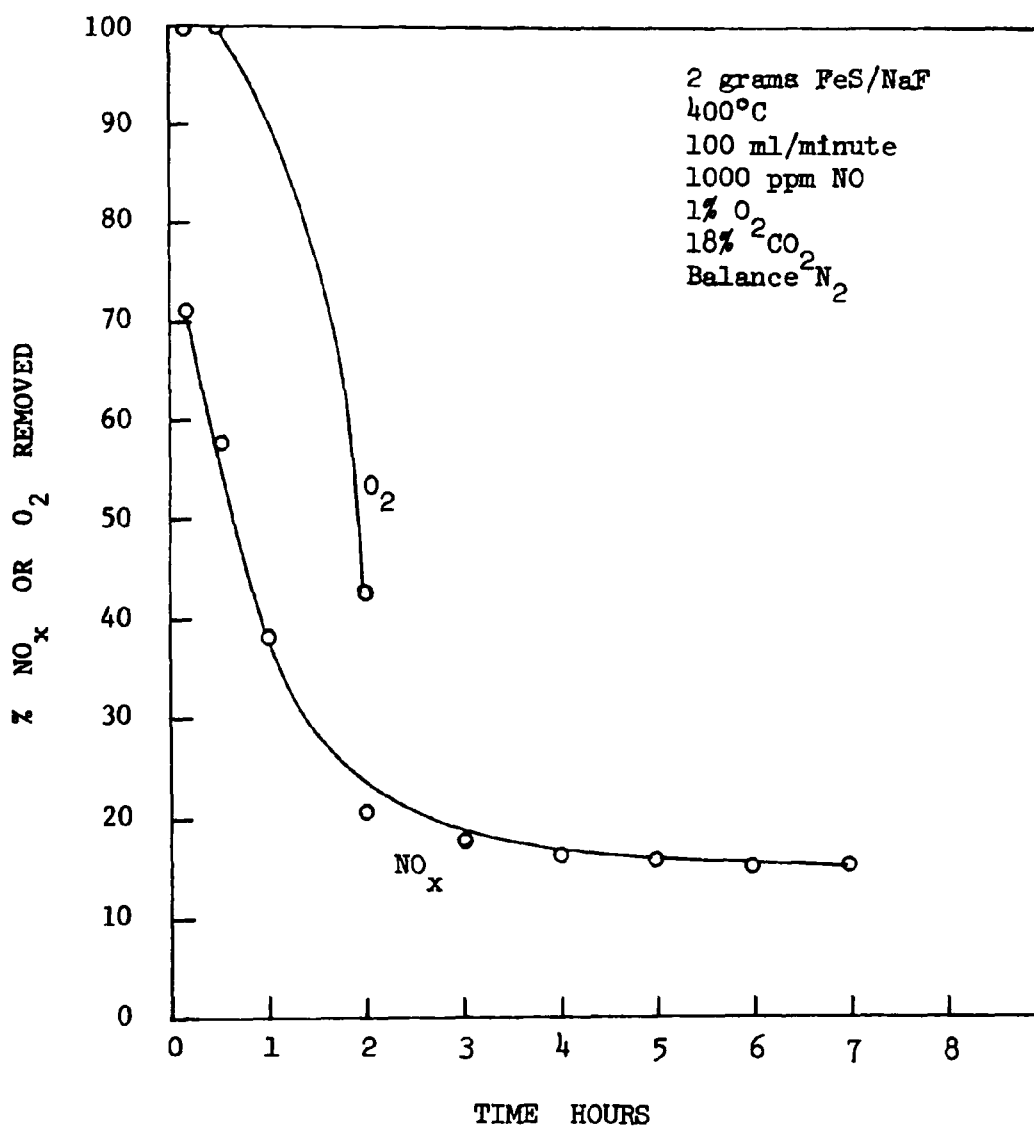BY 2 GRAMS OF BaS/Fe$_2$O$_3$ AT 400°C

FIGURE 34. THE PERCENT NO_x AND O_2 REMOVED
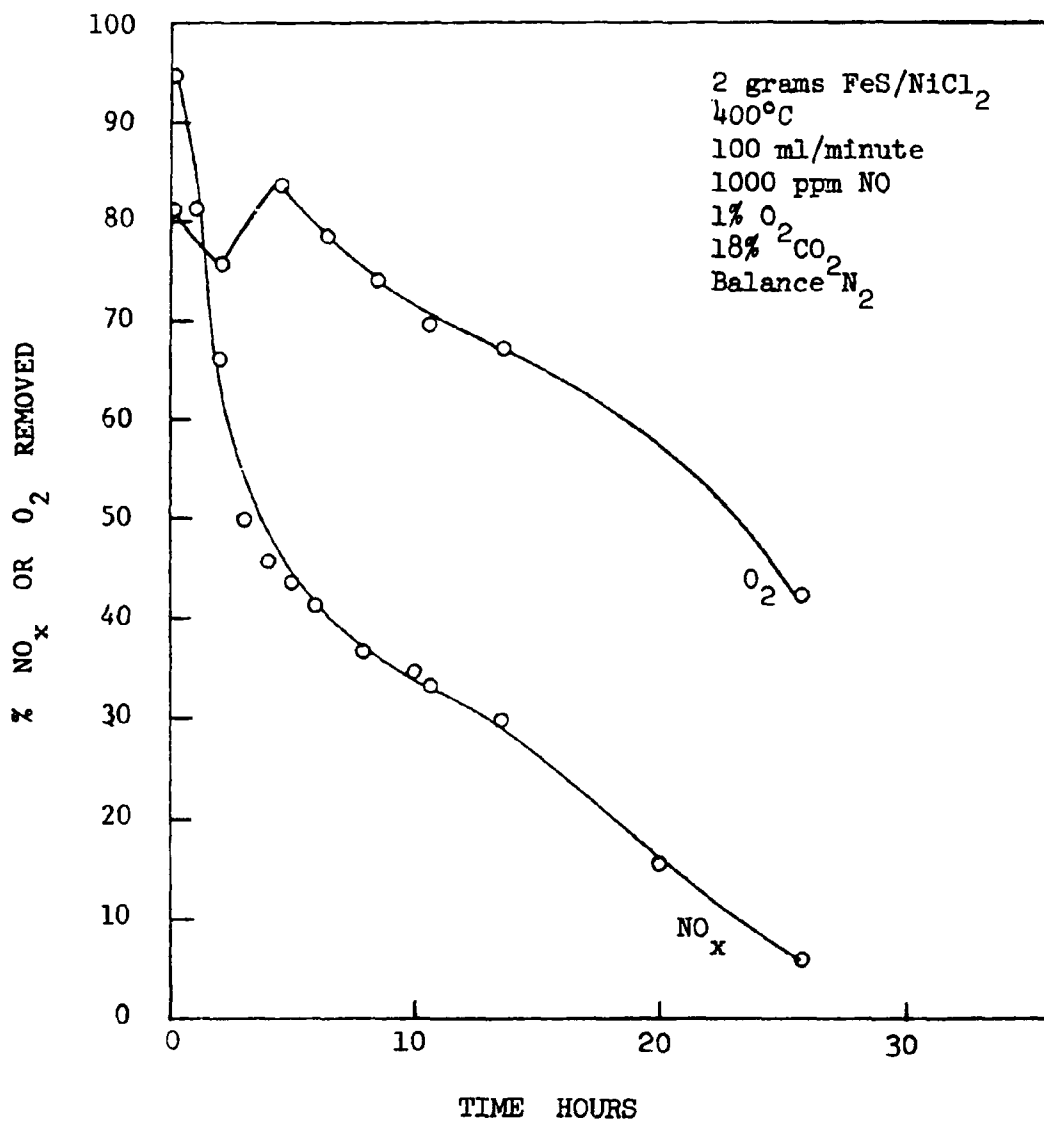BY 2 GRAMS OF FeS/NaF AT 400°C

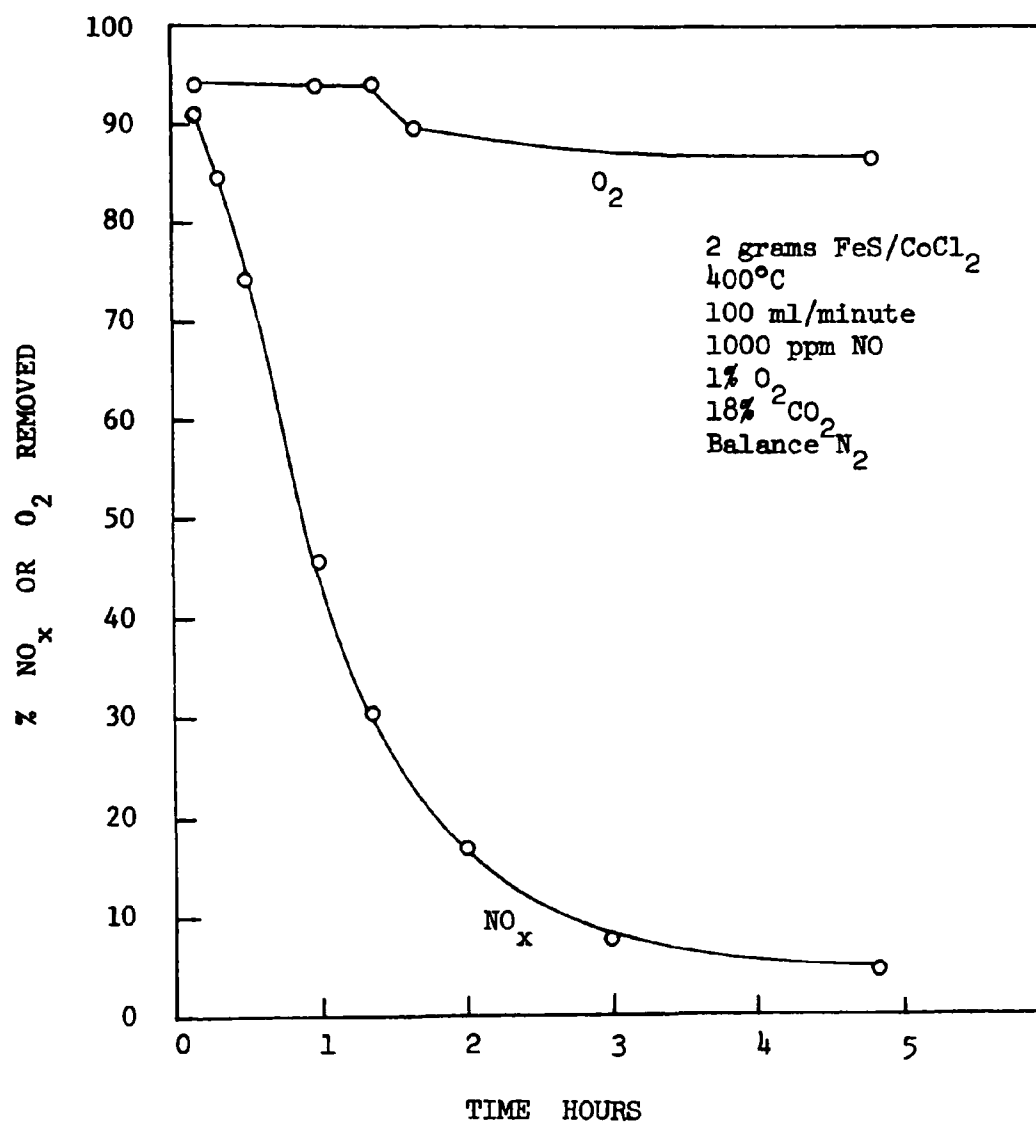FIGURE 35.   THE PERCENT NO$_x$ AND O$_2$ REMOVED

BY 2 GRAMS OF FeS/NiCl$_2$ AT 400°C

FIGURE 36.   THE PERCENT NO$_x$ AND O$_2$ REMOVED
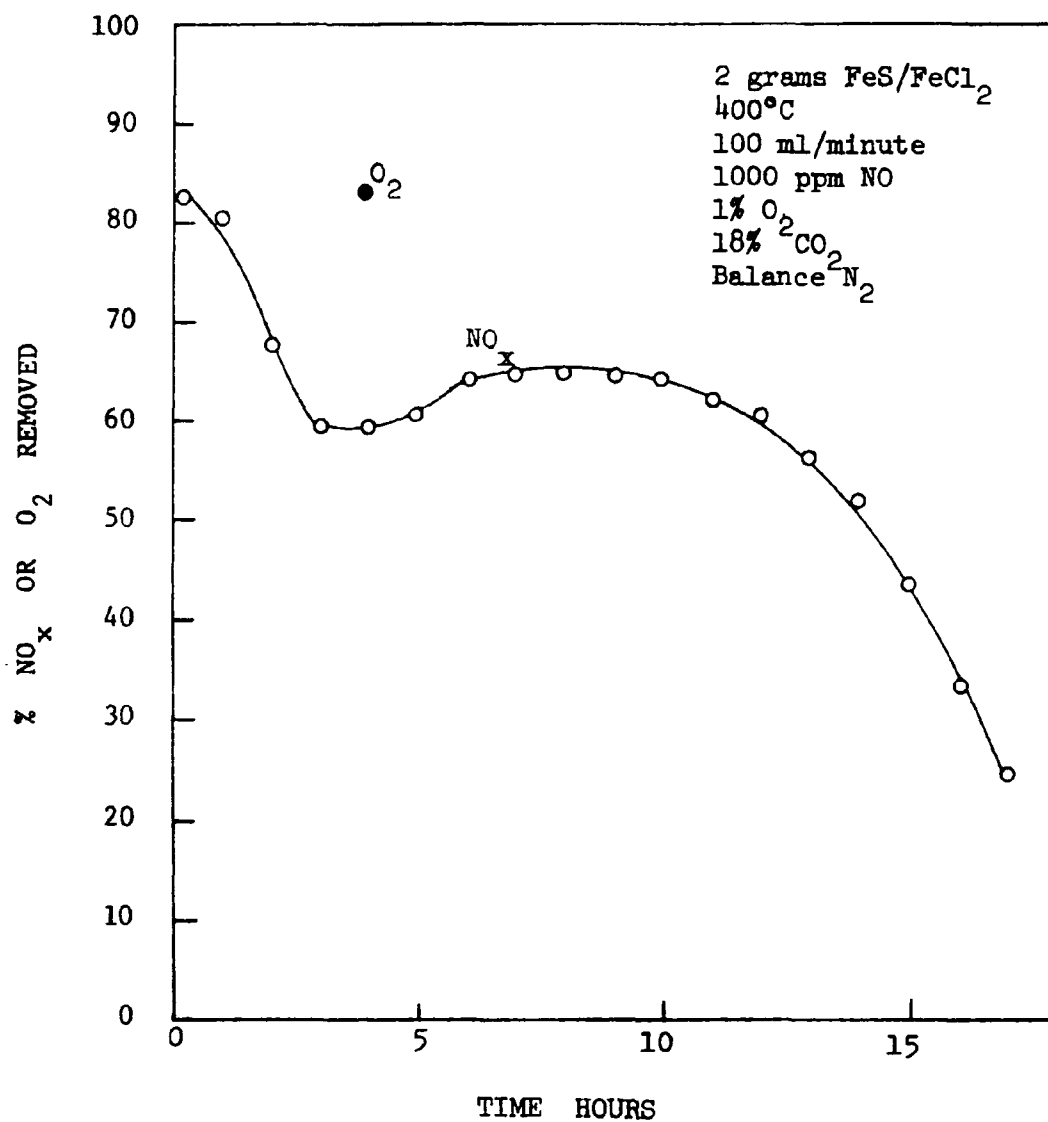
BY 2 GRAMS OF FeS/CoCl$_2$ AT 400°C

FIGURE 37.   THE PERCENT NO$_x$ AND O$_2$ REMOVED
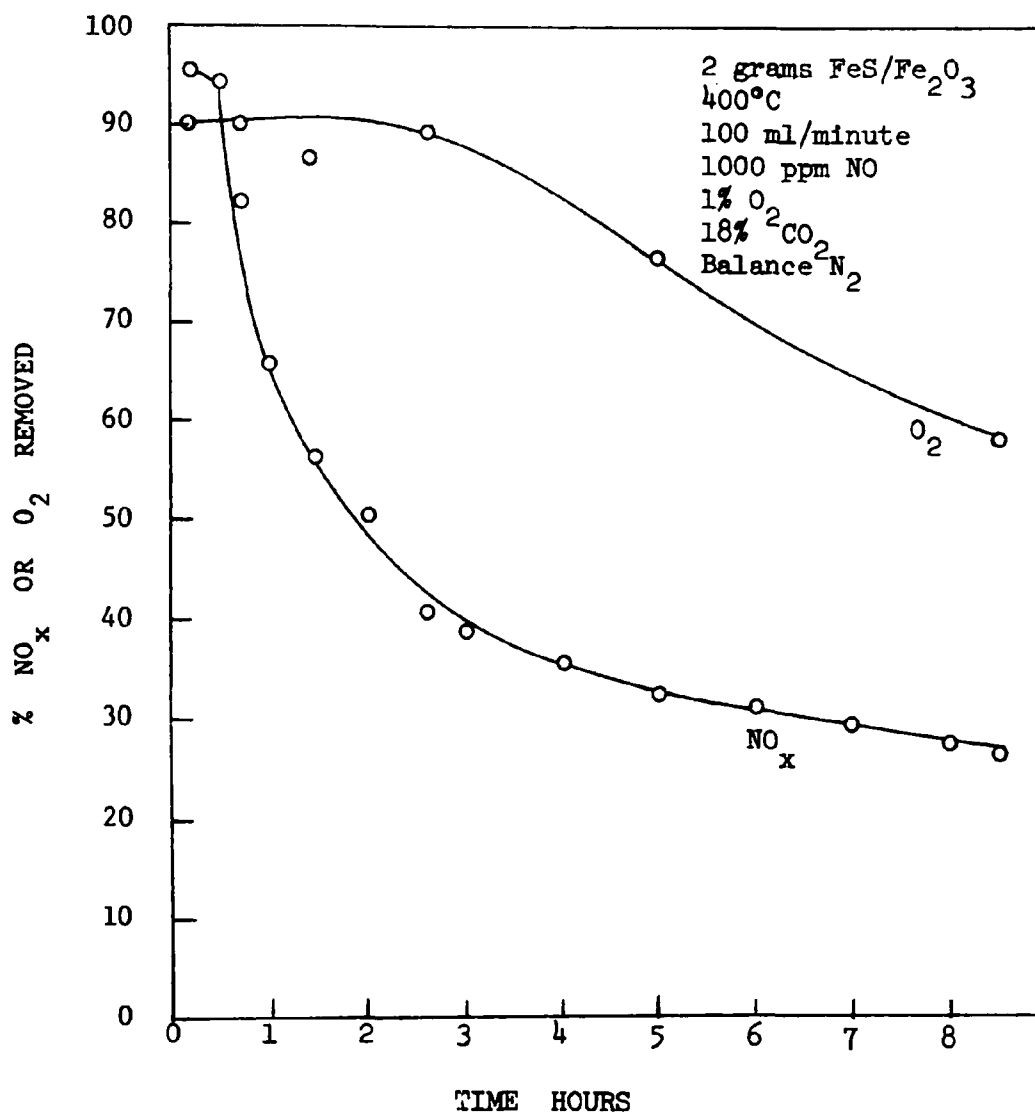
BY 2 GRAMS OF FeS/FeCl$_2$ AT 400°C

FIGURE 38.   THE PERCENT NO_x AND O_2 REMOVED

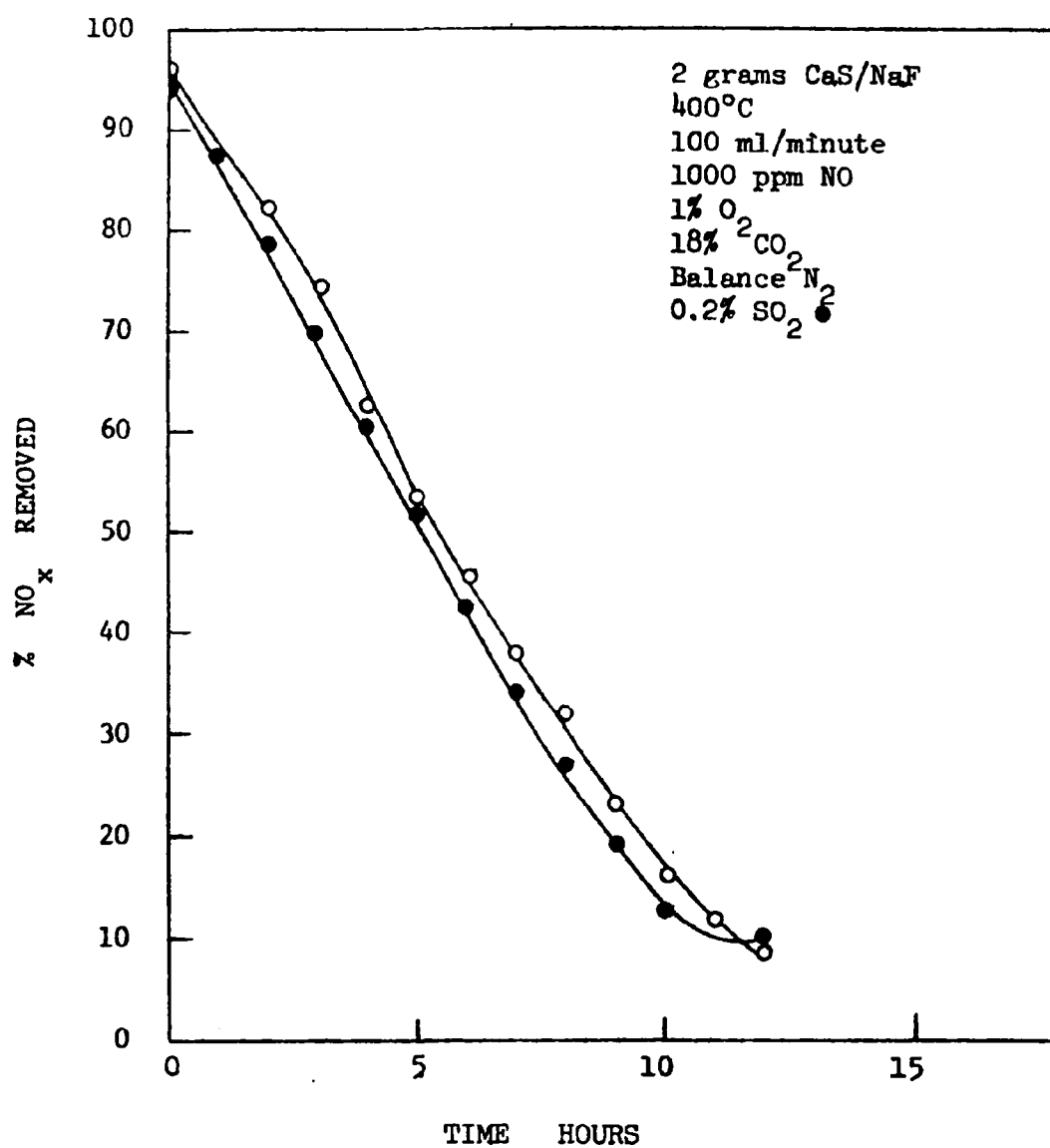BY 2 GRAMS OF FeS/Fe_2O_3 AT 400°C

FIGURE 39.   THE EFFECT OF SO_2 IN THE FEED GAS

STREAM ON NO_x REMOVAL AT 400°C WITH CaS/NaF
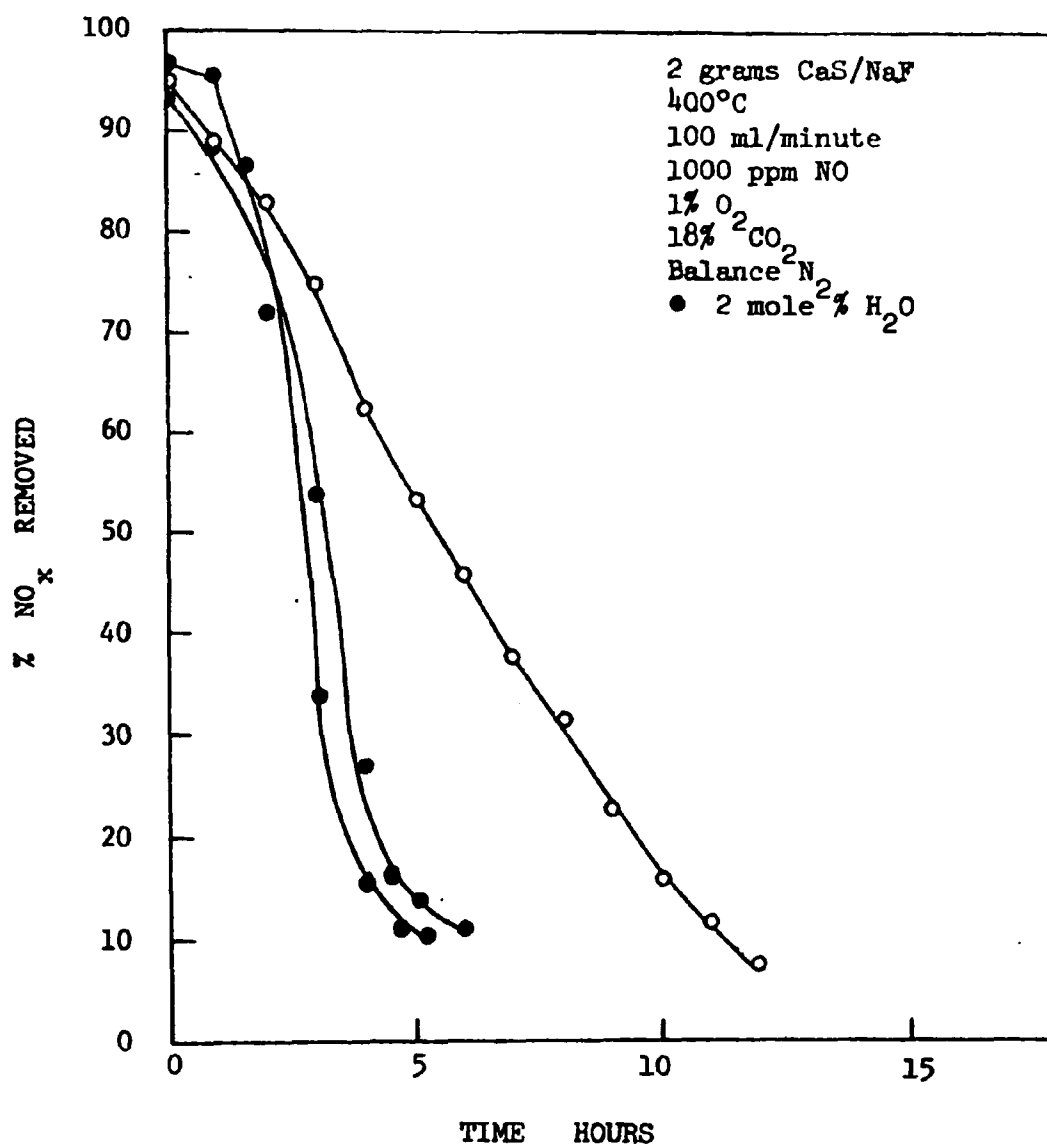
FIGURE 46. THE EFFECT OF H_2O ON NO_x REMOVAL
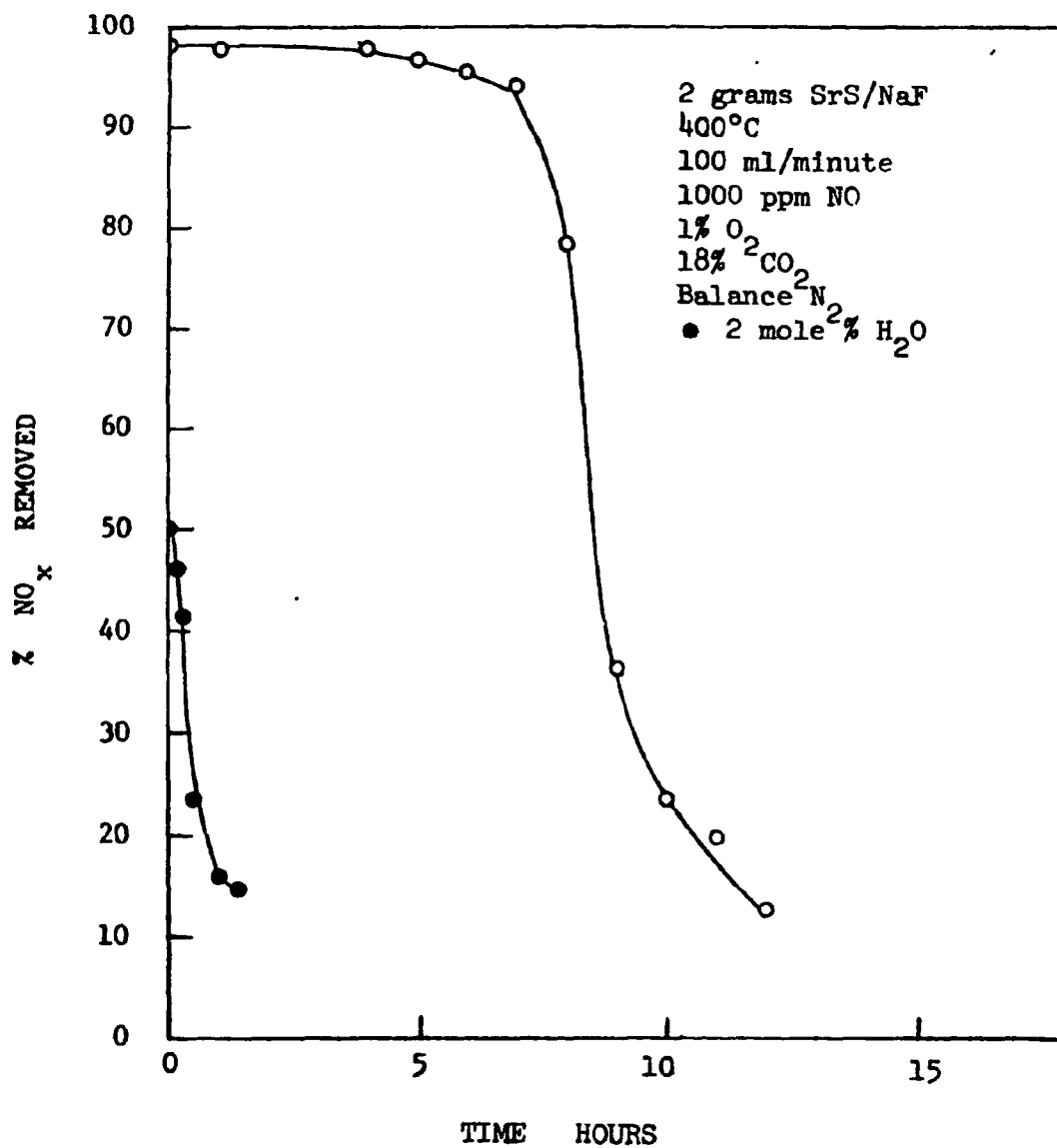
BY CaS/NaF AT 400°C

FIGURE 41. THE EFFECT OF H_2O ON THE REMOVAL

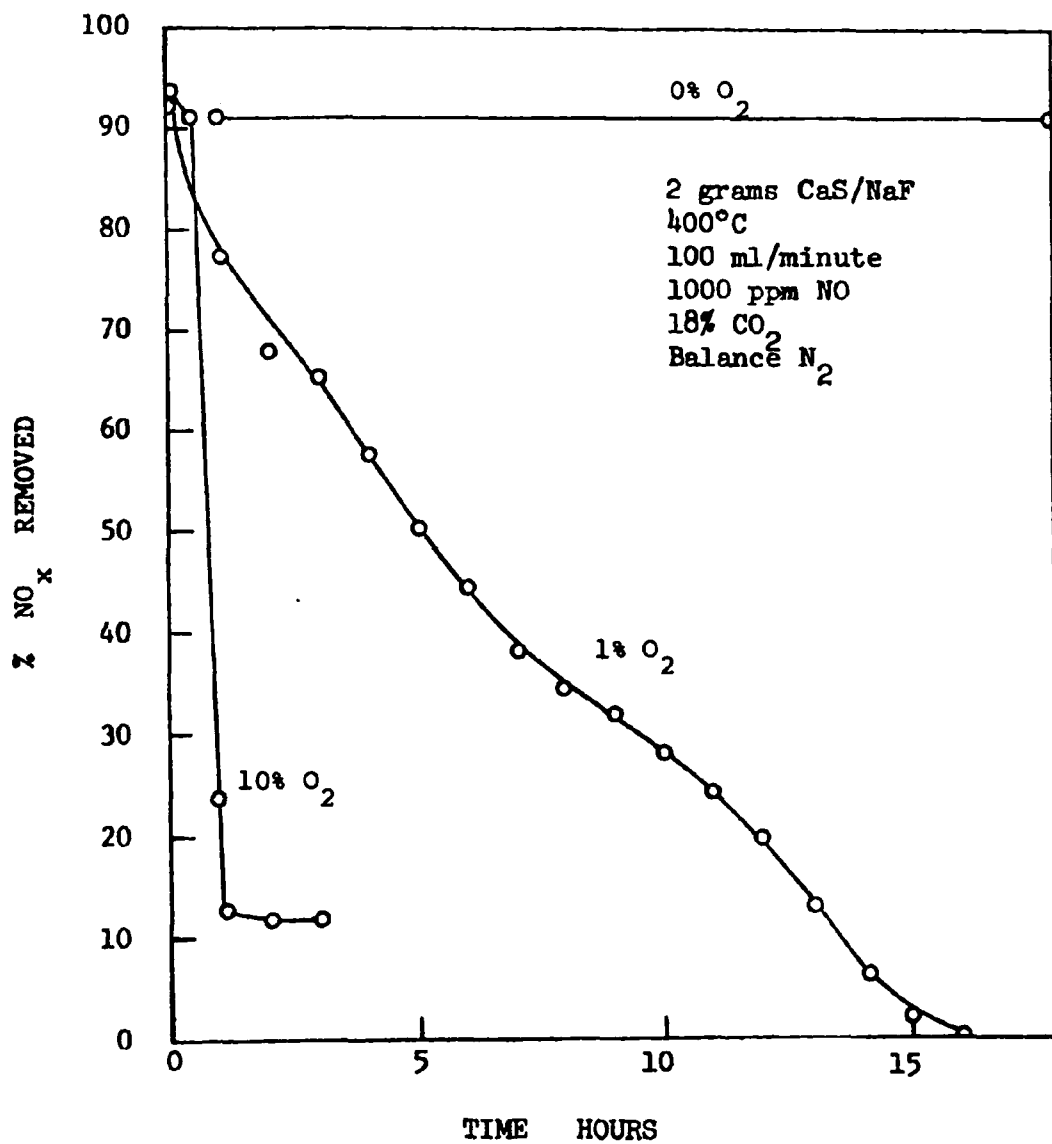OF NO_x BY 2 GRAMS OF SrS/NaF AT 400°C

FIGURE 42. THE EFFECT OF O_2 CONCENTRATION ON NO_x REMOVAL

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Finally, two runs investigated the removal of NO_x from the synthetic
flue gas by 5% CaS (only) impregnated on the high surface supports Harshaw
1602-T and Linde TM-0-1114. The results are shown in Figure 43. As can be
seen, performance curves of the pellets are much better than the best
sulfide-promoter mixtures in bulk form. The capacity of the pellets for NO_x
reduction was calculated to be 0.76 and 0.91 grams NO/grams initial sulfide
in the pellets for the Harshaw and Linde pellets respectively, over 20 times
that of the best bulk sulfide-catalyst mixture.

Discussion

Of the 19 metal sulfides tested for NO reduction only eight (BaS, CdS,
CaS, Cu_2S, PbS, SrS, ZnS, and NiS) showed a weight gain. Of these, the
alkaline earth sulfides (CaS, BaS, SrS) were thought to have the most prom-
ise because of the stability of the sulfides and corresponding sulfates.
Other factors being equal, CaS would be the most desirable sulfide because
of its potential abundance and low cost. It can readily be produced from
gypsum by reduction using a number of reducing agents including coke, carbon
monoxide and hydrogen (15,16). Thus, it would be possible to regenerate the
CaS, and this would result in a process where the reducing agent was coke or
carbon monoxide:

$$CaS + 4NO \rightarrow CaSO_4 + 2N_2$$

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2$$
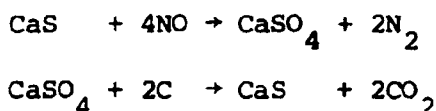
Alternatively, since gypsum is so abundant and cheap it may be econom-
ical to have a throw away process where $CaSO_4$ is not regenerated.

Because of these considerations, much of the research effort concen-
trated on using CaS as the reducing agent. However, some of the data in the
research program indicated that SrS may be superior to CaS when reducing NO
in the presence of O_2. In addition, FeS was investigated further because of
its abundance and high rate of reaction even though SO_2 was formed in the
reduction of NO by FeS.

The rate of reaction is significantly increased by intimately mixing
certain materials with the sulfides. K_3FeF_6 was one of the most active pro-
moters but electrobalance studies showed that it reacted with NO at tempera-
tures between 200 and 500°C resulting in a weight gain. $CoCl_2$ gained weight
when exposed to NO at 300°C but lost weight at 400°C. Fe_2O_3 gained weight
at 300°C. NaF, $NiCl_2$ and $FeCl_2$ did not react with either NO or O_2 at 300
and 400°C. These materials significantly increased the rate of reduction
with some of the sulfides at these temperatures and thus the action appears
to be catalytic in nature. The electrobalance study showed that Fe_2O_3 mixed
with FeS, SrS and CaS significantly increased the rate of reaction with NO in
the absence of O_2 but results using the synthetic flue gas containing 1% O_2
were poor with the sulfide-Fe_2O_3 mixtures. This indicates that O_2 may inter-
fere with any catalytic activity exhibited by Fe_2O_3 under these conditions.
Other trends of the sulfide-catalyst mixtures obtained during the simulated
flue gas generally agree with the data obtained in the electrobalance study.

A very active form of sulfide is obtained by impregnating it on a high
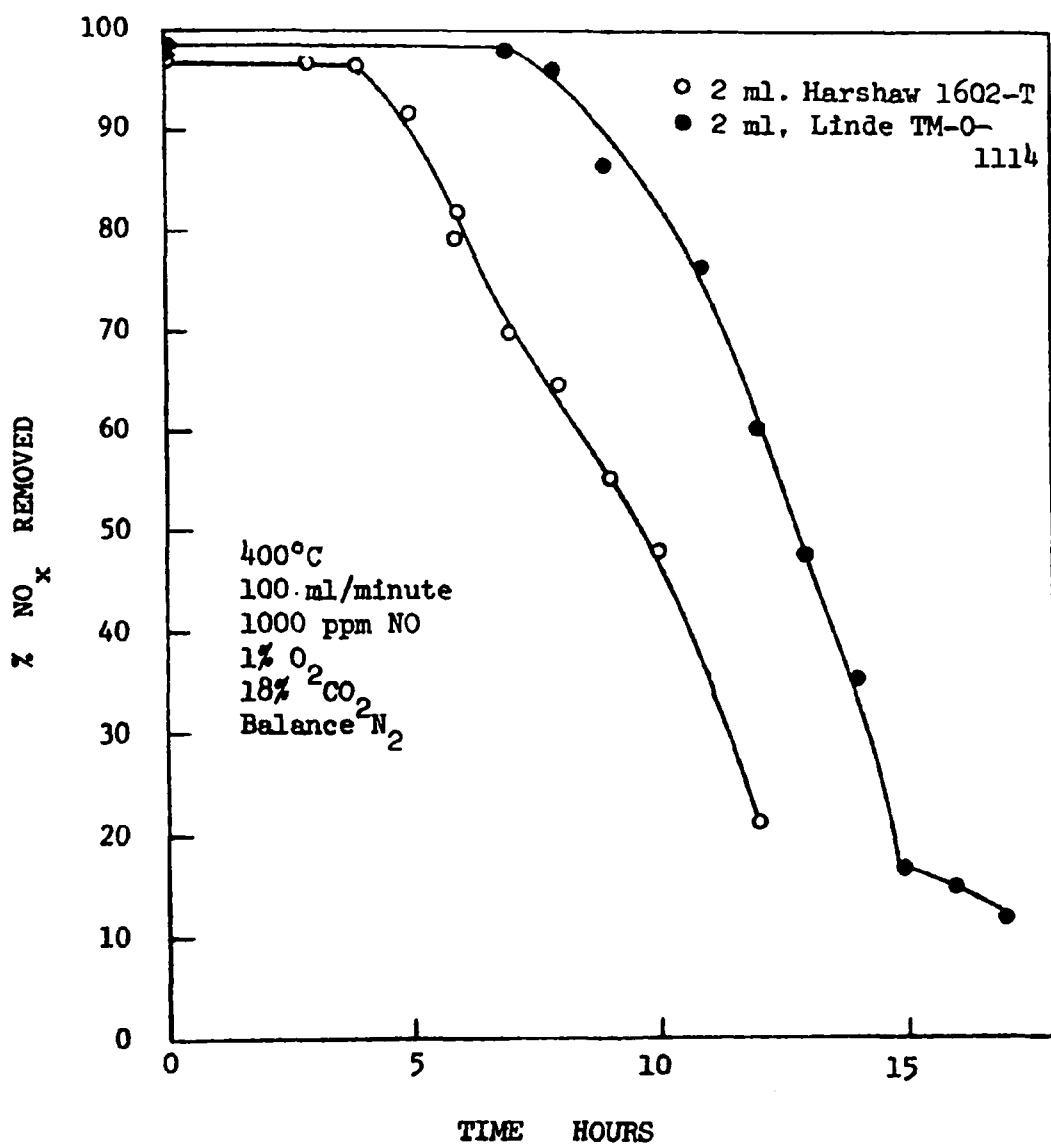surface area support but these are so active that there is a rapid oxidation

FIGURE 43. THE REMOVAL OF NO$_x$ BY HARSHAW PELLETS
AND LINDE MOLECULAR SIEVES IMPREGNATED WITH CaS

of the pellets in air at room temperature. If the sulfide pellets were used in a flue gas environment containing limited amounts of O_2, NO_x reduction would be significant but the pellets would also be rapidly consumed with the O_2. The selection of the support material would be very important since supports of different compositions behave differently. From the limited data obtained, it appears that activated alumina containing very little silica would be the best.

The reaction of the sulfides with O_2 is very important in determining the usefulness of the sulfides for the control of NO_x emissions from flue gases. Flue gases from power plants typically would contain much more O_2 than NO_x (O_2/NO ratios as high as 50/1 are probable) and so when O_2 reacts with the sulfide most of it would be consumed by a non-pollutant. Tests of CaS-NaF at 400°C increasing the O_2 concentration to 10 percent greatly decreased the capacity of the mixture for NO_x reduction. However, the electrobalance studies indicated that, for CaS-NaF mixtures at 200°C, NO reacted at a finite rate while no reaction with O_2 was detected. This could not be verified using the CaS-NaF mixture in the tubular reactor with the simulated flue gas, however, probably because the reaction rate was too low to detect a change in NO_x concentration under the conditions of the test. Apparently the rate of reaction is higher at the higher NO_x concentration used for the electrobalance tests.

The presence of water vapor at lower temperatures lowered the rate of NO_x reduction at least for CaS. This conflicts with the earlier data which showed H_2O had no effect. This indicates that the H_2O probably interferes with the action of the catalyst.

SO_2 and CO_2 had no apparent effect on the performance of the sulfide for NO_x reduction.

The tests using the synthetic flue gas indicate that each sulfide-catalyst mixture behaves quite differently. The performance of the various mixtures generally followed the trends seen in the electrobalance studies but there were some inconsistencies with the FeS-FeCl$_2$ system. The electro-balance studies showed that FeS-FeCl$_2$ had a high rate of weight gain at 300°C but that the mixture lost weight at 400°C using 2.5% NO in He. However, in the synthetic flue gas tests the FeS-FeCl$_2$ had the highest capacity for NO_x reduction of any of the mixtures at 400°C but the capacity was quite low at 300°C. At the low temperature mass transfer may be limiting the reaction rate while at 400°C the rate of reaction is limiting.

FeS forms SO_2 when it reacts with NO and thus it would probably be unsuitable for NO_x control although the rate and capacity is quite high at 400°C.

The capacity (defined as the weight of NO reduced per unit weight of sulfide initially present from the start of the run until the exit concentration exceeds 600 ppm) was quite low for all of the bulk sulfide-catalyst mixtures under the conditions of the tests using the synthetic flue gas test mixture. The two highest were .0372 and 0.0317 grams NO/grams sulfide for FeS-FeCl$_2$ and SrS-NaF mixtures respectively. The best CaS mixtures were .0186 and .0134 grams of NO/grams sulfide for CaS-NaF and CaS-FeCl$_2$ mixture respectively. These compare with the capacity of the 5% CaS (only) high

surface area pellets of 0.76 and 0.91 grams/NO gram sulfide in the Harshaw and Linde pellets, respectively. Thus, it appears that the capacity of the bulk sulfide beds is being limited by poor gas-solid contacting. For comparison, assuming the reaction:

$$CaS + 4NO \rightarrow CaSO_4 + 2N_2,$$
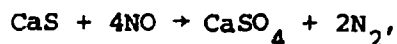
the maximum capacity for CaS would be 1.66 grams NO reduced/gram of sulfide.

The pellet tests indicate that the capacity can be greatly increased by impregnating the sulfide on high surface area supports and it may be possible to further increase it by including a catalyst on the pellets. Reaction in a fluidized bed reactor should also greatly increase the capacity if the bulk material were used.

The tests to date have been limited to a synthetic flue gas containing 1 percent O_2. This would be typical of a flue gas from burning of coal with 10 percent excess air. A more realistic O_2 concentration probably would be about 5 percent O_2 which would result from using about 25 percent excess air, however. The capacity of the sulfides for NO_x reduction would probably be reduced in the flue gas containing the higher O_2 concentration, but it may be possible to obtain a reasonable capacity with the proper choice of sulfide-catalyst-support material at lower temperatures.

The study is continuing and the results will be the topic of a future publication.

REFERENCES

1. Environmental Protection Agency Publication NO. AP-67. Air Quality
    Criteria for Nitrogen Oxide, January 1971.

2. McCutchen, G.D. NO_x Emission Trends and Federal Regulation. Chemical
    Engineering Progress, August 1977, pp. 58-63.

3. Hopper, T.G., and W.A. Manone. Impact of New Source Performance
    Standards on 1985 National Emissions from Stational Sources. EPA 450/
    3-76-017 (May 1976).

4. Karp, I.N., and O.I. Golobov. Paper SM-107181, Magnetohydrodynamics
    Symposium, Warsaw, 5:2875, 1968.

5. Ando, J., H. Tohata, K. Naguta, and B.A. Laseh. NO_x Abatement for
    Stationary Sources in Japan. EPA-600/7-77-1035, Sept. 1977.

6. Henschel, D.B. Emissions from FBC Boilers. Environmental Science &
    Technology 12(5):534-38, 1978.

7. Jain, L.K., E.L. Calvin, and R.L. Looper. State of the Art for Con-
    trolling NO_x Emission, Part I. Utility Boilers, EPA-R-2-72-072a
    (Sept. 1972).

8. Hall, H.J., and W. Bartolk. NO_x Control from Stationary Sources.
    Environmental Science Technology, 5(4):320-6, 1971.

9. Shelef, M., and J.T. Kummer. Chemical Engineering Progress, Symposium
    Series, 67(115):74-93, 1969.

10. Bartok, W., A.R. Crawford, H.J. Hall, E.H. Maury, and A. Skopp. Sys-
    tems Study of Nitrogen Oxide Control Methods for Stationary Sources.
    Clearing House for Federal Scientific and Technical Information,
    PB 184 479, May 1969.

11. Ando, J., and H. Tohata. Nitrogen Oxide Abatement Technology in Japan
    --1973. EPA-R2-73-284 (June 1973); NTIS PB-22 143.

12. Faucett, H.L., J.D. Maxwell, and T.A. Barnett. Technical Assessment of
    NO_x Removal Processes for Utility Application. EPRI AF-568, EPA-600/
    7-77-127, Office of Research and Development, U.S. Environmental
    Protection Agency, Nov. 1977.

13. Fulton, C.H. Metallurgical Smoke. Bulletin 84, Dept. of the Interior,
    Bureau of Mines, 1915, pp. 72-77.

14. Young, S.W. The Thiogen Process for Removing Sulfur Fumes. Trans.
    AIChE, 8:81-89, 1915.

15. George, D'Arcy, L. Croker, and J.B. Rosenbaum. Current Research on the Production of Sulfur from Gypsum at the Salt Lake City Metallurgy Research Center of the U.S. Bureau of Mines, March 1968.

16. Zadick, T.W., R. Zavalita, and F.P. McCandless. Catalytic Reduction of Calcium Sulfate to Calcium Sulfide with Carbon Monoxide. Ind. Eng. Chem. Process Res. Develop, 11(2):283-7, 1972.

17. Berty, J.M. Reactor for Vapor-Phase Catalytic Studies. Chemical Engineering Progress, 70(4):78-84, May 1974.

18. Carberry, J.J. Designing Laboratory Catalytic Reactors. Industrial and Engineering Chemistry, 56:39, Nov. 1974.

TECHNICAL REPORT DATA
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1. REPORT NO. EPA-600/7-78-213	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Reduction of Nitric Oxide with Metal Sulfides		**5. REPORT DATE** November 1978
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) F. P. McCandless and Kent Hodgson		**8. PERFORMING ORGANIZATION REPORT NO.**
9. PERFORMING ORGANIZATION NAME AND ADDRESS Montana State University Department of Chemical Engineering Bozeman, Montana 59717		**10. PROGRAM ELEMENT NO.** INE624
		11. CONTRACT/GRANT NO. Grant R800682
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		**13. TYPE OF REPORT AND PERIOD COVERED** Final; 6/72 - 5/78
		14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is J. David Mobley, Mail Drop 61, 919/541-2915.

16. ABSTRACT The report gives results of research to determine the technical feasibility of using metal sulfides for the chemical reduction of NOx to N2. Nineteen different metal sulfides were investigated, using a test gas of pure NO. Although most sulfides resulted in some NO reduction, BaS, CaS, SrS, and FeS were the most promising. Several catalysts reduced the temperature at which the reduction process proceeds by as much as 200 C. A further temperature reduction was obtained by impregnating the sulfide and catalyst on high surface area supports of activated alumina or molecular sieves. The most promising catalysts were NaF, NiCl2, and FeCl2. All combinations of the most promising sulfides and catalysts were tested for NO reduction, using a synthetic flue gas containing 1000 ppm NO and 1% O2. The capacities of the six best were FeS-FeCl2 > SrS-NaF > CaS-NaF > BaS-FeCl2 > FeS-NiCl > CaS-FeCl2, and ranged from 0.0372 to 0.0134 g NO reduced/g initial sulfide present. Capacities of 0.91 and 0.76 g NO/g sulfide were obtained when using 5% CaS (only) impregnated on alumina and molecular sieves, respectively. It was concluded that these sulfides can reduce NO in the presence of O2, but more research is required to establish the economic feasibility.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Catalysis	Pollution Control	13B	07D
Nitrogen Oxides	Aluminum Oxide	Stationary Sources	07B	
Reduction	Absorbers	Metal Sulfides	07C	11G
Barium Inorganic Compounds		Activated Alumina		
Calcium Inorganic Compounds		Molecular Sieves		
Strontium Compounds				

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 94
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)