



Kinetic studies on absorption of NO_x by alkali carbonate-metal oxide sorbents
by Christopher John Evoniuk

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF
PHILOSOPHY in Chemical Engineering
Montana State University
© Copyright by Christopher John Evoniuk (1978)

Abstract:

Mixtures made from alkali carbonates and transition metal oxides were tested for their NO_x (NO + NO₂) absorption capabilities. A packed bed reactor and a recycle reactor were used in testing the solid sorbent mixtures and a NO_x Chemiluminescent Analyzer was used to measure NO and NO_x concentrations. The sorbents were tested in the form of powders and as flat plates with test gases composed of 1000 to 9000 ppm NO_x, 0 to 10% O₂, and 0 to 15% CO₂. Sorbents were also tested to determine the effect of SO₂ and H₂O on NO_x absorption.

Of the sorbents tested, K₂CO₃ + Fe₂O₃, K₂CO₃ + MnO₂, and Na₂CO₃ + MnO₂ were the most-promising absorbers of NO_x. It was found that 7.5 grams of these sorbents at temperatures ranging from 360 to 450°C could absorb 99% of the NO_x from a gas stream flowing at a rate of 620 ml/min and containing 9000 ppm NO_x, 2% O₂ and 15% CO₂. The rate of NO_x absorption could be increased by increasing the O₂ concentration and by decreasing the CO₂ concentration. Capacities of the sorbents were equal to the theoretical amount of NO required to convert the alkali carbonate to an alkali nitrate. SO₂ was absorbed by the sorbents forming an alkali sulfate which did not absorb NO_x. H₂O was found to not have any effect on absorption.

Regeneration of the sorbents was accomplished by heating them at temperatures ranging from 500 to 700°C. Sorbents made with Na₂CO₃ required lower temperatures to desorb than those made with K₂CO₃.

It was found that sorbents made with MnO₂ underwent changes when heated above 560°C which reduced their NO absorption ability. Sorbents made with Fe₂O₃ did not show a loss in NO_x absorption ability when desorbed at temperatures as high as 700°C. The NO absorbed by the sorbents can be recovered at concentrations greater than 10% when the sorbents are regenerated.

© 1980

CHRISTOPHER JOHN EVONIUK

ALL RIGHTS RESERVED

KINETIC STUDIES ON ABSORPTION OF NO_x BY
ALKALI CARBONATE-METAL OXIDE SORBENTS

by

CHRISTOPHER JOHN EVONIUK

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

of

DOCTOR OF PHILOSOPHY

in

Chemical Engineering

Approved:

W. M. C. C. C.
Chairperson, Graduate Committee

L. R. R.
Head, Major Department

W. L. P.
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

May, 1978

ACKNOWLEDGMENTS

The author wishes to thank the faculty and staff of the Department of Chemical Engineering for their assistance, especially Dr. Giles Cokelet and Dr. Phil McCandless for their helpful suggestions. Very special thanks is extended to the author's wife, Marian, for her patience and understanding during the course of the research and for editing and typing the thesis.

A note of gratitude is extended to the scientists of the past whose efforts have provided us with a wealth of knowledge and understanding which enables us to better perform our work. And, most of all, a thank you goes to the Creator of what we have and are.

TABLE OF CONTENTS

	Page
VITA	ii
ACKNOWLEDGEMENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
ABSTRACT	x
I. INTRODUCTION	1
Typical Conditions Encountered	4
NO Absorption	5
Previous Studies on Solid Sorbents	7
II. OBJECTIVES	13
III. EXPERIMENTAL APPARATUS AND PROCEDURE	14
Analytical Equipment	18
Gas Mixtures	20
Sorbent Preparation	21
IV. REACTOR ANALYSIS	23
V. RESULTS	26
Analysis of Feed Composition	26
Sorbent Comparisons on Flat Plates with Unmodified	
Feed Line	30
Effect of O_2 and CO_2 on NO_x Absorption using the Flat	
Plates and the Unmodified Feed Line	37
Effect of O_2 and CO_2 using the Modified Feed Line	40

Effect of the Ratio of Carbonate to Metal Oxide on Absorption	43
Effect of Gas Composition on Desorption of NO_x from Flat Plates	46
Effect of O_2 and NO_x on Absorption using Packed Beds ..	46
Loading Studies using Packed Beds	50
Effect of Mole Ratio of Carbonate to Oxide on Absorption	50
Absorption using Carbonates Impregnated on Harshaw Pellets	54
Effect of SO_2 and H_2O on Absorption	57
Desorption Studies	58
Absorption after Desorption	69
Mechanism Study	69
VI. THERMODYNAMIC AND EQUILIBRIUM RELATIONSHIPS	80
VII. MATHEMATICAL CORRELATIONS	85
VIII. ECONOMIC CONSIDERATIONS	91
IX. GENERAL DISCUSSION	96
X. CONCLUSIONS	99
XI. RECOMMENDATIONS	102
XII. BIBLIOGRAPHY	103

LIST OF TABLES

Table		Page
1	Typical Flue Gas Compositions	5
2	Data on Sorbents Tested by Gidaspow	10
3	NO _x Absorption by Carbonates and Fe ₂ O ₃	32
4	NO _x Absorption by Mixtures of Oxides and Carbonates ...	33
5	Compounds Showing Deactivation after Desorption	35
6	Miscellaneous Compounds	36
7	Materials Tested as Powders	38
8	Carbonates on Oxide Pellets	56
9	Chemical Equilibrium Constants	81
10	Equilibrium Compositions at Atmospheric Pressure	82
11	Selected Free Energies of Formation	83
12	Loading Capacities and Rate Constants	90
13	Costs of Sorbents	92

LIST OF FIGURES

Figure		Page
1	Experimental Apparatus	15
2	Reactor Diagram	17
3	Effect of CO_2 and O_2 Concentration on NO Conversion in Feed Line	27
4	Equilibrium Ratio of NO to Total NO_x	29
5	Effect of O_2 and CO_2 on NO Conversion in Modified Feed Line	31
6	Effect of O_2 Concentration on NO_x Absorption (High NO_x)	39
7	Effect of CO_2 Concentration on NO_x Absorption (High NO_x)	39
8	Effect of O_2 and CO_2 Concentration on NO_x Absorption (Low NO_x)	41
9	Effect of O_2 Concentration on NO_x Absorption by Carbonates (High NO_x)	41
10	Effect of O_2 on NO_x Absorption (High NO_x)	42
11	Effect of CO_2 on NO_x Absorption (High NO_x)	42
12	Effect of O_2 on NO_x Absorption (Low NO_x)	44
13	Effect of CO_2 on NO_x Absorption (Low NO_x)	44

Figure		Page
14	Effect of $K_2CO_3:Fe_2O_3$ Ratio on NO_x Absorption (15% CO_2)	45
15	Effect of $K_2CO_3:Fe_2O_3$ Ratio on NO_x Absorption (0% CO_2)	45
16	Effect of Gas Composition on Desorption	47
17	Effect of O_2 Concentration on NO_x Absorption for Packed Beds	48
18	Loading of 1:1 $K_2CO_3 + Fe_2O_3$ at Low NO_x	51
19	Loading of 1:1 $K_2CO_3 + Fe_2O_3$ at High NO_x	52
20	Effect of the Molar Ratio of $K_2CO_3 + Fe_2O_3$ on Absorption (Packed Bed)	53
21	Effect of the Molar Ratio of $K_2CO_3 + MnO_2$ and $Na_2CO_3 + MnO_2$ on Absorption (Packed Bed)	55
22	Effect of Temperature on Desorption of $Na_2CO_3 + MnO_2$ and $K_2CO_3 + Fe_2O_3$	59
23	Effect of Temperature on Desorption of 1:4 $K_2CO_3 + Fe_2O_3$	60
24	Effect of Temperature on Desorption of 1:1 $Na_2CO_3 + MnO_2$ (Packed Bed)	62
25	Desorption of O_2 from MnO_2 as a Function of Temperature	64

Figure		Page
26	Desorption of 1:1 $K_2CO_3 + Fe_2O_3$	65
27	Desorption of 1:2 $K_2CO_3 + Fe_2O_3$	66
28	Desorption of 1:1 $Na_2CO_3 + MnO_2$	68
29	Oxidation of NO to NO_2 by Fe_2O_3 , MnO_2 and Ag_2O	70
30	Oxidation of NO to NO_2 by V_2O_5 , CuO , NiO , Cr_2O_3 and Co_2O_3	71
31	Effect of Temperature on Absorption by $Na_2CO_3 + Fe_2O_3$ and $Na_2CO_3 + MnO_2$	73
32	Effect of Temperature on Absorption by $K_2CO_3 + Fe_2O_3$ and $K_2CO_3 + MnO_2$	74
33	Effect of Separating Na_2CO_3 from MnO_2	75
34	Effect of CO_2 on NO_x Absorption by K_2CO_3 (Packed Bed)..	77
35	Log Plot for Data on Figure 18	88
36	Equilibrium Composition of NO as a Function of Temperature	95

ABSTRACT

Mixtures made from alkali carbonates and transition metal oxides were tested for their NO_x ($\text{NO} + \text{NO}_2$) absorption capabilities. A packed bed reactor and a recycle reactor were used in testing the solid sorbent mixtures and a NO_x Chemiluminescent Analyzer was used to measure NO and NO_x concentrations. The sorbents were tested in the form of powders and as flat plates with test gases composed of 1000 to 9000 ppm NO_x , 0 to 10% O_2 , and 0 to 15% CO_2 . Sorbents were also tested to determine the effect of SO_2 and H_2O on NO_x absorption.

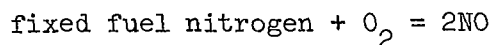
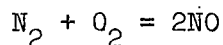
Of the sorbents tested, $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$, $\text{K}_2\text{CO}_3 + \text{MnO}_2$, and $\text{Na}_2\text{CO}_3 + \text{MnO}_2$ were the most promising absorbers of NO_x . It was found that 7.5 grams of these sorbents at temperatures ranging from 360 to 450°C could absorb 99% of the NO_x from a gas stream flowing at a rate of 620 ml/min and containing 9000 ppm NO_x , 2% O_2 and 15% CO_2 . The rate of NO_x absorption could be increased by increasing the O_2 concentration and by decreasing the CO_2 concentration. Capacities of the sorbents were equal to the theoretical amount of NO required to convert the alkali carbonate to an alkali nitrate. SO_2 was absorbed by the sorbents forming an alkali sulfate which did not absorb NO_x . H_2O was found to not have any effect on absorption.

Regeneration of the sorbents was accomplished by heating them at temperatures ranging from 500 to 700°C. Sorbents made with Na_2CO_3 required lower temperatures to desorb than those made with K_2CO_3 . It was found that sorbents made with MnO_2 underwent changes when heated above 560°C which reduced their NO_x absorption ability. Sorbents made with Fe_2O_3 did not show a loss in NO_x absorption ability when desorbed at temperatures as high as 700°C. The NO_x absorbed by the sorbents can be recovered at concentrations greater than 10% when the sorbents are regenerated.

I. INTRODUCTION

The oxides of nitrogen, NO and NO₂ are components in the formation of photochemical smog and are considered air pollutants. Mixtures of NO and NO₂ are termed NO_x but emission sources and standards are based on NO₂ under the assumption that the NO is ultimately oxidized to NO₂ by the reaction $\text{NO} + 1/2 \text{O}_2 = \text{NO}_2$. Bartok reported that in 1968 stationary sources accounted for 60% of the total NO₂ emitted in the United States (Bartok et al. 1968). Of that 60%, electric power generation accounted for 38%, industrial boilers 29%, stationary combustion engines 21%, small combustion sources 10%, and noncombustion sources 2%. Fossil fuel combustion, coal and gas, accounted for 40% of the NO_x emissions from stationary sources (Bartok 1971).

Current EPA emission standards for NO_x from coal fired steam generators are 0.70 lb. of NO₂ per million BTU's of heat input or approximately 600 ppm (Walters and Goodwin 1974). The amount of nitric oxide (NO) present in flue gases is dependent on the concentration of oxygen and nitrogen, temperature, and type of fuel used in the combustor. Nitric oxide is formed in the high temperature combustion zone of the burners by the chemical reactions:



U.S. coals contain from 1.15% to 1.74% fixed nitrogen and this will produce 880 - 1330 ppm NO if 40% of the fixed N₂ is converted to NO

(Pershing 1973). Current estimations of the NO_x emissions from the MHD process, which uses temperatures approaching 3000°K , range from 600 ppm to 30,000 ppm (3%) depending upon the combustion scheme used (Hals and Lewis 1973).

Current technology for the control of NO_x ($\text{NO} + \text{NO}_2$) consists of combustion modification, denitrification of the fuel, catalytic reduction and absorption by solids or liquids. Combustion modification includes staged combustion, flue gas recirculation and low excess air firing. The problems encountered in combustion modification are reduced efficiency, excess CO formation and unresolved slagging and corrosion problems (Pershing 1973). In the case where NO_x is derived from the nitrogen in the fuel, reducing the oxygen supply is required to reduce NO_x emissions rather than reducing the temperature of the combustor (Clay 1975, Pershing et al. 1973, Turner et al. 1972). The advantages of combustion modification are low cost and ease of implementation. Catalytic reduction systems need to operate in a net reducing atmosphere and thus it is necessary to carry out combustion under sub-stoichiometric oxygen conditions or it is necessary to add CO, H_2 or CH_4 to the flue gas (Bartok 1971). In either case emissions from the uncombusted material occur resulting in overall combustion inefficiency. Selective reduction of NO with ammonia using a catalyst in a net oxidizing atmosphere has proven to be effective. However, catalyst poisoning and the cost of ammonia present a problem for large scale applications

of the process. It has been estimated that if catalyzed ammonia reduction systems for NO_x were used extensively in Japan, consumption of ammonia would reach 400,000 tons/yr. This is about half of Japan's current nitrogen fertilizer use (Ricci 1977).

Liquid scrubbing systems have been found to be useful for SO_2 but NO has to be oxidized to at least 50% NO_2 before efficient absorption occurs because absorption is due to the mixed oxide N_2O_3 (Koval and Roberts 1960, Chappell 1973, Hals and Lewis 1973). Other problems associated with liquid scrubbing are low capacity, limitations in operating temperature due to high vapor pressure of liquids, and the possible formation of volatile pollutant compounds especially in the case of the ammonia and amine solutions which are reportedly the best absorbers of NO (Chappell 1973).

Solid sorbents show a technical promise primarily for the absence of some of the basic problems affecting the liquid systems. They have the advantage of higher operating temperature, and the absence of problems of flue gas reheating, contacting liquids or slurries with gases and the crystallization phenomena that is usually associated with flue gas scrubbing (Clay 1975). Although a solid sorption system looks promising there has been limited data published. Sorbent attrition under the conditions required for flue gas treatment is another problem facing the application of solid sorbents. However, the technology needed to prevent sorbent attrition has been reportedly developed in the

Shell Flue Gas Desulfurization Process which uses a solid sorbent to absorb SO_2 (Groenendaal 1976).

An area in which absorption of NO_x could be valuable is in the MHD electrical generation process. This system operates at high temperatures and consequently is capable of forming large amounts of NO. It has been reported (Wright and Youderian 1976, Hals and Jackson 1969) that the sale of nitric acid recovered from the NO produced in a 1000 MW MHD generator could produce more income than the sale of the electricity. An alternative which would not produce nitric acid but would reduce NO_x levels is to absorb the NO from the flue gas with a sorbent then desorb the NO and recycle it to the combustion chamber where it would decompose to equilibrium levels. The remaining NO would then be reabsorbed and the cycle repeated.

Typical Conditions Encountered

In applying sorbents for the absorption of NO_x , other materials are present which could interfere, such as H_2O , O_2 , SO_2 and particulate matter. Table 1 presents an approximate analysis of the other flue gas components. Other parameters of importance include flow rates and temperatures. Gas flow rates are as high as 75×10^6 scf/hr. for a 1000 MW (electrical) MHD plant and 70×10^6 scf/hr. for a 750 MW (electrical) gas fired plant (Bartok 1971). Combustor temperatures range from 2727°C for an MHD plant, $1650\text{--}2090^\circ\text{C}$ for a typical coal fired plant to $671\text{--}1204^\circ\text{C}$ for a fluidized bed combustor and the flue gas tem-

perature ranges from 127-177°C (Kube and Gronhovd 1977). Due to these high temperatures and flow rates, NO oxidation is limited and the NO comprises about 90% of the NO_x (Bartok 1971).

Table 1. Typical Flue Gas Compositions (Chappell 1973)

Component	Volume % from Combustion of		
	Coal	Oil	Gas
N_2	76.2	77	72.3
CO_2	14.2	12	9.9
H_2O	6.0	8	16.8
O_2	3.3	3	1.8
SO_2	.2	.15	---
NO_x	?	.07	?
Particulate	.5	.01	---

NO Absorption

As was mentioned earlier the absorption of NO by aqueous scrubbing requires that some of the NO (at least 50%) be oxidized to NO_2 before efficient absorption can occur. The absorption of NO is due to the formation of the mixed oxide N_2O_3 ($\text{NO} + \text{NO}_2$) which is absorbed by the water to form nitrous acid (HNO_2). For NO to be absorbed by aqueous solutions of other materials such as alkali sulfites and hydroxides, the NO also has to be oxidized to NO_2 (Chappell 1973). Although the liquid scrubbing methods are attractive because of the low cost of the

materials, there are major problems associated with them. The most prominent one is the oxidation of NO to NO₂.

It has already been found in the case of nitric acid plants to be highly uneconomical to limit NO_x emissions below 1500 ppm by aqueous scrubbing (Newman 1971). The reason for this is the size of the equipment which would be necessary to carry out the oxidation of NO. The oxidation reaction is $\text{NO} + \text{O}_2 = 2\text{NO}_2$ and the rate of oxidation is written as:

$$-\frac{d(\text{NO})}{dt} = k (\text{NO})^2 (\text{O}_2)$$

where: k = reaction rate constant which decreases with temperature

(NO) and (O_2) = partial pressure of each component

t = time

When the NO concentration is decreased by a factor 2, the rate of oxidation decreases by a factor of 4. It is evident that as the NO concentration drops, the volume needed (holding time) to oxidize the NO increases quite fast. To further complicate matters, the reaction rate constant decreases with increasing temperature.

For a typical energy generating process, the amount of flue gas produced is quite high and the NO_x concentration is quite low. These two factors along with the fact that the flue gas temperatures are usually above 100°C makes absorption processes requiring prior oxidation of NO not very desirable. If the rate of oxidation was increased,

there would still remain the problem of disposal of the weak acid solution formed by aqueous scrubbing of N_2O_3 . In the case of the alkali solutions, disposal of the nitrate and nitrite solutions formed when N_2O_3 is absorbed, would also be a problem.

It is apparent that a process which would absorb NO without prior oxidation would prove to be valuable. If the absorbed NO could then be desorbed to produce a more concentrated NO_x stream, the process would be even more valuable. The concentrated NO_x stream could be either made into nitric acid or fed to an efficient NO_x reducing system. Liquid absorption processes do not look promising at this time. However, the following discussion on solid sorbents indicates that there are some sorbents which may be useful for NO (NO_x) emission control.

Previous Studies on Solid Sorbents

A number of sorbents have been reported in the literature which absorb NO at temperatures ranging from 26°C to 700°C. Ogg and Ray developed a sorbent by decomposing a 2:1.1 mole mixture of $NaNO_3$ + Fe_2O_3 at 700-900°C (Ogg and Ray 1954). Using 7.8 grams of the mixture and a gas flow rate of .16 ft.³/min., they were able to absorb better than 90% of the NO at 400°C from a gas containing .7% NO and an undetermined amount of O_2 . The advantages of this sorbent are that prior oxidation of the NO is not required, the absorbed NO formed nitrates and not nitrites and the NO can be recovered by heating the sorbent at

700-900°C. No mention was made of the amount or effect of CO_2 , H_2O or O_2 on the NO absorption. It was reported (Leung and Gidaspow 1974) that this sorbent could not be used for flue gas treatment due to the formation of carbonates or nitrates which could not be decomposed at reasonable temperatures. However, Leung and Gidaspow did not present evidence to substantiate this claim.

Evoniuk had gathered data on the $\text{NaNO}_3 + \text{Fe}_2\text{O}_3$ sorbent developed by Ogg and Ray and had found it also to be an active absorber of NO (Evoniuk 1976). The absorbed NO could be easily desorbed at temperatures between 500 and 600°C. However, absorption of NO was significantly decreased when CO_2 was present in the gas. Evoniuk also tested alkali carbonates, transition metal oxides and mixtures of the two. It was found that neither the carbonates nor the metal oxides were good absorbers of NO, but mixtures of the two were very active absorbers of NO. The sorbent $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ was found to be just as active as the $\text{NaNO}_3 + \text{Fe}_2\text{O}_3$ but CO_2 also decreased its NO absorption ability. In light of this data the claims made by Leung and Gidaspow appear to be unjustifiable. But, due to the effect of CO_2 on NO absorption, the sorbents may not be suitable for flue gas treatment. However, Evoniuk had found that the sorbent $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ was capable of absorbing NO in the presence of CO_2 . This sorbent had a capacity of .2 gm of NO/gm of sample at a temperature of 460°C and was capable of absorbing better than 90% of the NO_x from a gas containing 9000 ppm

NO_x , 17.5% O_2 and 15% CO_2 . By desorbing the NO_x at temperatures ranging from 500-700°C, the sorbent was regenerated and at the same time a concentrated stream of NO_x was produced. Since the $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ sorbent appears to be very promising, it is one of the sorbents which will be further investigated in this work.

Gidaspow et al. had also developed a high capacity NO sorbent (Gidaspow et al. 1977). The sorbent has a capacity of .1282 gm of NO/gm of sorbent and was made from a solution containing 15.17 gm $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 16.96 gm $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Na_2CO_3 . The pH of the solution was adjusted from 7 - 9.7 and the precipitates washed and then calcined at 650°C. In Table 2 the conditions under which the sorbent was tested is shown along with data for other sorbents tested by Gidaspow and his associates. Although the capacity of the sorbent is high the effects of CO_2 , SO_2 or H_2O on NO absorption were not determined. It was reported that the low capacity sorbents (shown in Table 2) were affected by H_2O and would probably be not suited for flue gas treatment. The high capacity sorbent was thermally regenerable at 520°C but showed a decline in NO capacity after continuous sorption and desorption of NO.

A study performed by Onischak and Gidaspow indicated that $\text{FeSO}_4 + \text{LiCl}$ supported on silica gel was an active absorber of NO between 21° and 93°C (Onischak and Gidaspow 1973). The capacity of the sorbent was less than 1.9×10^{-3} gm of NO/gm of sorbent. It was noted that dry

Table 2. Data on Sorbents Tested by Gidaspow et al.

Sorbent	Temp.	Capacity gm NO/gm sample	Differential Rate constant l/gmole.min
Cobalt Oxide Alumina Coprecipitated	270°C	2.56×10^{-3}	1.8×10^4
Chromium Oxide Alumina (Harshaw Cr-1404)	25	3.0×10^{-3}	2.0×10^4
Manganese Oxide Alumina (Harshaw Mn-0201)	25	4.85×10^{-3}	---
Manganese Oxide Alumina Coprecipitated	25	7.2×10^{-4}	3.52×10^4
$\text{FeSO}_4\text{-CoNO}_3\text{-Na}_2\text{CO}_3$	300	.1282	52*

- feed composition was 680 ppm NO, 3% O_2 and 0% CO_2 .

* - capacity was measured up to NO out = 85% of the NO in and the feed rate was 700 ml/min.

FeSO_4 did not absorb NO and a hygroscopic material like LiCl is needed to draw in H_2O . This was attributed to a complex similar to $\text{Fe}(\text{H}_2\text{O})_5\text{NO}^{++}$ being formed. The sorbent could be used for flue gas treatment if temperatures were below 100°C and the gas was saturated with H_2O . Regeneration of the sorbent was done at 204°C using CO or H_2 . The researchers also tested dry coconut charcoal, dry molecular sieves, saturated coconut charcoal and silica gel at room temperature and found that they were less efficient than $\text{FeSO}_4 + \text{LiCl}$ for absorbing NO. Effects of CO_2 , SO_2 and O_2 on NO absorption by $\text{FeSO}_4 + \text{LiCl}$ were not reported.

Leung and Gidaspow reported that supported ferric oxide and reduced ferric oxides were better for absorbing NO than $\text{FeSO}_4 + \text{LiCl}$, because the $\text{FeSO}_4 + \text{LiCl}$ was not useful for NO absorption above 100°C and it required an expensive catalyst for regeneration (Leung and Gidaspow 1974). The ferric oxides could absorb NO between 200°C and 350°C and be regenerated with air at 450°C . Unfortunately, water vapor interfered with the NO absorption. Reduced ferric oxides are not affected by water vapor and can be regenerated with 1% CO. Gidaspow, Leung and Dharia reported the capacity of reduced ferric oxide as being .054 gm of NO/gm of sample at 270°C (Gidaspow et al. 1974). However, the presence of water vapor at concentrations greater than 1% reduced the capacity of the sorbent. Oxygen also decreased the capacity since it oxidized the reduced ferric oxide. Due to the effects of H_2O and O_2 on the sorbent, it does not appear that it would be useful for flue gas treatment.

Molecular sieves, which are also affected by water (i.e. absorb it preferentially), have been used for control NO emissions from nitric acid plants (Ricci 1977). In the process the gas is dried prior to passing it to the molecular sieve bed. The sieve bed catalytically oxidizes the NO to NO_2 and then selectively absorbs the NO_2 (Brennan 1962, Joithe 1972, Sunderson et al. 1967). Because the molecular sieve preferentially absorbs water it could not be used in the treatment of flue gases where the water vapor is usually over 6% and the gas flow

rates are high. Also, the cost of molecular sieve processes is about the same as for catalytic reduction systems but their energy requirements are higher (Ricci 1977).

In summary, very few solid absorbents are available which have a large capacity for absorbing NO and are not affected by CO_2 , O_2 or H_2O . Of the sorbents reviewed the alkali carbonate-metal oxide mixtures appear to be the most promising (i.e. the $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$). The high capacity sorbent developed by Gidaspow et al. contains cobalt which is expensive and the sorbent loses capacity with continual use. It is evident that further research is warranted to determine if the $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ sorbent and others similar to it are useful for controlling NO_x ($\text{NO} + \text{NO}_2$) emissions. Applicability of the sorbent can only be determined if the effects of CO_2 , O_2 , H_2O and SO_2 are known. Determining these effects is the objective of this research along with developing new sorbents for NO_x absorption.

II. OBJECTIVE

The objectives of this research are:

1. investigate in detail the effects of CO_2 , O_2 , NO_x , H_2O and SO_2 on the absorption of NO_x by the alkali carbonate-transition metal oxide sorbents, and the $\text{NaNO}_3\text{-Fe}_2\text{O}_3$ sorbent developed by Ray and Ogg.
2. determine the effect of changing the ratio of the two compounds in the mixture on absorption of NO_x .
3. determine the effect of O_2 and CO_2 on the desorption of NO_x from the sorbent.
4. gather thermodynamic data on selected sorbents.

III. EXPERIMENTAL APPARATUS AND PROCEDURE

Figure 1 is a schematic diagram of the research apparatus. Gas flows of individual feed components were measured by rotameters and then passed to the main feed line where they mixed. A magnetic stirrer was placed in the line to facilitate mixing but it was found that the mixing provided by the stirrer did not change the gas composition (i.e. the amount of NO_2 formed from the NO) or the experimental results. Further analysis indicated that under laminar flow conditions, diffusion would cause almost complete mixing within the first 10 centimeters of the line for the gas flow rates used (Perry and Chilton 1973). The pressure downstream of the rotameters was kept constant at 10 inches of mercury by adjusting the valve downstream of the manometer. Maintaining the pressure constant assured a constant reproducible flow rate at varying pressure drops across the reactor. The feed gas could bypass the reactor system and be fed directly to the NO_x analyzer where the inlet concentration of NO_x ($\text{NO} + \text{NO}_2$) and NO were determined. Gas samples for determining CO_2 and O_2 could be taken through a sample port located on the bypass line.

After determining the NO_x , CO_2 and O_2 concentrations in the feed gas, the bypass line was closed and the gas mixture passed to the reactor system and back to the NO_x analyzer. If gas flow rates were below that needed to operate the analyzer a diluting gas could be fed to the stream to bring the total flow rate up.

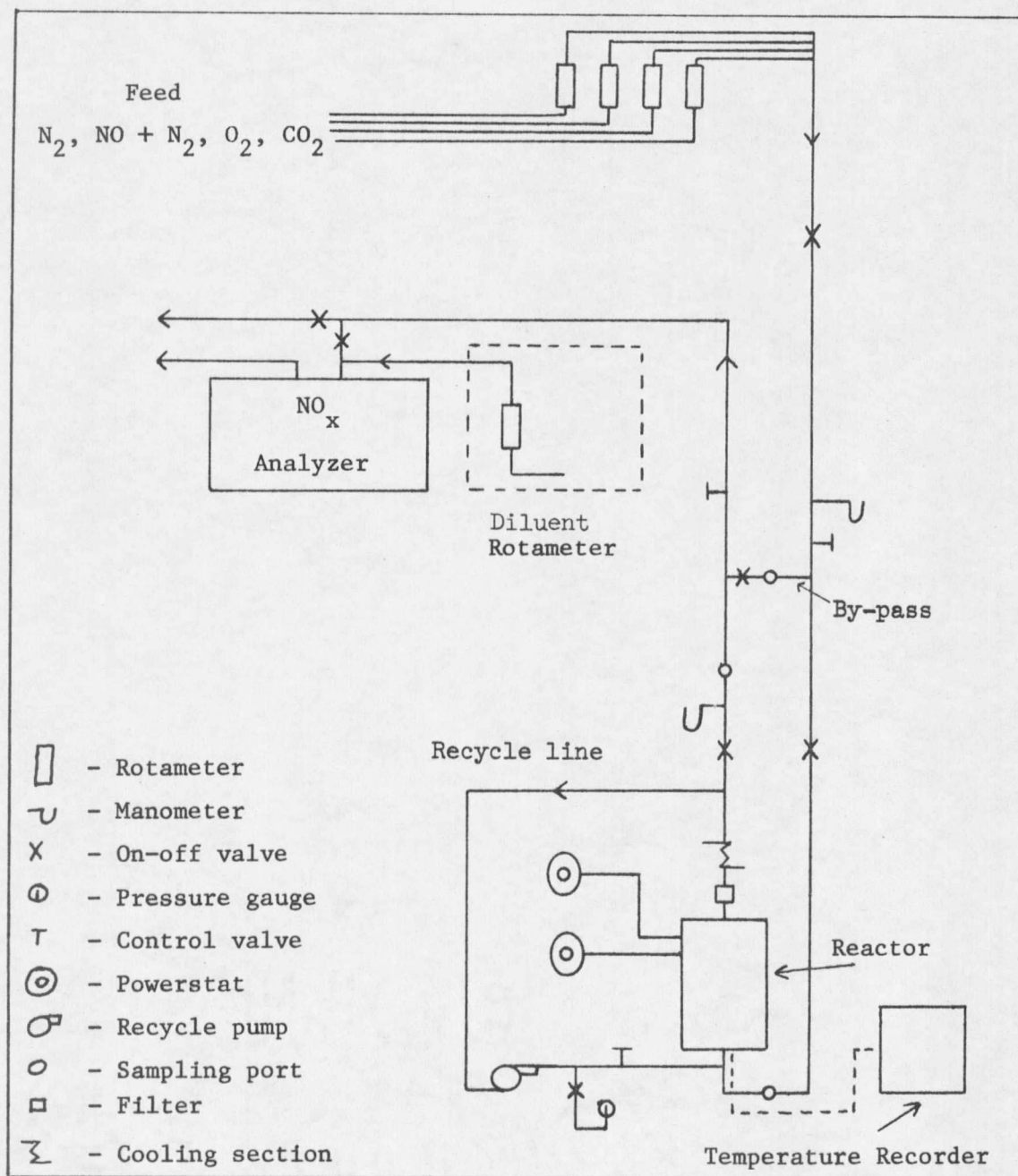


Figure 1. Experimental Apparatus

Sampling ports were located upstream and downstream of the reactor to permit sampling of the entering and exiting gas. A water cooling jacket and a glass wool filter were used for cooling the exiting gas and removing sorbent fines. The pressure downstream of the reactor was measured by a mercury manometer and kept slightly above atmospheric pressure. A recycle line equipped with a stainless steel metal bellows pump (Metal Bellows Corporation) was used when the recycle reactor was in operation.

Figure 2 is a schematic diagram of the reactor and housing. The reactor consisted of a 20 inch stainless steel pipe (SS-316), 7/8" O.D. and 5/8" I.D., with appropriate fittings for attaching a thermocouple well and inlet-exit lines. The first 10 inches of the reactor served as a preheat section for the feed and recycle gas. A thermocouple well made of 1/8 inch stainless tubing extended up through the preheat section. Attached 1 inch below the top of the thermocouple well was a perforated stainless steel disk and screen which served as a support for the sorbents. When powdered sorbents were tested, a layer of sand was poured over the disk to prevent material from falling through. Another layer of sand was poured over the powder and then a retaining pipe (which served as a weight) and screen were put on the sand. Glass wool was inserted in the top of the reactor to catch any powder which worked out of the sand. The sand, glass wool and retaining pipe were found to have no effect on the experimental results

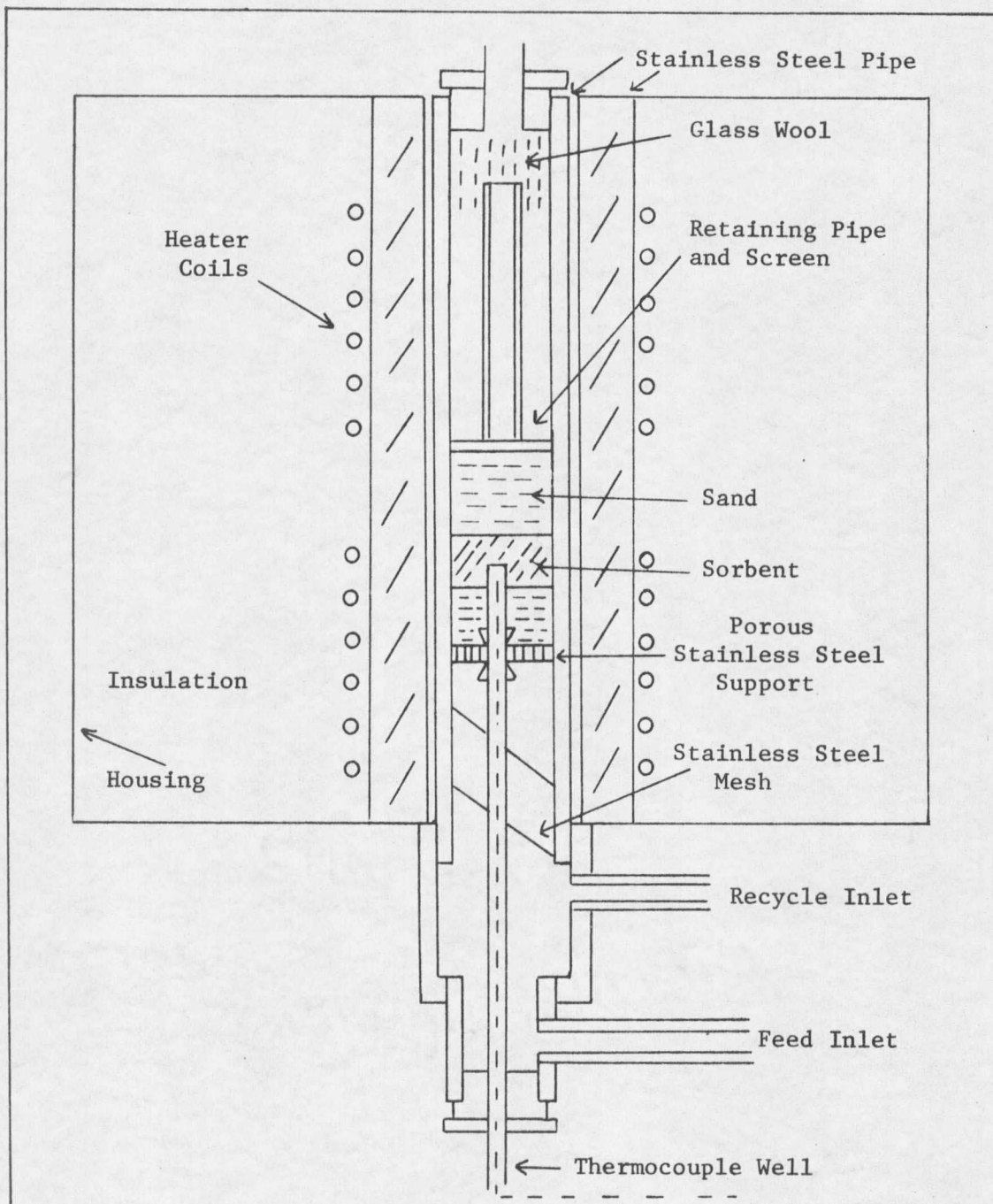


Figure 2. Reactor Diagram

(i.e. they did not absorb NO_x or change the composition of the gas). When pellets or plates of sorbents were tested the sand and retaining pipe were eliminated from the reactor.

The reactor was surrounded by a stainless steel block 18 inches long, 3 inches O.D. and 15/16 inch I.D. Two sets of beaded nichrome wire (6.5 feet long, .9 ohm/ft.) were wrapped around the block and the voltage across the heater coils was controlled by transformers. A 10 inch diameter housing 19 inches high, filled with zeolite, surrounded the reactor heating block. The temperature at the center of the reactor was monitored by an iron-constantan thermocouple attached to a continuous recorder. Estimated accuracy of the temperature reading was $\pm 1.5\%$.

Analytical Equipment

NO_x and NO concentrations were determined using a Thermo-Electron Model 10-A Self Contained Chemiluminescent Analyzer. The instrument was capable of measuring in a range of 8 scales from 0-10,000 ppm NO or NO_x ($\text{NO} + \text{NO}_2$) with an accuracy of $\pm 1\%$ of each scale. To operate the instruments a constant flow of at least 400 ml/min of sample was required. Therefore, when flow rates used to test sorbents were below this value a makeup stream of N_2 was added. It was found necessary to increase the NO_x converter temperature from the recommended 650°C to 850°C to eliminate O_2 interference. The analyzer was calib-

rated using a certified standard 5050 ppm NO in N₂ gas mixture (Matheson Co.).

Nitrogen and oxygen analyses were performed on an Aerograph Gas Chromatograph using a column of molecular sieve type 13-X at a temperature of 50°C. Carbon dioxide analysis was performed on the same chromatograph using a column of Porapak Q-S (Waters Associates). Accuracy of the chromatographic methods is estimated at $\pm 5\%$.

Standards for O₂, CO₂ and N₂ analysis were made by pressurizing a tank to 50% of each component in nitrogen and then successively diluting the mixture by reducing the pressure and repressurizing with N₂. An ideal gas state was assumed in calculating the compositions since the pressure was below 2 atm. Mixing of the gas was accomplished by suspending a plastic vane inside of the tank and then tilting the tank to cause the vane to mix the gas. Accuracy of the pressure readings used to determine the amount of dilution is estimated at $\pm .5\%$. This accuracy was achieved by using a manometer which could be read within $\pm .05$ inches of mercury.

Sulfur dioxide analysis was attempted on a Varian gas chromatograph using the Porapak Q-S packing. The packing and operating conditions of the column were the same as for the CO₂ analysis. Due to the inability to change the chromatograph operating conditions without interfering with the CO₂ and O₂ analysis the SO₂ peaks were of such poor quality that an accurate determination of the SO₂ concentration

in gas could not be made. An estimation of the SO_2 concentration was done by measuring the amount of pure SO_2 or SO_2 in N_2 , that flowed through the calibrated rotameters. From this flow rate and the total flow rate of the feed the concentration of SO_2 was calculated.

It was also decided that if a solid sorbent was affected by SO_2 (i.e. became deactivated) then a gravimetric procedure would be used to determine if the SO_2 was converted to a sulfate. A precipitation method using BaCl_2 to precipitate any $\text{SO}_4^{=}$ formed by the absorption of SO_2 was used and was found to be acceptable for determining how much SO_2 was absorbed. The water soluble fraction of the sorbent containing $\text{SO}_4^{=}$ and $\text{CO}_3^{=}$ ions was treated with HCl acid to decompose the $\text{CO}_3^{=}$ species before BaCl_2 was added. From the gravimetric analyses and the calculation of the amount of SO_2 in the feed, the amount of SO_2 absorbed could be determined.

Gas Mixtures

N_2 , CO_2 and O_2 were delivered from cylinders containing the gases and calcium sulfate was used to remove moisture from the CO_2 and O_2 streams. Nitric oxide was taken from cylinders containing either pure NO or a mixture of NO and N_2 . An approximate 9% NO in N_2 mixture was made by pressurizing a cylinder to 90 psia with pure NO , then pressurizing to 1000 psig with N_2 . The 9% NO mixture was then diluted in the process of mixing with the other components in the feed gas to

either approximately 1000 ppm or 9000 ppm.

A 2000 ppm SO_2 mixture in N_2 was made in a similar fashion as the NO mixtures. The $\text{N}_2 + \text{SO}_2$ mixture was substituted for the pure N_2 used in the feed gas when the SO_2 tests were made. Since N_2 comprised approximately 83% of the feed gas mixture, the substituted $\text{SO}_2 + \text{N}_2$ gave a calculated concentration of SO_2 close to 1660 ppm.

Test gases containing water vapor were made by bubbling N_2 through water. A 3% water vapor composition was calculated from the vapor pressure of water at the temperature of the container.

Sorbent Preparation

A $\text{NaNO}_3 + \text{Fe}_2\text{O}_3$ sorbent was made by heating a dry mixture of 2:1.1 mole ratios of $\text{NaNO}_3 + \text{Fe}_2\text{O}_3$ in a rotating canister over a bunsen burner. Decomposition was assumed complete after 1 hour of heating. Alkali carbonate and transition metal oxide sorbents (e.g. $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$, $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$) were made by intimately mixing the dry chemicals (reagent grade) together in a beaker. Other sorbent materials were prepared similarly. One series of $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ sorbents were prepared by dissolving K_2CO_3 in a minimum of water and then adding the Fe_2O_3 to the solution. The mixture was then heated to dryness on a hot plate and ground to a powder. No difference in absorption performance was found between sorbents made by dry mixing and those made by dissolving in water.

Plates of sorbent were made by compressing 1.88 gm of powder on rectangular stainless steel channels. The channels were 3 inches long, 7/16 in. wide and 5/16 in. high. Sorbent material was placed only on the first two inches of the plate. To secure the sorbent in the channel, a stainless steel screen was formed and laid in the bottom of the channel. Total area of the sorbent surface, as measured by plate surface area, was approximately .875 square inches (5.65 cm^2).

Sodium and potassium carbonates were also deposited on manganese dioxide and ferric oxide pellets. The 1/8 inch pellets were Harshaw Fe-0301 (20% Fe_2O_3 on Al_2O_3) and Mn-0201 (19% MnO_2 on silica). Each of the carbonates were dissolved in a minimum amount of water and then 9 gm of pellets were added to absorb all the solution. A basis of 1:1 mole ratio of carbonate to transition metal oxide was used to calculate the amount of alkali carbonate to use. The ferric oxide pellets appeared to absorb the carbonates internally while the manganese dioxide pellets when dried had clumpy deposits of the alkali carbonate on the exterior surface.

IV. REACTOR ANALYSIS

In determining the effects of CO_2 , O_2 , NO_x , SO_2 , H_2O and sorbent composition on the NO_x absorption rate, two types of reactor systems were used. One system used was the fixed bed integral reactor in which the observed NO_x absorption is the integrated result of the material passing through the reactor bed. In the classical case the total conversion (X_A) of species A undergoing a reaction at a rate r_A is:

$$\int_0^V dV/F_A = \int_0^{X_A} dX_A / -r_A$$

where F_A = constant feed rate of component A.

V = volume of reacting mass including voids.

The assumptions used in this equation are a uniform distribution of mass in a tubular reactor in which there are no axial or radial gradients of temperature and mass transport of material by diffusion is negligible. Under condition where the conversion is small, the integral reactor can be treated as a differential reactor (Smith, 1970).

The expression for the rate of reaction then becomes:

$$-r_A = X_A (F_A/V)$$

This expression is more useful for treating experimental data than the integrated expression since the exact form of rate equation does not have to be known.

The second type of reactor system used was the recycle reactor. When the ratio of recycle to feed is greater than 20:1, it can be assumed that the system behaves as a backmix reactor (Carberry 1976, Berty 1974). The well known expression describing this system is a material balance:

$$V/F_A = X_A / -r_A$$

$$-r_A = X_A (F_A/V)$$

While this expression has the same form as the equation for the differential reactor, it is valid over a conversion range from 0 to 100%.

As is true in many cases the application of theory to experiment is difficult. In the case of the recycle reactor which is ideal for determining kinetic data, the pressure drop across packed beds becomes excessive at high recycle rates. This problem was solved by using plates of absorbent but the potential of diffusion controlled kinetics becomes a factor. However, for calculating rates the recycle expression is better than the integral or differential expression. This is due to the fact that it is almost impossible to achieve the ideal operating conditions needed to satisfy the assumption for the integral or differential expressions. Therefore, the recycle expression will be used to calculate rates (i.e. NO_x absorption rates) from experimental data from the recycle reactor. Data from experiments with the integral reactor (packed beds) will be represented as % NO_x absorbed at specified

conditions, with the understanding that ideal conditions do not actually exist.

V. RESULTS

Analysis of Feed Composition

In Figure 3 the fraction of NO originally in the feed which is unconverted to NO_2 in the feed line is plotted against the amount of O_2 in the feed at 0% and 14% CO_2 . The conversion of NO to NO_2 follows normal trends at high concentrations of NO_x and at low concentrations of NO_x with CO_2 (i.e. more conversion of NO to NO_2 with increased O_2 concentration). But at low concentrations of NO with no CO_2 , the normal trend is reversed. The explanation of this behavior was found in the manner in which the gases were fed to the main line. CO_2 , 9% NO in N_2 , and O_2 were fed together upstream from the N_2 , and the flow of CO_2 was normally greater than that of NO or O_2 . When the CO_2 flow rate was decreased the residence time and concentration of NO and O_2 increased in the section of line upstream from the N_2 inlet. This caused a rapid oxidation of the NO to NO_2 .

At high concentrations of NO the flow rate of the NO + N_2 mixture was large enough that the residence time did not have as large an effect on NO_2 formation as did the O_2 concentration, hence the normal decline in NO as the O_2 was increased. At low concentrations of NO (low flow rates of NO + N_2) and zero flow rate of CO_2 , the increased O_2 flow rate (increased % of O_2) decreased the residence time and hence decreased the amount of NO converted to NO_2 .

The oxidation of NO to NO_2 in the feed gas prior to the feed

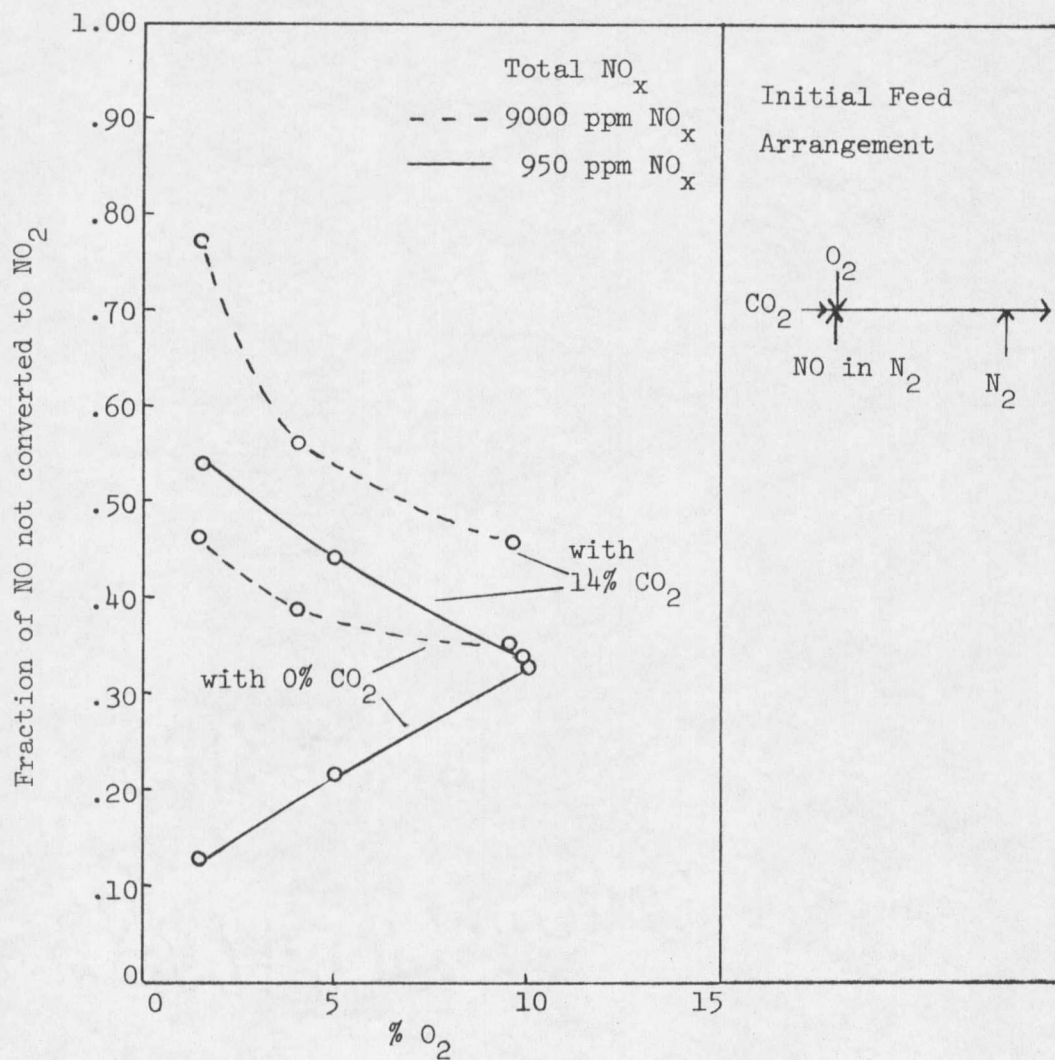


Figure 3. Effect of CO₂ and O₂ Concentration on NO Conversion in Feed Line

reaching the reactor is not highly desirable because NO_2 is rapidly absorbed by compounds which do not readily absorb NO. Furthermore, in typical flue gases which contain less than 1000 ppm NO_x , NO usually comprises 90% of the total NO_x (Bartok 1971).

The effect of the NO_2 formation when screening sorbents is an important factor. But if the same gas composition is used for all sorbents and the amount of NO_2 present is known, then sorbents which absorb more NO_x than the known amount of NO_2 in the feed gas present are probably also absorbing NO. However, when the effects of O_2 and CO_2 are determined the results would be inconclusive because it is possible that increased absorption is due to more formation of NO_2 when the O_2 is increased or the CO_2 decreased. It is also necessary to test the sorbents under conditions where the NO concentration approaches that found in actual feed conditions. Figure 4 is a plot of the equilibrium fraction of NO in the total NO_x ($\text{NO} + \text{NO}_2$) as calculated from the thermodynamic values (Chilton, 1968). At 450°C the fraction of NO in NO_x is from .67 to .8 and at 400°C from .47 to .7. The values in the feed are below the values in Figure 4, indicating that the NO_2 formed would have to decompose if equilibrium conditions were to be reached. Therefore, the feed system was modified so a minimum of NO_2 would be formed. This was accomplished by having the N_2 , $\text{NO} + \text{N}_2$ and CO_2 enter upstream from the O_2 . This insured that the NO would be diluted from the 9% value to a low concentration before contacting the O_2 and a

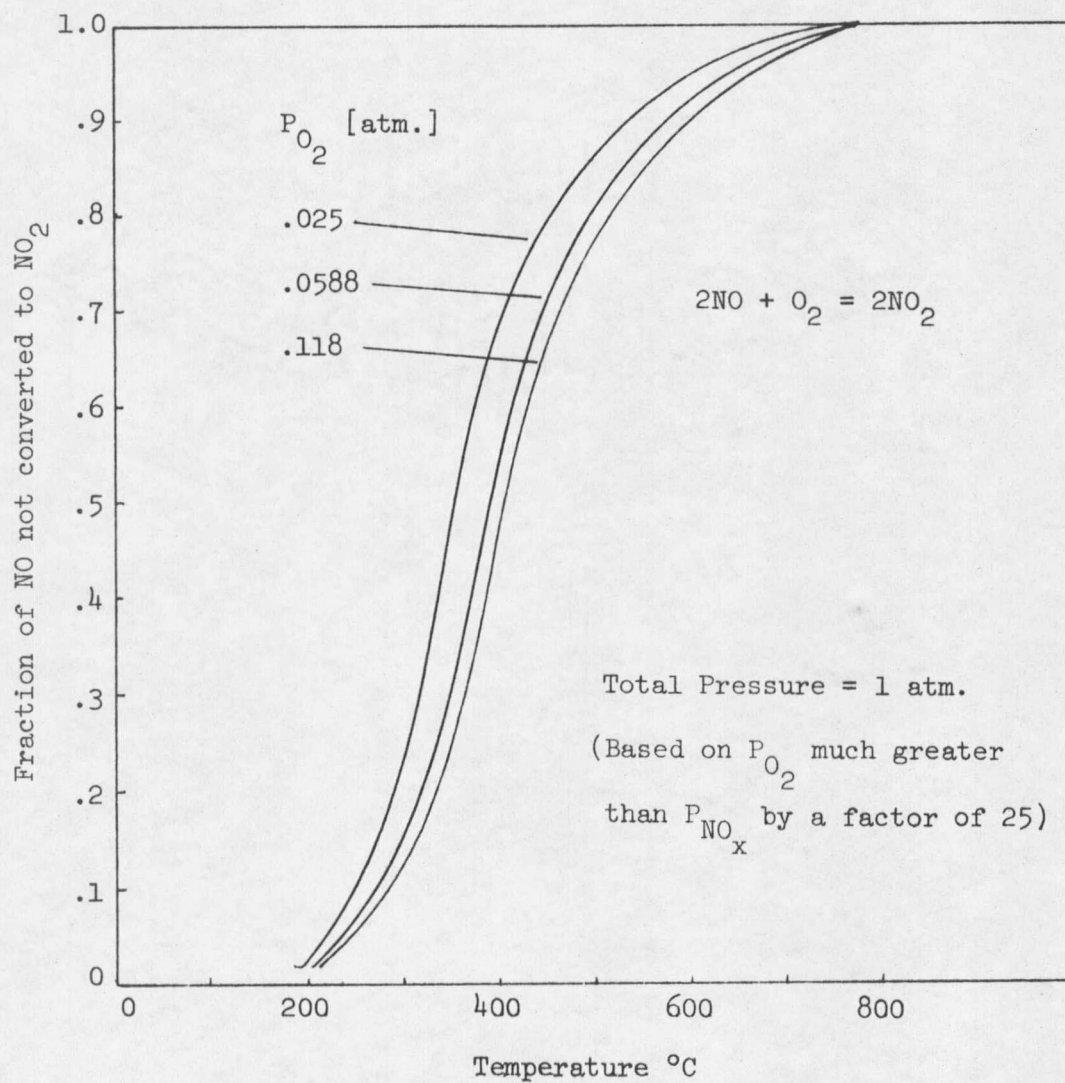


Figure 4. Equilibrium Ratio of NO to Total NO_x

change in the flow of CO_2 would not affect NO_2 formation.

Figure 5 shows the effect of CO_2 and O_2 on NO conversion in the modified feed line. No effect of CO_2 on the oxidation of NO in the feed line was found and the amount of NO oxidized at the 900 ppm level was kept to less than 10%. NO oxidation at the 8800 ppm level has been kept to less than or near the equilibrium values for temperatures from 400 - 450°C.

Sorbent Comparisons on Flat Plates with Unmodified Feed Line

The percent and initial rates of NO_x absorption by various carbonates and ferric oxide when tested in the recycle reactor are shown in Table 3. Cesium carbonate (Cs_2CO_3) was the most active absorber of NO_x but it was found that the material evaporated off the plate during the absorption process. The data also indicates that the temperature at which maximum absorption occurs increases with molecular weight of the alkali metal carbonate. Of the alkaline earth carbonates only magnesium carbonate showed some NO_x absorption ability.

Ferric oxide showed no observable NO_x absorption. In a previous study (Evoniuk 1976) it was shown that the first row transition metal oxides (TiO_2 -CuO) showed very little or no capacity for NO_x absorption under test conditions similar to those used for the ferric oxide.

Table 4 shows the performance of sodium and potassium carbonates when mixed with the metal oxides. Included in this table are the re-

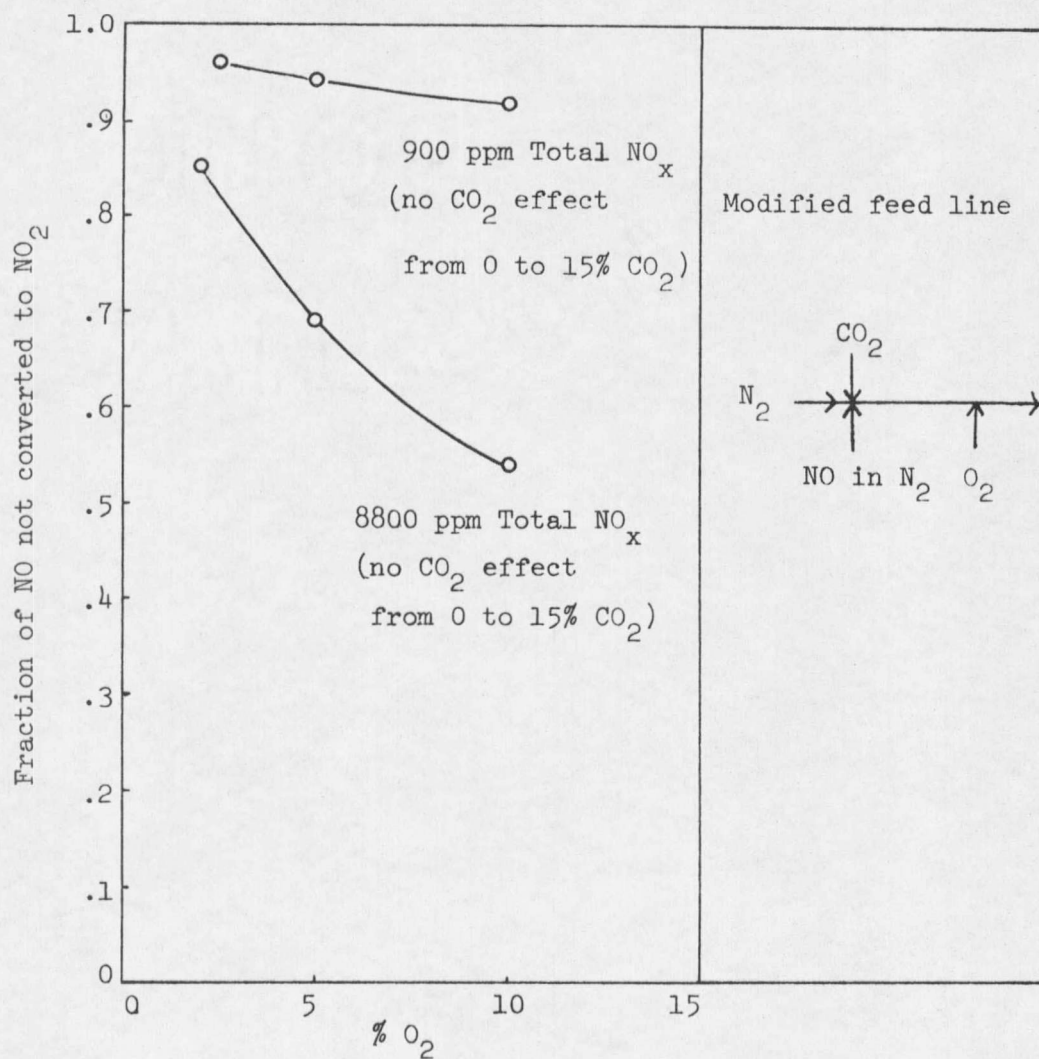


Figure 5. Effect of O₂ and CO₂ on NO Conversion in Modified Feed Line

Table 3. NO_x Absorption by Carbonates and Fe_2O_3

Compound	Rate		% Absorbed	Temperature °C
	$\frac{\text{g NO}}{\text{min-g sorbent}}$	$\frac{\text{g NO}}{\text{min-cm}^2}$		
Li_2CO_3	3.7×10^{-5}	1.22×10^{-5}	1.1	350
Na_2CO_3	5.1 "	1.26 "	1.2	425
K_2CO_3	53.3 "	8.67 "	8.1	475
Cs_2CO_3	154.3 "	51.3 "	45.6	585
MgCO_3	29.8 "	9.91 "	9.9	250-300
MgCO_3	29.8 "	9.91 "	9.9	400-420
CaCO_3	0	0	0	50-620
SrCO_3	0	0	0	50-620
Fe_2O_3	0	0	0	50-620

Feed 620 ml/min, 2% O_2 , 15% CO_2 , and 8400-9000 ppm NO_x

Recycle 12.5 liters/min

Sorbent material was placed on 5.65 cm^2 of surface parallel to flow

Approximately 1 gram of material was used

Rates are initial values which were constant for the first 30 min.

Temperatures reported are for where absorption was maximum

% Absorbed was calculated from the expression:
$$\frac{100 \times (\text{NO}_x \text{ in} - \text{NO}_x \text{ out})}{(\text{NO}_x \text{ in})}$$

Table 4. NO_x Absorption by Mixtures of Oxides and Carbonates

Compound	Rate		% Absorbed	Temperature °C
	$\frac{\text{g NO}}{\text{min-g sorbent}}$	$\frac{\text{g NO}}{\text{min-cm}^2}$		
$\text{NaNO}_3 + \text{Fe}_2\text{O}_3$	1.28×10^{-3}	2.11×10^{-4}	19.3	425
$\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$	.95 "	1.86 "	17.2	425
$\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$	2.8 "	3.72 "	35.3	475
$\text{K}_2\text{CO}_3 + \text{Co}_2\text{O}_3$	.63 "	1.11 "	1.09	470
$\text{K}_2\text{CO}_3 + \text{NiO}$	1.04 "	1.8 "	17.6	470
$\text{K}_2\text{CO}_3 + \text{MnO}_2$	3.45 "	6.1 "	52.4	470
$\text{Na}_2\text{CO}_3 + \text{Co}_2\text{O}_3$	1.05 "	1.86 "	17.0	400
$\text{Na}_2\text{CO}_3 + \text{NiO}$	.70 "	1.24 "	11.5	415
$\text{Na}_2\text{CO}_3 + \text{MnO}_2$	2.80 "	4.96 "	47.6	400
$\text{Na}_2\text{CO}_3 + \text{MO}_3$	0	0	0	50-620
$\text{Na}_2\text{CO}_3 + \text{WO}_3$	0	0	0	50-620
$\text{Cs}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$	1.63 "	2.88 "	2.47	500

Recycle 12.5 liters/min.

Sorbent material was placed on 5.65 cm^2 of surface parallel to flow.

Approximately 1 gram (1:1 mole ratio) of material was used.

Feed 620 ml/min., 2% O_2 , 15% CO_2 , and 8400-9000 ppm NO_x .

Rates are initial values and temperatures are for where absorption was maximum.

sults for the decomposed $\text{NaNO}_3 + \text{Fe}_2\text{O}_3$ sorbent developed by Ogg and Ray. Sorbents made from the sodium carbonate and sodium nitrate absorb the maximum NO_x at approximately 410°C while the potassium mixtures absorb NO_x best at 460°C . The most efficient sorbents are $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$, $\text{K}_2\text{CO}_3 + \text{MnO}_2$ and $\text{Na}_2\text{CO}_3 + \text{MnO}_2$.

After regenerating the sorbents by desorbing the NO_x at high temperatures ($500\text{--}700^\circ\text{C}$), selected sorbents were again tested for their NO_x absorption ability. Compounds which showed a large loss in absorption ability are shown in Table 5. Manganese dioxide mixed with sodium carbonate showed the least amount of deactivation after desorption, but each additional desorption continued to lower its performance. The amount of NO_x absorbed dropped from 47.6% to approximately 20% and then remained constant. Also the temperature at which the absorption was maximum changed from 400°C to approximately 430°C . Ferric oxide mixed with either potassium or sodium carbonates did not show any change in the absorption temperature or in the amount of NO_x absorbed after regeneration.

Table 6 shows the performance of calcium compounds mixed with ferric oxide (1 to 1 mole ratio). Other mixtures tested are also shown in Table 6. The calcium mixtures performed poorly under the test conditions used. Potassium permanganate showed an initial high NO_x absorption but as was shown in Table 5 absorption ability drops off after desorption.

Table 5. Compounds Showing Deactivation after Desorption.

Compound	% Absorption	
	Initial	After 1 Desorption
1:1 K_2CO_3 + NiO	17.6	9.4
1:1 K_2CO_3 + MnO_2	52.4	24.4
$KMnO_4$	45.6	18.5
Na_2CO_3 + MnO_2	47.6	39.5
1 K_2CO_3 .5 Fe_2O_3 .5 Co_2O_3	37.8	24.4
1 K_2CO_3 .5 Fe_2O_3 .5 MnO_2	44.0	28.4
1 Na_2CO_3 .5 Fe_2O_3 .5 MnO_2	37.5	34.0

Feed 620 ml/min., 2% O_2 , 15% CO_2 , and 8400-9000 ppm NO_x .

Recycle 12.5 liters/min.

Sorbent material was placed on 5.65 cm² of surface parallel to flow.

Approximately 1 gram (1:1 mole ratio) of material was used.

Table 6. Miscellaneous Compounds

Compound	Rate		% Absorbed	Temperature °C
	$\frac{\text{g NO}}{\text{min-g sorbent}}$	$\frac{\text{g NO}}{\text{min-cm}^2}$		
$\text{CaO}+\text{Fe}_2\text{O}_3$	$.22 \times 10^{-3}$	$.74 \times 10^{-4}$	6.4	217
$\text{Ca}(\text{OH})_2+\text{Fe}_2\text{O}_3$	.15 "	.50 "	4.5	200
$\text{CaCO}_3+\text{Fe}_2\text{O}_3$	0	0	0	50-620
$\text{Li}_2\text{CO}_3+\text{Fe}_2\text{O}_3$	0	0	0	100-620
KMnO_4	1.54 "	5.11 "	45.6	400-460
$\text{PbO}_2+\text{Fe}_2\text{O}_3$	.53 "	1.76 "	16.1	305
$\text{PbO}_2+\text{K}_2\text{CO}_3$	.89 "	2.97 "	25.8	355-500
$\text{K}_2\text{SO}_4+\text{Fe}_2\text{O}_3$	.37 "	1.24 "	10.9	280
Fe_2SO_4	.37 "	1.24 "	11.1	95-300
Silica Gel	.37 "	1.24 "	11.1	100-250
$\text{MgCO}_3+\text{Fe}_2\text{O}_3$	.22 "	.74 "	6.4	390&400

Recycle 12.5 liters/min.

Sorbent material was placed on 5.65 cm^2 of surface parallel to flow.

Approximately 1 gram (1:1 mole ratio) of material was used.

Feed 620 ml/min., 2% O_2 , 15% CO_2 , and 8400-9000 ppm NO_x .

Rates remained constant in the temperature interval listed.

Table 7 is a list of materials tested in an earlier packed bed reactor system. The reported NO_x absorption percentages are larger than for the plates but this is probably due to the presence of more sorbent material, better contacting in the packed bed, larger O_2 concentration and the absence of CO_2 . The high concentration of O_2 is probably causing a large fraction of the NO to be oxidized to NO_2 which is more easily absorbed by the solid sorbents. A comparison of the data in Table 7 with the previous data gives an indication of the importance of testing sorbents with gas compositions that are closer to actual flue gas compositions.

Effect of O_2 and CO_2 on NO_x Absorption using the Flat Plates and the Unmodified Feed Line

Figures 6 and 7 show the effect of O_2 and CO_2 on NO_x absorption by $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$, $\text{NaNO}_3 + \text{Fe}_2\text{O}_3$ (decomposed) and $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ for high levels of NO_x . As shown in Figure 6, all three sorbents showed a strong dependency of NO_x absorption on the oxygen concentration. The potassium carbonate system performed better than the other two sorbents at all levels of oxygen. It is not possible to conclude that NO is being absorbed by the sodium carbonate and decomposed sodium nitrate mixtures because the percent NO_2 in the feed is greater than the total NO_x absorbed. However, for the potassium carbonate mixture in Figure 6, it is clear that NO is being absorbed at O_2 concentrations below 10%.

Table 7. Materials Tested as Powders

Compound	Temperature °C	% NO _x Absorbed
K ₂ CO ₃ +Fe ₂ O ₃	490	99.5
CaCO ₃ +Fe ₂ O ₃	300	66.0
CaCO ₃ +MnO ₂	325	83.8
CaCO ₃ +Co ₂ O ₃	325	68.8
CaCO ₃ +NiO	325	66.3
CaO+Fe ₂ O ₃	370	89.4
CaO+MnO ₂	375	61.1-76.3
CaO+Co ₂ O ₃	270	77.5
MgCO ₃	300	38.5
Ca(NO ₃) ₂ +Fe ₂ O ₃	425	31.3
SrCO ₃ +Fe ₂ O ₃	300	25
Sr(NO ₃) ₂ +Fe ₂ O ₃	375	25
Ba(NO ₃) ₂ +Fe ₂ O ₃	425	58.8
CaO+sand	350	40

Feed = 500 ml/min., .8% NO_x, 21% O₂, 0% CO₂.

Sorbent = .025 moles of 1:1 mole mixture.

Material was tested in a packed bed reactor with no recycle.

The temperature was varied at a constant rate and the temperature at which maximum absorption occurred is listed.

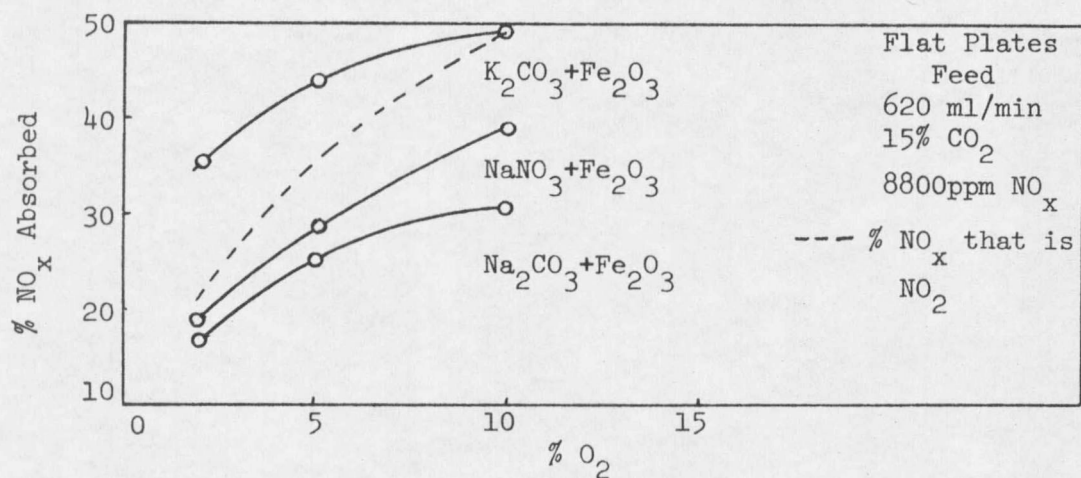


Figure 6. Effect of O₂ Concentration on NO_x Absorption
(High NO_x)

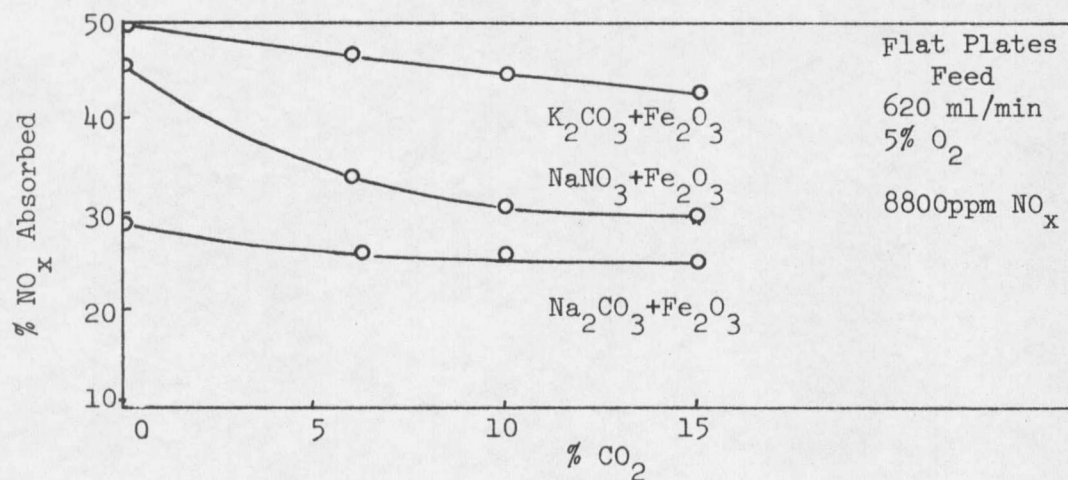


Figure 7. Effect of CO₂ Concentration on NO_x Absorption
(High NO_x)

In Figure 7 the effect of CO_2 on NO_x absorption is shown. But, due to the dependence of NO_2 formation on CO_2 concentration it is impossible to conclude that the increased absorption is due to the decrease in CO_2 concentration.

The effect of oxygen concentration on NO_x absorption at low levels of NO_x is shown in Figure 8. Of the three sorbents, sodium carbonate + ferric oxide showed the most oxygen dependency. Absorption with no CO_2 present is shown by the three points in the upper left hand corner. All the sorbents absorb more NO_x when no CO_2 is present. Again it is not possible to conclude if CO_2 or O_2 affected NO absorption since the amount of NO_2 was much greater than the total NO_x absorbed.

The results of testing the carbonates for O_2 dependency is shown in Figure 9. An oxygen dependency was found but no CO_2 dependency was seen even though the CO_2 was varied from 0 to 15%. This indicates that CO_2 may interfere with a step in the mechanism of absorbing NO_x which takes place on the ferric oxide. The data also shows that the carbonates alone do not have a high rate of NO_x absorption.

Effect of O_2 and CO_2 Using Modified Feed Line

Figures 10 and 11 show the effect of O_2 and CO_2 on absorption by the three sorbents at high levels of NO_x . Oxygen effects stayed approximately the same but the effect of CO_2 has become more pronounced for the NaNO_3 and Na_2CO_3 sorbents. The K_2CO_3 system shows approximately

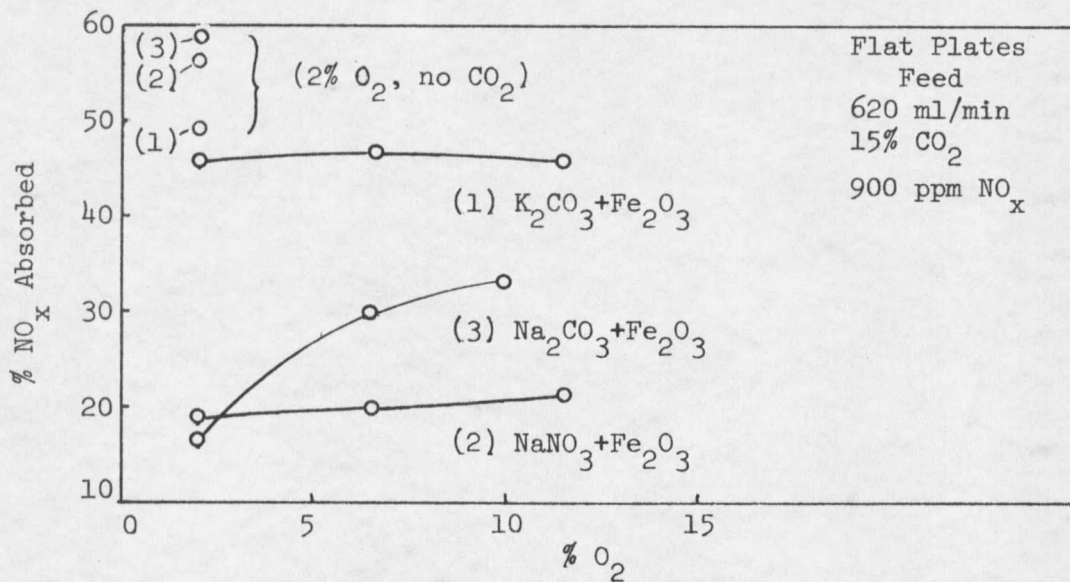


Figure 8. Effect of O₂ and CO₂ Concentration on NO_x
Absorption (Low NO_x)

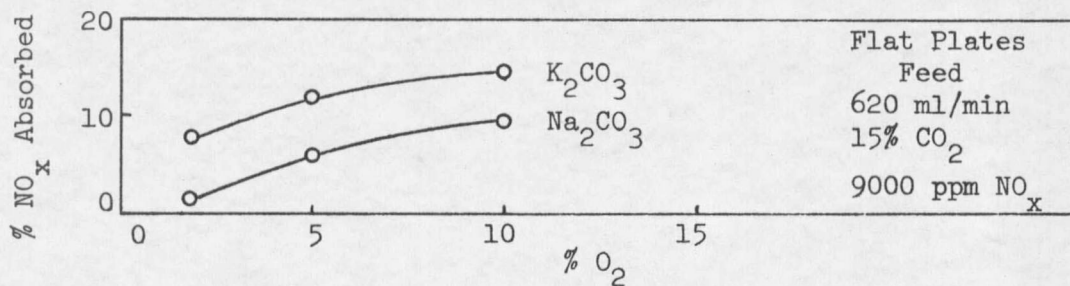


Figure 9. Effect of O₂ Concentration on NO_x Absorption
by Carbonates (High NO_x)

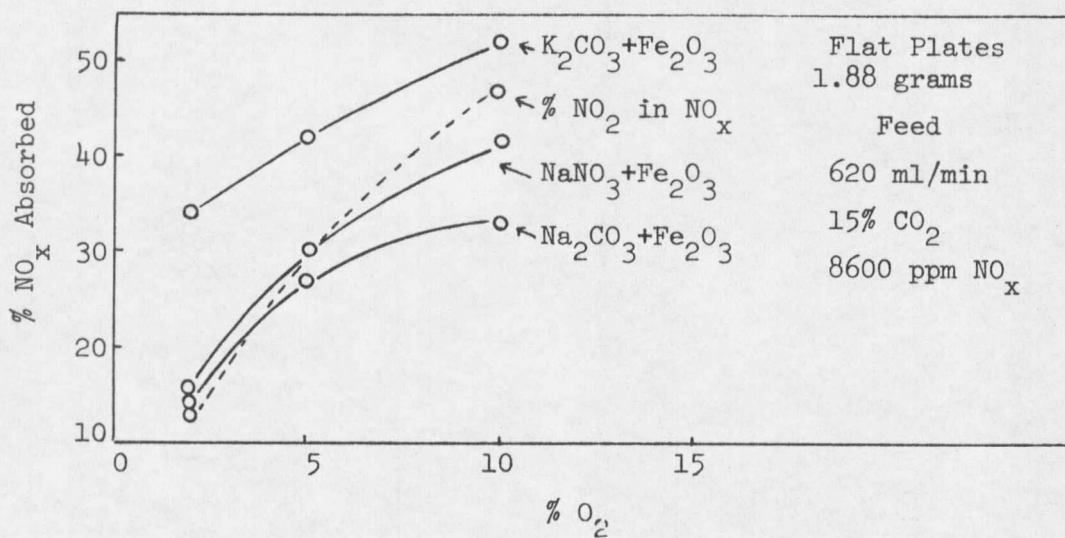


Figure 10. Effect of O₂ on NO_x Absorption (High NO_x)

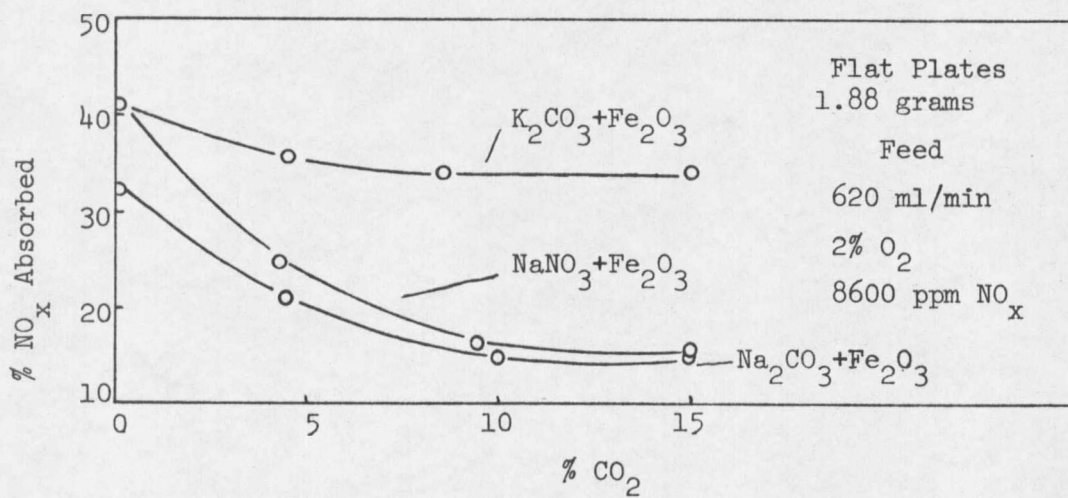


Figure 11. Effect of CO₂ on NO_x Absorption (High NO_x)

the same CO_2 interference as before and all three sorbents absorbed less NO_x than before probably because there is less NO_2 in the feed.

At low concentrations of NO the performance of the sorbents dramatically changed. Figures 12 and 13 show the effect of O_2 and CO_2 at low NO_x levels. The $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ system was the only sorbent that was able to absorb appreciable amounts of NO_x and it showed a strong O_2 and CO_2 dependency. The NaNO_3 and Na_2CO_3 system absorbed significant amounts of NO_x only when CO_2 was absent from the feed. Some NO_x was absorbed initially by both sodium mixed sorbents. This initial amount increased as the oxygen increased but if the O_2 was cut back from 10% to 2% some NO_x was then desorbed. Desorption of NO_x occurred if the CO_2 concentration was increased from 3% to 15%. The behavior of the sodium system indicates that their absorption ability is strongly affected by the amount of NO_2 present in the feed.

Effect of the Ratio of Carbonate to Metal Oxide on Absorption

Figures 14 and 15 show the effect of changing the ratio of K_2CO_3 to Fe_2O_3 on NO_x absorption. The total mass of material tested was kept constant but the molar ratio of K_2CO_3 to Fe_2O_3 was changed. Absorption increased with an increase in ferric oxide and leveled out at about a ratio of 1:2 for feed compositions containing from 5% to 10% O_2 . At 2% O_2 and 15% CO_2 an increase in ferric oxide did not increase NO_x absorption as greatly as with 0% CO_2 and 2% O_2 . This data indicates that

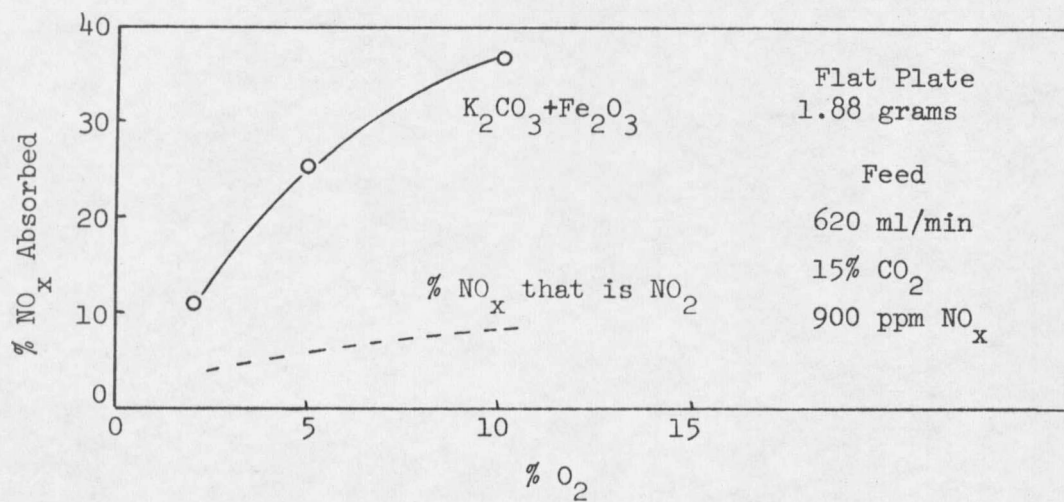


Figure 12. Effect of O_2 on NO_x Absorption (Low NO_x)

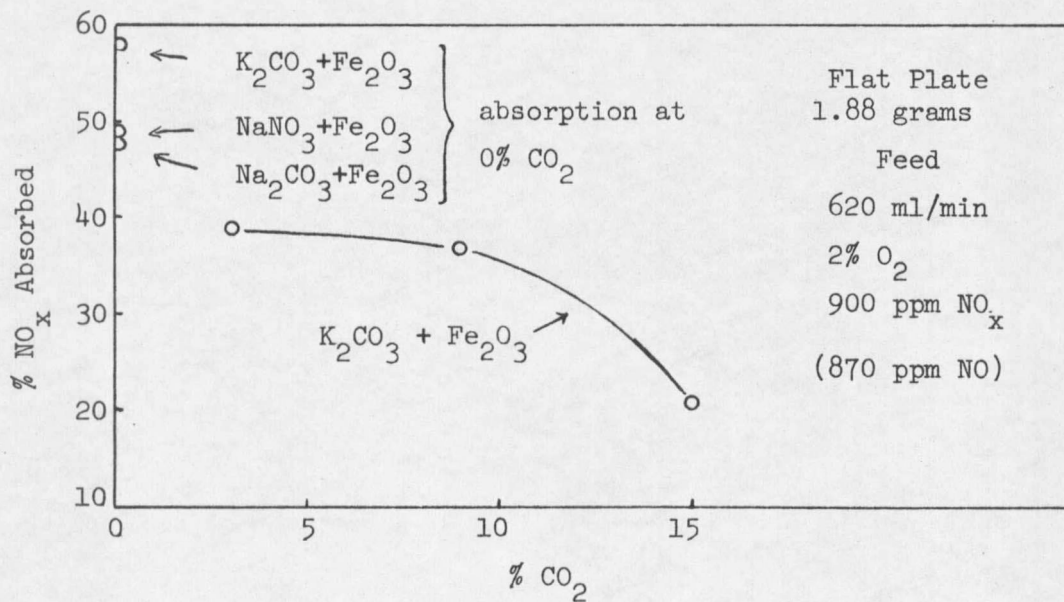


Figure 13. Effect of CO_2 on NO_x Absorption (Low NO_x)

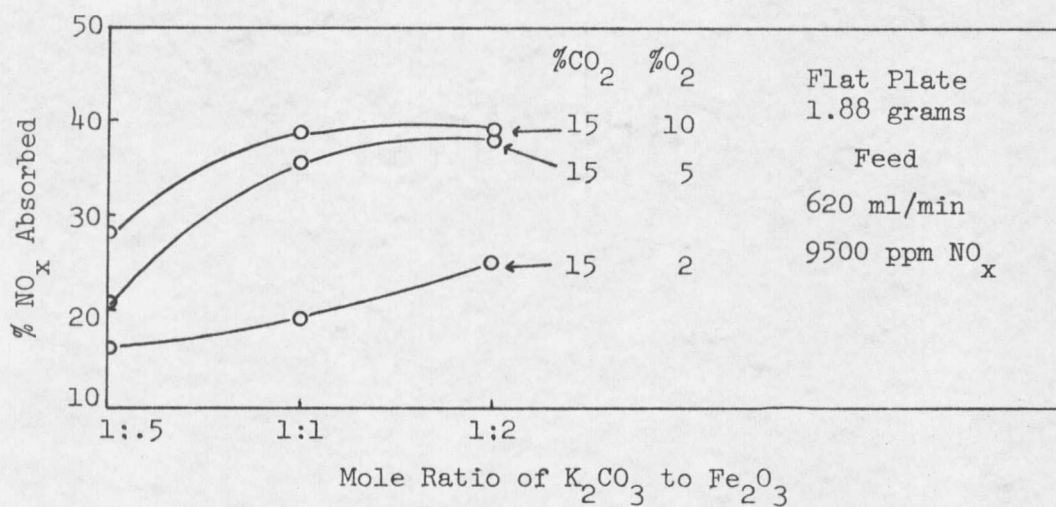


Figure 14. Effect of K₂CO₃:Fe₂O₃ Ratio on NO_x Absorption
(15% CO₂)

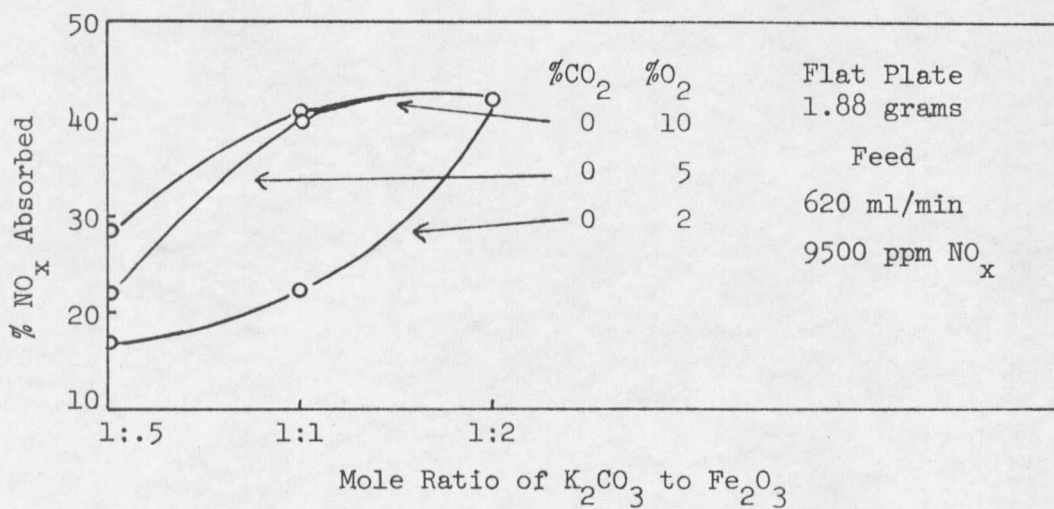


Figure 15. Effect of K₂CO₃:Fe₂O₃ Ratio on NO_x Absorption
(0% CO₂)

CO_2 interference is important at low concentrations of O_2 and is somewhat nullified at high concentrations of O_2 . At ratios of 1:5, absorption is unaffected by CO_2 and as the ratio is increased CO_2 interference increases. This indicates there is a rate controlling absorption step on the Fe_2O_3 which is influenced by CO_2 and O_2 . The evidence for a rate controlling step on Fe_2O_3 is the fact that for any gas composition the rate of NO_x absorption increases with an increase in Fe_2O_3 . CO_2 and O_2 are also affecting the rate of absorption since at 1:1 molar ratio an increase in O_2 or a decrease in CO_2 increases NO_x absorption.

Effect of Gas Composition on Desorption of NO_x from Flat Plates

The effect of gas composition on desorption of loaded $\text{NaNO}_3 + \text{Fe}_2\text{O}_3$ (decomposed prior to loading) and 1:1 $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ is shown in Figure 16. Higher temperatures are required for desorption of $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ than for $\text{NaNO}_3 + \text{Fe}_2\text{O}_3$. $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ desorption temperatures were the same as those for the $\text{NaNO}_3 + \text{Fe}_2\text{O}_3$. All three sorbents required higher temperatures to desorb with increased O_2 concentration and lower temperatures with increased CO_2 concentration.

Effect of O_2 and NO_x on Absorption using Packed Beds

The effect of O_2 concentration on NO_x absorption by packed beds containing 1.8 grams of sorbent material is shown in Figure 17.

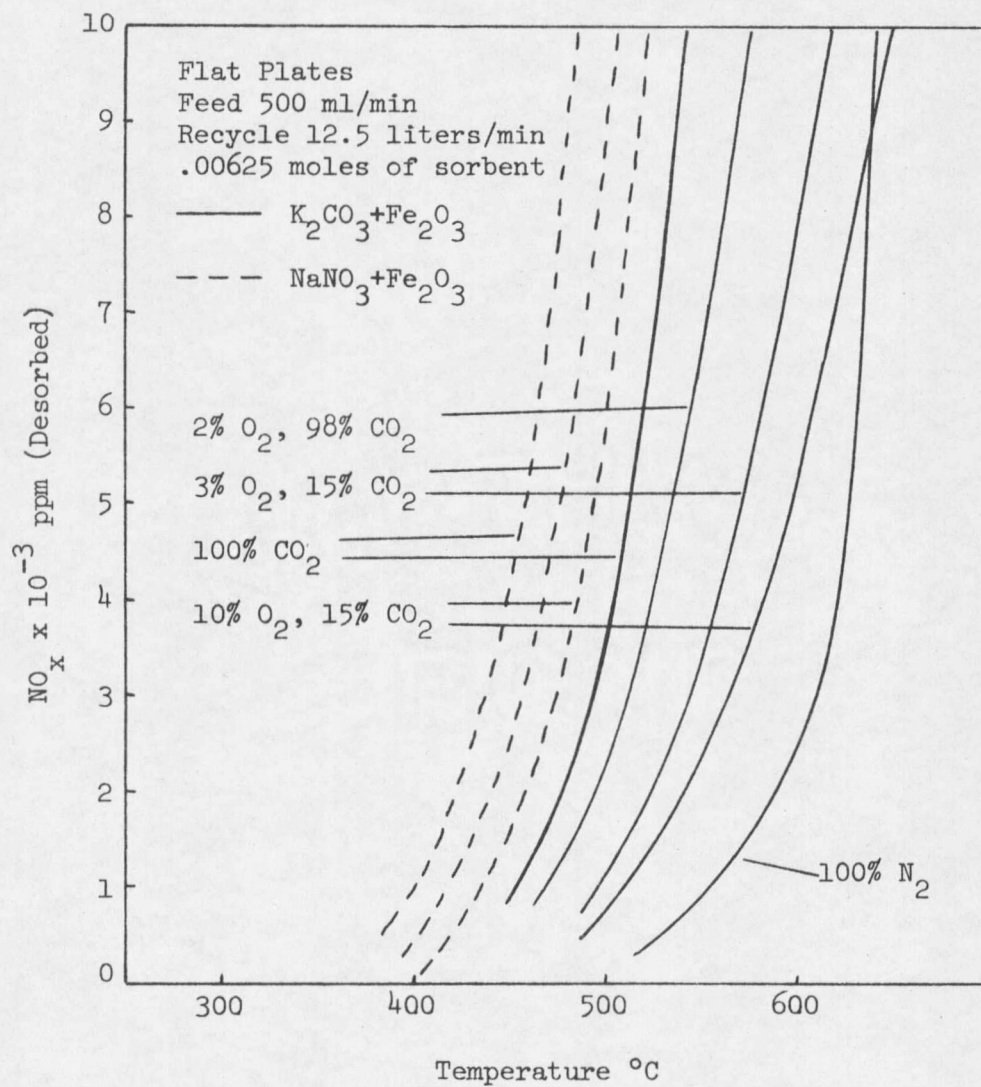


Figure 16. Effect of Gas Composition on Desorption

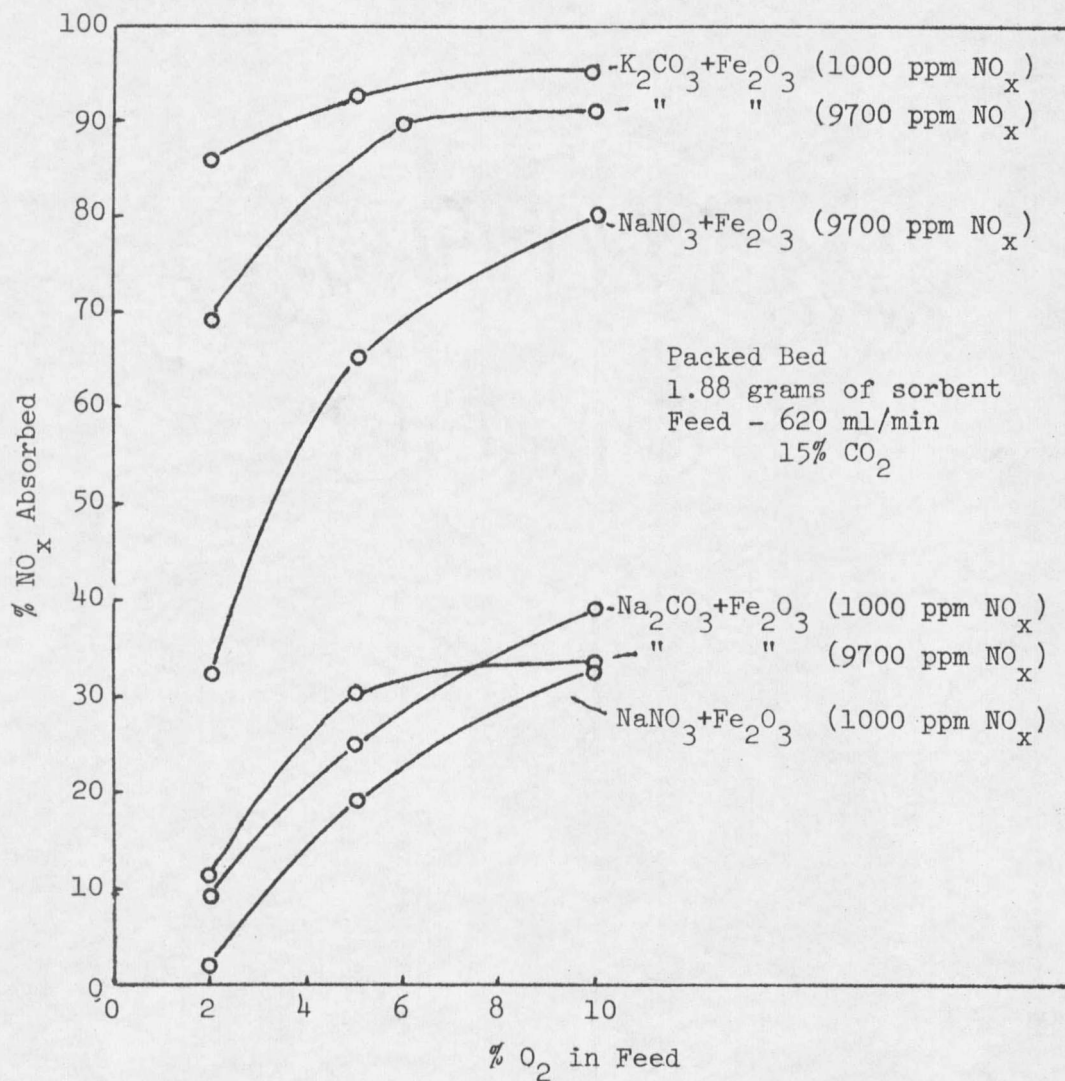
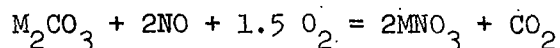


Figure 17. Effect of O_2 Concentration on NO_x Absorption for Packed Beds

$K_2CO_3 + Fe_2O_3$ sorption ability increased greatly above that from the plates. This would be expected because a bed of powder offers more fluid-solid contact than a pressed plate of material. Absorption did not increase dramatically for the $Na_2CO_3 + Fe_2O_3$ at high NO_x concentration but there was significant absorption at low NO_x concentrations. $NaNO_3 + Fe_2O_3$ absorption increased with increasing O_2 concentration for both low and high NO_x concentration. All three sorbents show the same general dependency on oxygen. Analysis of the feed and exiting gas showed that for every 2 moles of NO absorbed, 1 mole of CO_2 was desorbed and 1.5 moles of O_2 were consumed. This indicates a reaction of the form:



where M_2CO_3 is either K_2CO_3 or Na_2CO_3 . The fraction of NO_x absorbed by $K_2CO_3 + Fe_2O_3$ and $Na_2CO_3 + Fe_2O_3$ at high and low levels of NO_x is approximately the same. This indicates that the reaction order for NO_x in the system for these sorbents is close to unity. The reaction order for NO_x with decomposed $NaNO_3 + Fe_2O_3$ appears to be greater than unity because the percent absorption is greater for higher NO_x concentrations than for lower NO_x concentrations.

Loading Studies using Packed Beds

Figures 18 and 19 are the results for the loading studies of 1.88 grams of 1:1 $K_2CO_3 + Fe_2O_3$ for 820 and 8800 ppm of NO_x respectively. From the loading curves the amount of NO_x absorbed was calculated and the results show the capacity of the sorbent is equal to the theoretical amount of NO required to convert all of the K_2CO_3 to KNO_3 . For 1:1 molar ratio of $K_2CO_3 + Fe_2O_3$ the capacity at 450°C is .2 gram NO/gram of sorbent and the capacity is unaffected by the concentration of NO in the feed. Figure 19 shows that the material either becomes more reactive or changes occur in the bed after the material is desorbed. It was found that by shaking the reactor housing the absorption rate could be increased but the total NO absorption capacity was unaffected. This indicates that possibly channeling, bulk diffusion, changes in the bed structure or other processes are occurring. These processes are probably responsible for the differences in the curves.

Effect of Mole Ratio of Carbonate to Oxide on Absorption

The effect of the molar ratio of K_2CO_3 to Fe_2O_3 on capacity and absorption rate is shown in Figure 20. As was evident before, the capacity decreased with a decrease in the amount of K_2CO_3 . However, the amount of K_2CO_3 converted to KNO_3 before the exit concentration reached 600 ppm increased with increasing Fe_2O_3 . The conversion for 1:1, 1:2, 1:3 and 1:4 was respectively 68%, 71%, 74% and 76% of the theoretical

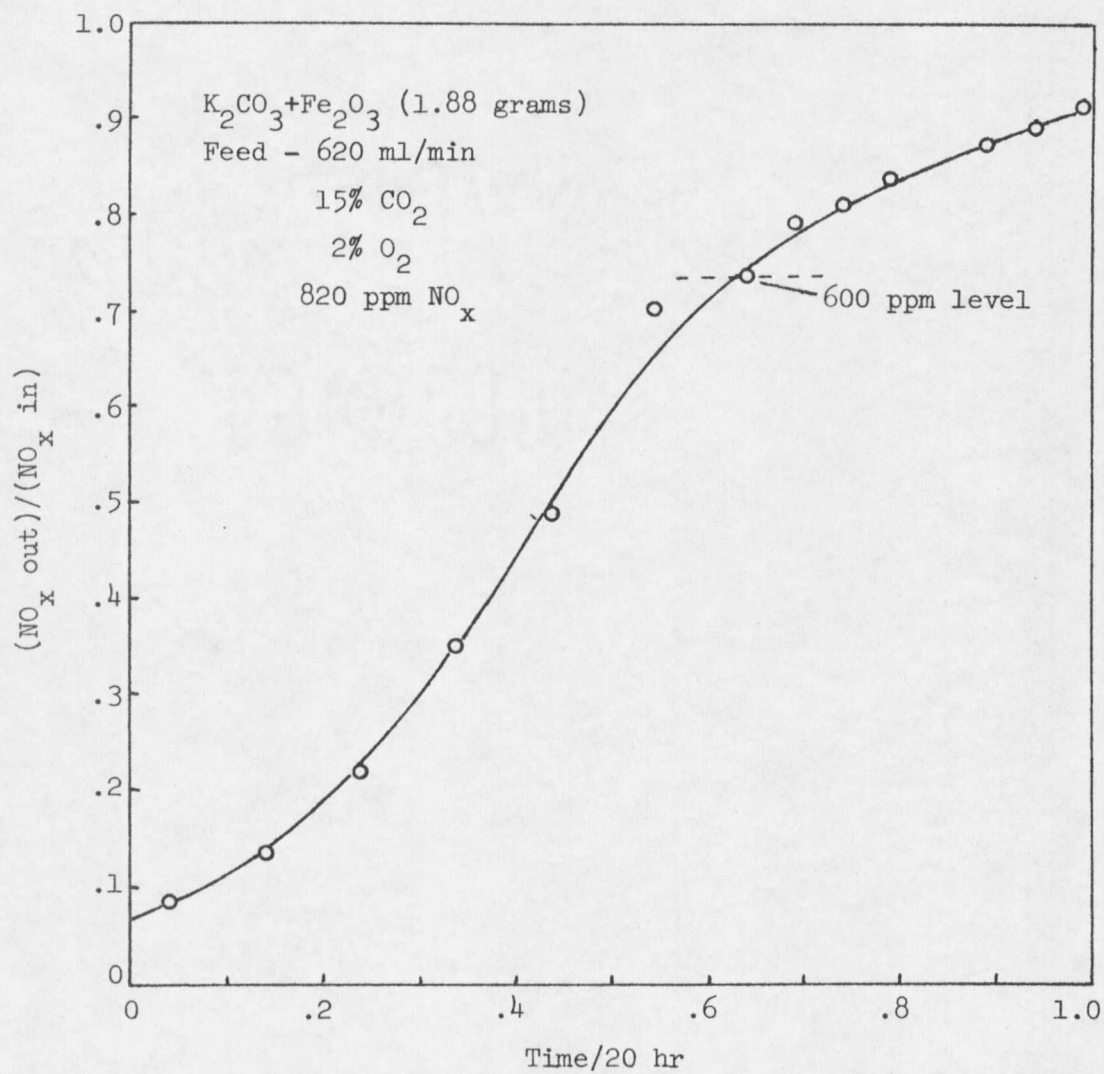


Figure 18. Loading of 1:1 $K_2CO_3 + Fe_2O_3$ at Low NO_x

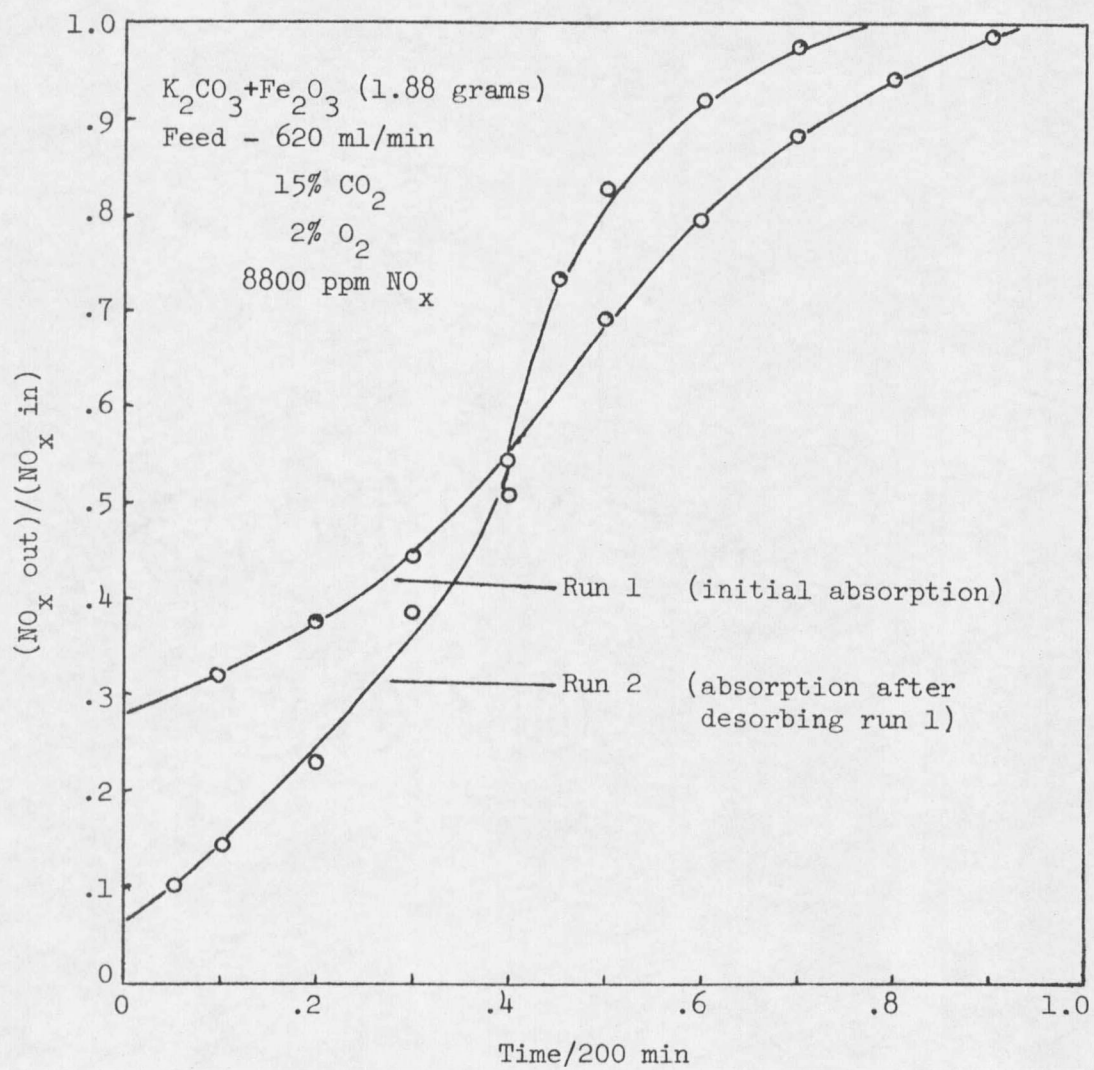


Figure 19. Loading of 1:1 $K_2CO_3 + Fe_2O_3$ at High NO_x

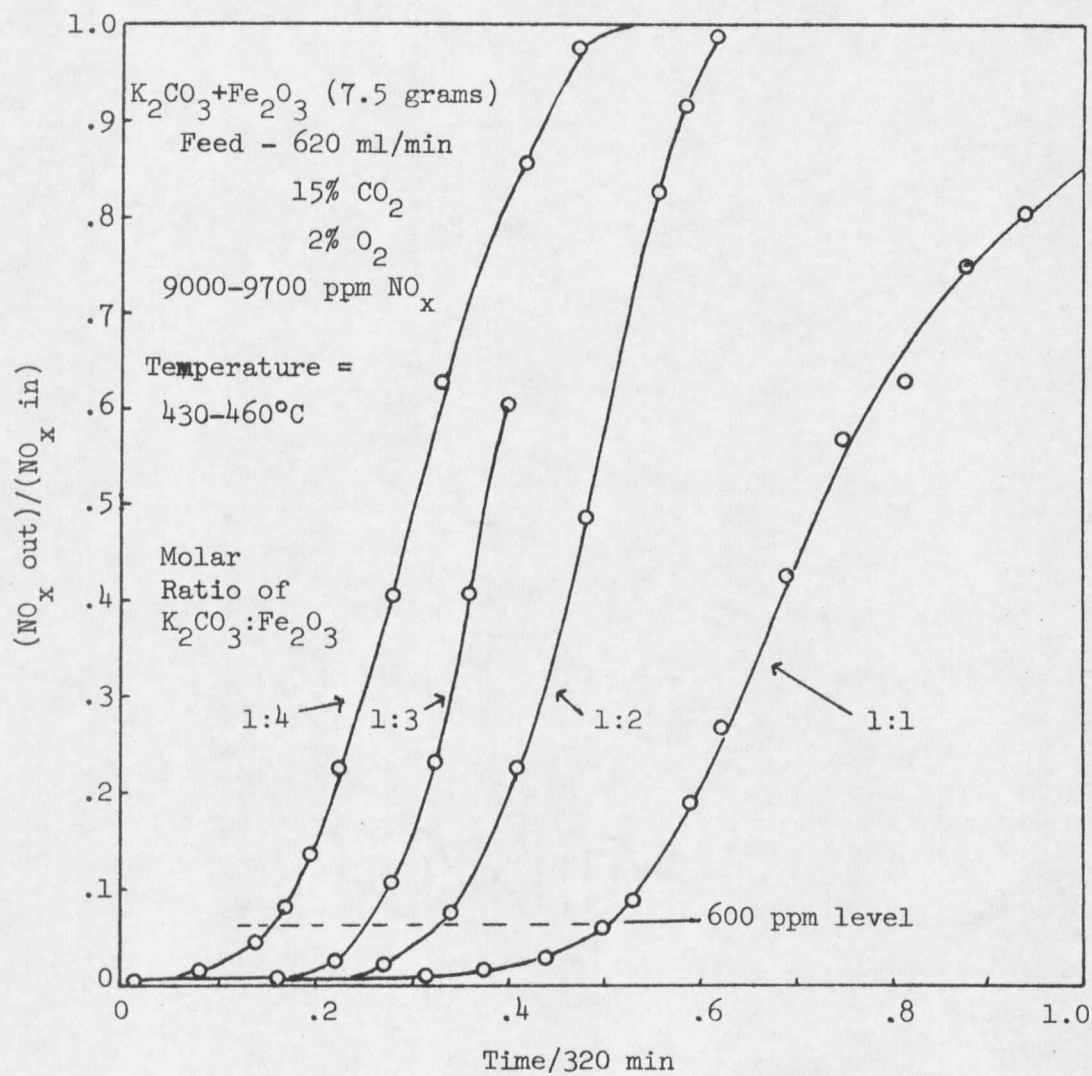


Figure 20. Effect of the Molar Ratio of $K_2CO_3 + Fe_2O_3$ on Absorption (Packed Bed)

capacity. These figures give an indication of a faster rate of absorption, but due to the possibilities of channeling the proof is not as conclusive as that with the plates.

Similar results were found for mixtures of $K_2CO_3 + MnO_2$ and $Na_2CO_3 + MnO_2$ (see Figure 21). The loading of the sorbent before the exit concentration reached 600 ppm for the 1:1 $K_2CO_3 + MnO_2$, 1:2 $K_2CO_3 + MnO_2$, 1:1 $Na_2CO_3 + MnO_2$ and 1:2 $Na_2CO_3 + MnO_2$ was 39%, 61%, 45% and 66% respectively.

Absorption Using Carbonates Impregnated on Harshaw Pellets

Potassium carbonate and sodium carbonate were deposited on commercial Harshaw catalyst pellets as described in the Experimental Procedures. The 1/8 inch pellets, Fe-0301 (20% Fe_2O_3 on Al_2O_3) and Mn-0201 (19% MnO_2 on silica), were soaked in solutions of the carbonates and then dried. Results of these runs are shown in Table 8.

In all tests except the second run with Na_2CO_3 on Fe_2O_3 , the initial material was more active than the desorbed material (i.e. second run). This can be attributed to either surface changes or pore changes on the sorbent support or a change in bed arrangement. Surface and pore changes seem the most likely since the desorbed material could easily flux over the surface and reduce the total accessible surface area. The fact that the carbonates are active when deposited on commercial supports containing the oxides may be important for in-

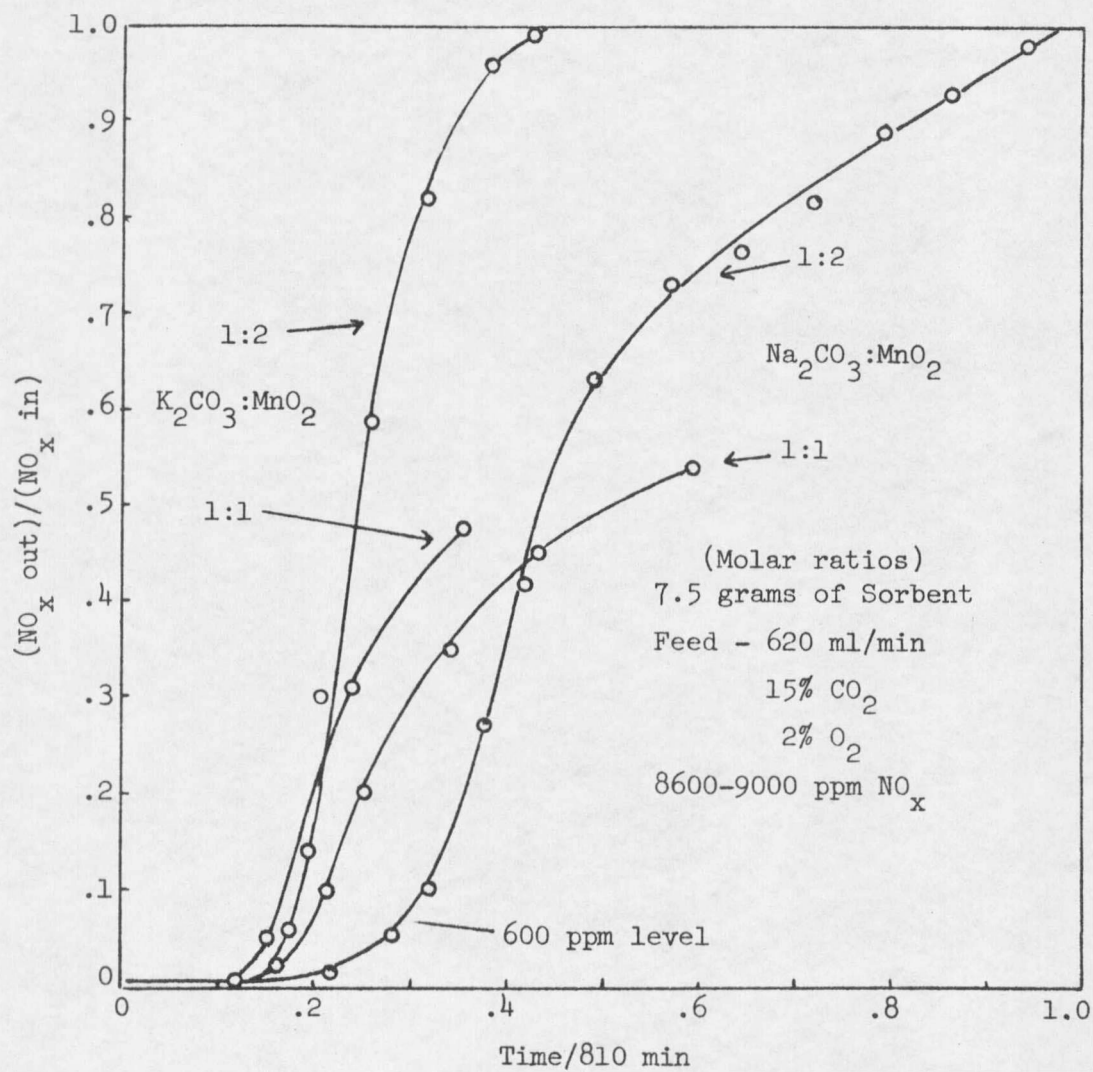


Figure 21. Effect of the Molar Ratio of $\text{K}_2\text{CO}_3 + \text{MnO}_2$ and $\text{Na}_2\text{CO}_3 + \text{MnO}_2$ on Absorption (Packed Bed)

Table 8. Carbonates on Oxide Pellets

Sorbent	Temperature °C	% NO _x Absorbed	
		Run 1	Run 2
Fe ₂ O ₃	26-600	0	0
K ₂ CO ₃ on Fe ₂ O ₃	415-510	87.2	64
Na ₂ CO ₃ on Fe ₂ O ₃	400	24.7	47.4
MnO ₂	26-600	0	0
K ₂ CO ₃ on MnO ₂	440	98.1	96.6
Na ₂ CO ₃ on MnO ₂	406-430	88.2	37.4

Feed 620 ml/min., 15% CO₂, 2% O₂, 9000 ppm NO_x.

Absorption remained constant in the temperature range listed.

Run 2 was done after desorbing the NO_x from run 1.

dustrial application. To be able to optimize the proper ratio of carbonate to oxide it would be necessary to make surface area measurements and determine pore size distributions for which equipment was not available. These measurements along with the absorption rates would indicate what factors to vary to maximize absorption.

Effect of SO_2 and H_2O on Absorption

No effect of H_2O on the absorption rate or capacity of the sorbents was found. The results from experimental runs made with the H_2O present were identical to those made when H_2O was absent. SO_2 was found to reduce capacity and reduce the rate of absorption. The SO_2 test consisted of feeding 1460 ppm SO_2 , 8700 ppm of NO_x , 15% CO_2 and 2% O_2 at 620 ml/min. to 1.88 grams of 1:1 $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$. Basing the initial capacity of the sorbent at 100%, the capacity dropped to 50% after one loading, and was down to 9% of theoretical after the second absorption. The rate of absorption dropped proportionally to the amount of material left unreacted with the SO_2 . After complete deactivation with SO_2 the sorbent was tested for sulfate by BaSO_4 precipitation and the test showed that all the K_2CO_3 was converted to K_2SO_4 . This indicates that possibly SO_2 is oxidized and absorbed in the same manner as NO . Tests also showed that SO_2 would cause desorption of NO_x . In this test the sorbent was loaded with NO_x and then a stream containing the SO_2 was fed to the reactor under the same conditions as used for absorption.

The NO_x concentration leaving the reactor was 2100 ppm indicating that better than 70% of SO_2 was absorbed (assuming an equation of the form: $2\text{KNO}_3 + \text{SO}_2 = \text{K}_2\text{SO}_4 + 2\text{NO}_2$).

Tests also showed the SO_2 would desorb NO_x from the sorbent when NO_x was present in the feed at a concentration of 8700 ppm. Sorbent capacity could not be regained after desorption at 600 to 700°C, which indicates that the sulfate formed does not decompose significantly.

Desorption Studies

From the plate studies it was evident that desorption should be done with pure CO_2 streams to get the maximum concentration of NO_x . Figure 22 shows the effect of temperature on desorption of loaded 1:1 $\text{Na}_2\text{CO}_3 + \text{MnO}_2$ and 1:1 $\text{K}_2\text{CO}_3 + \text{MnO}_2$. The temperature was increased at a rate of 5°C/min. and the amount of NO_x desorbed was recorded. When the temperature rise was interrupted and the temperature held constant the concentration of NO_x also leveled out. This indicates that no transient effect was affecting the recorded NO_x concentration. As was evident with the plate studies, the sorbent containing sodium desorbs at a lower temperature than the sorbent containing potassium. Comparison of Figure 23, which shows the effect of temperature on desorption for 1:4 $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$, with Figure 22 indicates that sorbents made with $\text{K}_2\text{CO}_3 + \text{MnO}_2$ have somewhat different desorption characteristics than those made from $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ for temperatures below 600°C.

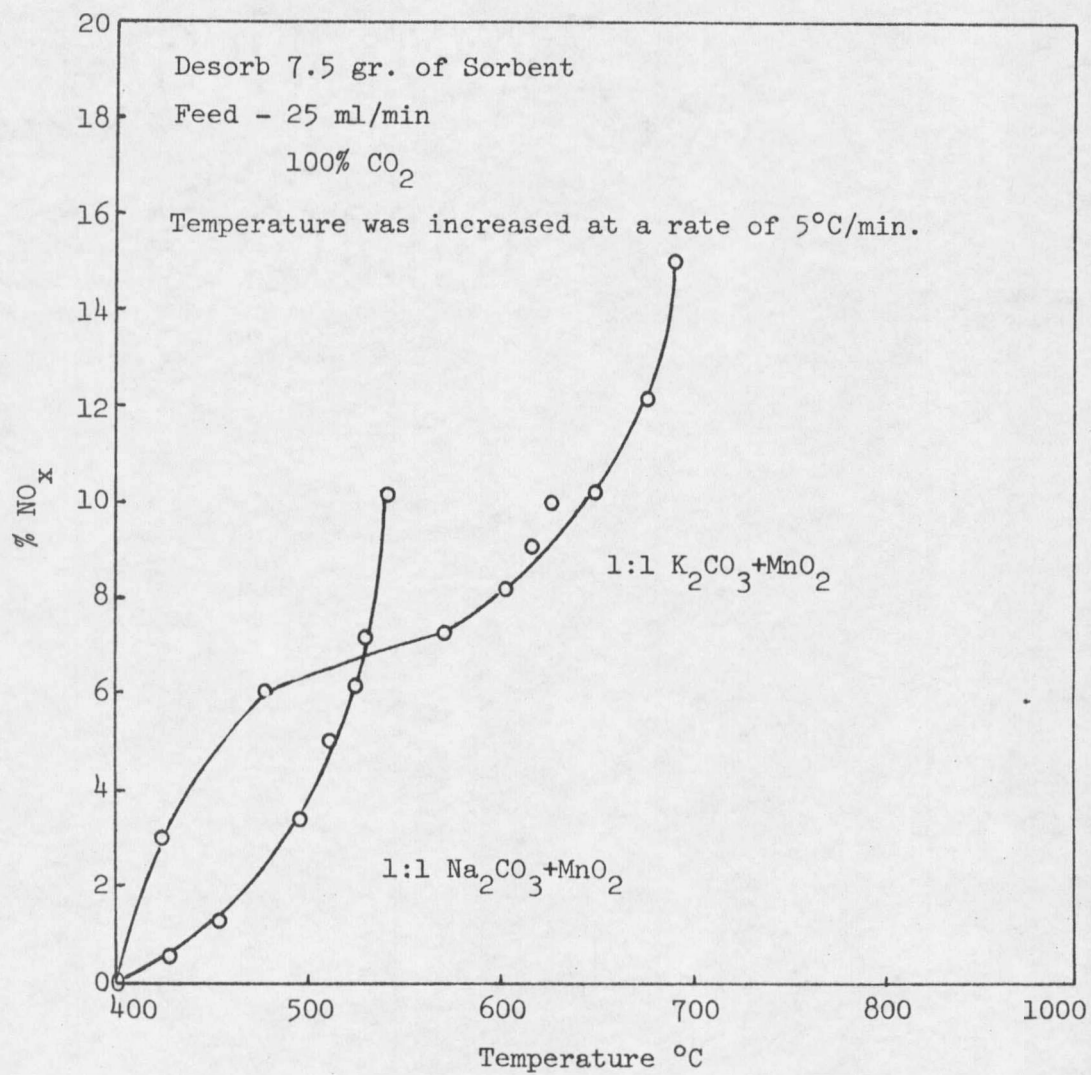


Figure 22. Effect of Temperature on Desorption of
Na₂CO₃ + MnO₂ and K₂CO₃ + Fe₂O₃

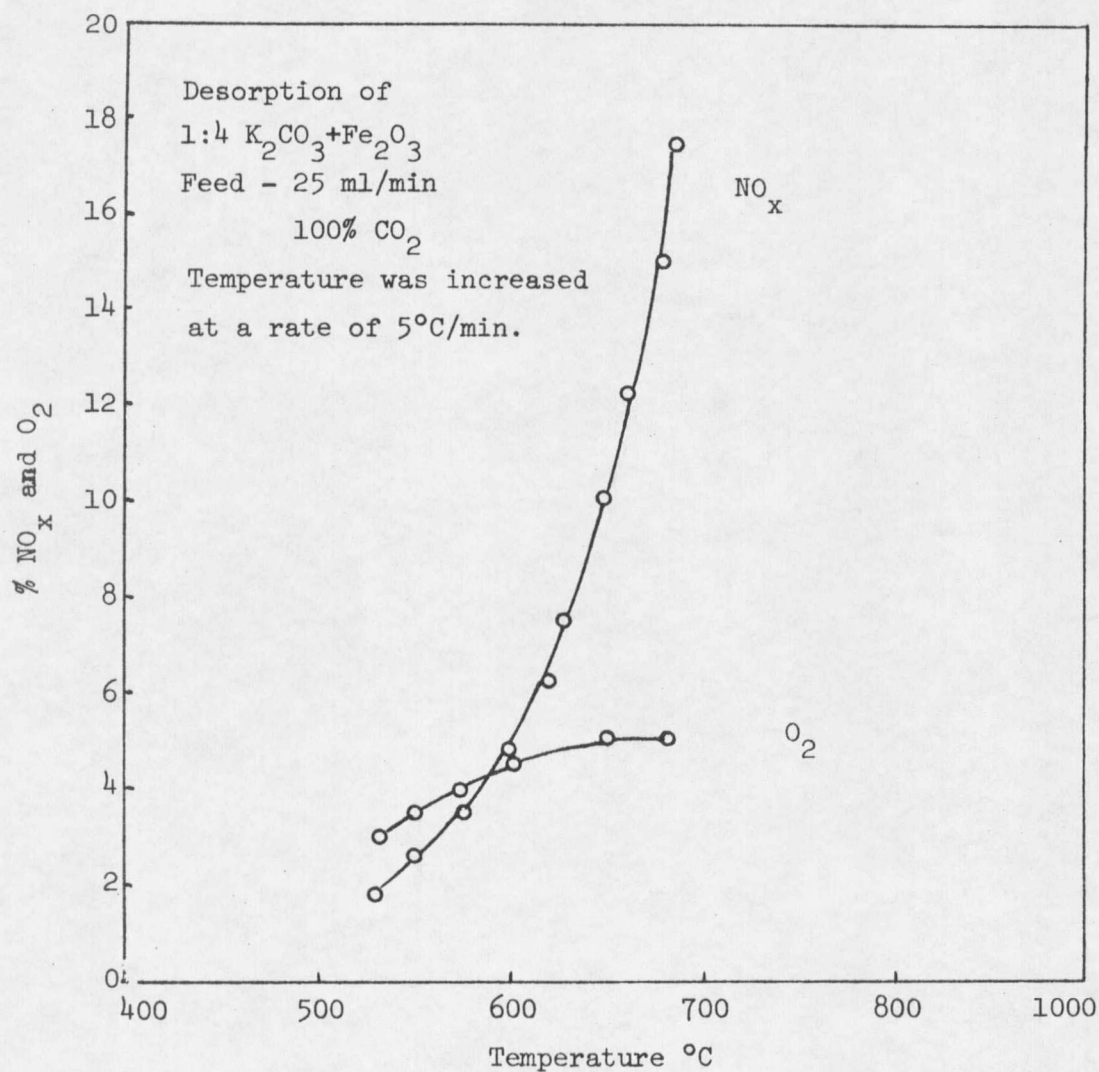
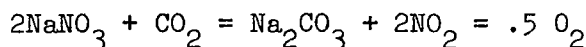


Figure 23. Effect of Temperature on Desorption of 1:4
 $K_2CO_3 + Fe_2O_3$

However, the difference appears to disappear at temperatures past 600°C since the NO_x concentrations become approximately the same. In general, desorption was dependent on temperature, gas composition and the type of carbonate used, and independent of the type and quantity of oxide used for absorption.

Figure 24 shows the results for desorption of 1:1 $\text{Na}_2\text{CO}_3 + \text{MnO}_2$ up to a temperature of 650°C. The graph shows that around 600°C the NO_x and O_2 concentration rises sharply. The fraction of NO_x that was NO was less than .01 (1%) at the flow rate used. If the flow rate was increased to 600 ml/min. it was found that the NO would increase to 90% of the NO_x . This indicated that the NO is being oxidized to NO_2 by the O_2 given off during desorption. After the initial rise in NO_x and O_2 , the concentrations steadied out to approximately 24% and 6% respectively at 655°C. This indicated a desorption equation of the form:



This equation gives the observed ratio of NO_2 to O_2 of 4:1 and is consistent with the tests showing that when CO_2 is present the material is converted to a carbonate. When desorption is done with O_2 and no CO_2 the material is converted to a mixture of alkali oxide and metal oxide. In the case of $\text{K}_2\text{CO}_3 + \text{MnO}_2$ when no CO_2 is present a potassium permanganate is probably formed, this was evident by a purple-blue color formed on dissolving the desorbed material which is characteristic of permanganates.

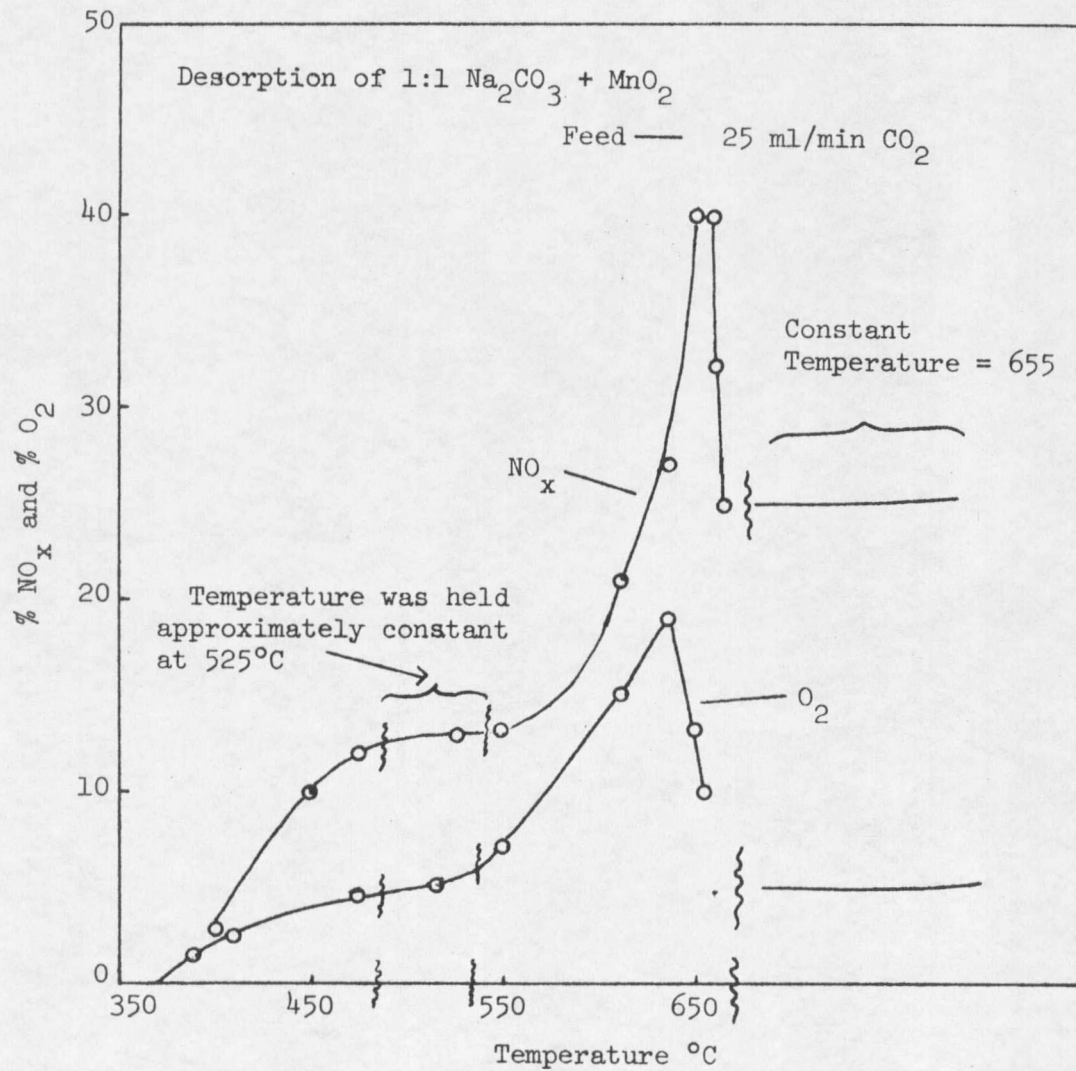
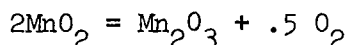


Figure 24. Effect of Temperature on Desorption of $\text{Na}_2\text{CO}_3 + \text{MnO}_2$ (Packed Bed)

The sharp increase in O_2 concentration is attributed to a chemical change in the MnO_2 . Figure 25 is a graph of the O_2 desorbing from MnO_2 as temperature is increased. The observed increase in O_2 is from the decomposition reaction:



which takes place at 400 to 600°C (Samsonov 1973). In comparison to Figure 23 where Fe_2O_3 was used, no sharp peak of O_2 was observed but there is some initial O_2 given off which cannot be attributed to nitrate decomposition.

Figures 26 and 27 are graphs showing desorption of 1:1 $K_2CO_3 + Fe_2O_3$ and 1:2 $K_2CO_3 + Fe_2O_3$ at constant temperature. A number of possibilities exist which may explain the desorption curve. The rate of desorption could be controlled by a diffusional process in which the desorbed NO_x has to diffuse out of the sorbent material, by heat transfer limitations in which the rate at which energy is transferred is controlling, or by the kinetics of the desorption mechanism. However, when the flow of CO_2 is cut off and the material is allowed to set at 600°C overnight, no sharp peak of NO_x is observed when the flow of CO_2 is started again. This would rule out diffusion, heat transfer and kinetic limitations, since these processes would have continued to increase the NO_x concentration. The sensitivity of NO_x concentration to temperature also indicated a kinetic or equilibrium situation. Since kinetic limitations were checked out as described above, the equilibrium

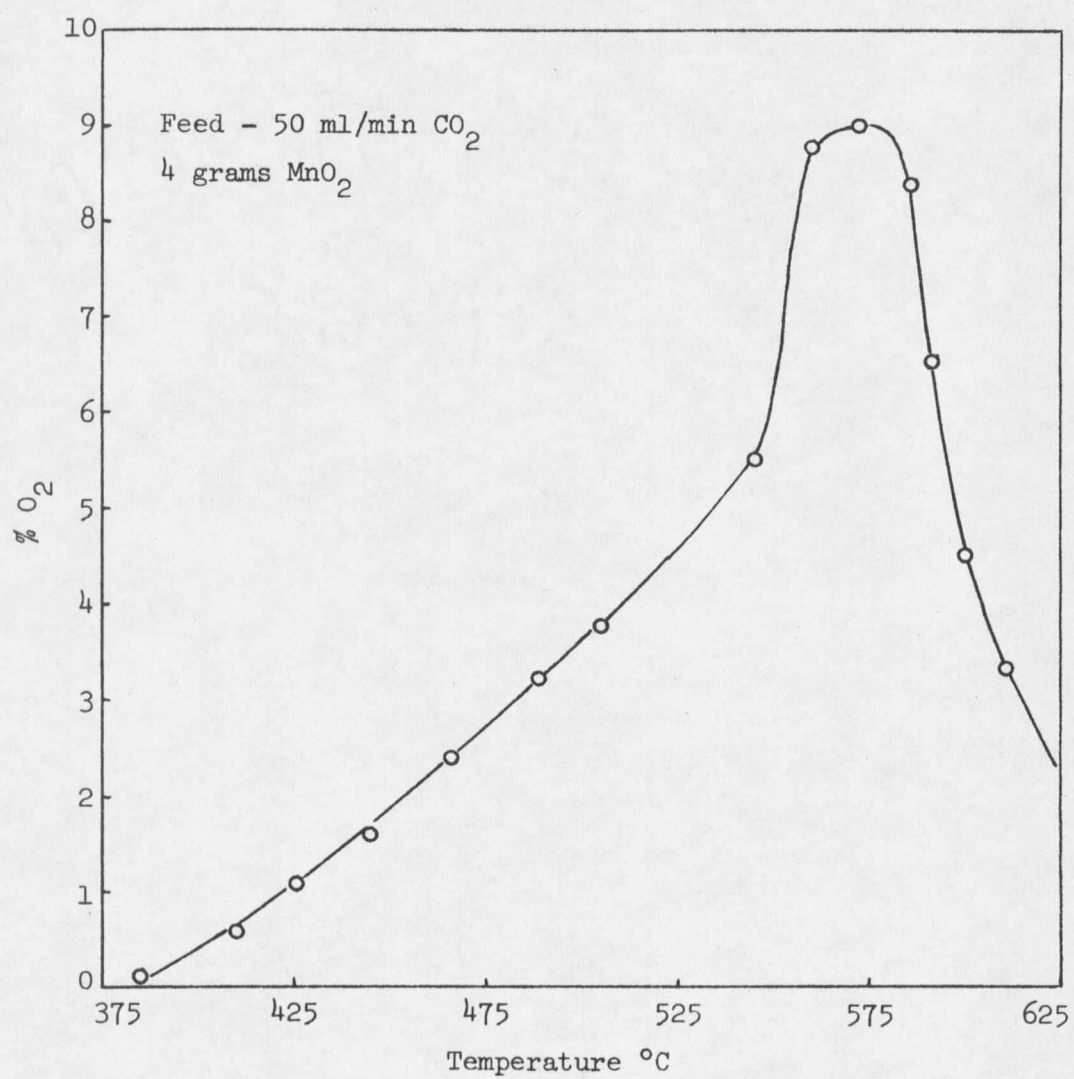


Figure 25. Desorption of O_2 from MnO_2 as a Function of Temperature

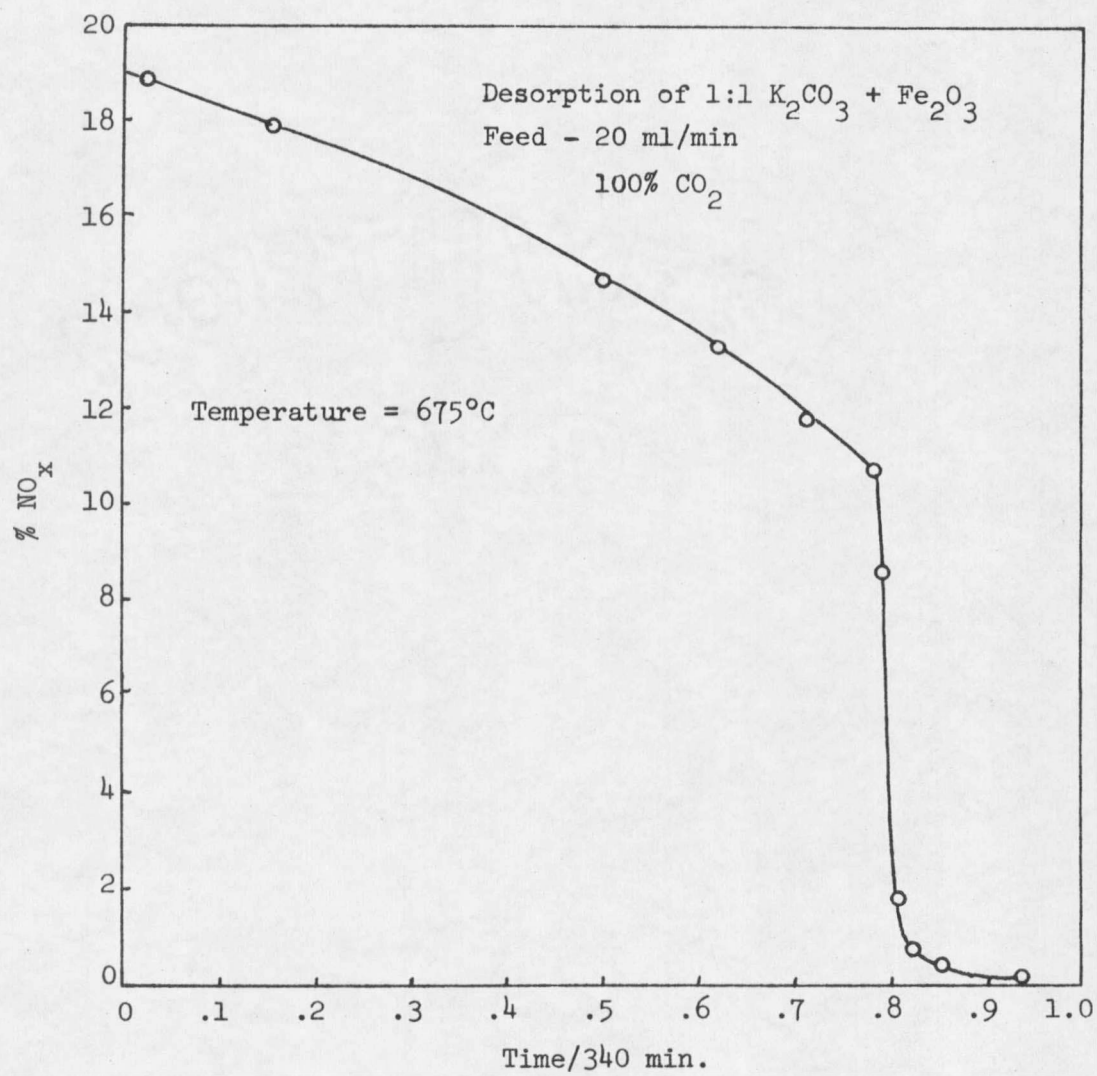


Figure 26. Desorption of 1:1 $K_2CO_3 + Fe_2O_3$

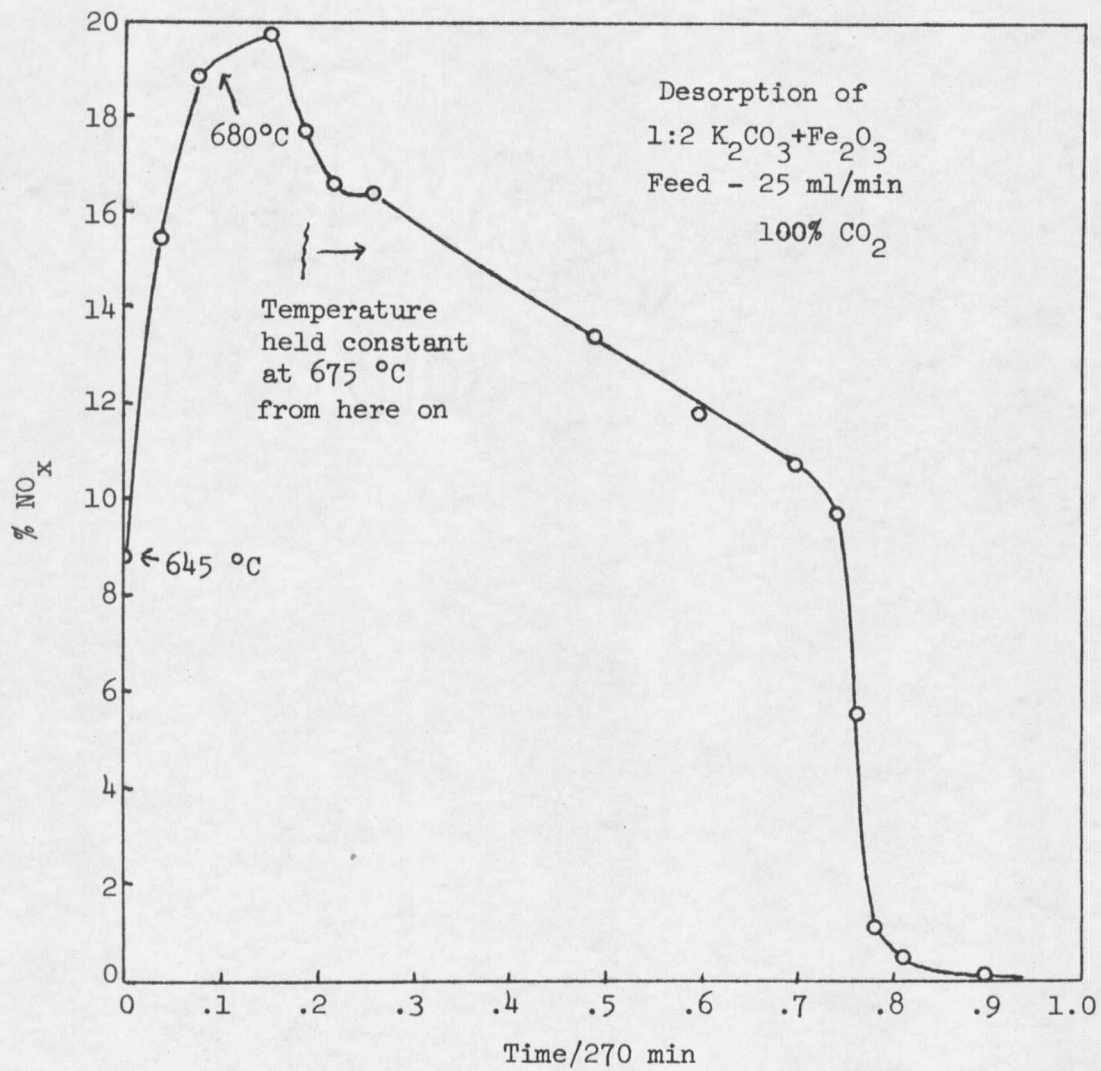


Figure 27. Desorption of 1:2 $K_2CO_3 + Fe_2O_3$

situation remains. If equilibrium is assumed then the slow drop with time would have to be due to a temperature gradient in the reactor.

The rapid drop would then be attributed to the complete depletion of the material and the final slow decline would then be due to diffusion out of the porous structure. Approximate measurements of the volume of the material after it was taken out of the reactor indicated that the material could be compacted to at least 50% of its original volume, indicating that the material was highly porous. The compaction was done in a graduated cylinder by taking a piece of the material and tamping it with an iron rod. Evidence for diffusion in the last stage was the slow or nonexistent increase in NO_x concentration when the temperature was increased. Other evidence for equilibrium is that loaded and partially loaded sorbents give the same NO_x concentration when desorbed at the same temperatures. Also when $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ was completely desorbed and then brought to 550°C and a gas containing NO_x was fed to the reactor, the concentration of NO_x leaving was approximately the same as the NO_x concentration during desorption at 550°C . This indicates a very fast reaction was occurring which permitted equilibrium to be reached before the gas left the bed.

Figure 28 is a graph of desorption of 1:1 $\text{Na}_2\text{CO}_3 + \text{MnO}_2$ at 550°C . This desorption curve is similar to those in Figures 26 and 27. The slight rise in NO_x concentration during the early stage of desorption is due to increasing the temperature from 540°C to 550°C . Of the NO_x de-

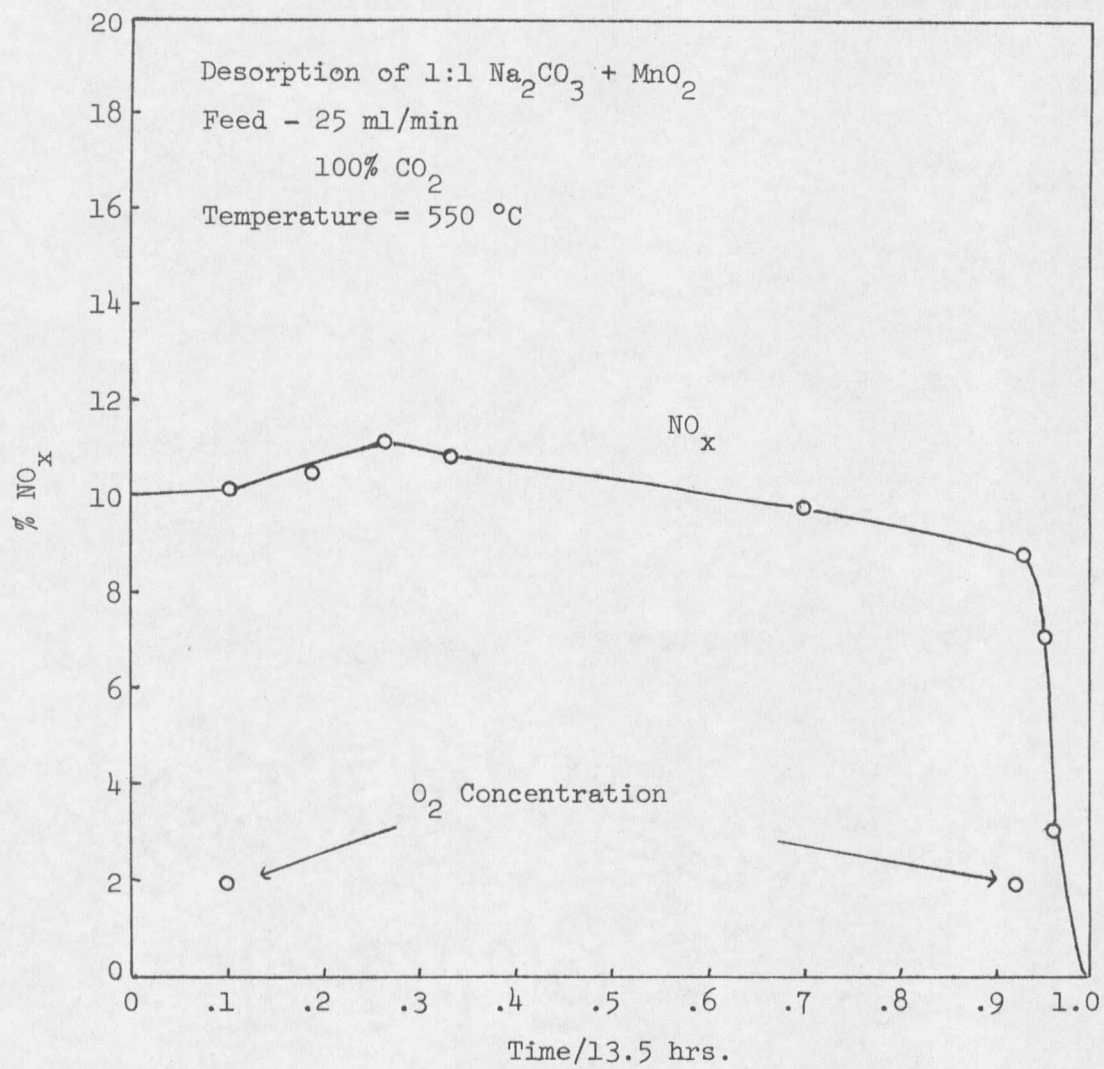


Figure 28. Desorption of 1:1 $\text{Na}_2\text{CO}_3 + \text{MnO}_2$

sorbed approximately 2% or less is NO and the remainder is NO₂.

Absorption After Desorption

It was found that for the MnO₂ sorbent mixtures the temperature at which maximum absorption occurred changed from 330-365°C to 400-460°C if the first desorption was carried out above 560-600°C. Mixtures made from ferric oxide did not have a change in absorption temperature. It was also found that if desorption of MnO₂ mixtures took place below 550°C the absorption temperature did not change. This can be attributed to little or no conversion of MnO₂ to Mn₂O₃.

Mechanism Study

Metal oxides were tested for their ability to oxidize NO to NO₂ under conditions used during absorption. The results of these tests are shown in Figures 29 and 30. Although total conversion of NO to NO₂ would be a function of surface area the effect of temperature would be unique for each material. It was found that MnO₂ and Co₂O₃ had optimum temperatures in the 300 to 360°C range. While NiO, CuO and Fe₂O₃ had optimum temperatures around 400°C. Experimentally it was found that the fraction of NO oxidized to NO₂ by the metal oxides was not changed even if 15% CO₂ was added to the feed. This is interesting because in the earlier studies it was found that CO₂ did affect the fraction of NO_x absorbed by mixtures of alkali carbonate and metal oxide. Comparing Figure 29 with Figure 4 (equilibrium curve for NO₂ and NO)

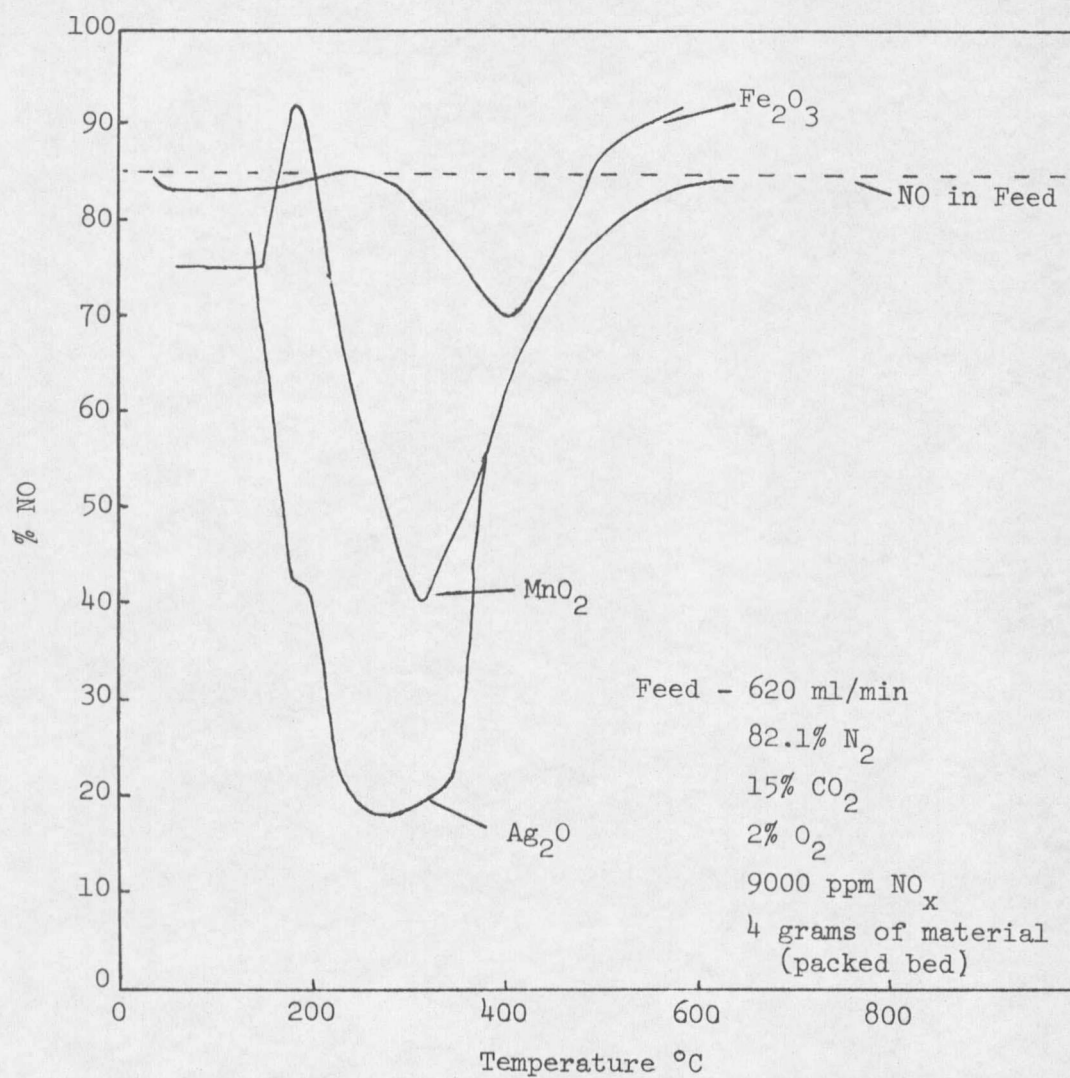


Figure 29. Oxidation of NO to NO_2 by Fe_2O_3 , MnO_2 and Ag_2O

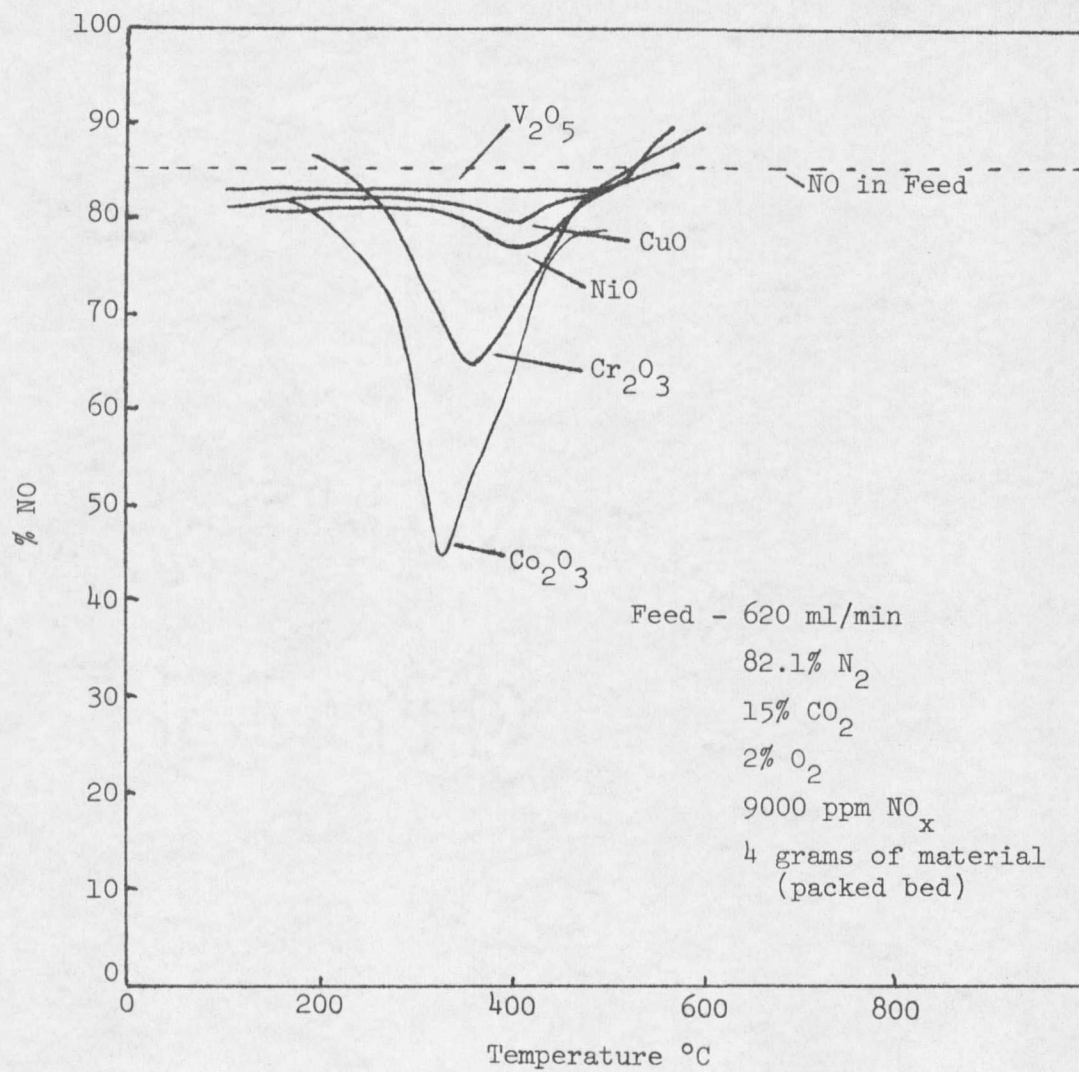


Figure 30. Oxidation of NO to NO_2 by V_2O_5 , CuO , NiO , Cr_2O_3 , and Co_2O_3 .

indicates that the MnO_2 oxidizes the NO to equilibrium or near equilibrium is reached for most of the oxides at temperatures of 400°C . Silver oxide (Ag_2O) oxidized NO quite well initially, but after heating above 400°C and then cooling down the material oxidized less than 30% of the NO. Mixtures of Ag_2O and sodium carbonate absorbed less than 20% of the NO_x fed to the reactor. The temperature at which absorption was maximum for mixtures of carbonate and MnO_2 or Fe_2O_3 corresponds very closely to the optimum temperatures found for the oxidation of NO to NO_2 (see Figures 31 and 32). It was also found that during the oxidation studies of NO to NO_2 with the metal oxides that very little (less than 1-5%) of the NO_x was being absorbed. This gives very conclusive evidence that the metal oxide acts as an intermediate (catalyst) for the absorption process. Further evidence for this is shown in Figure 33 where the Na_2CO_3 had been separated from the MnO_2 and the NO_x and NO leaving the reactor was measured. The results show that even though 50% of the NO_x is converted to NO_2 not much of the NO_2 is absorbed by the Na_2CO_3 . In Figure 31 where the materials were mixed together strong absorption occurs. This indicates that a surface species and surface diffusion is taking place. Investigators have shown that when NO is absorbed on a metal oxide the nitrate (NO_3^-) species is formed (Knozinger 1976, London and Bell 1973) and if NO_3^- diffuses on the surface it is possible that it is the reactive intermediate formed.

The effects of O_2 and CO_2 can be explained in the following manner.

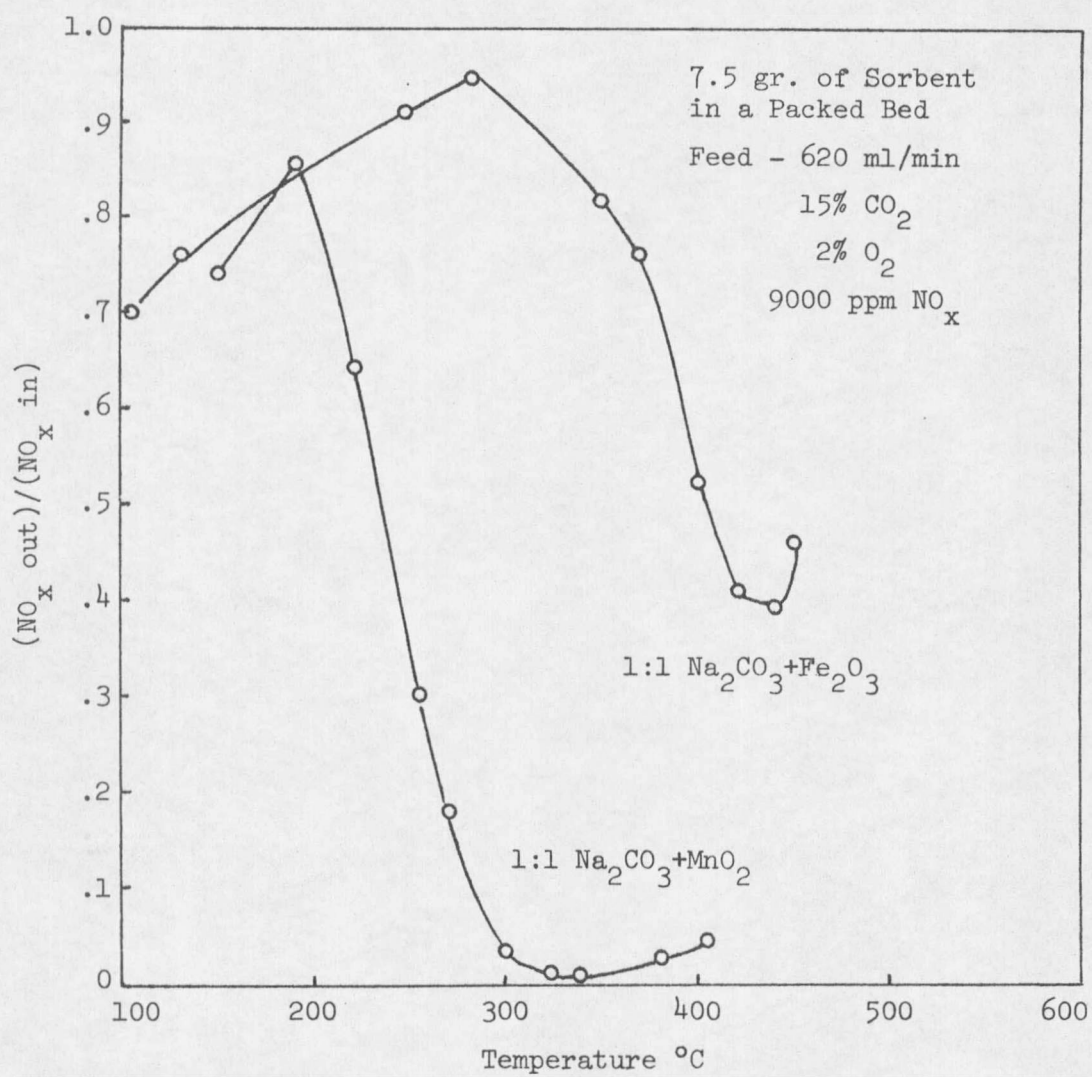


Figure 31. Effect of Temperature on Absorption by
Na₂CO₃ + Fe₂O₃ and Na₂CO₃ + MnO₂

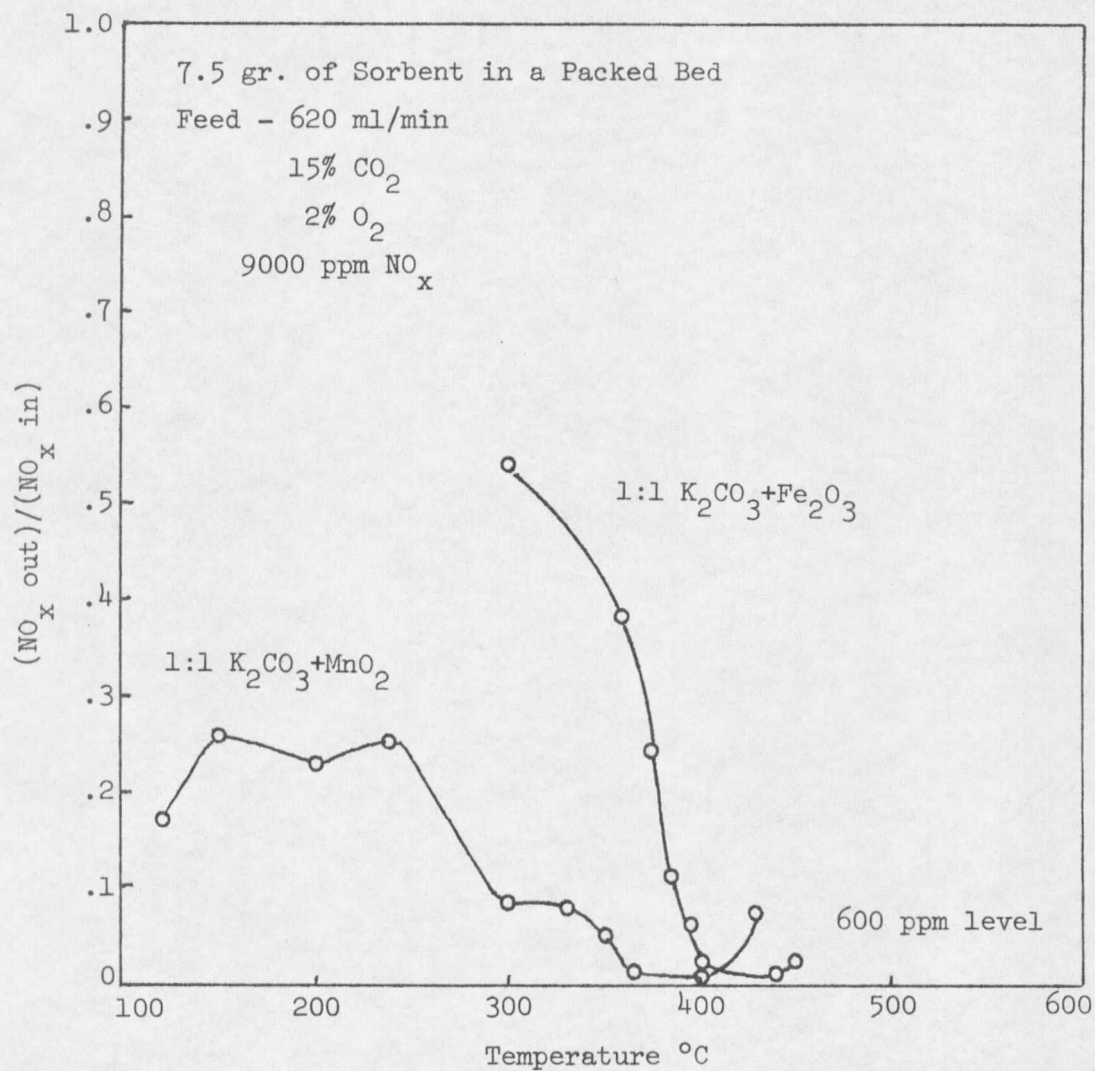


Figure 32. Effect of Temperature on Absorption by
 K₂CO₃ + Fe₂O₃ and K₂CO₃ + MnO₂

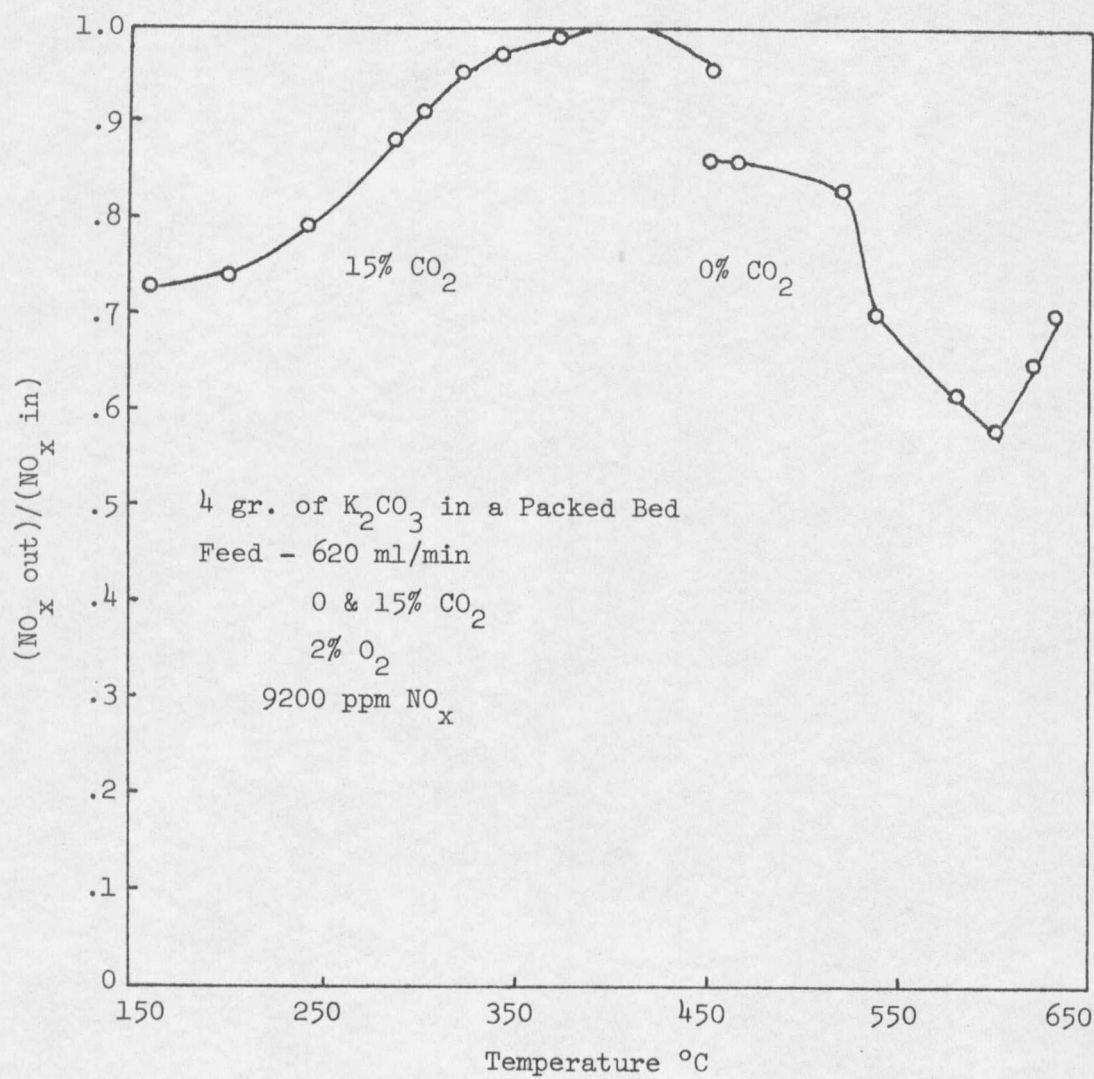


Figure 34. Effect of CO_2 on NO_x Absorption by K_2CO_3
(Packed Bed)

If the NO reacts with the metal oxide to produce NO_2 or NO_3^- which then reacts with the carbonate, then reoxidation of the surface would be important and affected by the O_2 concentration. CO_2 dependence could be attributed to interference with the surface diffusion process, by either absorption on active oxidation sites or interference with the reaction with the carbonate. The plate studies with pure carbonate indicated that CO_2 did not severely affect the absorption of NO_x . However, Figure 34 shows that some interference is found for the packed bed. K_2CO_3 absorbs NO_x at low temperatures and absorption drops off as the temperature increases. The material began to desorb NO_x at 400°C until the absorbed NO_x was mostly depleted.

If the temperature is again increased no absorption will take place and desorption will start again. However, if the CO_2 is shut off, absorption increases until the temperature reaches $600\text{--}620^\circ\text{C}$. Therefore, some CO_2 interference can be attributed to the carbonate but not all of it. It has been reported that NO and CO_2 can exist together on an oxide surface but NO is more strongly bonded and will eventually displace the CO_2 (Alexeyev and Terenin 1965). During a loading study it was found that if the CO_2 was shut off absorption would increase sharply and level off. However, if CO_2 was then added to the feed, absorption slowly dropped off and gradually leveled out to the previous value. This type of response would appear to fit the data presented in the literature, indicating that the bulk of CO_2 interference occurs on the

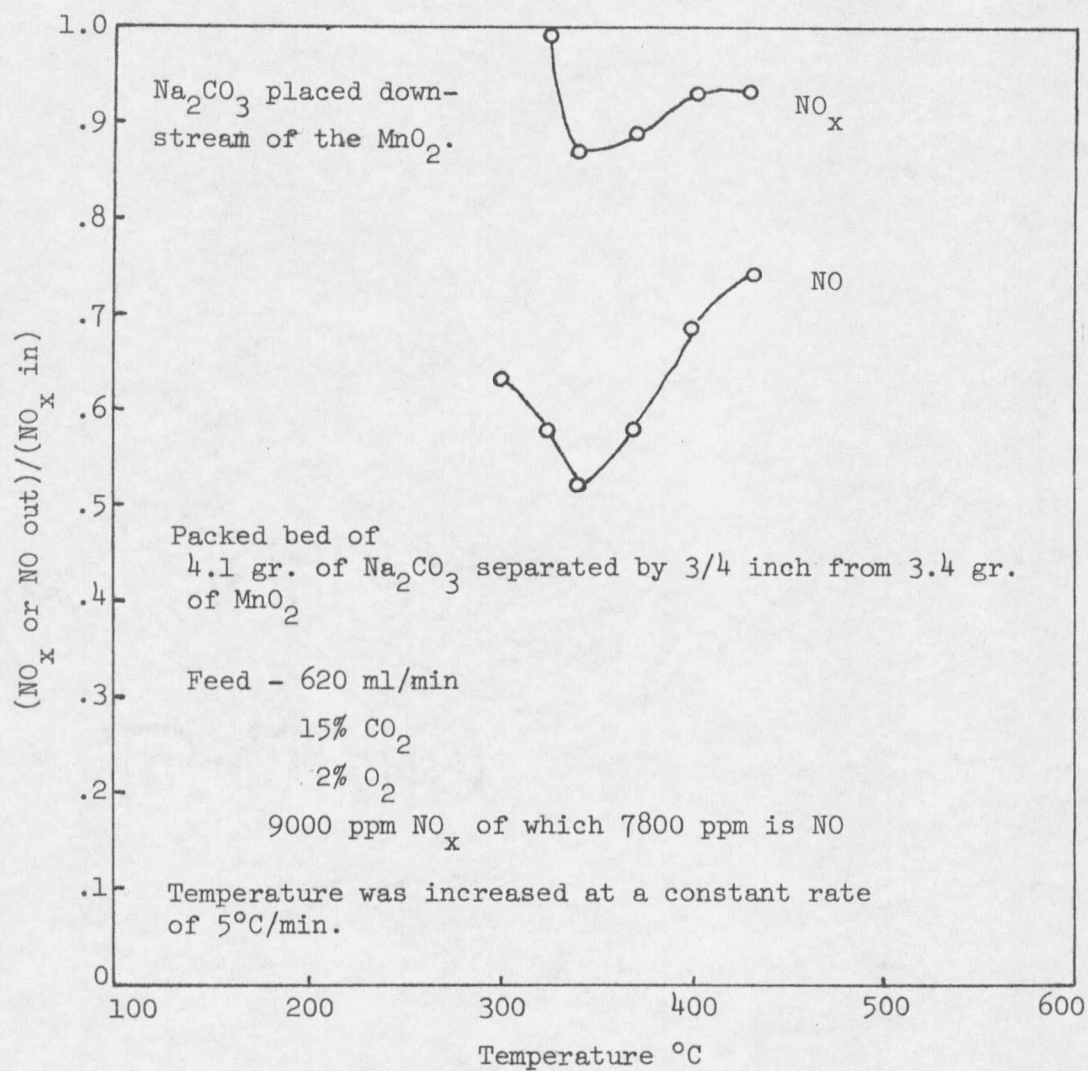


Figure 33. Effect of Separating Na₂CO₃ from MnO₂

metal oxide.

In summary, the absorption process appears to be made of the following steps. Absorption of NO on the surface oxide, followed by oxidation of NO to NO_2 or NO_3^- and then migration of the oxidized NO to the carbonate where it reacts to form a nitrate. The migration of the oxidized NO to the carbonate could not be a rate limiting step for the following reason. No significant difference in NO_x absorption was found between sorbents made by dry mixing the materials together and those made by dissolving the carbonate in water and then adding the metal oxide. The amount of intimate contact between materials is conceivably quite different for the two methods of preparation. This difference should have affected absorption if migration was limiting. Desorption occurs by spontaneous decomposition of the nitrate or by reaction of CO_2 with the nitrate to form the carbonate. It is interesting to note that desorption of K_2CO_3 sorbent increased fastest at about 620°C , which is the temperature at which absorption drops off for the pure carbonate (see Figure 34).

A question that remains is why do the oxides not oxidize NO at low temperatures (26°C to 300°C)? In an article by Halpern and Germain (1975) the desorption of oxygen from transition metal oxides was studied. They had found that there were a series of desorption O_2 peaks from the different oxides as the temperature was increased. There were three states labeled 0, 1 and 2 and an activation energy

associated with each state. For example Fe_2O_3 had 3 states 0 = 16 kcal/mole, 1 = 39 kcal/mole and 2 = 62 kcal/mole while MnO_2 had 2 states 0 = 16 kcal/mole and 1 = 30 kcal/mole. A comparison of their data with Figures 29 and 30 (oxidation of NO to NO_2) indicated that after peaks having a desorption energy from 37 to 48 kcal/mole, the temperature corresponding to the minimum in their curve corresponded to the temperature of maximum absorption and oxidation of NO in Figures 29-32. This indicates that sites left vacant by O_2 having a desorption energy from 37 to 48 kcal/mole are active for NO oxidation. Further evidence for this is that Cr_2O_3 , MnO_2 , Fe_2O_3 , Co_3O_4 , NiO and CuO have desorption energies of 37, 30, 39, 37, 44, 48 (kcal/mole) respectively and also showed an oxidation of NO to NO_2 . MnO_2 has the lowest energy and also shows the lowest temperature for NO oxidation. Furthermore, V_2O_5 had its first desorption state energy of 57.5 kcal/mole and did not show an ability to oxidize NO to NO_2 . Since equilibrium of NO to NO_2 comes into play around 400°C, the increase in NO after the minimum is probably due to thermodynamic limitation.

VI. THERMODYNAMIC AND EQUILIBRIUM RELATIONSHIPS

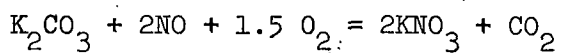
Table 9 lists the equilibrium constants for selected chemical reactions calculated from the data in Table 11. Conversion of the carbonates to nitrates is favored below 500°C and the reverse reaction is favored at 700°C. The reaction of SO_2 with the nitrates and carbonates to form sulfates is also favored below 500°C. It can also be predicted from the equilibrium calculations that H_2O would not affect the loading capacity of the sorbents since the assumed reaction is not favored.

The equilibrium concentration of NO was calculated for several initial gas compositions and the results are shown in Table 10. Although the results are subject to the accuracy of the original data, they give a very good indication of what NO concentrations can be expected. Thermodynamic data for the nitrates above 450°C has the greatest error because the equations used were derived from experimental data for temperatures below 450°C. The equations expressing enthalpy as a function of temperature were fitted to the experimental data between 26°C to 450°C. This equation was then used to calculate thermodynamic values at 700°C. Since the nitrates are liquids above 340°C it is possible that solutions are formed with either the metal oxides or the carbonates which are both solids at 700°C. The formation of a solution would nullify the assumption of unit activity for the nitrates and carbonates which was used in calculating the equilibrium compositions.

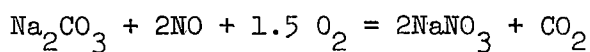
Table 9. Chemical Equilibrium Constants (K_{eq})

Reaction	Temperature °C		
	400	470	700
$K_2CO_3 + 2NO + 1.5 O_2 = 2KNO_3 + CO_2$		1.30×10^9	7.74×10^{-10}
$Na_2CO_3 + 2NO + 1.5 O_2 = 2NaNO_3 + CO_2$	2.60×10^7		.523
$2KNO_3 + SO_2 = K_2SO_4 + 2NO + O_2$		1.43×10^{12}	
$2NaNO_3 + SO_2 = Na_2SO_4 + 2NO + O_2$	3.12×10^{13}		
$2KNO_3 + H_2O = 2KOH + 2NO_2 + .5 O_2$		2.74×10^{-18}	
$2NaNO_3 + H_2O = 2NaOH + 2NO_2 + .5 O_2$	1.16×10^{-32}		

Table 10. Equilibrium Compositions at Atmospheric Pressure



Initial Composition (%)				Approximate Equilibrium Concentration of NO at Temperature	
N ₂	CO ₂	O ₂	NO	470°C	700°C
82.2	15	2	8000 ppm	400 ppm	
82.9	15	2	1000 ppm	200 ppm	
83.0	15	2	0		22%
0	100	0	0		57%



Initial Gas Compositions (%)				Approximate Equilibrium Concentration of NO at Temperature	
N ₂	CO ₂	O ₂	NO	400°C	700°C
82.2	15	2	8000 ppm	1200 ppm	
82.9	15	2	1000 ppm	1000 ppm	
83.0	15	2	0		21.7%
0	100	0	0		54.4%

$$\text{calculated from } K_{eq} = \frac{Y_{CO_2}}{Y_{NO}^2 Y_{O_2}^{1.5} P^{2.5}}$$

where Y = mole fraction

P = total pressure

Table 11. Selected Free Energies of Formation

	673°K	743°K	973°K
KNO_3	-227,977	-60,390	-17,667
K_2CO_3		-223,156	-207,711
K_2SO_4		-282,346	
KOH		-74,958	
NaNO_3	-57,073		-36,256
Na_2CO_3	-225,041		-205,719
NaSO_4	-273,480		
NaOH	-77,288		
NO	19,575	19,364	18,670
NO_2	17,891	18,958	22,468
NO_3	41,433	43,975	52,260
CO_2	-94,496	-94,530	-94,619
CO	-41,032	-42,390	-42,390
SO_2	-71,623	-71,997	
H_2O	-50,250	-49,369	
O_2	0	0	0

Data for the KNO_3 and NaNO_3 were taken from the article by Jang, et al. 1964; all other data are from JANAF Thermochemical Tables (1965).

From the equilibrium expressions it can be inferred that NO absorption is favored by an increase in pressure, a decrease in CO_2 , or an increase in O_2 concentration. Desorption of NO would be favored by just the opposite factors. The experimentally observed trends follow those projected by the equilibrium expressions and therefore give some validity for the assumed chemical reactions.

VII. MATHEMATICAL CORRELATIONS

To be able to correlate the data into a model it is necessary to know if mass transfer limitations are affecting the kinetics. For laminar flow over a flat plate the gas film boundary layer can be approximated by the Blasius solution for fluid flow. The boundary layer thickness is inversely proportional to the square root of the free stream velocity. Therefore by increasing the flow rate the boundary layer should decrease in thickness and if diffusion through this layer is controlling an increase in absorption should be seen. Film diffusion was checked for in the plate studies by increasing the recycle flow rate and no increase in absorption was found. However, more absorption occurred for the packed powder beds of sorbent material than for the plates of sorbent material. This indicates, that in part, diffusion through the sorbent material was controlling the absorption rate for the plate studies. Diffusion effects are less important for the packed bed studies from the evidence of the effect of temperature on absorption and the "S" shaped loading curves. If diffusion were limiting, an increase in temperature should continually increase absorption by increasing the diffusion coefficient. Also, an increase in temperature should increase the rate of chemical reaction. Experimentally, absorption reached a maximum at a particular temperature and quickly dropped off as the temperature was further increased. The "S" shaped loading curve indicates that absorption is affected by

the amount of sorbent material while a steady absorption rate would have indicated a diffusion controlled reaction.

From the results of the loading data the mathematical model will have to be able to describe the change in absorption rate with time. A simple expression developed by Chu and Houser (1964) and Vogel et al. (1974) which can be used to describe the loading curves is:

$$\log \left(\frac{C_o}{C_e} - 1 \right) = \frac{k_r EV}{2.3F} - \frac{k_r C_o E}{2.3m_\infty} t$$

where: C_o = concentration of reactant at inlet mole/cc.

C_e = exit concentrant of reactant.

t = reaction time in minutes.

m_∞ = maximum capacity mole/cc. sorbent.

k_r = reaction rate constant in min.^{-1} (pseudo).

C = gas reactant concentration, mole/cc.

E = void volume of sorbent cc/cc. of sorbent.

V = volume of sorbent, cc.

F = total gas flow rate cc/min.

The model assumes:

1. Plug flow through a bed of sorbent material.
2. Sorbent capacity decreases as material is absorbed.

$$\frac{dm}{dt} = k_r CE \left(1 - \frac{m}{m_\infty} \right)$$

m = loading capacity at time t .

C = gas reactant concentration.

3. That the effects of other gaseous species present (CO_2 and O_2) can be neglected (i.e. assumed constant).
4. The capacity of sorbent is much greater than the concentration of the material being removed.

The validity of the model can be checked by plotting the $\log (C_o/C_e - 1)$ vs t and determining if a straight line is produced. Figure 35 is the curve produced when the data from Figure 18 was plotted. The line produced is not straight indicating that the model does not exactly describe the process. Deviations from the straight line can be attributed to changes in the void fraction, channeling and diffusion limitations and other factors which have been neglected. Gidaspow et al. has analyzed the absorption of NO on solid sorbents taking into account diffusion and structural changes of the sorbent (Gidaspow et al. 1976 and 1977, Leung and Gidaspow 1974, Gidaspow et al. 1974). Although their model attempts to describe the effects of diffusion, channeling in the bed is not considered. For an irreversible reaction their model reduces to the same type of expression as that of Vogel's. Gidaspow has performed research on sorbents similar to those presented in this work (i.e. powder metal oxides with other materials added) and has calculated rate constants from packed bed reactor data by plotting the data in the same manner as was used for Figure 35. For ease of calculation, the rate constant was defined as:

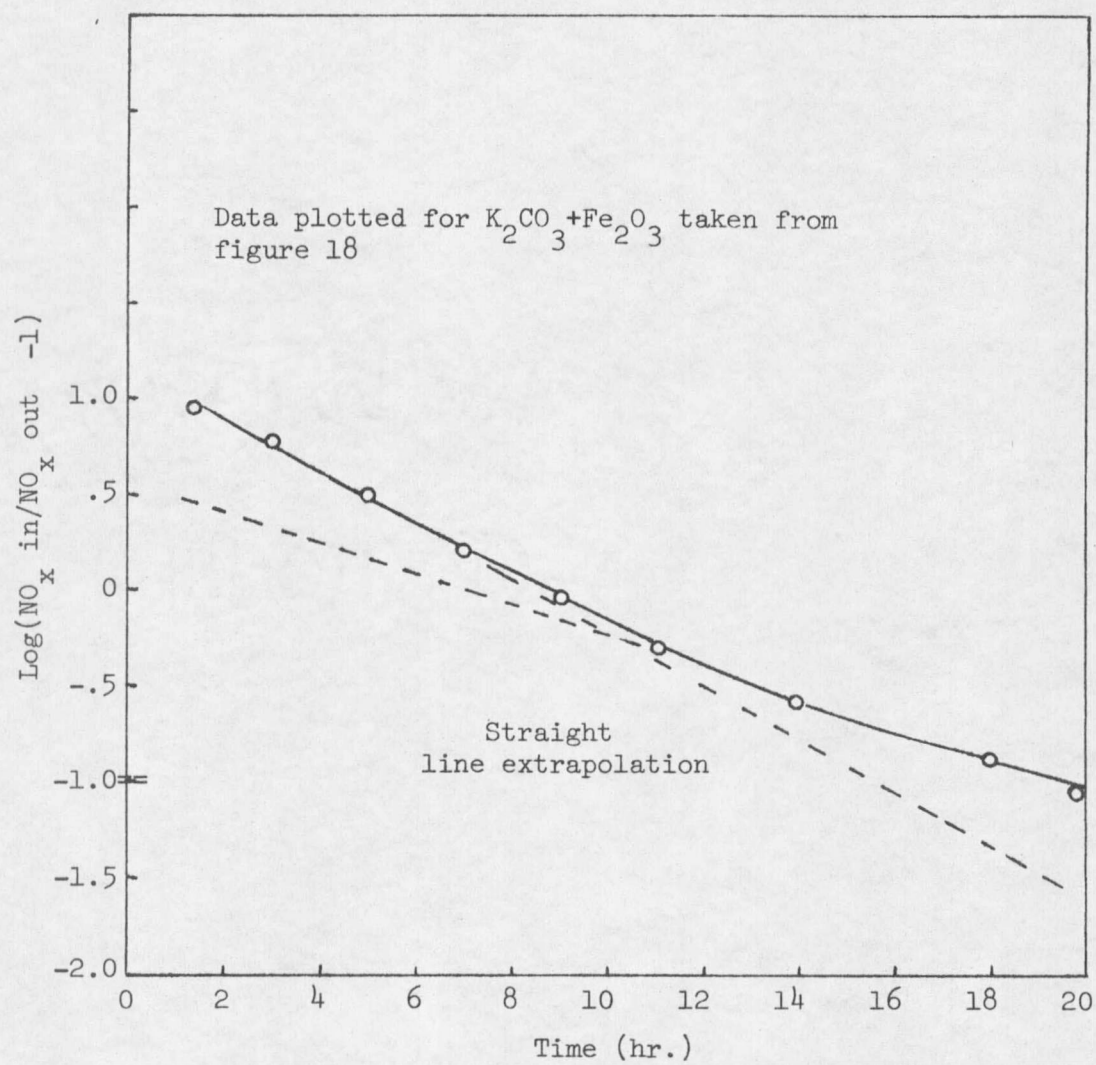


Figure 35. Log Plot for Data from Figure 18

$$k = k_r \frac{E}{m_{\infty}} \quad \text{liter/g mole-min.}$$

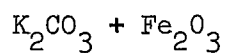
Table 12 lists the rate constants and capacities for the curves presented in Figures 18, 20 and 21. The reported rate constant of 52 L/g mole-min. for the high capacity sorbent in Table 2 (Gidaspow's) agrees fairly well with rate constants in Table 12. However, the highest capacity sorbent in Table 12 exceeds Gidaspow's by a factor of 2.4 even in the presence of CO₂.

The analysis presented here indicates a fairly good agreement with data gathered by other authors working in the same area. Although the mathematical model is far from perfect, it does give a basis on which experimental data can be compared (i.e. by the pseudo calculated rate constant and the sorbent capacities).

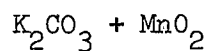
Table 12. Loading Capacities and Rate Constants

For Feed 620 ml/min, 15% CO₂, 2% O₂, 9000 ppm NO (7.5 gr of sorbent)

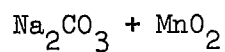
Molar Ratio	Total Capacity gr NO/gr sorbent	Capacity to 90 ppm	Capacity to 600 ppm	Rate Constant 1/g mole-min
-------------	------------------------------------	-----------------------	------------------------	-------------------------------



1:1	.2	.093	.14	40.0
1:2	.13	.066	.092	63.2
1:3	.0976	.057	.071	40.8
1:4	.076	.034	.058	53.3

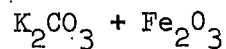


1:1	.264	.081	.10	51.3
1:2	.19	.088	.117	71.7



1:1	.311	.136	.20	35.9
1:2	.215	.099	.14	30.9

For Feed 620 ml/min, 15% CO₂, 2% O₂, 820 ppm NO (1.88 gr of sorbent)



1:1	.20	.02	.15	57.7
-----	-----	-----	-----	------

VIII. ECONOMIC CONSIDERATIONS

Table 13 lists the material costs per pound of sorbents and the costs per pound of absorbed NO. Costs were based on prices of individual chemicals reported in the Chemical Marketing Reporter as of February 20, 1978. Other factors which can enter into the selection of a sorbent are the operating costs and regenerating temperatures for the sorbent. The sorbents containing MnO_2 and Fe_2O_3 have maximum absorbing temperatures at 360°C and $400 - 460^\circ\text{C}$ respectively. However, if MnO_2 is regenerated above 560°C its absorbing temperature increases to $400 - 460^\circ\text{C}$. Sorbents containing Na_2CO_3 can be regenerated at approximately 100°C lower than sorbents containing K_2CO_3 . The $\text{Na}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ sorbents cannot be used for NO_x control because their absorption rate is too low in the presence of CO_2 . Therefore, the two cheapest sorbents are the 1:1 $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$ and the 1:1 $\text{Na}_2\text{CO}_3 + \text{MnO}_2$. From the standpoint of regenerating costs the 1:1 $\text{Na}_2\text{CO}_3 + \text{MnO}_2$ would be the most inexpensive if it would not change on desorption (i.e. change its desorption temperature and have a lower rate of NO_x absorption). The data in Table 13 also indicates that if the carbonate content of the sorbent is increased, costs would go down. Experimentally, increasing the carbonate above a 1:1 ratio causes the NO_x absorption rate to be lower.

For commercial application the powders would be unsatisfactory because of the large pressure drop across the bed. Forming the sor-

Table 13. Costs of Sorbents

Sorbent	\$/pound of sorbent	\$/pound of absorbable NO
$K_2CO_3 + Fe_2O_3$		
1:1 molar ratio	.116	.576
1:2 " "	.092	.708
1:3 " "	.080	.822
1:4 " "	.073	.960
$K_2CO_3 + MnO_2$		
1:1 " "	.202	.765
1:2 " "	.203	1.07
$Na_2CO_3 + MnO_2$		
1:1 " "	.108	.347
1:2 " "	.138	.642
$Na_2CO_3 + Fe_2O_3$		
1:1 " "	.039	.174
1:2 " "	.0416	.276

The cost per pound of absorbable NO is calculated by dividing the cost per pound of sorbent by the NO capacity of the sorbent (lb. of NO/lb. of sorbent)

bents into pellets or plates would reduce the pressure drop but the sorption rate would decrease due to diffusion limitations.

A rough indication of sorbent material cost can be made using the sorbent capacity and sorbents cost. For a plant operating at a gas flow rate of 75×10^6 scf/hr. and containing .9% NO, the total amount of NO to be recovered is 5.30×10^4 lb/hr. or 94% of the NO (assuming an EPA standard of 600 ppm, Walters and Goodwin, 1974). If the gas contained only .1% NO (1000 ppm) then only 2.51×10^3 lb/hr. of NO has to be recovered. The loading curve for 7.5 grams of 1:1 $K_2CO_3 + Fe_2O_3$ from Figure 20 gives a break-through at 600 ppm of 2.7 hr. for an hourly space velocity of 4000 (volume of gas passed per volume of sorbent). Using this data the amount of sorbent needed to control .9% NO in 75×10^6 scf/hr. is 9.46×10^5 pounds. Since the sorbent has to be regenerated every 2.7 hr., two beds of material are needed and the initial material cost is approximately \$110,711 for 1:1 $K_2CO_3 + Fe_2O_3$. If the desorbed NO is converted to nitric acid which is worth \$.11/pound, the income per hour is \$12,243. Since the major expense in a nitric acid plant is the ammonia used for making NO (Shrieve 1967), the recovery of NO from stack gases by the solid sorbents could be profitable if other costs associated with the process are not formidable.

If nitric acid is not made, the sorbents can still be used to absorb the NO. The desorbed NO can be cycled to the combustion chamber where it would be decomposed either thermally or catalytically to an

equilibrium composition. Figure 36 is a plot of the equilibrium concentration of NO at various temperatures. The remaining NO could then be reabsorbed and the cycle repeated.

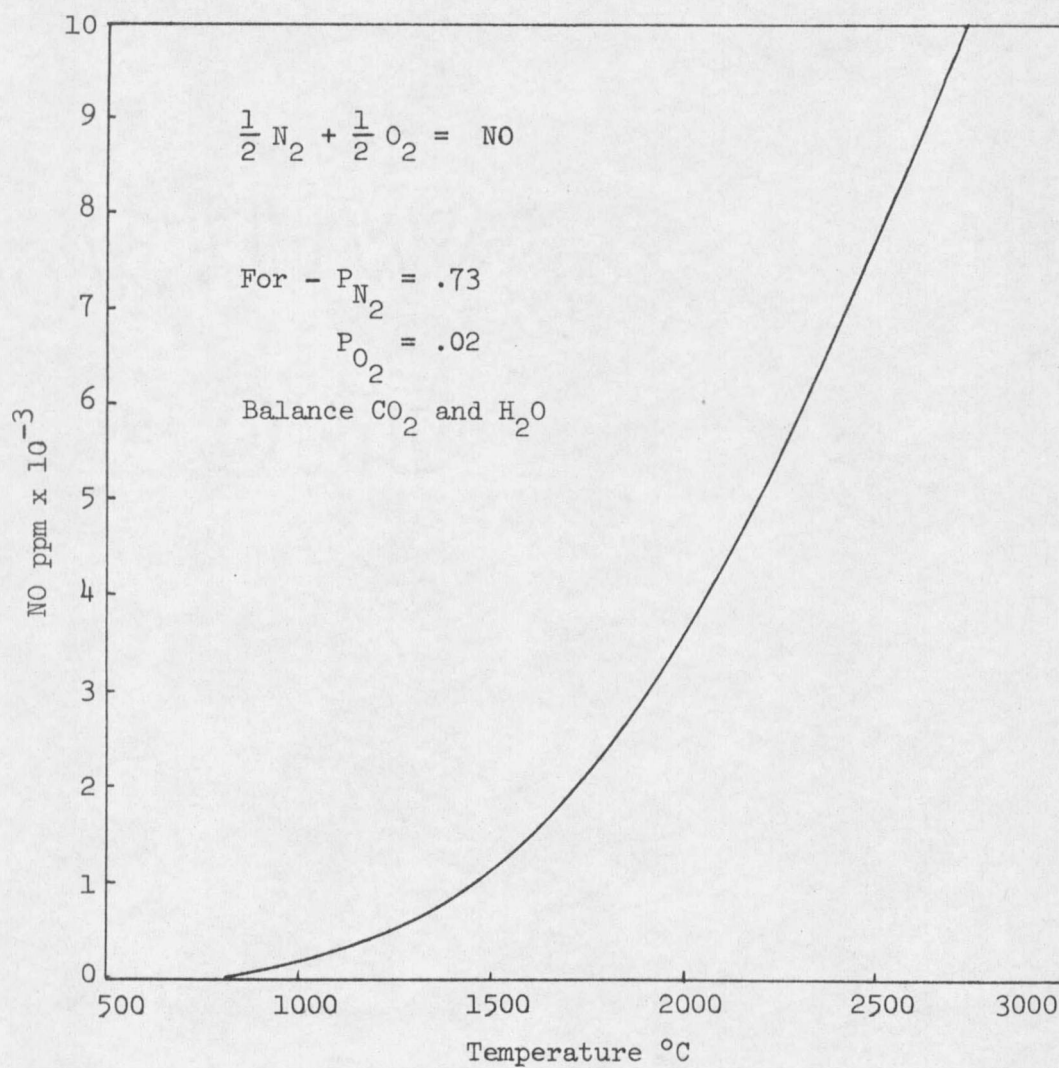


Figure 36. Equilibrium Composition of NO as a Function of Temperature

IX. GENERAL DISCUSSION

Sorbents made by mixing K_2CO_3 or Na_2CO_3 with either Fe_2O_3 or MnO_2 have been shown to be active absorbers of NO_x ($NO + NO_2$). Effects of CO_2 , O_2 , NO_x and SO_2 on absorption of NO_x by the alkali carbonate-metal oxide sorbents have been shown to be very important in the performance of the sorbents. CO_2 and SO_2 reduce the rate of NO_x absorption and in the case of SO_2 , complete deactivation of the sorbent occurs. This indicates that gases containing SO_2 will require a process for removal of SO_2 before the sorbents can be used. It may be possible to use sorbents similar to the carbonate-oxide sorbents for a SO_2 removal process.

Oxygen concentrations above 2% are needed if the sorbents are to be used when CO_2 is present. The increased absorption due to increased O_2 starts to level out in the range of O_2 concentration from 5 to 10%. At 2% oxygen the effect of CO_2 starts to level out in the range of 5 to 10% CO_2 . Of the sorbent mixtures those made with K_2CO_3 absorb NO_x the best and are least affected by CO_2 .

The molar ratio of carbonate to metal oxide is also an important parameter in the absorption of NO_x . For sorbents made with K_2CO_3 and Fe_2O_3 a 1:1 or 1:2 ratio appears to be satisfactory. Total capacity of the sorbents is determined by the theoretical amount of NO required to convert the carbonate to a nitrate. The temperature at which the sorbent is most active is closely related to the optimum

temperature at which the metal oxide oxidizes NO to NO₂.

Desorption of the absorbed NO_x is determined primarily by the type of carbonate, temperature, and the composition of the gas used for desorption. In general, sorbents made with sodium carbonate require lower temperatures to desorb than those made from potassium carbonate. The presence of O₂ causes the desorption rate to be lower at any given temperature while the presence of CO₂ increases desorption at any given temperature. Temperatures above 500°C are required to regenerate (desorb) the sorbents.

NO_x can be recovered from the sorbents at concentrations of greater than 10%. The composition of the NO_x is primarily NO₂ when desorption is carried out at low flow rates (25 ml/min.), while at higher flow rates (600 ml/min.) the NO_x consists mainly of NO. This indicates that NO is oxidized to NO₂ by the O₂ given off during desorption.

Sorbents made from Fe₂O₃ do not lose their absorption ability after repeated desorptions. However, after desorption the rate of absorption and the temperature at which absorption of NO_x is maximum changes for sorbents made from MnO₂. These changes were thought to be caused by the decomposition of MnO₂. Since sorbents made from MnO₂ have lower absorption temperatures than those made from Fe₂O₃, it would be advantageous if a method can be found which would reverse the changes that occur in MnO₂.

Thermodynamic calculations give an indication of what the maximum NO_x concentration can be achieved for desorption but due to data approximations the values are only a guideline. The mathematical model, although it is very crude, enables a comparison to be made with data reported by other researchers. Further work on a model is definitely needed if a preliminary design and cost estimations are to be made. However, before the model can be accurately constructed, the sorbents have to be made into a commercially usable form such as plates and pellets.

In summary, this work has shown that the sorbents are affected by a number of parameters which are important for their application. The most promising sorbents are $\text{K}_2\text{CO}_3 + \text{Fe}_2\text{O}_3$, $\text{K}_2\text{CO}_3 + \text{MnO}_2$ and $\text{Na}_2\text{CO}_3 + \text{MnO}_2$. Due to the problems associated with MnO_2 , further work is needed to determine if its activity can be maintained. The feasibility of making the sorbents into commercially usable forms should be studied and a model which can be used to predict their performance should be developed.

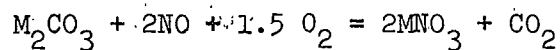
X. CONCLUSIONS

The following conclusions have been reached based on the experimental work performed:

1. Potassium carbonate mixed with either ferric oxide or manganese dioxide and sodium carbonate mixed with manganese dioxide can absorb 99 percent of the NO_x present in gas streams containing 15% CO_2 , 2% O_2 , 3% H_2O and 1000-10,000 ppm NO_x at an hourly space velocity of 4000 hr^{-1} .
2. Maximum absorption occurs at $330\text{--}360^\circ\text{C}$ for sorbents containing MnO_2 and at $390\text{--}460^\circ\text{C}$ for sorbents containing Fe_2O_3 . The temperature at which maximum absorption occurs for MnO_2 shifts to $400\text{--}460^\circ\text{C}$ if desorption is carried out above 560°C and remains there for repeated regeneration. NO_x absorption rates for sorbents containing MnO_2 dropped to approximately 50% of the initial rates after repeated regenerations. Sorbents made with Fe_2O_3 did not show a shift in absorption temperature or a decrease in the NO_x absorption rate after repeated regenerations.
3. NO_x absorption ability of the mixtures is related to the ability of the metal oxide to oxidize NO to NO_2 . The temperatures at which maximum NO oxidation occurred for Ag_2O , MnO_2 , Cr_2O_3 , Co_2O_3 , Fe_2O_3 , CuO and NiO are respectively 250, 310, 360, 325, 400, 400 and 400°C .
4. Total absorption capacity of the mixed sorbents is determined by the theoretical amount of NO required to convert the carbonate to

nitrate. For 1:1 molar ratios of $K_2CO_3 + Fe_2O_3$ the capacity is .2 grams of NO per gram of sorbent and for 1:1 $Na_2CO_3 + MnO_2$ the capacity is .311 grams of NO per gram of sorbent. Total capacity is unaffected by NO , O_2 , H_2O or CO_2 concentrations at the absorption temperature.

5. The rate of absorption is determined by a combination of CO_2 and O_2 concentrations, temperature, and the ratio of carbonate to oxide. High absorption rates are favored by low CO_2 , high O_2 and a low ratio of carbonate to oxide.
6. Absorption rates and capacities are affected by SO_2 to the extent that the active alkali carbonates are converted to alkali sulfates. SO_2 will desorb NO in a ratio of 2 moles of NO for every mole of SO_2 absorbed. The rate of SO_2 absorption is comparable to the rate of NO_x absorption.
7. The reaction order of NO with the sorbents is approximately 1 and reaction rate constants agree with the literature values for high capacity sorbents. The stoichiometric equation which fits the observed reaction is:



where M is either Na or K.

8. Desorption of NO_x from sorbents containing sodium occurs at lower temperatures than for those containing potassium. O_2 lowers the

desorbed NO_x concentration while the presence of CO_2 increases it.

XI. RECOMMENDATIONS

This research has indicated that mixtures of alkali carbonates and metal oxides are capable of absorbing NO under approximate flue gas compositions. Design data and cost estimates are now necessary to evaluate the sorbents for commercial application. Therefore the following work needs to be done.

1. Check sorbents made with commercial grade chemicals under exact flue gas compositions.
2. Using this data, develop a preliminary model for the absorption and desorption process and perform a preliminary economic analysis.
3. Sorbents should be formed into pellets and plates with the aid of high surface area supports and kinetic parameters evaluated.
4. Since SO₂ deactivates the sorbent, a SO₂ removal process should be evaluated in conjunction with the NO_x removal process.

To evaluate the kinetic parameters as accurately as possible a gradientless reactor system should be built or purchased. Surface area measuring equipment would also be very valuable for screening support materials and determining kinetics.

XII. BIBLIOGRAPHY

- Alexeyev, A., and Terenin, A., "Mutual Displacement of NO, CO and CO₂ Adsorbed on NiO, Shown by Infrared Studies", Journal of Catalysis, 4, p. 440-445 (1965).
- Bartok, W., Crawford, A. R., and Skopp, A., "Control of NO_x Emissions from Stationary Sources", Chemical Engineering Progress, 67 (2), p. 64-72 (1971).
- Bertry, J. M., "Reactor for Vapor Phase Catalytic Studies", Chemical Engineering Progress, 70 (5), p. 78-84 (1974).
- Brennan, J. A., "Removal of Nitrogen Oxides from Combustion Gases", U.S. Patent 3,015,369, 1962.
- Carberry, J. J., Chemical and Catalytic Reaction Engineering, McGraw-Hill Inc., 1976.
- Chappell, G. A., "Aqueous Scrubbing of Nitrogen Oxides", Pollution Control and Energy Needs, Advances in Chemistry Series 127, American Chemical Society, p. 207, 1973.
- Chemical Marketing Reporter, Schnell Publishing Co., Feb. 20, 1978.
- Chilton, T. H., Strong Water, Mass. MIT Press, p. 53-87, 1968.
- Clay, D. T., and Scott, L., "Reduction and Removal of SO₂ and NO_x from Simulated Flue Gas using Iron Oxide as Catalyst/Absorbent", AIChE Journal, 21 (3), p. 466-473 (1975).

- Dewing, E. W., "Heat Capacities of Liquid Sodium and Potassium Nitrates", Journal of Chemical and Engineering Data, 20 (3), p. 221-223 (1975).
- Evoniuk, C. J., "Solid Sorbents for the Recovery of Nitrogen Oxides (NO and NO₂) from MHD Exhaust Gases", Masters Thesis, Montana State University, 1976.
- Gidaspow, D., Arautoopour, H., and Hariri, H., "NO_x Removal with High Capacity Metal Oxides in the Presence of Oxygen", AIChE Houston Meeting, March 20-24, 1977.
- Gidaspow, D., Dharla, D., and Leung, L., "Gas Purification by Porous Solids with Structural Changes", Chemical Engineering Science, 31, p. 337-344 (1976).
- Gidaspow, D., Leung, L., and Dharla, D., "Design of Reaction Controlled Sorbers for Environmental Control: Removal of Nitric Oxide with a High Capacity Reduced Iron Oxide Sorbent", AIChE Symposium Series, 152, 71, p. 6-13 (1974).
- Groenendaal, W., Naber, J. E., and Pohleng, J. B., "The Shell Flue Gas Desulfurization Process: Demonstration on Oil and Coal Fired Boilers", AIChE Symposium Series 156, 72 (1976).
- Halpern, B., and Germain, J. E., "Thermodesorption of Oxygen from Powdered Transition Metal Oxide Catalysts", Journal of Catalysis, 37, p. 44-56 (1975).

- Hals, F. A., and Jackson, W. D., "MHD Power Generation - Economic and Environmental Implication", Tenth Symposium on Engineering Aspects of MHD, MIT, Cambridge, Massachusetts, 1969.
- Hals, F. A., and Lewis, P. F., Control Techniques for Nitrogen Oxides in MHD Power Plants, New York, ASME Publication, 1973.
- Henry, J. M., McCann, C. R., Demeter, J. J., Bienstock, D., "NO_x Control by Flue Gas Recirculation in Pulverized Fuel Coal", AICHE Symposium Series 148, 71 (1975).
- Hugh, C. N. and Houser, T. J., "A Method of Determining the Absorption Rate Constant of the Nonregenerative Catalyst", Journal of Catalysis, 3, p. 368-371 (1964).
- JANAF Thermochemical Tables, Dow Chemical Company, Midland, Michigan, Aug. 1965.
- Jang, G. J., Kelley, F. J., and Perano, J. L., "Melting and Premelting Phenomena in Alkali Metal Nitrates", Journal of Chemical and Engineering Data, 9 (1), January, p. 133-136 (1964).
- Joithe, W., Bell, A. T., Lynn, S., "Removal and Recovery of NO_x from Nitric Acid Plant Tail Gas by Adsorption on Molecular Sieves", Industrial and Engineering Chemistry: Process Design and Development, 11, p. 434 (1972).
- Knozinger, H., Advances in Catalysis 25, p. 230-232, New York, Academic Press, Inc., 1976.

- Koehler, R. G., "New England SO_2 Recovery Project System Performance", AICHE Symposium Series 148, 71, p. 289 (1975).
- Koval, E. J., and Roberts, M. A., "How Does Nitric Oxide Affect Reaction of Aqueous Nitrogen Dioxide", Industrial and Engineering Chemistry, 52, p. 1011 (1960).
- Kube, R. W., and Gronkovd, G. H., "Technology and Use of Lignite", Proceeding of Symposium Sponsored by the U.S. ERDA and the University of N. Dak., Grand Forks, N. Dak., May 14-15, 1977.
- Leung, L., and Gidaspow, D., "Iron Oxides Sorbents for Regenerative Sorption of NO_x ", AICHE Journal, 20 (5), p. 840, September (1974).
- London, J. E., and Bell, A. T., "A Simultaneous Infrared and Kinetic Study of the Reduction of NO by CO over Copper Oxide", Journal of Catalysis, 31, p. 96-107 (1973).
- Modell, M. and Reed, R. C., Thermodynamics and Its Application, Prentice-Hall, p. 396, 1974.
- Ogg, R. A., and Ray, J. D. "Method of Recovering Dilute Nitrogen Oxides from Gaseous Mixtures", U.S. Patent 2,684,283, 1950.
- Onischak, M., and Gidaspow, D., "Kinetics of Regenerative Sorption of Nitric Oxide by Solid FeSO_4 for Environmental Control", AICHE Symposium Series 134, 69, (1973).
- Perry, R., and Chilton, C. H., Editors, Chemical Engineering Handbook 5th Edition, McGraw-Hill Book Company, p. 14-4, 1973.

- Pershing, D. W., and Berhau, E. E., "The Chemistry of Nitrogen Oxides and Control Through Combustion Modification", Pollution Control and Energy Needs, Advances in Chemistry Series 127, American Chemical Society, p. 206, 1973.
- Pershing, D. W., Martin, G. B., and Berhau, E. E., "Influence of Design Variable on the Production of Thermal and Fuel NO from Residual Oil and Coal Combustion", AIChE Symposium Series 148, 71, p. 18 (1975).
- Reed, T. B., Free Energy of Formation of Binary Compounds, Mass. Inst. of Tech., 1971.
- Ricci, L. J., "Mixing NO_x Emissions", Chemical Engineering, April 11, 1977.
- Ricci, L. J., "Mixing NO_x", Chemical Engineering, April 25, 1977.
- Samsonov, G. V., Editor, Oxide Handbook IFI/PLENUM, 1973.
- Shrieve, N. R., Chemical Process Industries, McGraw-Hill Book Co., p. 319, 1967.
- Smith, J. M. "Chemical Engineering Kinetics", McGraw-Hill Book Co., p. 137-140 (1970).
- Sunderson, B. B., Harding, C. I., May, P. P., and Hendrickson, E. R., "Adsorption of Nitric Oxides from Waste Gas", Environmental Science and Technology, 1, p. 151 (1967).

- Turner, D. W., Andrews, R. L., and Siegmund, C. W., "Influence of Combustion Modification and Fuel Nitrogen Content on Nitrogen Oxides Emission from Fuel Oil Combustion", AIChE Symposium 126, 68, p. 55 (1972).
- Vogel, R. F., Mitches, B. R., and Massoth, F. E., "Reactivity of SO₂ with Supported Metal Oxide-Alumina Sorbents", Environmental Science and Technology, 8 (5), p 432-436, May (1974).
- Walters and Goodwin, "Federal Emission Standard for Stationary Sources", AIChE Symposium Series 137, 70 (3), (1974).
- Wright, S., and Youderian, R., "Economic Analysis of Nitric Oxide and Ammonium Nitrate Production Facilities on MHD Exhaust", Montana State University, Dept. of Chemical Engineering, 1976.

MONTANA STATE

3 1762 10005445 9

D378

Ev64

cop.2

Evoniuk, Christopher J

Kinetic studies on
absorption of NO_x ...

[illegible]

D378

EV64

cop. 2