Solid sorbents for the recovery of nitrogen oxides (NO and NO□2) for MHD exhaust gases
by Christopher John Evoniuk

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemical Engineering
Montana State University
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Abstract:
Nitrogen oxides (NO and NO2) are air pollutants produced in high, temperature combustion processes. Th generating power by the Magnetohydro dynamic (MED) process high temperatures are used and subsequently nitrogen oxides are produced. Two methods which:' are technically feasible for the control of the nitrogen oxides (NO) are: combustion modification to reduce the amount of NO produced and recovery of the NO for the manufacture of nitric acid or nitrate fertilizer. This research was performed to study solid sorbents for the recovery of nitrogen oxides.

Results of this work indicate that the carbonates of lithium, sodium or potassium and the first row transition metal oxides are not effective absorbents. However, mixtures of sodium or potassium carbonate with manganese dioxide or ferric oxide are very effective absorbents of NO and NO2. Ten grams of a 1:1 mole mixture of alkali carbonate and metal oxide in a temperature range from 380-450°C reduced the NO concentration from 9000 ppm to less than 100 ppm from a feed of 500Xml/min consisting of 15% CO2, 18% O2, 66% N2 and .9% NOx in a contact time of less than 4 seconds. Other equally effective sorbents were potassium manganate and decomposed mixtures of sodium nitrate and ferric oxide.

Sorbents could be regenerated and then reused by heating in a temperature range of 600-700°C. During the regeneration process, NOx could be recovered at concentration levels from 20 to 50% and the major component of the NOx was NO2.

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A thesis submitted in partial fulfillment
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ABSTRACT

Nitrogen oxides (NO and NO_2) are air pollutants produced in high temperature combustion processes. In generating power by the Magnetohydrodynamic (MHD) process high temperatures are used and subsequently nitrogen oxides are produced. Two methods which are technically feasible for the control of the nitrogen oxides (NO_x) are: combustion modification to reduce the amount of NO_x produced and recovery of the NO_x for the manufacture of nitric acid or nitrate fertilizer. This research was performed to study solid sorbents for the recovery of nitrogen oxides.

Results of this work indicate that the carbonates of lithium, sodium or potassium and the first row transition metal oxides are not effective absorbents. However, mixtures of sodium or potassium carbonate with manganese dioxide or ferric oxide are very effective absorbents of NO and NO_2. Ten grams of a 1:1 mole mixture of alkali carbonate and metal oxide in a temperature range from 380-450°C reduced the NO_x concentration from 9000 ppm to less than 100 ppm from a feed of 500 ml/min consisting of 15% CO_2, 18% O_2, 66% N_2 and .9% NO_x in a contact time of less than 4 seconds. Other equally effective sorbents were potassium manganate and decomposed mixtures of sodium nitrate and ferric oxide.

Sorbents could be regenerated and then reused by heating in a temperature range of 600-700°C. During the regeneration process, NO_x could be recovered at concentration levels from 20 to 50% and the major component of the NO_x was NO_2.

INTRODUCTION

Removal and control of nitric oxide from exhaust gases is a primary concern for all combustion processes. Nitric oxide (NO) is not considered as an irritant in itself and is not considered to have adverse health effects at concentrations found in the ambient atmosphere. Its greatest toxic potential is due to its oxidation to nitrogen dioxide (NO_2). Nitrogen dioxide exerts a toxic effect on the lungs and concentrations of greater than 100 ppm are lethal to most animal species, including man. Long term exposure to low concentrations does not cause acute inflammatory responses but does have an accumulative sustained effect. Results of community exposure to NO_2 levels of .062 to .109 ppm for long periods of time (6 months) gave an increased respiratory illness rate of 18% (Pollution Control Technology, 1973).

On a global basis the total amount of nitrogen dioxide generated by nature exceeds that made by man-made technological sources. Natural scavenging processes in nonurban areas keep background levels on the order of 2 - 4 ppb. In urban areas the levels are frequently higher because pollutants are added faster than scavenging processes can control them.

Fuel combustion is a major source of nitrogen dioxide in air pollution. Combustion of coal, oil and gasoline accounts for the majority of man-made emissions. The estimated global breakdown of nitrogen dioxide emissions in the year 1965 is as follows (Seinfield, 1975):

Source	Emissions in Trillion grams of NO_2
Coal combustion	24.4×10^9
Petroleum processes and combustion	20.2 "
Natural gas combustion	1.9 "
Miscellaneous (fires, etc.)	1.5 "

EPA emission standards for NO_2 from coal fired steam generators are 0.70 lb. per million Btu of heat input or approximately 600 ppm (Walters and Goodwin, 1974). For a 1000 Megawatt MHD generator having an efficiency of 50% it is estimated that the exhaust gas flow rate would be 1.25 million standard cubic feet per minute and could contain from less than 600 ppm NO to greater than 30,000 ppm NO (3%) depending on the combustion process used (Hals and Lewis, 1973).

To comply with EPA standards the MHD process would have to limit NO_x (NO and NO_2) emissions. Of the methods which appear promising, the most practical would be either combustion modification or absorption of the NO_x produced.

Previous Work

Combustion modification would reduce the amount of NO formed by lowering of the combustion temperature (Pepper, Eustic and Kruger, 1972). However, a preliminary economic analysis indicated that if the nitric oxide is collected and converted to nitric acid or a nitrate fertilizer, the income from marketing the product would be much greater

than that from the sale of electricity produced by the MHD generator (Wright and Youderion, 1976; Hals and Jackson, 1969). Since profitability is the prime concern of any industrial process, collection of the nitric oxide would be preferred over combustion modification.

A method which is technically feasible for the recovery of the nitric oxide is absorption by liquids or solids. Liquid absorption appears promising for it can be used to absorb both NO and SO_2. Usually alkaline solutions or sulfuric acid are used in conjunction with equimolar concentrations of NO and NO_2 (Hals and Jackson, 1969). Absorption of NO_x by liquid systems is improved by having equimolar concentrations of the two oxides rather than just NO_2 (Koval and Roberts, 1960). The increased absorption is due to the formation of N_2O_3 from the NO and NO_2, which is then absorbed to form nitrous acid. Nitrogen dioxide would have to be recycled to the incoming gas stream to achieve the equimolar concentration.

Among the alkaline scrubbing systems which have been tested, lime-water or magnesium hydroxide solutions have been reported as showing the most promise (Bartok, et al, 1971). The magnesium hydroxide is said to be better due to advantages in regeneration of the nitric oxide from the nitrite formed.

From the standpoint of forming a nitrate fertilizer, liquid absorbents form nitrites which would have to be oxidized to nitrates. Also the regeneration of liquid sorbents produces NO and little NO_2

which means that an added investment would be needed to oxidize the NO to NO_2.

Among solid sorbents, metal oxides, especially manganese and ferric oxides, have been reported to show technical potential (Leung and Gidaspow, 1974). Patent literature indicates that sodium and calcium carbonate or calcium oxide can be used to absorb NO_2 but not NO (Harres, Morello, and Peters, 1969). Nitric oxide is removed at normal temperatures and pressures by inorganic salts of hydroxy acids ($FeSO_4$, $KMnO_4$, $KClO_3$) by inorganic oxides (Na_2O_2, PbO_2) or by inorganic halides (KI, $CuCl_2$) (Lewis, 1975).

A ferric oxide-sodium oxide sorbent developed by R. A. Ogg and J. D. Ray (U.S. Patent 2,684,283) absorbs NO at 400°C forming sodium nitrate and little sodium nitrite. The sorbent was prepared by heating 2 moles of sodium nitrate ($NaNO_3$) and 1 mole of ferric oxide (Fe_2O_3) in a temperature range of 700 to 900°C until the sodium nitrate was largely decomposed and no nitrogen oxides were being given off. When a gaseous mixture consisting of 0.7% NO, oxygen and nitrogen was contacted with the sorbent the NO was absorbed and sodium nitrate was formed. Nitrogen oxides could then be recovered in a concentrated form on heating the sorbent to a temperature of over 700°C. A sorbent of this type would be particularly useful since a nitrate fertilizer could be directly formed or a concentrated stream of nitrogen oxides could be produced for the manufacture of nitric acid.

The importance of NO and NO_2 concentrations in the formation of nitric acid is best shown by the following example: For a gas mixture at 1 atm and 25°C containing 5% NO_x of which 80% is oxidized to NO_2 the equilibrium strength of nitric acid with this gas mixture is 55% by weight (Chilton, 1968), while if the gas contains 50% NO_x of which 80% is oxidized to NO_2 then the equilibrium strength of nitric acid is 70% by weight. The increased concentration is useful if the nitric acid is to be concentrated. Also by increasing the pressure of the concentrated NO_x stream the equilibrium strength of nitric acid would be well over 70%.

OBJECTIVES

The purpose of this research was to develop a solid for the removal of NO and NO_2 (NO_x) from the MHD exhaust gases and either convert them to a nitrate or on regeneration produce a more concentrated stream of NO_2 or NO. Other objectives were to determine the factors which affect the absorption and regeneration processes.

APPARATUS AND PROCEDURE

Figure 1 is a schematic of the apparatus used. Individual gas streams were passed through rotameters and into a mixing chamber to form a test gas of similar composition to that expected for the MHD exhaust. From the mixing chamber the gas could be passed directly to the NO_x analyzer to determine the NO_x composition or it could be passed to the reactor and then to the NO_x analyzer. Septum ports were located on both sides of the reactor to permit taking of gas samples for analysis of CO_2, N_2 and O_2.

Figure 2 is a schematic of the reactor. The reactor consisted of a stainless steel pipe 10.5 inches long with an outside diameter of 7/8 inch and an inside diameter of 5/8 inch. A stainless steel thermocouple well made from 1/4 inch O.D. and 5/32 I.D. tubing was situated in the center of the reactor. Approximately 7 inches from the top of the reactor a stainless steel porous disk was placed. Beneath the disk the reactor was packed with stainless steel rings which served to preheat the gas coming in. Materials to be tested were placed on top of the disk. Glass wool packing at the exit of the reactor prevented solid particles from blowing out. After each run the reactor was cleaned with dilute hydrochloric acid, rinsed with distilled water and dried.

The reactor was heated by an inconel pipe wrapped with 6.5 feet of ceramic beaded nichrome wire (.9 ohm/ft) and insulated by a 6.5 inch diameter housing packed with zeolite.

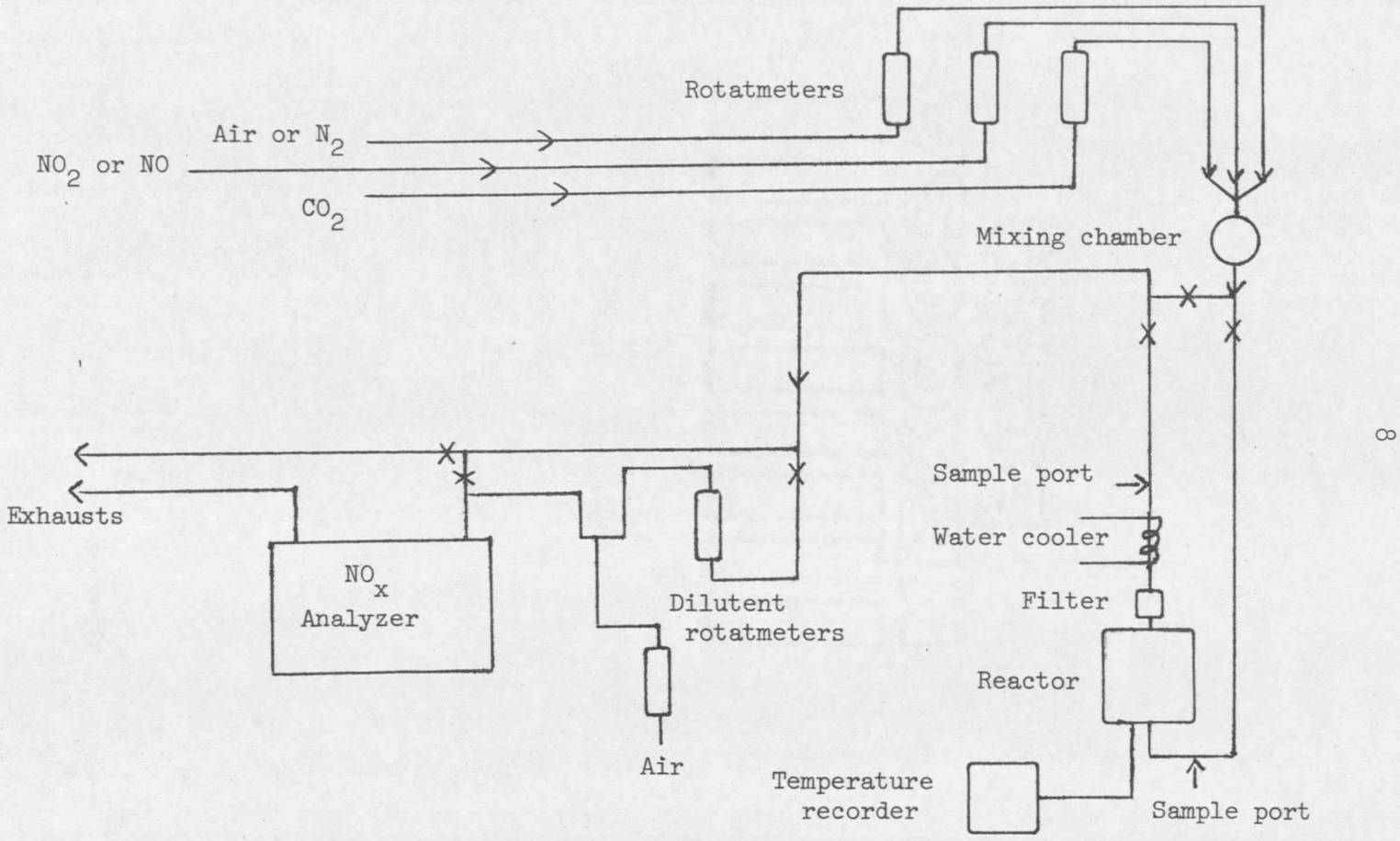


Figure 1. Flow Diagram of Apparatus

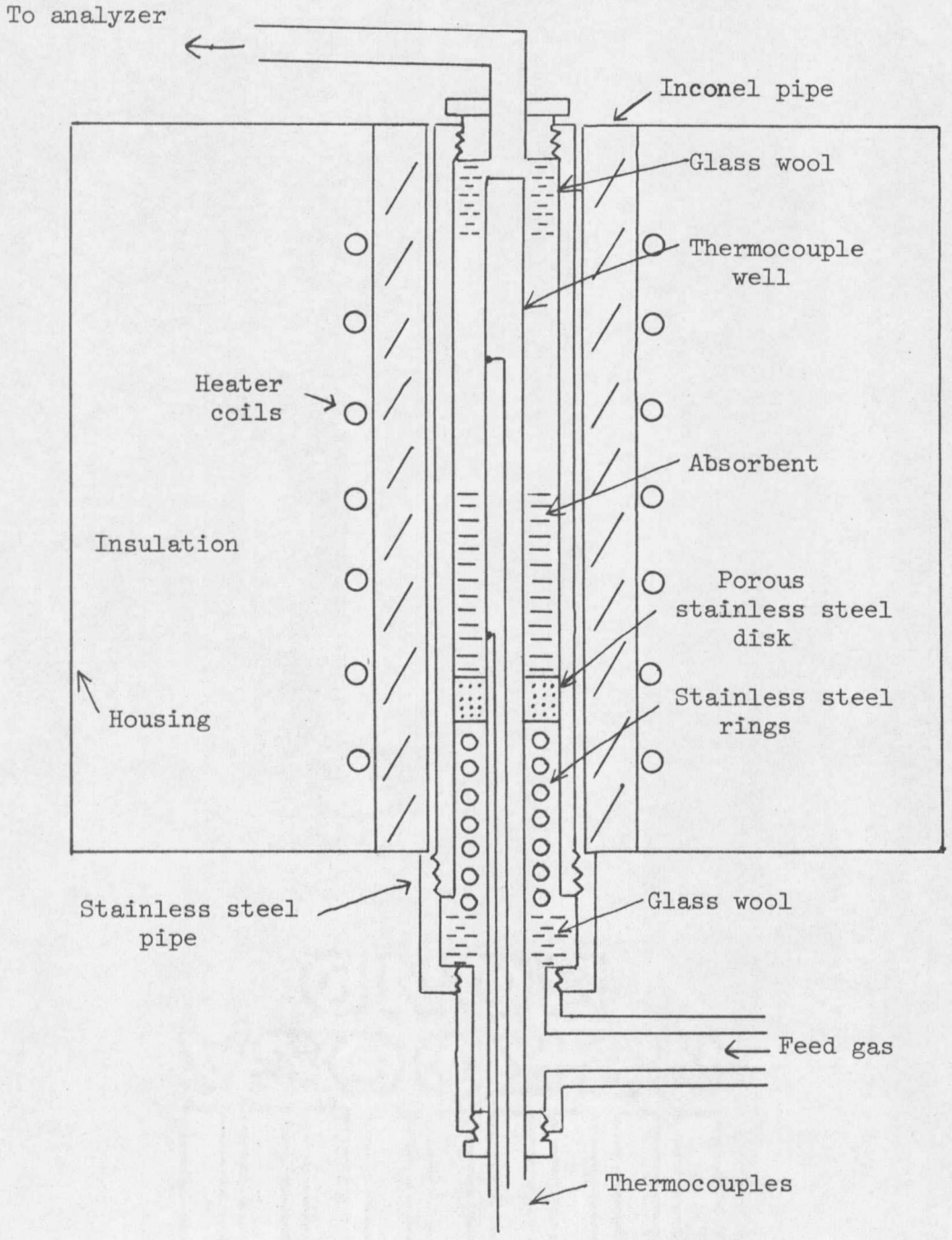


Figure 2. Reactor Cross-section

Sorbents

The sodium oxide-ferric oxide sorbent was prepared by heating a 2:1 mole ratio mixture of sodium nitrate and ferric oxide at red heat in a small rotating kiln over a large burner for approximately one hour. Gravimetric analysis indicated a weight loss of approximately 31% which corresponded to a formula of $Na_2OFe_2O_3$ for the remaining material. Bulk density of the substance when loosely packed was between 1.33 and 1.44 g/cm^3.

Transition metal oxides and the alkali carbonates were tested in the form that they were obtained from reagent grade chemicals. Mixtures of the oxides and carbonates were made on a 1:1 mole basis and 10 g. of the resulting mixture was used for testing. The chemicals were dry mixed with a mortar and pestle.

Gas Mixtures

Standards for calibrating the analyzer were made by diluting .50% NO (5000 ppm) with room air. The reactant gas mixtures also contained NO diluted with room air to produce the desired NO_x concentration, generally between .75% (7500 ppm) and 1% (10,000 ppm). Nitric oxide reacted with oxygen in the air to produce a final gas mixture containing approximately .5% NO and .5% NO_2.

Carbon dioxide was added to the feed stream and the resulting concentration of CO_2 was approximately 15%. Due to plugging of the

analyzer by high concentrations of moisture, no appreciable amount of H_2O was included in the feed gases other than what was in the room air. To determine the effect water had on the absorption, the air was saturated prior to being mixed with NO at 24°C to get a moisture content of approximately 2 - 3%.

Analysis of NO and NO_2 was accomplished using a Thermo-Electron Model 10A Self-Contained Chemiluminescent NO-NO_x Gas Analyzer, which has the capability of measuring from 0-10,000 ppm of NO or NO_2. Nitrogen and oxygen analysis was performed on a Beckman gas chromatograph using a column packed with molecular sieve type 13-X. Carbon dioxide analysis was performed on a Varian gas chromatograph using a column packed with Porapak Q-S (Waters Associates).

Nitrate Analysis

Nitrate analysis was performed by using an Orion specific ion electrode model 93-07. The solid sorbent was dissolved in water and the pH of the resulting solution was adjusted to approximately 5. The resulting solutions were then compared to known mixtures containing nitrate and nitrite ions. Presence of the nitrite ions was determined in the following manner: The amount of NO_x absorbed by the sorbent was determined from the absorption versus time curves. Standard solutions of nitrate and nitrite ions were made to approximate the concentration anticipated when the sorbent was dissolved in water.

Comparison of the reading for the sorbent solution and for each standard solution was then made to determine if nitrite or nitrate ions were predominately present.

RESULTS

Due to the reaction of NO with O_2 to form NO_2, it was necessary to determine the actual composition of the gas entering the reactor. Writing the chemical equation for the oxidation of NO to NO_2 as:

$$2NO + O_2 = 2NO_2$$

the rate expression for the formation of NO_2 can be written as:

$$dP_{NO_2}/dt = kP^2_{NO} P_{O_2}$$

where,

dP_{NO_2}/dt = rate of change in the partial pressure of NO_2

k = reaction rate constant

P_{NO} = partial pressure of NO

P_{O_2} = partial pressure of O_2

The rate expression can be written in a more useful form by letting

a = initial partial pressure of NO (atm)

b = initial partial pressure of O_2 (atm)

c = partial pressure of NO_2 at time t

t = time from start of reaction (sec.)

k = reaction rate constant: $k = \exp(641/T - 0.725)$ $(atm^{-2}sec^{-1})$ and T is in °K (Chilton, 1968)

substituting these variables in the original rate equation gives the expression:

$$dc/dt = k(a - c)^2(b - c/2)$$

If b is much larger than c/2 then the last term on the right hand side

reduces to b. The resulting expression can be easily integrated and solved for c to give:

$$c = a(1 - 1/(akbt + 1))$$

If a = .01, b = .21, k = 38 and t = 27 then

$$c = .0068 \text{ atm } (6800 \text{ ppm})$$

If a = .008 and the other variables remain the same then

$$c = .00506 \text{ atm } (5060 \text{ ppm})$$

Approximately 50% of the original NO is oxidized to NO_2 in the time (27 sec) it takes the feed stream to reach the reactor.

To determine if the NO_2 decomposes significantly as it passes through the preheat section, the equilibrium constant (K_p) and the rate constants for the forward (k_f) and reverse (k_d) reactions need to be known. Table I lists values of k_d calculated from the expression:

$$k_f/k_d = K_p = P^2_{NO_2}/P^2_{NO}P_{O_2}$$

TABLE I: Equilibrium Constants and Rate Constants (Chilton, 1968)

°C	38	200	400	600	800
K_p	1×10^{11}*	1×10^{5}	1×10^{1}	1×10^{-1}	1.7×10^{-3}
k_f	2.2×10^{1}	4.3	1.69	1.02	.745
k_d	2.2×10^{-10}	4.3×10^{-5}	.169	10.2	7.45×10^{2}

As can be seen from the table the decomposition reaction does not proceed at a significant rate until the temperature exceeds 400°C.

Since the decomposition reaction will be important above 400°C, it is important to know what the equilibrium concentrations of NO and NO_2 will be above this temperature. Table II lists some values for the concentrations of NO and NO_2 when the initial amount of NO added to a stream containing 21% O_2 is known.

TABLE II: Equilibrium Values of NO and NO_2

Initial NO concentration = 10,000 ppm			
°C	400	600	800
NO_2(ppm)	6774	1740	4
NO(ppm)	3226	8260	9996
Initial concentration = 8,000 ppm			
NO_2(ppm)	5420	1390	3
NO(ppm)	2580	6610	7997

Comparison of these values with the values calculated for the feed composition indicates that the concentration of NO and NO_2 entering the reactor will be close to the equilibrium concentration of NO and NO_2 at 400°C. Other nitrogen oxide species that could form from the mixture of NO and NO_2 are dinitrogen trioxide (N_2O_3) and dinitrogen tetroxide (N_2O_4). Equilibrium values for these are shown in Table III and Table IV.

TABLE III: Equilibrium Values for N_2O_3 (Chilton, 1968)

Reaction $NO + NO_2 = N_2O_3$	$K_p = P_{N_2O_3}/P_{NO}P_{NO_2}$		
°C	25	35	45
K	0.475	0.272	0.145

TABLE IV: Equilibrium Values for N_2O_4 (Chilton, 1968)

Reaction $2NO_2 = N_2O_4$	$K_p = P_{N_2O_4}/(P_{NO_2})^2$, atm^{-1}				
°C	0	20	40	60	80
K_p	65	12	2.7	.67	.20

Inspection of the equilibrium values indicates that neither of these species would be significant at temperatures above 100°C.

Graphs and Order of Presentation

Some points which are important in reading of the graphs are as follows: The feed concentration is in ppm of NO while the exit concentration is in ppm of NO_x ($NO + NO_2$). It should also be noted that desorption is occurring when the exit concentration (NO_x) exceeds the original NO concentration in the feed. Since absorption tests were performed with changing temperature, the concentration of NO_x in the gas stream leaving the reactor and the corresponding temperatures are

plotted against time.

The original order of testing sorbents was to examine the sodium oxide-ferric oxide sorbent in detail since it was reported to be a very effective solid sorbent. Then mixtures of alkali carbonates and metal oxides were tested as was the individual components of the mixtures to determine if a more effective sorbent could be found. For unification the results are presented in the order that follows.

NO_x Absorption by the Alkali Carbonates

The concentration of NO_x leaving the reactor and temperature curves for runs made with 10 grams of Li_2CO_3, Na_2CO_3, and K_2CO_3 are shown in Figure 3, 4 and 5. Each carbonate has an initial absorption maximum at approximately 100°C and at 350 - 450°C.. The absorption at 100°C does not occur after the carbonates have been heated. Absorption capacity increases from lithium to potassium. Potassium carbonate is unique in that it reduces the NO_x ($NO + NO_2$) concentration leaving the reactor below the NO_2 concentration entering the reactor at temperatures between 350 and 450°C. It should be remembered that of the original NO that is injected into the feed stream, approximately half is oxidized to NO_2 before reaching the reactor. Also as NO_2 is absorbed the possibility exists that the rate of NO oxidation will increase creating more NO_2 which can be absorbed.

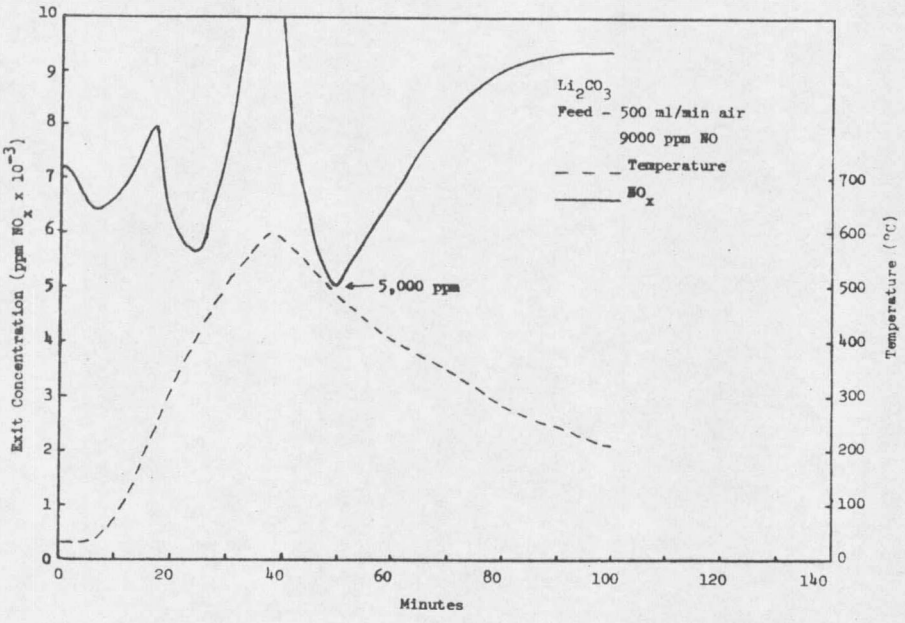


Figure 3. NO_x Absorption Curve for Li_2CO_3

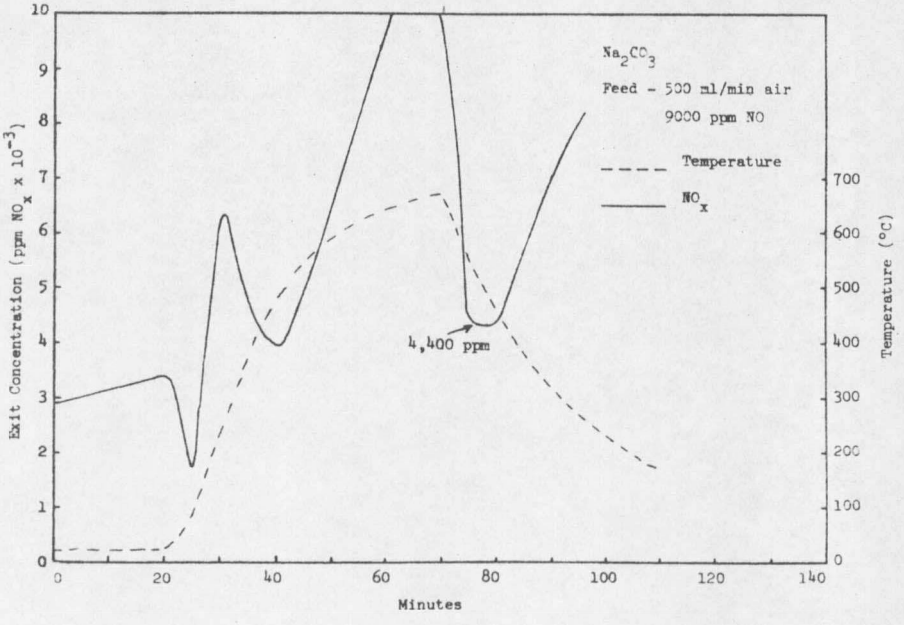


Figure 4. NO_x Absorption Curve for Na_2CO_3

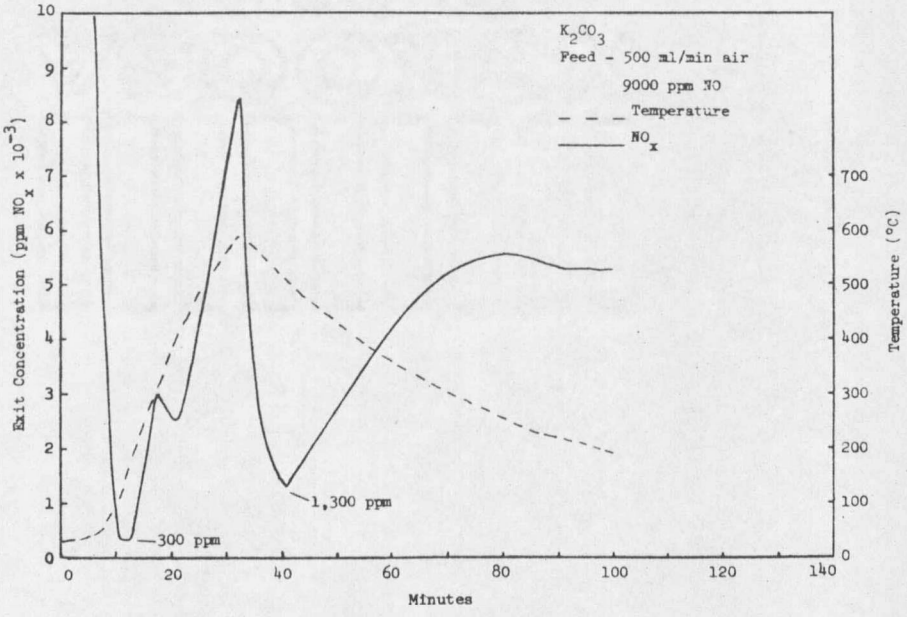


Figure 5. NO_x Absorption Curve for K_2CO_3

Absorption of NO_x by Metal Oxides

Figures 6 through 11 are the results of the runs made with metal oxides TiO_2, MnO_2, Fe_2O_3, Co_2O_3, PbO_2 and Al_2O_3 (activated alumina). Of these oxides, alumina and lead dioxide showed the greatest potential for absorbing NO_x.

At room temperature Al_2O_3 absorbs NO_2 and possibly some NO (Figure 11) while PbO_2 absorbs primarily NO_2 (Figure 10). Both oxides have an absorption maximum at about 300 - 400°C, but Al_2O_3 desorbs in the temperature region from 20°C to 300°C. Above a temperature of 400°C Al_2O_3 and PbO_2 desorb NO_x and after the desorption Al_2O_3 will absorb more NO_x at 400°C than previously (9200 ppm compared to 800 ppm), while PbO_2 absorbs less (3500 ppm compared to 6250 ppm).

Manganese oxide absorbs mostly NO_2 at room temperature but as the temperature increases from 26°C to 500°C desorption occurs (Figure 8), then as the temperature decreases from 500°C to 300°C some absorption occurs again. Table 5 summarizes the performance of the metal oxides.

TABLE V. NO_x Absorption by the Metal Oxides

Oxide	From(ppm)	To(ppm)	Oxide	From(ppm)	To(ppm)
TiO_2	9,000	7,000	Co_2O_3	9,000	6,800
MnO_2	10,000	7,500	Fe_2O_3	10,000	8,900
PbO_2	7,000	750	Al_2O_3	10,000	800

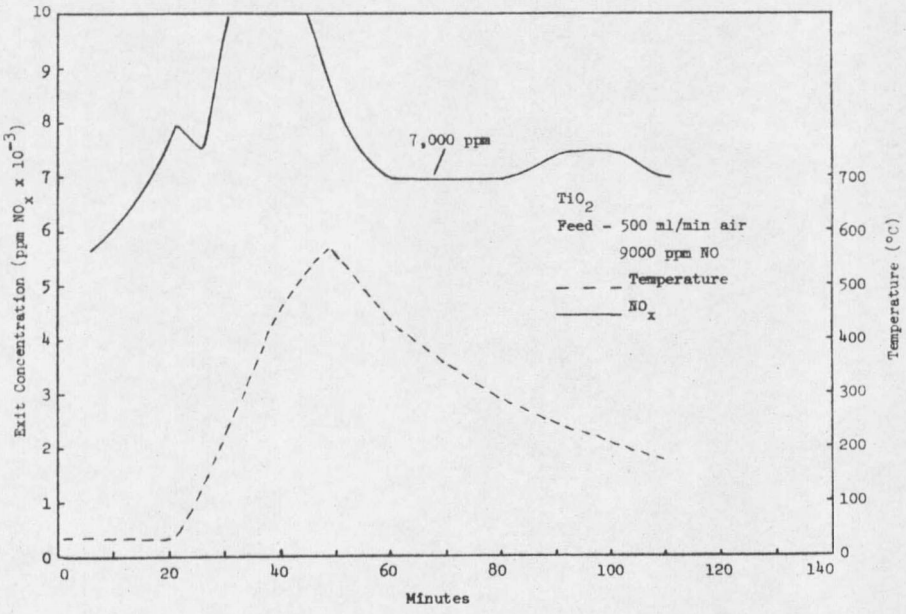


Figure 6. NO_x Absorption Curve for TiO_2

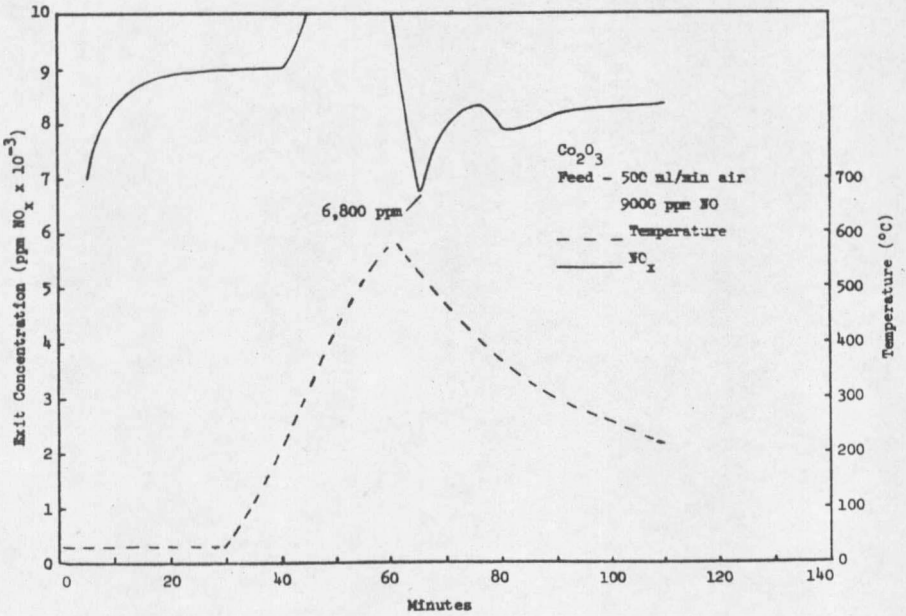


Figure 7. NO_x Absorption Curve for Co_2O_3

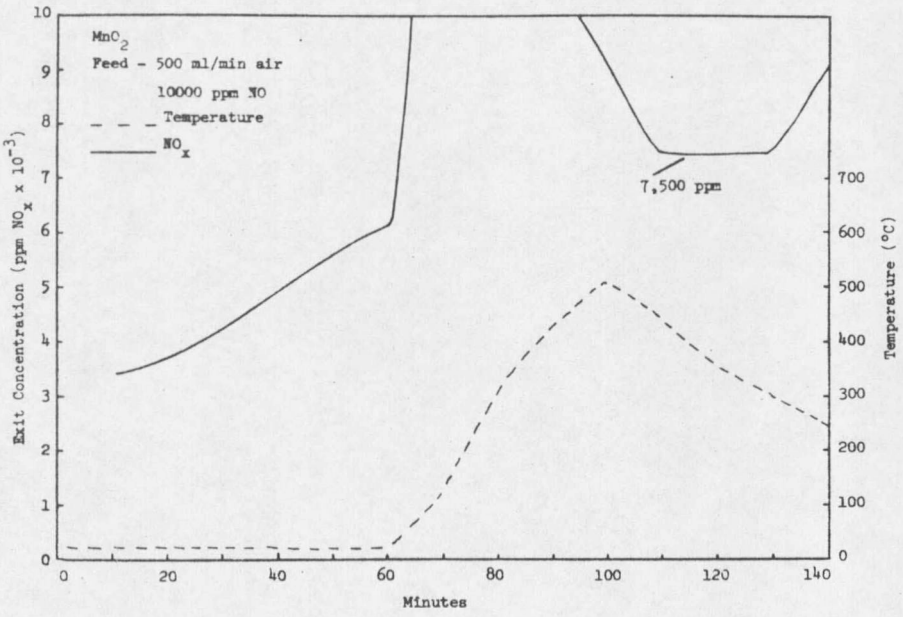


Figure 8. NO_x Absorption Curve for MnO_2

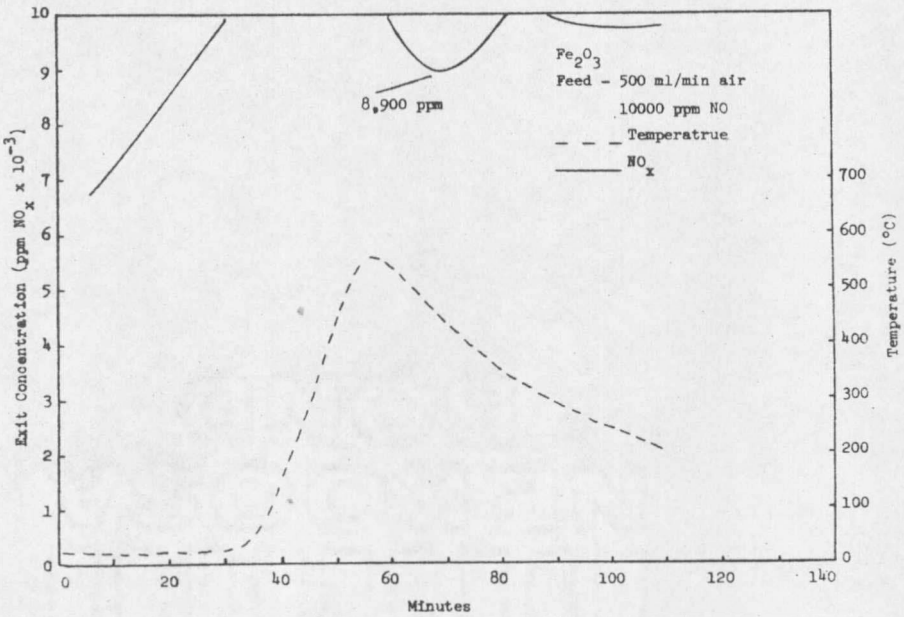


Figure 9. NO_x Absorption Curve for Fe_2O_3

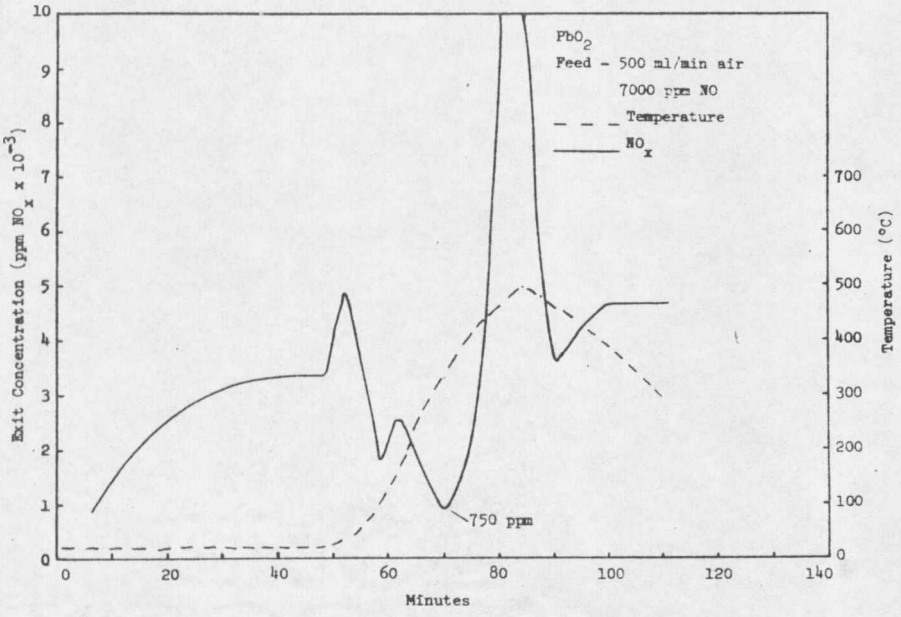


Figure 10. NO_x Absorption Curve for PbO_2

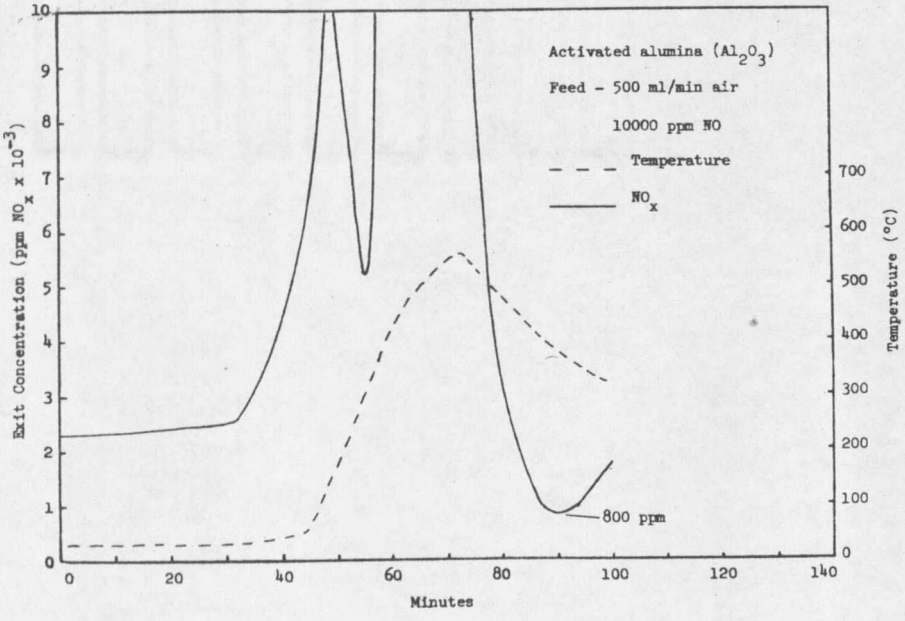


Figure 11. NO_x Absorption Curve for Al_2O_3

It should be noted that these absorption tests were performed when no CO_2 was present in the feed.

NO_x Absorption by Mixtures of Metal Oxides and Alkali Carbonates

Results of the runs made with mixtures of the first row transition metal oxides and sodium carbonate are shown in Figures 12 to 21. In all cases a maximum absorption occurs in the temperature range from 350 to 450°C. No increase in absorption of NO_x occurs over that for Na_2CO_3 until oxides of manganese, iron, cobalt, nickel, or copper are used. The oxides of manganese, iron, nickel, and cobalt when mixed with sodium carbonate reduce the NO_x concentration leaving the reactor to less than 100 ppm. (Note that CO_2 was present in the run made with MnO_2). Table VI summarizes the performance of mixtures of Na_2CO_3 with metal oxides.

TABLE VI. NO_x Absorption by Mixtures of Na_2CO_3 and Metal Oxides

Oxide	From(ppm)	To(ppm)	Oxide	From(ppm)	To(ppm)
TiO_2	10,000	3,000	Co_2O_3	9,000	100
V_2O_5	8,000	1,900	NiO	8,000	30
Cr_2O_3	8,000	3,200	CuO	8,000	800
MnO_2	8,000	50	Cu_2O	8,000	550
Fe_2O_3	7,500	25	Al_2O_3	10,000	600

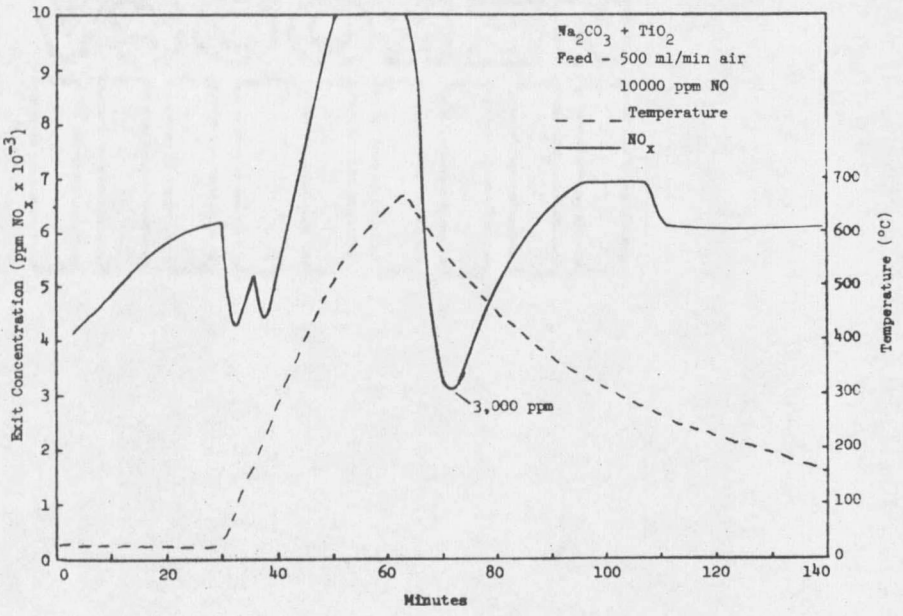


Figure 12. NO_x Absorption Curve for $Na_2CO_3 + TiO_2$

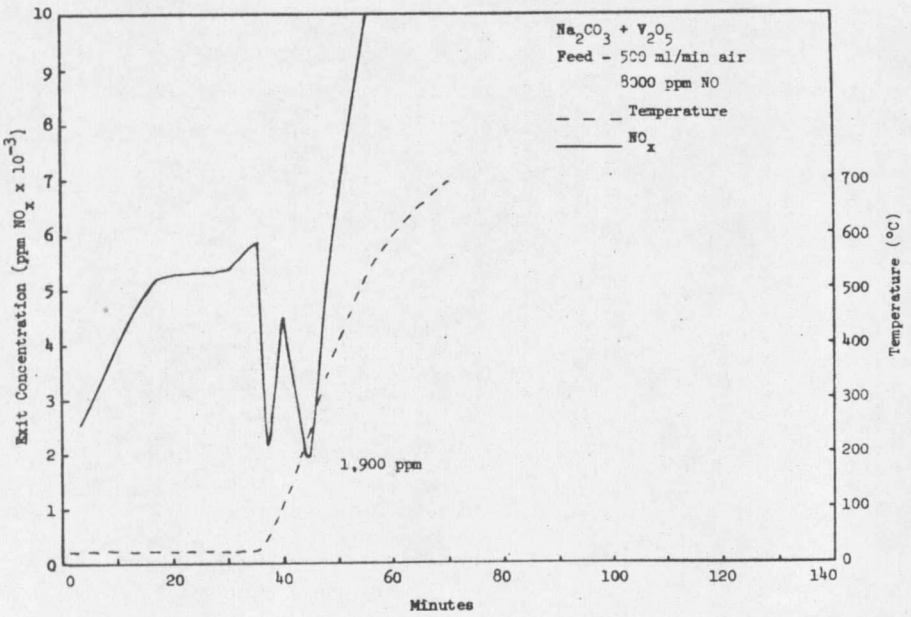


Figure 13. NO_x Absorption Curve for $Na_2CO_3 + V_2O_5$

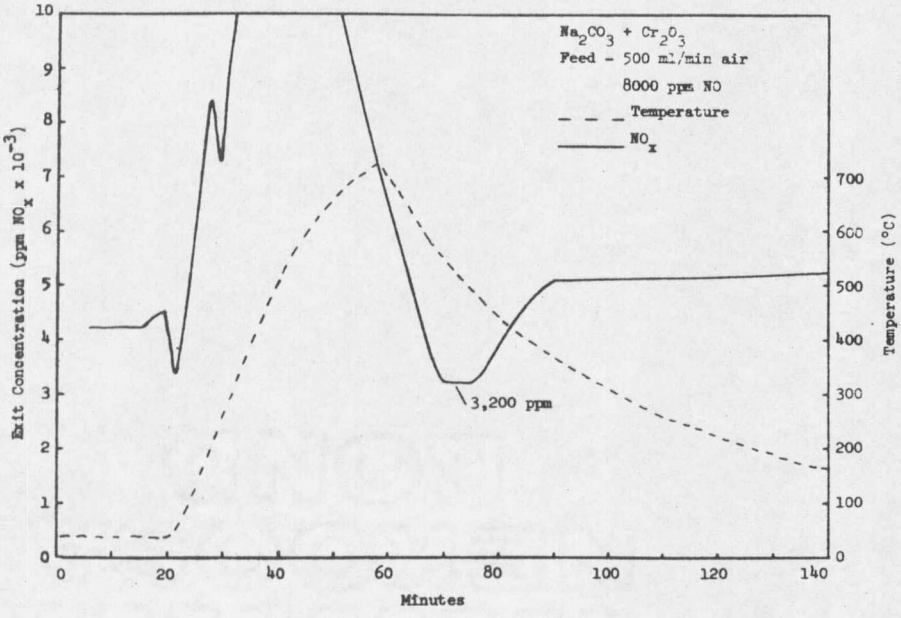


Figure 14. NO_x Absorption Curve for $Na_2CO_3 + Cr_2O_3$

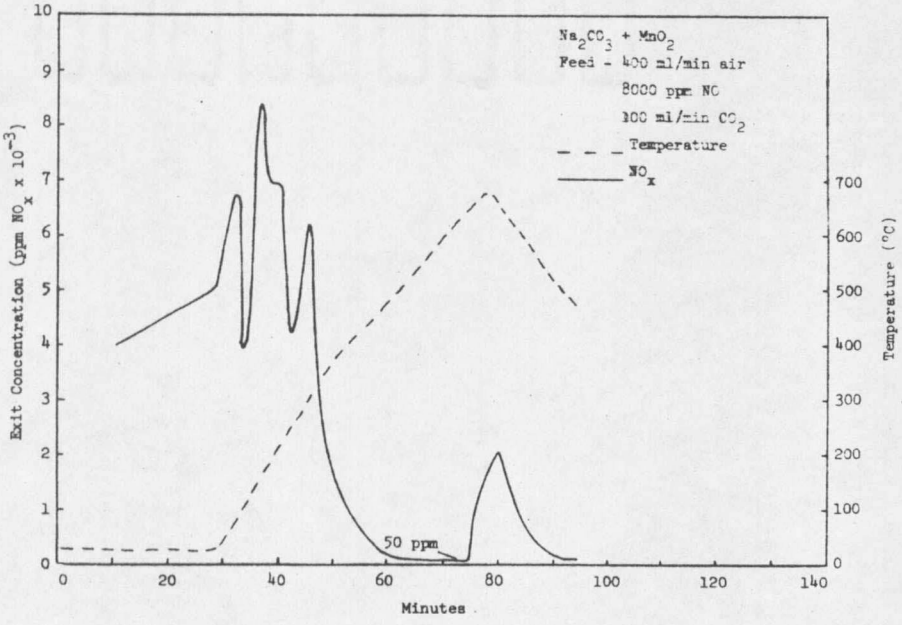


Figure 15. NO_x Absorption Curve for $Na_2CO_3 + MnO_2$

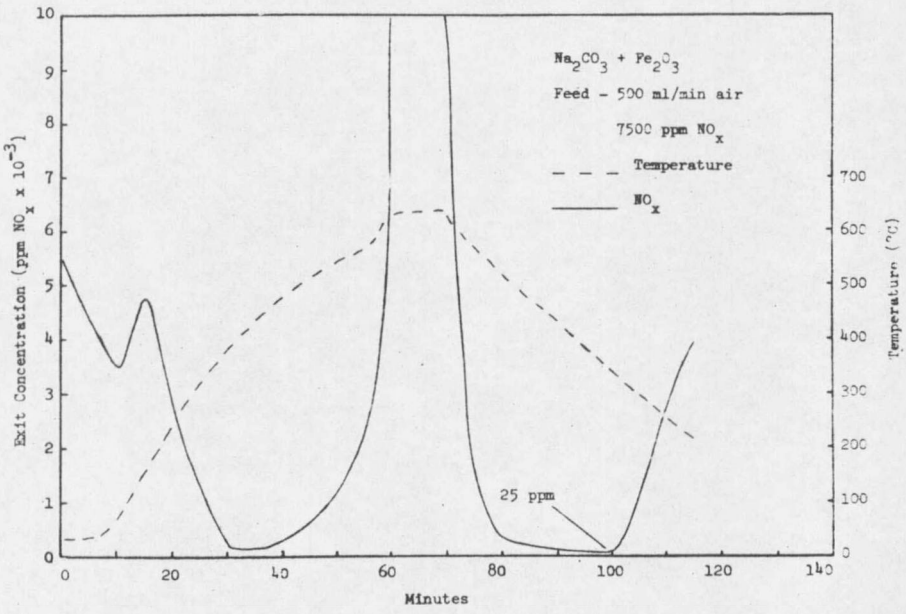


Figure 16. NO_x Absorption Curve for $Na_2CO_3 + Fe_2O_3$

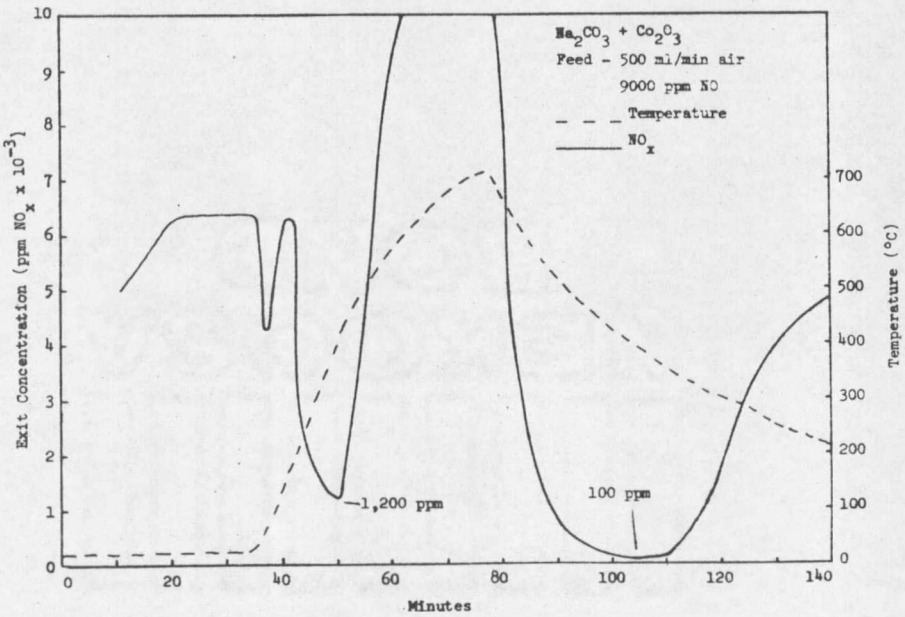


Figure 17. NO_x Absorption Curve for $Na_2CO_3 + Co_2O_3$

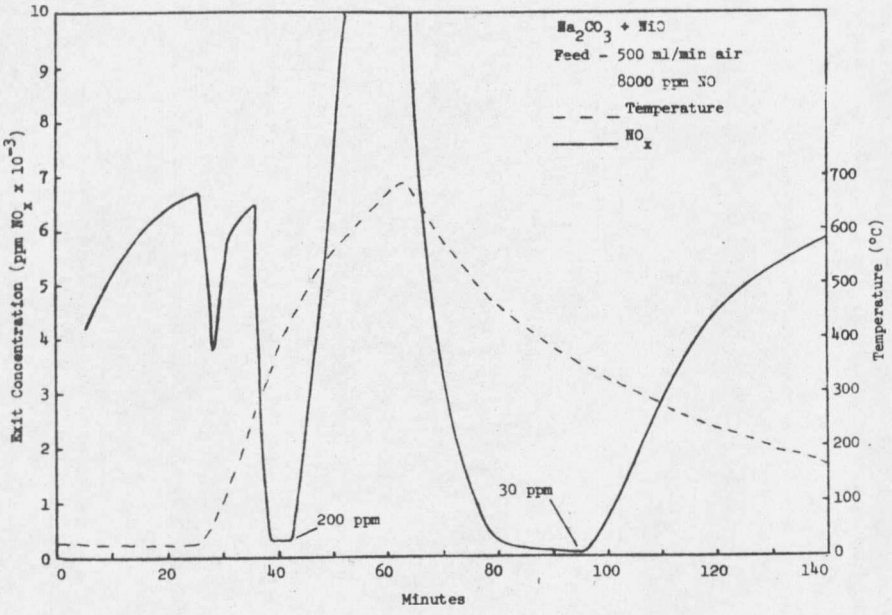


Figure 18. NO_x Absorption Curve for Na_2CO_3 + NiO

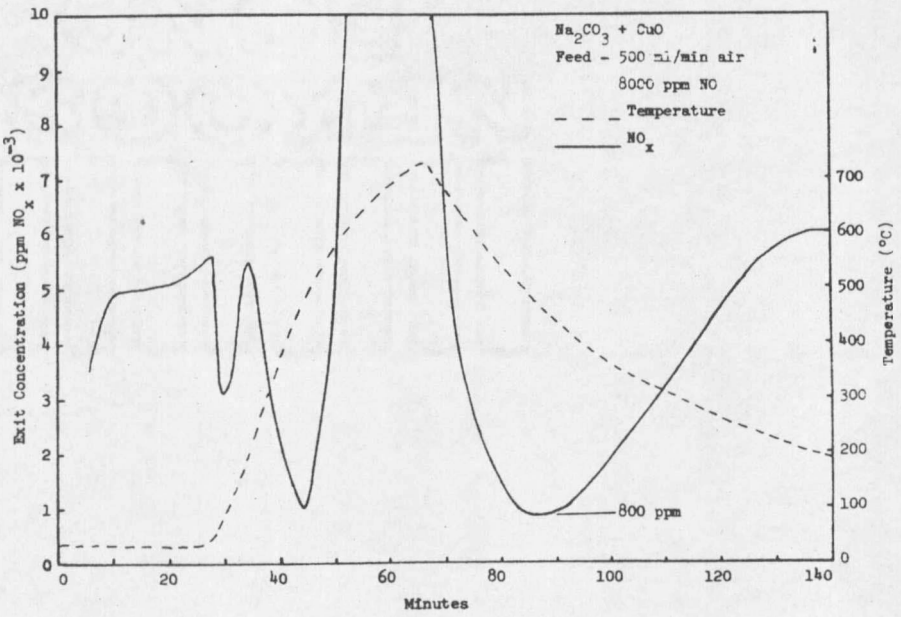


Figure 19. NO_x Absorption Curve for Na_2CO_3 + CuO

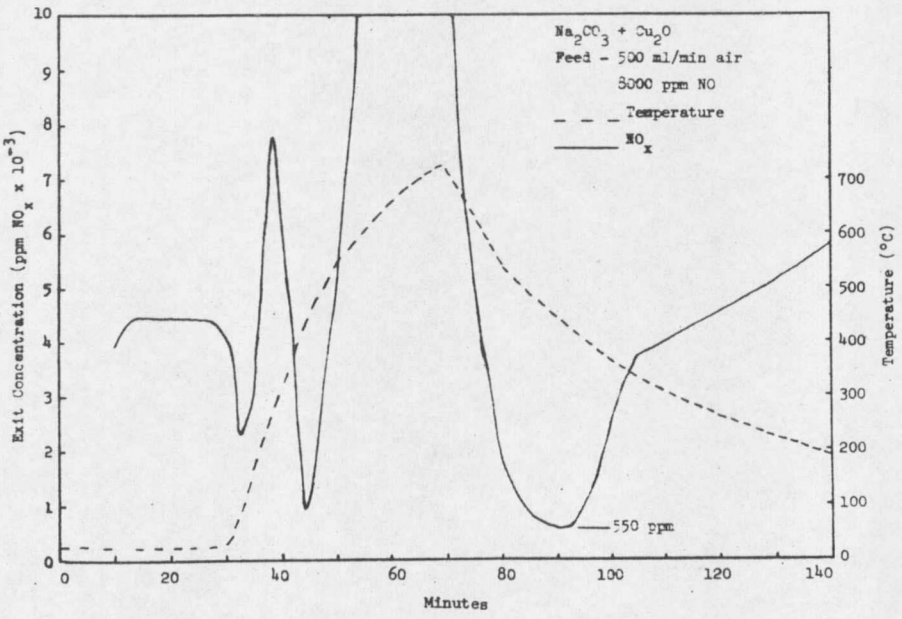


Figure 20. NO_x Absorption Curve for $Na_2CO_3 + Cu_2O$

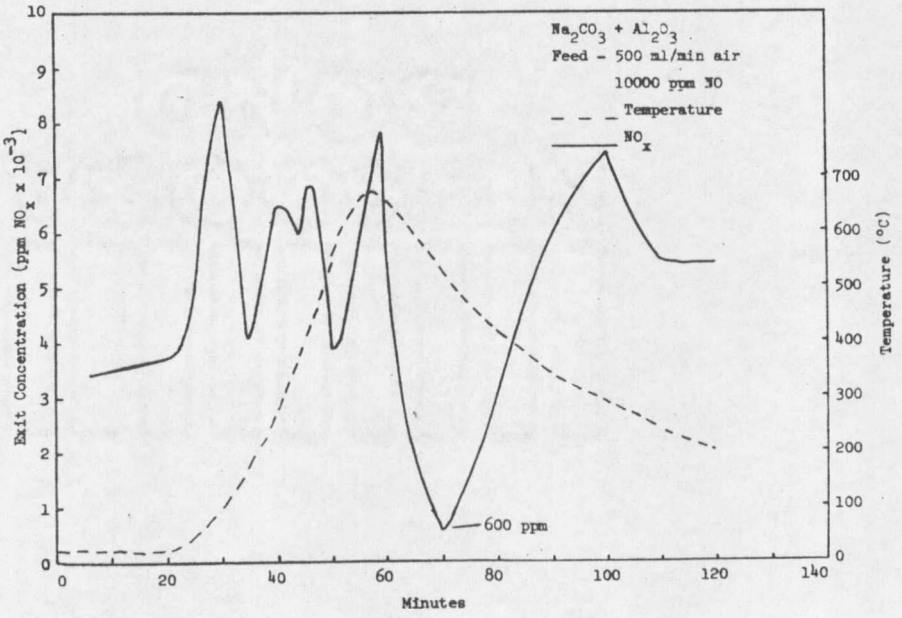


Figure 21. NO_x Absorption Curve for $Na_2CO_3 + Al_2O_3$

NO_x Absorption by Sodium Oxide and Ferric Oxide Mixtures (Ferrates)

A mixture of sodium nitrate and ferric oxide was heated to decompose the nitrate and form a sodium oxide-ferric oxide mixture. Also a sample of commercial sodium ferrate ($Na_2Fe_2O_4$) was obtained and tested. Even though both substances had the same molecular formula, the commercial ferrate was red while the ferrate made from nitrate was yellow. (Note: When pure $NaNO_3$ was decomposed, a yellow substance was produced, presumably sodium peroxide (Na_2O_2)).

The results of runs made with these two ferrates are shown in Figure 22 and 23. Both absorb NO_2 at low temperature and also absorb NO and NO_2 at approximately 380 - 500°C, reducing the exit concentration of NO to less than 100 ppm. (CO_2 is present in the $NaNO_3$ + Fe_2O_3 test). It is interesting to note that the temperature where absorption starts to occur is also the temperature at which the sodium nitrate starts to decompose and give off NO (380°C).

The extended temperature range in which absorption occurs may be due to temperature gradients in the reactor (see Table VII). It can be assumed that the middle of the reactor is where absorption first occurs and also the point at which the temperature first reaches 380°C. A test on the effect temperature had on absorption is shown in Figure 24. In this test no CO_2 was present. Absorption of NO_x starts to drop off at approximately 380°C.

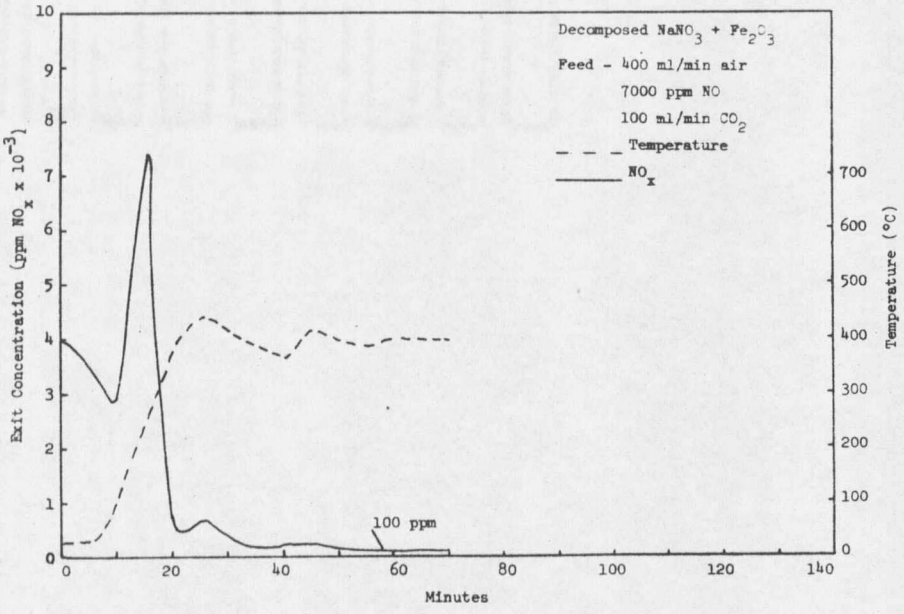


Figure 22. NO_x Absorption Curve for Decomposed $NaNO_3$ + Fe_2O_3

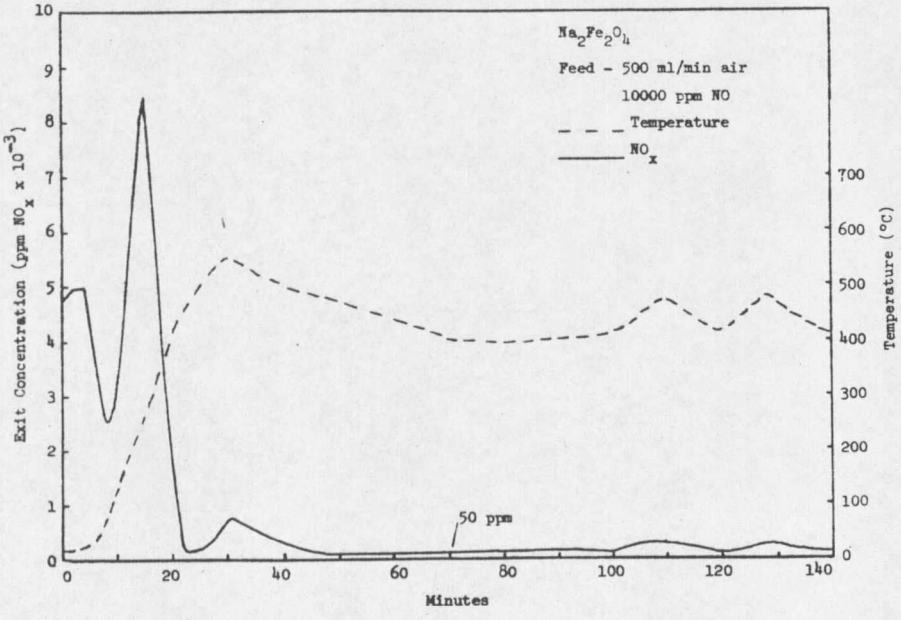


Figure 23. NO_x Absorption Curve for $Na_2Fe_2O_4$

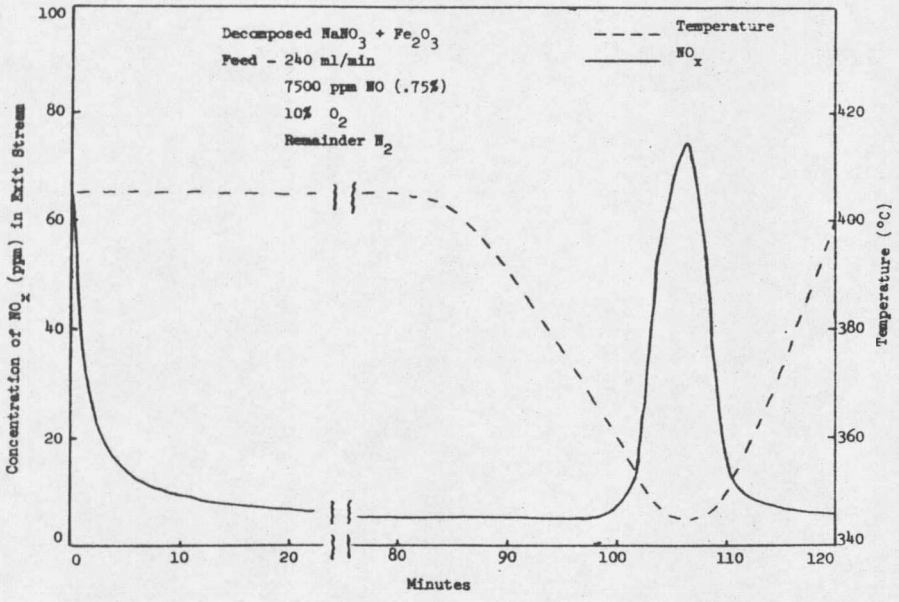


Figure 24. Effect of Temperature on NO_x Absorption by Decomposed $NaNO_3$ + Fe_2O_3

TABLE VII. Effect of Flow on Temperature Gradients in the Reactor and NO_x Absorption

Flow (ml/min)	600	800	1100	1200
T_w(°C)	457	457	457	457
T_t(°C)	402	400	395	395
T_m(°C)	445	445	400	435
T_b(°C)	330	330	320	310
NO_x(ppm)	20	16	18	20

T_w = temperature of outside wall of reactor across from T_m

T_t = temperature 1 inch below the top of reactor

T_m = temperature 1 inch above the porous disk (middle of reactor)

T_b = temperature .5 inch below the porous disk

NO_x = concentration of exit stream (feed is 5000 ppm NO)

(Temperatures were measured by using thermocouples).

Also in Table VII the exit concentration of NO_x leaving the reactor at the various flow rates are listed. Even though the flow rate was doubled the absorption of NO_x was not affected.

Figures 25 and 26 show the effect CO_2 and O_2 had on the absorption of NO and NO_2 at 400°C by the decomposed sodium nitrate-ferric oxide. The presence of carbon dioxide in amounts of 20% or greater affected the absorption of NO_x; and when the NO to O_2 ratio was below 1:2 the absorption of NO_x was also severely reduced.

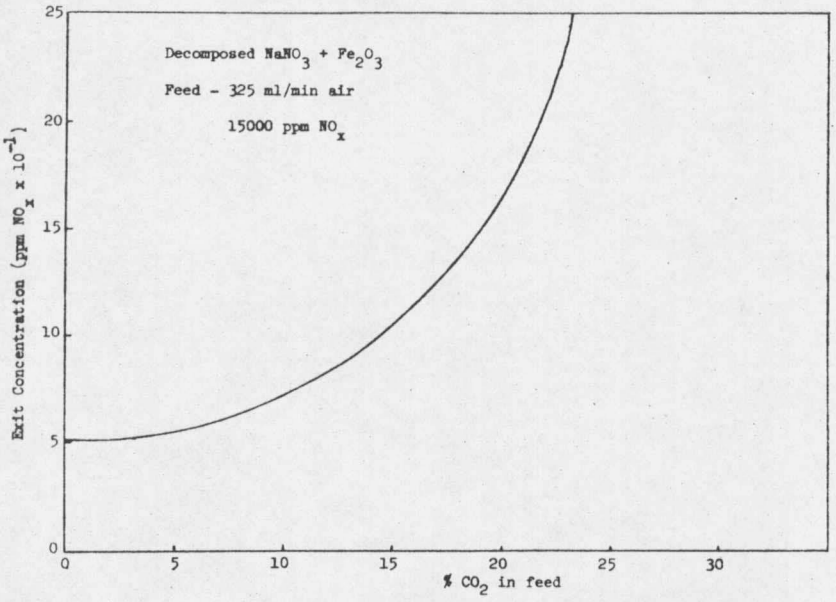


Figure 25. Effect of CO_2 on NO_x Absorption by Decomposed $NaNO_3$ + Fe_2O_3

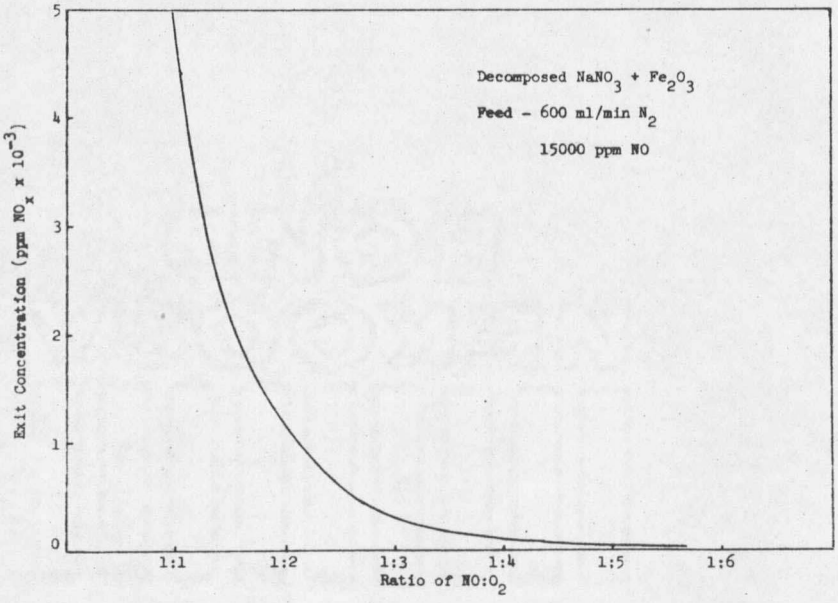


Figure 26. Effect of NO to O_2 Ratio on NO_x Absorption by Decomposed $NaNO_3$ + Fe_2O_3

Performance of Sodium and Potassium Carbonates and Nitrates with Manganese and Iron Oxides

Figures 27 through 32 are the results of tests made with different combinations of manganese and ferric oxides with the carbonate and nitrates of potassium and sodium. (The results are summarized in Table VIII). In these tests equal volumes of 20-30 mesh ottawa sand and sorbent (.025 moles) were mixed together and poured into the reactor to form a packed bed. The volume between the bed and top of reactor was then filled with ottawa sand to keep the sorbent from separating out.

TABLE VIII. NO_x Absorption by $KMnO_4$ and Mixtures of $NaNO_3$, Na_2CO_3, K_2CO_3, KNO_3 with Fe_2O_3 and MnO_2

Sorbent	NO_x Concentration Reduced From 9000 ppm To (ppm)
$Na_2CO_3 + Fe_2O_3$	200
$NaNO_3 + Fe_2O_3$	150
$K_2CO_3 + Fe_2O_3$	25
$KNO_3 + Fe_2O_3$	250
$Na_2CO_3 + MnO_2$	150
$K_2CO_3 + MnO_2$	50
$NaNO_3 + MnO_2$	2500
$KMnO_4$	25

Sodium nitrate-ferric oxide mixtures absorbed slightly more NO_x than did the decomposed sodium carbonate-iron oxide. The first absorption at 380°C reduced the NO_x concentration to 1900 ppm for the carbonate and 45 ppm for the nitrate, while NO_x at the second absorption at 380°C was reduced to 200 ppm and 150 ppm by the carbonate and nitrate respectively. It was found that upon successive regeneration, the carbonate mixture steadily improves and surpasses the performance of the nitrate mixture.

Similarly with the potassium carbonate and decomposed nitrate mixtures with ferric oxide (Figures 29 and 30), the carbonate performed much better than the nitrate, reducing the NO_x concentration to less than 50 ppm, compared to 400 ppm for the nitrate. A few factors worth noting about the potassium carbonate-ferric oxide mixture are: (i) it absorbs more than $Na_2CO_3 + Fe_2O_3$ or decomposed $NaNO_3 + Fe_2O_3$, (ii) absorption starts at a lower temperature (300°C) compared to 380°C for the sodium carbonate, (iii) a higher temperature is needed for regeneration (this may be caused by the temperature gradient in the reactor), and (iv) more NO_2 is absorbed at lower temperature than for the previous mixtures.

The effect of using manganese dioxide with sodium and potassium carbonate is shown in Figures 31 and 32. Absorption was improved for the sodium carbonate (the NO_x concentration dropped to less than 100 ppm) and there was a slight improvement for the potassium carbonate

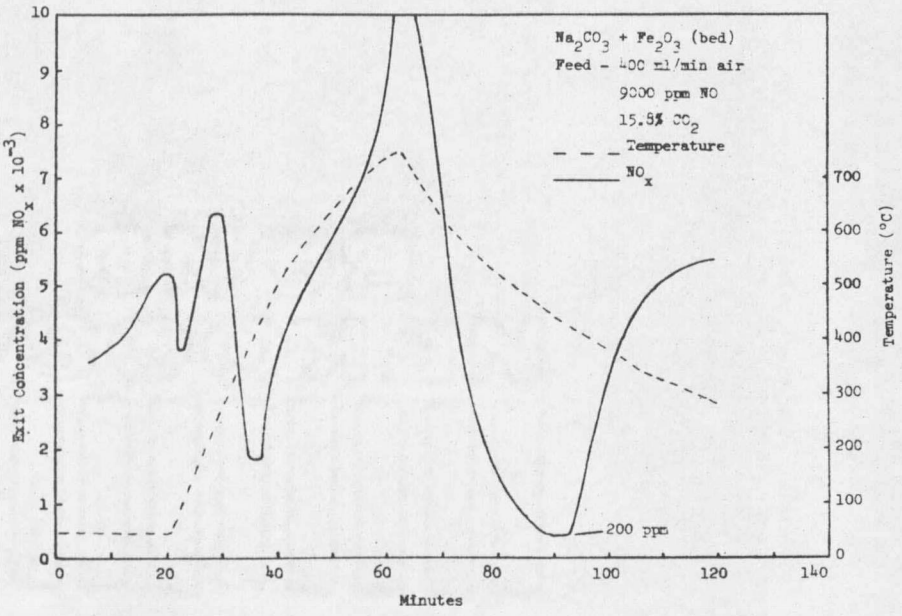


Figure 27. NO_x Absorption Curve for $Na_2CO_3 + Fe_2O_3$ (bed)

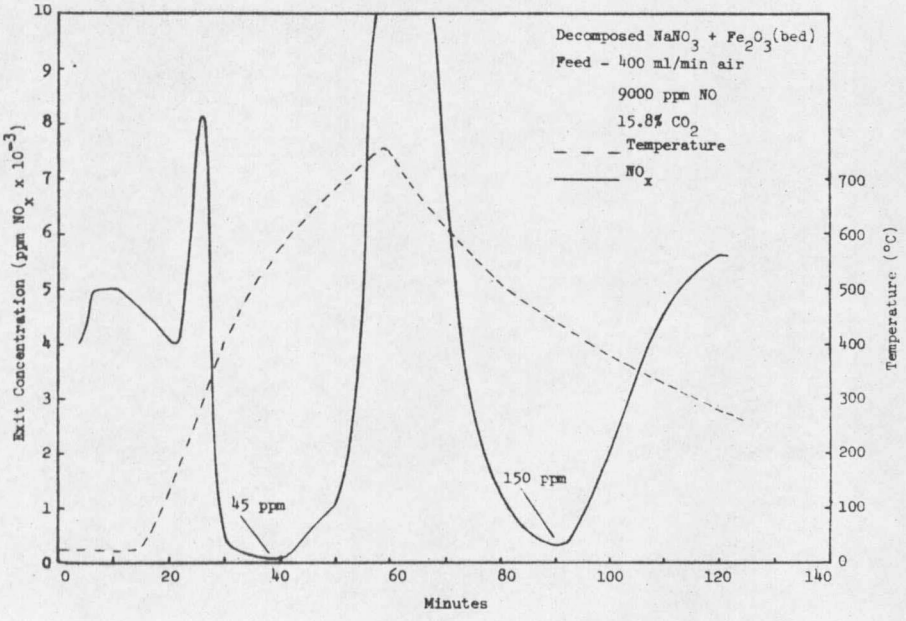


Figure 28. NO_x Absorption Curve for $NaNO_3 + Fe_2O_3$ (bed)

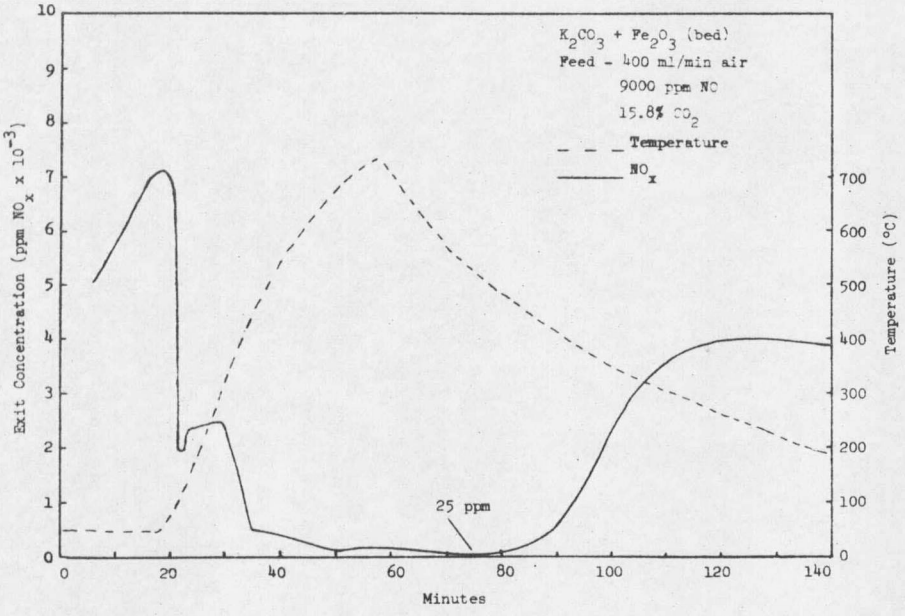


Figure 29. NO_x Absorption Curve for $K_2CO_3 + Fe_2O_3$ (bed)

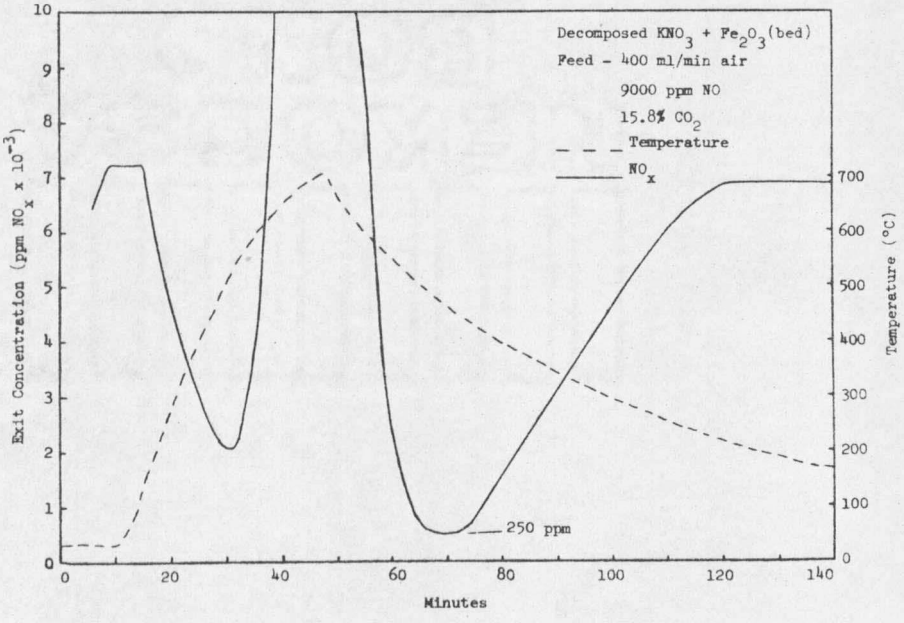


Figure 30. NO_x Absorption Curve for Decomposed $KNO_3 + Fe_2O_3$ (bed)

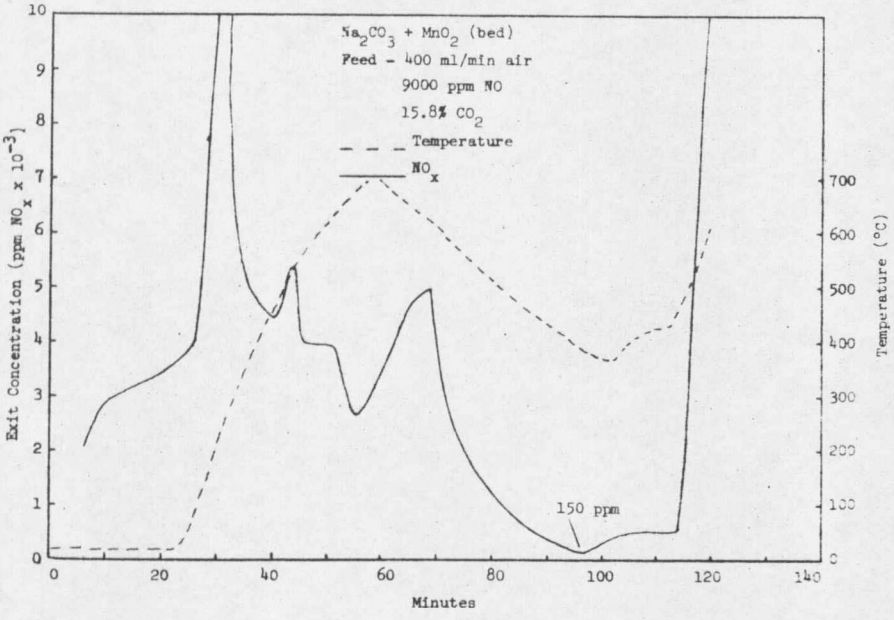


Figure 31. NO_x Absorption Curve for Na_2CO_3 + MnO_2 (bed)

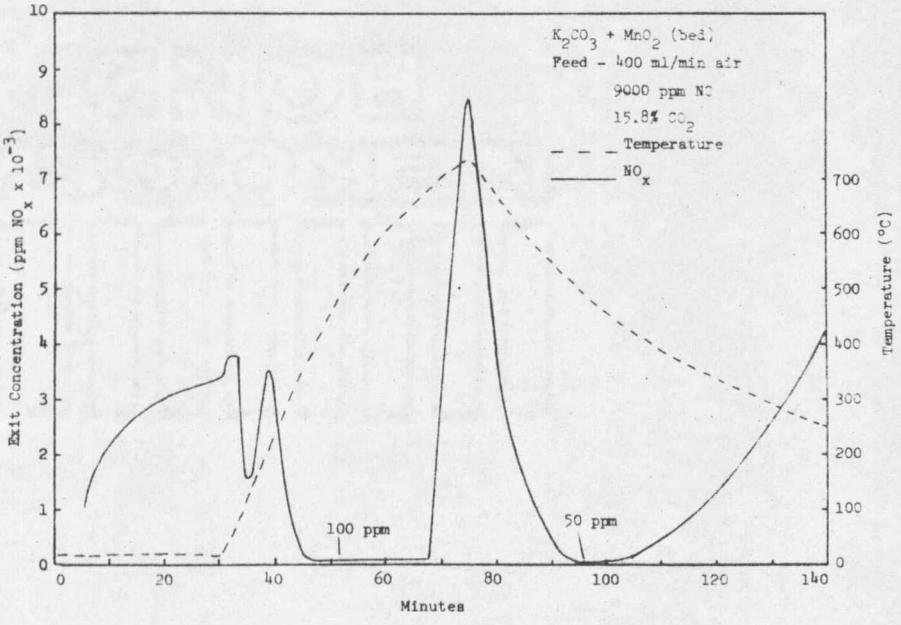


Figure 32. NO_x Absorption Curve for K_2CO_3 + MnO_2 (bed)

(NO_x dropped to less than 40 ppm). Again the mixture with K_2CO_3 absorbs more than the Na_2CO_3 mixture.

Unlike the potassium carbonate-ferric oxide mixture, the manganese mixture formed clumps which could cause problems in a large scale reactor. The clumpy material when dissolved in water produced a green colored solution which is characteristic of potassium manganate (K_2MnO_4) (Partington, 1921; Tyree and Knox, 1961). A test was performed in which a mixture of K_2CO_3 and MnO_2 was decomposed at a high temperature in an atmosphere of N_2. When the decomposition was considered to have proceeded sufficiently the reactor was cooled down and the material removed. This material was hard and initially had a blue color, indicating that potassium hypomanganate had formed (K_3MnO_4) (Partington, 1921). On being exposed to the room atmosphere, the blue material gradually turned green and became moist. The green material is presumably potassium manganate while the moisture may be due to the formation of potassium hydroxide which then absorbs moisture from the air.

Potassium permangante ($KMnO_4$) and a decomposed mixture of sodium nitrate and manganese dioxide were tested to see if they would absorb NO_x. Results of these two tests are shown in Figures 33 and 34. The performance of the decomposed nitrate mixture was poor. However, the potassium permanganate absorbed almost all the NO_x in the feed. The temperature at which the $KMnO_4$ started absorbing is the temperature

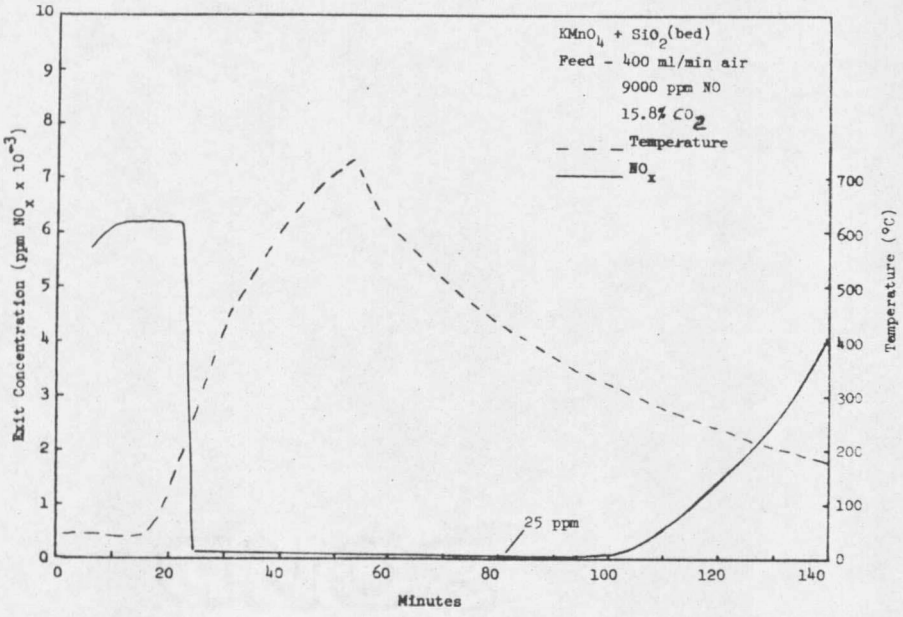


Figure 33. NO_x Absorption Curve for $KMnO_4$ + SiO_2 (bed)

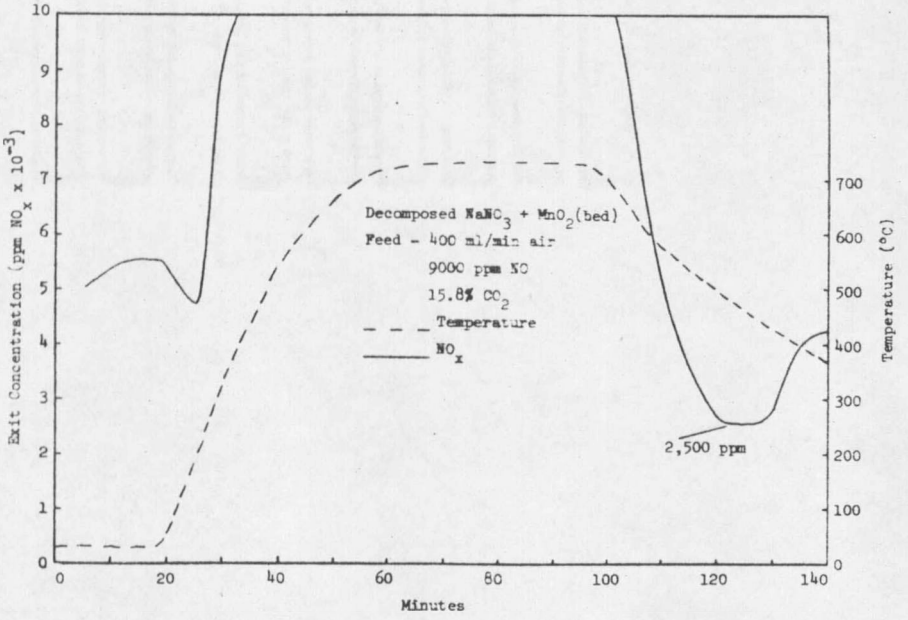


Figure 34. NO_x Absorption Curve for Decomposed $NaNO_3$ + MnO_2 (bed)

at which it decomposes (190°C) to potassium manganate (K_2MnO_4).

The possibility existed that SiO_2 in the ottawa sand reacted with the carbonate or manganese dioxide and increased their sorbent ability. It is known that SiO_2 will displace CO_2 from carbonates at high temperatures to produce silicates. Figures 35 through 37 are the results of potassium carbonate, sodium carbonate and manganese dioxide tested independently of each other with ottawa sand. The ottawa sand did not improve absorption.

Regeneration Studies

Figures 38 and 39 are typical regeneration curves for K_2CO_3-MnO_2. Four absorptions and regenerations were performed with the K_2CO_3-MnO_2 mixture and there was no indication of loss in sorbent performance. The concentration of NO_x obtained on regeneration depends on the flow rate used, the amount preabsorbed and the heating rate used in regeneration. An NO_x concentration of greater than 50% was obtained on regenerating MnO_2-K_2CO_3 sorbent at a temperature of 600 - 700°C using 10 ml/min of air. Furthermore, of the 50% NO_x, approximately 49.5% was NO_2 and only .5% was NO. It is interesting to note the large amounts of O_2 that are also given off during decomposition. This oxygen could be responsible for oxidizing NO to NO_2.

Similar regeneration results were obtained with K_2CO_3-Fe_2O_3 mixtures. After six cycles of regenerating and absorbing, no loss in

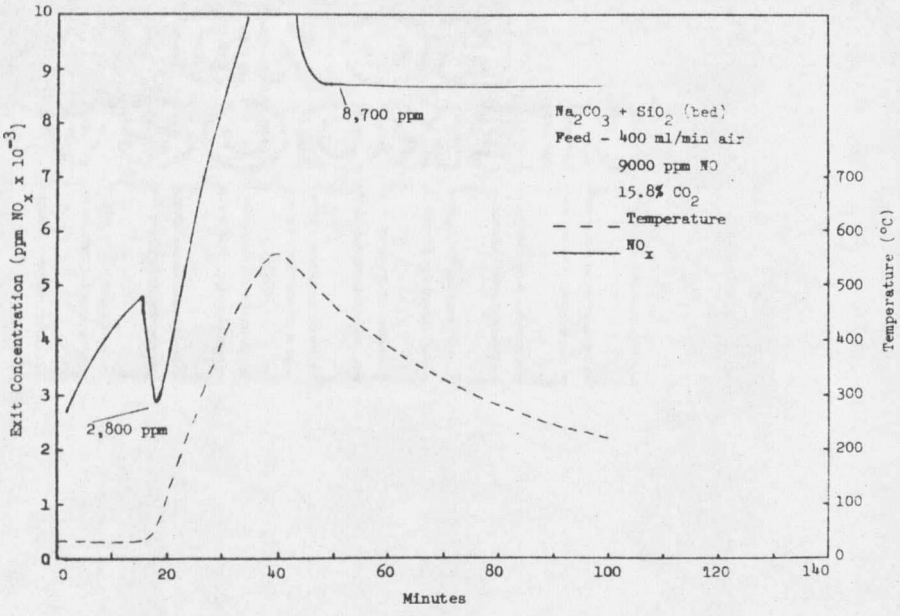


Figure 35. NO_x Absorption Curve for Na_2CO_3 + SiO_2 (bed)

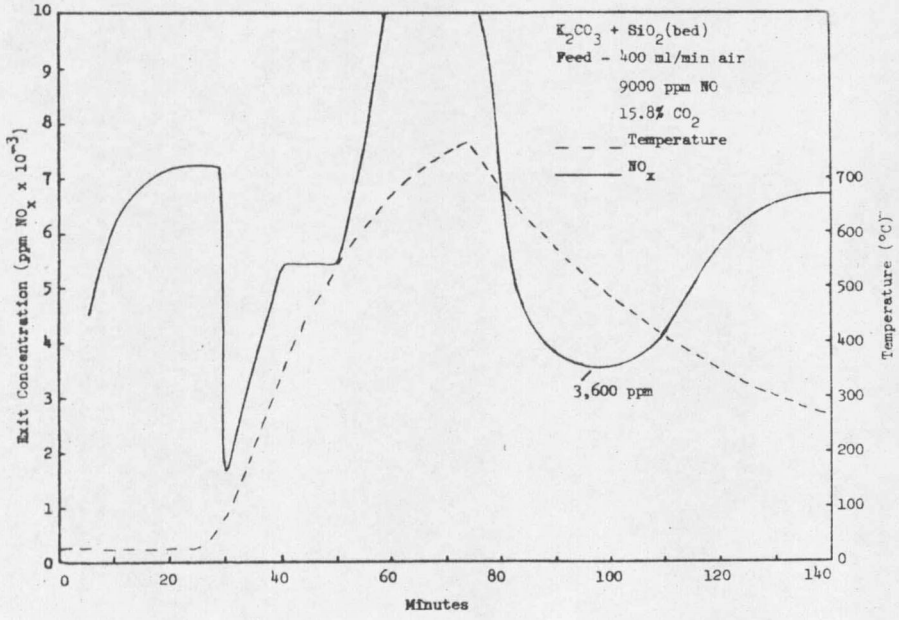


Figure 36. NO_x Absorption Curve for K_2CO_3 + SiO_2 (bed)

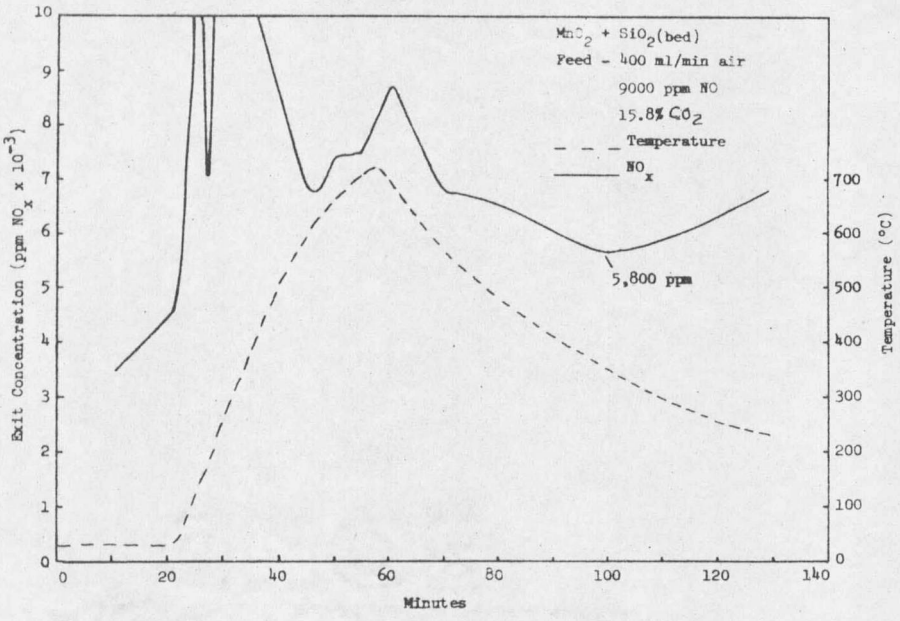


Figure 37. NO_x Absorption Curve for MnO_2 + SiO_2 (bed)

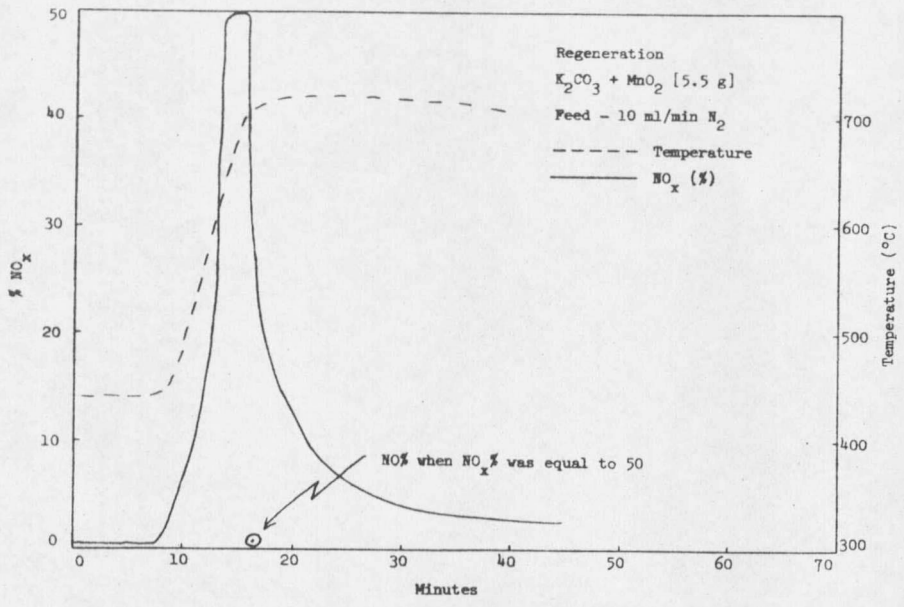


Figure 38. NO_x Concentration During Regeneration of K_2CO_3 + MnO_2

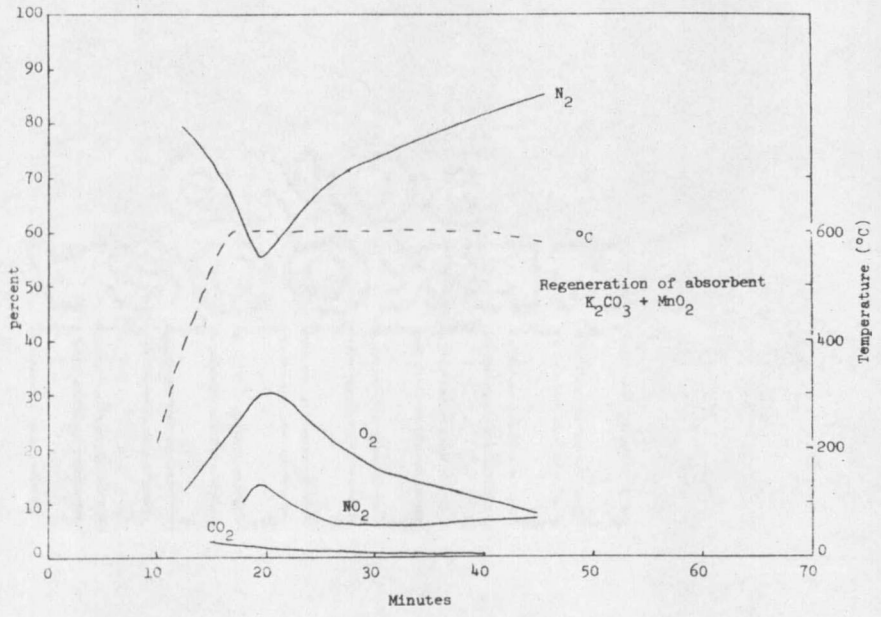


Figure 39. Regeneration of K_2CO_3 + MnO_2

sorbent performance was noted. Other tests on the potassium ferric oxide mixture indicated that when NO_x is absorbed at low flow rates (10 ml/min) on regeneration, NO is primarily given off, while if absorption occurred at higher flow rates (500 ml/min), NO_2 was primarily given off. Also after low flow rate absorptions, less oxygen is desorbed than after high flow rate absorptions.

When desorption was completed a feed of N_2 and NO was passed over the K_2CO_3-Fe_2O_3 sorbent at temperatures greater than or equal to 700°C. The N_2 and O_2 content of the exiting stream went up and hardly any NO was present. This indicates that the NO is reduced by the sorbent to N_2 and O_2, which corresponds to reports in the literature that alkali oxides reduce NO to N_2 and O_2 at high temperatures (Harris and Morello, 1969).

Loading Studies

The time taken for the concentration of NO_x in the exit stream to exceed 200 ppm was determined with and without CO_2 in the feed. Figures 40 and 41 are typical loading curves. If CO_2 was present the loading time was between 30 minutes and 60 minutes. This corresponds to a conversion of 8.5 to 17% of the .025 moles of sorbent present. When CO_2 was not present the loading time was about equal to the time needed to theoretically convert all the alkali carbonate or alkali oxide to an alkali nitrate (5 - 10 hr). It was found that

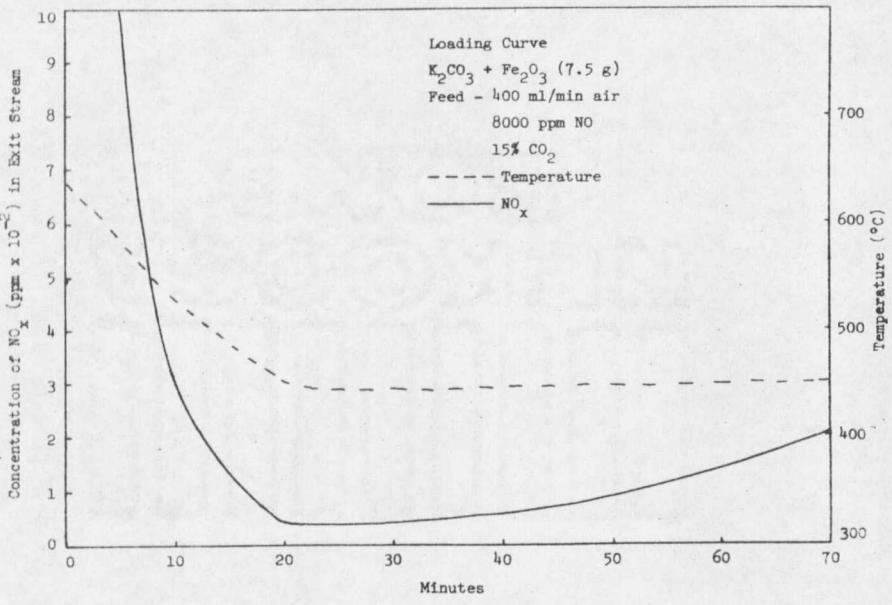


Figure 40. Loading Curve for K_2CO_3 + Fe_2O_3

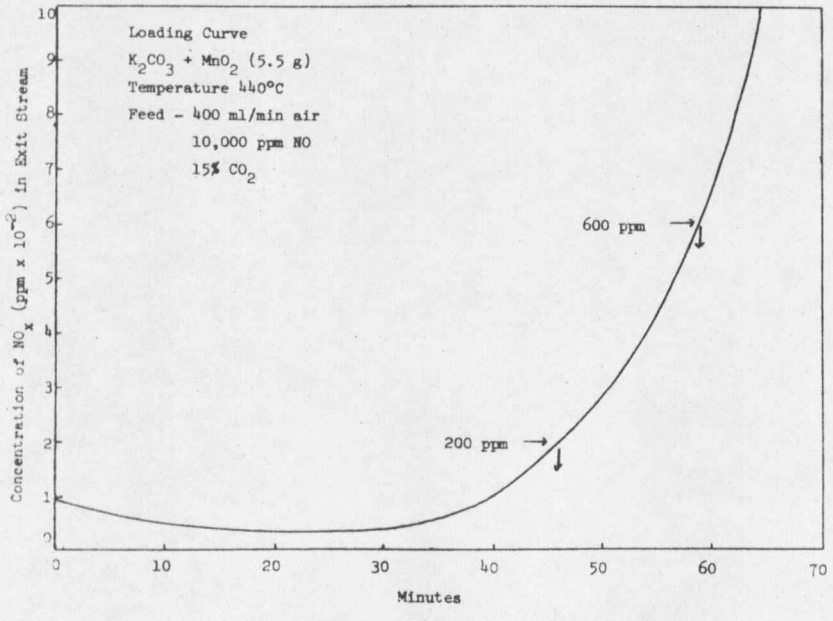


Figure 41. Loading Curve for K_2CO_3 + MnO_2

if the exit concentration reached 200 ppm when CO_2 was present, shutting off the CO_2 would cause the NO_x concentration to drop below 200 ppm.

CO_2 and H_2O Effects

As was mentioned carbon dioxide affects the absorption of NO and NO_x but tests showed that no detectable amounts of CO_2 are absorbed. The other affect of carbon dioxide is to limit the temperature range in which absorption occurs. Addition of carbon dioxide to the feed will narrow the temperature range from 80 to 20 degrees. This effect is less pronounced for the potassium carbonate than for the sodium carbonate and non-existant for K_2MnO_4.

It is possible by using the free energies of reaction to determine the equilibrium constants for reaction involving carbon dioxide and nitric oxide (see Table IX). The values calculated indicate that the carbonates do not appreciably decompose by themselves, but by reacting with NO and O_2, decomposition is favored.

When equal amounts (1%) of carbon dioxide and nitric oxide, along with 20% oxygen are fed into the reactor, no decrease in sorbent ability is seen. It isn't until the concentration of CO_2 is greater than 5% that sorbent performance drops off. Since the concentrations of carbon dioxide are far below the values predicted by equilibrium constants to cause the reaction to reverse, CO_2 possibly affects an inter-

TABLE IX: Equilibrium Constants for Reactions Involving NO and CO_2

Reaction	Free Energy Change at 425°C (Kcal/mole)	Equilibrium Constant
$Na_2CO_3 = Na_2O + CO_2$	52.128	5.09×10^{-17}
$K_2CO_3 = Ka_2O + CO_2$	68.42	4.3×10^{-22}
$Na_2O + 2NO + 3.5\ O_2 = 2NaNO_3$	-143.40	8.58×10^{44}
$Na_2CO_3 + 2NO + 3.5\ O_2 = 2NaNO_3 + CO_2$	-91.27	3.97×10^{28}
$Na_2Fe_2O_4 + 2NO + 3.5\ O_2 = 2NaNO_3 + Fe_2O_3$	-150 (estimate)	1×10^{47}
$Na_2CO_3 + Fe_2O_3 = Na_2Fe_2O_4 + CO_2$	58.24	5.63×10^{-19}

mediate reaction. Furthermore, if the sorbent has absorbed oxygen prior to the introduction of a stream of NO and N_2, the nitric oxide will be absorbed for a short period of time. As soon as the absorption of NO stops the introduction of oxygen to the feed will cause the absorption to begin again.

The effect of water on absorption of NO_x was tested by saturating the air stream at room temperature prior to adding NO to the stream. At moisture concentrations of 2-3% no effect on sorbent performance was detected. It has been reported that the NO_2 absorption by the carbonates is facilitated by the presence of water vapor in the feed (Lewis, 1975).

DISCUSSION

The potassium and sodium carbonate absorption maximums occurred at 100-200°C and from 300-400°C. Generally NO_2 was absorbed by the carbonates at low temperatures (below 100°C) and any NO that was not converted to NO_2 passed through the reactor. The absorption from 100 to 200°C is possibly due to water being released by the carbonate. For example potassium carbonate had a water content of approximately 8%. The water is probably due to the decomposition of bicarbonate and the release of hydrated water, both of which occur in the temperature range from 100 to 200°C. This would also explain why the low temperature absorption maximum does not occur after the carbonate has been heated. It was been reported that the presence of water vapor improves the absorption ability of carbonates (Harris, Morello and Peters, 1969).

The high temperature absorption is probably due to a compound formed during the heating of the carbonate. Decomposition with liberation of CO_2 and the formation of an oxide is a characteristic property of carbonates at high temperatures (Webb, 1970; pp 304). The rate of decomposition depends on the carbonate used and on any impurities present in the material. The oxide formed depends on its stability at the temperature in question and the amount of O_2 present. It is interesting to note that the reactivity of the carbonates for absorption of NO_x is in the reverse order of the stability of the

carbonates to thermal decomposition. Tables X and XI list thermal characteristics of the possible alkali oxides that could be formed. Thermal studies on NaO_2-Na_2O show that the sodium superoxide (NaO_2) decomposes with the rapid evolution of oxygen up to 280°C leaving only sodium peroxide (Na_2O_2) (Webb, 1970; pp 242). Decomposition of Na_2O_2 into Na_2O and oxygen does not take place until the temperature is above melting (460°C). In decomposing sodium carbonate in the reactor the compound formed had a yellow color indicating possibly that Na_2O_2 was formed.

Common oxides of potassium are potassium superoxide (KO_2) and potassium peroxide (K_2O_2); the superoxide is the most common. When KO_2 is heated, reversible decomposition into oxygen and a mixture of K_2O_2 and KO_2 takes place at 300 to 400°C (Yost and Russell, 1944). A yellow substance was formed when potassium carbonate was heated in the reactor indicating that the oxide formed was KO_2.

It is possible then, that the active species in absorption at higher temperatures is not the alkali carbonate but rather the alkali oxide which is formed from the carbonate. This would explain why absorption increases after the carbonate has been heated to high temperatures.

TABLE X: Melting and Boiling Points of Alkali Carbonates and Oxides*

Formula	Formula weight	mp(°C)	bp(°C)	Color
Li_2CO_3	73.89	735	d590	white
Na_2CO_3	105.99	854	d600	white
K_2CO_3	138.21	896	d670	white
Li_2O	29.88	1570		
Li_2O_2	45.88	d160	d193	
NaO_2	54.99	d280		
Na_2O	61.98	920		white
Na_2O_2	77.98	d460	d657	yellow
KO_2	71.1	402(380)	d	yellow
K_2O	94.20	d350	d881	
K_2O_2	110.20	490	d	white

*(Jang, 1967; Samsonov, 1973)

Table XI Thermal Stability Characteristics of Alkali Oxides*

Li_2O	Thermally stable. Volatility increases and thermal stability decreases in the series Li-Cs.
Li_2O_2	Decomposes with liberation of oxygen at 160°C. Decomposes completely at 315-343°C.
Na_2O	Volatile above 1300°C.
Na_2O_2	Some loss of active oxygen is observed on heating at 311-400°C vigorous decomposition begins at 540°C; gives up active oxygen completely above 675°C.
NaO_2	Decomposes on heating; decomposes completely above 540°C.
K_2O	Decomposes at 300-400°C without melting to metallic patassium and peroxide.
K_2O_2	Melts without decomposition. Thermal stability of peroxides rises from K to Cs.
KO_2	Decomposes completely at 543°C.

* (Samsonov, 1973)

Effect of Oxides on the Decomposition of Carbonates

As was discussed earlier the effect of impurities in the carbonate can markedly affect its decomposition rate. Shown in Figure 42 are the results of CO_2 released from mixtures of carbonate and metal oxide when decomposed in an air stream. The presence of the metal oxide increases the rate of decomposition of sodium and potassium carbonate considerably. This increase in CO_2 liberation may be responsible for the increased sorption ability of the carbonate due to the production of active alkali oxides. It was also found that the presence of oxygen or NO_x in the feed increases the rate at which CO_2 is released from the carbonate. A test was performed using iron powder and sodium carbonate as the sorbent, although the thermal conductivity of this mixture would have been higher than that of the other metal oxide-Na_2CO_3 mixtures, no increase in NO_x absorption occurred above that of just Na_2CO_3.

The alkali oxide formed from decomposition of a Na_2CO_3 or $NaNO_3$ is reactive and would combine with Fe_2O_3 to form a ferrite or ferrate (Na_2O-Fe_2O_3). The ferrates are known to be strong oxidizing agents and it is possible that if a nitrite was formed it would be oxidized to a nitrate. The possible reactions that may be occurring are as follows:

$$Na_2OFe_2O_3 + 2NO + 3/2\ O_2 = 2NaNO_3 + Fe_2O_3$$

$$Na_2OFe_2O_3 + 2NO_2 + 1/2\ O_2 = 2NaNO_3 + Fe_2O_3$$

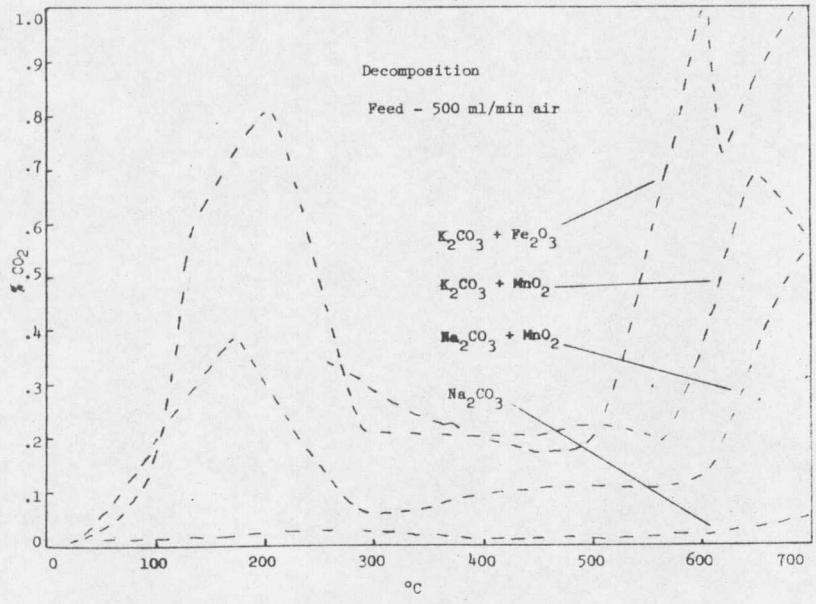


Figure 42. Effect of Metal Oxides on Decomposition of Carbonates

It is also possible that $Na_2O_2Fe_2O_3$ is formed and undergoes the same reactions except a half a mole less of oxygen would be needed. Other reactions are listed in Table XII. In a test using only nitrogen and NO the ferrate from the nitrate reduced the NO concentration from a level of 7500 ppm to 3500 ppm, indicating that a reaction will occur without oxygen present in the feed gas.

The temperature at which absorption occurs and the activity of the carbonate mixtures compared to those prepared from the nitrates might be explained by the following paragraph taken from Arvid Hedvall's Solid State Chemistry, "It is in many cases advantageous to start, not from original oxides but from structurally defect and consequently particularly active oxides which are formed by thermal decomposition. An example is the production of ferrites and chromites by homogenised heating of the required oxide with iron carbonate or of magnesium carbonate with chromium oxide, respectively. In powder mixtures of ferric oxide and oxides of alkaline-earth metals, the preparations with structural defects formed ferrites far more rapidly and completely than the preparations without defects. The differences only disappear at temperatures above 900°C as the irreversible defects vanish.

Innumerable experiments involving various types of changes of structure have provided a basis for a general rule which states that the temperature (or temperature range) where new phases are formed by transformation coincide with a relative maximum of reactivity in a substance."

Temperatures at which the nitrates undergo a change are listed in Table XIII. Sodium nitrate and potassium nitrate decompose in the temperature range at which NO_x is absorbed by the sorbents. Chemical analysis also indicates that nitrates are formed when NO_x is absorbed.

An alternate method by which the reaction could proceed is through an oxidation step on the metal oxide. Before discussing this

Table XII. Possible Reactions of the Sorbents

Reaction	ΔH_{298} (kcal/mole)
$Na_2CO_3 = Na_2O + CO_2$	76.8
$K_2CO_3 = K_2O + CO_2$	94.05
$Na_2CO_3 + 1/2\ O_2 = Na_2O_2 + CO_2$	55.6
$K_2CO_3 + 1/2\ O_2 = K_2O_2 + CO_2$	62.45
$2NaNO_3 = Na_2O + 2NO + 3/2\ O_2$	166.88
$2KNO_3 = K_2O + 2NO + 3/2\ O_2$	192.29
$2NaNO_3 = Na_2O_2 + 2NO + O_2$	145.68
$2KNO_3 = K_2O_2 + 2NO + O_2$	160.69
$Na_2CO_3 + 2NO + 3/2\ O_2 = 2NaNO_3 + CO_2$	-90.08
$K_2CO_3 + 2NO + 3/2\ O_2 = 2KNO_3 + CO_2$	-98.27

Table XII Continued:

Reaction	ΔH_{298} (kcal/mole)
$NO + 1/2\ O_2 = NO_2$	-13.51
$Na_2O + 2NO_2 + 1/2\ O_2 = 2NaNO_3$	-139.86
$K_2O + 2NO_2 + 1/2\ O_2 = 2KNO_3$	-166.30
$2NaNO_3 + Fe_2O_3 = Na_2Fe_2O_4 + 2NO_2 + 1/2\ O_2$	176.67
$Na_2CO_3 + Fe_2O_3 = Na_2Fe_2O_4 + CO_2$	121.75 (32.06)*
$Na_2Fe_2O_4 + 2NO + 3/2\ O_2 = 2NaNO_3 + Fe_2O_3$	-211.78
$K_2CO_3 + MnO_2 + 1/2\ O_2 = K_2MnO_4 + CO_2$	221.98
$Na_2MnO_4 + 2NO + O_2 = 2NaNO_3 + MnO_2$	-116.78
$K_2MnO_4 + 2NO + O_2 = 2KNO_3 + MnO_2$	-133.22

* Matsui, Mototaro and Sakamaki, Tomonosuke, J. Soc. Chem. Ind.(Japan) 30, 29-36 (1927)

TABLE XIII. Melting and Decomposition Temperatures of Alkali Nitrates, Nitrites and Hydroxides (Jang, 1967) (CRC Handbook 45th ed)

Compound	Formula Weight	mp(°C)	dp(°C)
$LiNO_3$	68.95	254	d600
$NaNO_3$	85.01	310	d300
KNO_3	101.10	337	d340
$LiNO_2$	52.95	100	d185
$NaNO_2$	69.00	271	d320
KNO_2	85.11	440	d350
LiOH	23.95	462	
NaOH	40.00	318	
KOH	56.11	360	

mechanism the oxides used in the oxidation of CO to CO_2 will be described. The catalytic activity series of metal oxides for the oxidation of CO is from the most active to the least active (Dixon and Longfield, 1960): Co^{+2}, Cu^{+1}, Ni^{+2}, Mn^{+4}, Cu^{+2}, Fe^{+3}, Zn^{+2}, Ce^{+4}, Cr^{+3}, Th^{+4}, Zr^{+4}, V^{+5}, Hg^{+2}, and Al^{+3}. There is also a qualitative connection between the activity of the oxide and their semiconducting properties. The most active oxides are the P type which include manganese dioxide (Ashmore, 1967; pp 239). In the P type oxides, electrical conduction occurs by changes of charge or motion of positive holes. N type oxides (eg. Fe_2O_3) which are the next most effective oxidizers of CO, conduct electricity by free electrons.

At high temperatures carbon monoxide attacks the surfaces of P and N type oxides to form carbonate ions. The proposed mechanism is one in which oxygen is absorbed as O^- and CO reacts with two O^- to form the carbonate, which decomposes to CO_2 (Ashmore, 1967; Thomas and Thomas, 1967). A similar scheme can be thought to occur for nitric oxide, since NO and CO are very similar molecules. The NO_3^- formed when NO is absorbed would decompose to produce NO_2 which would react with the alkali carbonate or oxide to form a nitrate. Absorption of NO_2 at low temperatures does occur for the carbonates and studies indicate that NO_2 is absorbed as NO_3^- ions on Al_2O_3 and NiO surfaces (Knozinger, 1976). It is also known that NO will displace CO from the surface of metal oxides, indicating that the NO molecule

has a strong affinity for metal oxide surfaces.

Release of Oxygen from Potassium Carbonate and Manganese Dioxide or Ferric Oxide Mixtures

Tests were performed to determine if oxygen was given off during decomposition of K_2CO_3 + MnO_2 or K_2CO_3 + Fe_2O_3. As is shown in Figure 43 and 44, the manganese dioxide mixture releases O_2 when decomposed, while the ferric oxide mixture does not. The decrease in N_2 at 200 - 250°C is not due to N_2 being absorbed, but from the decomposition of bicarbonate present to give off H_2O and CO_2.

Decomposition of manganese dioxide to Mn_2O_3 and O_2 is responsible for the large O_2 peak around 450 - 550°C. Integration of the O_2 peak indicates that approximately 1.5% of the original .025 mole of manganese dioxide releases O_2. It is possible that Mn_2O_3 is an active species in the absorption process if it doesn't revert back to MnO_2 below 450°C in the presence of O_2.

Decomposition of the carbonate appears to reach a final value for the MnO_2-K_2CO_3 mixture while the Fe_2O_3-K_2CO_3 decomposition continues for a longer period of time as indicated by the nitrogen composition of the exit stream. An approximate analysis indicated that 11% of the original .025 mole of carbonate present in both mixtures releases CO_2 and the total amount of carbon dioxide released after 70 minutes is the same for both mixtures.

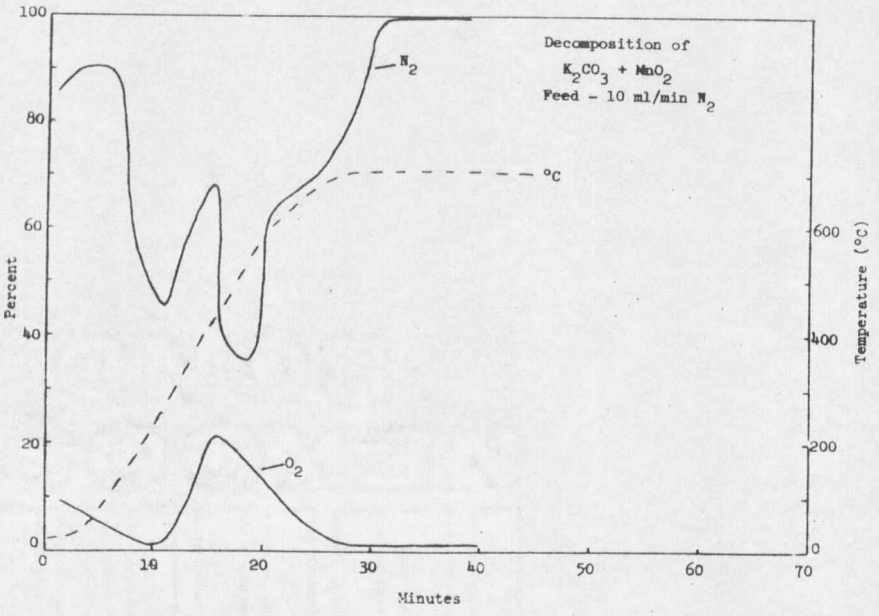


Figure 43. Amount of O_2 Released From K_2CO_3 + MnO_2

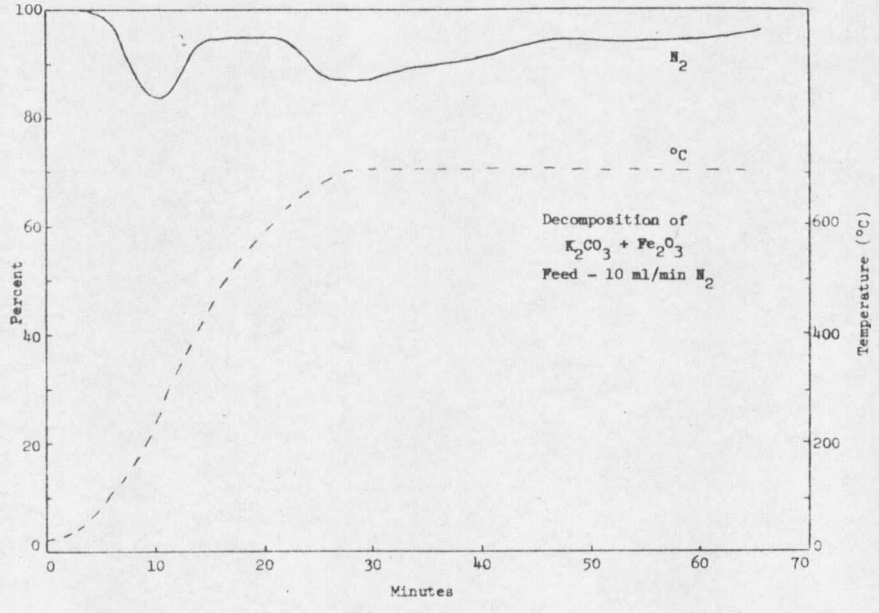


Figure 44. Amount of O_2 Released From K_2CO_3 + Fe_2O_3

The possible reactions of the manganese mixture in an N_2 atmosphere are as follows:

1) $K_2CO_3 = K_2O + CO_2$

2) $2MnO_2 = Mn_2O_3 + 1/2\ O_2$

3) $K_2CO_3 + MnO_2 = K_2MnO_3 + CO_2$

4) $K_2CO_3 + MnO_2 = K_2MnO_4 + CO$

5) $K_2CO_3 + 2MnO_2 = 2K_3MnO_4 + 2CO_2 + CO$

All of the reactions are endothermic and would be favorable at higher temperatures. Equilibrium calculations are not applicable since the gaseous products are removed by the nitrogen stream but the rates of the reaction may play an important role. Exactly to what extent each reaction takes place is hard to determine. The formation of K_2MnO_4 or K_3MnO_4 has been suggested earlier. The presence of O_2 in the exit stream indicates that reaction 2 takes place. Analysis of CO was not possible at the time so definite conclusions can not be drawn on the extent of any reactions.

Similarly, the reactions that take place between K_2CO_3 and Fe_2O_3 couldn't be positively identified but some of the likely ones that could take place in the inert N_2 atmosphere are:

1) $K_2CO_3 = K_2O + CO_2$

2) $K_2CO_3 = K_2O_2 + CO$

3) $K_2CO_3 + Fe_2O_3 = K_2OFe_2O_3 + CO_2$

4) $K_2CO_3 + Fe_2O_3 = K_2O_2Fe_2O_3 + CO$

Absorption of O_2 by Decomposed Potassium Carbonate, Ferric Oxide and Manganese Dioxide Mixtures

After decomposing the carbonate metal oxide mixtures in a N_2 stream, the feed stream was switched over to air and the amount of O_2 absorbed recorded (see Figure 45). The initial large absorption of O_2 by both mixtures is probably caused by the already existing compound formed when the carbonate decomposed and reacted with the metal oxide. Since the manganese mixture initially absorbs more O_2 and doesn't give off CO_2, the carbonate in this mixture is largely decomposed. Furthermore, once loaded, the manganate does not absorb O_2 until the temperature drops to below 600°C which corresponds to the reaction $Mn_2O_3 + 1/2\ O_2 = 2MnO_2$. The absorption of O_2 between 600 - 450°C was reversible in that O_2 was given off above this temperature and absorbed when the temperature was lowered. On the other hand, the ferric oxide-carbonate mixture continually absorbs oxygen and gives off carbon dioxide indicating that the carbonate isn't fully decomposed. Then when the temperature drops, the carbonate no longer decomposes and subsequently O_2 absorption stops. These tests indicate that the oxygen is absorbed, therefore NO may be reacting with the oxygen as an intermediate step in the absorption process.

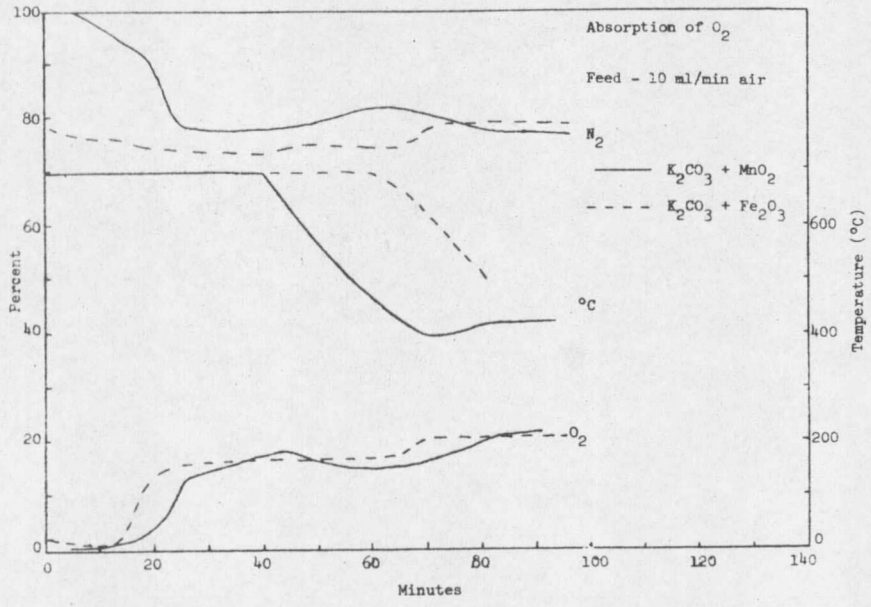


Figure 45. Absorption of O_2 by $K_2CO_3 + MnO_2$ and $K_2CO_3 + Fe_2O_3$

APPLICATION

It was estimated that approximately 1.25 million standard cubic feet per minute of gas containing 1.5% NO will have to be handled for a 1000 Megawatt MHD generator. In terms of moles of NO this comes out to be 2.37×10^{4} gmole/min. Under the test conditions used in the laboratory reactor, .025 mole of sorbent was able to absorb 1.63×10^{-4} mole/min of NO for 30 minutes before having to be regenerated. If the same conditions are applied to the MHD plant then 3.64×10^{6} moles of sorbent would be required every 30 minutes. Assuming a continuous process, taking a one hour cycle for completion, the total amount of sorbent that would have to be purchased is 7.28×10^{6} moles or approximately 40 tons. The initial costs of sorbent mixtures that could be used for absorption of NO_x is shown in Table XIV (individual costs for chemicals are listed in Table XV). In the study performed to determine the economic feasibility of producing nitric acid from a 700 Megawatt MHD generator, silica gel was used as the sorbent and oxidizer at

TABLE XIV. Costs of 7.28×10^{6} Moles of Sorbent Mixtures

Mixture	Cost in Thousands of Dollars
K_2CO_3-Fe_2O_3	520
Na_2CO_3-Fe_2O_3	165
Na_2CO_3-MnO_2	320
K_2CO_3-MnO_2	673

cost of over 2 million dollars (Wright and Youderion, 1976). Even with this high expenditure for a sorbent the plant showed a projected rate of return of 31%. Scaling up the cost of the silica gel for a 1000 Megawatt generator indicates an investment of over 3 million dollars. Comparing this cost to the cost of the solid sorbents shows that the solid systems could save over 2.5 million dollars. Furthermore, the optimum ratio for the sorbent mixture has not been determined nor has the maximum flow rate, both of which would further reduce the cost.

TABLE XV. Costs of Chemicals

Chemical	dollars/lb	dollars/lb mole
Na_2CO_3	.028	2.97
K_2CO_3	.20	25.00
Fe_2O_3	.046	7.36
MnO_2	.21	17.00
$KMnO_4$	.48	82.00
$NaNO_3$	.065	5.53
KNO_3	.10	10.11
KCl	.02	1.48
$CaCO_3$	.01	1.00
$CaCl_2$	.035	3.85
NiO	2.00	149.42
Co_2O_3	4.27	708.22
PbO_2	.66	157.74
Al_2O_3	.16	16.32

CONCLUSIONS

1. Ferric oxide or manganese dioxide mixed on a one to one mole basis with potassium or sodium carbonate will absorb NO_x in a temperature range from 380 to 450°C. Using these absorbents, the NO_x concentration can be reduced from 10,000 ppm to less than 200 ppm from a gas containing 1% NO, 15% CO_2, 17.5% O_2 and 66.5% N_2 at flow rates of 500 ml/min. The effective operating time of .025 moles of sorbent mixture was between .5 and 1 hour.
2. Decomposed mixtures of sodium nitrate and ferric oxide (ferrates) are effective NO_x absorbers when the ratio of O_2 to NO in the feed is greater than 3:1.
3. Nickel or cobalt oxides mixed with sodium carbonate show potential for absorbing NO_x at high temperatures.
4. The order of the solid sorbents for absorbing NO is as follows (in order of increasing ability): $LiCO_3$, Na_2CO_3, K_2CO_3, decomposed $NaNO_3 + Fe_2O_3$, $Na_2CO_3 + Fe_2O_3$, $K_2CO_3 + Fe_2O_3$, $Na_2CO_3 + MnO_2$, $K_2CO_3 + MnO_2$, $KMnO_4$.
5. Carbon dioxide at concentrations of greater than 5% reduced the effective operating times of sorbents from several hours to less than one hour. K_2CO_3 mixtures are less affected by the CO_2.
6. Water vapor at concentrations of 2-3% does not affect the sorption ability of the solid sorbents.

7. Alkali nitrates are formed when NO_x is absorbed by alkali carbonate-ferric oxide or manganese dioxide mixtures.
8. Nitrogen dioxide is absorbed at low temperatures by the carbonate metal oxide mixture.
9. Nitric oxide is not absorbed at room temperature but is absorbed at higher temperatures (400°C) by the carbonate-metal oxide sorbents.
10. Nitrogen dioxide is formed when sorbents are regenerated at temperatures between 600 and 700°C.
11. Formation of NO_2 during regeneration of ferric oxide-carbonate sorbent is affected by the flow rates used during absorption of NO_x. Higher flow rates favored the formation of NO_2.
12. Carbon dioxide is not absorbed in any detectable amounts by the sorbents.
13. At high temperatures (700°C) in an inert atmosphere, NO is reduced to N_2 and O_2 by potassium carbonate-ferric oxide mixtures.
14. The carbonate-oxide mixtures appear to be more economical than silica gel for the absorption of NO_x from the MHD exhaust.

RECOMMENDATIONS

The research performed has indicated that carbonate-oxide mixtures are effective NO_x sorbents. Data is now required to better evaluate the performance of each sorbent mixture. Therefore, the following factors need to be known:

1. Optimum flow rates, temperatures and stoichiometric ratios for sorbent mixtures.
2. Rates and mechanism of reaction for absorption and regeneration.
3. Effect of different concentration of CO_2, O_2 and NO.
4. Surface area of sorbents.
5. Heats of reaction for regeneration and absorption.

Since there is evidence indicating that oxidative properties of the metal oxides are important, mixtures known as Hopcalites (MnO_2 with metal oxides) should be tested with the carbonates. In conjunction with the oxidative properties, the semiconductive properties should be evaluated to help determine a mechanism.

Further investigations in the reduction of NO at temperatures greater than 700°C by the sorbents may also be valuable. Application of the sorbents for automobile emissions control should be investigated.

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