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NITRIC OXIDE (NO) REDUCTION BY RETORTED OIL SHALE

By

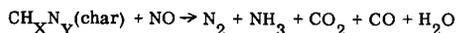
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INTRODUCTION

Oil shale, shale oil and retorted (spent) oil shale are rich in nitrogen. They contain 2 to 3 times as much nitrogen as found in coal, coal tar or coal char. Retorted oil shale contains char which can be burned. Some processes for recovering shale oil utilize the retorted shale as a fuel. The NO emission from the combustion of retorted shale has been measured by Lyon and Hardy (1) and by Taylor et al. (2). Lyon and Hardy's result suggests emissions of NO will probably exceed present standards for coal combustions (140 mg NO/MJ)*, but we found emissions of NO less than this value.

The concentration of NO and CO₂ in the exhaust gas as a function of time during the combustion of retorted shale in a fluidized bed has been reported (2). Only when the concentration of CO₂ decreased to 1/5 of its maximum value, signaling the end of char combustion, did the concentration of NO in the exhaust gas reach its maximum, as shown in Figure 1. The present work was initiated to explain this delay in NO emissions.

One explanation for the low NO emissions during most of the char combustion is that NO is reduced by the char. There are at least 5 possible products of this reduction as indicated by the following reaction:



Furusawa et al. (3) have found that coal char and activated petroleum coke reduce NO at elevated temperatures and they have measured the rates for the reduction reaction. They made the surprising discovery that char continues to reduce NO in the presence of oxygen even as the char is being consumed by oxidation. The principal products of the reaction at temperatures between 500 and 600°C were found to be N₂ and CO₂; above 775°C the concentration of CO exceeds CO₂ (4).

The object of the present work is to measure the rate of reduction of NO by retorted shale as a contribution to a general model of retorted shale combustion, leading to strategies for the control of NO emissions from retorted-shale combustors.

EXPERIMENTAL PROCEDURE AND RESULTS

Two kinds of experiments were performed to determine the rate of reduction of NO by retorted oil shale. In both kinds of experiments, NO, diluted in N₂, was passed through a shale bed and the decrease in NO concentration was measured. The rate was calculated from the transit (contact) time of NO through the bed. In one kind of experiment, the gas flow rate was held constant and the temperature was increased at a fixed rate. In the other experiments, the temperature was fixed and the gas flow rate was changed.

A fluidized bed was used both for the preparation of retorted shale and for reaction-rate measurements. It consisted of a silica-glass tube 4.2 cm inside diameter and 0.8 m long. The tube was mounted vertically inside an electric furnace. Preheated gas was passed upward through the tube. A perforated glass plate near the center of the tube retained the sample of crushed shale and distributed the gas flow. The sample of 104 L/Mg (24.8 gallons of oil per metric ton) shale came from Colorado tract C-a and had been crushed and sieved to a size distribution between 0.21 and 0.43 mm. A gas flow of approximately 3.5 L/min (STP) of nitrogen was sufficient to set the

* In the U. S. emission standards are written in units familiar to industry. For coal combustion, the NO_x standards are written in terms of pounds of NO₂ per 10⁶ Btu of fuel value in the coal, i. e., 0.5 lb NO₂/10⁶ Btu for new utility boilers. In metric units, this is equal to 140 mg NO/MJ. The standards are written in terms of NO₂ because NO is oxidized to NO₂ in the atmosphere.

100-g shale bed into a fluid like motion at a temperature of 500°C. Details of the bed are given in Table I.

TABLE I

Mass of raw shale bed	100.0 g
Mass of retorted shale bed	87 g
Organic carbon concentration (retorted)	2.9 wt %
Length of static bed	6.5 cm
Diameter of bed	4.2 cm
Volume of static bed (raw and retorted ^a)	90.0 cm ³
Shale density (raw)	2.22 g/cm ³
Shale density (retorted, calculated)	1.9
Bed void fraction (static, calculated)	0.50
Particle size range (diam.)	0.21 to 0.43 mm
Inlet concentration of NO	249 ppm

a. Particle size did not decrease with retorting; only the particle density decreased.

A 100-g sample of raw oil shale was retorted by heating it in flowing nitrogen to a temperature of 550°C at a rate of 25°C/min. The sample was kept at 550°C for 3 min and then cooled rapidly to room temperature in flowing nitrogen by opening the electric furnace. The retorted shale contained approximately 2.9 wt % organic carbon. The weight loss of the raw shale during retorting was 13%.

In all experiments, N₂ containing 249 ppm of NO was passed upward through the bed of retorted oil shale. The large amount of carbon (~3 g) and the low concentration of NO was planned to assure a nearly constant carbon concentration during each experiment. At the end of all the experiments, approximately 10% of the char could have been consumed.

The concentrations of NO and CO₂ in the gas stream from the reactor were measured by means of a mass spectrometer. The mass spectrometer was calibrated using purchased gas standards. Two standards for NO were purchased. When the mass spectrometer was calibrated by means of one standard, the concentration of NO in the other standard could be measured to within a few ppm.

In the first experiments, the temperature of the retorted shale was increased at the rate of 14.5 C/min in the NO-N₂ mixture flowing at 7.8 L/min (measured at 25° and 1 atm). At temperatures below approximately 175°C, the shale sample removed some of the NO from the gas stream by adsorption. As the temperature was increased above 175°C, the concentration of NO in the exit gas exceeded the inlet concentration of NO. At 200°C, the inlet and exit concentration were nearly equal and as the temperature was increased above 200°C, the concentration of NO decreased by reaction with the retorted shale as shown in Figure 2. The sample was again cooled to room temperature under pure N₂ and then reheated to 500°C at the same rate of heating and in the same gas mixture but at a flow rate of 4.9 L/min. A larger fraction of the NO was removed from the gas stream at the slower flow because of the 1.6 times longer period of contact between the solid sample and the gas.

In subsequent isothermal experiments using the same bed of retorted shale in the same apparatus, the temperature was held constant at various temperatures between 280°C and 400°C. The rate of flow of NO bearing N₂ gas through the bed was also kept constant. After measuring the exit gas concentration of NO at several flow rates, the temperature was changed and the process was repeated. In the course of these experiments, the bed was operated at a range of flow rates both below and above those required for fluidization. Whether or not the bed was fluidized made no discontinuity in the measured rate of reaction.

The effective rate constant (*k*) was evaluated at selected temperatures by the expression

$$k_{\text{eff}} (\text{s}^{-1}) = \frac{\ln \left[\frac{(\text{NO})_i}{(\text{NO})_o} \right]}{t}$$

where (NO)_i/(NO)_o is the ratio of the NO concentration into and out of the reactor and *t* is the actual transit time of the gas through the bed at temperature. The transit time was calculated from the bed volume, bed height and bed void volume (in a static, non fluidized condition, Table 1), using the measured inlet gas flow rate and the bed temperature. The results of the nonisothermal experiments are given in Figure 3. Because the temperature of the reacting bed changes only about 5°C during the gas transit time, the nonisothermal experiments can be analyzed as a series of

isothermal experiments (Table II). The results of the isothermal experiments are given in Figure 4. The reaction rate from both the isothermal and nonisothermal experiments is plotted as a function of temperature on Figure 5. An average value of the rate as a function of temperature, the line in Figure 5, can be expressed as

$$k_{\text{eff}} (\text{s}^{-1}) = 4.0 \times 10^5 e^{-E/RT}$$

where E is 59.7 kJ/mole.

TABLE II

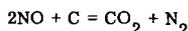
	Temperature of Fluidized Bed, °C								
	275	300	325	350	375	400	425	450	475
Flow = 7.8 L/min									
NO ^{out} , ppm	189	163	140	116	91	68	44	25	12
t, s	0.188	0.180	0.172	0.165	0.159	0.153	0.148	0.142	0.138
k, s ⁻¹	1.5	2.4	3.3	4.6	6.3	8.5	12	16	22
Flow = 4.9 L/min									
NO ^{out} , ppm	185	152	117	87	60	38	21	9	3
t, s	0.299	0.286	0.274	0.263	0.253	0.244	0.235	0.227	0.219
k, s ⁻¹	0.99	1.7	2.8	4.0	5.6	7.7	10	15	20

DISCUSSION

The results have been presented in terms of an effective rate constant for 87 g of a particular retorted oil shale. In order to make these results more general and to make comparisons to other measurements of NO reduction rates with other carbonaceous materials, it is necessary to take into account the amount and form of the agent effective in the NO reduction.

The principal reaction products of nitric oxide reduction by coal char are N₂ and CO₂ at temperatures from 502°C to 680°C. At 680°C, CO is also found and it becomes abundant at 775°C and the principal reaction product at 910°C, the maximum temperature investigated by Furusawa et al. (4).

We measured the concentration of CO₂ in the exit gas expecting to verify the principal NO reduction reaction as



However, the exit gas concentration of CO₂ was at most 45 ppm. This maximum concentration was found at the maximum temperature investigated (475°C), when all the NO flowing into the bed was reacted.

It appears possible that the principal agent for NO reduction by retorted oil shale at temperatures below 500°C is the hydrogen in the char. Oil shale retorted at 500°C contains a char of the approximate composition CH_{0.4}N_{0.07}. The coal char used by Furusawa et al. (4) had the composition CH_{0.17}N_{0.007}. The oil shale char used in this investigation has approximately twice the hydrogen concentration and ten times the nitrogen concentration of this coal char.

Furusawa et al. (4) measured the rate of reduction of NO by coal char in a packed bed reactor where the transit time was calculated from the "effective" length of the bed and the superficial gas velocity. The bed used was a mixture of inert aluminosilicate particles and char particles both approximately 0.6 mm in diameter. The "effective" length is the length of bed due to the char particles alone. The coal char contained 26% ash and it is not clear how this was taken into account. Retorted oil shale is also a mixture of "inert" silicate and carbonate minerals with char. The mixture is on a scale much smaller than the particle size; each particle contains many mineral particles and many zones or particles of char.

To calculate the effective residence time, Kunii, Wu and Furusawa (5) used the equation

$$Z = \frac{M_c}{\rho_b F}$$

where M_c is the mass of char, ρ_b is the bulk density of a pure char bed and F is the flow rate.

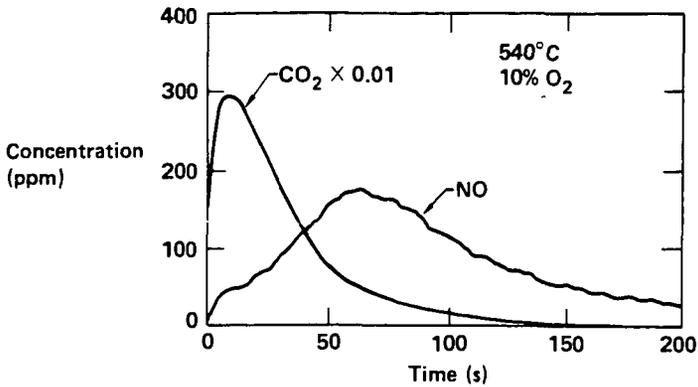


Fig. 1: Concentrations of CO_2 and NO as a function of time during the batch combustion of retorted Tract C-a oil shale in a fluidized bed.

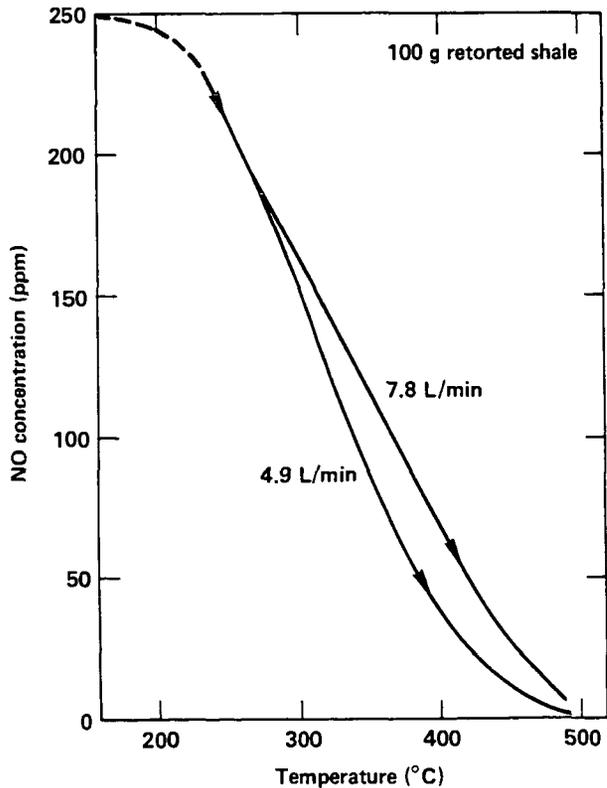


Fig. 2: Concentration of NO in the exit of a fluidized bed of retorted oil shale showing the removal of NO as the bed is heated (heating rate $14.5^\circ\text{C}/\text{minute}$). Inlet NO concentration, 249 ppm.

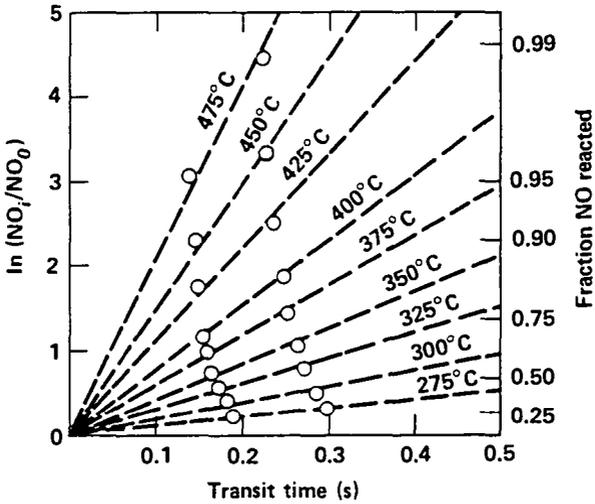


Fig. 3: Reduction of NO concentration as a function of transit time and temperature. The slope of these lines is equal to the reaction rate constant for the case of a constant rate of heating.

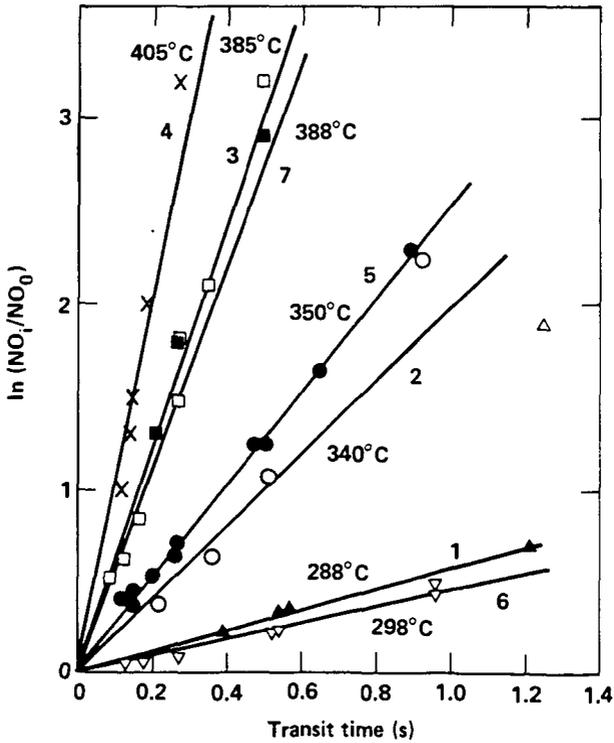


Fig. 4: Transit time (t) vs. $\ln(NO_0/NO_i)$ for isothermal experiments. The number on each line is the sequence in which the experiments were conducted.

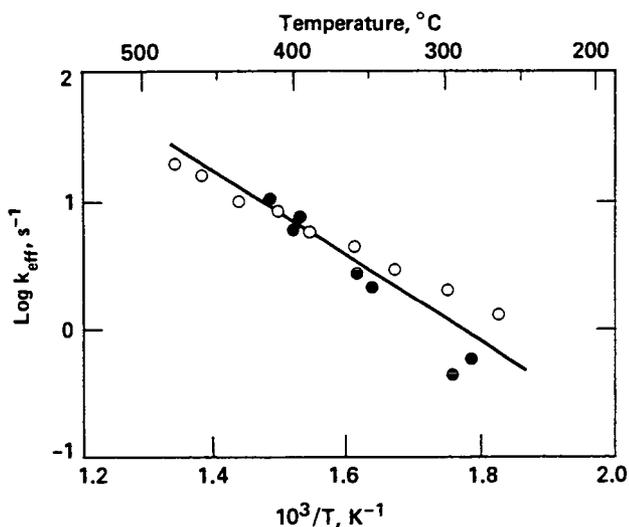


Fig. 5: Arrhenius Plot of effective rate constant for reduction of NO by retorted oil shale. The solid circles represent the results from heating the retorted shale bed at a constant rate; the open circles show the results when the bed was kept at the same temperature until a constant NO concentration was observed in the exit gas.

Using the same definition to calculate an effective residence time in our experiments results in residence times only 1/25 as long as those we used above, hence, a rate constant 25 x larger. Using this larger rate constant for comparison, we find that oil shale char is 10^3 times more reactive for NO reduction than is coal char.

An alternate approach for comparison is to convert the rate to units used by Chan, Sarofim and Beer (6) who show an Arrhenius plot indicating agreement of their results with those of Furusawa et al. We have not been able to make this comparison with certainty because of a confusing difference in units, but our preliminary comparison indicates oil shale char is $> 10^3$ times more reactive than the Montana Lignite Char used by Chan et al. While previous work (7, 8) has demonstrated that oil shale char is more reactive also towards oxidation and gasification than is coal char, the greater reactivity of oil shale char towards reduction of NO is more dramatic.

The reason for the greater activity is unknown. It may be due in part to the higher hydrogen content of oil shale char. The char in retorted oil shale (7) has a specific surface area of $\sim 360 \text{ M}^2/\text{g}$ which is similar to that of the coal char used by Chan et al. (6). However, the oil shale char may also be more accessible. Retorted oil shale is 97 wt % ash and contains 20 volume % interconnected porosity. The char in retorted oil shale is probably distributed primarily along these pores because they were created when the shale was retorted by the loss of volatile carbonaceous material. Thus, the char in retorted oil shale may be more available for NO reduction than char particles prepared by coal pyrolysis. Also, the great excess of ash in retorted oil shale may provide catalytic sites. Finally, we must not overlook the possibility that the NO is not reduced by char alone, but by some other reducing agent in the retorted shale, for example, iron-bearing minerals.

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