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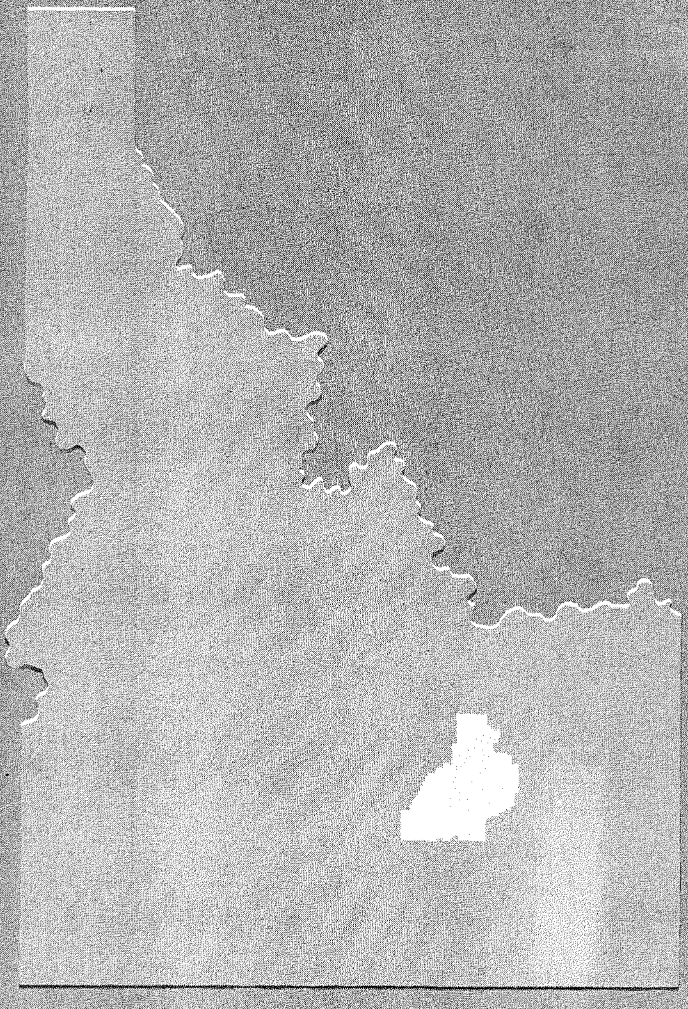
L. T. Lakey

April 17, 1961



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PLANT TESTS ON THE DECOMPOSITION OF NITROUS OXIDE OVER A HEATED RHODIUM CATALYST

by

L. T. Lakey

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ABSTRACT

Plant scale tests were conducted at the Idaho Chemical Processing Plant to determine the feasibility of decomposing the nitrous oxide in dissolver off gases with a heated rhodium catalyst. The test results from two fixed bed reactors operating on off gases containing between 14.2 and 19.8 volume per cent nitrous oxide show that the nitrous oxide content can be reduced to less than 0.05 per cent with catalyst bed outlet temperatures between 1300 and 1500° F and space velocities between 472 and 700 hr^{-1}. Rate constants appear to be comparable to those reported in the literature. Suggestions are made for the design of a permanent installation.

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PLANT TESTS ON THE DECOMPOSITION OF NITROUS OXIDE OVER A HEATED RHODIUM CATALYST

L. T. Lakey

I. INTRODUCTION

A low temperature process is used at the Idaho Chemical Processing Plant to recover valuable gaseous fission products released during the dissolution of spent fuel from nuclear reactors. Solidification of the higher freezing components, including nitrous oxide, present in the dissolver off gases makes it necessary to remove these components prior to the low temperature processing operation. In the process as originally installed, the nitrous oxide is reduced with hydrogen over a palladium catalyst heated by the energy released from the exothermic reaction. Since the use of hydrogen is both hazardous and costly, it is doubly desirable to find an alternate means of removing nitrous oxide from the off gas stream. Hydrocarbon fuels, which have been used in similar applications(1), cannot be used in lieu of hydrogen because of their incompatibility with the low-temperature process following the catalytic reactors.

From experimental work at BNL(2), the thermal decomposition of nitrous oxide in an externally-heated reactor containing rhodium, palladium, or platinum catalyst appeared to be a promising means of circumventing the disadvantages of hydrogen. In order to make a quick check of its potential advantages with minimum expenditure for facilities, this approach was tested in the existing ICPP gas processing equipment. Although conducting these tests on equipment installed in a production process meant that it was impossible to achieve the experimentally desired variations in conditions, it was possible to determine the effect of thermal decomposition of nitrous oxide on the downstream process components and to determine the operational flexibility of the catalytic reactors.

The BNL work(2) had indicated that essentially complete thermal decomposition of nitrous oxide can be accomplished over a rhodium catalyst maintained at temperatures ranging from 650 to 775° F and at space velocities between 525 and 2220 hr^{-1} (standard cubic feet of gas per hour per cubic foot of catalyst bed). Palladium and platinum catalysts were found to be equally effective but required temperatures 150 to 500° F higher, respectively.

The decomposition of nitrous oxide is exothermic according to the following equation: $N_2O \rightarrow N_2 + 1/2\ O_2 \quad \Delta H_{25} = -35{,}800$ BTU/lb mol N_2O(3). However, at flow rates and nitrous oxide concentrations experienced in the ICPP system, additional heating is required to maintain temperatures near 700° F in the catalyst beds. To reduce the heating equipment required for the plant tests, the catalytic reactors were insulated and the palladium catalyst replaced with rhodium catalyst.

II. TEST EQUIPMENT AND PROCEDURE

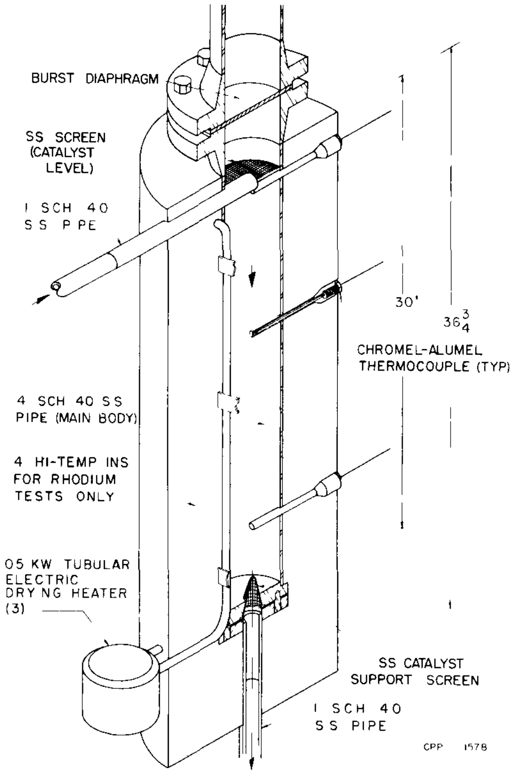

Fig. 1
Catalytic Reactor

Testing was conducted during the period from May 1959 through January 1960. For the initial test early in May, only one reactor was utilized. This reactor was a 5-inch I.D. by 28 inches long stainless steel tube holding 1/3 cubic foot of catalyst supported on a wire screen as shown in Figure 1. Available process instrumentation included inlet, outlet and center bed thermocouples, flow rate and pressure indicators, and an upstream gas sampling station. Strapped to the reactor case were three 0.5 KW tubular heaters used originally for drying the catalyst. For testing, the iron-constantan bed thermocouples in the reactor were replaced with chromel-alumel thermocouples connected to a 0-2000° F multipoint recorder. A temporary connection at a pressure tap downstream of the reactor was utilized to take effluent gas samples. The original palladium catalyst in the reactor was replaced with rhodium catalyst manufactured by Englehard Industries, Newark, New Jersey. This catalyst consists of a 1/8-inch diameter x 1/8-inch long alumina cylinder containing 1/2 wt. per cent rhodium as a surface coating. The reactors were covered with 4 inches of high temperature insulation to minimize heat losses. Gas samples, taken in evacuated bombs, were analyzed by mass spectrometer for the major gaseous components.

Before starting the initial test, the test reactor was heated with the catalyst-drying heaters until the center thermocouple was indicating 1000° F. Off gases were then passed through the unit for three hours at rates from 2 to 4 scfm. During this period, slow fluctuations in reactor temperatures, over a range in excess of 200° F at all thermocouple positions, made it evident that heater adjustment would not be a practical method for controlling reactor temperatures. Average inlet temperatures near 350° F and outlet temperatures near 1000° F were observed. Feed and effluent gas samples were taken when outlet thermocouple readings were near 1000° F. The gas flow rate was then raised to 8 scfm; however, the reactor outlet temperatures fell rapidly to below 500° F. Analysis of gas samples taken at a flow rate of 2.1 scfm showed that reactor effluent gases contained less than 0.05 volume per cent nitrous oxide (Table I). Other nitrogen oxides (NO, NO_2) were likewise found to constitute less than 0.05 volume per cent of the effluent gases. Valid samples at the 8 scfm flow rate were not obtained.

TABLE I

CATALYTIC DECOMPOSITION OF NITROUS OXIDE OVER A RHODIUM CATALYST
SUMMARY OF EXPERIMENTAL DATA$^{(a)}$

			Temperatures °F							$N_2O^{(c)}$		$NO + NO_2$		H_2		$CO_2^{(b)}$		Rate Constant Min^{-1}
			Reactor #1			Reactor #2			Flow scfm									
Date	Run	Time	Top	Mid.	Bott.	Top	Mid.	Bott.		In	Out	In	Out	In	Out	In	Out	
5-4	1	4:40P	-	-	-	375	450	950	2.1	5.1	<.05	<.10	<.05	.06	<.05			
5-4		6:30A	-	-	-	350	600	1000	2.1	5.1	<.05	<.10	<.05	.06	<.05			
5-19	2	2:30P	-	-	-	350	450	800	6	(16.8)	.05	-	<.05	-	<.05			44.0
5-19		4:20P	-	-	-	540	1075	1150	7.1	16.8	<.05	<.05	<.05	2.0	<.05	<.05	<.05	
5-20		9:00A	-	-	-	360	-	1150	4	15.0	<.05	.50	.50	1.8	<.05	<.05	<.05	
5-21		3:00P	650	1125	1000	525	1175	1025	7	-	<.05	-	.15	-	<.05	-	<.05	
5-22		8:30A	475	650	950	350	400	1050	7	10.8	0.10	.20	.20	1.4	<.05	<.05	<.05	49.5
5-26	3	10:00P	250	325	1025	225	325	1000	8	-	<.05	-	<.05	-	<.05			
5-27		2:00A	575	1150	1075	450	825	1075	-	-	.20	-	.15	-	<.05	-	<.05	
5-27		6:00A	425	525	1050	375	525	1100	7.8	-	.05	-	.40	-	<.05			
5-27		8:00P	350	675	1100	200	450	1100	7	-	.07	-	.10	-	<.05			
5-28		4:30A	375	650	925	275	600	1000	7	10.2	.05	<.05	.10	1.2	<.05	<.05	-	56.3
5-28		Noon	625	840	975	500	650	950	10.3	(10.2)	.06	<.05	<.05	1.2	<.05	-	<.05	80.0
5-29		12:30P	250	425	775	175	300	675	9.5	-	.18	-	.06	-	<.05			
5-29		8:00P	200	350	1100	150	300	925	9.5	-	.09	-	.10	-	<.05			
5-30		4:00A	450	825	1150	325	725	1200	7.5	-	.12	-	.13	-	<.05			
5-30		8:00P	300	600	1050	225	425	1075	5.7	-	.08	-	<.05	-	<.05			
5-31		4:00A	325	750	1050	325	1075	1125	5.7	-	.09	-	<.05	-	<.05			
5-31		12:30P	225	400	1075	175	375	1100	-	-	.09	-	.16	-	<.05			
5-31		8:00P	250	375	1175	225	450	1075	8.8	-	.06	-	.20	-	<.05			
6-1		4:15A	375	675	1125	200	425	875	9.7	12.6	.20	<.05	<.05	1.5	<.05			60.8
6-1		Noon	325	575	1075	225	475	925	9.7	(12.6)	.18	-	.20	-	<.05			62.3
6-1		8:00P	575	750	900	475	675	900	9.7	-	.07	-	<.05	-	<.05			
6-2		5:00A	670	820	975	550	740	1000	9.7	8.8	.18	<.05	<.05	1.1	<.05	<.05	-	57.2
1-16	4	1:00P	-	-	1200	-	-	1355	6.9	15.2	<.05	<.05	<.05	2.9	<.05			
1-19		11:00A	-	-	1450	-	-	1450	5.8	19.8	<.05	<.05	<.05	3.5	<.05			
1-19		3:00P	575	1400	1460	545	1400	1460	7.7	18.2	<.05	<.05	<.05	3.5	<.05	<.05	<.05	
1-25		1:45P	-	-	1355	-	-	1400	5.4	15.7	<.05	<.05	<.05	1.0	<.05			
1-25		2:00P	-	-	1380	-	-	1400	5.2	14.2	<.05	<.05	<.05	0.9	<.05			

(a) Concentrations given in volume per cent.

(b) Where CO_2 is not reported separately, it is included in N_2O concentration.

(c) N_2O values in parenthesis are estimated only.

Following the apparently successful initial run, the capacity of the rhodium catalyst test equipment was increased by placing another reactor in service paralleling the first. Additional heat was provided by inserting two 1.5 KW electrical preheaters in the feed line. Two extended runs were made with this configuration using flow rates up to 10 scfm and reactor outlet temperatures near 1000° F. As with the initial run, temperature fluctuations were large and difficult to control with the electrical heaters. It was also found necessary to shut down and defrost the low temperature unit at frequent intervals to remove solids frozen from the gas stream. Analysis of gas samples taken during this period showed up to 0.20 volume per cent of nitrous oxide and up to 0.50 volume per cent of other nitrogen oxides remaining in the effluent gas stream.

In January, 1960, a final run covering a period of fifteen days was conducted with reactor outlet temperatures between 1300 and 1500° F. Prior to this run, repairs to the dissolver element-charging chutes reduced air leakage into the off gas system resulting in higher nitrous oxide concentrations in the gas to the gas processing plant. This increased the reaction heat release in the catalyst beds and made it possible to hold temperatures between 1300 and 1500° F in the reactors. The nitrous oxide content of the dissolver off gas stream during this test period varied from 14.2 to 19.8 volume per cent. No operating difficulty attributable to contaminant buildup was experienced with the low temperature unit during this period. Analysis of reactor effluent gases showed less than 0.05 volume per cent of nitrous oxide or other nitrogen oxides remaining in the gas stream.

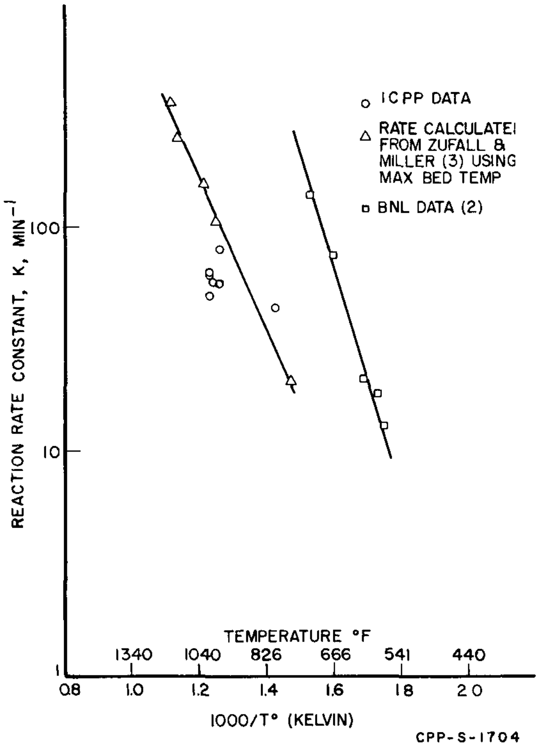

Fig. 2
Rate of Nitrous Oxide Decomposition

III. CORRELATION OF DATA

In an attempt to correlate the data, reaction rate constants were calculated for those conditions where both the inlet and outlet nitrous oxide concentration data were available. Assuming the decomposition of nitrous oxide is a first order reaction as was indicated by the test data of Steinberg(2), the reaction rate, k, can be expressed by:

$$k = \frac{\ln(C_o/C)}{\theta}$$

where k = reaction rate constant, min^{-1}
θ = residence time, min.
C_o = initial concentration, mol per cent
C = final concentration, mol per cent

The calculated values of k are given in the last column of Table 1 and are plotted in Figure 2 as a function of the reciprocal of the absolute temperature, $^{\circ}$K. The reaction rates of Steinberg(2) and the rates calculated from the test data of Zufall and Miller(4) have been included in Figure 2 for comparison.

IV. CONCLUSIONS AND RECOMMENDATIONS

Results of the tests are largely qualitative since processing committments at the gas plant prevented close control of the test conditions. Data were taken under actual processing conditions and as such were subject to varying feed compositions and flow rates.

The lack of control over test conditions is evident in the data scatter shown in Figure 2. However, the grouping of data indicates that higher temperatures than those reported by BNL are required. This has been substantiated by the recent work of Zufall and Miller(4) which is also shown in Figure 2. Since all of the reaction rate data shown in Figure 2 have been obtained in fixed-bed type reactors in which the temperature varies both longitudinally and laterally throughout the catalyst bed, the relative positions of the temperature-rate data plots are dependent on the location of the temperature sensing elements. The temperatures reported in the BNL plot were measured at a point near the inlet or cool end of the catalyst bed, while temperatures used in the present work and by Zufall and Miller are near maximum bed temperatures. It appears that the true rate-temperature relationship lies somewhere between these limits.

Because of the difficulties experienced in controlling reactor temperatures, the inadequate heating equipment, and concern for the durability of the catalyst support screens at high temperatures, use of the test reactors on a permanent basis is not advisable. For a permanent installation, a single double-pass reactor is suggested. This type of reactor does not require a bed support plate or screen and has an added advantage of conserving heat by the regenerative effect of the double-pass design.

The major problem in designing a reactor to meet conditions at the ICPP gas plant is that of attaining good temperature control. The method of temperature control must maintain the required temperature level at low nitrous oxide concentrations and yet have sufficient controllability to prevent reactor overheating at high concentrations. Overheating can lead to reactor failure and possibly to formation of other nitrogen oxides(4).

As shown by the tests, the existing external jacket heaters or preheaters have insufficient response and allow reactor temperatures to vary widely. A possible solution to this problem is the placing of electrical heaters in the catalyst bed. A better process design might include the use of dilution air or the recycle of effluent gas through a cooler back to the reactor inlet. Any of these alternatives should utilize automatic controls to minimize the need for an operator's attention and the possibility of his error.

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