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THE PURIFICATION OF GASEOUS WASTE STREAMS FROM
NITRIC ACID PLANTS WHICH CONTAIN NITROGEN OXIDES ^{1/}

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Table of Contents

	<u>Page</u>
I. Introduction	1
II. The Principles of the Process	3
III. Process Design and Economics	12

I. Introduction

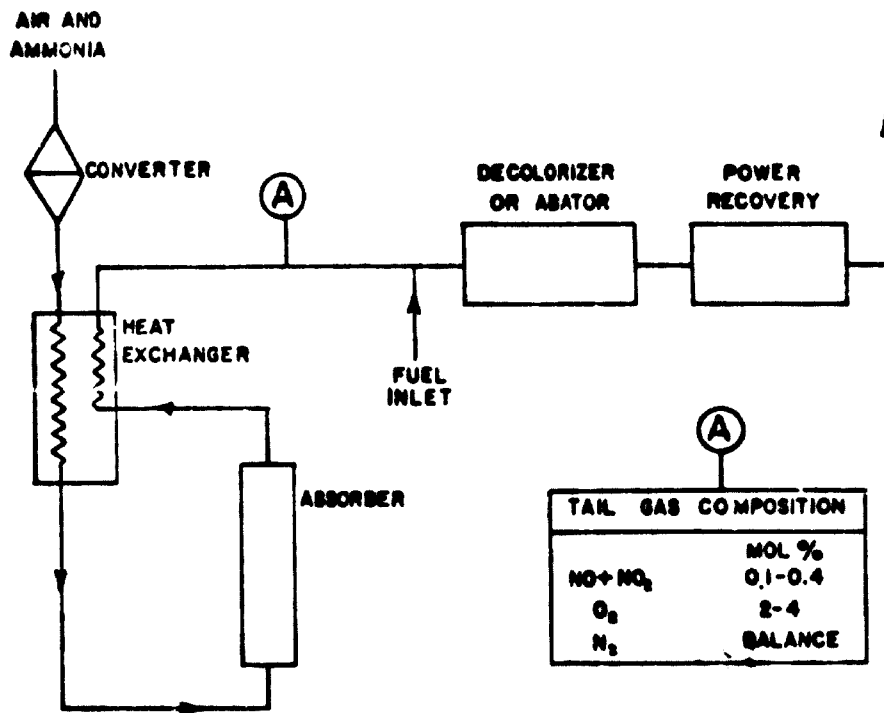
Most nitric acid needed in the production of fertilizers is produced by catalytic selective combustion of ammonia over platinum metals catalysts to convert the ammonia to nitric oxide. The nitric oxide is subsequently oxidized and absorbed in water to form nitric acid. Absorption usually is not entirely complete and the stack gases contain appreciable concentrations of oxides of nitrogen. Typically the tail gases have a composition in the range:

NO _x (NO + NO ₂)	0.2 - 0.5%
O ₂	2 - 4%
H ₂ O	Saturated at absorber conditions
N ₂	Balance

The oxides of nitrogen are toxic. Their NO₂ content causes the offensive reddish-brown plume characteristic for the off-gases from a nitric acid plant. A small amount of N₂O is also present in the tail gases which, however, is not considered to be an air pollution problem.

During the past 20 years it has been a commercial practice in the United States and other countries to at least decolorize the nitric acid tail gases by catalytic treatment with a fuel which converts the strongly colored NO₂ to colorless NO. This process turns a nuisance to an advantage because it generates energy which is utilized to contribute to the power requirements of the nitric-acid plant as shown schematically in the flow sheet of Fig. 1. The power of the fuel gases is used to drive the air compressors of the plants which supply the air for the ammonia oxidation.

Figure 1
Nitric Acid Manufacturing Process



In principle the same process is also employed for true pollution abatement required to an increasing degree as stricter NO_x emission standards become implemented. In the United States, for instance, Federal Standards permit a maximum of 1.5 Kg (measured as NO₂) per ton of acid produced for new plants and a maximum of 2.75 Kg/ton of acid for existing plants (1). In typical plant operation, these values correspond to NO_x concentrations in the tail gases of 209 and 400 ppm respectively.

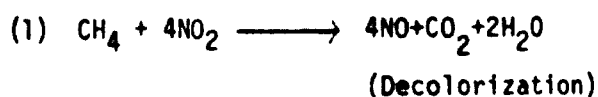
We have discussed earlier the benefit of catalytic treatment of nitric acid tail gases for the fertilizer industry (2). In the following, it will be shown that catalytic abatement systems can be retrofitted in existing plants or can be incorporated in the design of new plants. The economics of the process will also be indicated.

At this time, catalytic abatement systems are being constructed in the U.S. to meet legislated air quality standards.

II. The Principles of the Process

The catalytic treatment of the nitric acid tail gases can be carried out with a variety of fuels: natural gas (methane), hydrogen, purge gas from ammonia synthesis reactors, carbon monoxide, hydrocarbon mixtures, coke oven gas, vaporized kerosine or naphtha. When natural gas is the fuel the catalytic reactions can be described as follows:

4.



For decolorization to occur the combustion reaction (2) need not be complete; on the other hand full abatement requires complete removal of free oxygen and, in practice, the presence of some excess fuel, typically 10 per cent more than the stoichiometric demand.

The catalysts generally employed in either the decolorization or abatement operations consist in most cases of palladium or platinum on ceramic carriers in the form of either particulate or unitary "honeycomb" structures. The concentration of metal may vary from 0.3 to 1.0 percent. Typical specimens of such catalysts are shown in Fig. 2.

Spherical particulate catalysts have a diameter of typically 0.64 cm, unitary blocks may be 23 cm square by 7.6 cm deep, or 31.5 cm square by 2.5 cm deep. Comparative data of the two types of catalysts are given in Table 1. In commercial practice, catalyst choice is dictated by factors such as catalyst cost and vessel size. Both types of catalysts are being employed, the particulate catalyst exhibiting better aging characteristics, however, with proper procedures honeycomb type catalysts are quite suitable and offer a number of advantages for the design of abaters as indicated in Table 1. In practice the volume hourly space velocities have been in general 100,000 for honeycomb catalyst and 30,000 for particulate

Figure 2. Spherical (left) and honeycomb (right) tail gas catalysts.

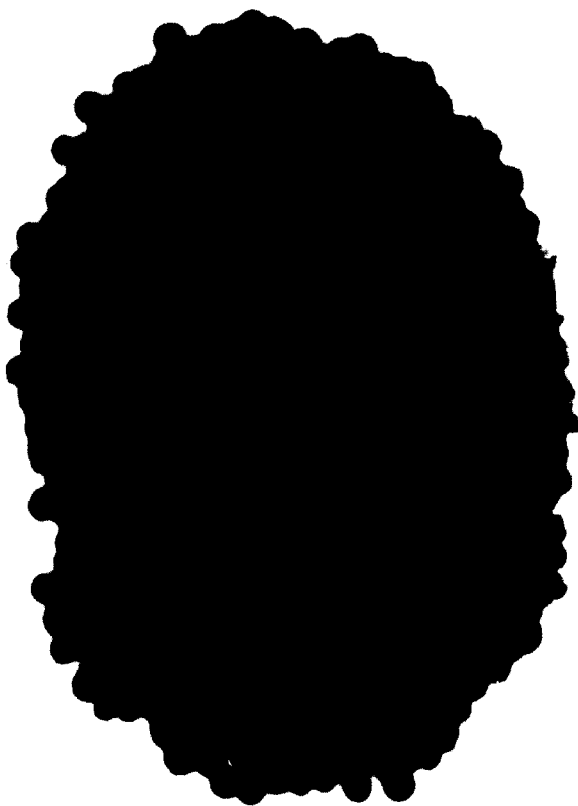


Table 1

Comparison of properties of monolithic catalysts with particulate spherical catalysts.

	Honeycomb catalyst with sinusoidal Channels 2.75 channels/cm	Particulate Type Diameter .635 cm
Superficial Surface Area (m ² /liter)	7.98	0.48
Voids in packed bed(%)	65-70	41.5
Pressure drop 10 cm of depth at Linear Velocity=6.1m/sec. Pressure =6.8 atm. gage Temperature =500°C	10mmHg	171mmHg
Relative Ratio of Vessel Diameter for $\Delta P=52\text{mmHg}$ at operating conditions: 100,000 Hrs. ⁻¹ vol. space velocity for honeycomb; 30,000 Hrs. ⁻¹ for particulate catalyst.	1	2
Commercially usable space Velocities (Volumetric)	90,000-140,000 Hrs. ⁻¹	20,000-60,000 Hrs. ⁻¹

catalyst.

The operating conditions of the abatement catalysts depend on the nature of the fuel. The most commonly used fuels are listed in Table 2.

Reaction Rate Limitations

Several publications (3,4) have shown that the rate of catalytic oxidation of CH_4 is first order in methane, and nearly zero order in oxygen. The rate equation for a catalyst may then be expressed as $r = k(C_s)(P_{\text{CH}_4})e^{-E/RT}$ where (C_s) is the surface concentration of metal of small crystallite size.

Table 3 lists relative catalytic reaction rates of CH_4 combustion at various temperatures (5). Obviously, Pd is much more active than Pt, and the rate increases much faster with increasing temperature over Pd than over Pt.

Although Pd-type catalysts are more sensitive to sulfur (present in most natural gas as H_2S and mercaptans) than Pt-type catalysts, the higher activity of Pd usually justifies use of a fuel desulfurization step.

Table 2

Properties of Typical Abatement Fuels

	Composition (Approximate) (Mole%)	Abater Design Inlet Temperatures (°C)	Temperature(1) Rise (°C)
Natural Gas	CH ₄ (abt. 99%)	480-510	128
Ammonia Synthesis Reactor Purge Gas	60H ₂ 14CH ₄ 26(N ₂ +A)	200	151
Synthesis Gas	75H ₂ 25N ₂	200	158
Naphtha (e.g. Udex Raffinate) ←	C ₆ -C ₈ M.W. = 91 Boiling range: 69-132° 1 ppm S; 1.1 ppm Cl, 2.0 ppm N.	400	(2)

- (1) Adiabatic Temperature Rise per Mole % O₂ in Tail Gas
(2) Value fluctuates dependent on naphtha composition

Table 3

Relative reaction rates of catalytic oxidation of methane.

	Activation Energy E Kcal./Mol.	Reaction Rates Relative to that of Pd/Al ₂ O ₃ at 400°C				Ref.
		400°C	450°C	600°C	800°C	
Pd/γAl ₂ O ₃	19.6	1.0	2.76	28.7	235.9	(3)(4)
Pt/γAl ₂ O ₃	9.2	0.44	0.71	2.1	5.7	(3)

In practice, under the conditions of operation catalyst deterioration or aging occurs. Various factors may cause deactivation: loss of active catalyst surface by thermal sintering of the refractory oxide support and simultaneous occlusion of the platinum group metal catalyst, agglomeration of precious metals crystallites forming larger crystallites with correspondingly reduced available surface area, or poisoning by trace materials in the feed stream.

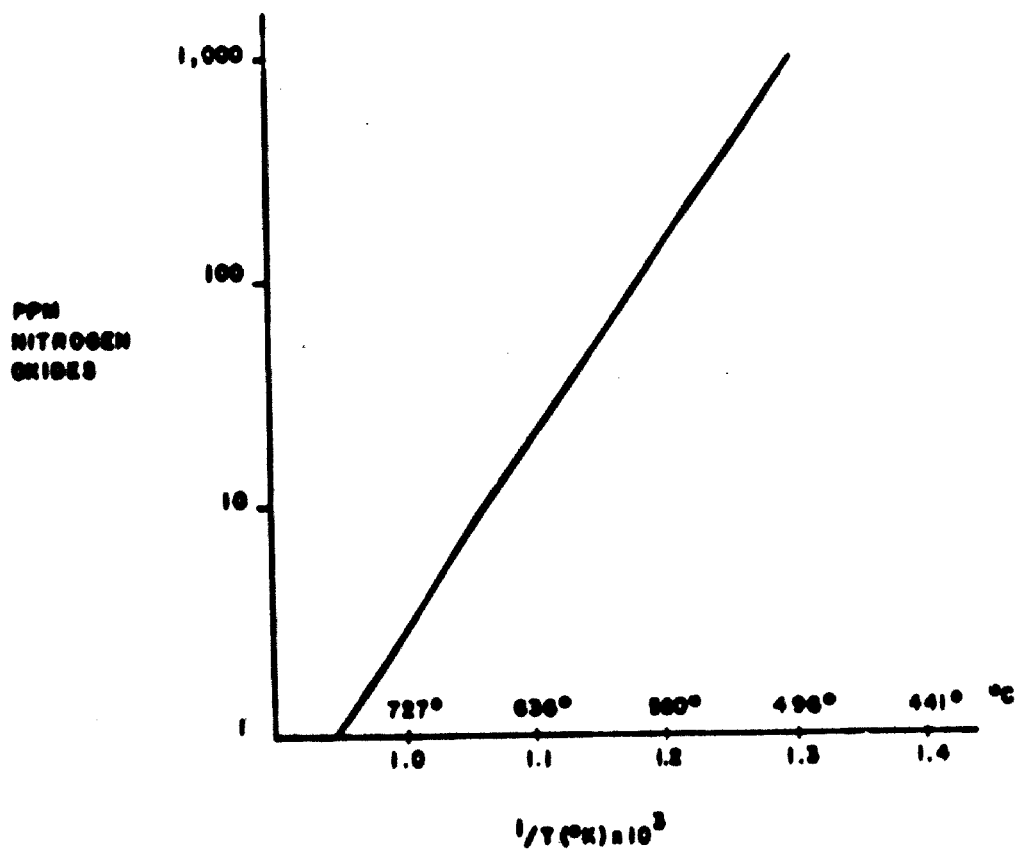
In the kinetically controlled reaction rate regime the effect of aging could be overcome by successively increasing the inlet temperature of the abater reactor. Practically however, this procedure could only be applied to a limited extent because of temperature limitation of the equipment.

Therefore, in order to obtain economic catalyst life, it is necessary to design the abatement reaction to proceed under mass transfer control, essentially throughout the entire period of catalyst use. Calculations can be made of the volume of virgin catalyst required to operate under mass transfer control, and allowing sufficient margin for catalyst aging. This is the basis of design criteria of tail gas abaters.

This design has to take into account the requirement that the outlet temperature has to reach a minimum value to achieve abatement. Indeed, the most critical temperature consideration in the design of the abater is the outlet temperature. The reactor effluent temperature equals nearly the temperature determined thermodynamically by the oxygen and NO_x content of the tail gas and by the heating value of the fuel as shown by the values of the temperature rise in Table 2. Experiments have been conducted to determine the relationship between the outlet temperature and the extent of abatement (6). The experimental results are shown in Figure 3.

Figure 3

Relationship of Nitrogen Oxides Concentration and Temperature at Reactor Exit



The data were obtained using a honeycomb Pd catalyst, a volumetric space velocity of $100,000 \text{ hrs}^{-1}$, a pressure of 6.8 Atm. gage, and a feed gas composition corresponding to the usual oxygen-and NOx content of tail gases.

In accordance with these data catalytic abaters are designed to have a maximum outlet temperature of approximately 800°C . This is close to the maximum allowable continuous operating temperature of the catalyst. Good design dictates that the preheat temperature be sufficiently high to allow the catalyst to operate at a temperature of around 750°C . Operation at these high temperatures allows good fuel efficiency and ensures that low concentrations of nitrogen oxides will be emitted. The higher the temperature of operation, however, the more accelerated becomes the thermal degradation of the catalyst.

III. Process Design and Economics

General Design Considerations

The proper design of the catalytic abatement system requires that the system not only reduce the concentration of environmentally objectionable NOx to acceptable concentrations but the system must also be compatible with nitric acid plant operation. The system must be flexible to allow its continued operation during minor plant upsets. Since the abatement reactions are exothermic and fuel is consumed, the system should produce power which will improve the economics of the abatement facility.

The function of the abatement equipment must be considered to ensure good performance of the system. Provision must be made to preheat the tail gas and introduce the fuel. The reactor must be properly designed to allow the abatement reaction and provisions must be incorporated to extract as much of the heat as

possible for useful power recovery. The waste heat is extracted by waste-heat boilers and power-recovery turbines.

Decolorizers, which are similar to abatement systems, have been used commercially since the Mid-1950's. Deficiencies in the design of these systems have shown that several problems can be encountered. One of these is poor fuel-tail gas mixing. As discussed earlier, the use of honeycomb catalyst with its parallel channels running the full length of the catalyst bed can result in performance problems if the fuel is not adequately mixed with the tail gas. Especially if hydrocarbon fuels are used, the presence of excessive quantities of fuel over the stoichiometric requirement can lead to cracking of the hydrocarbon which results in carbon laydown on the catalyst surface. Immediately, these local areas of the catalyst surface becomes covered by the carbon deposit and can no longer function as an active catalyst site. Moreover, if during shutdown larger oxygen concentrations become present in the hot catalyst bed, extreme temperatures can be reached at these catalyst sites as the carbon burns, and future use of the catalyst will be jeopardized.

With respect to operating temperatures the reactor is limited by a minimum inlet temperature or ignition temperature and a maximum exhaust temperature. The maximum exhaust temperature is either set by the catalyst temperature limitations or by the equipment downstream. Provisions must be made to allow the system to function with varying concentrations of oxygen without the risk of excessive temperature of either the catalyst or the downstream equipment. There always must be adequate fuel to consume the oxygen and nitrogen oxides. The catalyst is subject to poisoning by sulfur, halogens, and base metals. As stated previously palladium catalysts are especially sensitive to sulfur which is frequently present

in the fuel. This is most critical with natural gas as fuel whose sulfur content should be controlled to not more than 1 ppm V.

The abatement system must have several essential control features. These features include variability of the preheat temperature, control of the proper fuel to oxygen ratio, and control of the reactor temperature. The power recovery turbine must be protected against overtemperature.

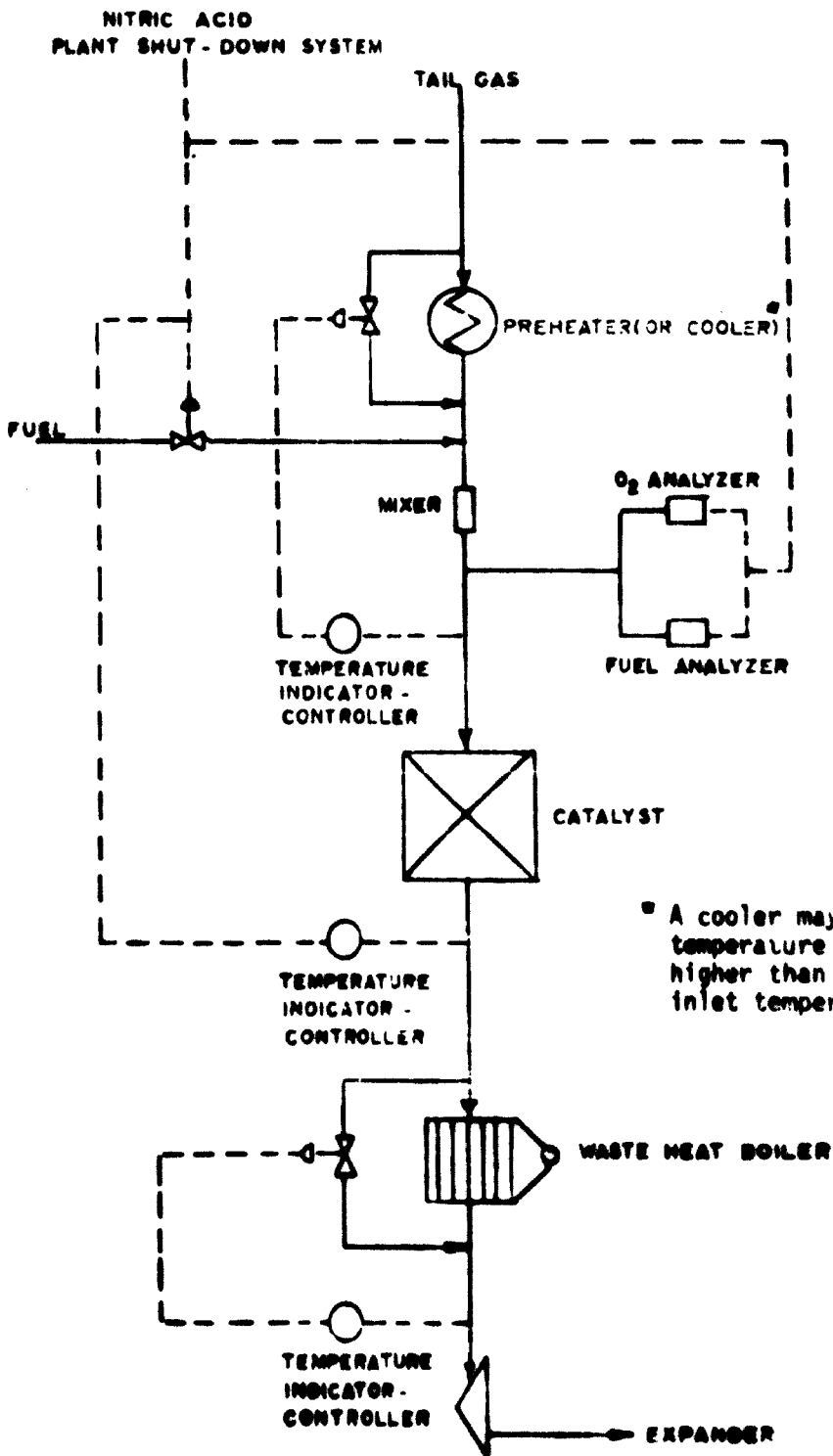
Specific Abatement Designs

In the following four possible abatement system designs are discussed and the economics of a system for a 500 metric ton per day (MTPD) plant.

The first system is simple and is shown schematically in Figure 4. This system uses a single catalyst bed and has the basic abatement control features. The single stage abatement system can be used where the temperature rise across the catalyst bed is less than the difference between the maximum outlet temperature (generally around 800°C) and the "ignition" temperature of the fuel/tail gas mixture. The tail gas is preheated to the desired temperature and fuel is added. A mixer is installed to ensure proper mixing, and the stream is fed to the reactor. The fuel flow is controlled by a fuel and oxygen analyzer/ratio control station which monitors the fuel/oxygen ratio to ensure that an excess of fuel is always present. Downstream of the catalyst bed is a temperature sensing point which provides the input to a control station for the preheat temperature or which will shut off the fuel if the maximum temperature is exceeded. The waste-heat boiler reduces the temperature of the exit stream to a temperature that is acceptable for the power recovery turbine.

Figure 4

Single Stage Abatement System



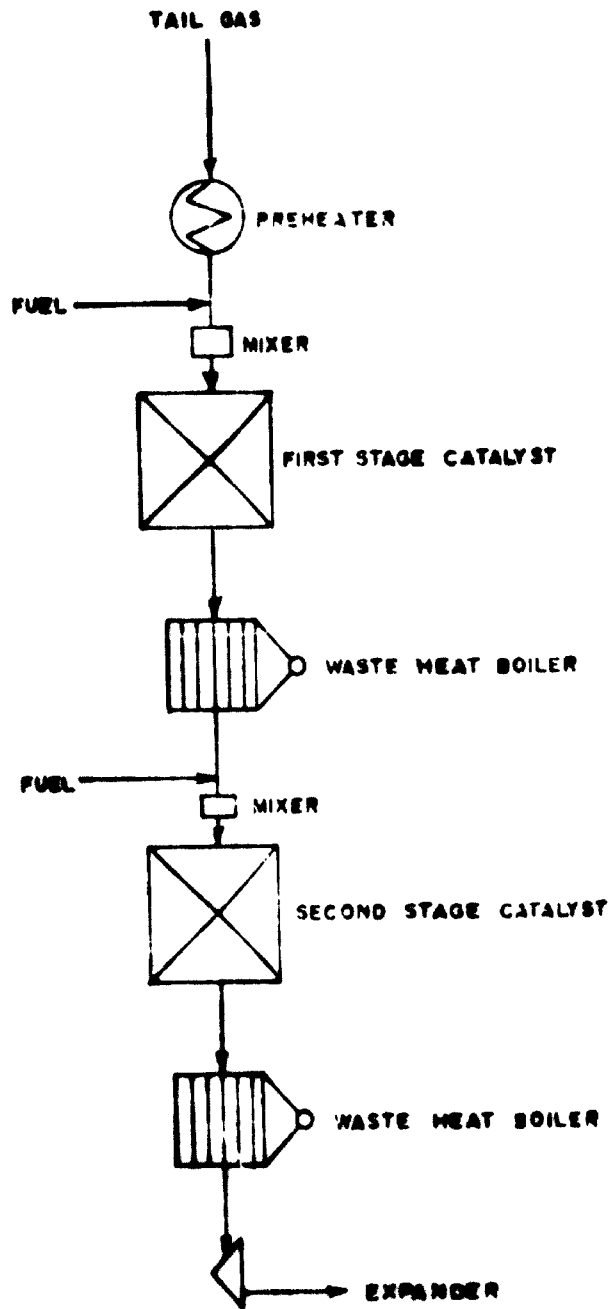
▪ A cooler may be required if the temperature of the tail gas is higher than the desired catalyst inlet temperature.

Different systems are required in cases where the oxygen concentration or the fuel heating value is such that the temperature rise developed in achieving abatement is greater than that which can be tolerated in a single stage system. The first of these equipment configurations is a two-stage unit which has interstage cooling. This system is shown in Figure 5. Again, the tail gas is preheated, fuel is added and mixed. The first stage fuel is added so that only a portion of the oxygen will be consumed. The oxygen concentration and some or all of the NO_2 is reduced to NO in the first stage, and the effluent gases are cooled by a waste heat boiler. A second amount of fuel is added in stoichiometric excess and the mixture is fed to the second stage catalyst. In this stage, abatement is achieved. There is a waste heat boiler to extract heat and to allow the expander to operate within acceptable temperature limits.

Figure 6 shows a variation of the two-stage abatement system (7). Here the tail gas is split, one portion going through a preheater. Fuel is added similarly to the previous example and the mixture is fed to the first stage catalyst. Here, as in the system described in Figure 5, some of the oxygen is consumed and NO_2 reduced to NO . The other portion of the tail gas which was not preheated is added to the effluent gases from the first stage. This cold tail gas cools the effluent from the first stage, more fuel is added in stoichiometric excess, and the mixture passes through the second stage catalyst where abatement is achieved. A waste heat boiler is used to cool the effluent.

The two dual-stage systems that have been described can be designed for reasonably high oxygen concentrations; however, they have certain inherent disadvantages. Generally, two stage abaters require considerable more catalyst than the one stage abaters. A waste heat boiler is employed downstream of the first stage in the

Figure 5
Two Stage Abatement System



case of the system with interstage cooling. In this case the catalyst requirement is twice that required if the reaction could be accomplished in a single stage. Two full-size reactors must be used and two waste-heat boilers of nearly same size must be incorporated. The second design which is shown in Figure 6 has some of the same disadvantages. If twenty percent of the tail gas must by-pass the preheater, and space velocity is the same in both stages, then the first catalyst bed will contain .8 of the catalyst requirement of the second stage resulting in a total catalyst requirement of approximately 1.8 times that which would be required if a single stage could be used, and the reactors will be correspondingly larger by the same factor. Both systems, Figures 5 and 6 require separate controllers for each catalyst stage and an overall coordinating control loop to allow the system to function as a single system.

The recognition of the disadvantages of the dual-stage systems, the high capital cost of these systems, and potential problems that may be inherently present, have led to the development of a new single-stage system with recycle (8). This system, which has been tested in pilot plant operation, is shown in Figure 7. The tail gas is preheated and passes through a recycle ejector. Part of the effluent from the catalyst bed which contains essentially no oxygen or NO_x is mixed with fresh tail gas, and the resultant mixture is fed to the reactor. The mixture is continuously analyzed and the proper fuel flow is set by the analyzer station. The mixture then passes through the catalyst bed which is a single stage and through the waste heat recovery equipment. The required recycle flow is withdrawn prior to the waste heat boiler. The oxygen concentration is monitored and the recycle rate varied to compensate for changes in plant operations. The catalyst bed is always exposed to the full fuel concentration and some of the excess fuel is recycled back to the bed, thus conserving fuel. Compared with the

Figure 6
Two Stage Abatement System with Bypass

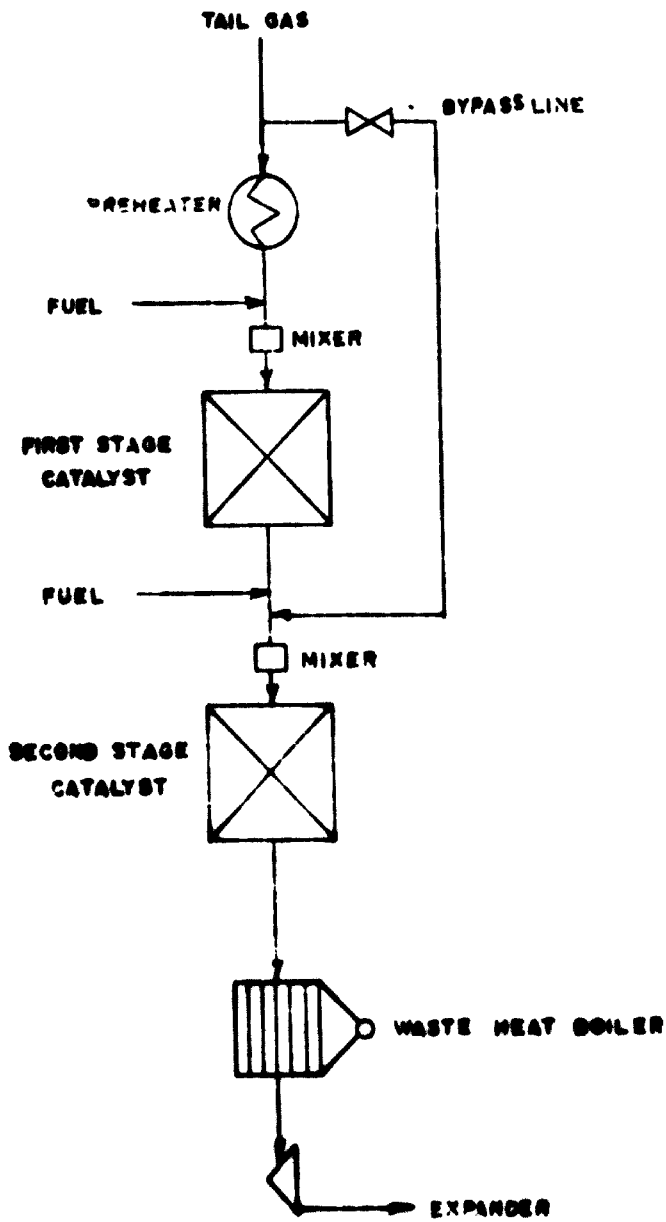
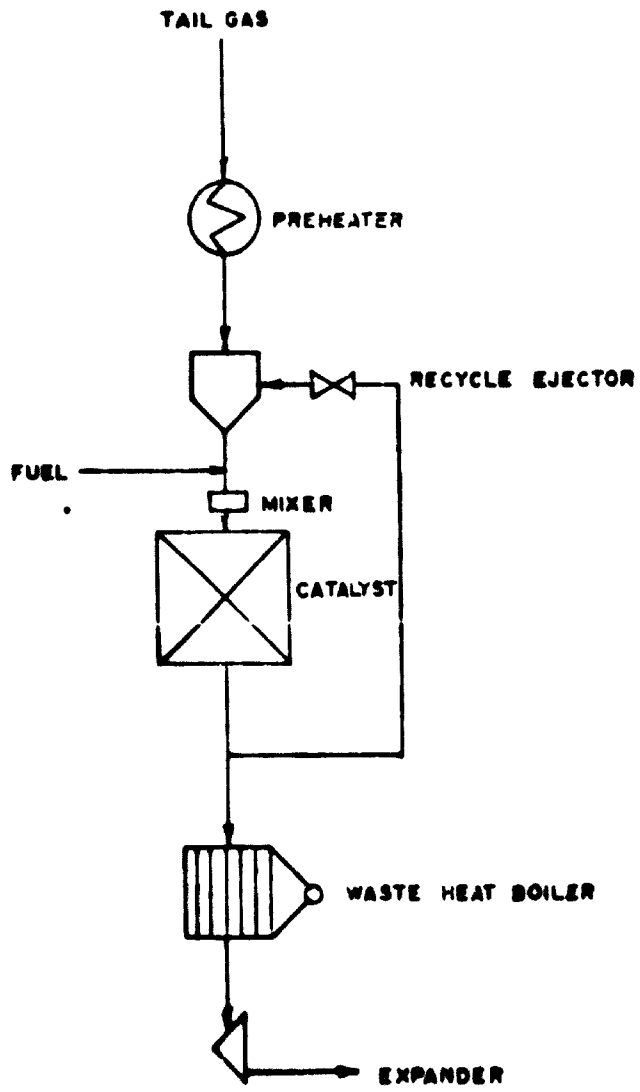


Figure 7
Single Stage Abatement System with Recycle



by-pass dual stage systems previously discussed where 20 percent of the gas was used for cooling purposes, at the same per cent of recycle, the catalyst requirement would be only 1.2 times that which would be required if a single stage could be used with no dilution, instead of 1.8 times in the case of the by-pass system. This leads to economies in the quantity of catalyst that must be purchased and reactor size. Only one waste heat boiler must be purchased. On the other hand, there is some loss of available power in the tail gases due to the pressure drop developed by the ejector recycle pump.

Economics

Selected cost and utility requirements as projected for a 500 metric tons per day plant are shown in Table 4. The basis for the data is as follows. The on-stream rate is 93%. The present price of the catalyst is about \$100 (honeycomb type) per kilogram and its life is two years. Tail gas composition is such that single stage operation can be used, and using natural gas as fuel 56.6 standard cubic meter of fuel are required per ton of nitric acid produced. As can be seen from Table 4, the fuel credit resulting from the generation of steam reduces the net fuel consumption to 16.4 standard cubic meters per ton of acid. This fuel value is utilized in the power recovery of the expander which thus represents the predominant economic benefit from the abatement process.

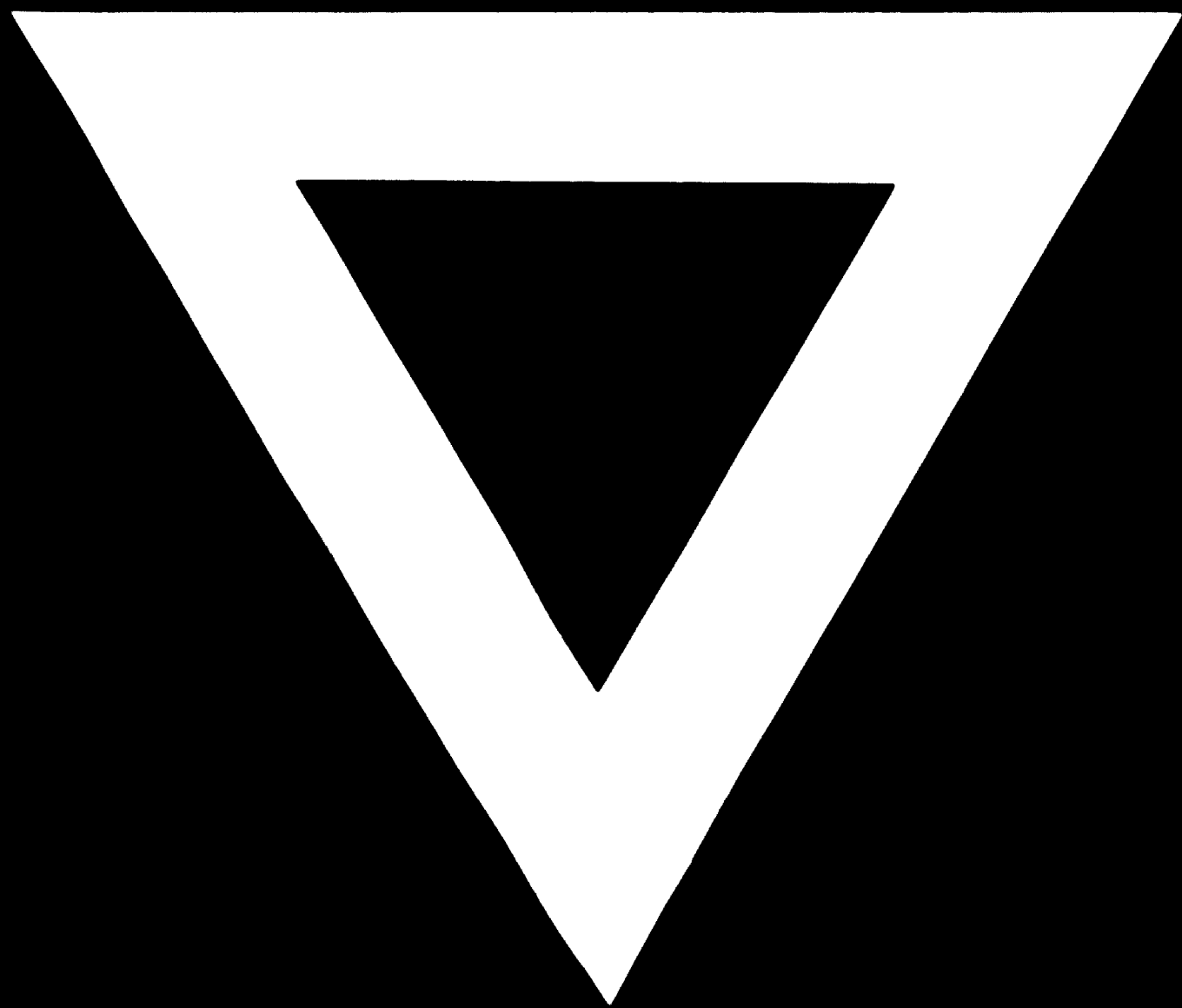
Table 4

Selected Cost and Utility Requirements for a
Catalytic Abatement System (500 Metric Ton
Per Day Plant Capacity and 340 Days Per Year
Operation)

Total erected cost	=	\$624,900
Catalyst Cost (2 yr. life)	=	\$0.17 per ton
Fuel Credit for Steam	=	40.2 standard cubic meters per ton
Fuel requirement	=	86.6 standard cubic meters per ton
Energy extracted in expander	=	9,778 kcal per ton

References

- (1) U. S. Federal Register, No. 247, 36 Part III, December 23, 1971.
- (2) Warsh, A. J. and Romeo, P. L., Recent Advances in Catalytic Processing as Applied to Nitrogen Fertilizer Complexes. Paper presented before the 57th Annual Meeting, American Institute of Chemical Engineers, December 8, 1964, Boston, Mass.
- (3) Malinsky, J., Catalytic Combustion of Methane, Erdoel, Kohle, Erdgas, Petroleum. 1971 24(2), 82.
- (4) Anderson, R. B., Stein, K. C., Feenan, J. J. and Hofer, L. J. E., Industrial and Engineering Chemistry 1961 53, 809.
- (5) Gillespie, G. R., Boyum, A. A. and Collins, M. F., Chemical Engineering Progress 1972 68(4), 72.
- (6) Adhart, O. J., Hindin, S. G., and Kenson, R. E., Chemical Engineering Progress 1971 67(2), 73.
- (7) Newman, D. J., Elimination of Nitrogen Oxides from Gas Streams, U. S. Patent 3,467,492 (1969) Assigned to Chemical Construction Corporation, New York.
- (8) Collins, M. F., and Michalek, R., Purification of Waste Gases Containing Oxides of Nitrogen and Oxygen. U. S. Patent 3,808,323 (1974) Assigned to Engelhard, Minerals and Chemicals Corporation.



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