

A typical nitric acid plant designed and built by C&I Girdler Inc.

Nitric Acid:

Nitric Acid Plant Fume Abaters

For both complete decolorization and low total nitrogen concentration of emissions, pelleted catalysts appear to render better service than either honeycomb platinum or palladium catalysts.

R. M. Reed, and R. L. Harvin,
C&I Girdler Inc., Louisville, Ky.

THE REDDISH BROWN PLUME RISING FROM A typical nitric acid plant vent stack has long been pointed out as a source of air pollution, principally because it is so visible. Actually, the nitrogen oxides in the brown plume are no different from the nitrogen oxides produced in the atmosphere by lightning flashes, which are washed down by rainfall, bringing as much as 10 lb./yr./acre of fixed nitrogen as natural fertilizer. The problem with the nitric acid plant effluent is first, that it can be seen, and second, that it is concentrated. One 500 ton/day nitric acid plant without fume abatement will throw out as much nitrogen oxides in one spot as nature produces in 300 sq. mi. While such concentration could, under certain conditions, result in damage to vegetation and accelerated corrosion of man-made structures, pollution from nitric acid manufacturing units is usually considerably less severe than from many other chemical and metallurgical operations. As a comparison, it has been estimated that automobile exhaust in Los Angeles produces as much nitrogen oxides as would be emitted by sixty 1,000 ton/day nitric acid plants without fume abatement.

Two different techniques are in general use for dealing with the nitric acid plant tail gas fume problem. The first of these is decolorization of the gas stream by high temperature catalytic reduction of the brown NO_2 to colorless NO by use of a reducing gas such as hydrogen or methane. This has proved satisfactory in locations where there are no stringent limitations on the concentration of NO that may be discharged. Where such limitations exist (i.e., 200 ppm or less of total nitrogen oxides in the effluent stream), the second technique is used. In this case, the catalytic reduction is carried to a greater extent to produce N_2O . This, however, requires considerably more drastic operating conditions than the decolorization, since the oxygen in the gas must be reduced before the nitrogen oxides can all be reduced to nitrogen.

For decolorization, there are two types of catalyst in general use. The first is the honeycomb catalyst, in which a platinum or palladium catalyst is impregnated on a ceramic support in the shape of a honeycomb which provides a large surface area, and permits gas flow with a low pressure drop. The second type of catalyst is a conventional pelleted catalyst, usually platinum or palladium on a ceramic support. The pelleted catalyst requires a higher pressure drop than the honeycomb, but has been found to have a longer operating life, and can be used under a wider range of conditions than the honeycomb catalyst.

Operation of the fume abater is greatly simplified if a source of hydrogen containing gas, such as ammonia plant purge gas, is available, for the catalytic unit will operate with an inlet temperature as low as 400°F, whereas with natural gas as reducing agent, the reaction may not take place below a temperature of 800- to 950°F. This results in a gas exit temperature of 1,400°F or higher for complete abatement, which may cause the catalyst life to be very short.

Problems with honeycomb catalysts

C&I Girdler's recent experience has been that it is difficult to obtain complete nitric acid plant tail gas decolorization with the available brands of honeycomb catalysts, when natural gas is used as the reducing agent in the catalytic unit. In one plant, the design for a single stage unit with honeycomb catalyst specified an inlet temperature of 875°F and an exit temperature of 1,250°F, when decolorizing a tail gas containing about 0.25% nitrogen oxides and 3% oxygen, with an expected fuel efficiency of above 90% (fuel used to obtain the required temperature rise). The catalyst manufacturer had supplied the design of the complete installation, and guaranteed its performance.

When the plant was placed in operation, it was found that the inlet temperature had to be increased to about 905- to 960°F to maintain reduction, and that even with 136% of the design natural gas usage, the exit stack gas was still colored, and the exit temperature was only 1,100°F instead of 1,250°F. After struggling with the unit for four months without success, the catalyst manufacturer acknowledged the failure of the unit to meet guarantees, and withdrew its catalyst. After reviewing the process conditions, a second catalyst manufacturer felt that their catalyst would perform, and agreed to supply a new charge. Unfortunately, its performance was no better than that of the original charge.

After a month, suspecting a defective batch, the second supplier decided to replace the catalyst with another charge. Again there was no improvement. The required inlet temperature was too high, the outlet temperature was too low, and the fuel usage was much too high (fuel efficiency about 20- to 30%).

At this point the piping to the abater was revised to provide an axial inlet gas flow with a distributing baffle. This gave a slight improvement in fuel efficiency, but did not improve the temperature conditions or give decolorization.

Operating data taken over a period of 1 yr. showed an average inlet temperature of 973°F, an average outlet temperature of 1,072°F, and an average temperature at the inlet of the power recovery turbine of 1,110°F, with fuel efficiencies ranging from 19- to 43%.

The temperature at the inlet of the power recovery turbine varied from zero to as much as 100°F higher than the temperature at the exit of the fume abater. This indicated that further reaction was occurring at times in the exit pipe, which was undesirable, since it caused substantial temperature fluctuations at the inlet to the power recovery turbine.

After the last batch of honeycomb catalyst had been in use for four months, the vessel was opened and the catalyst was inspected. It was reported to be normal in

appearance, with no catalyst breakage, and no indication that gas might be bypassing the catalyst. Activity tests made by the catalyst supplier indicated that the activity was normal. However, the actual performance of the unit was not satisfactory. During the year that this catalyst was in service, the inlet temperature needed to sustain reaction increased from 900- to 960°F or higher, indicating some loss of activity.

The final solution to the fume abater problem in this plant was replacement with a new fume abater unit using a pelleted catalyst. With this unit, the inlet temperature was maintained at 1,000°F, and the exit temperature was about 1,200°F. The fuel efficiency was somewhat above 80%, and there was no temperature rise between the fume abater and the power recovery turbine inlet. A substantial improvement was obtained in the decolorization of the stack. The high inlet temperature was not required to initiate the reaction, but resulted from other causes. It was estimated that this could be reduced to 900°F and still obtain reduction.

A third brand of honeycomb catalyst was used in another fume abater, also operating with natural gas. In this case, a tail gas containing 4% oxygen and 0.24% nitrogen oxides was to be treated to obtain a colorless stack. Design conditions were 900°F for inlet temperature, 1,110°F for exit temperature, and a 75% efficiency after 1 yr. when using natural gas. On initial operation, it was found that an inlet temperature of 960°F was required in order to get appreciable reaction, with a natural gas input about twice the design flow. At an inlet temperature of 910°F, the exit temperature was 935°F, indicating very little reaction. After many tests, including catalyst changes, and varying operating procedural changes in accordance with recommendations of the catalyst manufacturer, it has been concluded that, in order to get satisfactory decolorization and reasonable fuel efficiency, the amount of honeycomb catalyst must be increased, and the unit operated with inlet and outlet temperatures of 1,000- and 1,350°F, with the exit gas being cooled down to 1,100°F in a waste heat boiler before entering the power recovery turbine.

Granular or pelleted catalysts

For many years, granular or pelleted catalysts have been available for reacting nitrogen oxides with reducing gases. Three types are available commercially at present. Catalysts and Chemicals, Inc. offer their tableted C-53 platinum hydrogenation catalyst, Chemetron's Catalyst Division has a pelleted platinum catalyst, G-43, and Englehard Industries offer a spherical palladium catalyst, their DS 4/8 (formerly DS 1/4). All three of these catalysts are in commercial use, and reports of satisfactory operation have been obtained. They appear to be capable of long operating life, reports having been received of catalysts in service for 7 yr. or more.

With natural gas, the manufacturers recommend inlet temperature of 800- to 1,000°F, with at least 200°F temperature rise being required for decolorization, while complete reaction of the oxygen and nitrogen oxides is required for total abatement. A temperature rise of about 230°F is obtained for each per cent of oxygen and nitrogen oxides reacted.

In certain designs, the outlet temperature is limited by the allowable temperature into a turbine expander, and in others the catalyst may pose a limitation. When operating conditions would result in an excessive temperature rise in the abater, means must be provided for intermediate cooling.

In one of the first units using Chemetron's G-43 platinum catalyst, which went in operation in 1958 (1), this was accomplished by using two beds of catalyst, in series, with provision for by-passing part of the tail gas around the first bed to cool the gas entering the second bed, with separate natural gas feed to the two beds. This unit was installed primarily to heat tail gas from 650- to 1,200°F before entering a power recovery turbine, so a

second by-pass was provided around both beds to cool the exit to 1,200°F. It was found that decolorization was obtained when 1,200°F tail gas was supplied to the turbine. Nitrogen oxide removal as high as 90% was obtained in the gas leaving the second bed, with bed temperatures about 900- in and 1,300°F out of each bed. The lowest operable inlet temperature using natural gas was 750°F, with 125% excess natural gas required. At 1,050- to 1,100°F inlet temperature, the unit operated with no excess methane required. When ammonia plant purge gas containing hydrogen was used instead of natural gas, the unit operated satisfactorily with an inlet temperature of 550°F.

A similar two-stage process with by-passed tail gas being used for cooling the second catalyst bed has recently been announced (2). Inlet temperatures of 900°F to both beds are used with natural gas, with the exit temperature from the second bed being about 1,250°F. It was stated that this process would remove both the red-orange nitrogen dioxide and the colorless nitric oxide.

Another unit using Chemetron's G-43 catalyst was designed primarily for fume abatement (1). The unit has operated successfully since 1958, and has met the requirements of Orange and Los Angeles Counties in California. A catalyst service life of 7 yr. has been reported. The design was based on a single catalyst bed with natural gas fuel, an inlet temperature of 800°F, and an outlet temperature above 1,400°F.

Various other methods have been used for controlling the temperature rise to avoid overheating the catalyst, such as a waste heat steam boiler to cool the gas between beds, as well as a direct water quench.

A number of patents have been issued on other methods for removing nitrogen oxides from gas streams, but few have found any commercial use. These other methods include adsorption with molecular sieves, chemical reaction with urea or ammonia to convert nitrogen oxides to nitrogen and absorption with ammonia, caustic soda or lime.

In conclusion

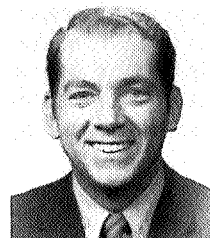
Obviously, when designing and building plants, contractors are normally governed by their own experiences with previous installations and equipment. At the present time, if both complete decolorization and low total nitrogen oxide concentration are required, C&I/Girdler would select pelleted catalysts. It is possible that other contractors on the basis of different experiences could make a different selection. Because of their lower cost, honeycomb platinum or palladium catalysts may prove attractive for applications where ammonia purge gas or some other hydrogen-bearing gas can be used in the fume abatement unit. #

Literature cited

1. Cronan, C.S., *Chem. Eng.*, 66, 66 (January 12, 1959).
2. Anon., *Chem. Eng.*, 76, 64 (October 20, 1969).



R. M. Reed is an engineering consultant, specializing in synthetic nitrogen fertilizers, gas purification and hydrogen manufacturing. He holds a number of patents and has published numerous articles in these fields. He obtained a Ph.D. degree at the University of Washington, and retired in 1969 as technical director of C&I/Girdler Inc.



R. L. Harvin is director of commercial development, C&I/Girdler Inc. He received his B.Ch.E. and M.Ch.E. degrees from the University of Louisville and his Ph.D. from the University of Florida. His experience includes process engineering, research and development, and environmental control. He is a registered professional engineer in Florida.

DISCUSSION

Q. In using natural gas for firing one of these abaters, how far down do you have to take the sulfur and how would you suggest getting it there?

REED: I would believe that the natural gas should be taken down to the same degree of purity that you use in feeding a primary reformer. In other words, down to a matter of very few parts per million because these catalysts are susceptible to sulfur.

Q. In other words, if we could take it down to less than a part per million sulfur it should be adequate.

REED: Oh, yes, I would say so.

Q. Very good. In abating down to a level of, say, around 200 parts per million NO_x max, what would you say would be the minimum abater outlet temperature you could operate to take it to about that level?

REED: I think as was mentioned that about a minimum temperature rise of around 200 degrees at least would be required to get satisfactory heat colorization.

Q. But how about, say, taking it down below the decolorization level, down to, say, about, less than - say, 200 parts per million?

REED: I would think there that it would be necessary to probably go up to 1400 degrees or something like that.

Q. What would be, say, the minimum practical operating temperature inlet to sustain burning methane at some reasonable efficiency?

REED: The catalyst manufacturers I believe are currently reporting a minimum inlet temperature of 800 degrees. Some operating experience that we have had contact with indicates that while this low a temperature may be attainable with the new catalyst, it in some instances has - the catalyst has shown some aging, and inlet temperatures have had to be increased somewhat above that. So that again is a question I would prefer to defer to the catalyst manufacturers for their recommendations and guarantees.

Q. I noticed in some of your data, you reported firing up to say 1350 and then cooling to 1100 before you went to a power recovery device. Is that for the protection of the device, or is that to prevent a shift in equilibrium?

REED: For the protection of the device. It's simply a case in which the power recovery turbine temperature is limiting. As far as we know, there is no shift occurring in the short time that this material is at this temperature.

Q. What were the space velocities in these three examples, and what were the actual percents of oxygen in these three examples that failed?

REED: The question was concerning the space velocities in these cases that we mentioned, and as I recall the space velocities were roughly in the range of 100,000. That is the space velocity, I believe, that is normally used (somewhere in that range) with the honeycombed type catalyst. The oxygen contents varied between about 2 1/2 to 3 1/2 %, somewhere in that range. They were, as far as we knew, completely nitric acid plant tail gas. There was nothing unusual, and we checked with quite a number of other companies that were using similar catalysts. In many instances they were obtaining performances which appeared to be considerably better than what was being obtained in these plants. To date there has not been any complete satisfactory explanation of the differences in performance.

We're merely reporting what happened to us, and we really don't know all the answers other than that we do not know of any special circumstances that would have made these less favorable than others.

BOB KROEHLING, DuPont Co.: I have a series of questions based on some of the comments you made in your paper. Bob just mentioned something about oxygen contents, and you mentioned 3% here in that first example. Is it possible that in the early days of the operating of that plant the oxygen content was quite a bit over 3%?

HARVIN: I believe not. There were quite a few analyses made at various times, and variations in oxygen content were made deliberately in some cases for other reasons in the plant. But I think in general it was in that range. It may have at times gone up as high as 4% but it's been some little time since I looked at those figures, so I'm not quite sure.

KROEHLING: At another point you mentioned that the design of the abater was altered so that the inlet was put on an axial direction, and you mentioned that this gave a slight improvement in fuel efficiency. How slight?

HARVIN: I think that where previously it had been running from, oh, say, 15 to 30, I think some of the results went up to 40 or a little higher, per cent fuel efficiency.

KROEHLING: I had heard through plant contacts that it doubled from 20 - 25% efficiency to 40 - 50% efficiency.

HARVIN: Well, 15 to 30.

KROEHLING: Indicating that the design of the reactor is quite important.

HARVIN: It's a factor all right.

KROEHLING: Another question. After you went over to the pelleted catalyst and the new reactor, at what space velocity was it operated? Versus the 100,000 and over at which we understand the honeycomb type catalysts were operated?

HARVIN: I'm speaking here strictly from memory, but as I recall the space velocities used with that type of catalyst would be in the range of somewhere around 40,000. So it is quite a bit lower than done with the other catalyst.

KROEHLING: At that point in the paper you mentioned that there was a substantial improvement in the decolorization. Was color completely removed? Or was there any color left at all?

HARVIN: Not completely removed.

KROEHLING: You mentioned also that the 1000°F. degree inlet temperature on that job was not required to initiate the reaction, but was the result of other causes. What were these causes?

HARVIN: These were simply considerations within the heat utilization in the plant.

KROEHLING: I'd like to make a comment about the whole idea of honeycomb catalysts; that is that there is an important need to learn how to operate with honeycomb catalysts. That is, you have to provide sufficient mass transfer. I see no comment about mass transfer characteristics of the pelleted catalyst or honeycomb catalyst in their particular volumes, one being used at perhaps one fourth the volume of the other. I'd like to comment that if properly designed (and unfortunately many of the honeycomb catalysts have been utilized in the existing equipment where there was no opportunity to change the design), taking into consideration the low pressure drop characteristics of the honeycomb catalysts, the catalyst bed must have a relatively narrow cross section and a deep configuration to provide the turbulence or mass transfer characteristics that are necessary to get the job done.

HARVIN: Thank you. That's probably good advice. The cases we cited here all were designs approved by the

honeycomb suppliers, and that's the way it turned out.

DAN NEWMAN, Chemical Construction Corp.: We've suffered with catalysts and catalytic combustors even longer than C&I, and suggest the obvious conclusion that it's rare that you get the same new catalyst twice. Catalyst manufacture is not quite the science it should be as yet, so it is necessary to design plants well beyond the supplier's minimum criteria. There are many things that have been said that should be commented on but I don't want to go over the paper in any detail. I would like to mention one point.

In this country, we do have three Dual Combustion systems operating with honeycomb catalyst for total abatement, that is, with less than five hundred parts per million of NO_x in the tail gas. In addition we have another half a dozen Dual Combustors operating on honeycomb throughout the world, although, not necessarily on full abatement since local requirements aren't that severe as yet.

Chemico will offer combustors with either type of catalyst and we don't believe there should be a decision as yet to eliminate the honeycomb from consideration. In so far as life expectancy is concerned, the first honeycomb in a nitric acid plant was the one we installed at Phillips in 1964 for heat recovery and decolorizing. It has run for eight years so far, which isn't a bad record for any catalyst.

REED: Are these combustors using hydrogen or natural gas for fuel?

NEWMAN: I'm sorry, I should have stated that I was only talking about natural gas as a fuel. As one of the vendors has often said, hydrogen can practically burn on hot rocks. It's methane that's hard to burn in these applications.

ASMUND BOYUM, Engelhard Industries: I'd like to make a comment in support of some of the earlier remarks that have been made here. In a way, I'm surprised that such general conclusions have been derived from a test done in a single plant, when there are many honeycomb decolorizers that are working successfully in industry. For instance, in the test cited, a fixed bed operation with pelleted catalyst at higher inlet temperature and lower space velocity was compared with honeycomb at a lower inlet temperature and higher space velocity. This comparison is clearly unfair. In addition, it was admitted that mixing or the location of

the fuel injection point had a significant effect on decolorization.

Another thing, I was surprised that the temperature rise in the abater was smaller than the temperature rise from the abater to the turbine where one supposedly has no catalyst. This would indicate to me that there were certain design problems in the reactor.

Now from these tests to make the conclusion, the general conclusion, that pelleted catalyst is better than honeycomb catalyst is, I think, stretching the test's slope. One more thing, the 1400°F that was necessary for abatement, I assume you mean it was required for your catalyst, you don't intend this, do you, to be a general statement about all catalysts?

HARVIN: Assume which -

BOYUM: That 1400°F that was stated as necessary for abatement, I assume that applies to Girdler's catalyst and should not be taken as a general statement.

HARVIN: Well, in regard to our general conclusions, this of course is not a final conclusion on our part. We are always open to new evidence. We are certainly guided by our most recent experience, and any time we see new evidence come along we can always modify this. So you speak of a sweeping generalized conclusion; it isn't final, certainly.

BOYUM: In terms of mass transfer, was the possibility ever looked into of igniting the gas before going into the abater or the decolorizer to make sure that you get the temperature of the catalyst up to near adiabatic flame temperature?

HARVIN: I don't believe there was.

BOYUM: What my last question refers to is if mass transfer is controlling - as was indicated earlier - that means that the catalyst temperature could be set by the adiabatic flame temperature rather than by the temperature of the gas itself; And therefore, it would be very important to get to a point where one does have a good fuel efficiency to get the catalyst up in temperature. When you talk about 15% fuel efficiency, my suspicion is you never reached that point.

HARVIN: Well, that could very well be, but there is—as mentioned—the fact the feed stream was preheated over 900 degrees, and even then the apparent degree of reaction was quite small.