

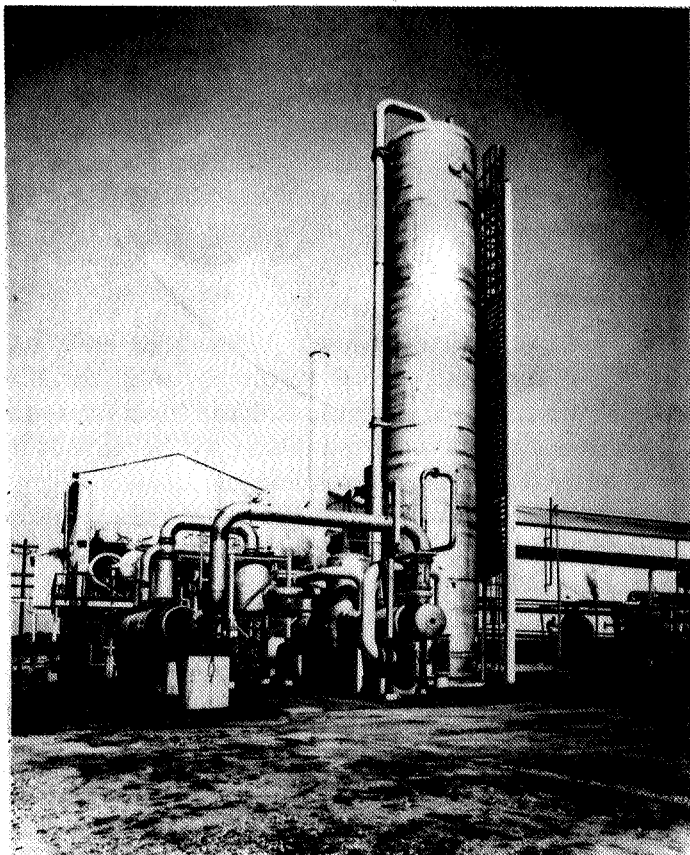
Nitric Acid Plant Emission Standards - A Compliance Problem

About 175 nitric acid plants are presently unable to comply with federal regulations regarding emission levels. Achieving this compliance will take a great deal of effort and money.

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Probably the most significant recent development in the nitric acid manufacturing industry occurred in 1971 when the U.S. Government established standards and regulations covering pollution in the form of NO_x from nitric acid plants. The standards are applicable to both existing and new plants (1, 2, 3).

The impact of the regulations and standards on the nitric acid industry is both unparalleled and unprecedented as to capital investments required over a very short period of time. This article will examine the effect of the standards and regulations on the industry.



About six months of work is required to adapt an existing nitric acid plant so that it complies with the U.S. Government emission standards.

U.S. Government Standards

Two separate standards have been established by the U.S. Government. One of these standards is for existing nitric acid plants, while another has been established for new plants.

The standard established for existing plants requires that the emission of nitrogen oxides, calculated as nitrogen dioxide, be limited to 5.5 lb./ton of 100% acid produced (1). This emission limitation is about equivalent to a nitrogen dioxide concentration of 400 parts/million by volume. The regulations appear to indicate that this standard must be met by existing plants no later than August, 1975.

The U.S. Government standards for new nitric acid plants (a plant on which the construction is to commence after December 23, 1971) must limit the emission into the atmosphere of nitrogen oxides to not in excess of 3 lb./ton of 100% acid produced, expressed as nitrogen dioxide. This emission level is approximately 200 parts/million of NO_x expressed as nitrogen dioxide.

Exact and precise information on the number of nitric acid plants operating in the U.S., and the annual production of each plant, is difficult to assemble. It appears that there are approximately 190 plants existing in the U.S. Approximately 15 of these plants are equipped to comply with the U.S. Government standards (4). Approximately 60 additional plants are equipped with catalytic decolorizers, but are not equipped to comply with the standards (4). This information means that approximately 175 plants exist in the U.S. that cannot now comply with the standards.

Nitric Acid Manufacture

In a typical nitric acid plant built within the past 15 yr., nitric acid is synthesized based on the oxidation of ammonia to nitrogen dioxide and absorbing this material in water to form nitric acid. The other raw materials for manufacturing nitric acid are air and water.

The process scheme usually employed incorporates the filtration of atmospheric air prior to compression in a

centrifugal compressor. The compressor can be driven by one or more types of prime movers including a hot gas expander, steam turbine, and electric motor. Ammonia is vaporized, superheated, and filtered, after which it is mixed with the compressed air stream. Both of these raw materials are carefully metered to the mixer to provide proper proportions of each to obtain high yields.

The combined ammonia-air mixture passes over a catalyst, usually platinum-rhodium and burns very rapidly to form nitric oxide and water vapor. The hot reaction products exit the catalyst, pass through a waste heat boiler and one or more additional heat exchangers where the process gas is cooled, while at the same time recovering heat by the generation of steam and recovering power by heating the tail gas for use in the hot gas expander.

The partially cooled process gas from the heat exchanger system enters the cooler condenser where most of the water formed during the burning of the ammonia is condensed. Part of this reacts with the nitrogen dioxide to form weak nitric acid which is separated from the gas and transferred to the absorber tray which most nearly matches it at the concentration. Process gas leaving the cooler condenser enters the absorber where nitrogen dioxide reacts with water fed to the top of it resulting in the formation of product acid.

Process gas leaving the top of the absorber contains a quantity of nitrogen oxides in excess of those allowed by the U.S. Government standards. This gas passes through one or more heat exchangers where it is heated either to the temperature required by the hot gas expander or to a temperature satisfactory for introduction to a catalytic tail gas reaction system. The typical catalytic reaction system installed in the U.S. utilizes a fuel to react with the residual oxygen in the tail gas stream, thereby increasing the temperature of the tail gas to that which is required for the hot gas expander. The hot gas expander recovers all or part of the power required to drive the centrifugal air compressor.

Most of the existing nitric acid plants equipped to meet the Government standards for emissions from them employ a catalytic abatement system. It is not the purpose of this article to examine the various systems available to the industry for abatement. Such system can be obtained from several suppliers.

Each abatement system employs a reaction system involving a reaction between the oxygen and the fuel to eliminate free oxygen and, after completing this step, providing for the reaction between NO_x and fuel to produce a tail gas substantially free of oxides of nitrogen (5).

Nitric acid plants are available from suppliers with abatement systems to meet the U.S. Government standards and have been demonstrated according to an EPA publication (6). The further examination of the effect on the nitric acid industry is based on employing catalytic abatement systems.

What to do

Based on the current status of the standards and regulations, it appears that nitric acid manufacturers,

assuming the continued existence of a market for products made therefrom, are faced with two possible choices: they can either purchase a new plant which will comply with the emission standards, or they can modify the existing plant so as to cause it to comply with the standards for existing plants.

The Weatherly Co., and this is probably true for all other nitric acid plant designers, is constantly called upon to render an opinion concerning how a specific nitric acid manufacturer can comply most economically with the standards. This implies, and usually gets around to the question as to whether or not it is more economical to fix up an existing plant than to purchase a new one. There is no clear answer to this question that is universally applicable.

We undertook a study to obtain a general answer to this question. Shown in Table 1 is an analysis of the factors that affect the cost of producing nitric acid which should be considered in connection with NO_x abatement in a new plant built in 1972. Included in Table 2 is a comparable cost in a plant built in 1962 without NO_x abatement facilities. Table 3 sets forth the cost of producing nitric acid in the 1962 plant when catalytic type NO_x abatement facilities are added to it.

All of the costs and quantities shown in the tables are only relative and do not necessarily apply to any existing plant nor any plant currently under construction. Since this is the case, the only conclusion that should be drawn from the tables is that the cost of manufacturing nitric acid in the 1972 model plant is less than in an older plant such as the 1962 model. It is much easier from an engineering standpoint, in our opinion, to design a new plant to meet the emission standards than to attempt to modify an existing facility. Each existing plant must be carefully studied, and probably the method exemplified in Tables 1, 2, and 3 is applicable, utilizing cost information peculiar to the existing site in order to arrive at a satisfactory answer to the question; What do I do?

Conclusions

It appears that approximately 175 existing nitric acid plants are currently unable to comply with the U.S. Government standards governing emission levels from such plants. Major efforts and expenditures will be required by the industry to meet the current deadline.

The capacity of engineering contractors and specialized suppliers of the equipment and catalyst for nitric acid plants has never been asked to fill such a major requirement in such a short time. Approximately 15 months are required from the time an order is placed until a new nitric acid plant can be placed in operation. Approximately six months is required to carry out a modification program to an existing plant. These times indicate deadline for the nitric acid manufacturers concerning when they must decide what they will do about complying. #

Literature cited

1. Federal Register No. 158, Part II (August 14, 1971).
2. Federal Register No. 67, Part II (April 7, 1971).

**Table 1. Cost of producing nitric acid (300 ton/day plant
built in 1972 – NO_x abatement included).**

<u>Raw Material & Catalyst</u>	<u>Unit</u>	<u>Quantity</u>	<u>Cost/Unit</u>	<u>Cost/Ton</u>
Ammonia	Tons	0.290	\$35.00	\$10.15
Abatement Catalyst	Dollars			0.15
Utility Consumption				
Cooling Water	thousand gal.	20.502	0.41
Steam	Export thousand lb.	2.430	0.92	(2.24)
Electricity	Kw.-hr.	3.00	0.010	0.03
Fuel	1 x 10 ⁶ Btu.....	1.75	0.650	1.14
Other Cost				
Maintenance				\$ 0.49
Depreciation				1.31
Operating Labor				0.20
				<u>\$11.64</u>
Basis				
Investment	\$2,000,000			
Production	102,000 ton/yr.			
Maintenance	\$50,000/yr.			
Depreciation	15 yr.			
Operating Labor	2,000 man-hours/yr. at \$10,00/hr.			

**Table 2. Cost of producing nitric acid (300 ton/day
plant built in 1962 – without NO_x abatement).**

<u>Raw Material & Catalyst</u>	<u>Unit</u>	<u>Quantity</u>	<u>Cost/Unit</u>	<u>Cost/Ton</u>
Ammonia	Tons	0.2998	\$35.00	\$10.49
Utility Consumption				
Cooling Water	thousand gal.	34.0	0.02	0.68
Steam	Import thousand lb.	0.610	0.92	0.56
Electricity	Kw. hr.	6.00	0.01	0.06
Other Cost				
Maintenance				0.71
Depreciation				1.18
Operating Labor				0.86
				<u>\$14.54</u>
Basis				
Investment	\$1,800,000			
Production	102,000 ton/yr.			
Maintenance	\$72,000			
Depreciation	15 yr.			
Operating Labor	8,760 man-hours/yr. at \$10.00/hr.			

Table 3. Cost of producing nitric acid (300 ton/day plant built in 1962 – NO_x abatement added 1972).

<u>Raw Material & Catalyst</u>	<u>Unit</u>	<u>Quantity</u>	<u>Cost/Unit</u>	<u>Cost/Ton</u>
Ammonia	Tons	0.2998	\$35.00	\$10.49
Abatement Catalyst				\$ 0.15
Utility Consumption				
Cooling Water	thousand gal.	34.00	0.02	0.68
Steam	Export thousand lb.	1.090	0.92	(1.00)
Electricity	Kw. hr.	6.0	0.01	0.06
Fuel	1 x 10 ⁶ Btu.	1.75	0.65	1.14
Other Cost				
Maintenance				\$ 0.88
Depreciation				1.47
Operating Labor				<u>0.88</u>
				\$14.75
Basis				
Investment	\$2,200,000			
Production	100,000 ton/yr.			
Maintenance	\$88,000			
Depreciation	15 yr.			
Operating Labor	8,760 man-hours/yr. at \$10.00/hr.			

3. Federal Register No. 247, Part II (December 23, 1971).
4. Private communication to the author.
5. Gillespie, G.R., A.A. Boyum, and M.F. Collins, *Chem. Eng. Progr.*, 68, 72 (April 1972).
6. "Background Information for Proposed New-Source Performance Standards." EPA, Research Triangle Park, N.C. (1971).

DISCUSSION

ANON: It is mentioned in the literature that urea is used for the complete removal of nitrogen oxide from nitric acid plant tail gas. Is there any advantage in the U.S.A. in using this process?

WEATHERLY: No plant in the U.S.A., to the best of my knowledge, is using urea to destroy oxides of nitrogen in nitric acid plant tail gases.

ED JOHNSON, Allied Chemical: What do you think of the possibilities of using refrigerated absorbers as an interim measure in meeting the emission standards for existing nitric acid plants?

WEATHERLY: The current EPA standard for emission from existing nitric acid plants is equivalent to approximately 400 ppm of NO_x. It is technically feasible to meet this standard by adding a refrigerated absorber system to existing plants. The capital investment for this addition to a 300 TPD plant may be approximately \$500,000. The increased operating cost of such a system will probably be in excess of \$1.00 per ton of nitric acid.

TOM SEGAR, St. Paul Ammonia Products, Inc.: Recently the EPA found that the nitrogen oxides in the ambient air are not as high as they originally predicted. Will this delay the implementation of our NO_x abatement program?

WEATHERLY: I have recently talked to EPA about this. They advise me that the question was raised because of test procedure utilized to determine the NO_x content in the atmosphere. They are currently rechecking the data previously obtained and checking on test methods that may be more satisfactory than the previous method. I was advised that such current work will have no effect on the emission standards for nitric acid plant tail gases.

CROMEANS: I think this is a subject that we'll be coming back to in another year. These emission standards will have to be met. The industry's having problems meeting them at present. There will be substantial expenditures required by the nitric acid manufacturers to meet them.



WEATHERLY, D. M.