

8.8 Nitric Acid

8.8.1 General¹⁻²

In 1991, there were approximately 65 nitric acid (HNO₃) manufacturing plants in the U. S. with a total capacity of 11 million tons of HNO₃ per year. The plants range in size from 6,000 to 700,000 tons per year. About 70 percent of the nitric acid produced is consumed as an intermediate in the manufacture of ammonium nitrate (NH₄NO₃), which in turn is used in fertilizers. The majority of the nitric acid plants are located in agricultural regions such as the Midwest, South Central, and Gulf States because of the high demand for fertilizer in these areas. Another 5 to 10 percent of the nitric acid produced is used for organic oxidation in adipic acid manufacturing. Nitric acid is also used in organic oxidation to manufacture terephthalic acid and other organic compounds. Explosive manufacturing utilizes nitric acid for organic nitrations. Nitric acid nitrations are used in producing nitrobenzene, dinitrotoluenes, and other chemical intermediates.¹ Other end uses of nitric acid are gold and silver separation, military munitions, steel and brass pickling, photoengraving, and acidulation of phosphate rock.

8.8.2 Process Description^{1,3-4}

Nitric acid is produced by 2 methods. The first method utilizes oxidation, condensation, and absorption to produce a weak nitric acid. Weak nitric acid can have concentrations ranging from 30 to 70 percent nitric acid. The second method combines dehydrating, bleaching, condensing, and absorption to produce a high-strength nitric acid from a weak nitric acid. High-strength nitric acid generally contains more than 90 percent nitric acid. The following text provides more specific details for each of these processes.

8.8.2.1 Weak Nitric Acid Production^{1,3-4}

Nearly all the nitric acid produced in the U. S. is manufactured by the high-temperature catalytic oxidation of ammonia as shown schematically in Figure 8.8-1. This process typically consists of 3 steps: (1) ammonia oxidation, (2) nitric oxide oxidation, and (3) absorption. Each step corresponds to a distinct chemical reaction.

Ammonia Oxidation -

First, a 1:9 ammonia/air mixture is oxidized at a temperature of 1380 to 1470°F as it passes through a catalytic convertor, according to the following reaction:



The most commonly used catalyst is made of 90 percent platinum and 10 percent rhodium gauze constructed from squares of fine wire. Under these conditions the oxidation of ammonia to nitric oxide (NO) proceeds in an exothermic reaction with a range of 93 to 98 percent yield. Oxidation temperatures can vary from 1380 to 1650°F. Higher catalyst temperatures increase reaction selectivity toward NO production. Lower catalyst temperatures tend to be more selective toward less useful products: nitrogen (N₂) and nitrous oxide (N₂O). Nitric oxide is considered to be a criteria pollutant and nitrous oxide is known to be a global warming gas. The nitrogen dioxide/dimer mixture then passes through a waste heat boiler and a platinum filter.

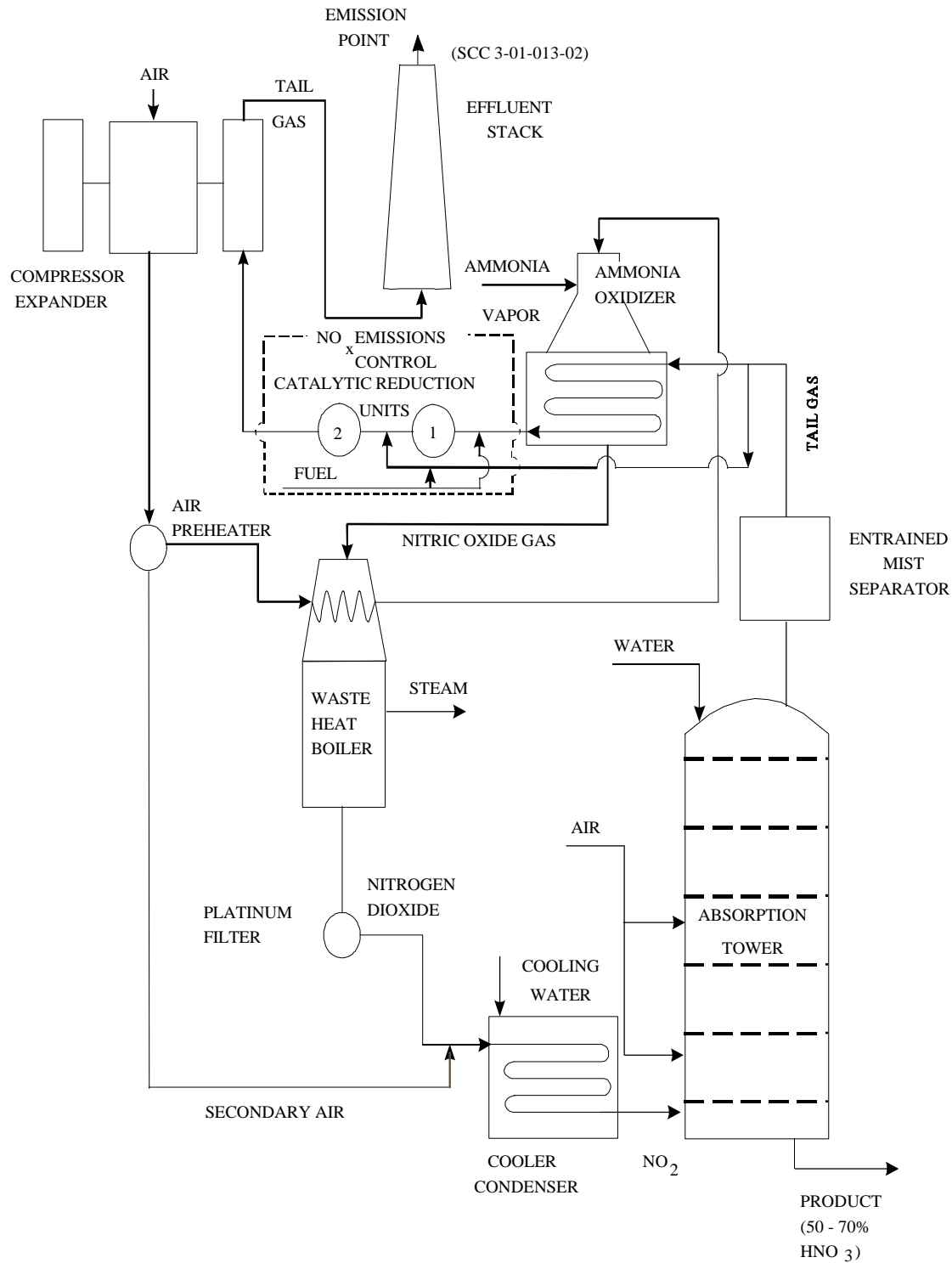


Figure 8.8-1. Flow diagram of typical nitric acid plant using single-pressure process (high-strength acid unit not shown). (Source Classification Codes in parentheses.)

Nitric Oxide Oxidation -

The nitric oxide formed during the ammonia oxidation must be oxidized. The process stream is passed through a cooler/condenser and cooled to 100°F or less at pressures up to 116 pounds per square inch absolute (psia). The nitric oxide reacts noncatalytically with residual oxygen to form nitrogen dioxide (NO₂) and its liquid dimer, nitrogen tetroxide:



This slow, homogeneous reaction is highly temperature- and pressure-dependent. Operating at low temperatures and high pressures promotes maximum production of NO₂ within a minimum reaction time.

Absorption -

The final step introduces the nitrogen dioxide/dimer mixture into an absorption process after being cooled. The mixture is pumped into the bottom of the absorption tower, while liquid dinitrogen tetroxide is added at a higher point. Deionized process water enters the top of the column. Both liquids flow countercurrent to the nitrogen dioxide/dimer gas mixture. Oxidation takes place in the free space between the trays, while absorption occurs on the trays. The absorption trays are usually sieve or bubble cap trays. The exothermic reaction occurs as follows:



A secondary air stream is introduced into the column to re-oxidize the NO that is formed in Reaction 3. This secondary air also removes NO₂ from the product acid. An aqueous solution of 55 to 65 percent (typically) nitric acid is withdrawn from the bottom of the tower. The acid concentration can vary from 30 to 70 percent nitric acid. The acid concentration depends upon the temperature, pressure, number of absorption stages, and concentration of nitrogen oxides entering the absorber.

There are 2 basic types of systems used to produce weak nitric acid: (1) single-stage pressure process, and (2) dual-stage pressure process. In the past, nitric acid plants have been operated at a single pressure, ranging from atmospheric pressure to 14.7 to 203 psia. However, since Reaction 1 is favored by low pressures and Reactions 2 and 3 are favored by higher pressures, newer plants tend to operate a dual-stage pressure system, incorporating a compressor between the ammonia oxidizer and the condenser. The oxidation reaction is carried out at pressures from slightly negative to about 58 psia, and the absorption reactions are carried out at 116 to 203 psia.

In the dual-stage pressure system, the nitric acid formed in the absorber (bottoms) is usually sent to an external bleacher where air is used to remove (bleach) any dissolved oxides of nitrogen. The bleacher gases are then compressed and passed through the absorber. The absorber tail gas (distillate) is sent to an entrainment separator for acid mist removal. Next, the tail gas is reheated in the ammonia oxidation heat exchanger to approximately 392°F. The final step expands the gas in the power-recovery turbine. The thermal energy produced in this turbine can be used to drive the compressor.

8.8.2.2 High-Strength Nitric Acid Production^{1,3} -

A high-strength nitric acid (98 to 99 percent concentration) can be obtained by concentrating the weak nitric acid (30 to 70 percent concentration) using extractive distillation. The weak nitric acid cannot be concentrated by simple fractional distillation. The distillation must be carried out in the presence of a dehydrating agent. Concentrated sulfuric acid (typically 60 percent sulfuric acid) is most commonly used for this purpose. The nitric acid concentration process consists of feeding strong sulfuric acid and 55 to 65 percent nitric acid to the top of a packed dehydrating column at approximately atmospheric pressure. The acid mixture flows downward, countercurrent to ascending vapors. Concentrated nitric acid leaves the top of the column as 99 percent vapor, containing a small amount of NO₂ and oxygen (O₂) resulting from dissociation of nitric acid. The concentrated acid vapor leaves the column and goes to a bleacher and a countercurrent condenser system to effect the condensation of strong nitric acid and the separation of oxygen

and oxides of nitrogen (NO_x) byproducts. These byproducts then flow to an absorption column where the nitric oxide mixes with auxiliary air to form NO_2 , which is recovered as weak nitric acid. Inert and unreacted gases are vented to the atmosphere from the top of the absorption column. Emissions from this process are relatively minor. A small absorber can be used to recover NO_2 . Figure 8.8-2 presents a flow diagram of high-strength nitric acid production from weak nitric acid.

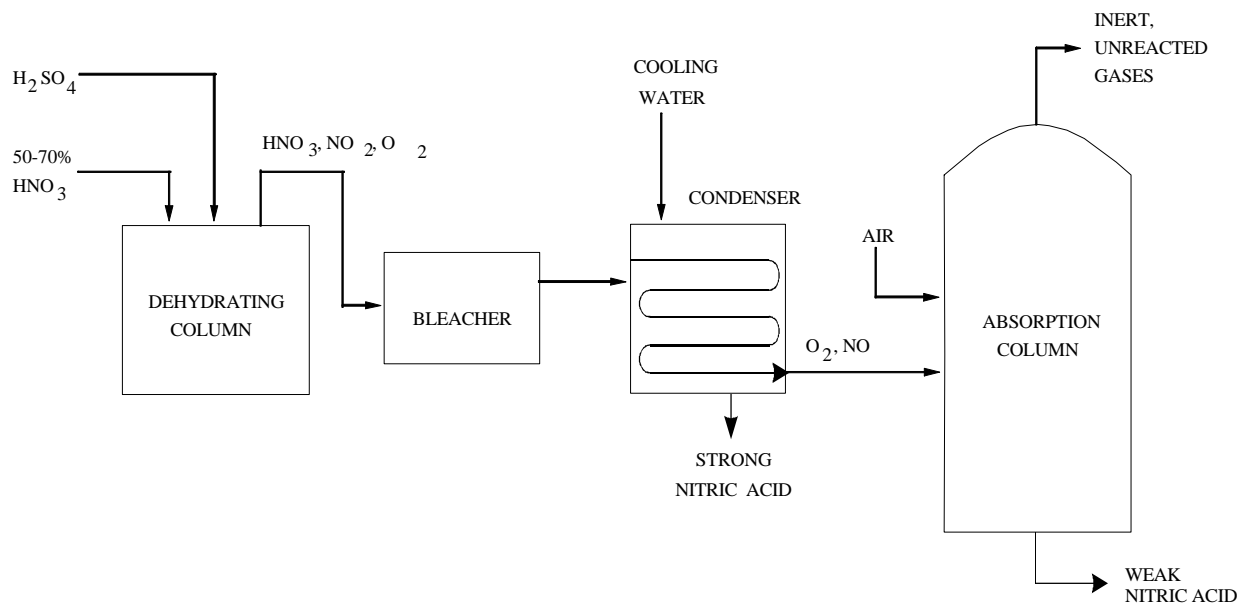


Figure 8.8-2. Flow diagram of high-strength nitric acid production from weak nitric acid.

8.8.3 Emissions And Controls³⁻⁵

Emissions from nitric acid manufacture consist primarily of NO , NO_2 (which account for visible emissions), trace amounts of HNO_3 mist, and ammonia (NH_3). By far, the major source of nitrogen oxides (NO_x) is the tailgas from the acid absorption tower. In general, the quantity of NO_x emissions is directly related to the kinetics of the nitric acid formation reaction and absorption tower design. NO_x emissions can increase when there is (1) insufficient air supply to the oxidizer and absorber, (2) low pressure, especially in the absorber, (3) high temperatures in the cooler-condenser and absorber, (4) production of an excessively high-strength product acid, (5) operation at high throughput rates, and (6) faulty equipment such as compressors or pumps that lead to lower pressures and leaks, and decrease plant efficiency.

The 2 most common techniques used to control absorption tower tail gas emissions are extended absorption and catalytic reduction. Extended absorption reduces NO_x emissions by increasing the efficiency of the existing process absorption tower or incorporating an additional absorption tower. An efficiency increase is achieved by increasing the number of absorber trays, operating the absorber at higher pressures, or cooling the weak acid liquid in the absorber. The existing tower can also be replaced with a single tower of a larger diameter and/or additional trays. See Reference 5 for the relevant equations.

In the catalytic reduction process (often termed catalytic oxidation or incineration), tail gases from the absorption tower are heated to ignition temperature, mixed with fuel (natural gas, hydrogen, propane, butane, naphtha, carbon monoxide, or ammonia) and passed over a catalyst bed. In the presence of the catalyst, the fuels are oxidized and the NO_x are reduced to N_2 . The extent of reduction of NO_2 and NO to N_2 is a function of plant design, fuel type, operating temperature and pressure, space velocity through the

reduction catalytic reactor, type of catalyst, and reactant concentration. Catalytic reduction can be used in conjunction with other NO_x emission controls. Other advantages include the capability to operate at any pressure and the option of heat recovery to provide energy for process compression as well as extra steam. Catalytic reduction can achieve greater NO_x reduction than extended absorption. However, high fuel costs have caused a decline in its use.

Two seldom-used alternative control devices for absorber tailgas are molecular sieves and wet scrubbers. In the molecular sieve adsorption technique, tailgas is contacted with an active molecular sieve that catalytically oxidizes NO to NO_2 and selectively adsorbs the NO_2 . The NO_2 is then thermally stripped from the molecular sieve and returned to the absorber. Molecular sieve adsorption has successfully controlled NO_x emissions in existing plants. However, many new plants elect not to install this method of control because its implementation incurs high capital and energy costs. Molecular sieve adsorption is a cyclic system, whereas most new nitric acid plants are continuous systems. Sieve bed fouling can also cause problems.

Wet scrubbers use an aqueous solution of alkali hydroxides or carbonates, ammonia, urea, potassium permanganate, or caustic chemicals to "scrub" NO_x from the absorber tailgas. The NO and NO_2 are absorbed and recovered as nitrate or nitrate salts. When caustic chemicals are used, the wet scrubber is referred to as a caustic scrubber. Some of the caustic chemicals used are solutions of sodium hydroxide, sodium carbonate, or other strong bases that will absorb NO_x in the form of nitrate or nitrate salts. Although caustic scrubbing can be an effective control device, it is often not used due to its incurred high costs and the necessity of treating its spent scrubbing solution.

Comparatively small amounts of nitrogen oxides are also lost from acid concentrating plants. These losses (mostly NO_2) are from the condenser system, but the emissions are small enough to be controlled easily by inexpensive absorbers.

Acid mist emissions do not occur from the tailgas of a properly operated plant. The small amounts that may be present in the absorber exit gas streams are removed by a separator or collector prior to entering the catalytic reduction unit or expander.

The acid production system and storage tanks are the only significant sources of visible emissions at most nitric acid plants. Emissions from acid storage tanks may occur during tank filling.

Nitrogen oxides and N_2O emission factors shown in Table 8.8-1 vary considerably with the type of control employed and with process conditions. For comparison purposes, the New Source Performance Standard on nitrogen emissions expressed as NO_2 for both new and modified plants is 3.0 pounds of NO_2 emitted per ton (lb/ton) of 100 percent nitric acid produced.

8.8.4 Changes Since July, 1993

- Reformatted for the Fifth Edition, released in January 1995
- Supplement D update (February 1998) - added a N_2O emission factor for weak acid plant tailgas.

Table 8.8-1. NITROGEN OXIDE EMISSIONS FROM
NITRIC ACID PLANTS

EMISSION FACTOR RATING: E

| Source | Control Efficiency % | NO _x , lb/ton Nitric Acid Produced ^a | N ₂ O, lb/ton Nitric Acid Produced ^m |
|--|----------------------|--|--|
| Weak acid plant tailgas Uncontrolled ^{b,c} | 0 | 57 | 11.70 |
| Catalytic reduction ^c | | | |
| Natural gas ^d | 99.1 | 0.4 | ND |
| Hydrogen ^e | 97 - 98.5 | 0.8 | ND |
| Natural gas/hydrogen (25%/75%) ^f | 98 - 98.5 | 0.9 | ND |
| Extended absorption | | | |
| Single-stage process ^g | 95.8 | 1.9 | ND |
| Dual-stage process ^h | | 2.1 | ND |
| Chilled absorption and caustic scrubber ⁱ | ND | 2.2 | ND |
| High-strength acid plant ^k | ND | 10 | ND |

^a Assumes 100% acid. Production rates are in terms of total weight of product (water and acid). A plant producing 500 tons per day of 55 weight % nitric acid is calculated as producing 275 tons/day of 100% acid. To convert lb/ton to kg/Mg, multiply by 0.5. ND = no data.

^b Reference 6. Based on a study of 12 plants, with average production rate of 230 tons (100% HNO₃)/day (range 55 - 750 tons) at average rated capacity of 97% (range 72 - 100%).

^c Single-stage pressure process.

^d Reference 4. Fuel is assumed to be natural gas. Based on data from 7 plants, with average production rate of 340 tons (100% HNO₃)/day (range 55 - 1077 tons).

^e Reference 6. Based on data from 2 plants, with average production rate of 160 tons (100% HNO₃)/day (range 120 - 210 tons) at average rated capacity of 98% (range 95 - 100%). Average absorber exit temperature is 85 °F (range 78 - 90 °F), and the average exit pressure is 85 psig (range 80 - 94 psig).

^f Reference 6. Based on data from 2 plants, with average production rate of 230 tons (100% HNO₃)/day (range 185 - 279 tons) at average rated capacity of 110% (range 100 - 119%). Average absorber exit temperature is 91 °F (range 83 - 98 °F), and average exit pressure is 79 psig (range 79 - 80 psig).

^g Reference 4. Based on data from 5 plants, with average production rate of 540 tons (100% HNO₃)/day (range 210 - 1050 tons).

^h Reference 4. Based on data from 3 plants, with average production rate of 590 tons (100% HNO₃)/day (range 315 - 940 tons).

^j Reference 4. Based on data from 1 plant, with a production rate of 700 tons (100% HNO₃)/day.

^k Reference 2. Based on data from 1 plant, with a production rate of 1.5 tons (100% HNO₃)/hour at 100% rated capacity, of 98% nitric acid.

^m Reference 7.

References For Section 8.8

1. *Alternative Control Techniques Document: Nitric And Adipic Acid Manufacturing Plants*, EPA-450/3-91-026, U. S. Environmental Protection Agency, Research Triangle Park, NC, December 1991.
2. *North American Fertilizer Capacity Data*, Tennessee Valley Authority, Muscle Shoals, AL, December 1991.
3. *Standards Of Performance For Nitric Acid Plants*, 40 CFR 60 Subpart G.
4. Marvin Drabkin, *A Review Of Standards Of Performance For New Stationary Sources — Nitric Acid Plants*, EPA-450/3-79-013, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 1979.
5. *Unit Operations Of Chemical Engineering*, 3rd Edition, McGraw-Hill, Inc., New York, 1976.
6. *Atmospheric Emissions From Nitric Acid Manufacturing Processes*, 999-AP-27, U. S. Department of Health, Education, And Welfare, Cincinnati, OH, December 1966.
7. R. L. Peer, *et al.*, *Characterization Of Nitrous Oxide Emission Sources*, U. S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, NC, pp. 2-15, 1995.