How to Control NO_X

Hydrogen peroxide can eliminate NO_X in some treatment situations.

by Nicholas J. Rossi

Because the Clean Air Act Amendments of 1990 target ozone, NO_X emissions, a precursor of ozone, also are being scrutinized. NO_X is primarily composed of nitric oxide (NO) and nitrogen dioxide (NO_2). Both NO and NO_2 are considered toxic to humans, and emissions of NO_2 can be readily identified as an unsightly orange-brown gas. NO_X is produced in a variety of different processes, including combustion in a car engine or power plant.

NO_X also is emitted from processes where nitric acid is an oxidant, as in metal surface cleaning or metal dissolution. The steel industry runs sheets of steel through pickling baths of nitric acid. NO_X is emitted from the bath as a gas. Plating or catalyst recovery involves the reaction of nitric acid and transition metals, also forming NO_X. Substantial amounts of NO_X also can be generated in the specialty chemical industry when nitric acid is used as a reagent.

As potential generators of NO_X, the chemical and metal industries face mounting pressure from federal regulations such as the Clean Air Act to reduce discharges.

Treatment options

A number of methods can control emissions of NO_X gases that result from the use of nitric acid. Some of these are summarized in Table 1.

In general, treatment options can be placed in three categories: NO_X can be treated at the discharge site; by suppression of NO_X at the source; and by elimination of nitric acid from the process.

Treatment at the discharge site. Gas scrubbers are widely used for the treatment of NO_X gases. They involve the transfer of pollutants from a gas phase to a liquid phase by putting the two phases in contact. The liquid phase can comprise various chemicals.

Sodium hydroxide is the most commonly used chemical in scrubbing solutions. Although sodium hydroxide is fairly inexpensive, it produces nitrates which have to be eliminated from the process and disposed of at an additional cost.

Sodium hydrosulfide also is widely used in scrubber solutions. Care has to be taken when handling sodium hydrosulfide, as it is a hazardous chemical regulated by RCRA. In addition, sodium hydrosulfide inadvertently released to the effluent could convert to reduced sulfur compounds.

While hydrogen peroxide (H_2O_2) is more expensive on a per-pound basis than either sodium hydroxide or sodium hydrosulfide, its product of reaction is nitric acid, which can be recovered and recycled into the process. Hydrogen peroxide decomposes to water and oxygen, and loses less than 1 percent of its concentration per year when stored properly. However, improper application or handling could create hazardous conditions or injure personnel.

NO_X gases emitted from a process can be vented to a selective catalytic reduction system instead of a scrubber. In selective catalytic reduction, the gases are heated, then passed over a catalyst as ammonia is injected to reduce the NO_X. This

Table 1. Ways to Control NO_X

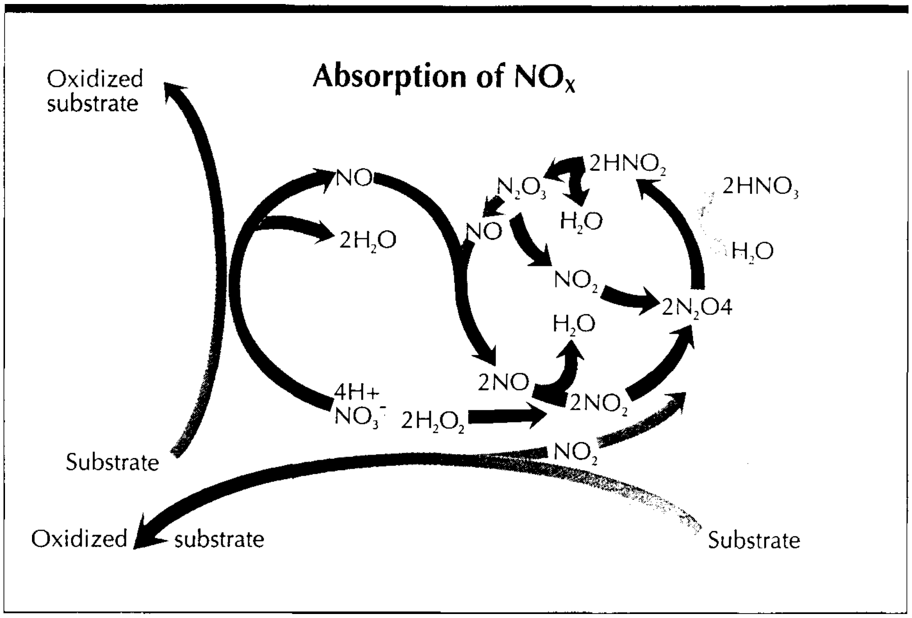
Treatment	Catalytic reduction by NH_3	Gas scrubbing-NAOH	Gas scrubbing-NASH	Gas scrubbing-H_2O_2	Addn. to bath $CO(NH_2)2$	Addn. to bath-H_2O_2
Capital cost	very high	high	high	high	low	low
Variable costs	low	low	low	high(1)	low	high (1)
HNO_3 consumption	no influence	no influence	no influence	lower	higher	lower
NO_X removal	very high	high	high	very high	low	very high
By-products	no problem	sodium nitrite difficult	difficult to discharge	nitric acid recovered	no problem to discharge	nitric acid recovered

(1) A portion of the variable cost is offset by nitric acid production.

technology is capable of high NO_x reduction (90 percent), but requires capital investment and high operating expenditures due to periodic catalyst replacement. In addition, the anhydrous ammonia used in the process is considered a hazardous gas.

Treatment at the source. The most effective way to prevent the emission of NO_x into the atmosphere is to suppress it at its source before it evolves from solution.

Hydrogen peroxide can be added directly to a process using nitric acid. The H_2O_2 reacts instantaneously with HNO as it is formed, before it decomposes to NO and NO_2. As in the case of gas scrubbing with hydrogen peroxide, nitric acid is formed as a reaction product.



• *Figure 1. The reaction between NO_x and hydrogen peroxide is the same for various treatment methods.*

Urea also can be used to suppress the formation of NO_x, but this method requires an increased consumption of nitric acid. Also, when used in stainless steel pickling, urea may adversely affect the quality of the final product.

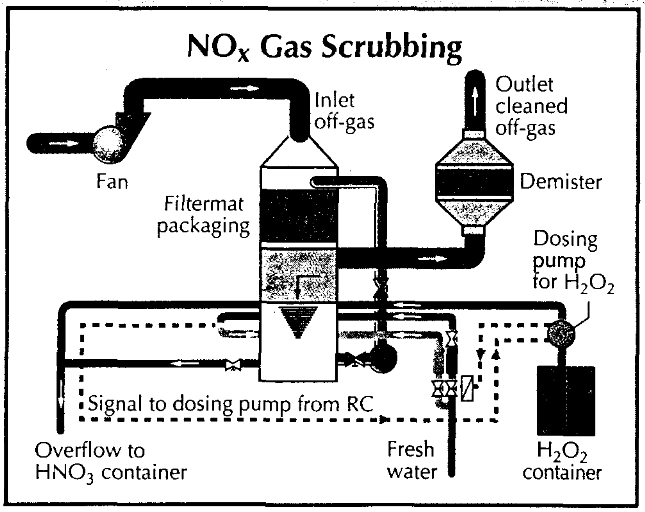
Elimination of nitric acid. Substituting hydrogen peroxide for nitric acid in the manufacturing process provides the best solution to the problem of NO_x emissions. For example, in the stainless steel pickling process, nitric acid acts as both an acid and an oxidant. These functions can be replaced by using sulfuric acid and H_2O_2, respectively. Review of this treatment alternative is ongoing.

The reaction of NO_x with H_2O_2

Hydrogen peroxide can be used to eliminate NO_x in various treatment methods. The chemistry involved in the reaction of NO_x with H_2O_2 is the same for the various alternatives.

NO_x must first be absorbed into the liquid phase. NO_2 tends to absorb more readily than NO and thus NO_x emissions with a high $NO:NO_2$ ratio will have relatively low

A Case Study: NO_x Gas Scrubbing using H_2O_2



• *A gas scrubbing plant using hydrogen peroxide delivers removal efficiencies of 80 percent.*

A chemical company produced an offgas of 3800 cfm, containing approximately 1000 ppm NO_x with an $NO:NO_2$ ratio of 1:9. The company was attempting to limit emissions to 300 ppm.

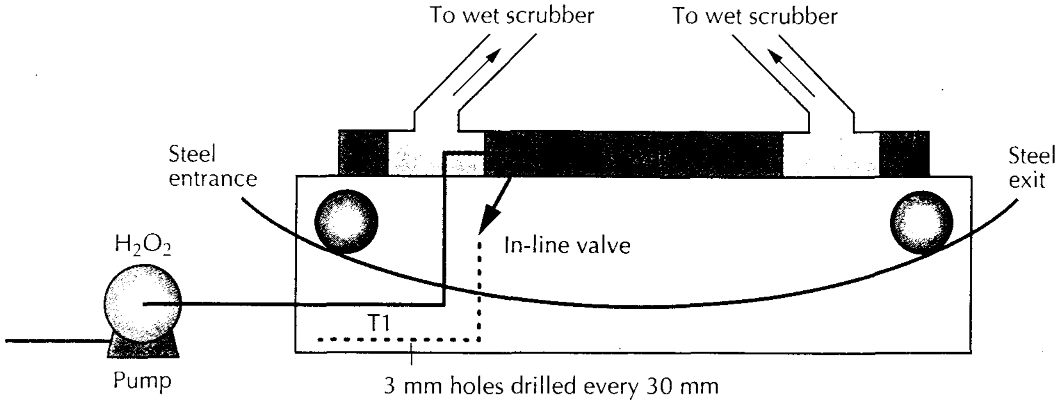
After extensive internal investigation, the manufacturer contacted an engineering firm engaged in gas scrubbing plant fabrication, which recommended the use of H_2O_2. The developed design passed the offgas and scrubbing liquor concurrently through a dense mat packing.

This method employed a hydrogen peroxide consumption slightly in excess of the chemical stoichiometry, for a usage rate of 300 lb/day, as 100 percent H_2O_2. Successfully installed, it proved to have a removal efficiency of 80 percent.

VARIABLE	INLET	OUTLET
NO_x, ppm	1000	200
Temperature (8F)	86	—

Substituting hydrogen peroxide for nitric acid may be the best response to NO_x concerns.

NO_x Abatement in a Pickling Bath



• ***Figure 2. Hydrogen peroxide is added to the pickling bath to eliminate NO_x.***

absorption rates and will be more difficult to eliminate. When NO_x is absorbed into the liquid phase, it reacts with water to form nitrous acid (HNO_2). Nitrous acid is unstable and will decompose to NO and NO_2 once again; however, H_2O_2 rapidly oxidizes HNO to the more stable and reusable nitric acid. The nitric acid, in turn, enhances the absorption of NO because nitric acid oxidizes NO to NO_2 in the gas phase.

Figure 1 shows these reactions schematically.

Hydrogen peroxide in gas scrubbers

When hydrogen peroxide is used as a gas scrubbing solution, it is normally used in packed towers, the most commonly used equipment for gas scrubbing. The liquid flows down the tower, while the gas flows up. Packing in the tower provides surface area to enhance the contact of the two phases. The diameter of the tower is determined by the flow rates of the two phases, and the tower's height is determined by the amount of pollutant to be removed.

A Case Study: NO_x Suppression in the Pickling Bath using H_2O_2

A stainless steel manufacturer employed a pickling liquor which consisted of 12 percent nitric acid and 1 percent hydrofluoric acid, and which contained 4 percent dissolved iron. Stainless steel, grades 304, 316, 321 and 301, were pickled in a continuous strip with the bath temperature controlled to 130° to 140°F. The volume of the bath was 8500 gallons.

Hydrogen peroxide (35 percent) was introduced via a $^3/_8$-inch-diameter pipe positioned 2 inches above the floor of the tank, and extended to a distance of approximately 20 feet. Holes $^1/_8$ inch in diameter were drilled in the pipe at 1-ft. intervals.

A 95 percent reduction in NO_x emissions was achieved by the introduction of hydrogen peroxide at a flow rate of approximately 9.6 gal/hr. The flow rate varied, depending on line speed, bath temperature, steel type and degree of scale present. The savings in reduced nitric acid consumption partially offset the cost of the hydrogen peroxide.

Hydrogen peroxide in the process

Suppression of NO_x gases at the source effectively reduces treatment cost by eliminating the need for a scrubber. Hydrogen peroxide added to the nitric acid process solution oxidizes the nitrous acid (HNO_2) formed before it decomposes to NO_x. Hydrogen peroxide also has a tendency to decompose by its reactions with other ions in the process. The oxidation reaction with HNO_2 is faster than the hydrogen peroxide decomposition reaction. Nonetheless, efficient mixing is essential with hydrogen peroxide.

In a stainless steel pickling bath, for example, a recirculation loop that changes the bath liquor about five to 10 times per hour effectively ensures mixing. Another method uses a sparge to inject hydrogen peroxide directly into the pickling bath. See Fig. 2. When H_2O_2 is used for NO_x suppression in the bath, the stainless steel surface quality is improved.

Conclusions

One of the advantages of using hydrogen peroxide for NO_x suppression is the formation of nitric acid as a reaction product. This positively impacts the cost of systems such as gas scrubbing and pickling, which use nitric acid as a raw material. Also, the nitric acid in gas scrubbing operations assists in the absorption of NO into the liquid phase, making the process more efficient. Since no solids handling is involved in using a hydrogen peroxide system, plant upsets are minimized.

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