



## NITROGEN OXIDES (NO<sub>x</sub>) ABATEMENT WITH HYDROGEN PEROXIDE

### Introduction

Nitrogen oxides are major pollutants in the atmosphere and are a precursor to acid rain, photochemical smog, and ozone accumulation. The oxides are mainly nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), both of which are corrosive and hazardous to health.

### Stationary Source Focus

With the use of catalytic converters on automobiles, the initial regulatory focus of controlling mobile NO<sub>x</sub> emissions has reached the point where further restriction has become economically impractical. Consequently, the stationary sources of NO<sub>x</sub> emissions are now being subjected to more stringent standards in many areas of the U.S. These stationary sources include nitric acid manufacturing plants, manufacturers of nitrated materials such as fertilizer and explosives, and industrial manufacturers such as metallurgical processors, glass manufacturers, cement kilns and power generators where high processing temperatures are used. Because of the environmental concerns posed by air pollution, a great deal of research and money has been expended to develop methods for controlling NO<sub>x</sub> emissions.

### Regulations

Regulations concerning the limitation of atmospheric emission of NO<sub>x</sub> from industrial sources vary from region to region. Following the Clean Air Act amendments in 1990, the EPA has reviewed the current national standards, and has subsequently updated the standards pertaining to non-attainment areas. The EPA standard for new nitric acid manufacturing plants is three pounds of NO<sub>x</sub> per ton of nitric acid produced. This means that new plants must reduce NO<sub>x</sub> emission levels from 1500-3000 ppm to 200 ppm. The requirements for existing plants are complicated by controversy over methods for measuring ambient NO<sub>x</sub> levels, as well as the wide variations in state and regional requirements. Typically, existing nitric acid plants are allowed to produce 5.5 pounds of NO<sub>x</sub> per ton of nitric acid produced. Standards for other industries are being promulgated.

### Sources of Nitrogen Oxide

There are five major sources of nitrogen oxide.

1. Combustion of fuels: At high temperatures, oxygen and nitrogen present in air combine to form nitrogen oxides. Typical flue gas samples contain 100-1500 ppm of nitrogen oxides.
2. Nitric acid manufacturing: Waste gases which cannot be economically recovered in the final absorber usually contain 2-3% nitrogen oxides based on weight of acid produced.
3. Metal finishing operations: Metal surface treatment operations using nitrates, nitrites, or nitric acids, which evolve nitrogen oxides. Examples include bright dipping, phosphatizing, desmutting and pickling of stainless steel.
4. Chemical processes: Nitric acid, nitrates, or nitrites are used as reagents evolve nitrogen oxides. Examples include the production of explosives, plastics and dyes.
5. High temperature processes: Materials made at high temperatures, such as glass manufacturing, electric furnaces and cement kilns, which all evolve nitrogen oxides.

## Controlling NOx Emissions

There are several methods for controlling NOx emissions. Gas scrubbing is one of the most common forms of NOx treatment, with sodium hydroxide being the conventional scrubbing medium. The absorbed NOx, however, is converted to nitrite and nitrate, which may present wastewater disposal problems. Scrubbing solutions containing hydrogen peroxide are also effective at removing NOx, and can afford benefits not available with NaOH. For example, H<sub>2</sub>O<sub>2</sub> adds no contaminants to the scrubbing solution and allows commercial products such as nitric acid to be recovered from the process. In its simplest application, H<sub>2</sub>O<sub>2</sub> (0.5-1 wt.%) and nitric acid (35-45 wt.%) are used to scrub both nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) – the chief components of NOx from many industrial sources. The reactions are rapid at moderate temperatures (30-80 deg-C), with about 1.7 and 0.37 lbs H<sub>2</sub>O<sub>2</sub> required per pound of NO and NO<sub>2</sub>, respectively. The chemistry controlling the process is outlined in Figure 1.

The Kanto Denka, Nikon and Ozawa processes also use hydrogen peroxide to remove NOx. The Kanto Denka process employs a scrubbing solution containing 0.2% hydrogen peroxide and 10% nitric acid while the Nikon process uses a 10% sodium hydroxide solution containing 3.5% hydrogen peroxide. The Ozawa process scrubs NOx by spraying a hydrogen peroxide solution into the exhaust gas stream. The liquid is then separated from the gas stream, and the nitric acid formed is neutralized with potassium hydroxide. The excess potassium nitrate is crystallized out and the solution is reused after recharging with hydrogen. A series of Japanese patents also describe efficient processes and equipment for reducing NOx to nitrogen using hydrogen peroxide and ammonia, but they must be carried out at higher temperatures.

Another approach to controlling NOx emissions involves its elimination at the source. This typically involves adding H<sub>2</sub>O<sub>2</sub> directly to HNO<sub>3</sub> contained in metal pickling baths, where

the H<sub>2</sub>O<sub>2</sub> reacts instantly with HNO as it is formed, thereby eliminating its decomposition to NO and NO<sub>2</sub>. In this way, the nitric acid is regenerated in-situ without the expense of scrubbers. Compared to urea, which is also used for in-situ control, the H<sub>2</sub>O<sub>2</sub> process affords true nitric acid recovery and does not degrade the quality of the finished product.

Figure 1. Controlling NOx Emissions



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## About USP Technologies

USP Technologies is the leading supplier of peroxygen-based technologies and services for environmental applications. We have been serving the water, wastewater and remediation markets for over 20 years and have offices and field service locations throughout North America. Our consultative approach to problem solving includes application assessment, technology selection and development of a tailored treatment approach. Our full service programs successfully integrate storage and dosing equipment systems, chemical supply, inventory and logistics management, and ongoing field and technical support. This approach provides cost-effective, "hands-off" solutions to our customers. USP Technologies also can provide access to experienced application partners for a turn-key program encompassing engineering, site characterization and technology selection, program implementation, execution and report generation.

## Getting Started

We look forward to supporting your treatment needs, whatever the scale of your requirements. To obtain a streamlined treatment solution tailored to your specific project, give us a call at (877) 346-4262.

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