

Nitrogen Oxide (NO_x) Abatement with Hydrogen Peroxide

Introduction

Nitrogen oxides are major pollutants in the atmosphere. The oxides, mainly nitric oxide (NO) and nitrogen dioxide (NO₂) are both corrosive and hazardous to health. The control of NO_x emission from automobiles has reached the point where further restriction has become economically impractical. Consequently, the emission of NO_x from stationary sources is now subject to more and more stringent standards in many areas of the U.S. Stationary sources include nitric acid manufacturing plants, manufacturers of nitrated materials such as fertilizer and explosives, and industrial manufacturers (glass manufacturers, cement, power generators, etc.) where high processing temperatures are used. Because of environmental concerns, a great deal of research time and money has been expended to develop methods for controlling concentrations of these noxious gases in the atmosphere. The 2003-2007 year window is rapidly approaching which is the transition period for many US industries to comply with the most recent NO_x standards.

Regulations

Regulations concerning limitation of atmospheric emission of NO_x from industrial sources vary from region to region. The EPA has undertaken a review of its current national standards as mandated by the 1977 Clean Air Acts Amendments (to examine short-term standards). The EPA standard for new nitric acid manufacturing plants is 3 pounds NO_x per ton of nitric acid produced. This means that plants must reduce NO_x emission levels from 1500-3000 ppm to 200 ppm. The requirements for existing nitric acid manufacturing plants are complicated by controversy over methods for measuring ambient NO_x levels, as well as the wide variations in state requirements alluded to earlier. Typically, existing nitric acid plants are allowed to produce 5.5 pounds of NO_x per ton of nitric acid produced.

Standards are being determined for other industries. The 1990 Clean Air Act Amendment required the EPA to establish regional rules tightening the NO_x allotments. The minimum emission factor for fuel combustion units is 0.15 lb of NO_x per hour per million BTU/hour for units east of the Mississippi. California and Texas have standards that are even more stringent.

Nitrogen Oxide Sources

Combustion of fuels: (600-2300 °F)

At high temperatures the oxygen and nitrogen of air combine to form nitrogen oxides. Typical flue gas samples contain 100-1500 ppm of nitrogen oxides.

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Nitric acid manufacture:

Waste gases which cannot be economically recovered in the final absorber usually contain 2-3% nitrogen oxides based on weight of acid produced.

Metal finishing operations:

Many metal surface treatment operations which use nitrates, nitrites, or nitric acid evolve nitrogen oxides. Examples of such operations include bright dipping, phosphating, desmutting, and pickling.

Chemical processes:

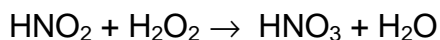
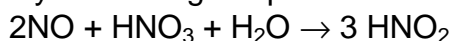
Many processes where nitric acid, nitrates, or nitrites are used as reagents evolve nitrogen oxides. Examples include manufacture of explosives, plastics, dyes, etc.

High temperature processes (2600-2800 °F)

Processes where materials are made high temperatures such as glass manufacturing and cement manufacturing evolve nitrogen oxides.

Processes for Nitrogen Oxide Removal

There are several wet methods for removing nitrogen oxide contaminants from gases emitted to the atmosphere. Scrubbing solutions containing hydrogen peroxide are effective in destroying these contaminants. FMC has developed a process in which a scrubbing solution composed of 0-5-1% hydrogen peroxide and 35-45% nitric acid effectively removes both nitric oxide (NO) and nitrogen dioxide (NO₂). These oxides are the chief components of NO_x from many industrial sources. The reactions are rapid at moderate temperatures (30-80°C). The chemistry controlling the process is outlined below.



There are several other processes which also use hydrogen peroxide to remove NO_x. 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. Generally, the NO: NO₂ ratio has the most significant effect on removal efficiency. Removal efficiencies did increase with increasing H₂O₂ concentrations. When NO_x concentrations varied from 1000-3000 ppmv and the ratio NO: NO₂ was 1:0 to 1:1 to 0:1 the removal efficiency was nearly 100% at one g/L H₂O₂ concentrations

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A fourth process, the Ozawa process, scrubs NO_x 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 reused after recharging with hydrogen peroxide.

In addition to the methods cited above in which NO_x is oxidized to nitric acid or nitrate salts, a series of Japanese patents describe processes and equipment for reducing NO_x to nitrogen using hydrogen peroxide and ammonia. The processes are efficient but must be carried out at higher temperatures than the processes cited earlier.

Test Procedure

The approved EPA monitoring method and the sampling method are described in the Federal Register