

FIRST AID FOR AIR POLLUTION

STEVE ROBINSON
Solvay Interlox
Houston, TX

Hydrogen peroxide, increasingly the oxidant of choice for wastewater treatment, also finds new applications in the stepped up battle against air pollution. Faced with rigorous controls mandated by the 1990 Clean Air Act Amendments, industry continues to take a closer look at hydrogen peroxide and the benefits of peroxygen technology. The versatility of hydrogen peroxide lends itself to solving problems with air emissions in three ways:

1. *By absorbing gaseous pollutants into liquid hydrogen peroxide in scrubbing systems;*
2. *By modifying processes to prevent production of pollutants by integrating hydrogen peroxide in upstream processes; and*
3. *As an alternative to air stripping.*

WHY CONSIDER PEROXIDE

Worldwide, industry uses hydrogen peroxide to treat a wide range of industrial and municipal effluents, thus eliminating contaminants that range from sulfides, to phenols, to cyanides. Used to control air emissions, hydrogen peroxide successfully removes NO_x, SO₂, hydrogen sulfide (H₂S), mercaptans, aldehydes, and odors that result from numerous other compounds.

While other oxidizers prove successful in treating the same spectrum of pollutants, hydrogen peroxide stands apart as a non-toxic, non-polluting, and powerful chemical oxidant. It breaks down into just water and oxygen. Safe, easy-to-use, and stable in commercial storage, hydrogen peroxide generally represents a cost effective, low-capital alternative to traditionally accepted methods of air pollution control.

H₂O₂ AND GAS SCRUBBING

Hydrogen peroxide's strong oxidizing properties offer two primary benefits in gas scrubbing systems:

1. Depending on the application, hydrogen peroxide may enhance the rate

of absorption and thus reduce the scrubber size; and

2. As an environmentally-compatible chemical, hydrogen peroxide eliminates liquor disposal problems since the scrubber effluent can be safely disposed of or recycled.

NO_x and H₂O₂

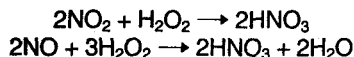
NO_x denotes a variety of nitrogen oxide compounds, known contributors to acid rain and photochemical smog. Unsightly as well as hazardous, NO_x identifies itself by forming a brownish-orange cloud when released. During the early years of industrialization, coal burning contributed heavily to NO_x production, and the so-called "London fog" of Sherlock Holmes' day actually consisted of a hazardous smog caused by coal smoke.

Today, in the U.S., we have varied sources of NO_x. Since nitrogen combines with oxygen at high temperatures to form the nitrogen oxides, a car engine, for example, provides the ideal mechanism for production of NO_x. And while automobiles contribute significantly to the atmospheric load of NO_x, industry remains another significant source. Common sources of NO_x include power plants, nitric acid production plants, and industries using nitric acid (metallurgical processes and chemical manufacturing). Also, because nitrogen makes up about 78 percent of the atmosphere, it can readily undergo oxidation by substances discharged from incinerators, with NO_x as the net result.

Typical NO_x concentrations range from a few parts per million to several thousand ppm. The concentration and composition depends on the source, and varies significantly in batch-processing operations. Essentially, NO_x contains nitric oxide (NO) and nitrogen dioxide (NO₂) in varying proportions. This fluctuating ratio, and the fact that these compounds dissolve at different rates, complicate the treatment of NO_x.

Absorption of NO_x into water produces nitric and nitrous acid. To prevent the subsequent decomposition of nitrous acid to NO and NO₂, the scrubbing process requires another step. The followup reaction involves either neutralization, oxidation, or reduction. These reactions can pose extended problems to NO_x abatement.

Absorption of NO_x into an aqueous solution of hydrogen peroxide, however, prevents decomposition of nitrous acid by oxidizing it almost instantly to nitric acid, thus eliminating the need for further reactions:



Computer programs that simulate the performance of a NO_x scrubber demonstrate that scrubbing efficiency increases noticeably with additional NO₂ concentration, and increases marginally when nitric acid concentration rises to 40 percent. Around the world, case studies demonstrate the success of hydrogen peroxide against NO_x. Applications cross a broad spectrum of industries and nationalities, but even with the unpredictable proportions of NO and NO₂, hydrogen peroxide is successful.

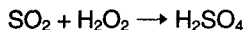
SO₂ and H₂O₂

SO₂, or sulfur dioxide, reacts in the atmosphere to form sulfuric acid, another component of acid rain. It also contributes to photochemical smog and represents a deadly factor in air pollution disasters. Scientists target SO₂ as the source of acid rain that now eats away at the Acropolis in Athens, Greece, not to mention other historical monuments around the world. SO₂ also takes the blame worldwide for increases in respiratory infections, asthma attacks, and other diseases. Mountain forests have been decimated by sulfuric acid mist resulting from SO₂ emissions. Fossil-fuel smokestacks, primarily in the domain of utility companies, produce significant amounts of SO₂. Other industrial processes, ranging from copper smelters to manufacturers and users of sulfuric acid also contribute SO₂ to the atmosphere—as well as those industries that still burn high-sulfur coal.

SO₂ emission control traditionally involves wet scrubbing. While some processes use an alkali, such as lime, disposal problems can offset the benefits of using cheap alkali. Other processes recover sulfur as a byproduct by further processing the scrubber effluent, but these may not yield the best economy.

Scrubbing with hydrogen peroxide produces strong reusable sulfuric acid

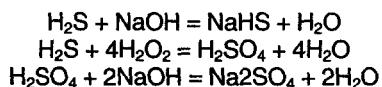
without unwanted byproducts. Hydrogen peroxide reacts almost instantaneously with dissolved SO₂:



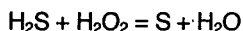
The reaction generates heat, so SO₂ contents of greater than 1 percent require cooling of the scrubbing liquor. Also, with increased concentrations of hydrogen peroxide in the scrubbing solution, the concentration of sulfuric acid also increases.

H₂S and H₂O₂

Hydrogen sulfide gas, or H₂S, is known to many for its smell of rotten eggs. More importantly, H₂S poses a lethal threat to those who breathe it. Oil refineries, chemical manufacturers, pulp and paper mills, and municipal wastewater systems all produce hydrogen sulfide. Not only a potentially lethal gas, H₂S corrodes pipes, equipment, and electrical contacts, and impairs operations. Absorption, adsorption, and incineration represent various methods of combating hydrogen sulfide. Hydrogen peroxide, used for more than 20 years to destroy sulfides in municipal wastewater systems, can also be effective in the treatment of sulfides in air emissions. Where treatment of hydrogen sulfide at the source seems impractical due to the presence of other pollutants or other constraints, hydrogen peroxide works well against sulfide gas in a scrubbing system. The process requires an alkali, such as sodium hydroxide, to raise the pH to at least 10 for increased hydrogen sulfide solubility. Hydrogen peroxide oxidizes the hydrogen sulfide to sulfuric acid, which is then neutralized to sodium sulfate for safe disposal:



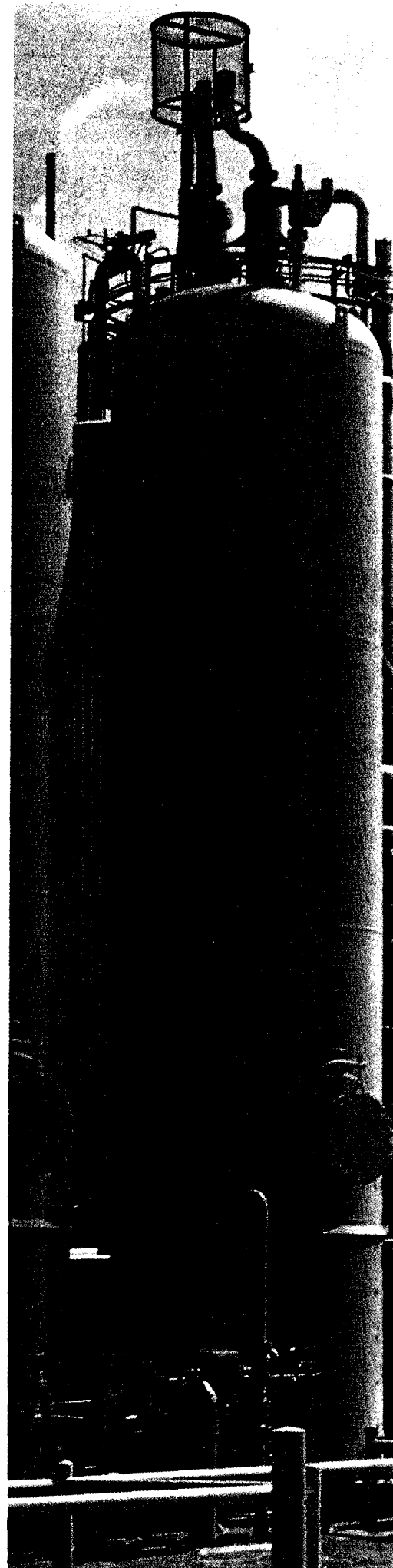
Under acidic to neutral conditions, oxidation of H₂S produces sulfur:

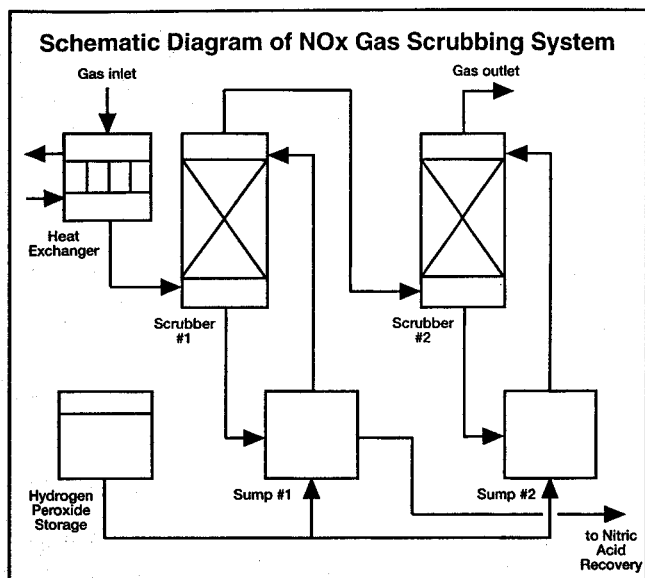


These acidic and/or neutral conditions require about a fourth of the amount of hydrogen peroxide compared to reactions under alkaline conditions. However, the lower solubility at these conditions means that a much larger scrubber is required. If the gas also contains a high proportion of acidic gas, such as carbon dioxide, an alkaline scrubber may consume extra alkali and precipitate salts. Scrubbing the gas under acidic or neutral conditions overcomes this problem.

Mercaptans

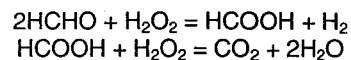
Mercaptans plague refineries, pulp and paper mills, sewage treatment plants, and processes involving the synthesis of organic sulfur compounds. Mer-





The instantaneous reaction with sodium hydroxide represents the first step. The dissolved mercaptan is then oxidized by hydrogen peroxide, then oxidizes to the corresponding sulfonic acid. This reaction also occurs quickly. The resulting disulfide further oxidizes, but due to low solubility, the reaction takes place slowly. Where applicable, a skimmer can remove the insoluble oil layer formed by the generation of disulfides.

formic acid then slowly oxidizes to carbon dioxide and water:



Metallic salts can catalyze the reaction. Generally, aldehydes have a relatively high solubility in alkaline solutions and can be scrubbed efficiently from a gas stream.

Odor Control

Sewage treatment plants, food processing plants, animal feed manufacturers, and animal carcass rendering plants are typical industries that have problems with malodorous gases. Highly odorous gases can contain a multiple of compounds in low concentrations, including hydrogen sulfide, mercaptans, aldehydes, ketones, phenols, fatty acids, ammonia, and amines.

Hydrogen peroxide also effectively oxidizes phenols and some amines. Since many streams contain both acidic and basic malodorants, scrubbing with an acidic solution followed by an alkaline hydrogen peroxide solution offers a cost-effective method of odor control. The first stage, using acidic solution, removes basic compounds such as amines and ammonia. The second stage, using an alkaline hydrogen peroxide solution (pH 10 to 12), removes acidic compounds such as hydrogen sulfide and mercaptans.

PROCESS MODIFICATION: PREVENTION VS. CURE

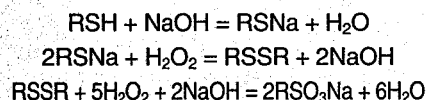
While hydrogen peroxide is effective in the removal of contaminants from gaseous effluents, certain upstream applications of hydrogen peroxide prevent the generation of pollutants.

NOx: Suppression vs. Removal

The previous discussion highlighted the use of hydrogen peroxide to remove hazardous NOx from air emissions. However, in the metal finishing industries, the addition of hydrogen peroxide to the pickling bath can reduce the need for post-process scrubbing. Metal-surface treatments, particularly stainless-steel pickling, represent major generators of NOx. Pickling processes use a liquor containing nitric acid and hydrofluoric acid. The reaction between the nitric acid and transition metals generates NOx fumes.

Scrubbing represents a capital-intensive approach, while catalytic reduction using ammonia represents an even greater capital outlay. However, adding hydrogen peroxide to the pickling bath offers a low-capital approach to minimiz-

captans have a low molecular weight and create intense odors. The process of absorbing mercaptans resembles the absorption of hydrogen sulfide, beginning with the addition of sodium hydroxide to increase solubility:



Aldehydes

Processes that use resins containing formaldehyde, such as particle board production and metal casting, will produce formaldehyde vapors. Formaldehyde and other low-molecular weight aldehydes undergo rapid oxidation with hydrogen peroxide under strong alkaline conditions. With formaldehyde, the reaction produces formic acid and hydrogen, and the

Get The Facts On Clean Air With A Portable Emissions Analyzer, Starting At Under \$3,000

THE ENERAC MODEL 2000



- LOWER FUEL COSTS - COMPLY WITH EPA
- OBTAIN/STORE EMISSIONS DATA EASILY
- SUBSTANTIAL RETURN ON INVESTMENT
- SIMPLE - NO SPECIAL TRAINING REQUIRED
- EASILY EXPANDABLE
- ENERAC™ SERIES OFFERS YOU THE POWER TO KNOW STACK TEMP, O₂, CO₂, CO, NO_x, SO₂, AND CALCULATE EFFICIENCY LEVELS RAPIDLY, EASILY, ACCURATELY

Energy Efficiency Systems, Inc.
1300 Shames Drive, Westbury, New York 11590
(800) 695-3637 FAX (516) 997-2129

ing NOx emissions, and proves to have no detrimental effect on the process.

The chemistry follows that given previously for hydrogen peroxide and NOx in the gas scrubbing liquor. In the pickling bath, the hydrogen peroxide rapidly oxidizes nitrous acid to form the more stable nitric acid, thus preventing the formation and emission of NOx. Additionally, this reduces the nitric acid consumption of the pickling process.

Other Opportunities for Process Modification

Industry increasingly looks to perox-ygen technology for ways to avoid air pollution problems through process modification. In addition to NOx suppression, hydrogen peroxide finds upstream applications in the reduction or elimination of other problematic emissions.

For example, as regulation of absorbable organic halides discharge gains momentum, pulp mills continue to discover that by integrating hydrogen peroxide into the bleaching process, they achieve a 50-90 percent reduction in airborne chloroform. The hydrogen peroxide serves as a substitute, either partially or totally, for chlorine dioxide or hypochlorite; this ultimately represents a reduction in the use of chlorine and the generation of chloroform.

Another example of a successful preventive (vs. "curing") use of hydrogen peroxide is the elimination of hydrogen sulfide at its source. Municipal wastewater treatment plants may find that upstream peroxide dosing eliminates the need for costly gas scrubbers downstream.

ALTERNATIVES TO AIR STRIPPING

Air emissions from the treatment of contaminated groundwater represent a growing problem. Historically, air stripping removed volatile organic compounds (VOCs) from groundwater, with the net result amounting to a transfer of contaminants from groundwater to the atmosphere. As air discharges became more restrictive, vapor phase treatment with activated carbon was added to the end of the air stripper, adding cost and complexity to this approach.

Innovative technology provides a new alternative to traditional stripping methods. This new technology uses ultraviolet light to catalyze hydrogen peroxide, producing free radicals that destroy hard-to-treat organics in groundwater. Using this technology, hydrocarbon oxidation carried to completion yields carbon dioxide and water, and groundwater treatment generates

zero air emissions of hydrocarbons.


The ultraviolet/hydrogen peroxide system has proven superior to stripping in some applications. The results depend on a number of reaction variables, including the type and concentration of the organic contaminant and the required dosages of ultraviolet light and hydrogen peroxide. Many of these installations have been successful in removing contaminants ranging from benzene, to trichloroethylene, to vinyl chloride. At these sites, former air strippers sit idle in the wake of minor capital outlays and a superior technical and

environmental approach for modular systems using ultraviolet light and hydrogen peroxide.

Hydrogen peroxide is already used in many industries, and when applied properly, is a valuable and environmentally-safe chemical. However, as with most powerful chemicals, improper application or handling could create hazardous conditions or cause injuries. Before experimenting with, designing, installing, or modifying an application system using hydrogen peroxide, a manufacturer or other knowledgeable resource should be consulted. □

Monitoring,
analyzing,
and
reporting.

You got it.


METCO
ENVIRONMENTAL

1-800-394-1194