Controlling Reduced Sulfur Compounds with INTEROX® Hydrogen Peroxide

Hydrogen sulfide and other reduced sulfur compounds can present problems in both industrial and municipal treatment plants.

In municipal collection and treatment systems, hydrogen sulfide is produced via the reduction of sulfates by bacteria under anaerobic conditions. In the presence of aerobic bacteria, hydrogen sulfide forms sulfuric acid, which corrodes metals and concrete. INTEROX® Hydrogen Peroxide oxidizes hydrogen sulfide to elemental sulfur or sulfate. It can also provide residual hydrogen peroxide to a system. The residual hydrogen peroxide decomposes into dissolved oxygen, helping maintain an aerobic environment and preventing the formation of sulfide. The dissolved oxygen is also beneficial to biological treatment processes.

Reduced sulfur compounds also plague refineries, chemical plants, tanneries, food processing operations, pulp and paper mills, and many other industrial facilities. Scrubbers can recover marketable sulfur from gases containing hydrogen sulfide and sulfur dioxide, but liquid waste streams with lower concentrations of reduced sulfur must be treated with other methods. Today, much of this liquid waste disappears untreated into deep injection wells. As federal and state regulations tighten, this simple solution is less available and the need for an inexpensive, effective chemical treatment is increasing.

INTEROX® Hydrogen Peroxide has a long track record of controlling sulfide odors and corrosion in municipal sewage operations. It also offers a cost-effective solution for a wide variety of industrial sulfur problems.

Treatment alternatives

Many different approaches have been used to treat reduced sulfur compounds. A comparison is shown in Table One.

Hydrogen peroxide. In use since the 1970s, it has gained in popularity because it specifically oxidizes sulfur compounds without producing toxic byproducts.

Chlorine gas. A powerful, inexpensive oxidizer, it is also very hazardous to handle. If misused or overdosed, chlorine can also react with organics in the wastewater stream to form chlorinated organics such as chloroform.

Hypochlorite. Easier to handle than chlorine, but considerably more expensive. Like chlorine, hypochlorite can also form chlorinated organics.

Chlorine dioxide. Another powerful oxidizer, it does not form chlorinated organics as readily as chlorine or hypochlorite. It is, however, much more expensive than either chemical and requires on-site generation equipment.

Ozone. Another strong oxidizer that will eliminate hydrogen sulfide and other reduced sulfur compounds. Ozone requires expensive, on-site generation equipment and is difficult to handle. For these reasons, it is generally considered too expensive for sulfide control.

Potassium permanganate. This is another strong but relatively expensive oxidizer. It comes as a purple powder that can be difficult to handle. Spent permanganate may also precipitate manganese oxide - an unsightly brownish-black stain.

Precipitation. Ferrous chloride and ferrous sulfate are inexpensive chemicals used to precipitate iron sulfides. Their use, however, actually increases oxygen demand by increasing the “sourness” of a pond or other biological treatment system. Disposal of the iron sludge is another problem that must be addressed.
The oxidation of reduced sulfur compounds by hydrogen peroxide is a complex reaction controlled by a number of variables, including pH, catalysts, temperature, peroxide concentration and reaction time. These variables control the rate of the reaction, the consumption of hydrogen peroxide and the end products formed. The variables are interdependent, and changing one will affect the others.

**Nitrate.** In lagoons and holding ponds, adding nitrate will help establish a nitrate-reducing organism population, thus crowding out the population of sulfate-reducing organisms. Because this method takes time, it is ineffective in dynamic systems. It is also relatively costly, requiring 10 to 20 parts of nitrate to destroy one part of hydrogen sulfide.

**INTEROX® Hydrogen Peroxide advantages**

INTEROX® Hydrogen Peroxide combines advantages not obtainable with any other single form of chemical control. It is cost-effective and specific, forming no toxic byproducts. It is safe to work with when handled properly and produces soluble sulfates (and in some circumstances, thionates), thus avoiding the sludge problem. Hydrogen peroxide has a low freezing point, unlimited solubility in water, and it reacts very quickly. Finally, oxygen that remains after the sulfur oxidation reaction increases the oxygen content of wastewater, helping to prevent future production of sulfides by anaerobic bacteria.

The oxidation of reduced sulfur compounds by hydrogen peroxide is a complex reaction controlled by a number of variables, including pH, catalysts, temperature, peroxide concentration and reaction time. These variables control the rate of the reaction, the consumption of hydrogen peroxide and the end products formed. The variables are interdependent, and changing one will affect the others.

**Sulfides.** The reaction between sulfides and hydrogen peroxide depends greatly on the pH of the solution. The speciation chart (Figure One) shows that at an acid pH, sulfide exists primarily as molecular hydrogen sulfide, \( \text{H}_2\text{S} \), which reacts on a 1:1 (w/w) basis with hydrogen peroxide to form elemental sulfur. This is the most efficient use of hydrogen peroxide.
At a neutral pH, H₂S and HS⁻ exist and hydrogen peroxide reacts at a 1.5:1 (w/w) ratio with the sulfides. At an alkaline pH, it takes four times as much hydrogen peroxide to turn the S= ion into sulfate. The reactions that occur in each pH range are:

**Acid pH**

H₂S + H₂O₂ → S⁰ + 2H₂O

**Neutral pH**

H⁺ + HS⁻ + H₂O₂ → S⁰ + 2H₂O

HS⁻ + 4H₂O₂ → SO₄²⁻ + 4H₂O + H⁺

**Alkaline**

S= + 4H₂O₂ → SO₄²⁻ + 4H₂O

**Thiosulfates.** The oxidation of thiosulfates by hydrogen peroxide proceeds through a series of reactions, forming tetrathionates, then trithionates, then sulfites, and finally sulfates:

2SO₃²⁻ + H₂O₂ → S₄O₆²⁻ + 2OH⁻

S₄O₆²⁻ + 3H₂O₂ → S₃O₆²⁻ + 2H₂O + 2H⁺

S₃O₆²⁻ + H₂O₂ + H₂O → 3SO₃²⁻ + 4H⁺

SO₃²⁻ + H₂O₂ → SO₄²⁻ + H₂O

In most cases tetrathionate is acceptable for disposal.

In acid solutions with low concentrations of hydrogen peroxide, the tetrathionate is the primary end product. As the concentration of peroxide increases, the reaction proceeds to the formation of trithionates, sulfites and sulfates.

Most waste streams are alkaline and in these systems, the reaction normally proceeds through to sulfates, thus requiring considerably more hydrogen peroxide. There is, however, a patented Solvay Chemicals catalyst system that can both speed up the reaction and significantly reduce the amount of hydrogen peroxide needed.

**Sulfites.** Regardless of pH, sulfites react with hydrogen peroxide to form sulfates:

SO₃²⁻ + H₂O₂ → SO₄²⁻ + H₂O

This reaction is fast, requires no catalyst, and uses relatively little hydrogen peroxide, and unlike systems which use air, all of the sulfite is oxidized to sulfate.

**Mercaptans and disulfides.** Mercaptans or thiols are the sulfur analogs of alcohols, containing the -SH (sulfhydryl) group. They react with hydrogen peroxide in alkaline conditions to form disulfides:

2RSH + H₂O₂ → RSSR + 2H₂O

Disulfides generally form an insoluble oil layer that is easy to separate. Disulfides also react with hydrogen peroxide to form sulfonic acid:

RSSR + 5H₂O₂ + 20H⁻ → 2RSO₃⁻ + 6H₂O

Carrying the reaction to the sulfonic acid using a peroxide to pollutant molar ratio of 5:1 is generally enough to control odors. The reaction proceeds best with a copper or iron catalyst in the presence of a chelating agent, such as EDTA. The chelating agent helps prevent the catalyst from coming out of solution, and increases the pH range over which the reaction takes place.
Typical applications

In many cases of sulfur pollution, hydrogen peroxide will reduce extremely high levels of sulfides, thiosulfates and sulfites (e.g., above 1000 mg/L to less than 10 mg/L). The following examples show the diversity of suitable applications:

**Treatment of biological upsets in ponds and lagoons.** In both the food processing and pulp and paper industries, biological treatment systems can suffer anaerobic conditions that lead to the formation of H₂S and other sulfides. Batch treatment with hydrogen peroxide not only rids ponds and lagoons of odor and poisonous sulfides, it also leaves behind a residue of excess oxygen that helps prevent future anaerobic conditions.

**Treatment of sour waters from a refinery.** One refinery compared the use of hydrogen peroxide to stripping to remove sulfides from a sour water stream. Using an H₂O₂:S = ratio of 3:1 at a pH of 8.5, the refinery successfully reduced sulfides to required limits and avoided the capital cost of the stripper.

**Pretreatment of process wastewater.** In another refinery, sulfide remaining in the waste stream after sour water stripping was first oxidized by air and steam to thiosulfate. Hydrogen peroxide was then used to convert the thiosulfate to sulfate. The municipal collection system accepted this treated wastewater.

**Hydrogen sulfide scrubbers.** A West Coast municipality experienced problems with high sulfide levels after primary treatment of sewage. A caustic scrubber system was installed to absorb the hydrogen sulfide. Hydrogen peroxide introduced into the scrubber solution oxidized the sulfide to sulfate.

**Geothermal applications.** Condensed steam from geothermal power plants contains high levels of sulfides. Several plants on the West Coast treat the condensate by using hydrogen peroxide with an iron catalyst.

**Industrial water reuse.** A midwestern commercial car wash operating under a zero discharge permit began experiencing hydrogen sulfide odors in its water despite the fact that the water had gone through settling, ion charge and carbon absorption treatment units. By adding a hydrogen peroxide step after the carbon unit, the odors were completely removed.

**Municipal odor control.** A southeastern U.S. wastewater treatment plant had a severe hydrogen sulfide odor problem. The odor spawned several citizen complaints, and finally led to court action. Solvay Chemicals worked with the county, conducting a cost analysis and on-site trials. These led to a hydrogen peroxide dosing strategy that allowed the county to control its dissolved and airborne sulfides.

---

**Table Two: Hydrogen Peroxide Chemistry**

<table>
<thead>
<tr>
<th>Sulfur Compound</th>
<th>pH</th>
<th>Weight Ratio H₂O₂: Pollutant 100% Basis</th>
<th>Reaction Time</th>
<th>Catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfides</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid</td>
<td>1.00:1</td>
<td>Minutes</td>
<td>Fe²⁺ can be used to speed reaction time.</td>
<td></td>
</tr>
<tr>
<td>Neutral</td>
<td>1.5:1</td>
<td>Minutes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkaline</td>
<td>4.25:1</td>
<td>Minutes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thiosulfates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid</td>
<td>0.15:1 (min)</td>
<td>Minutes</td>
<td>Patented Solvay Chemicals catalyst used in alkaline systems to reduce mole ratio of H₂O₂ required.</td>
<td></td>
</tr>
<tr>
<td>Alkaline</td>
<td>1.21:1 (max)</td>
<td>Minutes or seconds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfites</td>
<td>All</td>
<td>0.43:1</td>
<td>Minutes</td>
<td>Catalyst not required.</td>
</tr>
<tr>
<td>Mercaptans, Disulfides</td>
<td>Alkaline</td>
<td>5:1 mole ratio (Weight ratio depends molecular weight of organic component)</td>
<td>Minutes</td>
<td>Chelated Fe²⁺ or Cu²⁺ generally required.</td>
</tr>
</tbody>
</table>
Sludge treatment. In the Midwest, a wastewater treatment plant experienced high levels of hydrogen sulfide in sewage sludge. The hydrogen sulfide was volatilizing at the thickener and causing severe odor and health problems. By adding hydrogen peroxide prior to sludge thickening, the plant was able to successfully combat hydrogen sulfide and related problems.

Treatment of sludges in pond closings. Many industries are closing and/or refurbishing treatment ponds to meet stringent RCRA guidelines for permeability. Some of these ponds contain sludges high in sulfides. One refinery met EPA guidelines for disposal by treating the pond with hydrogen peroxide. This reduced the sulfide level from several thousand mg/L to less than 20 mg/L.

Quality
Solvay Chemicals strives to bring you the best in products, service and technology. Exceeding, not just meeting, your expectations is the basis for our pursuit of continual improvement. To demonstrate our commitment, Solvay Chemicals’ Quality Management System is registered to the ISO 9001:2000 International Quality Management System Standard.

Our registration encompasses the production and distribution of hydrogen peroxide at both of our manufacturing facilities in Deer Park, Texas and Longview, Washington, as well as administrative activities at our Houston, Texas headquarters.

Solvay Chemicals will continue to pursue excellence in everything we do. We dedicate ourselves to this effort because we know that our success depends on satisfying you.

Safety
Like all other powerful chemicals, hydrogen peroxide must be treated with respect and handled appropriately. For a full discussion of safe handling of this product, please see our publication “Hydrogen Peroxide Safety and Handling”, available on request, or as a download from our website at www.solvaychemicals.us.

Delivery
In North America, Solvay Chemicals ships product from two plant sites and a number of strategically located distribution terminals. We operate a fleet of high-purity aluminum and stainless steel tank trucks and rail cars dedicated to hydrogen peroxide service.

We also provide stainless steel IM101 ISO containers to deliver, store and dose hydrogen peroxide. These isotainers are ideally suited to seasonal or short-term needs. In emergency situations, our Quick Response program will get isotainers of hydrogen peroxide to your site right away. For the information on our excellent delivery capability, call 1-800-765-8292 (1-800-SOLVAY-C), or see our brochure “Isotainers for a Quick Response”, which is available on our website at www.solvaychemicals.us.

Responsible Care® Program
Recognizing the importance of preserving the environment of the planet we share, and the health and safety of the employees who produce our products, Solvay Chemicals actively supports the Responsible Care program of the American Chemistry Council.
To our actual knowledge, the information contained herein is accurate as of the date of this document. However, neither Solvay Chemicals, Inc. nor any of its affiliates makes any warranty, express or implied, or accepts any liability in connection with this information or its use. This information is for use by technically skilled persons at their own discretion and risk and does not relate to the use of this product in combination with any other substance or any other process. This is not a license under any patent or other proprietary right. The user alone must finally determine suitability of any information or material for any contemplated use in compliance with applicable law, the manner of use and whether any patents are infringed. This information gives typical properties only and is not to be used for specification purposes. Solvay Chemicals, Inc. reserves the right to make additions, deletions or modifications to the information at any time without prior notification.

Copyright 2005, Solvay Chemicals, Inc. All Rights Reserved.