

Hydrogen Peroxide

Controlling reduced sulphur compounds

Solvay
Interox



Hydrogen Peroxide for controlling reduced sulfur compounds

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. 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 regulations tighten, this simple solution is less available and the need for an inexpensive, effective chemical treatment is increasing.

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 out as manganese dioxide – an unsightly brownish-black stain.
- *Precipitation*. Ferrous chloride and ferrous sulfate are inexpensive chemicals used to precipitate iron sulfides. Their use, however, can actually increase oxygen demand by increasing the “sourness” of the biological treatment system. Disposal of the iron sludge is another problem that must be dealt with.
- *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.

Peroxide advantages

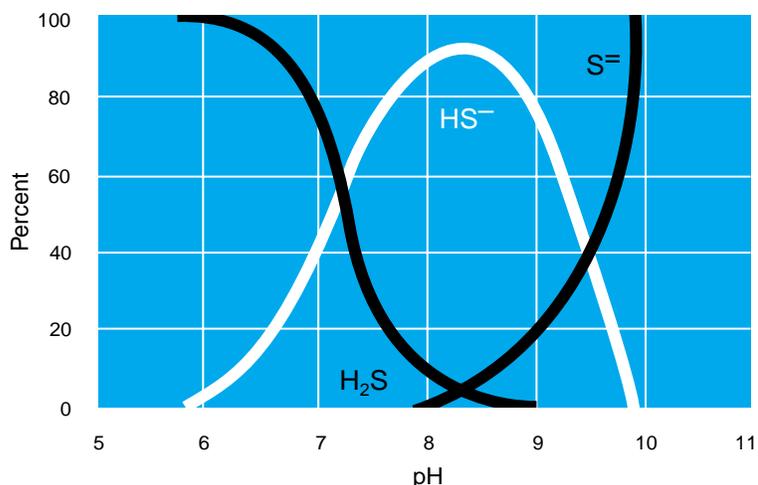
Hydrogen peroxide combines advantages not obtainable with any other single form of chemical control. It is cost effective and specific, forming no toxic byproducts. It is safe to work with when handled properly and produces soluble sulfates (and in some circumstances, thionates), thus avoiding the sludge 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.

Peroxide chemistry

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 acid pH, sulfide exists primarily as molecular hydrogen sulfide, H_2S 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.

Figure One: Speciation chart

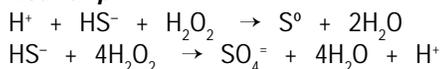


At neutral pH, H₂S and HS⁻ coexist and hydrogen peroxide reacts at a 1.5:1 (w/w) ratio with the sulfides. At alkaline pH, it takes four times as much hydrogen peroxide to turn the S²⁻ ion into sulfate. The reactions that occur in each pH range are:

Acid pH



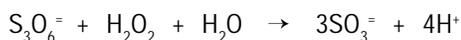
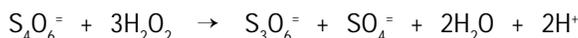
Neutral pH



Alkaline pH



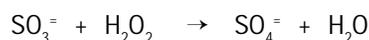
Thiosulfates. The oxidation of thiosulfates by hydrogen peroxide proceeds through a series of reactions, forming tetrathionates, then trithionates, then sulfites, and finally sulfates:



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 more hydrogen peroxide. There is, however, a patented Solvay Interlox 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:

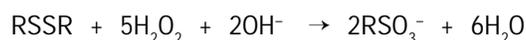


This reaction is fast, requires no catalyst, and uses relatively little peroxide and, unlike systems which use air, all of the sulfite is oxidized to sulfate.

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:



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



Carrying the reaction to 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.

Table Two: Peroxide chemistry

<i>Sulfur Compound</i>	<i>pH</i>	<i>Weight Ratio H₂O₂:Pollutant, 100% Basis</i>	<i>Reaction Time</i>	<i>Catalysts</i>
Sulfides	Acid	1.00:1	Minutes	Fe ⁺² can be used to speed reaction time
	Neutral	1.5:1	Minutes	
Thiosulfates	Alkaline	4.25:1	Minutes	Patented Solvay Interlox catalyst used in alkaline systems to reduce mole ratio of H ₂ O ₂ required
	Acid	0.15:1(min)	Minutes	
	Alkaline	1.21:1(max)	Minutes or seconds	
Sulfites	All	0.43:1	Minutes	Catalyst not required
Mercaptans, Disulfides	Alkaline	5:1 mole ratio (Weight ratio depends on molecular weight of organic component)	Minutes	Chelated Fe ⁺² or Cu ⁺² generally required

Typical applications

There are a wide variety of industrial applications involving sulfur pollution. In many cases, hydrogen peroxide will reduce extremely high levels of sulphides, thiosulphates and sulphites (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 H_2S and other sulphides. Batch treatment with hydrogen peroxide not only rids ponds and lagoons of odor and poisonous sulphides, 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 sulphides from a sour water stream. Using an $H_2O_2:S^{2-}$ ratio of 3:1 at a pH of 8.5, the refinery successfully reduced sulphides to required limits and avoided the capital cost of the stripper.

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

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

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

Industrial water reuse. A midwestern commercial car wash in the USA operating under a zero discharge permit began experiencing hydrogen sulphide odours in its water despite the fact the water had gone through settling, ion exchange and carbon adsorption treatment units. By adding a hydrogen peroxide step after the carbon unit, the odours were completely eliminated.

Municipal odour control. One southeastern U.S. wastewater treatment plant had a severe hydrogen sulphide odour problem. The odour spawned several citizen complaints and finally led to court action. Solvay Interlox 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 their dissolved and airborne sulphides.

Sludge treatment. In the Midwest of the USA, a wastewater treatment plant experienced high levels of hydrogen sulphide in the sewage sludge. The hydrogen sulphide 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 the hydrogen sulphide and related problems.

Treatment of sludges in pond closings. Many industries are closing and/or refurbishing treatment ponds to meet stringent EPA guidelines for permeability. Some of these ponds contain sludges high in sulphides. 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.

Solvay Interox is dedicated to customer satisfaction

We strive to make your experience with Solvay Interox safe, efficient, and cost effective. Most of the important product and contact information is readily available at www.solvayinterox.com.au. You may also contact us by phoning 61 2 9316 8000, faxing 61 2 93166445 or writing to Solvay Interox, Pty.Ltd. at 20-22 McPherson Street, Banksmeadow, NSW 2019.

Solvay Interox Quality Policy

"Total Customer Satisfaction through Operational Excellence"

This policy means that we pursue the highest standards of excellence in every facet of our business. We dedicate ourselves to this effort because we know that our success depends on satisfying you.

Our Quality Management System demonstrates this commitment by meeting the requirements of the ISO 9002:1994 International Quality Standard. The manufacture and distribution of hydrogen peroxide at our plant in Banksmeadow, NSW, as well as the support activities at the Banksmeadow headquarters, are all registered to ISO 9002:1994.

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 upon request, or as a download from our website at www.solvayinterox.com.au. Solvay Interox also conducts safety training sessions as part of its *PARTNERS* program.

Delivery

Solvay Interox distributes product from the Banksmeadow site and a number of strategically located distribution warehouses. Hydrogen peroxide is packed in 25 kg carboys or 250 kg Mauser drums. Bulk hydrogen peroxide is shipped in 1,200 kg Intermediate Bulk Containers (IBCs), 2,500 kg Road Tanks and 20 or 24 tonne Isotanks.

Responsible Care

Recognising the importance of preserving the environment of the planet we share, and the health and safety of the employees who produce our products, Solvay Interox actively supports the Responsible Care® program of PACIA.

***PARTNERS* PROGRAM**

PARTNERS is a collaborative program of development between Solvay and its customers. It aims to establish the appropriate levels of cooperation and services to be exchanged as part of the product provided by Solvay Interlox. Issues such as Safety Training, Audits, Engineering and Technical Support can be covered by the *PARTNERS* program.

PARTNERS aims to more effectively focus resources from Solvay Interlox on those issues of significance to our customers. This is achieved by an ongoing dialogue to develop programs and projects, which improves in total the on-site performance of peroxygens and the operations of both organisations.

The nucleus of *PARTNERS* commences with safety and safety related topics such as operator training and safety audits. Other areas of potential development include engineering, design, HAZOP, production performance auditing and technical process investigations. The level of partnership development will evolve through time to include those areas of importance to both partners.

Structured *PARTNERS* IN SAFETY training for your customers, staff, contract drivers etc.

- 24 hour emergency response hotline 1800 023 488.
- Safety audits of storage facilities.
- Technical service and advice.
- Staff training on efficient use of peroxygens and operational audits of processes.
- Access to our research and development findings.
- Participation in HAZOP studies.
- Engineering support for bulk installations and dosing systems.

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Disclaimer: " This Product Leaflet summarises our best knowledge of the health and safety hazard information of the product and how to safely handle and use the product in the workplace. Each user should read this Product Leaflet and consider the information in the context of how the product will be handled and used in the workplace including in conjunction with other products.

If clarification or further information is needed to ensure that an appropriate risk assessment can be made the user should contact this company.

Our responsibility for products sold is subject to our standard terms and conditions, a copy of which is sent to our customers and is available on request."