

The Use of Hydrogen Peroxide for the Oxidation of Sulfur Chemical Wastes

Introduction

This paper discusses the results of both laboratory and field studies of the reactions of sulfur compounds, including mercaptans, sulfides, and sulfur dioxide with peroxygen chemicals. The overall goal of these studies was to determine the optimum conditions for the treatment of liquid and gaseous industrial wastes containing the above compounds.

Treatment with hydrogen peroxide, has proven to be a convenient way to oxidize the toxic and obnoxious reduced sulfur compounds present in many of today's industrial effluents. The oxidation products are harmless, mainly sulfate, and impose little or no oxygen demands on subsequent waste treatment systems.

Approximately 60 industrial and municipal waste treatment plants in the United States are currently known to be using hydrogen peroxide to control their sulfur chemical wastes.

Chemistry

Sulfides and Mercaptans – Hydrogen sulfide and mercaptans are waste products of petroleum refining, tanneries, the evaporation of black liquor in kraft pulping, viscose rayon manufacture and the purification of natural gas. Hydrogen sulfide is frequently the cause of odor problems when organic waste products are collected and stored in non-aerated lagoons. Sulfide-containing gases may be scrubbed with alkaline solutions. These are also a source of liquid sulfide wastes requiring treatment before discharge into a sewer or stream.

Many of these compounds are toxic and corrosive. Both hydrogen sulfide and the common mercaptans, such as methyl mercaptans, have odor threshold limits as low as 1 ppb in air.

Because hydrogen sulfide is of such common occurrence, its deadly character has been largely ignored. By comparison hydrogen cyanide is widely recognized as a dangerous poison. Hydrogen sulfide has approximately the same level of toxicity as HCN, and deaths have been reported at levels as low as 300 ppm of hydrogen sulfide.

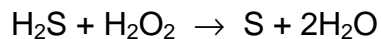
The rate at which hydrogen sulfide or mercaptans can escape from solution into the air is largely dependent upon the pH of the solution.

Table I shows the effect of pH on the equilibrium vapor concentration of hydrogen sulfide with a water solution initially containing 70 mg/l of dissolved sulfide at 25°C.

Table I

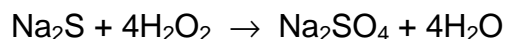
<u>pH</u>	<u>H₂S Vapor Conc. (ppm by Vol.)</u>
5	18,300
6	17,200
7	10,900
8	2,400
9	260
10	26

Hydrogen sulfide under neutral conditions will react with hydrogen peroxide to give sulfur and water



In pure solutions the reaction is relatively slow requiring 15 to 30 minutes for completion. Trace amounts of iron salts (2-4 ppm Fe) will greatly accelerate this reaction. Reaction time is reduced to 1-2 minutes at room temperature and 2-6 seconds at 60°C (140°F).

In alkaline solution of pH 8 or greater the dominant reaction is:



This reaction is fast without catalysts and is completed in a few minutes at room temperature. The reaction is stepwise and a 1:1 ratio of H₂O₂:H₂S will eliminate all the sulfide. However, to transform all the sulfur into the form of sulfate, 4 moles of hydrogen peroxide per mole of S⁼ are needed.

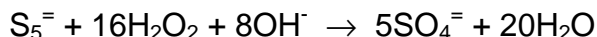
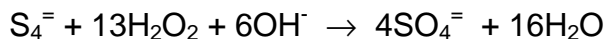
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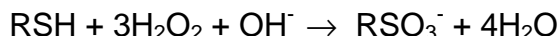
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Polysulfides, S_x^{-2} in alkaline solutions react the same way as sulfides. This is not unexpected since polysulfides are actually intermediate species in sulfide oxidation. The exact stoichiometry depends on the species present, i.e.,



At pH below 8, polysulfides decompose into sulfide and elemental sulfur.

Mercaptans (RSH) are oxidized with hydrogen peroxide according to the equation:

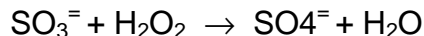


Sulfones and sulfonic acids are the initial reaction products. At room temperature the reaction is slow. Again traces of iron salts are effective in accelerating this reaction. For instance, a Kraft pulp mill waste containing 22 ppm total sulfides (primarily methyl mercaptans) was treated with 66 ppm of hydrogen peroxide. After 10 minutes the total sulfide of the treated sample read 10 ppm. When a duplicate sample was treated with 66 ppm hydrogen peroxide plus 4 ppm Fe^{++} the total sulfide was 1 ppm after 10 minutes. When 7 ppm Fe^{++} was used together with hydrogen peroxide no detectible sulfide was found after 10 minutes.

Higher temperatures (60°C) also accelerate the reaction.

Sulfur dioxide and sulfites are waste products of sulfuric acid manufacture, sulfite pulping, roasting operations, power plants, and chemical manufacture. The sharp irritating odor of sulfur dioxide may be detected at levels as low as 0.5 ppm (Manufacturing Chemists Association).

Sulfite, (SO_3^-) is oxidized to sulfate. In acid solution the reaction is very rapid; in alkaline solution it is slower. The reaction is:



The times necessary for 90 to 99% SO_3^- oxidation at several pH levels, when initial SO_3^- concentration was 7.2 g/l and 10% excess of hydrogen peroxide was used were:

Oxidation Time – Minutes

pH	% Oxidation	
	90	99
7.9	0.4	2
9.2	1.4	5
9.4	5.0	20
10.8	.5	25
11.4	11.0	43

Several recent patents have proposed the use of hydrogen peroxide to oxidize sulfur dioxide emissions from sulfuric acid manufacture. This process is believed to be used commercially in at least one U.S. installation. The oxidation of sulfite wastes to reduce BOD and COD loadings is also a commercial reality.

Thiosulfates

Thiosulfate wastes are products of such diverse industries as steel manufacturing and photography.

Sodium Thiosulfate pentahydrate, the common “hypo” of the photographic industry, reacts quantitatively with peroxide in alkaline solution.



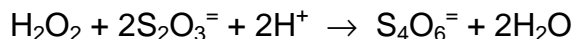
Thus 0.55 parts of hydrogen peroxide oxidize 1.0 part of sodium thiosulfate pentahydrate. The reaction was found to be 90 percent complete in 10 minutes and 98 percent complete within 30 minutes. Results from a typical experiment are tabulated below:

Sodium Thiosulfate Pentahydrate Conc. mg/l	H ₂ O ₂ Conc. mg/l	BOD ₅ mg/l	
		Before H ₂ O ₂	After H ₂ O ₂
20,000	11,000	4,000	40

The initial pH of the thiosulfate solution should be 8.0 or higher.

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In acid solution only partial oxidation occurs and tetrathionates are formed.



Scrubbing Tests

Laboratory studies were conducted to determine the optimum conditions for the oxidation of gaseous sulfur compounds with hydrogen peroxide.

The two most important considerations in designing a liquid scrubber are (1) the selection of a scrubbing medium which will give rapid absorption of the pollutant and (2) providing sufficient contact time to give good absorption and to allow sufficient time for the oxidation of pollutant. For this purpose a packed bed appears to be most satisfactory.

Figure 1 shows a schematic of the bench scale scrubber used in FMC's laboratory studies. This equipment consisted essentially of a two inch Pyrex pipe packed with ¼ inch Intalox saddles supported by a stainless steel screen. Below the support was an inlet for the gas and an outlet for the liquid. The liquid level was kept above the exit opening with a float controlled solenoid valve to avoid gas escaping this way. Above the packing were inlets for the liquid and a side arm outlet for gas.

The auxiliary equipment consisted of flow meters and valves for hydrogen peroxide, the alkaline water solution, test gas, air and the exhaust gas side stream for analysis. Exit liquid was sampled normally from the liquid outlet. Gauges were used for measuring pressure of inlet gas and pressure drop in the packing. The fluids were tested at ambient temperatures.

The air was taken from the house line, filtered and pressure adjusted with a pressure controller. The hydrogen peroxide was premixed with deionized water to obtain a concentration yielding a flow rate suitable for measurement in the flowmeter. The peroxide was pumped with a microbellow pump into a pressure chamber made of a short length of 2" Pyrex pipe. From here the peroxide solution was propelled into the scrubber with compressed air. The water was pumped with a centrifugal pump. Example of the data obtained are given below:

The packing height was 37 cm.

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Example 1

The air contained 1% by volume of hydrogen sulfide. The liquid contained 10 g/l of NaOH and 4.3 g/l of H₂O₂. The gas flow velocity in the packing was 56 cm/sec; the resident time of the gas in the contactor was 0.66 sec. The effluent gas contained less than 1 ppb H₂S. The effluent liquid had a pH of 12.5 and H₂S content was 0.5 mg/l. The pressure drop in the

column was, when the column was still dry with only gas flowing, 26 mm water column. With 1% NaOH solution the pressure drop was 51 mm. In the second run NaOH concentration was reduced to 0.5%, which corresponds to 1.35 times the necessary amount, leaving the other conditions the same. Initial pressure drop was 68 mm water column, in 30 minutes it was 72 mm and after an hour 77 mm. The solution remained clear at all times. The pH of the effluent was 0.5 ppm.

Example 2

The gas contained 0.1% by vol. H₂S and the liquid contained 0.165 g/l NaOH and 0.28 g/l H₂O₂. The effluent gas contained less than 1 ppb H₂S; the effluent liquid had a pH of 10.4 and the H₂S content was 7 mg/l.

Example 3

The gas contained 0.006% H₂S by volume and the liquid contained .1 g/l NaOH and 0.02 g/l H₂O₂. The effluent gas had less than 1 ppb H₂S. The effluent liquid had a pH of 9.3 and the content of H₂S was 1.7 mg/l.

Hydrogen sulfide was removed effectively in all examples.

In the tests with organic sulfur compounds the packing height was 70 cm. The total gas flow as 15 L/min. The gas contained 1000 ppm by volume methane thiol. The liquid flowrate was 1.35 L/min. The liquid consisted of an aqueous solution containing 1.0 g/l of NaOH and 1 g/l H₂O. The pH of the solution was 11.9.

After liquid-gas contacting the effluent gas contained 4 ppm methane thiol, a 99.6% reduction. The effluent liquid pH had dropped to 11.0 and the content of unoxidized sulfur compounds was below detection limits.

Example 2 & 3 Modified

The same conditions were used as in the previous example, only the gas contained 8000 ppm by volume H₂S and 200 ppm by volume methane thiol. The effluent gas contained no detectable H₂S and 2 ppm by volume methane thiol. The effluent liquid had a pH of 11.2 and the content of unoxidized sulfur compounds was below detection limits.

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Example 4

The same conditions were again used only the gas contained 1000 ppm by volume ethane thiol, 1000 ppm by volume dimethylsulfide and 100 ppm thiophene. The effluent gas contained no detectable sulfur compounds. The effluent liquid had a PH of 11.9 and none of the original sulfur compounds were present. The effluent did contain approximately 5 mg/l of diethyldisulfide.

In practice any conventional scrubber can be used which will provide the necessary contact time between the liquid and gas phase. Best are probably the packed bed scrubbers, because the characteristics of these are known and the operating parameters can be calculated. Some types of scrubbers i.e., venturi type, various spray chamber usually have insufficient contact for adequate gas absorption.

Some scale-up examples of packed bed scrubber are shown below.

The example describes a scrubber which can handle a gas flow of 50 m³/min. (1800 cu ft/min). Several choices of tower diameter and height combinations are given in the table. The packing chosen is 1" Intalox saddles (Norton Company). Two sets of values are given: One for removal of H₂S originally present in an amount of 200 ppm, the other for treatment of gas originally containing 20 ppm H₂S.

Diameter of Column m	Liquid Flow inches	Height of Column					
		200 ppm H ₂ S		20 ppm H ₂ S			
		1/min	gal/min	m	in.		
.782	30	86	23	1.27	50	.84	33
.798	31	120	32	1.06	42	.70	28
.824	32	158	42	.93	37	.62	24
.924	36	400	106	.62	21	.35	14
1.128	44	1200	318	.35	14	.23	9

The hydrogen peroxide consumption for a gas containing 200 ppm H₂S will be 56 gal/min (7.5 lbs/hour) calculated as 100% material. The consumption of NaOH will be 35 gal/min. (4.5 lbs/hour).

For other gas flow rates the height of packing will remain the same. The column diameter will change proportionally to the square root of the gas flow.

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Commercial Applications

Hydrogen peroxide is now widely used in both municipal and industrial applications for the control of sulfur containing wastes. In municipal treatment and collection operations the principal application is in the control of sulfide buildup in waste collection systems. Anaerobic conditions in long gravity and force mains lead to the formation of hydrogen sulfide and subsequent odor and corrosion problems. These problems are generally easy to treat by the addition of hydrogen peroxide upstream of the point of the odor or corrosion problem. Approximately two parts of hydrogen peroxide are required per one part of sulfides. About fifteen minutes time is required to complete the reaction unless catalytic salts such as iron are present to accelerate the reaction.

Industrial applications are quite varied. They include pulp and paper plants where the problem may be either sulfides or mercaptans, textile plant odors, pharmaceutical plants, cutting oils, soy bean oil manufacture, and the high BOD sulfur wastes from chemical manufacture.

Some typical examples of these applications are given below:

Paper Mill

A paper mill in the Northeast produces paperboard using largely recycled waste furnish. The waste treatment system, handling 2.5 MGD, consists of a primary settling tank, aerated lagoon, and secondary clarifier. Sludge from the secondary clarifier is returned to the primary settling tank, combined with primary sludge, and returned to the paper mill for use as the board furnish.

Chlorine was added to the sludge system for control of odors, including hydrogen sulfide. Chlorine usage was 300-400 lbs. Per day, or approximately 2000 ppm based on sludge weight. A problem of short life on the disc refiner plates was blamed on corrosion caused by the high 80 ppm chloride content of the furnish at the refiners. Cost for a monthly change of refiner plates was estimated at \$500. Handling of the ton chlorine cylinders was also a problem in cost and manpower.

A 35 day plant scale trial demonstrated the effectiveness of hydrogen peroxide in controlling waste treatment plant sludge odors. Seventy-three pounds/day of fifty percent hydrogen peroxide replaced 300 pounds of chlorine for this purpose at an estimated annual savings of \$2500/year. Overall waste treatment plant performance, as measured by effluent BOD, effluent solids and turbidity was equal or superior with the hydrogen peroxide system as compared with chlorine treatment. Examination of the disc refiner plates after 35 days operation on peroxide treated sludge furnish showed no signs of corrosion. The plant now routinely uses hydrogen peroxide in place of chlorine for odor control. After one year's service refiner plate life had doubled.

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Soybean Processing

Wastewater from soybean processing plant generated odors in a holding tank used to settle solids and decant oil. Subsequent discharge of the aqueous phase generated further objectionable odors when entering the municipal sewer.

Waste Treatment System

The 0.3 mgd combined wastewater stream from the soybean processing operation contains soybean solids and oil as well as significant sulfate from in-process neutralization of sodium soaps with sulfuric acid. Alum (0.04 wt %) is added to the wastewater and flocculated by adjustment of the pH to about 5.9. This facilitates settling of the solids when the mixture is fed into a 32,000 gallon holding tank. The settled solids are removed, the oil that rises to the surface is decanted, and the aqueous layer is discharged to the municipal sewer. The aqueous layer is discharged to the municipal sewer. The aqueous phase has a high BOD of the order of 1000 mg/l or more when discharged. Normal biological activity depletes the dissolved oxygen in the wastewater and the high sulfate content encourages generation of hydrogen sulfide in the hold tank, and later in the municipal sewer.

Procedure and Results

Initial attempts to control the odor problem by aeration, or addition of up to 75 ppm chlorine to the wastewater, were unsuccessful.

Addition of hydrogen peroxide to the waste water controls the odor problem. The hydrogen peroxide is added at a rate of 40 ppm (100% basis) to the waste water before it enters the 32,000 gallon holding tank. Supplemental hydrogen peroxide is added to the effluent from the holding tank on the rare occasions when some odor develops.

An ancillary advantage for hydrogen peroxide when compared with chlorine for controlling odors in the holding tank is recovery of soybean solids and oil with no objectionable chlorinated residues contamination.

Chemical Manufacture

A southern chemical manufacturing plant had a acidic waste stream high in sulfur dioxide. This resulted in objectionable effluent BOD and COD values. The addition of hydrogen peroxide corrected the problem with only minor equipment costs. Approximately 6.4 pounds of hydrogen peroxide (10% as solution) was found to be sufficient to destroy one pound of sulfur dioxide.

The above waste stream was from a sulfur recovery system in which sulfur chlorides were hydrolyzed to give an effluent containing both hydrochloric acid and sulfur dioxide. When

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hydrogen peroxide was added to this mixture the sulfur dioxide was rapidly oxidized to sulfuric acid.

This stream could then be blended with alkaline wastes to give an effluent having greatly reduced COD demand.

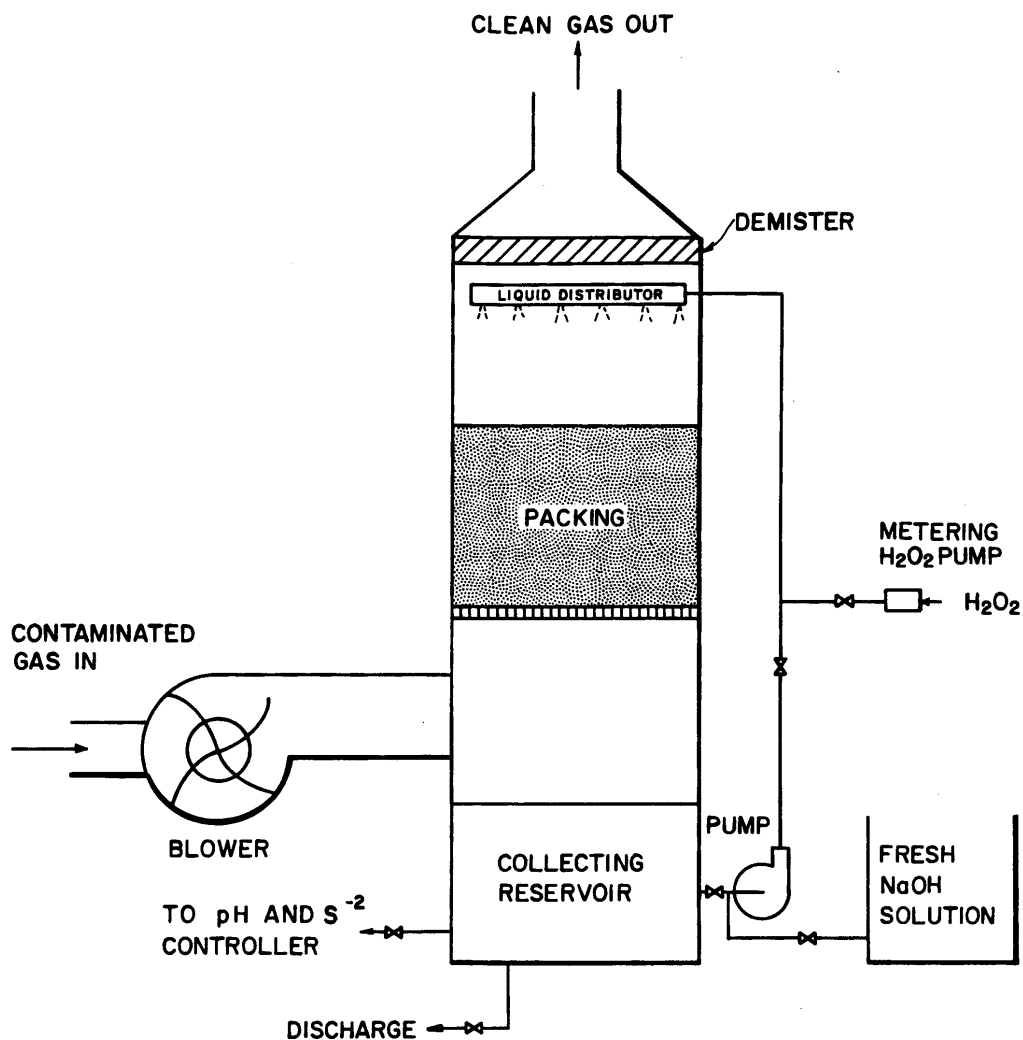
Summary and Conclusions

Hydrogen peroxide oxidation has been found to be a convenient process for the treatment of many sulfur containing wastes. Among its advantages are:

1. Ease of handling an all liquid system.
2. Has no toxic or corrosive fumes.
3. Economical.
4. Reduces odor, COD and BOD.
5. Hydrogen peroxide's decomposition products, water and oxygen, add no harmful products to the stream.
6. Can be used to add dissolved oxygen to the system.

It is hoped that the above discussion will stimulate thinking of other waste treatment uses for this chemical and in another year we will have many new examples to report.

**SCHEMATIC OF A HYDROGEN
SULFIDE SCRUBBER**



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