REMOVAL OF HYDROGEN SULFIDE IN DRINKING WATERS
WITH HYDROGEN PEROXIDE

by

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ABSTRACT

The presence of hydrogen sulfide is a common problem encountered in the field of water supply. This chemical imparts to the water unpalatable taste and odor, in addition to corrosive properties. The hydrogen sulfide problem is of major importance in New Mexico where it has caused many wells to be abandoned.

Hydrogen peroxide is a non-polluting, relatively inexpensive oxidizing agent, which has shown promise as a solution to the hydrogen sulfide problem. For this reason, the New Mexico Environmental Improvement Division (EID) has authorized the study of hydrogen peroxide as a potential oxidant for the removal of hydrogen sulfide from water supplies. The research presented in this paper demonstrates the technical feasibility of using hydrogen peroxide to remove hydrogen sulfide from drinking water supplies.

Favorable removal of hydrogen sulfide was obtained during the ongoing field implementation of hydrogen peroxide in the distribution system at Madrid, New Mexico (pop. 89). The removal efficiencies of 95 percent and higher obtained during these field studies demonstrate that the oxidation of hydrogen sulfide with hydrogen peroxide is a plausible solution to the taste and odor problems in rural communities' distribution systems. Treatment costs for typical rural facilities vary between 19 and 64 cents per thousand gallons, depending on the water storage capacity available on site. Design procedures and criteria for these facilities are also presented.

KEY WORDS: water treatment, chemical treatment, sulfides, chemical
             oxidation, potable water

INTRODUCTION

The study of the chemistry of the different sulfur species and their
removal from drinking water is important in the field of water supply
because many of the thermodynamically stable species of sulfur are envi-
ronmental pollutants. Sulfur and sulfates are potential pollutants,
but more significant than these are sulfides, due to their undesirable
properties and less-developed treatment methods. Hydrogen sulfide (H_2S)
in water at levels as low as 0.001 mg/l gives it a characteristic "rotten
egg" odor and a musty taste (Pomeroy 1969). Water containing H_2S is very
corrosive, reacting with iron, copper, or silver to form metal sulfides.
Contact between H_2S and oxygen causes the formation of sulfuric acid,
which corrodes concrete and steel. H_2S in the gaseous state is of major
concern because of its toxicity and explosiveness. The maximum safe
concentration of H_2S in air is 13 ppm by volume. However, much of the
danger lies in the fact that the H_2S paralyzes the olfactory nerves so
that it no longer ecomes detectable. Because the temperature of igni-
tion is only 250°C, when H_2S is present in concentrations between 4.5
and 45.5 percent by volume in air, the danger of explosion is present.

Sulfides do not accumulate in water except under anaerobic condi-
tions. The removal of sulfides from water can be effected through
biological oxidation, metal sulfide precipitation, volatilization or
chemical oxidation. Some of the removal alternatives that have been
studied include aeration, chlorination, ozonation, and oxygenation. In
addition, lime, sodium nitrate, sulfates of zinc, copper, ferrous iron,
and activated carbon have been used to remove sulfides. The selection
of a procedure for the removal of sulfides from water is very much depen-
dent on economic considerations, as well as the ease of implementing the
method.

Sulfides in drinking water are a problem of considerable importance
in New Mexico. In most cases, the problem has resulted in the abandon-
ment of wells, except in small communities that have no alternative sources
of available water. According to one EID study San Miguel County alone has

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35 wells still in use in spite of being contaminated with sulfides. In addition, sulfide levels as high as 2.0 mg/l have been detected in the radial collection system of the San Juan River. Because of this situation, it is desirable to study and implement a treatment process that is both practical and economically feasible for small communities as well as for the private well owner. A final maximum concentration of 0.05 mg/l, the limit set by the National Interim Secondary Drinking Water Standard, is desirable. Studies performed in Pennsylvania, Florida, and Illinois indicate that these treatment criteria can be met using hydrogen peroxide (H_2O_2) as an agent to oxidize sulfides in drinking water. The NMEID has given permission to determine the feasibility of this treatment method under actual field conditions with necessary modifications to existing water supply systems. The research presented in this paper considers the study of the kinetics of the oxidation of hydrogen sulfide with hydrogen peroxide in drinking water in both laboratory and actual field conditions.

OBJECTIVES

The purpose of this research project was to study the oxidation of
dilute hydrogen sulfide solutions by hydrogen peroxide. Understanding
of the kinetics of the reaction was desired for determining the feasi-
bility of sulfide removal with peroxide in the field of water supply,
as well as to provide a means for designing the removal systems for the
water supply under investigation. Specifically, the research project
considered four phases of study:

Literature review

A comprehensive literature review on the oxidation of sulfide con-
taminated waters was undertaken by both a direct and computer search.
Information regarding chemical reactions between various commonly used
oxidants and sulfides was considered for comparison with the alternative
oxidant proposed, hydrogen peroxide. Special emphasis was placed on in-
terpreting scarce literature available on the use of this chemical in
drinking waters.

Laboratory studies

The effects of pH, oxidant dose, and catalyst concentration on the
kinetics of the oxidation reaction were considered for various sulfide
contaminated waters. Parameters measured during the kinetic experiments
included remaining sulfide concentration and turbidity. Turbidity infor-
mation was used to rule out the need of filtration equipment for waters
generating colloidal sulfur at concentration equivalent to less than 1.0
Jackson Turbidity Units (JTU). A selection of a kinetic model was made
based on the nature of the experimental data. Reaction rate constants
for this model were calculated from raw experimental data and is present-
ed in the text.

Design criteria

Design criteria for sulfide oxidation with hydrogen peroxide are
presented in this report. Design of a given treatment facility was
based on actual laboratory determination of kinetic rate for the water
to be treated. Cost estimates for peroxide facilities are also presented.

Field implementation

Application of the developed technology was tested in an actual rural water supply system. Parameters measured field studies included pH and remaining sulfide concentration. Social reaction to the chemical oxidation plan is reported. A simple economic analysis on capital and operation and maintenance costs is also presented.

LITERATURE REVIEW

This literature review is comprehensive, in that many aspects of the problem of hydrogen sulfide in water are included. The overall picture begins with several paragraphs on the chemistry of the sulfur species in water. This is followed by a section on the removal of sulfides from the water supply and the various oxidants used. Upon introduction of the oxidant hydrogen peroxide, its application for hydrogen sulfide removal, as well as the kinetics of oxidation of hydrogen sulfide with hydrogen peroxide, are covered.

Chemistry of the Sulfur Species

Of the more than 30 possible sulfur compounds, only five are thermodynamically stable in aqueous solution at standard temperature and pressure. These are HSO_4^-, $SO_4^=$, S, H_2S and HS^-. Other compounds, such as sulfites, thiosulfates, and polysulfides, can be formed, but are not stable under conditions found in natural waters.

Elemental sulfur is found in nine possible crystalline forms with a range in specific gravity from 1.92 to 2.07, all insoluble in water. Elemental sulfur in colloidal form may be formed in water by the oxidation of other more reduced sulfur compounds. Colloidal elemental sulfur is soluble to the extent of 0.0032 mg/l and displays a "Tyndall beam effect", so that its presence can be detected turbidimetrically. The particle size of the colloid can reach 0.5 micrometers. When colloidal elemental sulfur is formed in water in the presence of sulfides, polysulfides can be formed immediately. Elemental sulfur easily can be removed from water by filtration processes.

Polysulfides are the result of the interaction between sulfur and an aqueous solution of sulfide. The aging and/or oxygenation of sulfides in water can also bring about this phenomenon. Polysulfides display a distinct yellow color in water, which disappears at sulfide concentrations of less than 2.0E-04 M (6.4 mg/l), though it can still be detected spectrophotometrically. Of the polysulfides, $S_4^=$ and $S_5^=$ are believed to be predominant, while $S_2^=$ and $S_3^=$ are unstable and generally undetectable.

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Interrelationships between the sulfur species are dependent on the redox potential and pH of the environment (figure 1). Many of the steps in the sulfur cycle in nature are due to transformations of the sulfur species by microbial mediation, and it is this microbial action that is believed to be one of the main sources of sulfides in water.

The question of the origin of sulfides in groundwater is not completely answered, but it is known that H_2S is formed under anoxic conditions in the bottom sediments of lakes, wells, and the ocean by geochemical or biological processes. If the water is trapped in the sediments, it may then become "fossil" water. Microbial formation of H_2S involves the reduction of sulfates or putrefaction of sulfur-containing amino acids. Bacteria of the genera Desulfovibrio and Desulfotomaculum are known to accelerate the reduction process. A water may also have a high concentration of H_2S from man-made sources, because sulfides are a by-product of such processes as kraft pulping, petroleum refining, tanning, coking, natural gas purification, and food processing.

Sulfides present in water impart to it many undesirable properties, among which are corrosiveness and a pronounced, unpleasant sulfuretted odor discernible even at a few tenths of a milligram per liter. With the exception of those from Groups I, II, and III in the periodic table of elements, metal sulfides are generally insoluble, so that even small quantities of sulfide in solution limit the concentrations of Fe(II) and Mn(II).

H_2S is a weak diprotic acid that dissociates according to the following equilibrium reactions:

$$H_2S \Longleftrightarrow H^+ + HS^-; \quad K_1 = 1.0E-07 \qquad [1]$$

$$HS^- \Longleftrightarrow H^+ + S^=; \quad K_2 = 1.0E-14 \qquad [2]$$
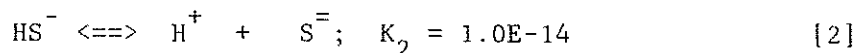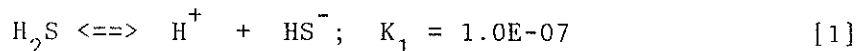
Values of 6.72-7.04 have been reported for pK_1, and the range for pK_2 is even greater, at 12.20-17.10, but 7.0 and 14.0 are generally used as good practical values. The variation in pK_2 values can be seen in figure 2, where a value of approximately 12.5 was used. Because H_2S is a weak diprotic acid, the relative quantities of its various forms in solution

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HSO₄ aq = 10⁻¹ → $HSO_4^- aq = 10^{-1}$

$SO_4^= aq = 10^{-1}$

$\frac{O_2}{H_2O}$

E_H

S

$(\Sigma S < 10^{-1})$

$H_2S aq = 10^{-1}$

$\frac{H_2O}{H_2}$

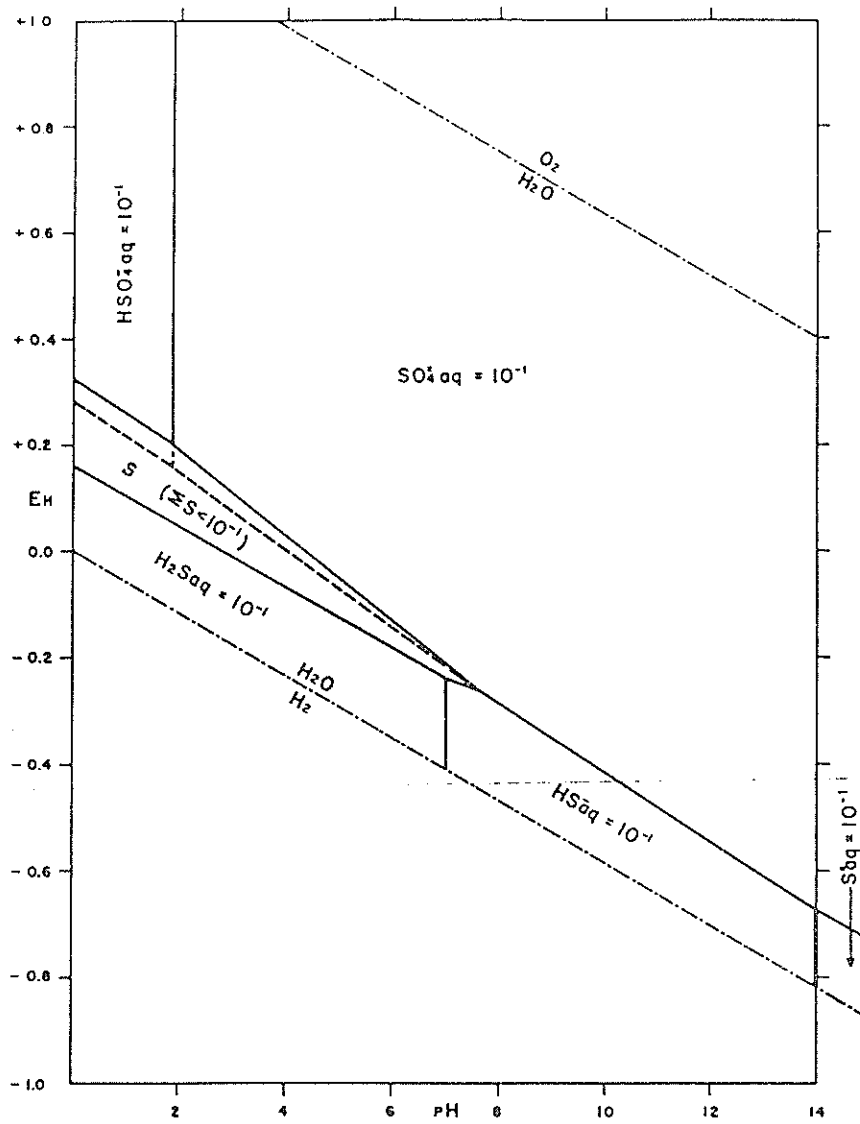$HS^- aq = 10^{-1}$

$S^= aq = 10^{-1}$

pH

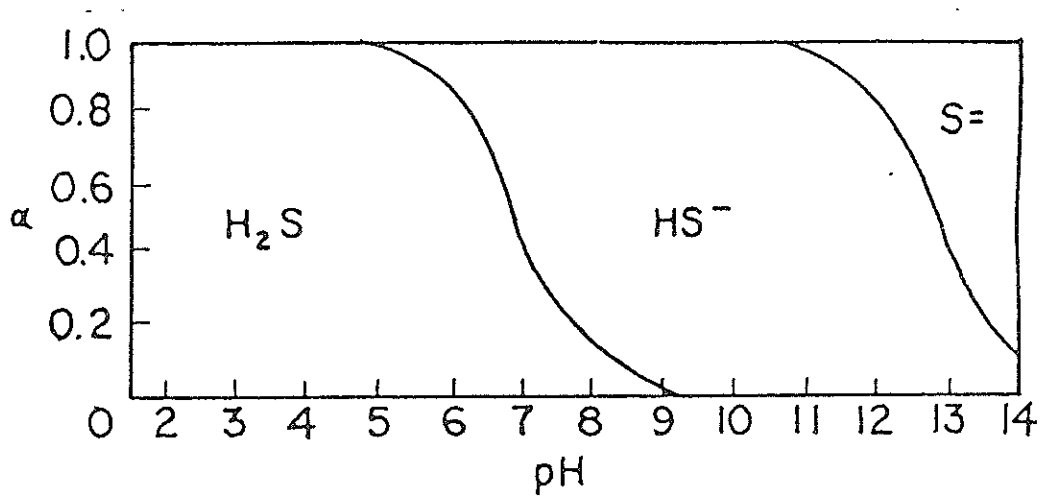Figure 1. E_H - pH Diagram for Inorganic Sulfur Species.

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Figure 2. Effect of pH on Sulfide Species Distribution.

are greatly dependent on pH. As shown in figure 2, H_2S is the predominant species present below a pH of 6.0, while HS^- is most abundant in the 8.0-11.0 pH range. $S^=$ does not become significant unless the pH exceeds 11.0. For this reason, it is common practice to refer to the total sulfide concentration, which is the summation of H_2S, HS^-, and $S^=$, rather than to each individual species. Of the three forms, HS^- is believed to be the most reactive species in oxidation-reduction reactions. In the gaseous form, H_2S is highly soluble in water, reaching 4000 mg/l at 20°C and a 1-atmosphere pressure of H_2S. However, it is rare in natural waters to find concentrations of H_2S greater than 10 mg/l.

Removal of Sulfides from Water Supplies

The removal of sulfides from water can be accomplished through biological oxidation, metal sulfide precipitation, volatilization, or chemical oxidation. Because time and economic factors are among the most important considerations for the removal process, only chemical oxidation is truly effective. Among the most common oxidizing agents which have been considered for sulfide removal are oxygen, chlorine, hypochlorite, chlorine dioxide, ozone, potassium permanganate, ferrate, and hydrogen peroxide. These are discussed in further detail in the following paragraphs. Little is known about the mechanisms of oxidation, due to the presence of minute quantities of catalysts and inhibitors in water and the difficulty of segregating end products of the reaction. These two factors are a significant problem in dilute aqueous solutions as are generally found in the field of water supply.

Oxidation by Oxygen. The use of atmospheric oxygen (O_2) through the process of aeration was the earliest method of H_2S control. It is the simplest of all methods, and it can be accomplished by water spraying or air diffusion, two relatively expensive processes. The removal mechanism is a combination of degasification and oxidation and is very slow due to the low solubility of O_2 in water and the slow reaction rate between sulfide and O_2 in the absence of catalysts. Aeration has proved effective in eliminating taste and odor problems, decreasing H_2S corrosiveness, and decreasing chlorination interferences without requiring other chemicals. However, some of the major disadvantages of the method

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are significant. For example, two or three hours of detention time are generally required to remove 2-3 mg/l of sulfide. Additionally, an aeration tank is required, which must be followed by an additional pump for repressurizing the water, and filtration systems must be installed to remove elemental sulfur formed in the process. An open aeration basin also is highly susceptible to bacteriological contamination. For these reasons, aeration has found its greatest use in the prevention of H_2S formation in impounded waters.

Extensive studies have been done on the kinetics and mechanism of oxygenation of sulfides, the complexity of which is evidenced by:

1. variation in the induction periods;
2. complex dependence of the reaction rates on the concentrations of O_2 and $S^=$;
3. sensitivity of the reaction to impurities;
4. the number of intermediates and their related products; and
5. great dependence of the specific rate on pH.

Chen and Morris (1972) suggested that polysulfides play an important role in the oxidation of sulfide in neutral and either slightly alkaline or slightly acidic solutions. The oxidation mechanism suggested involves a free radical chain reaction with elemental sulfur as the chain-determining product. This reacts with more sulfide to form polysulfides and eventually oxidizes to sulfite, thiosulfate, and sulfate according to the following mechanism:

$$HS^- + O_2 \; \longrightarrow \; HS\cdot + O_2^- \qquad\qquad [3]$$

$$HS\cdot + O_2^- \; \longrightarrow \; S + HO_2^- \qquad\qquad [4]$$

$$HS\cdot + O_2 \; \longrightarrow \; HO_2^-\cdot + S \qquad\qquad [5]$$

$$HS^- + (x-1)S \; \longrightarrow \; H^+ + S_x^=, \; (x=2\text{-}5) \qquad\qquad [6]$$
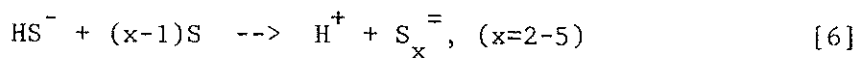
The reaction scheme following the polysulfide formation was presented as follows:

$$\begin{array}{l} \quad\; \lceil \text{---} +HS^- \text{-------} S \qquad\qquad\qquad\qquad\qquad [7] \\ \quad\; \downarrow \\ S_X^= + O_2 \text{------} \longrightarrow SO_3^= + O_2 \text{----} SO_4^= \\ \quad\; \uparrow \qquad\qquad\qquad \searrow S_2O_3^= + O_2 \text{----} SO_4^= \\ \quad\; \mid \qquad\qquad\qquad\qquad /\!/ \\ \quad\; \lfloor \text{---} +HS^- \text{-----} S + SO_3^= + O_2 \longrightarrow SO_4^= \end{array}$$
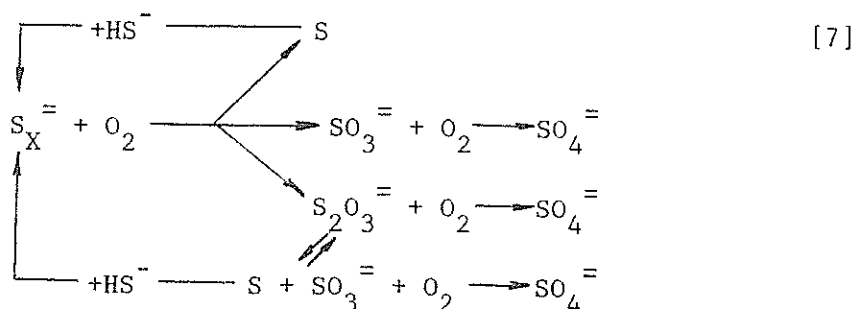
Above a pH of 8, little polysulfide formation was observed, so that another mechanism was needed to account for the complete oxidation to sulfate.

The catalytic effects of transition metals on the rate of oxidation of sulfides by oxygen were also studied by Chen and Morris (1972). They found that small additions of these transition metals could increase the reaction 10-100 fold. The catalytic effect was found to follow the sequence: $Mn^{+2} > CO^{+2} > Ni^{+2} > Fe^{+2} > Cu^{+2}$. EDTA and nitriloacetic acid have been found to act as inhibitors, reducing the reaction rate 33-90 percent.

Oxidation by Chlorine. Chlorine gas (Cl_2), a powerful oxidant, is the most common disinfectant used in the field of water supply. As the least expensive of the chemical oxidants, it has proved to be an economical method of removing sulfides from water. The reaction is a very rapid one, yielding both elemental sulfur and sulfates. In theory, 8.5 parts of Cl_2 are required per one part of H_2S, but it has been found in practice that a lesser dosage effectively removes all sulfides. The reaction takes place simultaneously or consecutively according to the following:

$$Cl_2 + S^= \longrightarrow 2Cl^- + S; \quad pH<8 \qquad\qquad [8]$$

$$4Cl_2 + S^= + 4H_2O \longrightarrow 8HCl + SO_4^=; \quad pH<8 \qquad [9]$$
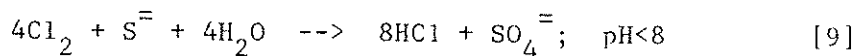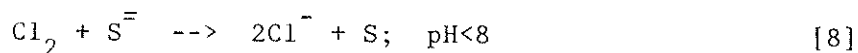
The ratio of the end products is affected by pH, temperature, reaction time, the concentration of the reactants, and the rate of reactant addition. The pH range 6.5-8.5 is optimum for maximum sulfide oxidation.

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In smaller facilities where the use of Cl_2 presents difficulties, sodium hypochlorite (NaOCl) is commonly used. Providing 95 percent available chlorine as compared to Cl_2, NaOCl also yields elemental sulfur and sulfates upon oxidation of sulfides, which occurs at a very rapid rate. It has the important disadvantage, though, that it is several times more expensive than Cl_2 gas.

In general, it can be said that chlorination with chlorine gas is advantageous because of its effectiveness, speed, and economy. However, specialized equipment and personnel are normally required for sulfide removal if chlorination is not already implemented. In addition, there also exists the possibility of creating potentially corrosive water, accompanied by a residual chlorine taste. It is also known that chlorine combines with organic compounds in water to form trihalomethanes, which are proven carcinogenics. Thus, it is common that small communities and individual well owners cannot afford the implementation of chlorination for the sulfide problem because of the high cost of NaOCl and the specialized equipment and personnel required to handle Cl_2 gas.

The rapid and almost complete reaction between sulfides and chlorine is uncontrollable. Thus, intermediate oxidation compounds, such as polysulfides may not be formed, because the reaction results in the formation of sulfur. The precipitation of sulfur in drinking water produces an unpleasant yellowish turbidity, frequently resulting in water with turbidity levels above drinking water standards. Additional capital investment is then typically required to remove sulfur turbidity by filtration.

Oxidation by Ozone. Ozone (O_3) is another strong oxidant widely used in Europe. It is mainly used to sterilize water, though it has also found application in taste and odor control and iron and manganese removal. Ozone converts sulfides in water to elemental sulfur and sulfates instantaneously. In contrast with Cl_2, O_3 leaves no residual so that water treated with ozone is palatable, and it reacts in a fraction of the time Cl_2 requires. Chen has proposed the following reactions for ozone with sulfide in dilute aqueous solution:

$$S^= + O_3 + H_2O \longrightarrow S + 2OH^- + O_2 \qquad [10]$$
$$S^= + 4O_3 \longrightarrow SO_4^= + 4O_2 \qquad [11]$$

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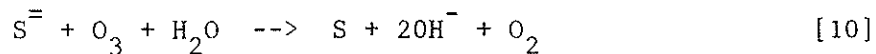
The decomposition of O_3 produces O_2 as the only by-product, so that in addition to being effective and fast, O_3 is also nonpolluting. But O_3 is very unstable in aqueous solution, having an effective life of only minutes at room temperature. This short life makes it necessary to generate O_3 on site. Optimum operation with O_3 is difficult because rigid monitoring of pH, temperature, dosage, bubble size, and influent oxidizing capacity are required. Therefore, in spite of the advantages over other oxidizing agents, high capital costs and the need to retrofit existing equipment, O_3 is impractical for sulfide removal.

Oxidation by Potassium Permanganate. Potassium permanganate ($KMnO_4$) is also an effective oxidant of H_2S in aqueous solution. In waters within the 6-10 pH range, permanganate reduction occurs via a 3-electron transfer with formation of manganese dioxide (MnO_2) as the end product. The reactions are as follows:

Basic solution:
$$MnO_4^- + 2H_2O + 3e- \longrightarrow 4OH^- + MnO_2 \qquad [12]$$

Slightly acidic and neutral:
$$MnO_4^- + 4H^+ + 3e- \longrightarrow 2H_2O + MnO_2 \qquad [13]$$
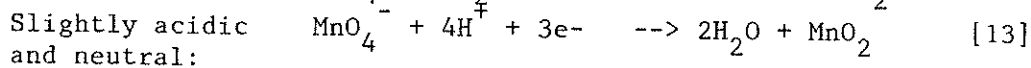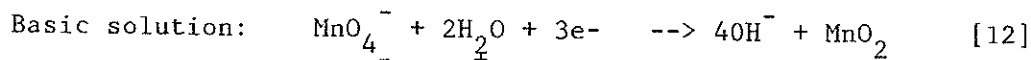
A molar ratio of 4:3 is required for the oxidation of H_2S as shown in the experimentally derived equation below:

$$4MnO_4^- + 3H_2S \longrightarrow 2SO_4^= + S + 3MnO + MnO_2 + 3H_2O \qquad [14]$$
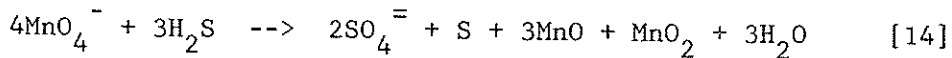
The reaction goes to completion within minutes. For this reason, in addition to interferences of color and the precipitation of MnO_2, kinetic studies of the reaction are difficult and have been limited. Potassium permanganate is available in liquid and solid form, making it easy to handle and dispense. A residual is easily detectable by a pinkish tint imparted to the water. Important to the application of $KMnO_4$ are retention time, pH, and filters. Filters are necessary for the removal of insoluble MnO_2 formed in the process.

Oxidation by Chlorine Dioxide. Chlorine dioxide (ClO_2) has characteristics similar to chlorine. On-site generation through the reaction between chlorine and sodium chlorite in acid solution is necessary due to its instability. Chlorine dioxide is several times more costly than chlorine for equivalent oxidation capacity. Because it presents no advantages over chlorine, ClO_2 is not discussed further.

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Oxidation by Ferrate. The study of the ferrate (VI) ion ($FeO_4^=$) as an oxidant is in its infancy, though it is known that it is powerful over the entire pH range. It has proved effective in studies as a disinfectant against E. coli. as an oxidant of allylbenzene and chlorobenzene, and as an agent for the removal of zinc and cadmium in industrial wastes. Donhalek and Fitzpatrick found ferrate effective in sulfide removal from drinking water in Elgin, Illinois, where it yielded complete sulfide removal, with a product distribution of 82 percent $SO_4^=$ and 18 percent S. Polysulfides were observed to form as intermediates. The greatest drawback to the utilization of ferrate for practical purposes is that is is extremely expensive.

Oxidation by Hydrogen Peroxide. Hydrogen peroxide (H_2O_2) is the oxidant considered in this paper. This oxidant is a weakly acidic, clear colorless liquid, miscible with water in all proportions. As pure H_2O_2, it has a melting point of -0.41°C and a boiling point of 150°C. It has a density at 25°C of 1.4425 g/ml at 100 percent purity. The variation in density at 25°C with respect to the weight percent of H_2O_2 in water is given in table 1. H_2O_2 has an acidic electrode potential of -1.76 volts, the half-reaction of which is (7):

$$2H_2O \iff H_2O_2 + 2H^+ + 2e- \qquad\qquad [15]$$
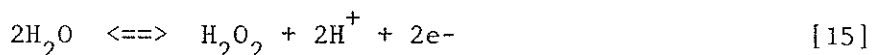
Hydrogen peroxide is a clean oxidant which decomposes to form H_2O and O_2. However, the decomposition must be controlled at all times because the resultant generation of gas and heat (100 kJ/mol) can cause safety problems. Decomposition is promoted by catalytic impurities and is proportional to both temperature and percent concentration of H_2O_2. The hazards of decomposition are minimized by purification during the manufacturing process, control of contaminants, and addition of stabilizers, so that the user, by applying a few precautions, need not be concerned. These precautions include using only clean, passive containers, such as aluminum or polyethylene, ensuring adequate ventilation in the storage area, and minimizing contact of the H_2O_2 with contaminants.

Hydrogen peroxide is irritating to the skin, eyes, and mucous membranes, and like any other chemical should be handled with care. Upon contact with H_2O_2, the affected area should be immediately flushed with

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Table 1

Density of Hydrogen Peroxide
at Different Percent Compositions[a]

Liquid Composition, wt. % H_2O_2	Density, g/ml[b]
10	1.0324
20	1.0694
30	1.1081
40	1.1487
50	1.1914
60	1.2364
70	1.2839
80	1.3339
90	1.3867
100	1.4425

[a] Encyclopedia of Chemical Technology, Vol. 19, John Wiley & Sons, Inc., Anthony Standen, Exec. Editor, 1969, (3).
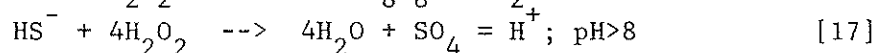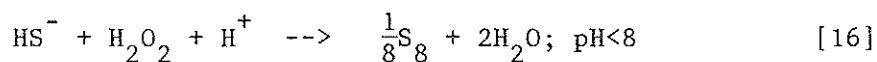
[b] at 25°C

water. Due to the extensive use of H_2O_2 in the food-processing industry as a sterilizing agent for polyethylene containers and for the control of microbial growth, there has been concern over the carcinogenic properties of H_2O_2. There have been studies published linking H_2O_2 with intestinal cancer; however, a review by the Food and Drug Administration has concluded that there is insufficient evidence in these studies to conclude that H_2O_2 is a duodenal carcinogenic.

Hydrogen peroxide is available in concentrations from 3-98 percent, though the most widely available concentrations are 30, 50, 70, and 90 percent. The H_2O_2 disinfectant solutions commonly found in drug stores are 3 percent pure. The Interstate Commerce Commission classifies solutions greater than 8 percent as corrosive, which means that special arrangements are necessary for the transport of the more concentrated forms.

Hydrogen peroxide is an oxidant of many applications. It is widely used in the preparation of other peroxygen compounds and as a non-polluting oxidizing agent. In the field of wastewater treatment H_2O_2 has been used to provide supplemental O_2 to systems, to assist in the flotation process, to control denitrification in secondary clarifiers, to control H_2S-associated odors, and to improve conditions caused by sludge bulking. The cotton industry uses it for bleaching textiles, while the leather industry uses it in tanneries for the removal of sulfides from their waste streams. It has been studied to a very limited extent in the removal of trihalomethane precursors from drinking water. More recently, the feasibility of utilizing H_2O_2 for the control of sulfides in drinking water has been investigated, but the research has been approached simply from a practical point of view, without considering the kinetics and mechanism of the oxidation process.

The stoichiometry of hydrogen sulfide oxidation by peroxide is greatly dependent on pH. In neutral or acidic solution, elemental sulfur is the primary product, whereas sulfate is formed in basic solution. The reactions are:

$$HS^- + H_2O_2 + H^+ \longrightarrow \frac{1}{8}S_8 + 2H_2O; \text{ pH<8} \qquad [16]$$

$$HS^- + 4H_2O_2 \longrightarrow 4H_2O + SO_4 = H^+; \text{ pH>8} \qquad [17]$$

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Hydrogen peroxide has displayed advantages over other oxidants which make it desirable for use in municipal water systems. These advantages are: (1) it has strong oxidizing power; (2) its products of decomposition are simply oxygen and water; (3) it is a liquid that can be readily and quickly applied when needed; (4) it produces no toxic or corrosive fumes; and (5) it may be competitive economically with other treatment systems.

Application of H_2O_2 for H_2S Removal

Elgin, Illinois, Case Study. Donhalek and Fitzpatrick have studied the application of various oxidants for sulfide removal for the City of Elgin, Illinois, where taste and odor problems have arisen with the addition to the water system ofseveral new deep wells. Sulfide concentrations in the raw water average 5.5 mg/l, and a maximum of 12 mg/l has been detected on occasion. The water treatment scheme in the city includes preaeration, aeration, lime precipitation, sedimentation, stabilization, dual-media granular filtration, and chlorination. Ferrous and ferric sulfate are utilized to catalyze the air oxidation of sulfide to sulfate, though economic considerations make it possible to add the required stoichiometric dosage for complete removal. This treatment produces water with an average sulfide concentration of 0.20 mg/l, which still exceeds the National Interim Secondary Drinking Water Standard (NISDWS) and odor threshold. The purpose of the research was to find an economical way to meet the NISDWS for sulfide, while improving the understanding of the sulfide oxidation mechanisms as they relate to groundwater chemistry.

The various oxidants were tested using a laboratory-scale treatment system to simulate the actual Elgin water treatment facility. The results for hydrogen peroxide indicated that at the required one-to-one stoichiometric dosage for the Elgin water (pH = 7.3) a final sulfide concentration of 0.01 mg/l could be achieved. This is well below the standard of 0.05 mg/l. Most of the removal occurred during the first few minutes of the reaction in the preaeration simulator. The product distribution was found to be 42 percent sulfate and 58 percent elemental sulfur. At twice the stoichiometric dosage, the reaction proceeded at a faster rate, yielding

47 percent sulfate and 53 percent elemental sulfur. An economic analysis of the various alternatives for sulfur removal, under the assumption that only sulfide treatment was to be added to an existing plant, showed that only ferrous iron (Fe[II]) had a lower total cost than H_2O_2. Other oxidants considered were $KMnO_4$, Cl_2, and O_2. However, they concluded that with certain economic refinements, peroxide and/or combinations of other oxidants could be as cost-effective as Fe(II).

Central Pennsylvania Case Study. Cole and Sharpe worked with H_2O_2 on a demonstration basis on a farm well after learning of several problem wells in central Pennsylvania in 1975. Because of its unpalatable quality, the water was used strictly for livestock watering. Chlorination was not considered because corrosion problems had been reported at another well where a chlorination-carbon filtration system had been used. At one of the problem wells, the carbon filtration system corroded and failed after only two years of operation. The well owner wanted a system that would be easier and cheaper to install than aeration; consequently, it was decided to evaluate the effectiveness of hydrogen peroxide in treating this hydrogen sulfide problem.

In a previous case in Florida where hydrogen peroxide was used for taste and odor control in a municipal water system, the U.S. Environmental Protection Agency (EPA) gave approval for the study on the basis of past use of peroxide. The EPA permitted a maximum dosage of 20 mg/l and a residual of 2 mg/l during the study. These values were used as guidelines for the Central Pennsylvania demonstration.

The H_2O concentration in the well varied from 0.5 to 1.5 mg/l, and the water was very high in total dissolved solids, bicarbonate, and total hardness. Preliminary jar tests indicated that H_2O_2 had great potential, as it reduced the sulfide concentration to 0.05 mg/l. Pressure injection of H_2O_2 into the system ahead of the pressure tank was begun in September 1975 and is known to have continued at least through 1979. An H_2O_2 dosage of 10 mg/l (10 ml/l of 0.1 percent pure H_2O_2) was the minimum dosage to provide H_2S levels below 0.1 mg/l. Without H_2O_2 the softened water remained unpalatable, but treatment of the water with H_2O_2 followed by softening produced a highly palatable water free of H_2S

taste and odor. The H_2O_2 treated unsoftened water still had a noticeable taste and odor, but it was considerably less than that of the raw water. An increase in detention time augmented the difference in palatability between the raw and unsoftened water.

Over a three-year period, the average raw water H_2S concentration was 0.49 mg/l, the H_2O_2 treated unsoftened water had an average of 0.08 mg/l, and the H_2O_2 treated softened water had an average of 0.04 mg/l. The residual H_2O_2 concentration after a 10 mg/l dosage was less than 0.2 mg/l for the softened water and 0.8 mg/l for the unsoftened.

Figure 3 is a schematic of a recommended feed system based on the Central Pennsylvania demonstration. It was suggested that a diluted H_2O_2 solution (0.1 percent concentration) be gravity-fed into a positive displacement pump, such that it was injected into the line before the pressure tank. Following the pressure tank additional contact time would be provided, either with a pressurized contact tank or with a large coil of plastic pipe. A carbon filter or an ion exchanger would follow the contact equipment, should the water also require softening. This would provide water free of H_2S taste and odor.

The above results were obtained without any attempt to optimize either the contact time or the peroxide feed rate under conditions of actual use, where water use and H_2S concentrations were not controlled. The results indicate that H_2O_2 is a promising alternative for sulfide taste and odor control in drinking water supplies.

Pressure switch   Pressure tank

Hydrogen
Peroxide
Supply

Pump

Pressurized contact
tank or coil

to use (washing or barn)

to softener

Well

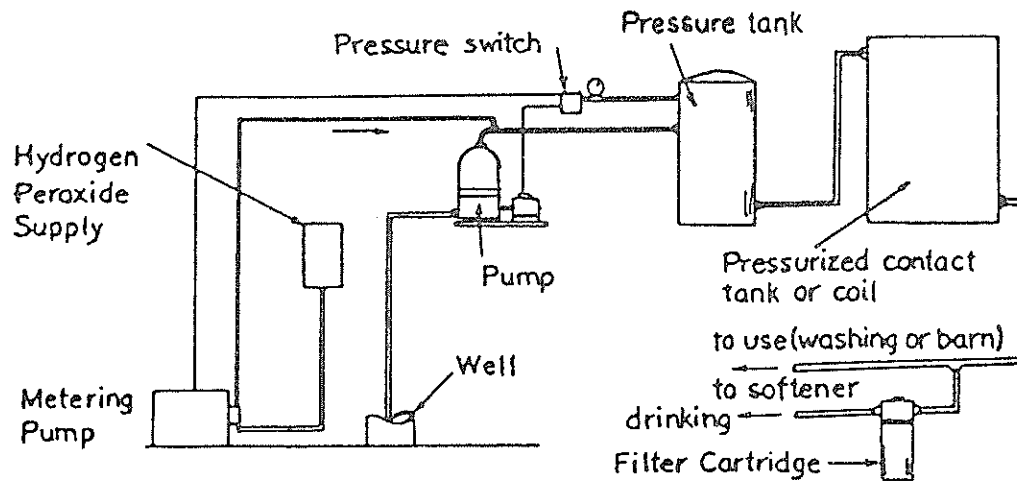drinking

Metering
Pump

Filter Cartridge

Figure 3. Hydrogen Peroxide Feed System[a]

[a]Cole, Charles A., and William E. Sharpe, "Hydrogen Peroxide, a New Addition to Conventional Methods of Treating Hydrogen Sulfide in Water," Proceedings of the Third Domestic Water Quality Symposium, American Society of Agricultural Engineers, 1979.

KINETICS OF OXIDATION OF HYDROGEN SULFIDE
WITH HYDROGEN PEROXIDE

Previous Studies

Even though hydrogen peroxide has been applied in many instances in the control of hydrogen sulfide-related problems in wastewater and to an extent in potable water, kinetic studies of the oxidation of hydrogen sulfide by hydrogen peroxide have been limited. This is a reflection of the analytical difficulties encountered with a complex solution containing a mixture of sulfides, elemental sulfur, sulfates, polysulfides, and possibly higher-order sulfur compounds with hydrogen peroxide.

Satterfield et al. studied the decrease in H_2O_2 versus time in a solution of H_2S maintained at saturation by continuous gas transfer. Tests were run at pH values of 1.2, 1.5, and 4.0 over the 24-61°C temperature range. Under these conditions it was found that the reaction between H_2S and H_2O_2 was first-order with respect to H_2O_2 and inversely proportional to the 0.4 to 0.5 power of the hydrogen-ion concentration. At the higher temperatures and pH values the reaction proceeded at the fastest rate.

Hoffmann studied the kinetics of hydrogen sulfide oxidation to sulfur and sulfate by hydrogen peroxide in aqueous solution. The rate law and other data obtained indicate that the reaction proceeds via a nucleophilic displacement by sulfide on hydrogen peroxide with the formation of polysulfide intermediates. The rate law proposed by Hoffmann is given by

$$-d(H_2S)/dt = k_1(H_2S)(H_2O_2) + k_2K_{a1}(H_2S)(H_2O_2)/(H^+) \qquad [18]$$

where $\quad k_1$ = 0.5 per M per min

$\qquad k_2$ = 29.0 per M per min

and $\quad K_{a1}$ = first dissociation constant of H_2S.

At constant pH and where $(H_2O_2) \ggg (S^=)$, the reaction can be described as pseudo-first-order, so that the rate equation can be given by

$$\text{rate} = K_{obs}(S^=) \quad \text{with} \quad K_{obs} = k(H_2O_2)/(H^+) \qquad [19]$$

according to Hoffmann's data. This equation is valid only in the pH range 5-8.

The polysulfide intermediates detected were $S_4^=$ and $S_5^=$, as would have been expected. Elemental sulfur and sulfates were the end products, their relative proportions dependent upon pH and H_2O_2 dosage. The elemental sulfur was determined to be orthorhombic cyclo-S_8. From the data presented in Hoffmann's article, it appears that all tests were run at an initial sulfide concentration of 1.5E-03 M (48 mg/l), with H_2O_2 concentrations ranging from 10 to 100 times this value.

Applicability of Kinetics Research

Both the high concentration of sulfide and the higher dosages of hydrogen peroxide in Hoffmann's study make the application of his findings limited. Seldom, if ever, in the field of drinking water supply would a sulfide problem of that magnitude be encountered, and such large peroxide dosages would eliminate any economic advantages that peroxide might have over other oxidants.

The pH range (1.2 to 4.0) over which Satterfield conducted his studies, takes the application of his findings out of the field of water supply. In addition, it seems that his research was in reality a study of the reduction of H_2O_2 with H_2S rather than an H_2S oxidation study.

For the reasons just presented, neither Hoffmann's nor Satterfield's findings are practical enough for engineering design in the field of drinking water supply. One aim of the research presented in this paper is that it be useful for design purposes for the removal of H_2S with H_2O_2.

EXPERIMENTAL PROCEDURES

Test Preparations

Each experimental run began the night before the test with the preparation of a sulfide solution. Advance preparation allowed time for any residual chlorine, dissolved oxygen, and other oxidizing or reducing agents in the sample tap water to complete their effects on the sulfide solution before the test with hydrogen peroxide was performed. Tap water, a variable quality water, was used in order to approximate conditions in natural waters. The solution was prepared by injecting with a syringe 1.0-1.5 ml of a saturated sodium sulfide solution into 8 liters of tap water contained in a 2.5 gallon plastic collapsible reactor, from which the air had been evacuated (fig. 4). To ensure complete diffusion of the sodium sulfide into the water, the system was magnetically stirred for 10-15 minutes and then allowed to sit until the experimental run was begun the next day. The sodium sulfide in solution completely dissociates into Na^+ and $S^=$, and the $S^=$ then combines almost immediately with the H^+ in solution to form HS^- and H_2S, the two principal forms of hydrogen sulfide under the pH conditions which were studied.

Before injection of hydrogen peroxide into the system, the pH was adjusted to the desired level by adding the required volume of either 1N HCl or 1N KOH with a syringe, depending on the adjustment direction required. A constant pH level was maintained thoughout the test by small additions of the HCl or KOH when the pH changed by 0.01 units. An Orion model 701A digital pH meter was used for monitoring this parameter. Initial calibration of the meter was done using pHydrion buffer capsules, dissolved in distilled water.

The amount of hydrogen peroxide to be added to the system was determined by taking a sample from the solution for a total sulfide determination. The volume required in order to obtain the desired molar ratio of peroxide to sulfide was calculated using the known percent composition of the peroxide and the total sulfide concentration. The percent composition of the peroxide was calculated from its density at 25°C, measured with a hydrometer.

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injection
port

rubber stopper

collapsible plastic
container

clamp

sampling port
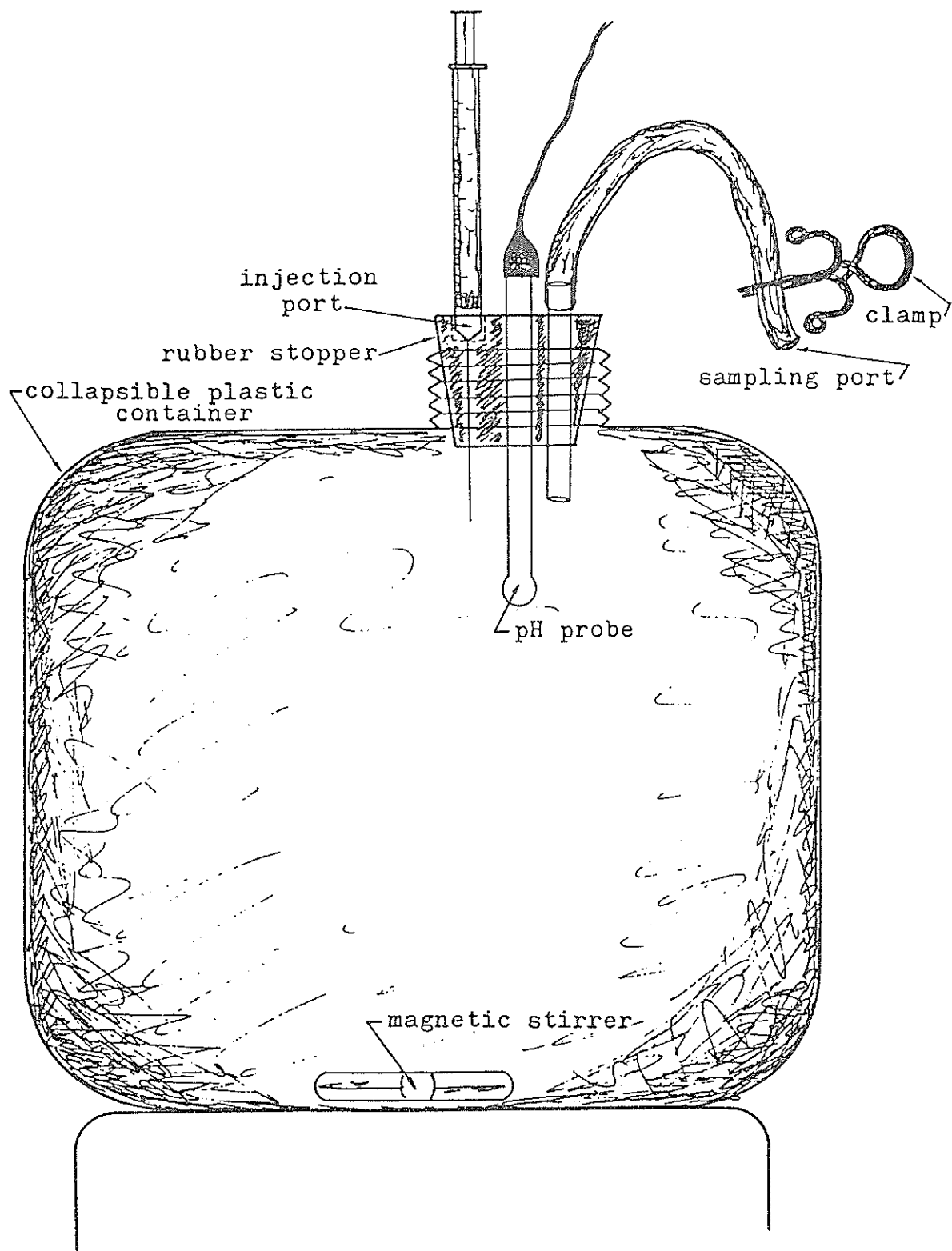
pH probe

magnetic stirrer

Figure 4. Laboratory Oxidation Reactor

Prior to injecting the peroxide, a second sample was taken to be used as the initial sulfide concentration, and the initial turbidity of the solution was determined. The peroxide was then injected into solution, and samples for sulfide and turbidity were taken at 15, 30, and 60 minutes.

The turbidity of the solution was used as an indicator of the presence of colloidal elemental sulfur in the system. The critical step in the turbidity determinations was to ensure that the exterior of the sample vial was clean and dry on the outside. A Hach Model #18900 ratio turbidimeter was used for turbidity determinations. Calibration of the instrument was verified using the Hach latex standards for 1.8 and 18 nephelometric turbidity units (ntu).

Samples were taken with care not to allow air into the system. This was done by simultaneously applying pressure to the reactor and releasing the clamp on the sampling port. With the reactor still under pressure, the sampling port was again clamped. At no time during the testing was air allowed into the system.

During the entire test, the system was kept mixed at a vigorous rate without the tossing about of the magnetic stirring bar. The water temperature for all tests was 22°C.

Sulfide Determinations

The total sulfide (H_2S + HS^-) laboratory determination was done by the methylene blue method given in Standard Methods for the Examination of Water and Wastewater (1980). Samples were obtained in standard 10-ml spectrophotometer tubes. Field determinations of total sulfides were conducted with a portable HACH kit, which operates under a principle similar to the methylene blue method.

EXPERIMENTAL RESULTS AND INTERPRETATION

Kinetic Model Selection

This section summarizes the results from laboratory kinetic studies on the oxidation of hydrogen sulfide with hydrogen peroxide. Interpretation of the kinetic data was based on the results by Pringle who found that the sulfide concentration in these types of studies could be described equally well by first-order and second-order kinetics. Thus, in order to simplify the application and interpretation of results, a first-order kinetic model was selected. The following simple relationship describes the decay of sulfides according to a first-order model:

$$d[S]/dt = - K1 \ [S] \qquad\qquad [20]$$

where $\quad$ [S] = sulfide molar concentration at any time t

$\qquad$ t = time in hours

$\qquad$ K1 = first-order rate constant in hr-1

Kinetic studies were conducted at New Mexico State University (NMSU) laboratories using natural water samples collected from the NMSU (two different wells), distilled water, and Madrid, New Mexico, well No. 1. Spiking of the NMSU water samples was performed according to the procedure outlined in the section on Experimental Procedures. Madrid water samples required no spiking, becausee they were found to be naturally contaminated with sulfides at a level of approximately 1.9 mg/l.

Effect of pH and H_2O_2 on Rate Constant

The raw data generated in our experiment was mathematically interpreted, according to the integrated form of the above equation, expressed in its linear form:

$$\ln \ [S/So] = -K1 \ t \qquad\qquad [21]$$

Best-fit analyses of the raw data to fit equation 21 provided the values of the first-order rate constants provided in tables 2, 3 and 4. It may be observed from these tables that the values of the constants are dependent on the following parameters:

1. type of water,

2. pH of the solution, and

3. molar ratio of peroxide to sulfide

It was observed in all the waters tested that the rate of the reaction decreases with the pH of the solution for H_2O_2:H_2S ratios below 4:1. However, for very large peroxide doses (i.e. 20:1) the trend is reversed. This acceleration of reaction rate for high oxidant dose is compatible with the results by Hoffman, who utilized peroxide to sulfide ratios higher than 50:1. The first-order rate constants for the Madrid water were 0.32 and 0.77 HR-1 for peroxide:sulfide ratios of 1:1 and 4:1, respectively. The pH of this water was 7.5 after equilibrium with atmoshperic CO_2 was attained.

The presence of dissolved minerals is known to affect the oxidation of sulfide by oxygen. Considering the similarity between oxygen and hydrogen peroxide, it is to be expected that the presence of such interferences will affect the oxidation rate of H_2S by H_2O_2. Thus, the kinetic results should be different for each water tested depending on the concentration of naturally occurring catalysts or inhibitors. The oxidation reaction proceeded in order of increasing rate in the following order: Madrid water < NMSU water No. 2 < Distilled Water < NMSU Water No. 1. The relatively slower rates observed in the first two natural waters is probably due to the presence of dissolved minerals that inhibit the oxidation reaction. On the other hand, the presence of a catalytic ion in NMSU Water No. 2 is obvious.

The rate of the reaction is accelerated by increasing the peroxide dose for a given sulfide concentration. This acceleration, even though stoichiometric, is not linear. The most marked effects of increasing peroxide dose are observed at higher pH values. With the exception of NMSU Water No. 1, turbidity did not increase in any set of experiments. The colloidal sulfur produced in the NMSU Water No. 1 was found to decrease as the pH of the sample increased. No turbidity was observed in any test at pH values above 7.5, as predicted by figure 1.

Effects of Catalysts on Reaction Rate

Chen and Morris have demonstrated that some metal ions have strong catalytic properties on the oxidation rate of sulfide in the presence of oxygen. These researchers found that for the metal ions tested, the acceleration by Ni+2 is greatest. These researchers also found that the

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Table 2

First-Order Rate Constants for NMSU Water No. 1 (hr-1)

pH	$H_2O_2:H_2S = 1:1$	pH	$H_2O_2:H_2S = 4:1$	pH	$H_2O_2:H_2S = 20:1$
6.75	2.26	6.00	3.89	6.60	5.68
7.00	2.24	6.52	4.61	7.91	7.37
7.00	2.54	7.00	2.51		
7.25	2.50	7.50	3.13		
7.50	2.44	8.00	2.29		
7.65	1.76	8.50	0.97		
7.70	2.20				
7.70	0.78				
7.75	1.94				
7.75	1.70				
7.85	1.43				
7.85	1.12				
8.00	1.31				
8.10	0.46				
8.10	0.49				
8.50	0.97				
8.50	0.33				

Table 3

First-Order Rate Constants for NMSU Water No. 2 (hr-1)

pH	$H_2O_2:H_2S = 4:1$
7.0	1.12
7.5	0.93
8.0	0.14

Table 4

First-Order Rate Constants for Distilled Water (hr-1)

pH	$H_2O_2:H_2S = 1:1$	pH	$H_2O_2:H_2S = 4:1$
7.0	0.83	7.0	1.17
8.0	0.17	7.0	1.43
		7.0	1.53
		8.0	0.20

catalytic order in the mildly basic range is: $Ni+2 > Co^{+2} > Mn^{+2} > Cu^{+2}$. They also demonstrated that even $Ca+2$ and $Mg+2$ have some accelerating effect on the oxidation of sulfide. Considering the similarity between the oxidation of sulfide by oxygen and hydrogen peroxide, the catalytic effect of various metal ions was examined in our study. Of those metal ions, manganese and copper are known to produce serious problems in water distribution systems. The first ion precipitates as a $MnO2$, an unpleasant black scale, while cupric ions corrode iron in contact with water. No limitations have been established in the drinking water standards regarding the presence of nickel and cobalt. However, recommended threshold limit values for these metals in the atmosphere are approximately equal to those of copper. Maximum USEPA contaminant level for copper in the secondary drinking water standards is 1.0 mg/l. Thus, the presence of either one of these three metals in drinking waters below this limit should result in no adverse toxic effects. However, additional literature and/or toxicological studies are recommended prior to field implementation of any of these metals as catalysts in a water distribution system.

Laboratory studies were conducted to determine the catalytic effect of Ni^{+2}, the most effective accelerant considered by Chen and Morris. The catalytic properties of Zn^{+2}, another potentially non-toxic metal ion were also studied in this research project. However, no significant effects on the reaction rate were observed when up to 10 mg/l of Zn^{+2} was used in oxidation studies. Thus, this metal ion has been ruled out as a catalyst in the oxidation of sulfides with hydrogen peroxide.

The first-order rate constants calculated from laboratory kinetic studies are presented as a function of $Ni+2$ concentration in table 5. The effect of Nl^{+2} as a catalyst on the oxidation reaction may be visualized in figure 5. All oxidation experiments presented in table 5 were conducted in distilled water at room temperature.

It may be observed in figure 5 that the kinetic results for the 1:1 and 4:1 ratios are not significantly different, except in the absence of catalyst. The influence of hydrogen peroxide dose on K1 is

insignificant, compared with the effect of increasing the catalyst con-
centration. The catalytic effects of nickel on the oxidation of sul-
fides is considerably more important at high pH values, where even
trace amounts of this element greatly accelerate the reaction rate.
This important catalytic phenomenon helps to explain the great differ-
ence in oxidation rates observed in various types of natural waters,
where trace amounts of catalysts or inhibitors may control the reaction
kinetics.

The information in table 5 shows that the effect of Ni^{+2} on the
reaction rate is stoichiometric over the range of concentrations studied.
In fact, this accelerating phenomenon is by far more important than the
effect of peroxide dose for concentrations of catalyst above 1.0 mg/l.
For instance, no significant difference is observed between the tests
conducted at peroxide:sulfide ratios of 4.0 and 1.0, at pH 7.0, and at
nickel concentrations greater than 1.0 mg/l. Least-square analyses of
information in table 5 yields equations 22 and 23, for waters with pH
values of 7.0 and 8.0, respectively (equation 22 was derived with data
from peroxide:sulfide ratios of 1.0 and 4.0).

$$K1 = 1.13 + 2.95 \ [Ni^{+2}] \qquad \text{at pH} = 7.0 \qquad [22]$$
$$K1 = -0.90 + 18.06 \ [Ni^{+2}] \qquad \text{at pH} = 8.0 \qquad [23]$$

Table 5

Catalytic Effect of Ni^{+2} on the First-Order Rate Constant

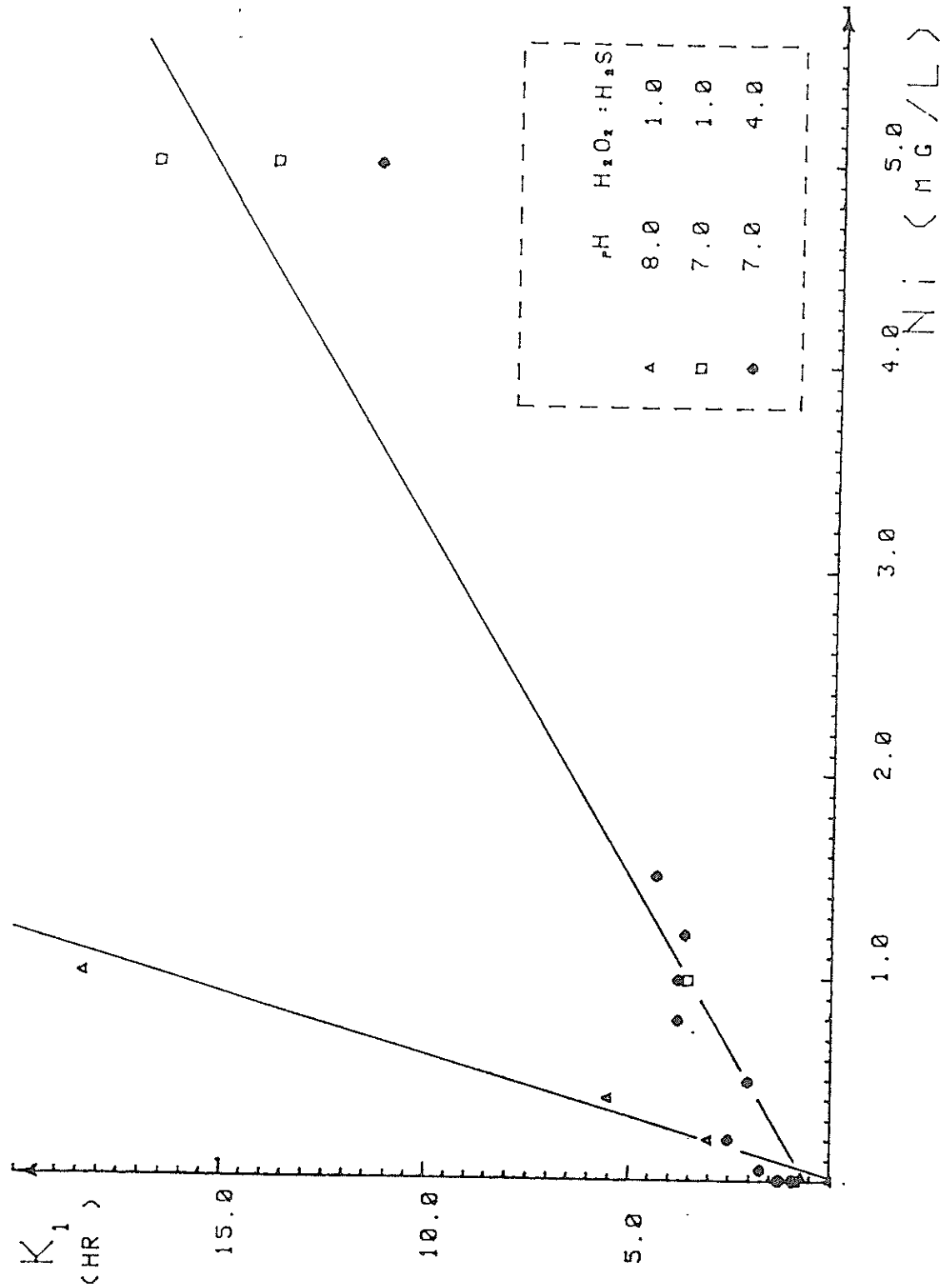| $H_2O_2:H_2S = 1:1$			$H_2O_2:H_2S = 4:1$		
pH	Ni (mg/l)	K1 (hr-1)	pH	Ni (mg/l)	K1 (hr-1)
7.0	0.0	0.83	7.0	0.0	1.17
7.0	1.0	3.57	7.0	0.0	1.43
7.0	5.0	13.93	7.0	0.0	1.52
7.0	5.0	16.86	7.0	0.05	1.76
7.0	10.0	24.28	7.0	0.2	2.57
8.0	0.0	0.17	7.0	0.5	1.83
8.0	0.2	3.03	7.0	0.8	3.83
8.0	0.5	5.47	7.0	1.0	3.80
8.0	1.0	18.42	7.0	1.2	3.70
			7.0	1.5	4.39
			7.0	5.0	11.35
			7.0	10.0	35.46

Figure 5. Effect of Ni^{+2} on Oxidation Rates.

DESIGN CRITERIA

Contact Basin Design

The reaction rate between hydrogen peroxide and hydrogen sulfide
varies greatly depending on the pH of the waters to be treated, and
the presence of trace catalysts and inhibitors in natural waters.
Attempting to establish general criteria for estimation of detention
times would involve a complete chemical analysis of the water to be
treated, including measurement of trace levels of heavy metals and
other potential catalysts and inhibitors, as well as an understanding
of how each of these substances affects the reaction rate. This the-
oretical, but general approach to the design of peroxide oxidation
systems is impossible at the present time due to the limited understand-
ing of how various trace components, other than nickel affect the reaction
rate.

A simpler, but more pragmatic design approach consists of insitu
measurement of the oxidative properties of the water. This second
approach would provide specific design criteria for the water tested
only. The design criteria developed in this report follows this simpler
and more reliable methodology.

Thus, water treatment design for the oxidation of sulfide with
hydrogen peroxide requires an experimental evaluation of the reaction
kinetics for the water to be treated, as described in the section on
experimental procedures. The goal of such evaluation is the determina-
tion of the first-order kinetic constant, a measure of the "speed" of
the reaction. This constant, K1, provides the engineer means to relate
the remaining sulfide concentration at various contact times, given the
original contaminant level. The equation that relates these parameters
is:

$$t = (1/K1) \ \ln[So/S] \hspace{4cm} [22]$$

where t is the time required (Hr) to reduce the initial sulfide concen-
tration So (mg/l) to the desired level S (mg/l). The desired level may
be established as 0.1 mg/l, the secondary drinking water standard for
sulfides. A safety factor F of 2 to 3 is recommended to compensate for

any non-ideal conditions encountered in field conditions. The contact basin volume, V (gallons) for a community with a peak day demand, Q, in gallons per day is computed according to:

$$V = F \ Q \ t/24 \hspace{3cm} [23]$$

An existing water reservoir may be used as contact basin as long as its volume is greater than the volume calculated by the above equation.

Chemical Dose

Food-grade hydrogen peroxide, with a purity of 35 percent is recommended for field applications. This chemical should be carefully metered into the water line feeding the contact basin. Hydrogen peroxide should never be combined with chlorine to prevent dechlorination and destruction of hydrogen peroxide. A chemical metering pump capable of handling this chemical should be used for this application. The metering pump may be connected to the circuit that activates the water supply pump, thus assuring constant concentration feed and avoiding the possibility of overdosing. The metering pump may then be calibrated to deliver the required peroxide rate to destroy the sulfide flow in the supply system. A dose of 4.0 mg of pure peroxide are required to completely oxidize 1.0 mg of total sulfides. This dose translates into 100 grams of total sulfides destroyed per liter of 35 percent hydrogen peroxide applied. Monthly chemical demand, M, in gallons per month, may be computed according to:

$$M = 3.0 \ So \ Qa \ / \ 10,000 \hspace{3cm} [24]$$

Where So is defined above, and Qa is the annual average demand. The metering pump flowrate, Qp in ml/min, for 35 percent peroxide may be computed based on the supply flowrate, Qs, in gpm, as follows:

$$Qp = So \ Qs \ / \ 26.42 \hspace{3cm} [25]$$

Field calibration to attain Qp must be performed when the metering pump is working against the pressure at the application point. This procedure may be safely accomplished by metering water from a graduated cylinder (or measuring cup) at operating pressure.

Economic Factors

Food-grade hydrogen peroxide (35 percent pure) is dispensed by FMC Corporation in 55 gallon drums, at a cost of 67 cents per pound FOB, Albuquerque, New Mexico, ($6.30/gallon). Sulfide test kits for field

analyses are also distributed by FMC at $19 each. Approximately 30 analyses may be expected from each kit. No more than two kits should be required to operate a rural treatment system for one year. Other operation and maintenance costs (O&M) associated with a peroxide treatment process are expected to be small, and considered negligible in this report. Adding the cost of two test kits to the chemical cost provides the expected O&M ($/month):

$$O\&M = 3.17 + 6.30 \ M \qquad [26]$$

Metering pumps specifically designed to handle hydrogen peroxide at low flowrates (Barracuda 475C) are available from the same manufacturer at a cost of $190 each. Installation of such a pump is simple and a cost of less than $100 is associated with such a task. Then, the total cost for the metering system, P, in dollars would be:

$$P = 290.00 \qquad [27]$$

Water storage tanks are available from various sources at a large range of prices, depending on the volume of the reservoir and the construction material. For instance, best-fit analysis of cost of underground fiberglass tanks, including installation is described by [28].

$$T = 2,400 + 1.08 \ V \qquad [28]$$

where T is the capital cost (including installation costs) in dollars, for a contact tank with volume, V, in gallons.

Example. A rural community reports taste and odor problems in its water distribution system. Field analyses show a sulfide concentration, So, of 1.9 mg/l. Water is supplied from a 690 foot well equipped with a 31 gpm pump. Water is then directly delivered to the distribution system (storage tank located at the opposite end of the system). Peak day and average demand are 7,000 and 4,400 gallons/day, respectively. A water treatment system design is requested to oxidize sulfides to secondary drinking water standards with hydrogen peroxide (S = 0.1 mg/l). The cost per 1,000 gallons treated is also requested assuming the community will borrow the required capital costs at 12 percent per annum. The life expectancy for the pump is 5 years and for the fiberglass contact tank is 20 years.

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Solution. Kinetic studies using a molar ratio of peroxide:sulfide of 4:1 (identical to 4 mg of peroxide applied to 1 mg of total sulfides), performed as indicated in the section on experimental procedures, result in a first-order kinetic constant of 0.77 Hr-1. Using a safety factor of 2.5 and equations 22 through 25, the following values would be obtained:

$$t = (1/0.77) \ln[1.9/0.1] = 3.82 \text{ Hr.}$$
$$V = 2.5 \times 7,000 \times 3.82 / 24 \sim 3,000 \text{ gal}$$
$$M = 3.0 \times 1.9 \times 4,400 / 10,000 = 2.5 \text{ gal/month}$$
$$Q_p = 1.9 \times 31 / 26.42 = 2.2 \text{ ml/min}$$

Costs associated with such a facility would be as follows:

$$O\&M = 3.17 + 6.30 \times 2.5 = \$18.92 \text{ /month}$$
$$P = \$290.00$$
$$T = 2,400 + 1.08 \times 2,785 = \$5,400$$

Thus, the total capital investment is $5,690. The capital recovery factors at a 12 percent interest rate are .02225 and .01102 for 60 and 240 monthly payments (5 and 20 years). Applying these factors to the previously calculated capital costs, $6.45 and $59.51 per month are required to amortize P and T, respectively. Total expenditures for the present example are then: $18.92 + $6.45 + $59.51 = $84.88 per month. The cost per thousand gallons is $84.88 / (4.4 x 30) or 64¢/1,000 gal. It is important to notice that the largest contribution to this cost is the amortization of the contact tank and that treatment costs may be greatly reduced in communities with reservoirs at the well site. For instance, given the same conditions in the present example, and a reservoir with capacity greater than 3,000 gallons at the well site would reduce total expenditures to 18.92 + 6.45 = $25.37 per month. The corresponding treatment costs would be 25.37 / (4.4 x 30) or 19¢/1,000 gal.

Safety Considerations

Food-grade hydrogen peroxide (35 percent pure) is a relatively safe liquid, but it may present certain hazards if not handled or fed properly. Rubber gloves, suitable protective clothing, and safety goggles should be worn when handling hydrogen peroxide. Although neither hydrogen peroxide nor its decomposition products are systemic poisons, concentrated solution irritates the skin, particularly mucous membrane tissue and the eye.

Clothing must be washed thoroughly with water should it come in contact with hydrogen peroxide. If allowed to dry in the fabric, the chemical may cause fire, particularly if the clothing is soiled.

Hydrogen peroxide is not considered explosive, but when mixed with organic substances (such as gasoline and lubricants), hazardous impact sensitive compounds may result. Also, small amounts of materials containing catalysts can cause rapid decomposition and rupture of the containing vessel if it is not properly vented. Hydrogen peroxide should be stored only in original containers. Once this chemical is removed from the original container, it should not be returned to it. Storage drums must be properly vented and located away from extreme heat and cold. Drums should always be placed in a vertical position, away from combustible materials and near a source of water for flushing in case of spillage. Concrete floors with a mild slope towards a drain are recommended for storage areas. Discarded drums may be used for other applications once they have been thoroughly washed with ample water. A relatively cool and protected place is recommended for storage because 35 percent peroxide will freeze at -27°F and may decompose at high temperature.

The metering pump selected for feeding peroxide into a pipeline should be designed to handle hydrogen peroxide in order to prevent "gas locking" or corrosion of the internal parts. Clean polyethylene tubing and fittings are recommended for this application as long as the pressure at the application point does not exceed 100 psi. The metering pump selected must be equipped with built-in check valves to prevent water backflow into the chemical reservoir.

FIELD TESTS

The community of Madrid, New Mexico, (pop. 89) has experienced
severe sulfide problems in its water supply well. Field measurements
of sulfide with a Hach sulfide kit indicate that the concentration of
total sulfides in this well is 1.9 mg/l, while the pH increases from
a natural 6.8 to a maximum of 7.5 as carbon dioxide evolves from solu-
tion. Water from this well is extracted with a submersible 31 gpm pump,
iodated for disinfection purposes and stored in a 30,000 gallon reser-
voir. Water is then delivered from the reservoir into the distribution
system.

Several field tests with hydrogen peroxide were conducted in this
water supply system to confirm the validity of the experimental labora-
tory results. A chemical metering pump was connected in parallel with
the main 31 gpm water pump. Hydrogen peroxide (food grade at 35 percent
concentration) was dosed into the system when the water pump was in
operation. By varying the stroke length in the metering pump, it was
possible to control the peroxide:sulfide ratio. A schematic diagram
of the water distribution and chemical systems is shown in figure 6.
Serious technical difficulties were encountered in the automatic dosing
of peroxide since the metering pump tended to "gas lock" unpredictably.
This undesirable performance may be eliminated in other sites if a meter-
ing pump designed to handle hydrogen peroxide is utilized, rather than a
standard chemical pump. In order to assure reliable results, the system
operator opted for manually injecting the chemical into the pressurized
water line prior to manually starting the main water pump.

Accurate records of water and peroxide volumes, date, and residual
sulfides were kept by the operator. Sulfide concentrations were measured
with the aforementioned field kit at various locations throughout the
distribution system. The limit of detection for the field kit is approx-
imately 0.05 mg/l as H_2S. A summary of the field records is shown in
table 6. Daily average flow rate and contact time in the reservoir were
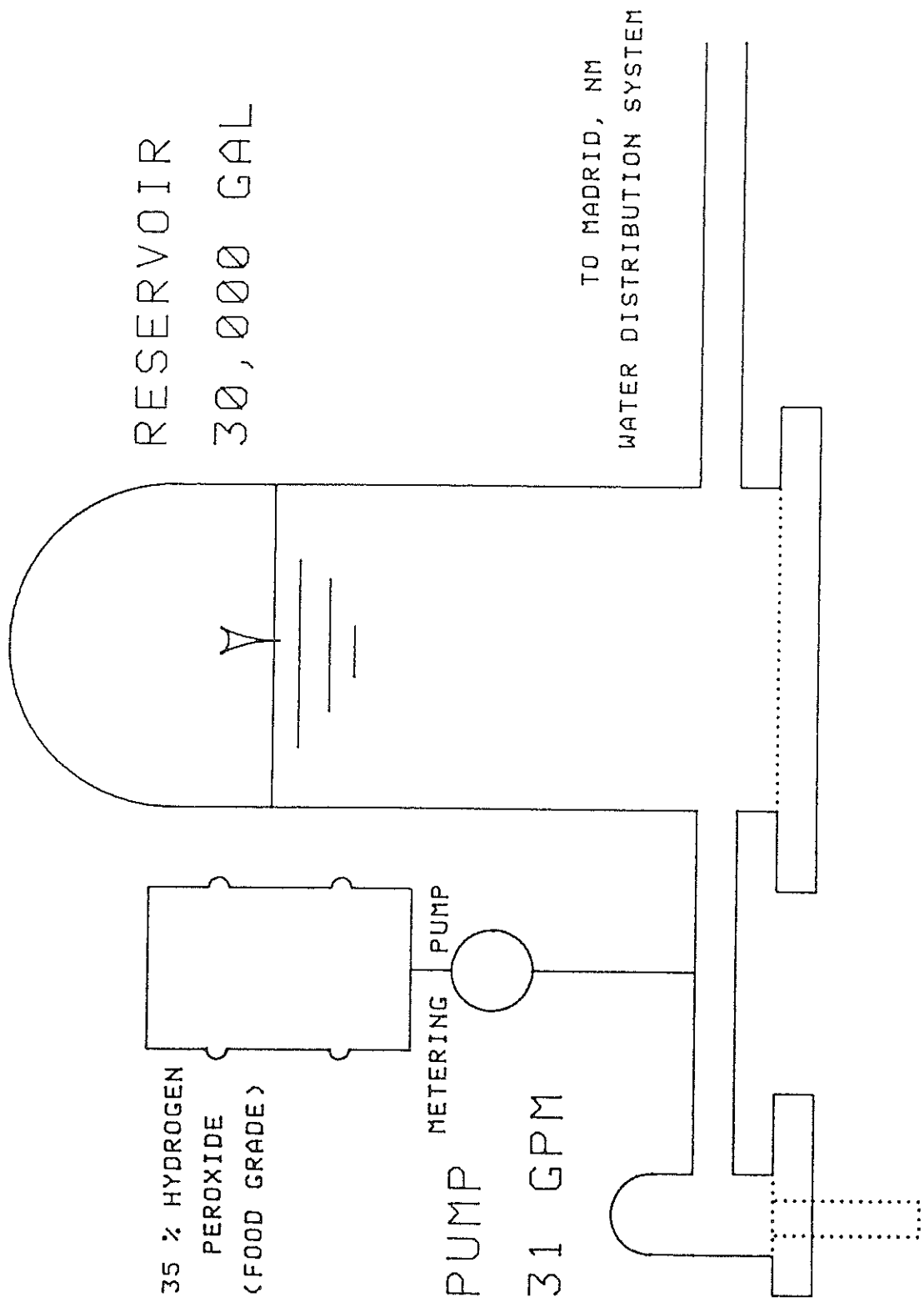4,400 gal/day and 6.8 days, respectively.

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RESERVOIR
30,000 GAL

35 % HYDROGEN
PEROXIDE
(FOOD GRADE)

PUMP
METERING
PUMP
31 GPM

TO MADRID, NM
WATER DISTRIBUTION SYSTEM

Figure 6.   Water Supply System in Madrid, N.M.

Table 6

Field Oxidation Results

Date (1984)	H_2O_2 (mg/l)	H_2S (mg/l)
8/23	0.88	1.90
8/26	2.03	1.30
8/29	2.67	1.30
8/30	2.88	1.20
9/03	3.03	0.58
9/07	3.15	0.64
9/11	4.11	0.80
9/14	4.84	1.10
9/17	5.38	0.43
9/24	5.47	0.31
9/28	6.45	0.32
10/06	7.15	0.36
10/13	7.15	<0.05

The time required to reduce the sulfide concentration from an initial 1.9 mg/l to the secondary drinking water standard of 0.05 mg/l may be calculated from equation 22 using the first-order rate constants, as determined in the laboratory (0.32 and 0.77 hr-1 for $H_2O_2:H_2S$ molar ratios of 1:1 and 4:1, respectively). Only 11 or 5 hours would be required to reduce the sulfide concentration from 1.9 to 0.05 mg/l for molar ratios of 1:1 or 4:1 respectively. No catalysts were tested in field conditions due to the limited information regarding effects of catalysts on human health and the more than adequate reaction time in the reservoir.

The information in table 6 shows that the peroxide program involved a gradual increase of peroxide concentration. The objective was to establish with certainty the minimum (optimum) dose of peroxide required to reduce the sulfide concentration to secondary drinking water standards. Plotting the residual sulfide concentration as a function of peroxide dose as shown in figure 7, one may observe that in order to accomplish such an objective in field conditions, 7.5 mg/l of pure peroxide are required to oxidize 1.9 mg/l of total sulfides. Therefore, the optimum mass ratio is approximately 4.0 mg of peroxide per mg of sulfide. The molar ratio of $H_2O_2:H_2S$ is also 4.0 since the molecular weights of both compounds are identical. This molar ratio is also indentical to the theoretical value predicted by reaction 17, which shows a complete reaction from sulfide to sulfate. Thus the end products of the field oxidation experiments are expected to be sulfates only.

The data provided for the previous design and cost analysis example are identical to those for Madrid's water supply. A 30,000 gallon water reservoir is available at the well site. The storage volume is, in this case, much greater than the calculated contact volume, V. Thus, no additional storage tank is required for this community. The treatment costs associated with the peroxide treatment facility are 19¢ per 1,000 gallons, and the capital investment is only $290.

Social acceptance to the chemical program was favorable. No community complaints were received by the researchers during the implementation of the program. The addition of peroxide at the optimum rate resulted in
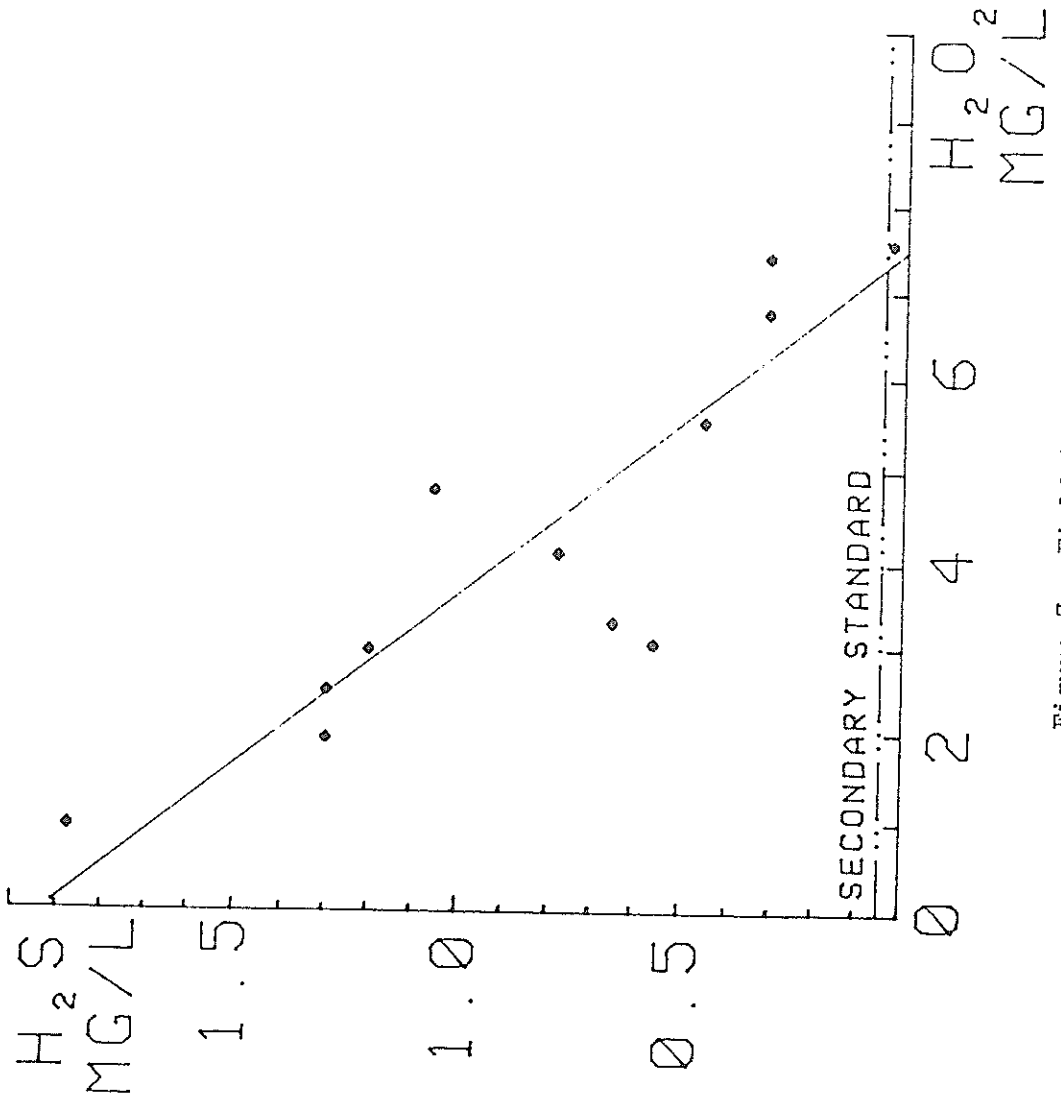
Figure 7. Field Oxidation Results

water free from taste and odor, which was welcomed in this community that has been plagued with odorous water for a considerable time. Comments were received regarding the unusually long times required by the operator to manually dose the chemical. This problem should not exist in this and other locations as metering pumps designed to handle hydrogen peroxide are used.

CONCLUSIONS

The purpose of this research was to study the oxidation of dilute aqueous solutions of hydrogen sulfide with hydrogen peroxide. Knowledge of the kinetics was desired for determining the feasibility of sulfide removal with peroxide in the field of water supply, as well as to provide a means for designing the removal systems with more than a trial-and-error approach.

Following is a summary of the findings of this research:

A review of the literature indicates that not only is hydrogen peroxide effective for sulfide oxidation, but it also is economically competitive with other oxidants. Additionally, the fact that it is easy to handle and non-toxic, as well as non-polluting and non-carcinogenic, makes it ideal for use by small communities and individual well owners.

The rate of sulfide removal decreases with increasing pH for peroxide-to-sulfide molar ratios of one-to-one and four-to-one. When the molar ratio is as high as twenty-to-one, this trend is reversed. The dependence of the oxidation rate upon pH decreases with increases in the molar ratio of peroxide-to-sulfide within the range one-to-one to twenty-to-one.

In some waters the formation of colloidal elemental sulfur may be displayed as an increase in the turbidity of the water at pH values below 7.75. Thus, in actual practice it may be necessary to include a filtration unit for this type of waters when the pH is less than 7.75. Elemental sulfur is not formed, and sulfate is the end product for all types of waters with pH values greater than 7.75.

Divalent nickel is a very efficient catalyst in the oxidation of sulfides by hydrogen peroxide. Its presence in concentrations above 1.0 mg/l is the most important kinetic factor studied. The acceleration of the reaction is more noticeable for solutions with higher pH values.

The presence of naturally occurring inhibitors and catalysts in drinking waters makes theoretical modeling of field oxidation rates impossible. Design of sulfide by peroxide facility is based on actual experimentation of the water to be treated.

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Even though the reaction rate of the oxidation of sulfides with hydrogen peroxide is slower than the ones observed with stronger oxidants, this chemical is an effective oxidant as long as adequate contact time is provided.

The optimum molar ratio of peroxide to sulfide is 4:1.

Total treatment costs associated with peroxide facilities in typical rural communities vary between 19 and 64 cents per 1,000 gallons.

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