corrosion prevention is
for its action on a film
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f dissolved oxygen. The
is low, but care in in-
, of dry surfaces above

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ecessary to use great care
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hich will insure syphoning
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r high enough in the neck
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$+ Na_2SO_4$

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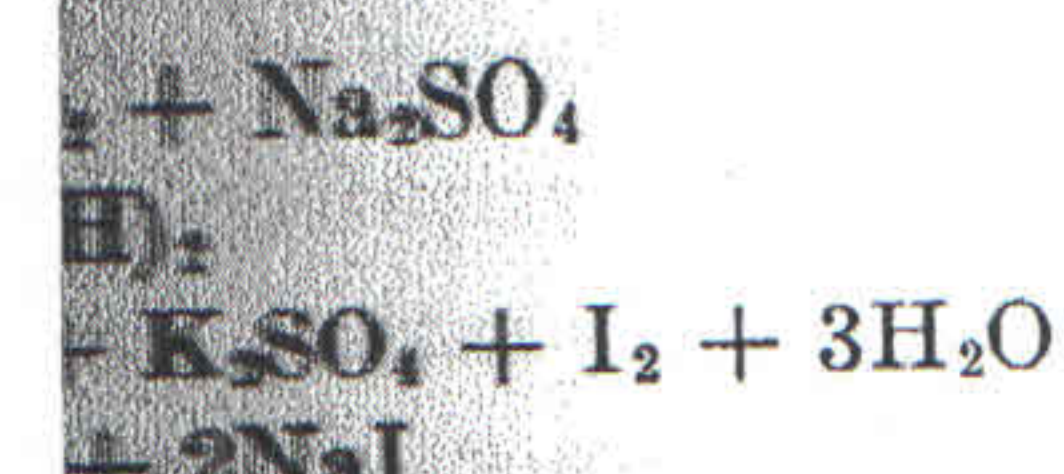
a number of modifications
purities and increase the
od is used for waters that

contain 1 ml/l or more of dissolved oxygen, while the Schwartz-Gurney modifications are used for testing deaerated waters.

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"Manual on Industrial Water—1956 Printing," ASTM Special Technical Publication No. 148-B, Am. Soc. for Testing Materials, Philadelphia, Pa.

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Hydrogen Sulfide

Waters which contain sulfides are commonly known as "sulfur waters." Their most prominent properties are their offensive, rotten-egg odor and their marked corrosiveness. This odor is the characteristic one of hydrogen sulfide gas. It is noticeable even in the cold when present in a water to the extent of 0.5 ppm or more, and when present to the extent of 1 ppm or more, it becomes very offensive. If the water has a high pH value, the odor may be slight, for in such a case much of the sulfur may be present as an alkaline sulfide instead of as hydrogen sulfide.

Most sulfur waters are ground waters. In Table 3-11 are listed the analyses of twenty-five such waters. It will be noticed that the sulfide content of these, when expressed as hydrogen sulfide, ranges from 0.7 to 70 ppm. Waters having higher amounts of hydrogen sulfide than this maximum are occasionally encountered, but nearly all of the usable sulfur waters will be found in the range below 10 ppm, and of these the great majority will range below 5 ppm.

Occasionally, a well yields a water which is black with ferrous sulfide (FeS). Usually, this is extremely finely divided, and it takes a very small quantity to blacken the water. Such black waters may also, at times, be encountered in dead-end mains where bacterial action has resulted in reducing some of the sulfate content to sulfide. In such cases, the black

water usually comes out in "shots." For instance, when a hydrant is opened, there may be a shot of black water for a few moments only and then the water will run clear, but on standing idle for a while, more black water will develop. The remedy for this is chlorination, heavy at first, with flushings to clear the mains; a slight chlorine residual should be maintained thereafter. Connate waters and oil-field brines also frequently contain very objectionable amounts of hydrogen sulfide and may be very corrosive.

While much of the corrosion deposits from sulfur waters is ferrous sulfide, analyses by Pomeroy indicate that in badly corroded pipe corrosion deposits may consist of FeS_2 instead of FeS. Aeration is widely employed for the reduction of the sulfide content of sulfur waters, but the reduction especially in waters of rather high alkalinity, is usually only partial. For instance, field tests that the author made on aerating three sulfur waters showed that aeration reduced the sulfide content, expressed as H_2S, only to the extent shown in Table 3-12.

TABLE 3-12. AERATION OF THREE SULFUR WATERS

Samples	Sulfide Content as ppm of H_2S	
	Raw Water	Aerator Effluent
Sulfur water A	3.5	1.3
Sulfur water B	2.0	1.0
Sulfur water C	2.2	0.8

It was noted that the aerated waters were alkaline to phenolphthalein, while the raw waters had all contained some free carbon dioxide and this suggested the addition of carbon dioxide to the water to lower its pH. In the first attempts to carry this out, various excesses of carbon dioxide were introduced into the water as it passed through the riser to the aerator. This did result in lowering the sulfide content of the water but not to the extent desired as it was found that nearly all of the carbon dioxide came out of the water in the top two or three trays of the aerator.

The next experiments were made in an enclosed, forced-draft type of aerator in which an artificial flue gas was blown upwardly through the aerator, counter-current to the descending water. This not only lowered the pH of the water but kept it low during its passage over all of the trays and effected the desired degree of reduction—to 0.2 ppm which was then eliminated by chlorination.

Both hydrogen sulfide and carbon dioxide, when dissolved in water, are very feebly ionized, and it is possible to displace either one of these

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EATMENT

Ortega, Fla.	well	1.1	214	584	224	8	124	17	81	0.1	8	7.5
Saratosa, Fla.	well	3.2	808	115	45	253	135	243	683	0.1	10	7.4
Shanghai Sulfur Spring, W. Va.	spring	3.2	160	111	62	39	122	15	62			
Torrance, Calif.	well	2.3	173	905	345	115	190	79	19			
White Sulfur Springs, W. Va.	spring	9.4	1250			143	194	23	100			

* Contains no carbon dioxide; has 20 ppm phenolphthalein alkalinity.

substances from its alkaline or alkaline earth salt by blowing a stream of the other gas through the solution. In treating sulfur waters, though, the important and unfortunate fact is that the carbon dioxide comes out much more easily than the more soluble hydrogen sulfide. Also, as it comes out, the pH value (assuming a normally alkaline water) rises, and this upsets the equilibrium between alkaline sulfides and hydrogen sulfide so that the reaction proceeds in the wrong direction for the removal as hydrogen sulfide. In this connection, Pomeroy has calculated, for a temperature of 20°C, a series of factors to show the amount of total sulfide existing as hydrogen sulfide at various pH values (Table 3-13).

TABLE 3-13.
HYDROGEN SULFIDE
FACTORS

pH Value	Factor
5.0	0.98
6.0	0.86
6.5	0.67
7.0	0.39
7.5	0.17
8.0	0.060
9.0	0.0063

According to this, if the determination of total sulfide, expressed as hydrogen sulfide, shows a certain figure and the pH value is 5.0, then about 98 per cent of the total sulfide is present as hydrogen sulfide and only some 2 per cent as an alkaline sulfide. On the other hand, if the water had a pH value of 9.0, only a little over one-half of one per cent would be present as hydrogen sulfide and the remainder would be present as an alkaline or alkaline earth sulfide.

Oxidation of sulfides by dissolved oxygen is apparently a rather slow process. In some experiments that the author made with aerated sulfur waters, standing in glass bottles for two hours at 82°F effected no measurable degree of oxidation. In these experiments, the amount of hydrogen sulfide in the aerated waters varied from a little below to slightly above 1 ppm. These waters were clear, contained less than 0.1 ppm of iron and the bottles were not in direct sunlight. In large reservoirs, aerated sulfur waters undergo a slow oxidation with the liberation of sulfur, much of which is so finely divided that it is colloidal. Such waters often appear clear when a glassful is viewed in direct sunlight. The same water, in a covered or darkened reservoir, shows the Tyndall effect when a beam of light is directed into it. The reaction that takes

Figure 3-5. Ex

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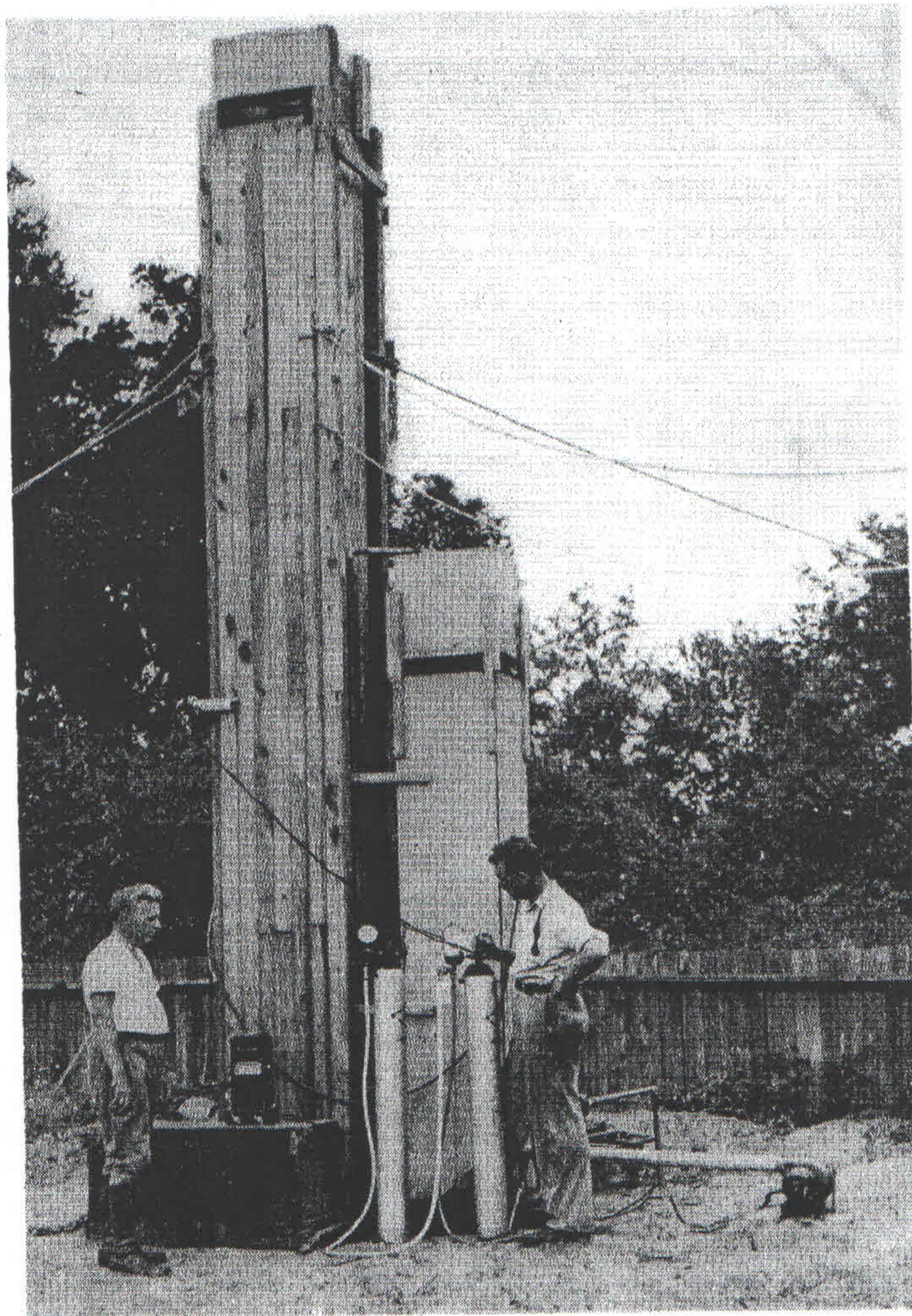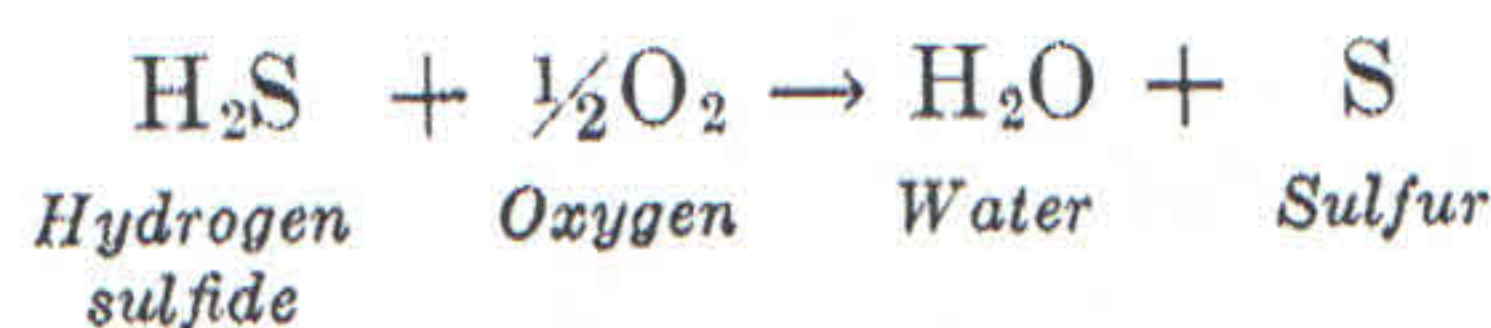irect sunlight.
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Figure 3-5. Experimental aerators for aeration of sulfur waters with synthetic flue gas.

place first is the oxidation of the hydrogen of the hydrogen sulfide as
follows:

$$H_2S + \tfrac{1}{2}O_2 \rightarrow H_2O + S$$

$$\text{Hydrogen} \quad \text{Oxygen} \quad \text{Water} \quad \text{Sulfur}$$
$$\text{sulfide}$$

Presumably, then, some of this finely divided sulfur oxidizes further,
with a sulfate as the final end product. Given infinite time and sufficient
oxygen, all of it should finally be oxidized to the sulfate. In practice,
however, such conditions do not exist and elemental sulfur is very evi-
dent. Also, most aerators and aerated water reservoirs, after operating

for some time on sulfur waters, show growths of sulfur bacteria which frequently play an important part in reducing the sulfide content.

Chlorine may also be used to oxidize sulfides but this process is rather expensive on raw sulfur waters because, depending on the pH of the water and the amount of sulfide present, it may take up to 8 atoms of chlorine to oxidize 1 molecule of hydrogen sulfide instead of the 2 atoms

TABLE 3-14. HYDROGEN SULFIDE: SOLUBILITIES AT 760 MM AND AT 0 TO 100°C

Temperature		Milliliters per Liter (ml/l)	Parts per Million (ppm)
(°C)	(°F)		
0	32	4590	7070
5	41	3900	6000
10	50	3320	5110
15	59	2870	4410
20	68	2500	3850
25	77	2190	3380
30	86	1940	2980
40	104	1530	2360
50	122	1220	1880
60	140	962	1480
80	176	497	765
100	212	0	0

TABLE 3-15. HYDROGEN SULFIDE: WEIGHTS
AND CONVERSION FACTORS FOR DISSOLVED
HYDROGEN SULFIDE

Weight (in grams at 0°C and 760 mm)
    1 liter = 1.539
    1 milliliter = 0.001539

Multiply ppm H_2S by 0.649 to convert to ml/l
Multiply ml/l H_2S by 1.54 to convert to ppm

theoretically required to oxidize the hydrogen of the hydrogen sulfide to water and liberate the sulfur. This is because either all or a great part of the sulfides are oxidized to sulfates and this oxidation takes place to a great extent even when a deficiency of chlorine is added. The consumption of chlorine at pH values ranging from 3.2 to 10.1 with a water containing 5 ppm of sulfides, expressed as H_2S, as determined by the author and E. K. Gilbert, is shown in Table 3-16. An excess of chlorine was used in these tests, the detention period was 10 minutes and all determinations were made by the iodometric method as that is not sensitive to colloidal sulfur.

TABLE 3-16. OXIDATION OF SULFIDES BY
CHLORINE AT VARIOUS pH VALUES
(Detention Period—10 Minutes)

Final pH Values	Sulfides as PPM H_2S	PPM Chlorine Added	PPM Chlorine Residual	PPM Chlorine Consumed
3.2	5	50	6	44
5.0	5	50	7	43
6.2	5	50	7	43
6.4	5	50	9	41
6.8	5	50	11	39
7.1	5	50	18	32
7.6	5	50	18	32
9.0	5	50	25	25
10.1	5	50	25	25

The amount of chlorine required to oxidize 1 ppm of H_2S to the sulfate is 8.32 ppm and the reaction is as follows:

$$H_2S \quad + \quad 4Cl_2 \quad + 4H_2O \rightarrow H_2SO_4 + \quad 8HCl$$

Hydrogen   Chlorine   Water   Sulfuric   Hydrochloric
sulfide   acid   acid

The amount of chlorine required to oxidize 1 ppm of H_2S to water and sulfur is 2.08 ppm and the reaction is as follows:

$$H_2S \quad + \quad Cl_2 \quad \rightarrow \quad S \quad + H_2O$$

Hydrogen   Chlorine   Sulfur   Water
sulfide

The amount of chlorine required to oxidize 5 ppm of sulfides, expressed as H_2S, is $8.32 \times 5 = 41.6$ ppm. In these tests, the sulfides were completely oxidized to sulfate at pH values below 6.4; at pH values around 7.0, about 70 per cent was oxidized to sulfate and 30 per cent to water and sulfur; and at pH values of 9.0 to 10, a little less than 50 per cent was oxidized to sulfate and slightly more than 50 per cent to water and sulfur.

NOTE: As shown in the reaction for the oxidation of hydrogen sulfide to sulfate, both sulfuric and hydrochloric acids are formed. These neutralize some of the alkalinity of the water, forming sulfates and chlorides. If the alkalinity of the raw water is low, this may appreciably affect the pH value.

While the chlorination of raw waters containing high contents of sulfides would be rather expensive, chlorination is of great value in eliminating the small residuals from the effluents of other sulfide removal processes. A water, for instance, that contained only 0.5 ppm of hydrogen sulfide would require only about 4 ppm or $\frac{1}{30}$ lb per 1000 gallons or 33 lb of chlorine per million gallons to oxidize the sulfide to sulfate.

When treatment of a sulfur water is under consideration, it seems
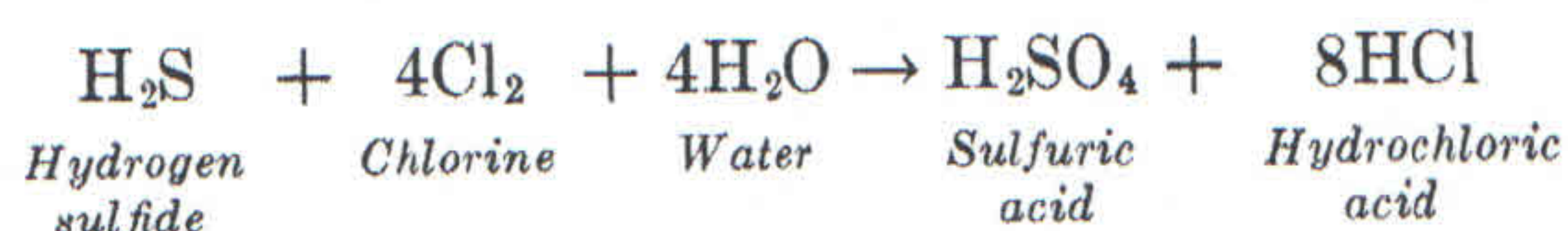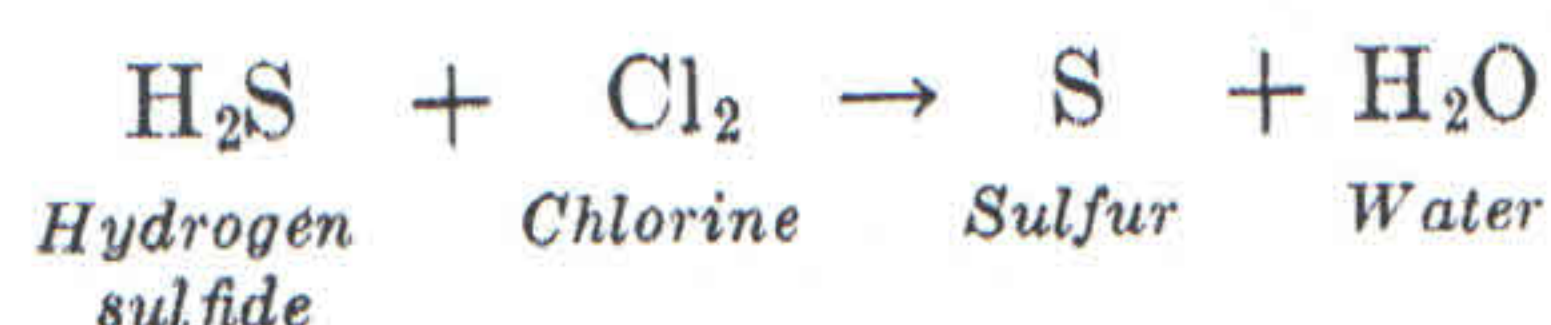
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CHLORINE AT VARIOUS pH VALUES
(Detention Period—10 Minutes)

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6.4	5	50	9	41
6.8	5	50	11	39
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7.6	5	50	18	32
9.0	5	50	25	25
10.1	5	50	25	25

The amount of chlorine required to oxidize 1 ppm of H_2S to the sulfate is 8.32 ppm and the reaction is as follows:

$$H_2S + 4Cl_2 + 4H_2O \rightarrow H_2SO_4 + 8HCl$$

Hydrogen sulfide   *Chlorine*   *Water*   *Sulfuric acid*   *Hydrochloric acid*

The amount of chlorine required to oxidize 1 ppm of H_2S to water and sulfur is 2.08 ppm and the reaction is as follows:

$$H_2S + Cl_2 \rightarrow S + H_2O$$

Hydrogen sulfide   *Chlorine*   *Sulfur*   *Water*

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When treatment of a sulfur water is under consideration, it seems

obvious that one of the first things to find out is how much sulfide is present. Strangely enough, this is usually not done. Instead the water is carefully analyzed for every other constituent. The reason for this absurd procedure is that sulfide determinations have to be made in the field, as shipped samples undergo sufficient oxidation, during shipment and handling, to vitiate the results.

NOTE: Stoppered samples of a water having 4.6 ppm of H_2S dropped to 2.9 ppm in 24 hours and to zero in 72 hours.

Various schemes have been tried, such as precipitating the sulfide as lead sulfide or cadmium sulfide before shipping, but none of these have been successful. In the cases of the lead or cadmium sulfide, it was found that they oxidized at least as readily during shipment as the sulfide content of the untreated water. Therefore, the shipped sample often shows no sulfide content when it reaches the laboratory. For this reason, field tests are recommended; these are relatively simple, rapid, and easily carried out.

NOTE: In sampling sulfur waters, the following procedure will be found satisfactory. If water is under pressure, connect one end of a length of ¼-inch gum rubber tubing to the sampling cock and place the other end at the bottom of a 500-ml glass sampling bottle, preferably one that has a glass stopper. Allow the water to flow through the bottle at a brisk rate for at least half a minute. Then withdraw the tubing while the water is still flowing. Add the standard iodine solution immediately, mix, let stand a few minutes, and then proceed with the titration. In the case of sulfur waters in tanks or reservoirs, the sampling bottle should be fitted with a two-holed rubber stopper through one hole of which passes a glass tube extending almost to the bottom of the sampling bottle. The other hole is fitted with a short piece of glass tubing, the inner end of which is flush with the bottom of the stopper. If the elevations will permit, a syphon can be established with some lengths of ¼-inch gum rubber tubing. In this case, the water is allowed to syphon through the sampling bottle for a minute or two before proceeding with the test. If the elevations are such that syphoning is impractical, the suction end of a hand pump may be connected to the discharge end of the sampling bottle and the water drawn through the sampling bottle in this manner. Where a pump is used, the rubber tubing should be heavy enough so that it does not collapse under the suction.

The sulfide content of sulfur waters may be reduced or removed by special methods of aeration or degasification, and/or chlorination. These methods are described in Chapter 10. Hydrogen sulfide is an exceedingly poisonous gas, and equipment for its removal should be out in the open and never in an enclosed room where there would be danger of trapping the gas. Fortunately, its repulsive odor usually gives a fair warning of its presence, but too much reliance should not be placed on this, for workmen have been killed by hydrogen sulfide while working in an atmosphere that did not seem too oppressive.

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