HYDROGEN SULFIDE IN WATER SYSTEMS: WHAT'S THAT SMELL?

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It is not uncommon for Hydrogen Sulfide (H_2S) to be found in Florida well waters. From a public health standpoint, the concentrations of H_2S found in these waters are not physically harmful. Adverse physical effects are from inhalation, not ingestion, and don't normally occur until the H_2S reaches levels around 20 to 50 mg/L. This is well above concentrations commonly found in most raw water supplies. The primary issue with its presence in drinking water is that, even at very low concentrations, it may contribute to taste and odor problems. Its existence is prototypically characterized as a "rotten egg" odor. In addition to the odor complaints, H_2S can contribute corrosiveness and other nuisance conditions within the distribution system and in home piping. This article will briefly discuss some of the issues commonly encountered while seeking to manage H_2S concentrations.

Water for the vast majority of Florida community water systems is pumped from wells (i.e., groundwater supplies). Because the water is below ground and not exposed to the atmosphere, the subsurface environment is generally classified as anaerobic or chemically reducing. This provides ideal conditions for the formation of H_2S. Oxidized forms of sulfur (primarily sulfates and bisulfates) tend to be reduced back toward its elemental form, where H_2S is an intermediate step. The generic equation for this transformation is shown in reaction 1.

$$SO_4^{2-} + (\text{sulfur-reducing anaerobic bacteria}) = H_2S + 2H_2O + 2OH^- \quad (1)$$

Not all groundwaters have these characteristics, but it is not uncommon for a water plant manager to have a well that does have a small quantity of H_2S among its chemical constituents.

Due to the aesthetic impacts of H_2S on drinking water, the Florida Department of Environmental Protection (FDEP) has promulgated rules covering its management in community water systems. The primary rule, located in Section 62-555.315 FAC, specifically addresses issues related to the removal of total sulfide from water. Depending on the concentration, different treatment methods may be warranted. For instance, if total sulfide is present at concentrations greater than 0.3 mg/L, the recommended method of removal is aeration. Depending on the concentration, different types of aeration may be used. These types include conventional, forced draft, or packed tower aeration. Aeration is the most common method of managing H_2S at water treatment facilities. To understand how this process works, a brief review of some basic water chemistry elements will be helpful.

H_2S Removal by Air Stripping

Aeration as a unit operation depends on two basic principles: equilibrium conditions and mass transfer considerations. The water to be treated is in equilibrium chemically with its component species and physically in equilibrium with the atmosphere above the water surface. These equilibrium conditions define the limits of the gas transfer process. Aeration is an effective removal mechanism because H_2S exists as a dissolved gas in the raw water. Incidentally, the function of aeration is not specifically to oxygenate the water; rather it is to strip the dissolved gas (H_2S) out of the raw water by changing the equilibrium conditions of the water and thus drive the dissolved gas out.

The removal of H_2S by air stripping is defined by application of Henry's Law. Henry's Law, which is generally associated with dilute solutions, relates the concentration of a gas in the water to the partial pressure of the gas above the liquid. It is recalled that partial pressure is pressure that a particular gas exerts as it moves toward equilibrium. Equilibrium occurs as gasses flow from regions of higher partial pressure to regions of lower pressure. The larger this difference, the faster the flow.

To remove the H_2S it is first necessary to determine how much of it exists in the water. This is a function of pH and temperature. pH is usually the primary variable because the raw water temperature remains fairly uniform. Hydrogen sulfide exists in equilibrium in three different forms as shown in reactions 2 and 3 and their respective pK (disassociation) values.

$$H_2S = HS^- + H^+ \qquad pK_a = 7.1 \qquad (2)$$

$$HS^- = S^{2-} + H^+ \qquad pK_a = 14 \qquad (3)$$

Figure 1 is a diagram showing the speciation of hydrogen sulfide as it varies with varying the water pH.

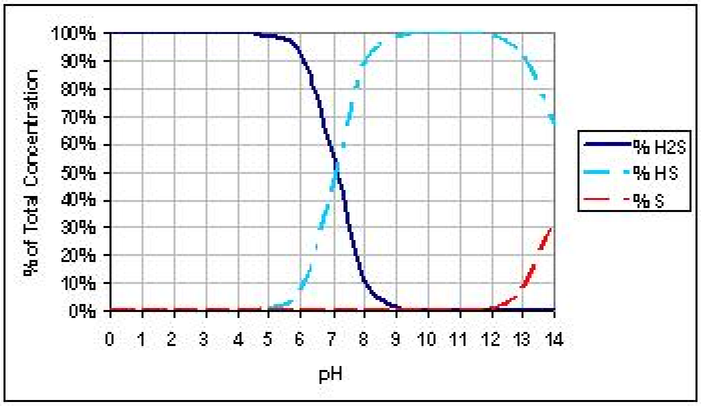

Figure 1: Hydrogen Sulfide - pH Dependence Diagram

In drinking water systems, total sulfide is primarily composed of H_2S and HS^-. At a pH equal to 7.0 for instance, approximately 56% of the total sulfide is H_2S while 44% is present as HS^-. At a pH equal to 8.0, only 11% of total sulfide is present in the H_2S form while the remaining 89% is HS^-. Of the different sulfide forms, only the H_2S molecule is removed by air stripping. It is important, therefore, to note that at elevated pH values the efficiency of aeration for the removal of hydrogen sulfide is significantly diminished. Again, only sulfur in the H_2S form can be removed by aeration by stripping.

It should be noted that Dalton's Law of Partial Pressures and Henry's Law also imply that the aeration process will affect all the dissolved gasses in the water. Recall that Dalton's Law states that in a volume that contains several gasses, each gas will exert its own partial pressure independent of the other gasses, and the total pressure of all gasses is the sum of all the partial pressures. In other words, as the water is aerated to remove hydrogen sulfide it will affect other water parameters. For instance, aeration also will strip other available gasses out of the water such as NH_3, Volatile Organic Carbons (VOC), dissolved radon, methane, and CO_2.

It is of particular importance to note that a decrease in CO_2 leads to a decrease in alkalinity and a corresponding increase in pH. A decrease in alkalinity also results in a decrease in the buffering capacity of the water. Buffering capacity is important because it promotes a stable pH environment, which is a key variable in corrosion characteristics of the water and various chemical equilibrium reactions (both good and bad).

H_2S Removal by Chemical Oxidation

In addition to removing H_2S by stripping the dissolved gas from the water, H_2S and HS^- can be removed by chemical oxidation. However, this treatment alternative must be used with caution. Oxidation of hydrogen sulfide or bisulfide ions converts these forms to elemental sulfur. Elemental sulfur exists as a finely divided solid that may contribute to high turbidity readings if sulfur is present at high levels. Unless removed, the sulfur will flow out of the plant and into the distribution system. This is not typically associated with any adverse health effects, but can cause taste and odor problems in the future if certain bacteria exist in the distribution system that reconvert the elemental sulfur back to H_2S.

Chlorination is the means of oxidation most commonly used for this purpose. Again, because elemental sulfur is formed, unless a turbidity removal process follows, oxidation is not recommended for hydrogen sulfide removal when hydrogen sulfide is present at concentrations greater than 0.3 mg/L.

By the way, in addition to removing H_2S by stripping, aeration will provide a nominal reduction of H_2S by direct oxidation. This occurs because aeration increases the level of dissolved oxygen in water, which reacts with hydrogen sulfide to produce elemental sulfur as shown in reaction 4. High DO levels in water may accelerate corrosion reactions.

$$2H_2S + O_2 = 2S_{(s)} + 2H_2O \qquad (4)$$

According to Section 62-555.315 F.A.C., if total sulfide is present in the water at concentrations less than 0.3 mg/L and dissolved iron is less than 0.1 mg/L, chlorination may be used for sulfide oxidation to elemental sulfur. Equation 5 outlines the oxidation of sulfide by chlorine species:

$$HS^- + OCl^- = S_{(s)} + Cl^- + OH^- \qquad (5)$$

It is noted that the species shown in reaction 5 are the ones typically found in water systems. As discussed, speciation is dependent upon the pH of the water, and water systems typically have pH values between 7.0 and 8.0. At such pH, bisulfide ions and hypochlorite ions are the predominant species with respect to hydrogen sulfide and chlorine, respectively.

Given the stoichiometry of the reaction and the fact that 1 mole of hypochlorite is equivalent to 1 mole of elemental chlorine, a minimum free chlorine dosage of 2.2 mg/L should be employed to oxidize every 1 mg/L of sulfide as sulfur. Removal of H_2S by chlorination can significantly increase the chlorine cost at the water plant due to the required dosage.

Because chlorine species oxidize sulfide, iron, and manganese to insoluble particulate products it is important to utilize chlorination with caution and closely monitor the concentration of these species when sulfide and iron exceed 0.3 mg/L and 0.1 mg/L, respectively. The FDEP requires the turbidity of the finished water not to exceed the turbidity of the raw water by more than 2 nephelometric turbidity units (NTUs). In events that result in elevated turbidity readings, a filtration step needs to be utilized downstream of the oxidation step.

In summary, removing hydrogen sulfide from water is not necessarily as easy as just adding an aerator at the treatment plant. It is important to understand how much sulfur is actually being removed and what forms the remaining sulfur takes. The remaining sulfur will flow into the distribution system. Because there are no regulatory restrictions on this, in one sense there is no problem with this practice. However, if sufficient elemental sulfur or bisulfide is incorporated into the biofilms of the distribution system, it is possible that under appropriate conditions the H_2S could re-form and cause taste and odor problems for the customers.

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