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Technical Bulletin

The Control of Hydrogen Sulfide Odors

The reduction and prevention of odors is a significant part of many wastewater treatment programs. Odors in wastewater typically develop in the collection system, sedimentation basins and in sludge handling areas. They are normally the result of biological activity creating anaerobic conditions. In these conditions sulfate reducing bacteria, convert sulfate ($SO4^{=}$) compounds into a variety of sulfide bearing compounds. These sulfide compounds can be simple hydrogen sulfide or more complex organic molecules. In wastewater systems these compounds are found both in their dissolved and gaseous forms. Control programs can address either or both forms, however, with persistent odor problems the program must address sulfides in the dissolved state.

The Effects of Sulfides

Sulfides are first and foremost odor nuisances. As population densities and public awareness increase, the pressure to mitigate and prevent nuisance odors is increasing.

Sulfides are corrosive. In the gaseous phase sulfides will be adsorbed by moisture on the exposed areas of pipes to form thin layers of sulfurous and sulfuric acids. In these layers relatively high concentrations of acid will corrode the pipe material leading eventually to line failures. The corrosion can shorten the life of any exposed metal and concrete equipment and fixtures. For plants with digester processes it is desirable to be able to eliminate the hydrogen sulfide from digester gases that will be used in energy production. High levels of hydrogen sulfide will corrode generators and restrict the use of digester gases for this purpose.

Sulfides are dangerous and hazardous to health. In moderately high concentrations hydrogen sulfide can be deadly. Enhancing this danger is hydrogen sulfide's ability to anesthetize the sense of smell. Creating a safe work place is not only a responsible thing to do, it is required by law; so the control of these substances in the work place is essential.

Hydrogen Sulfide Control Programs

Covering and Scrubbing

A common approach for addressing many odor situations is to physically cover the worst offending process areas and scrub the fumes. However, as odors can surface throughout an entire plant this approach is rarely fully effective unless the entire plant is covered and scrubbed.

Oxidation

Sulfides are produced in anaerobic conditions, which are indicated by a low to negative ORP (oxidation-reduction potential). Oxidizing chemicals such as oxygen, hydrogen peroxide, ozone, potassium permanganate and chlorine can be used to raise the ORP of the wastewater. The issues surrounding oxidation of wastewater with the various chemical oxidizers are as follows

Oxidizer	Pro's	Cons
Oxygen/ Air	Effective at sparging out H2S & Increasing ORP. No cost for air. Non-hazardous.	Scrubbing is generally necessary. High capital outlay with significant operating expense
Chlorine/ Bleach	Reacts with H2S & increases ORP	Forms THM's. Chlorine storage and use is hazardous. Dosage higher than theoretical due to high reactivity. Moderately high operating expense.
Hydrogen Peroxide/ Ozone	Reacts with H2S & increases ORP	Hydrogen Peroxide use and storage is hazardous. Dosage higher than theoretical due to high reactivity. Very high operating expense.
Potassium Permanganate	Reacts with H2S & increases ORP	Dosage higher than theoretical due to high reactivity. Very high operating expense.

Alkalinity/pH Adjustment

Low wastewater pH encourages the release of hydrogen sulfide and high pH discourages it, as seen in the following table. Another method for controlling odors is to raise the pH of the entire wastewater stream or a specific offending process.

pH	Percentage of H_2S	Percentage of HS^-
4	99.9	0.1
5	98.9	1.1
6	90.1	9.9
7	47.7	52.3
7.5	22.5	77.5
8	8.3	91.7
8.5	2.8	97.2
9	0.89	99.1

Alkalinity/ pH adjustment is accomplished with the following chemicals listed in order of normal relative cost of material. Depending on the alkalinity demand of the wastewater this approach can be high to very high in cost.

CaO	Quick Lime
$Ca(OH)_2$	Lime
Na_2CO_3	Soda Ash
NaOH	Caustic Soda
KOH	Caustic Potash

Odor Control with Ferric Chloride and Ferrous Chloride

Many communities and industries are successfully applying iron salts to mitigate existing odors and provide downstream protection for persistent odor problems. These products can be applied in wastewater systems to the collection system, the headworks of the plant, and in solids handling areas. Ferrous Chloride and ferric chloride provide adequate, economical odor removal. Both materials are shipped as highly concentrated solutions of the iron salt. As solutions, both materials are easy to store, handle and accurately apply to the process. Ferric Chloride provides the same odor control treatment as Ferrous Chloride along with a number of added benefits. The decision to use one or the other material will depend on treatment needs and economics. Below is a brief outline to highlight the major decision criteria.

Ferric Chloride Solution

Reacts with dissolved sulfides in water by the following summary reaction:

$$2FeCl_3 + 3H_2S \ddagger S\_ + 2FeS\_ + 6HCl$$

Dosage Ratio - ppm $FeCl_3$ to ppm H_2S (in solution) - **3.2 : 1.0**
(This ratio reflects theoretical stoichiometry)

Dosage Point – Interceptors, headworks, primary settling tanks

Cost – Low to moderate depending on geography

Handling - Easy to handle and feed

Applying a dosage beyond that dose required for initial H_2S removal, Ferric Chloride then reacts to form Ferric Hydroxide which is a coagulant/ flocculant. The result is enhanced settling of both the generated sulfide removal solids and other wastewater

particulates in the stream. The Ferric Hydroxide formed then resides in the sludge to react with H_2S that may form later on in the process. This is described in the following reaction:

$$2Fe(OH)_3 + 3H_2S \ddagger S\_ + 2FeS\_ + 6H_2O$$

Addition of an anionic flocculant just following the addition of the Ferric Chloride in a primary settling tank makes Advanced Primary Treatment possible.
Ferric Chloride is slightly oxidative and will raise the ORP of the wastewater. This translates into lower potential to form H_2S in the first place.

Ferrous Chloride Solution

Reacts with dissolved sulfides in water by the following reaction.

$$FeCl_2 + H_2S \ddagger FeS\_ + 2HCl$$

Dosage ratio ppm $FeCl_2$ to ppm H_2S (in solution) - **3.7:1.0**
(This ratio reflects theoretical stoichiometry)

Dosage Point – Interceptors, headworks, primary settling tanks

Cost – very low to moderate depending on existing market conditions and geography

Handling - Easy to handle and feed

Ferrous chloride odor removal programs are relatively inexpensive to maintain. Ferrous chloride does not provide any flocculation unless it is oxidized in the process to the ferric state.

Treatment Methods

California Water Technologies realizes that each treatment facility must be approached individually. While the basics of water treatment remain constant, differences in water quality, treatment requirements, facility capabilities and staff expertise require solutions to treatment that are custom designed for the facility. Contact your CWT representative at (866) 337-7427 for knowledgeable, insightful, and fully committed assistance in developing solid solutions to your treatment needs.