



TECHNICAL BULLETIN: Wastewater

Hydrogen Sulfide (H₂S) Control with Ferric Sulfate

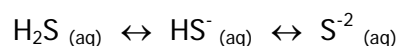
The presence of H₂S in wastewater systems can cause a variety of problems. It is responsible for the rotten-egg odor frequently associated with wastewater treatment facilities. Vapor phase H₂S concentrations greater than 10 mg/l can cause headaches, nausea, and respiratory distress. Concentrations over 300 mg/l are life threatening. Thiobacillus bacteria can metabolize aqueous phase H₂S into sulfuric acid, which can cause significant localized deterioration of concrete piping and structures.

H₂S in wastewater systems is primarily due to the metabolic activity of facultative anaerobes - bacteria that can conduct metabolic activity using either O₂ or SO₄⁻². In the presence of O₂, these bacteria behave as aerobes. In the absence of oxygen, these bacteria can utilize SO₄⁻² in their metabolic process. Sulfide is an end product of sulfate-based metabolism. Facultative bacteria are common throughout wastewater systems and can be found in sewers as well as anaerobic digesters.

A given section within a wastewater treatment facility will become oxygen deficient when its O₂ consumption rate exceeds the rate at which O₂ is replenished into the system. In order to optimize sludge digestion and methane generation, anaerobic digesters are specifically designed to operate under oxygen-deficient conditions. In contrast, sewers are not specifically designed to operate

anaerobically. Factors that lead to oxygen deficiency in sewers include high water temperatures, which induce high bacterial metabolic activity, and stagnant flow conditions.

H₂S is a weak diprotic acid, so the following acid-base equilibrium exists in aqueous solution:



The distribution of sulfide between these species varies with the system pH. At neutral pH typical of many wastewater systems, the speciation is nearly equally distributed between H₂S and HS⁻. H₂S in the vapor phase (the cause of rotten-egg odor) is the result of volatilization of liquid phase H₂S. Factors affecting this offgassing include pH, temperature and degree of turbulence in the aqueous phase. In general, for a specific concentration of total sulfide in solution:

- volatilization increases with increasing temperature
- volatilization decreases with increasing pH
- volatilization increases with increasing fluid turbulence

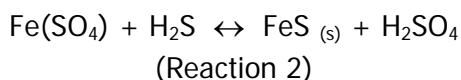
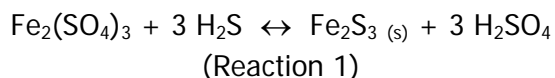
H₂S levels can be measured in both the liquid and vapor phases. Due to the rapid equilibria existing between the aqueous phase species, liquid phase methods typically measure the sum of the concentrations of all three species.

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The decision regarding which phase to analyze is based on the end-user's perception of the specific problem. For example, if the presence of H₂S is primarily an odor issue, treatment based on the vapor phase concentration may be the logical choice.

Solutions of iron salts control H₂S by precipitating it from aqueous solution, as shown in the following reactions:



These reactions demonstrate that Fe⁺³ is stoichiometrically more efficient than Fe⁺² for precipitating sulfide. Specifically, 1 mole of Fe⁺³ precipitates 1.5 moles of H₂S, compared to 1 mole of H₂S for Fe⁺². Table One summarizes the stoichiometrically required dosages of Fe₂(SO₄)₃ and Fe(SO₄) solutions to precipitate 1 mg/l of H₂S in solution.

In addition to this stoichiometric advantage, ferric-generated solids exhibit faster settling rates than ferrous-based solids. Also, due to ferric's excellent floc forming characteristics, several waste

treatment facilities have reported reduced polymer dosages in their sludge dewatering processes while using ferric sulfate for H₂S control.

Recommended ferric sulfate dosages for H₂S applications vary somewhat depending on the control strategy chosen by the end-user. For example, if the treatment objective is to control the liquid phase sulfide concentration, then the recommended ferric sulfate dosage is 110 - 125% of the stoichiometric dosage (based on the difference between the existing and target liquid-phase sulfide concentrations). Slight overdosing is recommended to insure achieving treatment objectives. If the treatment objective is to control the vapor phase H₂S concentration, then the recommended ferric sulfate dosage is 125% of the difference between the existing liquid phase sulfide concentration and an assumed "target" liquid phase sulfide concentration that will generate the target vapor phase H₂S concentration. Note that since these systems are open, there is no true equilibrium between the vapor and liquid phases. Thus, an inexact relationship exists between the vapor and liquid H₂S concentrations, making this a somewhat trial-and-error approach.

Table One: Stoichiometric Dosages for Fe-based Products

Solution	Fe Content (Wt. %)	Stoichiometric Dosage (mg/l of Neat Product/ppm H ₂ S)
50% Liquid Ferric Sulfate ⁽¹⁾	10.0	12
60% Liquid Ferric Sulfate ⁽¹⁾	12.0	10
28% Liquid Ferrous Sulfate ⁽²⁾	5.0	35

(1) Ferric Sulfate activity based on Fe₂(SO₄)₃•9(H₂O)

(2) Ferric Sulfate activity based on FeSO₄•7(H₂O)

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CORPORATE HEADQUARTERS

General Chemical
90 East Halsey Road
Parsippany, NJ 07054



CUSTOMER SERVICE

(800) 631-8050

TECHNICAL SERVICE

(800) 255-7589 or (315) 478-2323

WEBSITE

www.GeneralChemical.com