USP technologies™
Solutions for a clean environment

TECHNICAL BULLETIN
REFINERY

SULFIDE OXIDATION USING HYDROGEN PEROXIDE

Introduction

Sulfide is found throughout the environment as a result of both natural and industrial processes. Most sulfides found in nature are produced biologically (under anaerobic conditions) and occurs as free hydrogen sulfide (H_2S).

Manmade sources of H_2S typically occur as a result of natural materials containing sulfur, such as gas and oil, being refined into petroleum products. Sulfide-laden wastewater must be handled carefully and remediated before being released to the environment for aesthetic (odor control), health (toxicity), ecological (oxygen depletion) and economic (equipment corrosion) reasons. Typical sulfide discharge limits are <1 mg/L.

Sulfide Treatment Alternatives

There are dozens of alternatives for treating sulfide-laden waters, ranging from simple air stripping to elaborate sulfur recovery plants used to treating sulfide-laden waters at refineries, ranging from simple air stripping to elaborate sulfur recovery plants. There are processes based on chemistry such as oxidation, precipitation, absorption and combination as well as physics such as adsorption, volatilization and incineration. Each process occupies a niche that is often defined by the scale and continuity of treatment, whether the sulfide is in solution or is a gas, the concentration of sulfide involved and the disposition of the sulfide-containing medium. For convenience and flexibility, however, chemical oxidation using hydrogen peroxide (H_2O_2) continues to grow in its scope of application.

Treatment with Hydrogen Peroxide

H_2O_2 can control sulfides in two ways depending on the application:

- **Destruction -** by oxidizing sulfide to elemental sulfur or sulfate ion; and
- **Prevention -** by providing dissolved oxygen that inhibits the septic conditions that lead to biological sulfide formation.

This technical note focuses on the oxidation chemistry of odor control with H_2O_2, particularly as it is applied to wastewaters containing moderate to high levels of sulfide (50 - 10,000 mg/L). Oxidation of sulfide with H_2O_2 proceeds differently depending primarily on the pH of the wastewater.

Neutral - Slightly Acid Conditions

$$H_2S + H_2O_2 \rightarrow S_0 + 2\ H_2O$$

The product of the oxidation is predominately elemental sulfur, which appears as a yellow colloid if under dosed or a white colloid with complete oxidation. If clarity of the effluent is needed, the sulfur may be removed by flocculation with an anionic polymer followed by filtration.
The stoichiometry calls for 1.0 lb. H_2O_2 per lb. of H_2S and it is not unusual for efficiencies to approach 100%, particularly when the concentrations of other oxidizable substances such as thiosulfate are low.

There is very little heat generated in the reaction, even when sulfide levels are several thousand mg/L.

Alkaline Conditions

$$S^{2-} + 4\ H_2O_2 \rightarrow SO_4^{2-} + 4\ H_2O$$

The above reaction predominates at pH > 9.2 and yields soluble sulfate as the reaction product. The stoichiometry calls for 4.25 lbs. H_2O_2 per lb. S^{2-} and it is not unusual for reaction efficiencies to approach 100%, provided that the H_2O_2 is added in a controlled fashion and the reaction medium is thoroughly mixed. This is due to the much faster reaction brought by the increased reactivity of H_2O_2 at alkaline pH. Consequently, as the pH increases above 9 or 10, there is generally little benefit to catalyzing the reaction.

Slightly Alkaline Conditions

In moving from pH 7 to pH 9, both of the above reactions may occur with the following results:

- The reaction products transition from elemental sulfur to sulfate
- The H_2O_2 requirement transitions from 1:1 to 4.25:1
- The rate of reaction speeds up

To some extent, catalysts may be used to push the reaction one way or the other. Catalysts such as iron favor sulfate formation. These catalysts may be used to economize H_2O_2 use or to produce a clear effluent. In both cases, the speed of reaction is greatly accelerated.

The USP Technologies (USP) Advantage

The following advantages of H_2O_2 should be considered when evaluating treatment options:

- Rapid, complete oxidation of H_2S
- H_2O_2 decomposition liberates oxygen which helps maintain aerobic conditions, inhibiting H_2S regeneration
- No capital expenditures for storage and handling equipment when using USP's H_2O_2 dosing system

About USP Technologies

USP Technologies is the leading supplier of peroxygen-based technologies and services for environmental applications. We have been serving the water, wastewater and remediation markets for over 20 years and have offices and field service locations throughout North America. Our consultative approach to problem solving includes application assessment, technology selection and development of a tailored treatment approach. Our full service programs successfully integrate storage and dosing equipment systems, chemical supply, inventory and logistics management, and ongoing field and technical support. This approach provides cost-effective, "hands-off" solutions to our customers. USP Technologies also can provide access to experienced application partners for a turn-key program encompassing engineering, site characterization and technology selection, program implementation, execution and report generation.

Getting Started

We look forward to supporting your treatment needs, whatever the scale of your requirements. To obtain a streamlined treatment solution tailored to your specific project, give us a call at (877) 346-4262.

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