control of odors in the brewing and food processing industries

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abstract

Easily recognized by its rotten egg odor, hydrogen sulfide is responsible for most of the odor problems associated with brewery and food processing wastewater treatment. Heavier than air, colorless, corrosive and extremely toxic, its presence raises serious workplace health and safety concerns. This paper reviews the chemical treatment programs available to control H₂S as well as some nonsulfide odors. These include organic scavengers that react with reduced sulfur compounds, neutralizers that eliminate an odor’s objectionable characteristics, nitrates and inhibitors that prevent bacteria from producing sulfides, masking agents that replace one odor with another, and metal salts that remove sulfides as metallic precipitates. Biocides can control microorganisms that produce odors, but chlorine is rarely used to eliminate H₂S because of safety, handling and environmental problems. Case histories describe the application of advanced products that inhibit H₂S production, and neutralizers that neutralize non-H₂S odors.

introduction

Public complaints about odors can affect a brewer’s image in the surrounding community. Ultimately, these complaints may affect public relations in the greater marketplace where its products compete. Indeed, since the Clean Air Act Amendment (CAAA) went into effect, the onus has been placed on industry to reduce its odor emissions.

Within the brewery itself, the effect of odors can be observed in several definite ways:

- Safety concerns may arise about people being overcome by odors in the workplace.
- Productivity may be affected when odors or odor producing conditions cause employees to avoid an area or neglect their duties.
- Productivity can also be affected by odors that taint food products, rendering them unsaleable.
- Equipment integrity can be threatened by the presence of many odoriferous substances that are corrosive in nature.

It should be noted that not all manufacturing facilities produce odors or experience these problems, nor are all odors noxious or toxic in nature. However, one very large segment of the odor control market does fit this description and dictate immediate and complete attention, and that involves the control of hydrogen sulfide (H₂S) generation and evolution. Other non-reduced odors, such as those formed by certain compounds containing amines and other groups, also contribute to odor emissions and need to be controlled.

Under the CAAA, H₂S is not one of the 189 Hazardous Air Pollutants (HAPs). Therefore, hydrogen sulfide is not explicitly regulated. However, the CAAA does call for the elimination of offensive and toxic odors and H₂S falls into this category. State and local regulatory bodies use their own regulations as well as the CAAA to limit emissions of offensive and toxic compounds such as H₂S.
odor control in the brewing and food processing industry

Potential for odor control exists in many locations:

- Holding basins
- Lagoons
- Waste storage tanks
- Air stripping units
- Wastewater treatment systems
- Land applications

In the brewing industry, areas such as biological air filter units and plant effluent wastewater areas generate odors that may become fugitive emissions. The use of chemical neutralizers to control these odors is regarded as an acceptable treatment option because of the minimal amount of capital investment required. Other acceptable technologies, including combustion, oxidation and stripping, are also very efficient, but require considerable capital equipment investment. In many industrial applications outside of the brewing and food processing industries, odor control methods such as incineration, carbon adsorption, wet scrubbing, source modifications and odor masking may be found.

A chemical program will normally have a lower impact on the bottom line than immediate up-front capital expenditures. In addition, the time lapse between odor control conception and installation is shorter. Oftentimes, a chemical program can begin within days of inception.

background

Hydrogen sulfide (H\textsubscript{2}S) is the most commonly known and prevalent odoriferous gas associated with wastewater treatment systems. In addition to being toxic and corrosive to delicate instrumentation and other metals, it has a characteristic rotten egg odor that is objectionable and disagreeable.

In breweries, H\textsubscript{2}S odors may come from the biochemical reduction of inorganic sulfur compounds. It is generally recognized that under anaerobic conditions, sulfate-reducing bacteria (SRB) use sulfate as an oxygen source to metabolize organic matter in the waste stream.

Primarily, the SRB use a transport protein to bind sulfate in the bulk water. This provides the key to the sulfate entering into the periplasmic space (space outside and surrounding the cell membrane but inside the cell wall) of the bacteria where it can be further acted upon as an electron acceptor in the bacteria's complex energy process. This sulfate-binding protein has been isolated by A. B. Pardee and is known to contain one binding site for sulfate per molecule.

It is at the point where the water-soluble sulfate is reacted upon by the bacteria that proprietary inhibitors apparently interfere with the reaction. This means that the inhibitor either prevents the reaction from occurring or prevents subsequent reactions from going forward and producing hydrogen sulfide.

The exact means or reaction of the inhibitors that causes the inhibition of the sulfate uptake or reduction is not completely understood. Studies to isolate the exact mechanism are being done. Preliminary research suggests that there may be a quinone-like functionality in the inhibitor. This may be similar to the well-known anthraquinone mechanism of inhibition established in prior art. That is, certain cytochrome locations are involved in the SRB metabolic process. It may be that the inhibitors block the SRB's sulfate reduction at this site, among other possibilities.

Conditions favorable to the formation of H\textsubscript{2}S also increase the opportunity for the formation of other malodorous compounds such as mercaptans. At the same time, nitrogen-containing compounds such as amines may be present. These amine and ammonia compounds may also cause noxious odors that are disagreeable.

programs and solutions to control odors

At least four chemical means of controlling odors are generally used in the industrial setting:

1. Organic scavenging - Primary amines
2. Chemical oxidation - Chlorination, hydrogen peroxide, permanganate, ozone
3. Precipitation - Iron salts
4. Control by pH - Lime, soda caustic

Other solutions:

- Proprietary organic scavenger
- Biomodifiers - nitrates and proprietary inhibitors
Masking agents

Neutralizers

Organic scavengers are typically comprised of primary amines that react with reduced sulfur compounds that have acidic protons, as shown in the figure below:

\[ H_2S \leftrightarrow HS^- + H^+; \quad HS^- \leftrightarrow S^- + H^+ \]

Such nonproprietary compounds are not selective and will react with carbon dioxide as well, and in so doing will have a higher use cost than more selective compounds.

Proprietary organic scavengers such as ProSweet* are more specific in their reaction and will selectively react with the reduced species of sulfur compounds such as hydrogen sulfide and certain mercaptans. These organic scavengers tend to form side reactions; therefore, their use cost will tend to be lower. Of course, proper treatment levels for scavengers depend on many factors such as stream flow rate, temperature, H₂S concentration, desired H₂S removal efficiency and pH.

The benefits of using an organic scavenger include:

- No pH change
- Ease of handling and simple feed equipment
- No sludge generation.

Biomodifiers such as nitrate are commonly used in facultative and anaerobic lagoons to aid in controlling odors. Anaerobic bacteria use nitrate in preference to sulfate as an electron acceptor during their metabolism of organic substances. When nitrate is present, these sulfide-producing bacteria use it rather than sulfate. Thus the by-product of their activity becomes odorless nitrogen rather than objectionable H₂S. Some of the disadvantages of using nitrates are the limitation in effluent waterways and the necessity of significant contact time in order for proper utilization to occur.

Masking agents are increasingly being viewed negatively. Primarily, this negativity derives from the fact that in order to mask an odor the masking agent must create a significantly higher odor level. Once done, the perception is that something is being hidden. The masking of odors can present a severe health risk when H₂S is being masked. Masking does not mitigate the hazardous health effects of H₂S.

Oxidizers such as chlorine donating material have safety and handling problems. In addition, chlorine donors may contribute to the formation of carcinogenic trihalomethanes (THM).

Hydrogen peroxide oxidizes H₂S, and depending upon the pH of the water system will yield different products as shown below:

\[ \text{pH} < 8.5 \quad H_2O_2 + H_2S \rightarrow S + 2H_2O \]
\[ \text{pH} > 8.5 \quad 4H_2O_2 + S^- \rightarrow SO_4^{2-} + 4H_2O \]

At pH < 8.5, the stoichiometric H₂O₂ requirement is 1 gram H₂O₂ for each 1 gram of H₂S. In actual use, however, more H₂O₂ is required because H₂O₂ is not selective in what it attacks and therefore oxidizes other materials and organic matter in addition to H₂S. Many oxidizers have similar usage characteristics to that of H₂O₂.

Metal salts such as ferric chloride react as follows and precipitate the sulfide from water as ferric sulfide salts. In addition to sludge formation, handling of the iron salts presents a corrosion problem of its own.

\[ 2FeCl_3 + 3H_2S \rightarrow FeS_3\downarrow + 6HCl \]

Neutralizers function in a complex manner. This is because of the makeup of the neutralizers. Those neutralizers that contain essential oils primarily function by capturing odor molecules in a charge film that surrounds the essential oil-water complex. Neutralizers that contain other large organic molecules created by certain fermentation and blending processes function by absorbing odor molecules, by radical reaction, or by condensation reaction between the odor molecules and the neutralizer.

Oftentimes, the latter compounds produce a neutralizer reaction product that does not create or leave a detectable odor. Within the neutralizer grouping, the essential oils tend to control a wider range of odors. However, there may be a detectable odor of the essential oil present after odor neutralization.

**case history**

A large Midwestern brewer swept all gases from its reactors, tanks and other brewery processes through a biological gas-cleaning unit which consisted of iron impregnated chips that were periodically wetted by a spray system. The water from the gas cleaning unit went to the city sewer and
the cleaned, stripped gases were fed into the boilers.

This equipment purged many sulfur-containing compounds. However, a strong residual odor persistently wafted from the gas reaction chamber into the surrounding area. Various attempts to overcome the residual odor yielded only marginal results.

SUEZ Water & Process Technologies was asked to provide a cost-effective recommendation that would eliminate the fugitive odor from the gas-cleaning unit.

Bench testing helped determine that a very dilute solution of a ProSweet neutralizer product was the product of choice to completely neutralize the fugitive odors without producing a corresponding heavy masking odor. The neutralizer produced no odor.

A spray nozzle mist system was installed to provide two-nozzle coverage for each of eight openings in the 40’ X 20’ X 8’ biofilter unit; or a total of 16 nozzles. A dilute 0.3 % ProSweet neutralizing solution was delivered through this misting system.

• Once misted, odors were eliminated and neighbors and workers stopped complaining.
• No new masking odor was created.
• Neighbors became less aware of the brewery’s presence in their community.
• The ProSweet product use rate was cost competitive with the other programs previously tried.
• The ProSweet program was easy to set up and feed.
• A small amount of ProSweet neutralized a large amount of malodorous substances.

conclusion

At SUEZ, we have been successful at treating an array of odors that occur in the brewing and food processing industries. We continue to seek ways of providing unique ProSweet solutions for specific odors.

references