

Technical Paper

Control of Odors in the Sugar Beet Processing Industry

Clovis Sarmento, Industry Manager Food & Beverage
Terry Robbins, Consultant Water & Wastewater

INTRODUCTION

Driven by changes in the Clean Air Act Amendment (CAAA), the requirement for improved odor control may exist in many industrial facilities. Under this act, regulatory bodies will be forcing industrial plants such as paper mills, refineries and food processors to improve the quality of air they are emitting. This legislation is aimed at reducing toxic chemical emissions. Odor control has come into focus.

Odors emitted from manufacturing facilities can impact an operation in many ways:

- Public complaints about odor can negatively affect an industry's image in the marketplace and its ability to carry out an effective public relations policy with the surrounding community.
- Safety concerns can arise from people working in areas where odors can overcome them.
- Productivity impact can be seen in areas of a facility where objectionable odors exist due to employee avoidance or neglect.
- Production can be affected through the presence of odors and odor producing conditions, which taint product quality.
- Equipment integrity can be threatened by the presence of many odors 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, which does fit this description and dictates immediate and complete attention is the control of hydrogen sulfide (H₂S) generation and evolution.

Although the CAAA does not explicitly regulate hydrogen sulfide, it does call for the elimination of offensive and toxic odors.

ODOR CONTROL IN THE FOOD INDUSTRY

Potential for odor control technologies exists in many applications:

- Sugar Refining
- Meat Processing
- Rendering Plants
- Potato Processing
- General Food Processing Wastewater Treatment Systems

The use of chemicals as a method of odor control 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 of the industrial applications mentioned above such as paper making, oil refining and steel, odor control methods such as incineration, carbon adsorption, wet scrubbing, electrostatic precipitation, source modification, and odor masking may be found. In hospitals, office buildings and schools, other methods such as filtration and absorption are used. Many industrial facilities, however, find it is more cost effective to implement and operate a chemical based odor control program than to incur up front equipment purchases.

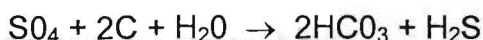
A chemical program is a direct benefit to those who have to put in place an odor control program now, with a low cost impact on their bottom line. With odor control programs involving equipment purchases, the time lapse between purchase and startup may involve months, consuming valuable time and becoming costly in fines and neighbor complaints.

BACKGROUND

H₂S is the most commonly known and prevalent odorous gas associated with wastewater treatment systems. It has a characteristic rotten egg odor, is extremely toxic, and is corrosive to metals.

Process and waste streams, in which the direct introduction of sulfides occurs, are likely candidates for odor problems.

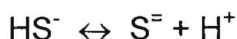
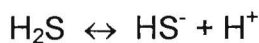
In addition to direct process sources of reduced sulfur compounds, the other primary contributor of hydrogen sulfide odors from wastewater streams is the biochemical reduction of inorganic sulfur compounds. Under anaerobic conditions, sulfate reducing bacteria use sulfate as an oxygen source to metabolize organics in the waste stream:



Most sulfate reduction occurs within a biological slime layer that protects the sulfate reducers from oxygen present within the bulk waste stream itself. The rate at which hydrogen sulfide is generated is dependent upon the concentration of sulfate and organics in the waste stream, the level of dissolved oxygen, pH, temperature, and the velocity of the water.

The conditions leading to H₂S formation generally favor the production of other malodorous organic compounds such as mercaptans, thiophenol, and thiocresol. Investigations of the conditions favoring H₂S formation can also help to quantify the potential for odor generation from other compounds. Thus, solving H₂S odor problems can often solve other odor problems as well.

H₂S dissolves in water and dissociates according to the following reactions:



Figures 1a and 1b show the distribution of sulfide species as a function of pH. The relative H₂S concentration increases with decreasing pH. At a pH of 7.0, H₂S represents 50 percent of the dissolved sulfides present; while at a pH of 6.0; over 90 percent of the dissolved sulfides is in the form of H₂S. If part of the dissolved H₂S escapes to the atmosphere, the remaining dissolved sulfide will be

divided between H_2S and HS^- in the same proportion as before because the equilibrium re-establishes itself almost instantly.

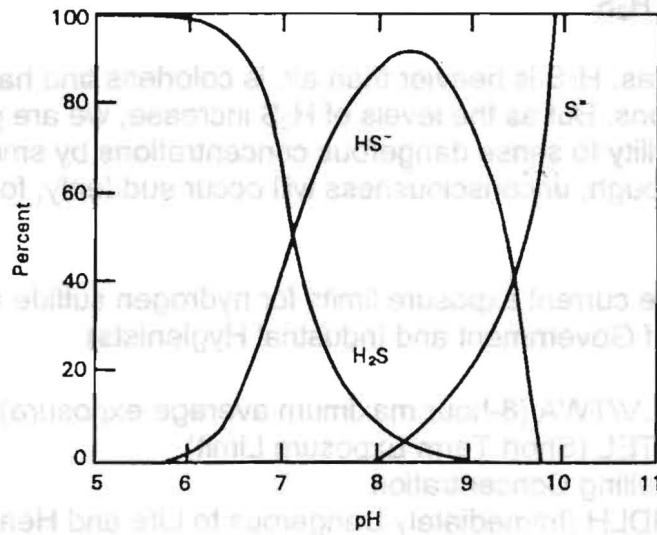


Figure 1a: Effect of pH on hydrogen sulfide equilibrium.

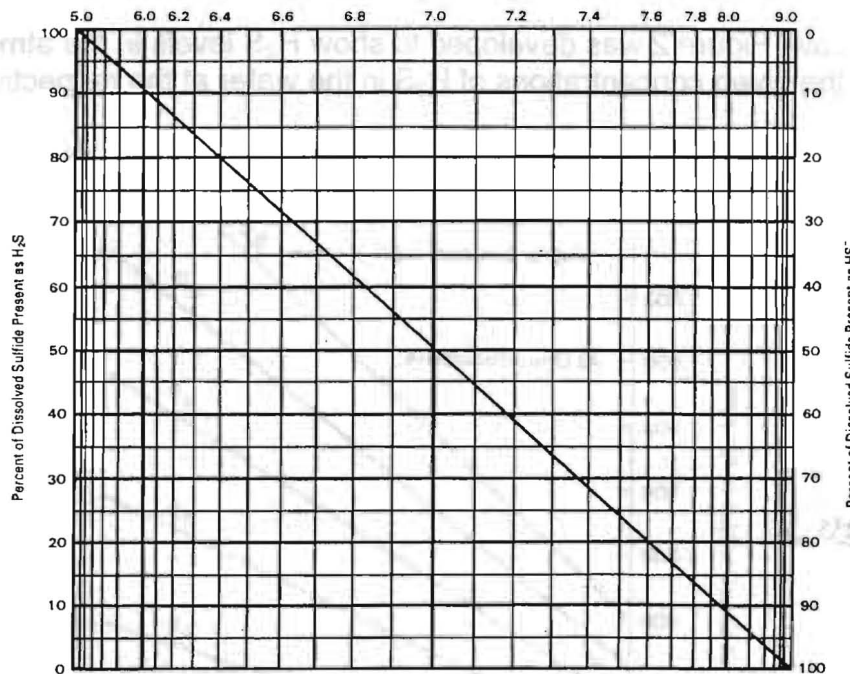


Figure 1b: Proportions of H_2S and HS^- as dissolved sulfide.

The distinction between the types of sulfide compounds is significant because only the H_2S can escape from solution and create odor, corrosion, and health problems. It is important, therefore, to quantify the total and dissolved sulfides present and the pH of the wastewater.

HEALTH EFFECTS OF H₂S

H₂S is an acutely toxic gas. H₂S is heavier than air, is colorless and has a characteristic rotten egg smell at low concentrations. But as the levels of H₂S increase, we are generally unaware of its presence. A person's ability to sense dangerous concentrations by smell is quickly lost. If the concentration is high enough, unconsciousness will occur suddenly, followed by death if there is not a prompt rescue.

The following outlines the current exposure limits for hydrogen sulfide as set by OSHA and ACGIH (American Conference of Government and Industrial Hygienists).

- 10 ppm (mg/L): TLV/TWA (8-hour maximum average exposure)
- 15 ppm (mg/L): STEL (Short Term Exposure Limit)
- 20 ppm (mg/L): Ceiling Concentration
- 100 ppm (mg/L): IDLH (Immediately Dangerous to Life and Health)

Very low concentrations of this gas can cause serious health hazards. Death has resulted from concentrations of 300 ppm (mg/L) by volume in air. Such concentrations can be obtained in an enclosed chamber with high turbulence, from wastewater containing 2 ppm (mg/L) of dissolved sulfide at a pH of 7.0.

Based on Henry's Law, Figure 2 was developed to show H₂S levels in the atmosphere (closed vessel) in equilibrium with the given concentrations of H₂S in the water at the respective wastewater temperatures.

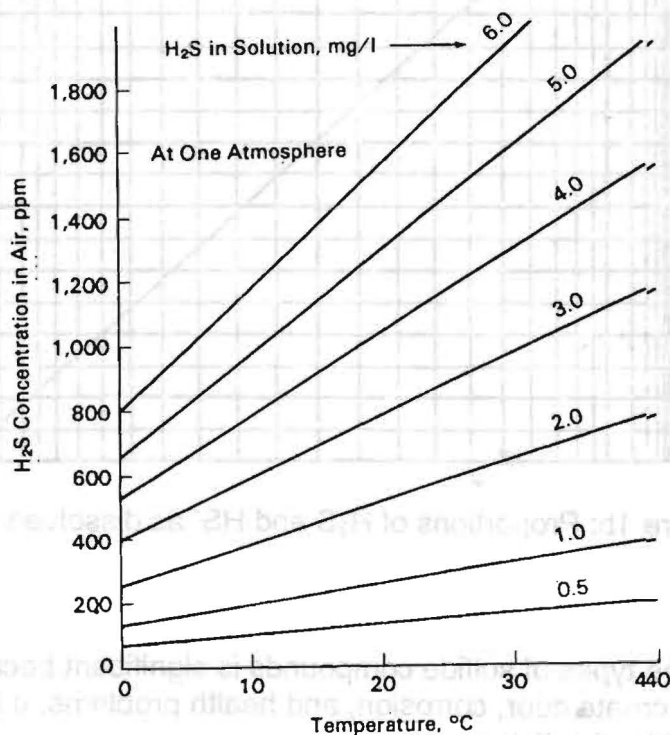


Figure 2: Equilibrium concentration of H₂S in air.

PRELIMINARY MONITORING PROGRAM

Normally, repeated odor complaints are the first indicators of potentially damaging sulfide generation within a system. In more extreme cases, the problems are manifested by deteriorated conditions in pipes and electrical equipment or by structural failures.

Evidence of sulfide generation warrants the implementation of a preliminary program to assess the overall potential for sulfide generation. Such a preliminary program should include a thorough investigation of odor complaints, and a systematic investigation of the wastewater collection and treatment system to identify major potential contributors.

CHEMICAL ADDITION

Numerous chemicals have been employed for control of sulfides in water systems. Chemical addition can control sulfides by:

1. Chemical Scavaging
2. Chemical oxidation (Cl₂, H₂O₂)
3. Precipitation (Metal salts)
4. pH control

OTHER SOLUTIONS

The current commercial products includes four distinct categories of technology:

- Organic Scavenger
- Counteractant
- Inhibitors
- Masking Agent

The organic scavengers are comprised of traditional primary amines as well as unique proprietary technologies.

Organic Scavenger- Scavengers will selectively react with any reduced sulfur compounds that have acidic protons. Therefore, many malodorous sulfur odors can be treated successfully with these products.

Proper treatment levels for scavengers depend on many factors such as stream flow rate, temperature, H₂S concentration, desired H₂S removal efficiency, and pH.

Dosages are often decreased based on actual operating conditions and the degree of scavenging required. It may not be necessary to scavenge all malodorous sulfide. Treatment levels will be dictated by perception and/or satisfactory monitoring levels.

The selection of single or multiple feed-points is site specific. Sulfide containing streams should be identified, in addition to locations, with high H₂S concentrations in the air. The feed point should be located upstream of the affected areas. Products can be fed with a standard metering pump to various locations such as full flowing pipelines, open channels, sludge lines, or sludge holding tanks.

The benefits of using scavengers include:

- A selective re-activity with many malodorous sulfur compounds
- No pH change
- Easy to handle and feed
- No sludge generation

Counteractant - These are chemicals that interfere with the malodor. The counteractant does not chemically react with the malodor, but reduces the perceived odor level by eliminating the objectionable characteristics of the malodor. This technology offers an effective way of dealing with a wide variety of odor types.

Biomodifiers - Nitrate has long been used in facultative and anaerobic lagoons to control odors. Facultative and obligate anaerobic bacteria, which are responsible for odor and sulfide production, prefer nitrate (to sulfate) as an oxygen source when available. When nitrate is present, these sulfide-producing bacteria use it to the exclusion of sulfate. This results in the production of nitrogen gas and other nitrogenous compounds rather than sulfide.

In some cases, it is appropriate to prevent the evolution of malodorous H₂S and mercaptans from water and wastewater streams.

Proper treatment levels for this technology depend on many factors such as stream flow rate, temperature, sulfate and dissolved oxygen concentrations, and pH. Assessment of these factors will aid in recommending treatment rates, control procedures, and specific application points.

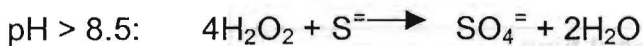
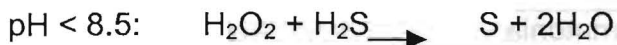
For optimum performance, these products should be fed in a declining dosage rate schedule. Higher feed rates are recommended initially, with decreasing rates following as the system begins to acclimate. Feed rates are often reduced until optimum maintenance dosages are established.

Masking Agent - Masking agents are primarily used where the level of odor is relatively low. Masking agents attempt to overpower the malodor with another odor, which is perceived to be more pleasant. In many cases, the end result is a fragrance-flavored version of the original malodor. There is no chemical reaction and the individual constituents of the odor remain unchanged. Masking agents are only effective on very mild odors and should be used only when no other practical solutions exist. **Use of masking agents to attack an H₂S problem is ill advised because it does not mitigate the severe health effects of the gas.**

Chemical Oxidation

Chlorine donating materials are rarely used because of their safety and handling problems and the probability of THM formation

Hydrogen peroxide chemically oxidizes H₂S according to the following reactions:

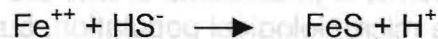


At pH < 8.5, the stoichiometric H₂O₂ requirement is 1g H₂O₂ / 1g H₂S. In practice, a greater weight ratio may be required because hydrogen peroxide can not selectively oxidize sulfides. The actual dosage rate will be proportional to the concentration of oxidizable compounds in the wastewater

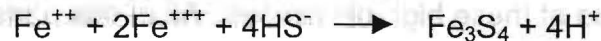
METAL SALTS

The salts of many metals will react with dissolved sulfide to form metallic sulfide precipitates, thus preventing H₂S release to the atmosphere. For effective removal of dissolved sulfides, the metallic sulfide formed must be highly insoluble.

Iron salts have been used for sulfide control. The ferrous ion reacts with sulfide as shown below.



Pomeroy found that the reaction of a mixture of iron salts with a molecular ratio of one part ferrous to two parts ferric was superior for sulfide control compared to the reaction of either one alone. The reaction of the mixed iron salts was hypothesized to occur as follows:



STRONG ALKALIES

Increasing the pH reduces the proportion of dissolved H₂S in the H₂S-HS⁻ equilibrium. For example, at a pH of 7.0, equal concentrations of dissolved H₂S and HS⁻ exist at equilibrium, while at a pH of 8.0, only about 10 percent of the dissolved sulfide exists as H₂S. Since dissolved H₂S is the only form which can be released to the atmosphere, it follows that increasing the pH would reduce odors and corrosion by maintaining the dissolved sulfides in the HS⁻ form.

Odor Control in Beet Sugar Operations

While it is a general practice to treat odor as a nuisance, several states are addressing the legal aspects of action taken by public or private citizens annoyed by odor. There are several point-sources of odor in the sugar process that are outlined below:

| Source | Odor Quality |
|---------------------------|--|
| Flume | Offensive - Rotten Eggs - H ₂ S |
| Pulp Dryer | Burnt Molasses |
| Diffuser Vent | Offensive-cooked cabbage |
| Vacuum Pan Vent | Very Offensive |
| 1 st Carb Tank | Offensive-cooked cabbage |
| Thin Juice Vent | Offensive-cooked cabbage |
| 2 nd Carb Tank | Offensive-cooked cabbage |
| Evaporators | Offensive-cooked cabbage |
| Diffuser Ammonia | Offensive-cooked cabbage |
| Thin Juice Boiler | Offensive-cooked cabbage |

| | |
|-------------------------------|--|
| White Pan | Offensive – Ammonia |
| Boiler | Sulfur |
| Lime Kiln | Weak – cement type |
| Lagoon / Wastewater Treatment | Offensive - Rotten Eggs - H ₂ S |
| Wet Scrubbers | Offensive – Ammonia |

Specific Odor Source Discussion and Control

Flume Water

Flume water has the problem of continuous inoculation of bacteria from soils and the lack of water loss from constant recirculation. Bacteria levels grow and in anaerobic conditions, significant amounts of H₂S develop.

To counteract these problems, high amounts of lime are added to the water to raise the pH to 10-12. This not only controls the microbiological population, but also keeps any H₂S in solution and out of the ambient air.

However, the high lime use has its costs: because of the high calcium levels and scaling conditions in the water, pumps and piping begin to clog and foul with scale. The high pH water causes an enormous amount of foaming so more foam control agents need to be applied. Ammonia-type odors are given off also at these high pH ranges. All of this adds to higher maintenance and operational costs.

Solution: Allow the pH to drop to a range of (8.5-9.0)- by reducing the amount of lime being fed. Add H₂S scavenging agents to control the H₂S levels along with biomodifiers to prevent the formation of H₂S. This will keep the odor causing agents in control while reducing the problem associated with high pH control. Maintenance cost can be reduced along with reducing the need for defoamers.

Wastewater Lagoon

Lagoon systems are used as holding ponds and often as a make-up source for the flume. By their nature, anaerobic conditions form and large amounts of H₂S are developed causing the classic rotten-egg odor problem. Solutions to this problem are similar to the flume water control systems – scavenge the hydrogen sulfide and prevent further formation through biomodifiers.

Scrubbers

Scrubbers are installed to “wash” the production air and air from various plant processes. Because they are not completely efficient, offensive odors are still produced and are emitted. Neutralizing agents can be fed into the post-scrubber air stream that counteracts with the offensive agents in the air and thereby reducing the odor problem.

Case History

Background

Due to increased urbanization, an increase in scrutiny was placed on the Sugar Mill for controlling odors. There arose a clash between some newer manufacturing facilities and the established Sugar Mill. To - be a good neighbor, the Sugar Plant put together a plan to identify and reduce odors in several areas of the plant. BetzDearborn's Odor Control Technology was a significant part of the plan.

Challenge

The first problem was to identify the source of the odors. The beet flume water system was recognized as a major odor source as well as the scrubber stack plume.

The second challenge was to specifically identify the odor so that the proper odor control program can be recommended.

Hydrogen Sulfide (H_2S) was quickly identified as a significant odor agent in the flume water. The average H_2S level in the flume water system was approximately 5 ppm. However, the hydrogen sulfide level in the plant air around the flume exceeded 40 ppm at times. This caused a concern from employee safety standpoint due to potentially high H_2S gas levels in the plant mostly from the flume water system.

Traditionally, lime was added to the flume water as a way of controlling odor. The pH was elevated to 10-12. Problems associated with high amounts of lime included pipe and pump scaling as well as the need to feed high amounts of a chemical-defoaming agent. Higher maintenance costs were also associated with this need for lime addition.

Solution

The BetzDearborn team recommended the treatment strategy of ProSweet OC 2521, the enzyme product to modify the anaerobic organism's product of hydrogen sulfide, and OC 2542, and the H_2S scavenger.

Initial feed-rates:

OC2521

- ✓ 25 ppm day 1
- ✓ 10 ppm day 2
- ✓ 5 ppm there after as maintenance dose

OC2542

- ✓ 7 ppm per ppm of H_2S

Various injection points for the program were evaluated. In addition, extensive water analysis was performed including pH, COD, H_2S , and the monitoring of microbiological activity. Hydrogen sulfide analysis and measurement was documented both in the bulk water system as well as in the air.

The pH was also allowed to drop. Lime feed was reduced to control the pH at just below 9.0.

To measure success and to monitor the program, various tools were used. The BetzDearborn BioScan ATP was used to measure microbiological activity, COD was testing in the flume water, and pH was monitored, as well as the H_2S levels in the water and in the air. Most importantly, the number and type of odor complaints were documented.

A misting program was initiated on the plant scrubber system. The products were fed in the scrubber plume based on a signal from an altimeter monitoring the wind direction.

Results

Odors were successfully controlled, both in the flume and on the scrubber. Complaints drastically reduced and the neighbors applauded the results. The plant was able to reduce the use of lime and antifoam for additional savings of \$158,472.

Other benefits to the plant include extending the time and use of the beet flume water from 50 to 90 days before dumping. This amounted to a savings in power, chemicals, and manpower for additional \$22,000 in savings.

Because the plant water was controlled at a lower pH, the bacteria consumed the BOD in the water more efficiently. By the end of the campaign, they found that they discharged 1.8 million pounds less of BOD to the city's POTW along with 6 million gallons less water. This equated to more savings of \$54,000 in sewer fees. A grand total savings of \$245,000.

