control of odors in the sugar beet processing industry

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introduction

Driven by changes in the Clean Air Act Amendment (CAA), the need for improved odor control may soon exist in many industrial facilities. Under this act, regulatory bodies will be forcing industrial plants, such as paper mills, refineries, steel mills and food processors, to improve the quality of the 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 when people are working in areas where odors can overcome them.
• Productivity can be impacted in areas of a facility where objectionable odors exist due to employee neglect.
• Production can be affected by odors and odor producing conditions that degrade 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 involves hydrogen sulfide (H₂S) generation and evolution. Although the CAAA does not explicitly regulate hydrogen sulfide, it does call for the elimination of odors with its offensive and toxic characteristics.

The potential for hydrogen sulfide emissions is especially strong in the food industry, in part because of its high levels of organic waste materials. As a result, there are opportunities for odor control technologies in many food processing applications, including:

• Sugar refining
• Meat processing
• Rendering plants
• Potato processing
• General food processing wastewater treatment systems

odor control methods

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 a considerable investment in capital equipment. In many industrial applications, such as papermaking, oil refining and steel production, the odor control methods used include incineration, carbon adsorption, wet scrubbing, electrostatic precipitation, source modification and odor masking. 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 an odor control program in place immediately 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 because of fines and community complaints.

**hydrogen sulfide background**

H$_2$S 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 bio-chemical reduction of inorganic sulfur compounds. Under anaerobic conditions, sulfate reducing bacteria use sulfate as an oxygen source to metabolize organics in the waste stream:

$$\text{SO}_4^- + 2\text{C} + \text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S}$$

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 H$_2$S formation generally favor the production of other malodorous organic compounds such as mercaptans, thiophenol, and thiocresol. Investigations of the conditions favoring H$_2$S formation can also help to quantify the potential for odor generation from other compounds. Thus, solving H$_2$S odor problems can often solve other odor problems as well.

H$_2$S dissolves in water and dissociates according to the following reactions:

$$\text{H}_2\text{S} \rightarrow \text{HS}^- + \text{H}^+$$
$$\text{HS}^- \rightarrow \text{S}^- + \text{H}^+$$

Figures 1a and 1b show the distribution of sulfide species as a function of pH. The relative H$_2$S concentration increases with decreasing pH. At a pH of 7.0, H$_2$S represents 50% of the dissolved sulfides present; while at a pH of 6.0, over 90% of the dissolved sulfides is in the form of H$_2$S. If part of the dissolved H$_2$S escapes to the atmosphere, the remaining dissolved sulfide will be divided between H$_2$S and HS$^-$ in the same proportion as before because the equilibrium reestablishes itself almost instantly.
The distinction between the types of sulfide compounds is significant because only the H$_2$S can escape from and create odor, corrosion and health problems. It is important, therefore, to quantify the total and dissolved sulfides present and the pH level of the wastewater.

**health effects of H$_2$S**

H$_2$S is an acutely toxic gas. H$_2$S is heavier than air, colorless and has a characteristic rotten egg smell at low concentrations. But as the levels of H$_2$S 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 table 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 (Eight 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)

**preliminary monitoring program**

Normally, repeated odor complaints are the first indication 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.

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**other solutions**

Currently available commercial products provide four distinct categories of odor control technology:

- Organic scavenger
- Counteractant
- Biomodifier
- Masking Agent

**Organic Scavengers**- The organic scavengers are comprised of traditional primary amines as well as unique proprietary technologies. 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, H$_2$S concentration, desired H$_2$S 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 H$_2$S 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 reactivity with many malodorous sulfur compounds
- No pH change
- Easy to handle and feed
- No sludge generation

**Counteractants** - These are chemicals that interfere with the malodorous substance. The counteractant does not chemically react with it, 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 over 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 H$_2$S 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 feedrates are recommended initially, with decreasing rates as the system begins to acclimate. Feedrates are often reduced until optimum maintenance dosages are established.

**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 H$_2$S according to the following reactions:

\[
\text{pH} < 8.5: \quad H_2O_2 + H_2S \rightarrow S + 2H_2O \quad \text{pH} > 8.5:
\]

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

At pH < 8.5, the stoichiometric H$_2$O requirement is 1g H$_2$O$_2$ / 1g H$_2$S. In practice, a greater weight ratio may be required because hydrogen peroxide cannot 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 H$_2$S 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.

**Table 1: Odor Sources and Quality**

\[
\text{Fe}^{++} + \text{HS}^- \rightarrow \text{FeS} + \text{H}^+
\]

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:

\[
\text{Fe}^{++} + 2\text{Fe}^{+++} + 4\text{HS}^- \rightarrow 3\text{FeS}_4 + 4\text{H}^+
\]
strong alkalies

Increasing the pH reduces the proportion of dissolved \( H_2S \) in the \( H_2S-HS^- \) equilibrium. For example, at a pH of 7.0, equal concentrations of dissolved \( H_2S \) and \( HS^- \) exist at equilibrium, while at a pH of 8.0, only about 10 percent of the dissolved sulfide exists as \( H_2S \). Since dissolved \( H_2S \) 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 \( H_2S^- \) 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 in Table 1.

**Flume Water** - Flume water is a problem because there is continuous bacterial inoculation from soils and a lack of water loss due to constant recirculation. Bacteria levels grow and, in anaerobic conditions, significant amounts of \( H_2S \) develop.

To counteract these conditions, high amounts of lime are added to the water to raise the pH level from 10 to 12. This not only controls the microbiological population, but also keeps any \( H_2S \) 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 at these high pH ranges. All of this adds up to higher maintenance and operational costs.

The solution is to allow the pH to drop to a range of 8.5 to 9.0 by reducing the amount of lime being fed. Adding \( H_2S \) scavenging agents to control the \( H_2S \) levels along with biomodifiers to prevent the formation of \( H_2S \) will keep the odor causing agents in control while minimizing the problem associated with high pH control. Maintenance costs can be reduced along with the need for defoamers.

**Table 1: Odor Sources and Quality**

<table>
<thead>
<tr>
<th>Source</th>
<th>Odor Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flume</td>
<td>Offensive - rotten eggs - ( H_2S )</td>
</tr>
<tr>
<td>Pulp Dryer</td>
<td>Burnt molasses</td>
</tr>
<tr>
<td>Diffuser Vent</td>
<td>Offensive - cooked cabbage</td>
</tr>
<tr>
<td>Vacuum Pan Vent</td>
<td>Very offensive</td>
</tr>
<tr>
<td>1st Carb Tank</td>
<td>Offensive - cooked cabbage</td>
</tr>
<tr>
<td>Thin Juice Vent</td>
<td>Offensive - cooked cabbage</td>
</tr>
<tr>
<td>2nd Carb Tank</td>
<td>Offensive - cooked cabbage</td>
</tr>
<tr>
<td>Evaporators</td>
<td>Offensive - cooked cabbage</td>
</tr>
<tr>
<td>Diffuser Ammonia</td>
<td>Offensive - cooked cabbage</td>
</tr>
<tr>
<td>Thin Juice Boiler</td>
<td>Offensive - cooked cabbage</td>
</tr>
<tr>
<td>White Pan</td>
<td>Offensive - ammonia</td>
</tr>
<tr>
<td>Boiler</td>
<td>Sulfur</td>
</tr>
<tr>
<td>Lime Kiln</td>
<td>Weak - cement type</td>
</tr>
<tr>
<td>Lagoon / Wastewater Treatment</td>
<td>Offensive - rotten eggs - ( H_2S )</td>
</tr>
<tr>
<td>Wet Scrubbers</td>
<td>Offensive – ammonia</td>
</tr>
</tbody>
</table>

**Wastewater Lagoon** - Lagoon systems are used as holding ponds and often as a makeup source for the flume. By their nature, anaerobic conditions form and large amounts of \( H_2S \) 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 the use of biomodifiers.

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

**case history**

**Background** - Due to increased urbanization, greater attention was given to the control of odors at this beet sugar mill. 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. SUEZ’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 could be recommended.

Hydrogen sulfide (H$_2$S) was quickly identified as a significant odor agent in the flume water. The average H$_2$S level in the flume water system was approximately 5 ppm (mg/L). However, the hydrogen sulfide level in the plant air around the flume exceeded 40 ppm (mg/L) at times. This caused a concern from an employee safety standpoint due to potentially high H$_2$S 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 to 12. Problems associated with high amounts of lime included pipe and pump scaling as well as the need to feed high amounts of lime.

**Solution** - The SUEZ team recommended a treatment strategy that utilized ProSweet* OC 2521, an enzyme product that modified the anaerobic organism’s production of hydrogen sulfide, and OC 2542, an effective H$_2$S scavenger.

Initial feedrates were:

ProSweet OC2521
- 25 ppm (mg/L) day 1
- 10 ppm (mg/L) day 2
- 5 ppm (mg/L) thereafter as maintenance dose

ProSweet OC2542
- 7 ppm (mg/L) per ppm (mg/L) of H$_2$S

Various injection points for the program were evaluated. In addition, extensive water analysis was performed including pH, COD, H$_2$S and the monitoring of microbiological activity. Hydrogen sulfide analysis and measurement was documented both in the bulk water system and 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 results and monitor the program, various tools were used. The BIOSCAN* ATP monitor was used to measure microbiological activity, COD was tested in the flume water, pH was monitored, and H$_2$S levels in the water and in the air were determined (Figures 3 and 4). Most importantly, the number and type of odor complaints were documented.

An identical program was initiated on the plant scrubber system. The treatment products were fed into the scrubber plume based on a signal from an altimeter monitoring wind direction.

![Figure 3: Flume water hydrogen sulfide levels](image1.png)

![Figure 4: Average levels of hydrogen sulfide in the air](image2.png)
results

Odors were successfully controlled in both the flume and the scrubber. Complaints were drastically reduced and neighbors in the community applauded the results. The plant was able to reduce the use of line and antifoam for saving of US$158,472.

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

Because the plant water was controlled at a lower pH, bacteria consumed the BOD in the water more efficiently. By the end of the campaign, the sugar will had found that they discharged 1.8 million pounds (816,500 kg) less of BOD to the city’s POTW along with 6 million gallons (2.7 million kg) less water. This equated to an additional savings of US$54,000 in sewer fees. The total net annual savings from all of these improvements was US$245,000.