Controlling anaerobic bacteria to improve product quality and mill safety

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Mills can prevent the buildup of explosive gases generated by anaerobic bacteria through a program of aeration, ventilation, and treatment with biocides.

In July 1987, workers in a Louisiana paper mill were welding a pipe on an unvented white-water storage chest when an explosion occurred. Investigators attributed the event to hydrogen gas generated by anaerobic bacteria. A year later, an explosion in Ontario, Canada, killed two welders who were installing a safety rail at the top of a white-water tank. The presence of hydrogen gas generated by anaerobic bacteria proved to be the cause of this accident, too.

Papermaking systems provide a moist, warm environment that is rich in nutrients for bacterial growth. Most bacteria produce gas when they metabolize food into energy. Aerobic bacteria produce carbon dioxide. Anaerobic bacteria can produce hydrogen, hydrogen sulfide, methane, or volatile fatty acids.

Uncontrolled growth of bacterial populations typically leads to production of slime, odors, or life-threatening gases. The generated gases do not have to be a concern if the mill operators understand the types of organisms involved, know their survival requirements, develop a control program, and monitor the bacterial populations and the gases they produce.

Most areas of a papermaking process do not support the growth of anaerobic bacteria. These organisms require an environment of reduced oxygen or no atmospheric oxygen. The high turnover in chests and the movement of stock and water limit the opportunity for growth of anaerobic bacteria. However, industry trends such as alkaline papermaking and mill closure will increase the opportunity for production of anaerobic bacteria. In mills converting to an alkaline process, slime problems are intensified because of increased bacterial growth in a more favorable pH environment (*1*).

More mills are recycling large volumes of process water. They do this because of the increasing emphasis on environmental protection as well as the potential profit from reclamation of fiber and additives. Many of these mills are experiencing an increase in the growth of anaerobic bacteria. An investigation of microorganisms in both open and closed mill water systems showed that the anaerobic colony counts in entirely closed water systems exceeded the aerobic counts. The authors concluded that system closure is accompanied by increased populations of anaerobic bacteria (*2*).

The primary problems caused by these bacteria are increased corrosion (from the hydrogen sulfide and organic acids formed), diminished product quality (because of spoilage of additives and stock from the presence of volatile fatty acids), and production of explosive/flammable gas in chests for recycled white water. All of these problems are caused by the metabolic end products generated by the bacteria.

Many species produce gases, such as hydrogen or methane, which are explosive once concentrated and ignited. Other anaerobic bacteria produce hydrogen sulfide, which not only corrodes machinery but also can be lethal when inhaled. Still other anaerobic bacteria produce volatile fatty acids whose odor contributes to additive spoilage and loss of product quality.

No single bacterial species produces each gas or volatile fatty acid, although many bacterial species can metabolize the same end products. As the environment, nutrient concentration, and population mix change, many bacteria adapt by metabolizing more than one end product. The generated end products can, in turn, be metabolized by other bacteria. Consequently, predicting which gas will dominate a system at a particular time is sometimes difficult.

In this article, the production of explosive/flammable gas and volatile fatty acids is discussed as separate issues. Methods of monitoring and controlling the production of these materials are also presented. First, however, we address the topic of anaerobic metabolism.

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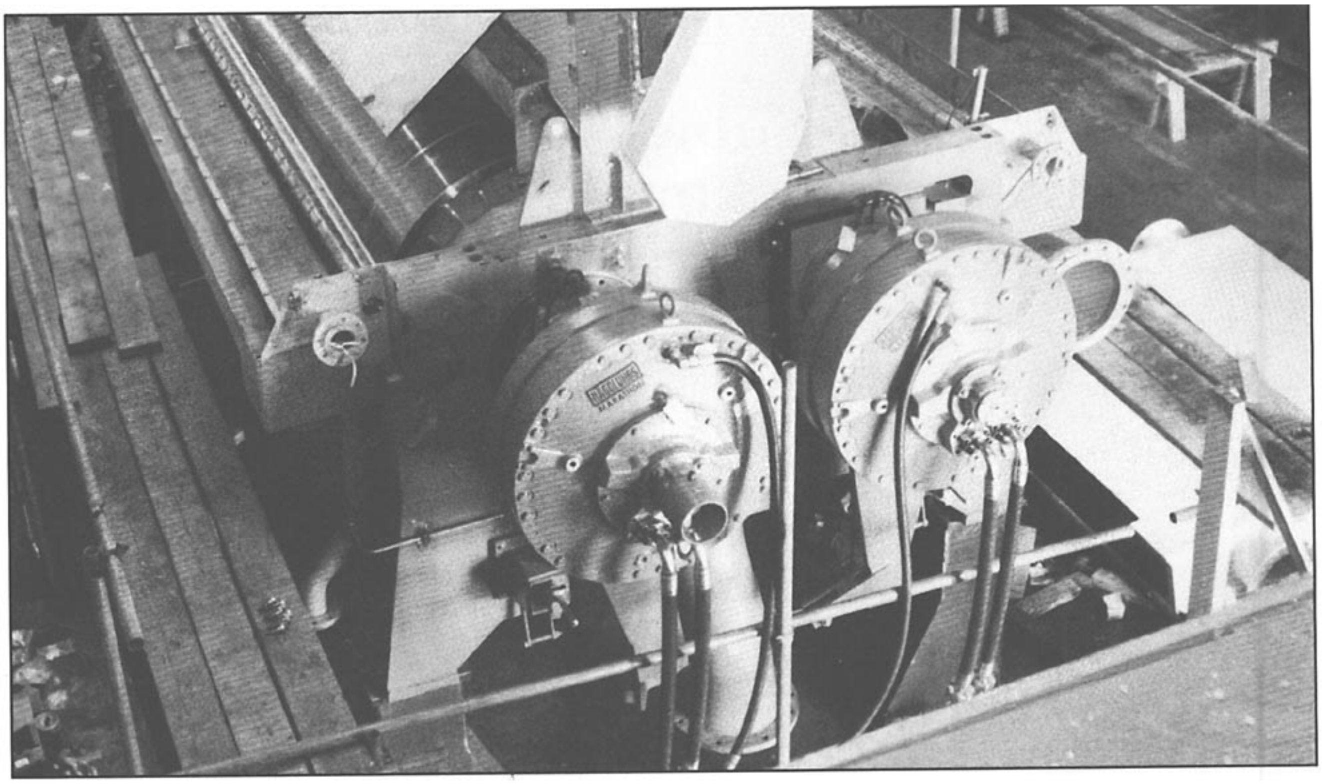
Gas build-up in the papermaking system can be controlled or prevented with aeration, ventilation, or biocide treatment.



Anaerobic metabolism

Bacteria derive energy from various compounds. They metabolize these compounds using aerobic respiration, anaerobic respiration, or anaerobic fermentation.

An aerobic bacterium uses oxygen to help extract maximum energy from a compound (such as glucose) and stores this energy as adenosine triphosphate (ATP). Using these ideal conditions, little acid is produced. Instead, carbon dioxide and water are produced and a maximum yield of energy is acquired.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}$$

In contrast, anaerobic bacteria liberate energy from molecules using anaerobic respiration. Inorganic compounds such as nitrate, sulfate, and carbon dioxide can be electron acceptors. The end products of anaerobic respiration are usually nitrogen, oxides of nitrogen, hydrogen sulfide, or methane.

For example, some species of anaerobic bacteria break down large organic materials into small molecules such as acetate, hydrogen, and methane. Other species convert sulfates to hydrogen sulfide. Yet other bacteria can use these gases, which are dissolved in water, and oxidize hydrogen sulfide back to sulfates or use the hydrogen and methane. In this way, materials are continually recycled in nature. From this, one can readily understand why anaerobic bacteria would be expected to develop in stagnant stock or a white-water chest, which are not balanced environments.

Explosive/flammable gas production

The anaerobic bacteria that are discussed in this section produce three separate gases: hydrogen, hydrogen sulfide, and methane. Each gas is produced by more than one bacterial genus. In addition, depending upon the available nutrients, some of these microbes can produce more than one type of gas.

Hydrogen producers

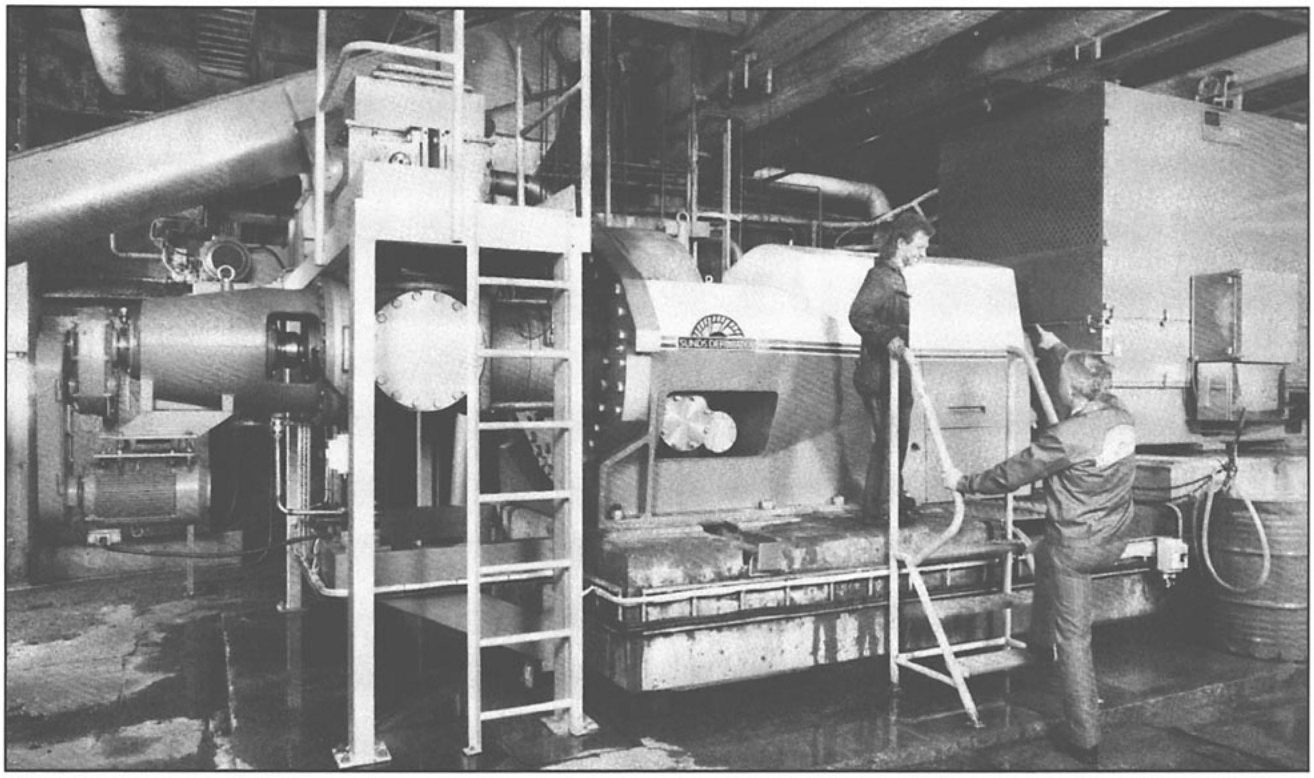
Many bacteria can produce hydrogen gas in an anaerobic environment. Hydrogen evolution is not unique to any particular bacterial species or genus. Genera of bacteria that can produce hydrogen include *Clostridium spp.*, *Eubacterium spp.*, and *Fusobacterium spp.*

Hydrogen sulfide producers

In anaerobic environments where the sediment or deposit contains sufficient amounts of dissolved sulfate, sulfate-reducing bacteria will use sulfate ions as their terminal electron acceptors to produce hydrogen sulfide. The sulfite ion acts like oxygen in conventional aerobic respiration. In the absence of sulfates, these bacteria can also release hydrogen.

Although hydrogen sulfide burns readily in an excess of air, it is most often identified by its "rotten egg" odor. Since hydrogen sulfide is denser than air, it usually stays in the lower levels of a tank.

All sulfate-reducing bacteria are strict anaerobes. None grow using oxygen as an electron acceptor. Oxygen always inhibits the growth of sulfate-reducing bacteria. Genera most often identified with the ability to produce hydrogen sulfide include *Desulfovibrio spp.*, *Desulfotomaculum spp.*, Anaerobic bacterial growth in closed systems, common in newer mills, can lead to the increased chance of gas accumulation and explosions.



and *Desulfomonas spp.*

Methane producers

Methane is produced by methanogenic bacteria, a diverse group of strict anaerobes. They rely on hydrogen generated by hydrogen-producing anaerobic bacteria. Methane gas is produced from oxidized hydrogen and reduced carbon dioxide.

These bacteria do not use complex organic compounds. Instead, neighboring bacteria such as *Clostridium spp.* and *Propionibacterium spp.* produce the organic acids and hydrogen needed by methanogenic bacteria as the components for energy derivation.

Since methane is poorly soluble in water and only about half as dense as air, it is easily released into the atmosphere as "swamp gas." When combined with oxygen, this mixture is highly explosive.

Methanogens are extremely sensitive to oxygen, and special techniques are required to culture them in the laboratory. Even a brief exposure to oxygen can quickly kill them. There are many methanogenic bacteria, including the genera *Methanobacterium spp.*, *Methanosarcina spp.*, and *Methanococcus spp.*

Volatile fatty acid production

Anaerobic bacteria that produce volatile fatty acids (such as acetic acid) reduce product quality, a serious concern in closed water systems (*3*). During anaerobic fermentation, most of the energy within the substrate molecule is not used. Minimal energy is stored as ATP. These bacteria convert a carbohydrate substrate to pyruvic acid, which can be metabolized to volatile fatty acids. Anaerobic bacteria are not capable of breaking these end products down further, resulting in a buildup of acid.

Some bacteria grow fermentatively even in aerobic conditions and produce organic acids that decrease the pH. However, anaerobic bacteria such as *Propionibacterium spp.*, *Clostridium spp.*, and *Fusobacterium spp.* can be problematic organisms in paper mills. High concentrations of microbial fermentation products such as volatile fatty acids in the process water and sludge are due to populations of facultative, anaerobic bacteria.

The volatile fatty acid fermentation products that most frequently cause odor-related quality problems are acetic acid (C_2), propionic acid (C_3), butyric acid (C_4), and valeric acid (C_5). Each has a characteristic odor and can be identified by gas chromatography (*1*).

A representative species of anaerobic bacteria prevalent in papermaking systems is *Clostridium sporogenes*. Butyric acid is one of the fermentation products *C. sporogenes* can manufacture in large quantities. This organic volatile fatty acid has a rancid butter odor that is detectable in process water and board samples.

This spore-forming bacterium can be found in soil, water, broke, additives, recycled fiber, and recycled sludge. In its vegetative phase, *C. sporogenes* is a unicellular rod-shaped bacterium similar in appearance to hundreds of bacterial species. Its thick spore coat can resist temperature extremes, desiccation, radiation, and exposure to many toxic chemicals. Since *C. sporogenes* can survive the dryer section of a paper machine, it can show up in the finished sheet, where it is transferred back to the process by way of the broke.

Prevention and control

There are several effective methods to prevent or control the buildup of volatile gas in the papermaking system. These methods include:

- Aeration by agitation or installing an air line
- Chest ventilation
- Biocide treatment.

The safety margin can be increased by combining the various techniques and incorporating a biocide treatment.

The explosions described at the beginning of this article occurred in closed, unvented white-water chests that had been stagnant. These operating conditions provided an environment where anaerobic bacteria could thrive. Control of these conditions and better chest designs will prevent future mishaps.

Aeration by agitation or installing an air line

When stock and white water circulate throughout the process, air has ample opportunity to mix with water. This alone can limit anaerobic bacterial populations. However, during a mill shutdown, aerobic bacteria quickly deplete the oxygen level in the white water and provide the anaerobic environment necessary to stimulate the growth of volatile-gas-producing microbes. The white-water oxygen content can be replenished by agitating the water in the chest or by aerating the water with an air line. While this control method is effective, power failures or a breakdown of aeration equipment must be considered. If the water is allowed to stagnate, oxygen will be consumed quickly and volatile-gas producers will thrive.

These procedures are not appropriate for stock chests because aeration will encourage the growth of aerobic bacteria. If stock is held for more than eight hours, aerobic populations will increase, providing a large inoculum to the paper system on startup. Stock chests often require a stock-preservation biocide to control aerobic populations during a mill outage.

Chest ventilation

Ventilation is a natural means of exhausting the light gases in the tank head space. The density differential between atmospheric air and hydrogen or methane provides the force for natural ventilation. A straight vent extending above the top of the chest and an air inlet (such as an overflow pipe) will ventilate the head space.

Although chest ventilation will not stop the generation of volatile gases by anaerobic bacteria, it will minimize the buildup of these gases and limit their concentrations to below the explosive threshold. Many chests are vented or have a manhole that can be opened and screened whenever the chest stagnates. Ideally, the chest should be permanently vented and periodically checked to assure the vent is not plugged. This is especially important during shutdown.

Precautionary safety procedures are typically followed during a mill shutdown. Enclosed stock and water areas, including the headbox, are tagged out and opened to allow fresh air to flush the gases from the container. A variation of this method is to provide forced ventilation by installing sparkless fans and explosion-proof motors to increase air-supply movement through the tank or chest (*4*).

Biocide treatment

Treatment with persistent, proprietary biocides can prevent stock degradation or additive spoilage during a mill shutdown. Such treatment kills vegetative forms of bacteria, prevents spores from becoming active, and minimizes the growth rate of bacteria over the shutdown period. Because shutdowns last for an unknown amount of time and sterilizing the system is difficult, oxidizing biocides (like chlorine) are not appropriate. They lack the necessary persistence.

Before shutdown, tests should be conducted to determine the biocide concentrations needed to control bacterial growth during outage. Although stock- and additive-preservation programs are not being used to prevent the buildup of flammable gas from anaerobic activity, a small amount of persistent biocide can provide an extra safety margin.

Draining a chest creates a large head space where gases can accumulate to dangerous levels. Even a few inches of water, stock, or sludge in the tank bottom will support the growth of large populations of anaerobic bacteria that are capable of generating an explosive concentration of gas. The amount of biocide needed to treat these few gallons of water costs only a few dollars.

Biocide treatment also suppresses production of hydrogen sulfide gas, which burns readily in an excess of air and is toxic by inhalation. Active aeration minimizes the growth of the organisms that can produce hydrogen sulfide. However, ventilation does not remove hydrogen sulfide from a stagnant chest, since the gas is denser than air and generally stays in the lower levels of a tank. Before checking gas levels in a chest, the surface tension of the stock or water should be broken to release any hydrogen sulfide below the surface. If the chest cannot be totally drained of water, then a one-time application of persistent biocide will establish control.

Monitoring methods

Mill or product odors, additive-preservation problems, pH swings, and corrosion should be routinely profiled, since they can signal the presence of large populations of anaerobic or facultative bacteria. Use the same serial-dilution techniques as with aerobic bacteria and monitor with an appropriate culture medium.

Culture media

Sulfate-reducing bacteria are easily cultured using National Canners media. Colonies of sulfate-reducing bacteria appear as dark spots in the light-colored medium. (The generated hydrogen sulfide reacts with iron and forms black iron sulfide.) The colony counts can be used to establish trends and monitor changes in populations.

General-purpose media that are used with an anaerobic chamber (Gas-Pak) can also support the growth of many (but not all) anaerobic and facultative species. Again, colony counts are used to establish trends.

Handling and shipping

Since many strains of anaerobic bacteria will not survive exposure to even minute amounts of oxygen, sample handling is critical. Oxygen is easily incorporated into the sample during collection and shipping, resulting in an inaccurate analysis of the sample.

If the bacteria are in their vegetative or growing stage, the sample must remain anaerobic during shipment. However, if the bacteria have formed spores in the sample before collection, the laboratory can recover and culture the spores.

Laboratory analysis of deposits usually takes 10-14 working days. The sample is cultured, isolated, and recultured under a variety of environmental and nutritive conditions. Species identification is not necessary, since the control measures for all anaerobes are similar.

Conclusion

The production of flammable gases is controlled by inhibiting the growth of anaerobic bacteria. Most of these anaerobic microbes are common and have always been present in papermaking systems. Control methods such as mechanical aeration of the water, ventilation, and biocide treatment will reduce populations of anaerobic bacteria to manageable levels.□

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