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Controlling Microbiological Growth and Foul Odors in Pulp & Paper Industry

Abstract: Papermaking systems provide a moist, warm environment that is rich in nutrients for microbiological growth. High nutrient levels and increased levels of contamination associated with the incoming recycled fibre and reduction in water reuse can lead to increased microbiological growth. With the increasing usage of recycled fibers, there are additional high nutrient levels to the papermaking wetend. Recycled fibers often contains residual sizing, coating, starches, polymers, and adhesives – components that are rich of nutrients. This recycled fiber is also contaminated with a higher loading of microorganisms than is typical with virgin pulp.

The biofilm generated by aerobic bacteria can form massive slime deposits that can be an inch or more in thickness. When these deposits break loose and fall into the paper furnish, they result in end product imperfections such as slime holes and defects or even slime breaks. When this occurs, the paper with the defects must be used as broke and re-pulped or downgraded. The rapid growth of aerobic organisms will also deplete the oxygen content of the stock and water system. This low oxygen content creates a reductive environment which favours the growth of anaerobic bacteria. Anaerobic bacteria can produce hydrogen, hydrogen sulfide, methane, or volatile fatty acids. Reduction in fresh water usage and recycling the process water will also cause changes in various physical and chemical parameters and microorganism populations in wetend. There will



be changes in microorganisms related problems including generation of odorous chemicals, microbiological influenced corrosion (MIC), and faster slime buildups in paper machine.

When the system turns to become more anaerobic, most biocide programs failed to perform well. This is mainly due to the inability of these biocides to deal with a very high level of contamination in a reductive environment. This paper reveals the changes in microorganisms population in wetend as the impact of furnish change and higher water closure, together with the mechanisms and problems caused by the change. Emphasis was made on the problems related to generation of foul odors. Possible solutions to the problems are also provided.

Key Words: Slime, anaerobic bacteria, Odors, VFA, H2S, WWTP, Biocide, Odor Neutralizer, Sulphide Neutralizer, MIC, Filamentous bacteria, biofilm, pink slime, Clostridia, SRB.

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Introduction

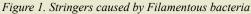
Microbial Slime Outbreaks: Papermaking wetend is considered as nutrient rich environment. Together with warm temperature and long retention time, this creates an ideal environment to support microbiological growth. Many additives in papermaking can be consumed by bacteria and fungi and allow rapid expansion of the population. The fast growth of microorganisms overload the wetend with mass of microbial biofilm that cause serious problems to machine runnability and sheet quality such as slime breaks, slime holes, downgraded papers, as well as higher wash-ups and unscheduled shuts.

Part of the microbial slime problem is the overgrowth of filamentous bacteria (1). This is a collective name for group of bacteria which has filament-like shapes. Their body is made of array of cells grouped together in a long filament structure and protected by a thick layer that protect them from extreme environmental conditions. This protective layer makes filamentous bacteria less sensitive to biocide attacks hence difficult to kill. Many of these filamentous bacteria are also active biofilm producer. The overgrowth of filamentous bacteria creates tangled web of filamentous mass covered with sticky layers of biofilm. They easily trap / captures other papermaking materials in wetend, and ended up as massive deposit all over the paper machine surfaces. Some of this filamentous bacteria develop yellowish-pinkish- orange pigments and the slime produced commonly known as pink slime

Results and Discussion

Figs.1 and 2. Pictures of filamentous bacteria and slime defects





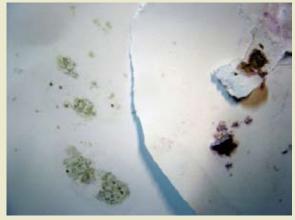


Figure 2. Slime spots in finish paper / board. Changed to purple color with slime test reagent

Overgrowth of Anaerobic Bacteria

Microorganisms are frequently grouped according to their ability or inability to grow in an environment containing oxygen. Aerobic organisms readily grow in such an environment while anaerobic organisms develop most favorably in an atmosphere in which the dissolved oxygen approaches zero. In Oxygen rich environment such as in highly agitated stock and white water, aerobic bacteria flourishes. Slime outbreak in paper machine is strongly related to overgrowth of aerobic bacteria.

The overgrowth of aerobic bacteria can also deplete the oxygen content of the stock and water system, especially in locations where agitation or penetration of oxygen from air is low. As the oxygen disappear, the condition is becoming more favorable for growth of anaerobic bacteria. As mill is closing their water circuit, Water temperature often increases while dissolved oxygen content in water decreases. Lower concentrations of dissolved oxygen creates more favorable growth condition for anaerobic bacteria. Various problems are related to the overgrowth

bacteria. In some cases, the odor problem also happens in finished paper and paperboard affecting finished product quality.

Many of the anaerobic Clostridia species produce cellulase enzymes. Cellulases degrade the cellulose polymers found as structural components of plant materials such as wood. If furnish is exposed to these cellulases, especially for extended periods of time, the structural integrity of the wood fibers may be sacrificed due to enzymatic activity. Loss of this structural integrity can lead to a decrease in sheet strength. Anaerobic colonization of broke towers has also been implicated with decreases in sheet brightness.

In addition to the factors mentioned above, the use of sulphite bleaching when recycling de-inked fibers,



Figure 3. Slime inside shower bar rich of iron sulfide depositindication of anaerobic growth

neutralizes the function of most biocide chemistries. These biocides are affected by the presence of reducing agents and can not function properly when sulphite bleaching is used. Therefore, a different biocide programme strategy is required when dealing with deinked pulp furnish.

Fig. 3 shows corrosion inside the shower bar with iron sulphide deposit with indication of anaerobic growth and Fig. 4 exhibits the pitting corrosion caused by microbiological attack.

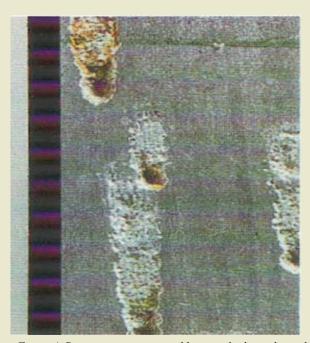


Figure 4. Pitting corrosion caused by microbiological attack

Mechanisms of Microbiological related Odors

Anaerobic degradation of organic materials leads to the intermediate formation of Hydrogen sulfide and volatile fatty acids (VFA) - primarily butyrate, valerate, propionate and acetate. Volatile fatty acids release pungent, unpleasant odors both in the process and in the finish products. The VFA related odors have been reported (2) in various grades of paper / board / tissue and cause very serious problems as the products are being rejected by customers or end users.

The chemical makeup and physical properties of many of paper additives form an environment conducive for microbial growth. Microbial spoilage can change the properties of the additives or cause physical or chemical changes that are detrimental to their use in paper making. Starch degradation will give you reduced strength, loss of brightness after the size press or in coatings (due to reducing sugars, which cause the starch to turn brownish), as well as a strong sour odor. Protein degradation in a coating are the malodors and color changes produced via microbial byproducts.

Water system closure has a profound influence on odor problems. Chemicals can cycle up in the process water, where years ago they were flushed out and did not cause problems. On the plus side costly additives and fines are retained, energy is conserved and water treatment costs are reduced. On the minus side, we find increased problems with odors.

Figure. 5 schematises the VFA as an intermediate in anaerobic degradation process

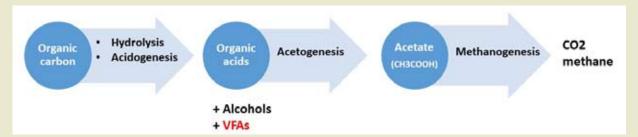


Figure 5. VFA as an intermediate in anaerobic degradation process

As the result of microbiological activity in the secondary treatment, the clarified water from waste water treatment plant is rich of residual bacteria, Volatile Fatty Acids (VFA), and various bacterial extracellular enzymes. In fact, VFA is present in big amount as VFA is the intermediate chemistry for complete degradation of organic chemistry in the anaerobic process into methane. When the methanogenesis reaction is not present or not running completely in WWTP, the VFA

can not be converted into methane and will finally be accumulated in WWTP. This will cause strong VFA odor in WWTP area and the water discharged from WWTP will also carry strong smell and often cause complaints from the community live nearby the mill area. When the clarified water from WWTP is reused in the wetend process, the VFA will increase the potential of odor problem in wetend process as well as in finish products.

Controlling Microbiological related Odors

From microbiological point of view, there are several effective methods (2) to prevent or control the buildup of microbiological contamination in the paper machine and WWTP areas, which include improvement in mechanical treatment, paper machine housekeeping and operation, WWTP operation, and through chemical actions (biocides or odor neutralizer).

Mechanical Treatment

Preventing the odor problem requires implementation of root cause analysis to identify what led to the odors in the first place. If the odor has a microbiological basis, the logical first step is to reduce the environmental factors favoring the growth of the microbes. The effective way to reduce odour caused by microbial activity will be to avoid VFAs and H₂S being formed. They are formed only under anaerobic conditions. Without proper VFA mapping, it may be difficult to trace the origin of the VFAs and H₂S in the process. Available technology exists for monitoring by-products of the anaerobic activity.

To avoid VFA and H₂S production, adequate oxygen concentration in the system should be ensured. Good water circulation, direct aeration, and avoiding stagnant water are all actions that can easily be implemented. VFA and H₂S mix well in the process flows. When stock and white water circulate throughout the process or agitated properly, this will increase air penetration into water. Higher oxygen level in water will help to limit anaerobic

bacterial populations. It is therefore important to ensure sufficient agitation inside the chest to maintain good oxygen concentration in water. Arrays of white water chests with cascade (gravitational) alignment also help to increase oxygen concentration in water. Oversized chests / tanks are not ideal as this will establish dead flow areas hence boost the anaerobic growth in that particular chest (3).

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. Ventilation in area of high oxidant vapors is recommended as this will help to avoid unnecessary accumulation of this vapors and reduce vapor phase corrosion potentials in these areas.

Paper Machine Housekeeping and Operation

Implementing an effective machine cleaning or boil out is very crucial for the success of any microbiological control program. Old deposits must be removed before the next production cycle so they will not damage the paper machine runnability and quality of finish products. Old biofilm deposit also provides seed for the next production batch (4). We can expect that the accumulation of deposits will be faster when mill closed its water circuit. It should be noted that inhibition / removal of biofilm deposits will also contribute to generation of anaerobic activities as it create a barrier for oxygen penetration while diffusing inwards. This effect has been demonstrated in relatively thin films, less than 0.2 mm thick. Very often, mill only conduct shortloop boil out while the long loop boil out will be conducted occasionally once or twice a year. The cleaning / boil out program must be carefully designed to address the most troublesome deposit, executed effectively using a carefully selected chemical treatment, and monitored closely to ensure maximum impact.

During mill shutdown, aerobic bacteria quickly consume the oxygen level in the white water and provide low oxygen environment ideal for the growth of anaerobic bacteria. Agitating the water in the chest or by aerating the water with an air line can help to maintain the oxygen level. If the water is allowed to stagnate, oxygen will be consumed quickly and anaerobic bacteria will thrive. However, this is not a recommended practice for stock chest as aeration will encourage the growth of aerobic bacteria during long shutdown (more than eight) and providing high aerobic bacteria count on machine startup. Stock preservation biocide is more recommended to avoid high microorganisms growth during long machine shut.

Maintaining effective chest / tower operating level can also help to control microbiological growth. Keeping high level of stock means higher retention time available for bacteria to grow and multiply, changing this stock to become a bioreactor. Big stock towers have potentially poor mixing hence create stock channeling problem. The stock in the center flows faster than the stock on the side of the tower wall hence encourage fiber spoilage and slime accumulation. Once the stock level drop, the spoiled stock and slime accumulated on the side of the wall will also collapse and sending highly contaminated material to the process.

WWTP Operation

Control of foul odours in WWTP area can be achieved by optimizing the function of each process stage, review each operating and control procedures and make required corrections if necessary. The design parameters must be used for comparison purposes. If the problem persists, then changes of process design can also be considered.

Prevention, or a reduction in malodour formation may be achieved by preventing the anaerobic growth in the aerobic stages, minimizing retention in systems where there is no aeration, such as in holding tanks or rising-main sewers. Aerobic conditions can be maintained in some cases by the addition of air, oxygen, or oxidizing agent.

Reduction in the input of sulphate, or modifications to the treatment processes, in order to reduce the formation of sulphide in the treatment and handling of sludges. A reduction in sulphate concentration is unlikely to have a significant impact on sulphide formation in sewage or the malodours associated with septic sewage. Addition of biocides has been used to reduce the high contamination of Sulphate Reducing Bacteria (SRB) growth of sewer wall slimes while Sulphide neutralizers are used to degrade / convert H₂S into non smelly sulfur forms. Use of oxidizers can also be considered to oxidize Hydrogen sulphide and volatile organic sulphides in sewage or sludge when conditions become aerobic. This will help to prevent high load of smelly H₂S in aeration tanks and secondary clarifiers. Hydrogen sulphide may also be controlled by the addition of precipitants, such as iron or Zinc salts.

Biocide Treatment

Management of microbiological activity is very important in allowing the papermaker to succeed in controlling microbiological related odors (5). Biocide treatment need to change from traditionally deposit focus to the overall aspect of microbiological related problems including ones from anaerobic bacteria. Type of biocide actives used in the program may need to be changed as well and the monitoring program should include the monitoring of anaerobic growth. One of the major drawbacks in the use most biocides are their inability to perform satisfactorily when dealing with a very high load of contamination and the reducing environment commonly found in the production of recycled paper and board. Some biocides that worked well in papermaking with virgin pulps and open system may no longer be products of choice for recycled pulps or with higher water closure. Therefore, toxicant test for biocide selection should be conducted again to determine if the best products are being used for the current environment. In addition, due to the high

competition in recycled paper markets, some recycled grades can only afford the use of relatively low cost chemical programmes. Proper product selection tests should be conducted to identify the most cost effective microbiological control programme required to meet these different challenges.

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. For white water tanks and towers, the white-water oxygen content can be replenished by agitating the water in the chest or by aerating the water with an air line. However, this 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.

Odor Neutralizers

There are many other non-biocide chemical applications that can be used microbiological related odors. They can be divided into two main groups: vapor-phase technologies, used to control odorous compounds in the air or gas; and liquid-phase technologies, used to control odorous compounds in the liquid at the source itself.

Vapor-phase technologies typically are used in point-source applications to prevent the "leakage" of odorous air from stacks, vents, manways, access hatches or other areas. The discharge from the ventilation system is the only route for the odorous air to escape, therefore it must be treated. Vapor-phase systems are very effective at preventing fugitive emissions from the ventilated sources and preventing odor problems associated with those

sources. The chemical is mixed with water, pumped through pipes/hoses and delivered via nozzles or fans to areas affected by odor. After the solution droplets are dispersed into the air they neutralize odors on contact. The major advantage of atomization nozzle systems is the level of control they provide. Through various means of control, depending on system style and design, the volume of product dispersed can be regulated.

Liquid-phase technologies typically are used in water collection / storage / sewer / scrubber / condensate / cooling systems with high concentration of soluble, odorous agents. Wide range of chemicals can be chosen to selectively react and neutralize the targeted organic odors. This treatment is highly effective as it reacts directly and specifically with the odorous agents and added near the source itself. Neutralization of odorous chemicals in recycled water or condensate allows safe and convenient reuse of these waters for various purposes while In the scrubber system, wet-gas scrubbing can remove or change the chemical composition of odorous contaminants with contacts the gas with a liquid phase. The contaminant either reacts with or dissolves in the liquid and is removed in the liquid phase. Careful selection of scrubber liquors is needed to ensure effective odor removal and ease of operation. The Sulphide neutralizer product can also be used to recover the brightness of dark furnish (6) due to Sulphide generation by SRB, in addition to removal of rotten egg smell.

Fig. 6 indicates the mill operation for odour neutralization via spray on dryer section vapor going to stack / chimney and Fig.7 presents the odor neutralization via spray in effluent dry sludge collection room in paper mill.

Odorous gas concentration reduced by 50-60% after the application.

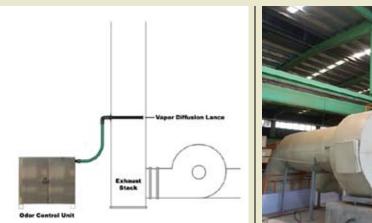




Figure 6. Example of odor neutralization via spray on dryer section vapor going to stack / chimney



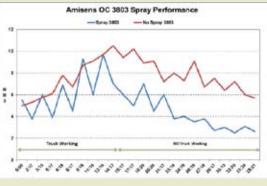


Figure 7. Odor neutralization via spray in effluent dry sludge collection room in paper mill. Odorous gas concentration reduced by 50-60% after the application

Case study on the use of Sulphide neutralizer product:

Mill experienced blackening of stock coming out from the stock towers, which is accompanied by foul smell. The presence of black contaminants lower the brightness of finish paper. The black furnish and foul smell is the results of Sulphate reducing bacteria growth. Mill agreed to trial AmiSense product addition into the stock storage tower with dosage variations, to look for the most cost effective treatment. After 30 mins contact time, change of brightness was observed, ORP and sulfides are measured, and hand sheets were made for brightness test. The trial result shows that the brightness stock improved At 300-500 ppm dosage of AmiSense product, and no rotten egg smell was detected.

The handset test shows that the dark furnish (marked as "0") gradually increases in brightness after addition of AmiSense product (Fig.8).



Figure 8. The handset test shows dark furnish (marked as "0") gradually increases in brightness after addition of AmiSense product.

Program Monitoring

For monitoring activities of anaerobic bacteria, test of Sulfate reducing bacteria and VFA are often used in the field (7). With increased water reuse the demand for antimicrobial oxidants and certain proprietary biocides may also increase. In many cases, it may be beneficial to use biocide active which works in reductive environment. Combination with oxidizing biocide can be applied to boost the system ORP and destroy the odor chemistries. Process or product odors, additive-preservation problems, pH swings, and corrosion could be routinely profiled, since they can signal the presence of large populations of anaerobic or facultative bacteria in the process. The use of portable gas testers and other test kit to measure concentration of odorous agents both in water phase and air phase should be considered.

Conclusion

Odour related problems in Pulp & Paper Industry is of raising importance. The odour may originate through many different sources. Some of the odour problems are microbiologically related, and becoming more severe with the higher use of recycled fibers and higher water reuse. However, by careful choice of raw materials, improved mechanical operations and housekeepings followed by effective application and monitoring of biocide programme and odour control applications, it is possible to produce paper process and products low in odour. The chemical applications should be carefully investigated to achieve maximum effectiveness and contribution to the performance and economics of the programme.

References

- 1) Al Piluso, The Paper Trade Journal, Lockwood Trade Journal Co., Inc., 1972.
- 2) Knut Wiik and Torbjørn Helle, Problems with the Paper Odour Possible ways to Solve Them, Norwegian University of Science and Technology, Department of Chemical Engineering
- Linda R. Robertson and William R. Schwingel, Microbial challenges unique to closed recycle paper systems, PIRÅ International Conference on Wet End Chemistry and Cost Work Shop, Gatwick, United Kingdom, May 28–29, 1997
- Robichaud, W.T., "Controlling Anaerobic Bacteria to Improve Product Quality and Mill Safety", Tappi Proceedings, 1990 Papermakers Conference, April 23-25, Atlanta, 305-308
- Corbel G. (2004) Pulp & paper. In: Paulus W. (eds) Directory of Microbicides for the Protection of Materials. Springer, Dordrecht.
- 6) Linda R. Robertson, Microbes in the Papermachine Environment, TAPPI Monograph: Microorganisms in Papermaking, Papercon, 2011
- The Nalco water Handbook, 3rd edition, Daniel Flynn, The McGraw-Hill Companies, Inc., 2009.