PAPER MILL FRESHWATER TREATMENT: LIFE AFTER CHLORINE

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TIPS FOR SELECTING ALTERNATIVE TREATMENT PROGRAMS

SYSTEM INNOCULATION IS A PRIMARY FACTOR INFLUENCING the performance of a microbiological deposit control program (1). Despite current trends toward increased closure of mill water loops, freshwater remains the largest raw material used in the papermaking process. As such, this water supply represents a significant source of microbial innoculation into the paper mill.

Successful microbiological control programs emphasize a system-wide approach to paper mill treatment. Experience typically shows that every effective microbiological control program begins with proper treatment of the incoming mill water. This water supply is crucial to pulping, shower operation, furnish preparation, additive makeup, chemical dilution, and white water makeup. While it may be possible to control microbial contamination at the paper machine directly, without adequate treatment of the freshwater, the cost of such an approach will most certainly be much higher.

The goal of any biological control program is to reduce the microbiological growth to a point where it is of no consequence to the operation of the paper machines. The quality of freshwater supplied to the paper mill can have a tremendous impact on paper machine performance. The results of inadequate microbial control are numerous and include sheet defects, sheet breaks, objectionable odors, increased machine downtime, and increased maintenance costs.

Traditionally, chlorine gas was the oxidant of choice to treat incoming mill water because it was economical, effective and simple to apply. Chlorine reacts with water to form the active biocidal compound, hypochlorous acid (HOC1). Hypochlorous acid is a weak acid that undergoes a pH-dependent dissociation to the H^+ and the $OC1^-$ (hypochlorite) ions. The bacterial efficiency of HOC1 is much higher than that of the $OC1^-$ ion due to its electrical neutrality. This allows HOC1 to easily pass through the negatively charged bacterial cell surface. Therefore, at pH >7.0, typical of most freshwater sources, the lower ratio of HOC1:$OC1^-$ leads to weaker biocidal activity (2).

Furthermore, chlorine, like any strong oxidizing agent, will react with many impurities found in the water including ammonia, proteins, Fe^{+2}, Mn^{+2}, or reduced sulfur compounds. These materials serve to deactivate the oxidizing agent, creating a demand for chlorine, which must first be overcome in order to control microbial growth. Environmental concerns have arisen due to chlorine reactions with organic compounds in freshwater supplies and the subsequent formation of halogenated organics (AOX compounds). AOX formation is typically a problem for paper mills due to the environmental toxicity associated with such compounds and the need to meet wastewater discharge requirements.

Many pulp and paper mills are currently reconsidering the use of chlorine gas for freshwater treatment due to safety and environmental concerns. While chlorine gas has been an inexpensive and proven technology, the advent of newer legislation has added cost to and focused attention on the risks associated with its use. Development of alternative chemistries may therefore preclude chlorine gas as the best choice for paper mill freshwater treatment.

Three pieces of legislation implementing regulations that can effect the use of chlorine gas are:

Process safety management (PSM) -- An OSHA regulation implemented to manage on-site worker safety. This regulation will need to be followed if there are more than 1500 lbs of chlorine gas on-site. Other chemicals can also require the implementation of PSM.

1. Best practices evaluation of the current freshwater treatment program
2. Alternate chemistries available for use
3. Biocidal efficacy of alternative chemistries
4. Safety and environmental impact associated with alternative chemistries
5. Impact of alternative chemistries on papermaking operations
6. Total cost determination of the new program

1. Key considerations for chlorine gas replacement

Risk management planning (RMP) -- An EPA clean air ruling scheduled to go into effect in June 1999. This regulation was established as a means to protect the public. It must be followed at sites with >2500 lbs of chlorine gas on-site. The regulation will require the potential for release of chlorine gas to be modeled, a procedure which can be quite expensive. In addition, the public will need to be notified of the chlorine gas that is on site and the mill must file with the government.

The Cluster Rule -- A set of EPA rules that combine air and water discharge regulations. This legislation was designed by the EPA to regulate paper industry discharges as a whole instead of separately. Regulations call for the complete substitution of chlorine gas, with chlorine dioxide as the currently recommended alternative.

While such regulations were primarily intended to monitor chlorine gas used in bleaching operations, many of these same mills utilize chlorine gas for freshwater treatment as well. This focus on chlorine gas provides an ideal opportunity to revisit its use as a freshwater biocide and to evaluate the performance of alternative oxidizing biocides. Several factors which must be considered when implementing a chlorine replacement program for freshwater treatment are listed in **Table I**.

BEST PRACTICES APPROACH

Considering a replacement for chlorine gas as a paper mill freshwater biocide can often have a wider impact than is initially anticipated. Therefore, a team approach to the evaluation of the mill water system is critical. Ideally, the audit team should include individuals responsible for mill water utilities and water treatment chemical programs, as well as pulp and paper production personnel who are ultimately affected by any changes in the freshwater treatment program. A list of key topics to be addressed by a mill freshwater audit team include the following:

1. It is essential to consider the mill water system as a whole and remember that any change can impact many other mill operations. The first step should be to obtain an updated flow diagram of the mill fresh water system. The diagram should include flow rates, chemical addition points and key sample points. System contact time and the reliability of feed equipment should also be investigated at this time.
2. Define the water quality specifications required for your system processes. Relying on historical data of machine runnability and mill freshwater parameters best makes this definition. Does the current treatment program meet these needs consistently?
3. Perform a freshwater system survey to assess the baseline performance of the current chlorine-based treatment program. Parameters to be considered throughout the system include temperature, pH, free halogen residuals, microbial counts and microscopic analyses. A makeup water analysis should also be run at this time.
4. Run a chlorine demand study to help estimate the amount of chlorine needed for microbial control.
5. Examine current monitoring and control procedures. Evaluate the risk of accidental chemical release and personnel safety with respect to transportation, storage and feed systems. Is the current program the most efficient means of meeting your freshwater needs?
6. Work together with a supplier to design a program to optimize performance in terms of paper machine cleanliness, runnability, paper quality, and cost economics. Be sure to include measurement and dosage control automation allowing targeted specifications to be met at all times. Poor system control is the most frequent cause of inadequate freshwater treatment.
7. Design a routine monitoring program to assess program performance. Relate program monitoring data to paper machine performance measures.
8. Document program results and benchmark the findings against other mills with similar issues.

ASSESSING FRESHWATER TREATMENT'S ROLE

Oxidants used in paper mill freshwater treatment are applied mainly for their biocidal properties; however, additional benefits such as color removal and oxidation of soluble iron and manganese may also be realized. Typical roles for oxidizing biocides in freshwater treatment are as follows:

1. Biocidal efficacy -- The principal program goal is to minimize the degree of microbial contamination entering the mill through the freshwater system. This will reduce slime formation in pipes, on heat transfer surfaces and, most importantly, on the paper machines. System parameters, which can

affect biocidal efficacy, include pH, available contact time, halogen demand, and product volatility. Each of these factors should be considered when evaluating the biocidal effectiveness of chlorine alternatives.
2. Color removal -- Removal of true color by chlorine is most effective over the acidic pH range between 4.0 and 6.8 (2). In most cases, highly colored, low turbidity waters are either naturally acidic or so lightly buffered that the application of gaseous chlorine may be sufficient to reduce the pH to the point required for optimal color removal (2). Changing programs from chlorine to an alternative oxidant may impact the pH of the freshwater supply, especially in waters with low alkalinity. Optimal color removal may then require a slight pH adjustment.
3. Soluble iron and manganese oxidation -- All forms of halogen will oxidize iron and manganese to a certain extent. Typically, soluble ferrous bicarbonate is oxidized to ferric hydroxide that is insoluble and can be removed by sedimentation and/or filtration, depending on how heavy a floc is produced. While this reaction will take place over a wide pH range (4.0 to 10.0), optimum activity is at pH 7.0. For manganese, the optimum pH for this reaction is between 7.0 and 8.0. At pH 8.0 and with alkalinities on the order of 50 ppm, the time required may be two to three hours (2). If the pH approaches 6.0, the time required may be as much as 12 hours. Temperature of the water does not appear to be a significant factor in manganese oxidation; however, iron oxidation will proceed slowly in colder waters. A change in oxidizing biocide can affect the rate of iron/manganese oxidation such that oxidized material can precipitate in different locations, perhaps onto metal surfaces, causing fouling problems. The oxidized material will also tend to precipitate phosphates used for corrosion inhibition. Manganese deposits on yellow metal-based surfaces can start under deposit or galvanic based corrosion.
4. Raw water clarification -- Oxidation prior to the clarifier can assist clarification of mill freshwater. This may reduce coagulant usage for the removal of turbidity in the water. Oxidant demand for this type of application will vary among the chlorine alternatives.

WHAT ARE THE ALTERNATIVES?

The arsenal of treatments for controlling microbial deposits in a paper mill freshwater system can be broadly classified into three categories: oxidizing biocides, non-oxidizing biocides and deposit control polymers. Oxidizing biocides such as chlorine have traditionally been used to treat paper mill freshwater due to their effectiveness and low cost, which allows a continuous feed approach for treatment of the large volumes of water involved (3). Non-oxidizing biocides have been utilized successfully for freshwater treatment; however, the cost of such programs generally inhibits this strategy. Finally, deposit control polymers are surfactants that prevent adhesion of microbial cells to system surfaces. They display no biocidal properties of their own but may be used to augment freshwater biocide programs. (This article discusses chlorine replacements belonging to the oxidizing biocide group.)

While each oxidizing biocide has its attributes and drawbacks, site-specific issues will ultimately determine the most practical chlorine alternative for a given freshwater system. Some of the issues that need to be considered include program performance, safety, feed and storage equipment, unloading frequency/spill risk, as well as unit chemical cost. A comparative summary of possible chlorine alternatives is provided in **Table II.**

EFFECTS OF ALTERNATIVE PROGRAMS

Freshwater treatment can have a large impact on many paper mill operations. When assessing the impact of changes to the freshwater treatment program, it is critical to evaluate the downstream benefits, such as the following:

1. Paper machine runnability -- The available contact time for an oxidizing biocide to work in a freshwater system is typically fixed and limited. Therefore, alternative chemistries should be chosen to offer enhanced biocidal efficacy and quicker speed of kill over traditional chlorine-based programs. Delivery of higher quality freshwater to the papermaking process will lessen the demand on the machine biocide program. Combined benefits include reduced spoilage of furnish and additives, decreased slime buildup on the machines, decreased downtime for wash-ups and boilouts, and improved sheet quality (1).
2. Machine clothing and system corrosion -- Halogenation can have a profound effect on the run-life of machine clothing and the corrosion rates of metal surfaces. The key to a successful freshwater treatment program is excellent control, especially with respect to oxidant dosage. Over-chlorination to rid the system of a microbial problem can considerably shorten felt life and is often extremely corrosive to steel and yellow metal-based heat exchangers. Residuals as low as

Chemistry	Pros	Cons
Sodium Hypochlorite (Bleach)	• Inexpensive, proven technology	• pH dependent dissociation to $OC1^-$ leads to decreased biocidal efficacy at pH >7.0. •Large volume storage and usage. Limited stability leads to degradation and loss of activity over time. •Reportable spill quantity = 800 lbs •Requirement for high residuals can degrade machine clothing and papermaking dyes. •Volatile. •High pH material.
Activated Bromine	•Biocidal efficacy at pH >7.0. •Fast microbial kill. •Less volatile than bleach.	•Need to activate on site creates requirement for two separate chemicals (bleach and sodium bromide) along with associated storage and feed systems. •High capital cost. •Same dosage and RQ issues as bleach.
Chlorine Dioxide	•May have supply already on site. •Relatively inexpensive. •pH independent activity over the neutral range. •Reduced AOX generation.	•Safety concerns - volatile, toxic gas. •Limited effectiveness against filamentous bacteria and molds. •Exists as dissolved gas in water. Extreme volatility leads to air stripping. •Increased corrosion. •Residual measurement is difficult. •Difficult to dechlorinate -- can cause demineralizer resin damage.
Stabilized Bromine (proprietary Nalco Technology)	•Single component program. • High spill RQ = 30,800 lbs. • Very low volatility (3). • Rapid and persistent action. •Low dosage requirements. •FDA approved. •Compatibility with scale and corrosion inhibitors (3). •Product contains no chlorine.	•More expensive than chlorine gas or bleach. •High pH product.
Bromochloro-dimethylhy-dantoin (BCDMH)	•Fast acting biocidal species is HOBr. •Good storage stability.	•Safety concerns due to dusting of dry product. •Low solubility leads to inconsistent product delivery and difficulty in responding to system upsets.

II. Summary of gaseous chlorine alternatives

0.3 ppm can increase corrosion rates 25-50% on clean yellow metal surfaces. Alternative oxidants should be evaluated for the ability to control microbial growth at lower residual dosages and with improved system control, eliminating the need to respond to system upsets following periods of interrupted oxidant feeds. The impact of alternative oxidants on the pH of the freshwater supply can also affect system corrosion. The application of chlorine gas to low alkalinity mill freshwater tends to lower the pH due to the formation of hydrochloric acid. Some alternative oxidants may increase the pH of the freshwater supply creating a less corrosive environment and reduced corrosion rates.

3. Demineralizer performance -- Ion exchange resins are susceptible to being oxidized and degraded by oxidizing biocides, leading to shorter run lengths, contaminant breakthrough and higher regenerant costs. Many mills feed a reducing agent to the water supply prior to demineralizer entry in order to lower the oxidation potential of the water. The ability to maintain effective oxidant doses at lower residual concentrations can eliminate or reduce the need to dehalogenate prior to the demineralizer resins.
4. Compatibility with other process additives -- Halogen residuals consume freshwater treatment chemicals such as scale and corrosion inhibitors, as well as papermaking additives such as dyes and retention aids. Alternative oxidants vary in their compatibility with such chemicals. Some, like chlorine dioxide, are known to be especially aggressive in this manner. Others will react much less aggressively than chlorine itself, creating the potential for considerable savings on chemical feed as well as process improvements.

Biocide	$/lb.	Dosage required	Feed & control equipment cost	Legislation compliance costs	Cost effect on other programs
Chlorine gas					
Chlorine dioxide					
Sodium hypochlorite					
Stabilized bromine					
Activated bromine					

III. Sample spreadsheet to assess costs of a chloine replacement program

DETERMINING CHLORINE REPLACEMENT COST

One method of assessing the cost of a chlorine replacement program is to design a spreadsheet that lists the alternative oxidants along with their associated costs in relation to their effects on the total mill water system. The cost impacts on other programs could be positive or negative. For example, a high required oxidant residual necessary to provide a good microbiological kill could shorten machine clothing life. Or, an increased mill water pH may reduce the cost of a corrosion prevention treatment program. An example of such a spreadsheet is outlined in **Table III**.

SUMMARY

Initiating a team approach to the global evaluation of the paper mill freshwater system can assist you in making the right decision about chlorine gas alternatives for freshwater treatment. Improved freshwater treatment will impact the paper mill in many ways, most noticeably by improving machine runnability and decreasing the costs associated with on-machine deposit control. Reevaluation of the freshwater treatment program often results in further benefits such as the ability to produce higher grade products, and more cost-effective production. Take advantage of this opportunity to justify the best paper mill freshwater chemical treatment program from safety to performance. TJ

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