

ABSTRACT

From June 1993 to August 1994, Newstech Recycling Limited Partnership, with assistance from several vendors, used various measures to combat or circumvent a problem of catalase contamination. In a mill whitewater environment, sufficient catalase can be generated to hamper or even disable an H_2O_2 treatment stage. The mill tested different options available to combat either the catalase itself or the bacteria generating the enzyme. Some of the options tried included biocide treatments, peracetic acid treatment, use of high H_2O_2 dosages, and steep bleaching. Others considered and tried on the laboratory scale without reaching mill-scale trial were very high doses of peracetic acid, alternative biocides, boilouts, and high operating temperatures (70–90°C). The successful solution was the use of an elevated H_2O_2 dosage in the pulper to both circumvent the problem and eliminate catalase.

Application:

This paper should help a mill suffering from a catalase problem to determine a course of action to eliminate or circumvent the problem.

CATALASE IS AN ENZYME OF THE oxidoreductase class that catalyzes the reaction $2H_2O_2 \rightarrow O_2 + 2H_2O$. It occurs naturally in most living cells. The purpose of this enzyme in nature is to destroy peroxides that occur as part of the cell's normal metabolism. As a naturally evolved defense mechanism, it is exceptionally effective at destroying peroxides both in and out of the cell.

Microorganisms are a normal part of the mill environment. The temperatures, availability of nutrients, and abundant habitats all encourage various forms of bacteria

Methods for controlling catalase in a deink pulp mill

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to grow, despite our best efforts to the contrary. In a typical recycle mill, these bacteria occur in various sections of the whitewater system. When a mill uses H_2O_2 , either in the pulper or in a post-bleaching stage, it is normal for a certain amount to remain after the conclusion of each stage. This residual H_2O_2 is carried into the whitewater, where it encounters the bacteria resident there. Typical residual H_2O_2 after a pulping state would be 0.1% to 0.3% H_2O_2 on oven-dry (o.d.) pulp, depending upon the dosage of H_2O_2 and the pulper conditions. Although H_2O_2 is a mild biocide, it is still dangerous to the bacteria, requiring them to take action against it. Thus they generate catalase.

Once the catalase is formed, it has several effects. The first is the intended (for the bacteria) effect of eliminating that troublesome H_2O_2 . The decomposed H_2O_2 yields a bonus of O_2 for the normally oxygen-limited bacteria. The bacteria usually have lots of nutrients in a mill whitewater, but the warm temperature of the water and closed nature of the vessels minimizes the amount of O_2 available. Now, with lots of food, oxygen, and a hospitable environment, the bacteria happily multiply and generate even more catalase. This catalase is not a reactant in the normal sense but is an enzymatic catalyst. Therefore it is not consumed in the course of converting the H_2O_2 to O_2 in the bacteria's immediate vicinity. The catalase-enriched whitewater travels throughout the mill—including back to the H_2O_2 -using stage. Once back in this stage, the catalase competes with the other reactions to

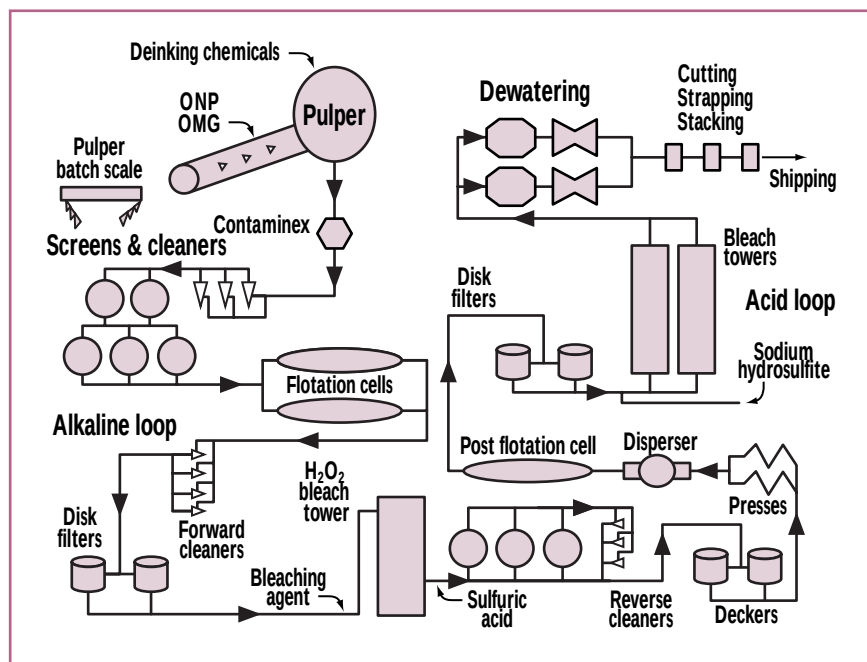
consume the H_2O_2 . Being an enzyme honed by a billion years of evolution, it competes very well—so well that it may consume much more H_2O_2 than either the normal brightening reaction or the usual forms of decomposition. The result of this consumption of H_2O_2 is that the expected brightening does not take place. The brightness gain may drop or even be reversed! The reversal, or brightness loss, is due to the fact that while the H_2O_2 is consumed by catalase, the NaOH is still present and now causes caustic yellowing unimpeded by the H_2O_2 . Increasing the dose of H_2O_2 may have little or no effect, as the catalase merely converts the additional H_2O_2 to O_2 as well. The end result is that the brightening stage, with its expensive equipment and costly chemicals, is not doing its job, all foiled by some bacteria and their enzyme—catalase.

THE PROBLEM

At the time of the first discovery of this problem, the mill had a dual-loop process—alkaline followed by acidic. A flowsheet of the process is shown in **Fig. 1**. H_2O_2 was applied conventionally in the pulper and following the flotation stage in a post-bleaching tower. The pulper conditions were 12.5% consistency for 8.5 min with conventional pulping chemistry, and the post-bleach conditions were 8% consistency, 4 h retention time, 50°C with about 1% H_2O_2 .

Symptoms

The symptoms of this problem were first noticed in June 1993, when a sudden loss of brightness gain occurred in the post-bleach stage. All



I. Newstech's flowsheet

parameters for the stage appeared normal; there was just no brightness gain. A standard series of diagnostic lab-scale tests were performed. They confirmed that, for no apparent reason, the expected brightness gain was not occurring. The pulper was unaffected. Although the symptoms were simple, the diagnosis was considerably more complex. As with car troubles and mechanics, the problem disappeared (initially) when we started to troubleshoot.

Diagnosis

Elimination of other causes. As the problem quickly returned, we continued to pursue causes for the post-bleaching difficulties through in-mill evaluations and consultation with industry experts. The initial first suspects of metals contamination in chemicals or furnish were easily ruled out. Suspect chemicals were tested by their suppliers; the furnish was tested by a third party. Other than having slightly elevated iron levels in the caustic, the chemicals were absolved of any blame. The furnish tested out to similar metal types and levels as found in previous tests,

prior to any problems. In addition, lab-scale brightening tests using elevated dosages of DTPA did not give any improvement in brightness gain. Another candidate, suggested by European colleagues, was the little-known (at the time) agent catalase. This candidate was considered and rejected on the suggestion of the mill's then-supplier of biocide. Such an exotic cause was considered unlikely.

Concurrent with testing for metals contamination, we considered other causes and undertook a comprehensive study of all aspects of the bleaching process in the mill. Bleaching studies, examination of tower parameters, and strength analysis of all bleaching chemicals proved negative.

Confirmation of catalase. After testing and eliminating all other possible causes, we returned to the one that had not been directly tested at the mill—catalase. A simple direct qualitative test clearly implicated catalase. To confirm this hypothesis, bleaching tests were performed on two pulps: one that had been pre-

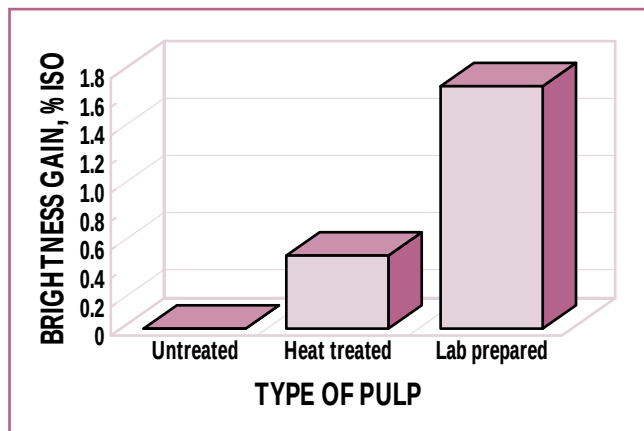
pared in the lab using tap water and the mill's furnish; and a second pulp that had come from the mill but was heat treated to eliminate either bacteria or enzymes. The results are shown in Fig. 2. Unlike previous tests, both pulps gained close to normal brightness! We had tracked down the cause of the problem. The easy part was over.

REMEDIES CONSIDERED OR TESTED IN THE LAB

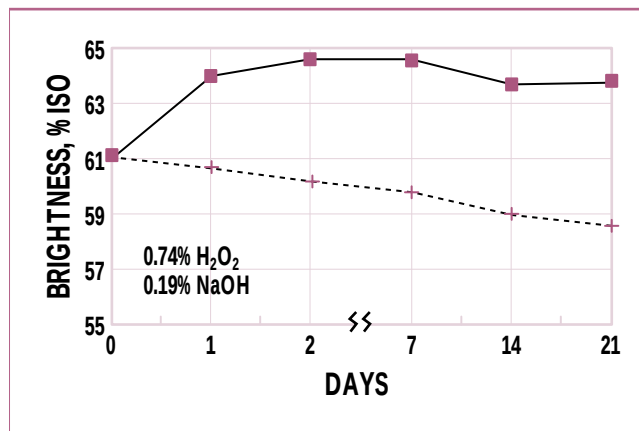
Although various options were tested in the lab at the same time as others were tried in the mill, we will consider the sequences out of chronological order and examine the lab-scale work first. It should be kept in mind that the problem was decomposition of the H_2O_2 by catalase, and that the catalase was bacterially generated. This allowed two potential avenues for solution: eliminate the catalase by direct action; or eliminate the source bacteria, preventing the formation of catalase. Elimination of catalase would give immediate results for the bleaching process. Elimination of the bacterial source would require waiting out the circulation of the whitewater system to "flush out" the residual catalase. Any solution chosen would have to include a long-term effect to prevent recurrence of the catalase at a later time.

High process temperature

A solution used successfully in Europe to eliminate catalase was to operate the mill with a whitewater temperature in excess of 70°C . This eliminated both the bacteria and catalase in the mill. This method was used successfully to treat pulp in the lab but could not be used in the mill for two reasons: steam limitations and concern about the effects on stickies. The concern was that the high temperature would soften stickies and allow them to pass through the screens.



2. Brightness gains with various pulp treatments



3. Lab results on steep bleaching wet-lap pulp

High H₂O₂ dosages

This option also had been used to combat catalase successfully in European recycle mills.

Peracetic acid (PAA)

PAA is a powerful biocide and oxidizer that has been used for years in other industries. As it is already somewhat known in the pulp and paper industry and is relatively easy to handle, it was considered a likely solution. There were two possible methods of application: elimination of catalase or elimination of the bacteria. In the lab, tests showed that it could eliminate catalase as well as the bacteria, but only at dosages of 200–400 ppm. Prior work in other industries had also shown that lower dosages, in the 10–20 ppm range, could eliminate the bacteria alone. For this solution however, the white-water system would have to be drained and refilled with water containing the required amount of PAA.

Biocides

There are a host of biocides available for a variety of purposes in the pulp and paper industry. Lab tests showed that there were several that could control the bacteria. However, any biocide treatment would have to include a program for ongoing treatment to prevent the bacteria from returning.

Boilouts

A typical paper machine-style

boilout was considered, but this procedure would have required extended downtime for the mill and would have to be repeated periodically.

Steep bleaching

As the mill produces a wet-lap pulp for shipment, steep bleaching was considered a viable “work around” solution for the catalase problem. It would not eliminate the catalase but would allow H₂O₂ bleaching to take place unaffected by the catalase. Lab tests showed significant brightness gains could be achieved with this method, as illustrated in Fig 3.

REMEDIES TESTED IN THE MILL: RESULTS AND EFFECTS

These procedures were used in the mill with varying degrees of success. The effects and side effects are discussed here.

High pulper H₂O₂ dosage

This was one of the first suggestions considered upon the determination of the presence of catalase. This option was tried for several days without success. The reason for its lack of success was not immediately known and was only determined later, as will be shown.

Institution of steep bleaching

Encouraged by the success of lab studies on steep bleaching, we instituted this remedy in the mill. It was a

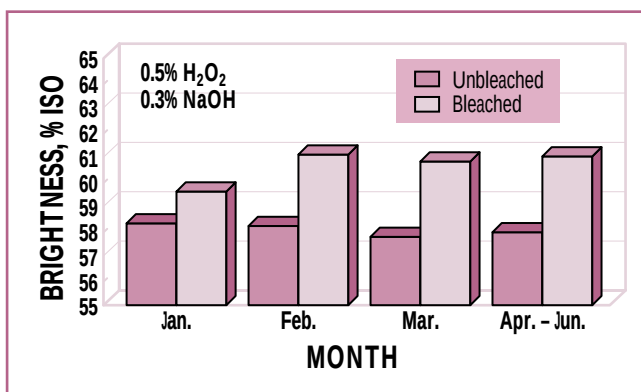
low-cost solution that gave sufficient brightness gain and could not be influenced by the catalase. Monthly average brightness gains are shown in Fig. 4. The wet lap was produced at the end of the acid circuit, while the catalase only occurred in the alkaline circuit and so was not present in the wet lap. An unfortunate consequence of the steep bleaching system was the presence of chemicals on the pulp bales being handled by the loaders. This meant that the pulp could not be touched with bare hands and gave rise to worker concerns about chemical exposure. These concerns led to the termination of steep bleaching.

First biocide trial

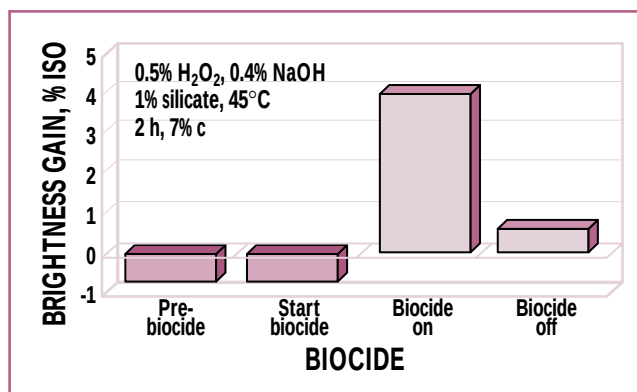
This trial was successful for as long as the biocide was being dosed. While the biocide was being added, the H₂O₂ bleaching tower was restarted with good brightness gains. As soon as the biocide was turned off, the catalase levels returned, and the H₂O₂ postbleaching lost its effectiveness and had to be discontinued. Figure 5 illustrates the results.

Peracetic acid trial

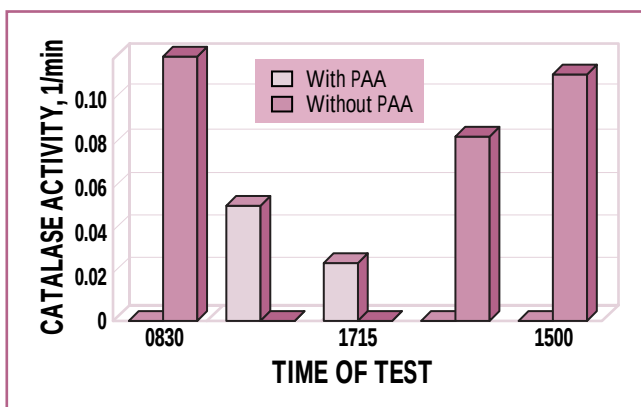
A trial using lower dosages of PAA was performed. It was considered that the amount of PAA required to bring the white-water to 200–400 ppm to eliminate catalase directly would be too expensive. However, knowing PAA's powerful biocidal



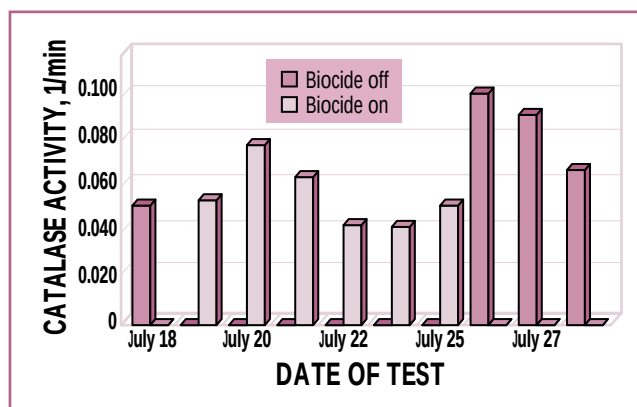
4. Monthly average brightness gains from steep bleaching wet lap pulp



5. Effects of first biocide trial on brightness gains in the H_2O_2 post-bleach stage



6. Effect of peracetic acid (PAA) on catalase in the mill



7. Effect of second biocide on catalase activity

effects, it was considered possible that the lower levels (10–20 ppm PAA) considered for whitewater replacement might have the desired effect by eliminating the bacteria without replacing the whitewater. So 800 kg of PAA was dosed directly into the whitewater system over a period of a few hours. This did have the desired effect upon the catalase activity, but the catalase returned in full force after the PAA was spent. **Figure 6** shows the results of this trial.

Second biocide trial

A second biocide supplier proposed a trial using a biocide claimed to have been successful elsewhere for this application. This trial was performed for one week with no appar-

ent effect upon the catalase activity, as shown in **Fig. 7**.

Pulper optimization—high pulper H_2O_2 dosage

While the battle against catalase was proceeding, other work in the mill had not stopped. Due to changes in the furnish and operating characteristics of the mill, it was considered worthwhile to reoptimize various chemical dosages to the pulper. Among the parameters varied was the H_2O_2 dosage to the pulper. The results from this series of tests in the pulper were closely monitored. Although the H_2O_2 was not to be increased to the levels originally recommended to eliminate catalase, any increase in H_2O_2 was considered to have a possible effect upon the bacteria and the catalase. The catalase

activity was monitored during the trial, and after two weeks of high H_2O_2 dosage in the pulper, the catalase was found to have been eliminated!

The continuous, slightly elevated dose of H_2O_2 slowly wiped out the bacteria, despite their best efforts with catalase. What is hypothesized to have happened is that the elevated dosage of H_2O_2 to the pulper caused a higher residual level of H_2O_2 to be carried over into the mill whitewater. This higher residual H_2O_2 overwhelmed the ability of the bacterial catalase to decompose it. A sufficiently high level of H_2O_2 residual remained to slowly destroy the bacteria. As the bacteria were gradually reduced, the amount of catalase that could be produced was

KEYWORDS

Biocides, biological control, deinking mills, enzymes, hydrogen peroxide, organic acids, peracetic acid, peroxides, peroxy acids, proteins, white water system.

decreased, hastening the demise of the bacteria.

CONCLUSION

The higher dosage of H_2O_2 has been continued in the pulper. There is a

significant brightness gain from the higher dosage, and the increased dosage of NaOH this permits has enhanced the ink removal in the following flotation stages. Due to the positive results of the pulper bleaching, the H_2O_2 post-bleaching stage has not been restarted. In addition, sufficient brightness is gained with the pulper bleaching and increased flotation brightness gains, so the hydrosulfite stage has been discontinued. The current brightening system of pulper bleaching and two stages of flotation is effective and free of any possible effects of cata-

lase. **TJ**

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