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# Bleaching Enzymes – Back from the Drawing Board

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Man has used enzymes since the first batches of beer, wine and cheese were made thousands of years ago. Our bodies use enzymes for the digestion of food amongst a myriad of other things to survive and to grow. In 1833 Anselme Payen was the first to discover an enzyme. Eduard Buchner received a Nobel prize in 1907 for his discovery of "cell free fermentation," which was in fact the use of an enzyme. The first commercial enzymes were produced by Röhm in 1914 for the detergent industry. This trypsin enzyme, isolated from animals, degraded proteins and was used as a detergent. It proved to be so powerful compared with traditional washing powders that German housewives' suspicions were aroused by the small size of the original package, so the product had to be reformulated and sold in larger packages(1). It has only been in the last 30 years that the paper industry has stepped into the arena.

Enzymes are proteins which act as catalysts in either accelerating or influencing specific chemical reactions. They are derived from living organisms, yet they themselves are not living. They do not reproduce, nor are they capable of mutation. They can be deactivated under certain conditions and can be destroyed under other conditions. Typically, most enzymes are destroyed at temperatures around 115°C (220°F) into innocuous organic materials.

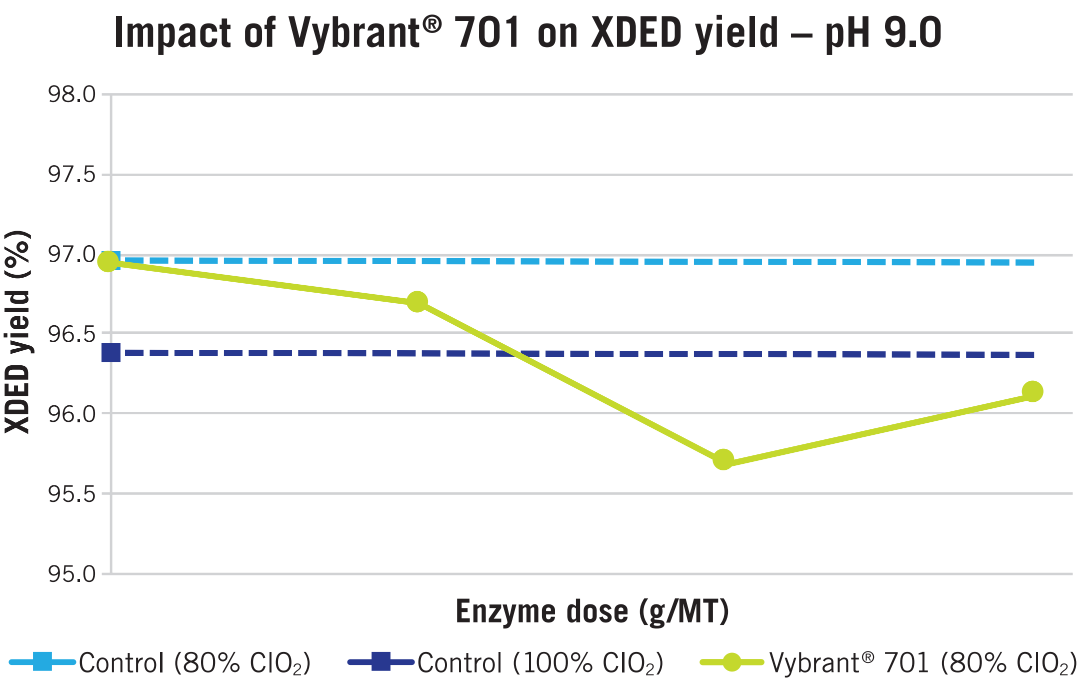


**Figure 1.** *Impact of Vybrant® 701 on XDED yield - pH 9.0*

The concept of using enzymes for the bleaching of pulp is not new. With the advent of ECF (elemental chlorine free) bleaching in the late 1990s, the industry quickly realized that bleaching with chlorine dioxide was much more expensive and adopted the use of various technologies such as oxygen delignification and acid pretreatment in an effort to reduce chlorine dioxide usage. To reduce chlorine dioxide usage further, investigation began into the commercial viability of using enzymes in the bleaching of pulp.

During the late 1980s and into the early 1990s, mill trials had already begun using xylanase enzymes in an effort to reduce the amount of chlorine dioxide used in bleaching. The industry encountered issues in that, in order for the enzymes to work, a very narrow operational band of pH and temperature had to be maintained over a period of 1-3 hours in order for the enzymes to be effective. Unfortunately, the required conditions were not native to the typical pulp mill, so extensive pH and temperature control strategies had to be employed. It was in the pH control that the bulk of the difficulties were encountered as the typical pH at the end of the brownstock washing system was somewhere between 9.0-11.5.

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This required extensive acidification at the end of the brownstock washers to achieve the required 6.5-7.5 pH range. The acidification of this pulp proved to be problematic as residual lignin, not washed out in the system, would reprecipitate causing more issues than could be overcome with the enzymes. There were also significant safety issues as hydrogen sulfide gas could be released during the acidification process. Some mills had limited success, but for the most part, the concept of bleaching enzymes was abandoned. For the mills that could implement the process, there were issues with substantial yield loss through the bleach plant. The issue was with the quality of the enzymes used as many of the commercially available products contained an unintended yet significant amount of cellulases which caused breakdown of the cellulose along with the hemicelluloses.

In the past few years, the technology of enzyme discovery, isolation and production has changed to the point where the new generation of materials warrant a closer look. Through careful manipulation of the biology producing the enzymes, not only have we been able to produce enzymes that perform in a wider pH regime, but we also have been able to remove residual cellulases and their undesired side effects in the bleaching process. This has provided the industry with another opportunity to not only reduce bleaching costs through the reduction of expensive chlorine dioxide, but also to produce a less toxic effluent through the reduction of chloro-organic compounds, some of which are measured as adsorbable organic halides (AOX). The less than stellar performance of the first generations of bleaching enzyme technologies has left many in the industry understandably wary of attempting to adopt this technology once again. Nonetheless, mills are increasingly venturing back into this arena with the new technology, and the results are promising. Several have commercialized this technology and are using it on a full-time basis. The rest of this article will address some of the typical concerns mills have when they are considering this technology. The main concerns include yield loss, adverse impacts to the wastewater treatment plants, and final pulp properties.

It makes sense to think that if the enzymes selectively act upon xylans, the potential exists to solubilise material and thereby cause a loss of yield through the bleach plant. All bleaching reduces yield in an absolute sense but we must look deeper into the relative change in yield when an enzymatically treated pulp is compared to one bleached with conventional methods. One has to remember that bleaching, by nature, results in a yield loss. Chlorine dioxide, while selective, still consumes not only the surface xylan but some of the cellulose as well. One must look at the selectivity of enzymes versus the selectivity of chlorine dioxide in total. Figure 1 presents the results of a meticulous lab study in which the post-bleaching yields of a pulp after pre-treatment with different dosages of a xylanase are compared against those of a conventionally bleached pulp. The xylanase pre-treated pulps are bleached with 80% of the chlorine

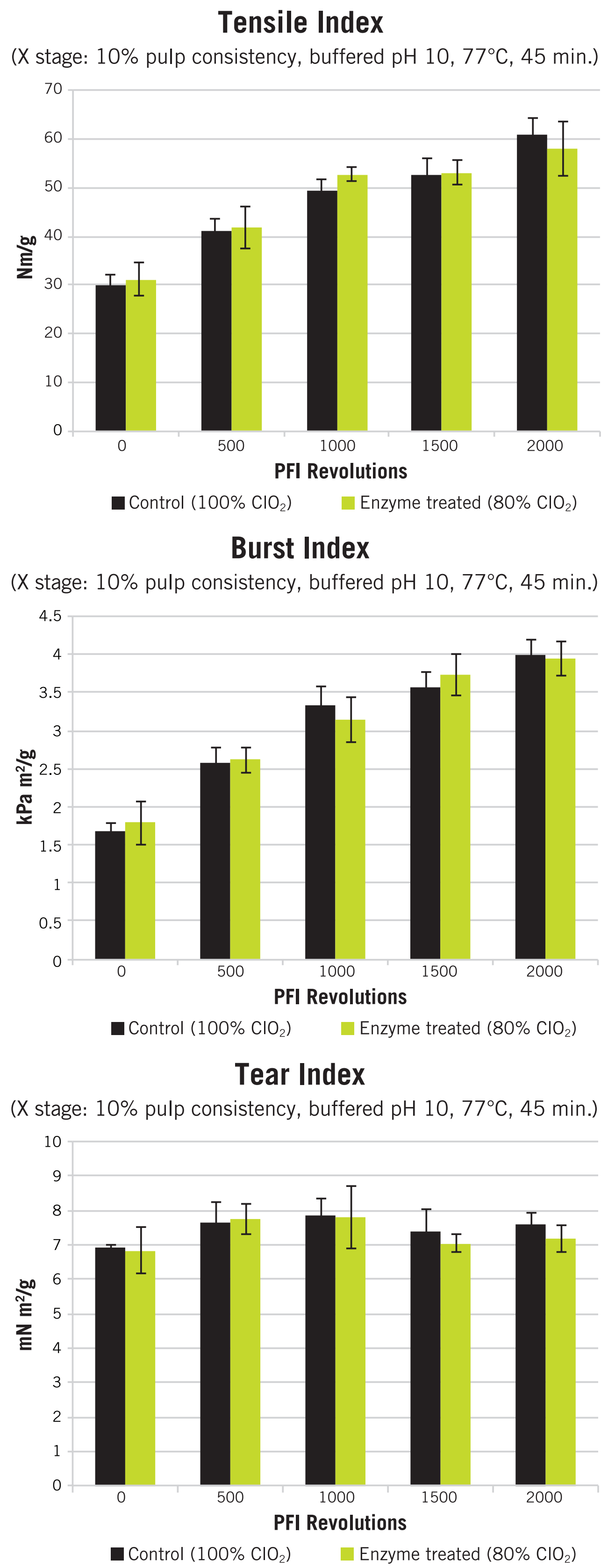



**Figure 2.** *Impact of enzymes upon standard beater curves (PFI revolutions)*

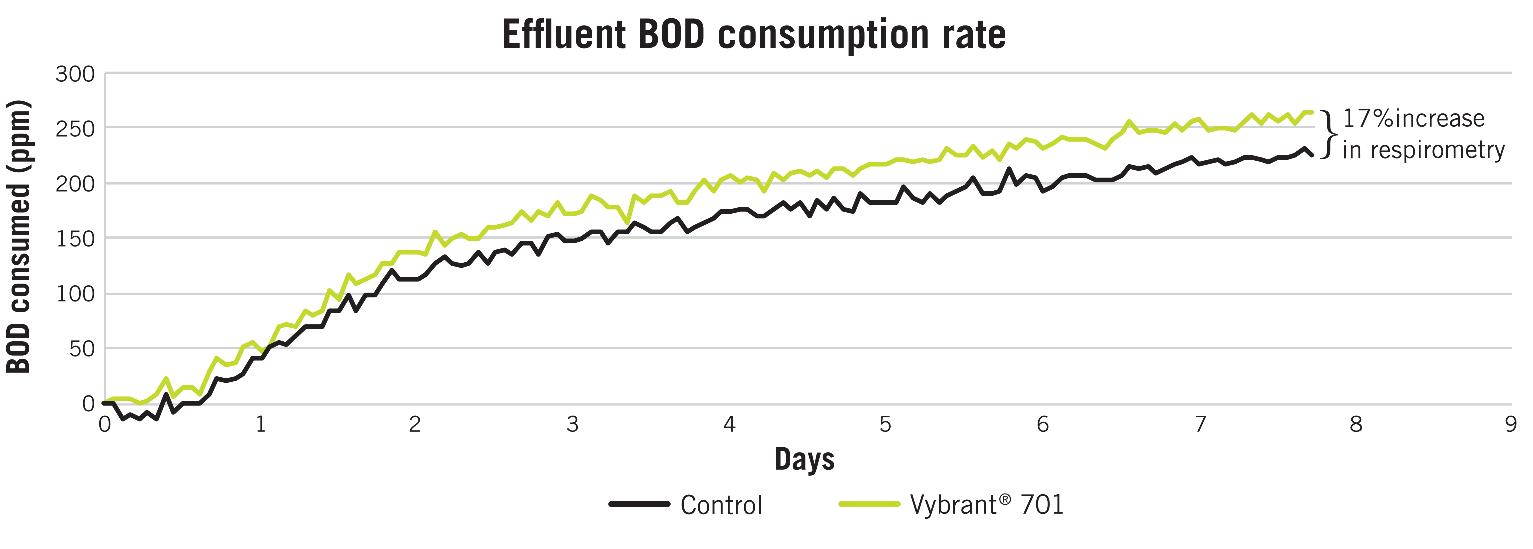
dioxide used in the conventional bleach sequence. At high dosages of xylanase, there can be a small yield loss. It is interesting to note that the maximum brightness is achieved at about the same xylanase dosage where the yield is equivalent to the conventionally treated pulp. Brightness gain was not observed at higher xylanase dosages but yield and COD release continue to be adversely impacted at higher dosages.

There is also concern about the impact of the removal of xylans with regards to final paper properties. There are many theories and hypotheses as to what the true impact is by removing xylan, some of which are contradictory. This is outside the scope of this paper; however, multiple mill trials have shown that the action of enzymes prior to bleaching has had no significant impact on paper properties. A sample of beater curves, with and without enzymatic pre-treatment is presented in Figure 2. Time and time again, the results are essentially the same. When the enzyme is applied at recommended levels, no significant impact upon paper properties was reported. End user characteristics in graphics papers have also been studied, and no ill effects have been found from paper produced from enzymatically treated pulp.

Another concern with the use of enzymes is the release of additional BOD/COD to the wastewater treatment plant. Enzymes do increase the release of lignin and xylan from brownstock (although the ratio is pH dependent). In mills where there is a prebleached washing stage between the brown High Density storage (the typical site of prebleaching enzyme addition), this organic loading is sent back to the recovery system and increases energy content of the black liquor. The net impact in these particular systems is a reduction in BOD/COD from the bleach plant to the wastewater treatment system. In principle, BOD is converted into usable Btus in the recovery cycle. One mill configured this way has seen a 14% reduction in effluent BOD where another mill has reduced COD loading to the wastewater treatment plant by about 10%.

**maximum brightness is achieved at about the same xylanase dosage where the yield is equivalent to the conventionally treated pulp**

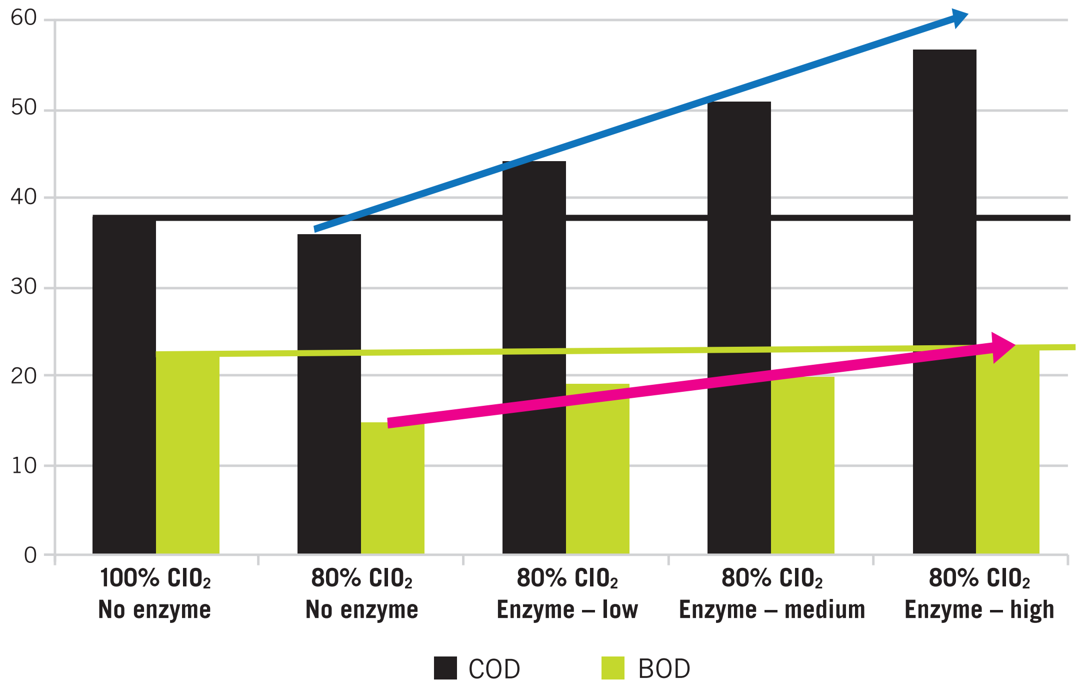
In cases where there is no prebleached washing, enzyme activity will cause an increase in BOD/COD loading; however, it should be pointed out that the increase is in the form of simple sugars and related organic acids. These materials are much easier to digest than the chlorinated phenolic compounds created in conventional bleaching. A study of the impact of filtrates from a xylanase treated pulp on biological oxygen uptake was conducted in the laboratory. The results indicated a 17% increase in respiration, an indicator of bioavailability, as is shown in Figure 3. In another study BOD and COD levels in the bleaching filtrates were compared against a baseline. Increasing xylanase dosage increases both BOD and COD loading; however, it takes a high dosage of xylanase to exceed the BOD loading equivalent to a conventionally bleached pulp. It is interesting to note that the increase in BOD loading was much more gradual than that of COD loading with an increase in xylanase dosage – a consequence of high lignin release relative to xylan release. The results of this testing are shown in Figure 4.



## Total COD and BOD liberated during XDEDP

**(mg/g of pulp)**

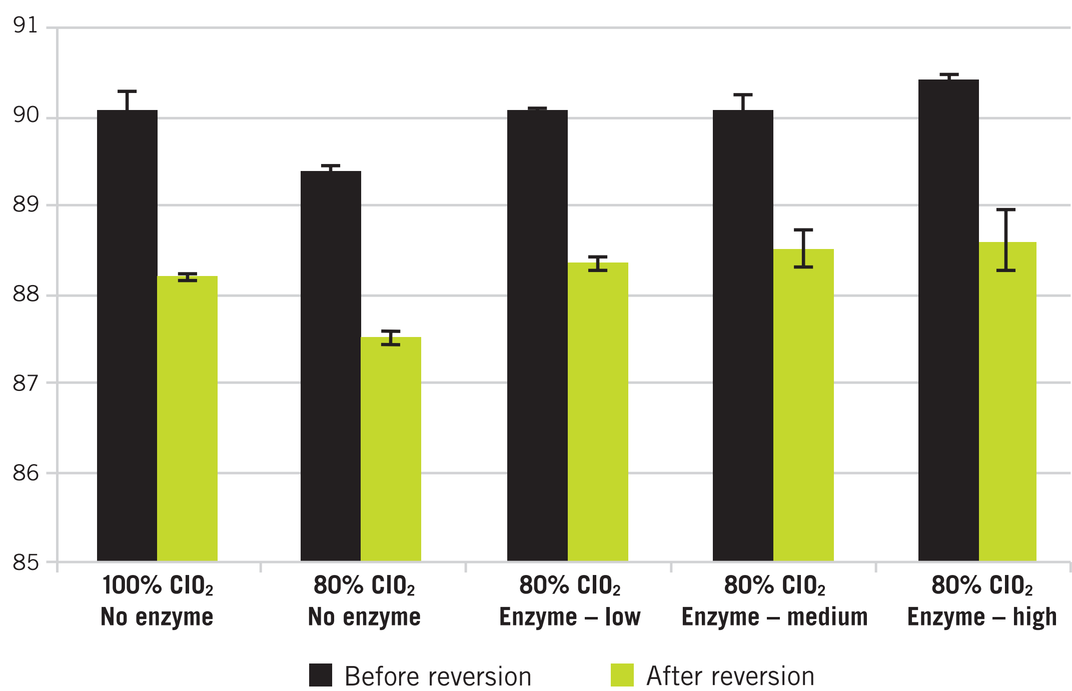
(X stage: 12% pulp consistency, pH 10.5, 90°C, 90 min)




## Brightness after XDEDP bleaching (%)

(X stage: 12% pulp consistency, pH 10.5, 90°C, 90 min)

(Reversion: 105°C for 4 hrs)




At least one mill has taken advantage of this mechanism to reduce the loading of their recovery boilers in order to increase production while maintaining a neutral impact upon the effluent discharge quality. We typically see a 15-20% reduction in chlorine dioxide usage, therefore, effluent from the bleach plant has a lower toxicity. The net result in the effluent quality from the wastewater treatment plant to the receiving body may have an increase in BOD/COD levels but will also have a lower AOX content. The impact of a bleaching enzyme upon the wastewater treatment plant must be closely monitored during mill trials. There have been cases where a mill has no prebleached washing and an overloaded activated sludge treatment system operating close to their permit discharge limits. In cases such as this, the additional inlet COD load could not be tolerated.

In conclusion, the use of xylanases in bleaching can result in significant savings to a mill in the reduction of chlorine dioxide. The perceived detrimental impacts caused by xylanases can be avoided by the judicious control of dosages. Adverse impacts, if any, are brought about by significantly overfeeding xylanases and/or significant adjustments of brownstock pH and should be avoided.

### REFERENCES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