Nonchlorine bleaching conference: the future is here

Paul C. Wollwage
Senior Research Scientist, Weyerhaeuser Company,
WTC 2G25, Tacoma, WA 98477

Nonchlorine bleaching is not the future, it is already with us! There are currently 34 kraft and sulfite pulp mills able to bleach pulp without chlorine-containing compounds.

Some 300 worldwide delegates participated in a four-day conference dealing with the pros and cons of no-chlorine and chlorine-compound-free bleaching. The conference was held in March at Hilton Head, SC, and was sponsored by *Pulp & Paper* and Emerging Technology Transfer, Inc. Program chairman was Rudra P. Singh.

Sessions, consisting of tutorials and testimonials, revolved around the areas of extended delignification, enzyme treatments, oxygen, ozone, and peroxide stages. The final session, on the current status and future trends of chlorine-free bleaching, provided for some active audience participation between those who are attempting to slow the demise of chlorine and chlorine dioxide and those who feel the immediate need to eliminate these compounds in response to market pressures.

The conference was directed at a rather broad slate of personnel ranging from mill executives to technical and operational personnel in pulp and paper companies, and equipment and chemical suppliers. More than half of the papers presented were reviews of past work. As such, little new scientific information was presented. The tutorials, however, were particularly useful for the inexperienced and those needing an understanding of current terminology.

One drawback of the conference was that approximately 65% of the speakers had hard copy materials. In addition, a number of speakers were promoting sales of product or a service rather than entering into a scientific exchange.

Delignification—where it's all at

The most impressive tutorial, in terms of clarity and presentation quality, was entitled "Extended delignification in kraft mills" by Martin MacLeod of PAPRICAN. As MacLeod pointed out, "we spend an enormous cost for the amount of lignin removed." The more work is performed in the digester, the less energy, chemical, and capital will be needed in the bleach plant. Indeed, the world is moving in this direction. In the last four years approximately 30 mills have begun operating with extended delignification, with more coming on line this year. Perhaps some day, and not too far into the future, we will bleach to 90 brightness in the digester and have a workable, closed-up process that will negligibly impact the environment.

How much can one extend delignification today? Several speakers talked in the range of 5–10 kappa number. The question that came up a number of times: "Is a kappa a kappa at the low kappa numbers encountered in the bleach plant?" Although no data were presented, it would appear from the discussions there was no clear consensus as to what one was measuring as lower kappa numbers were reached. The level may very well depend on the cooking chemistry and digester physics to reach a given kappa number. Thus the mode of cooking will influence the degree of lignin condensation and just how the aromatic rings are sterically linked together. Steric hindrance will reduce the reactivity of residual lignin to potassium permanganate (the oxidant employed in the kappa test), and to oxidizing chemicals such as chlorine dioxide and ozone used to bleach the pulp. Understanding the nature of residual lignin and how oxygen-based oxidants react with it will be a key to getting to 90 brightness with these chemicals.

The oxygen bleaching compounds and unanswered questions

Oxygen and hydrogen peroxide have been used in the industry for a number of decades. Ozone, which has been studied for a number of years in both laboratory and pilot plant, will be commercially implemented in conjunction with the kraft pulping process this year. Discussion about these compounds occupied the greatest portion of the conference time. While a great deal of scientific knowledge has been gathered regarding these compounds there is still much work to be done to fully utilize their potential in regards to maximization of pulp brightness and minimization of pulp strength loss and cost.

A specific area of interest was how heavy metals such as iron, copper, and manganese reduce pulp strength properties if present in oxygen and ozone bleaching stages. Metals management, it seems, has become a buzzword. Understanding the metal material balance around an oxygen-, ozone-, and hydrogen-peroxide stage will become more important as we recycle and close up mills to minimize effluents.

Ozone, like chlorine, is an electrophile, meaning it seeks out higher electron densities as found in the aromatic rings

in lignin. Thus, ozone would be a "natural" replacement for chlorine as ozone does not produce chlorinated products. There was much talk about multistage and medium-consistency ozonization. It appears many companies are studying and some are reinvestigating the use of ozone for bleaching. A question that arose several times concerned the toxicity of effluents from ozone stages. Currently little or no information is available on this subject, but perhaps the next nonchlorine or oxidative chemicals conference will provide some answers.

There was plenty of discussion regarding the costs to produce these chlorine-free and chlorine-compound-free pulps and effluents. There was little argument that costs could be significantly higher. Although current scientific data indicate that today's bleach plant effluents after secondary treatment are safe in terms of today's tests, some world markets are demanding changes with the elimination of chlorine-containing compounds. If you choose not to sell into these markets you must sell your product elsewhere or not sell your product at all.

The world of enzymes—will it last?

The enzyme world is expanding rapidly. Six enzyme suppliers were represented and numerous more are getting ready to sell a product. The current interest in enzyme technology is understandable as implementing the technology is relatively inexpensive from a cost standpoint. Many companies are running pilot trials with enzymes. A mixer, some piping, and pH control are all that is required. What's more, a 10–30% reduction in chlorine usage can result in reductions in adsorbable organic halogens (AOX). Reductions in hydrogen peroxide and oxygen can also be observed for the totally chlorine-free processes. The issue is that it is a relative reduction, dependent on the kappa number to the bleach plant. As we learn to go to lower and lower kappa numbers out of the digester we will be dealing with diminishing returns with enzymes. Interestingly, nothing was mentioned on how enzymes really work other than removal of xylan polysaccharide material from the surface of fibers, which then presumably allows lignin to be more readily dissolved in a subsequent alkaline stage. Perhaps as we begin to understand the mechanism by which enzymes unzip the hemicellulosic polymers, then we will be in a position to judge the future of enzymatic bleaching.

Current status and future trends in chlorine-free bleaching

Representatives from around the world gave their views on the impact of regional regulatory actions. The consensus, but not unanimous feeling, is that chlorine is out and chlorine dioxide may be out in 10 years. As previously mentioned, market and regulatory pressures to produce chlorine-free products and effluents are the drivers. There was much disagreement with the timing of the changes being thrust onto the pulp and paper industry. If your market is requiring chlorine-free product then you are making the necessary changes, but if your market is not requiring these changes then you do not feel the pressure to immediately change.

There was talk that regulatory authorities may soon understand that AOX is outdated and will be replaced by analyzing for specific classes of compounds or even specific compounds. There was much interest and concern in the declaration by British Columbia's government that industry effluents will be AOX-free by the year 2002. Based on the discussions that ensued, this type of regulation will spread.

Many felt that bleaching without chlorine dioxide will be impossible if today's brightness and pulp strengths are to be realized. The use of chlorine dioxide can result in ultra-low AOX levels with chloro-organics having low levels of chlorine substitution of the phenylpropane rings of lignin compared to the much higher chlorine substitution that occurs when bleaching with chlorine. This is an important point because the lower-substituted chloro-organics do not readily solubilize in fat deposits compared to the higher-substituted materials. Mother Nature is not adverse to chloro-organics and produces a significant quantity of natural AOX via biochemical mechanisms. If chlorine dioxide is to survive in the face of public pressure, the industry must demonstrate that the amount and type of AOX produced from bleaching with chlorine dioxide is similar to that generated by biochemical mechanisms. Perhaps more research into the nature, quantity, and chronic toxicity of chloro-organics in both paper and effluents is needed. The question is whether this research will be too late.

And just what is the future? Many more of these types of conferences. □