

## **Fundamental Topochemistry of Bleaching Stages Containing Chlorine Dioxide and Ozone (2004)**

### **A Dissertation by Ana M. Retzlaff**

Abstract: The combination of ozone and chlorine dioxide in two stages without intermediate washing allows for the elimination of elemental chlorine from the bleach plant or partial substitution for chlorine dioxide in the delignification stage. The substitution of ozone, in many cases, reduces the operating costs of the facility as well as reducing chlorinated by-products. To date, the research in this area has concentrated on D/Z and Z/D stages, the operating parameters of a combined stage, and the chemical and physical properties of the resulting pulps. Additional partial bleaching sequences to be used in this study include D/Z/D and Z/D/Z. The underlying chemistry of these combined stages is not well understood and further research is needed in this area. This research increased the understanding of the changes in the surface lignin content of the bleached pulp as well the lignin structural changes that occurred with the application of multiple bleaching agents.

Commercial brownstock and oxygen-delignified birch pulps were bleached with a combination of chlorine dioxide and ozone. The bleached pulps were then characterized for delignification, viscosity protection, and brightness. The mercurization of the bleached pulps allowed for the determination of the surface coverage of lignin using ESCA. Residual lignins were isolated from the ClO<sub>2</sub>/O<sub>3</sub> bleached pulp and characterized using <sup>13</sup>C NMR techniques.

The characterization of the bleached pulps from this research indicated that the lower substitution levels of ozone yielded pulps with greater delignification and less pulp degradation. To illustrate this concept, the D/Z/D stages (with 67% ClO<sub>2</sub> addition) had the highest selectivity of the combined ClO<sub>2</sub>/O<sub>3</sub> bleaching stages. Increased substitution of ozone leads to a higher final kappa number as shown by the Z/D/Z stages and the ozone reference stage. The pulps from these stages are also more degraded when compared to pulps that are bleached with an increased percentage of chlorine dioxide.

The structural characterization of the isolated lignin from the extracted pulp bleaching experiments has provided more information concerning the changes taking place in the lignin structure as a result of the ClO<sub>2</sub>/O<sub>3</sub> bleaching stages. A significant observation is the increased carboxylic acid contents of all pulps bleached with chlorine dioxide and ozone which is typically associated with the introduction of muconic acid-type structures into the lignin. The increased COOH content leads to increased solubilization and depolymerization of the lignin. Demethoxylation is also a significant pathway during delignification with chlorine dioxide and is confirmed by the large reduction in the methoxyl content seen with ClO<sub>2</sub> treatment. The changes in the lignin's methoxyl content are mirrored by changes in the methanol concentration of the stage effluent. As shown by the pulps in this study, increases in the effluent methanol content also result in decreases in the lignin methoxyl content.