Final Pulp Bleaching by Ozonation: Chemical Justification and Practical Operating Conditions

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Abstract: In an attempt to understand why, in pulp bleaching, the final brightness points are so difficult to gain despite the very low content of residual chromophores, several model compounds representing chemical structures which may still be present in semi-bleached pulp were submitted to various charges of chlorine dioxide and ozone. Depending on the model (quinones or lignin fragment) and on the reagent, different results were obtained. ClO₂, when it reacted with the lignin fragment, generated new coloured chromophores which were resistant to further degradation. O₃ also produced new coloured groups. However, the latter were easily degraded with an excess of reagent. Moreover, the quinone models were very resistant to degradation by ClO₂. On the contrary, they were easily destroyed by O₃. These results may explain the pulp resistance to chlorine dioxide in final bleaching and the better efficiency of an ozone treatment for this purpose.

The conditions of an ozone stage performed at the end of a bleaching sequence were not as critical as when ozone served as delignifying agent. It was shown that the ozone stage could be advantageously conducted at high temperature (80°C).

EXPERIMENTAL

Pulp samples

Two mixed hardwood kraft pulp samples (bright-
pulp bleaching

ness 83.7% and 85.1% ISO) were provided by the Alizay mill in France. The pulp had been bleached in the mill by the D0 (EP) D1 sequence and sampled ahead of the final D2 stage.

Reagents and bleaching stages
Ozone was produced in a laboratory ozone generator (LN 103, Ozonia) from pure oxygen at a concentration of 50-60 mg 1⁻¹. Chlorine dioxide was produced in the laboratory from the reaction between sulphuric acid and sodium chloride at a concentration of 8 g 1⁻¹ in water. For practical reasons the Z stages were carried out at high consistency. The Mill pulp was diluted in process water, then centrifuged to 35% consistency and fluffed. The ozone treatment was carried out in a rotating spherical glass reactor at the desired temperature (from 20 to 80°C). Ozone charges varied up to 0.2% on pulp. D stages were carried out at 10% pulp consistency in plastic bags placed in a thermostatically regulated water bath. D Stages were performed at 80°C for 3 hours.

After bleaching, brightness and cellulose state of polymerization (DP) were measured according to the ISO standards (ISO 3688 and 5351 respectively). Prior to DP measurement the pulp was reduced with 2% NaBH₄ and 1% Na₂CO₃ at 10% consistency and room temperature for 30 min. Post colour number was the difference (x100) between K/S after aging at 105°C for 24 h and before.

Model compounds
Para-benzoquinone (Lancaster Synthesis), sulphonated naphthoquinone, sulphonated naphthoquinone-4-sulfonic acid, sodium salt, Aldrich), and sulphonated softwood lignin (lignosulfonic acid sodium salt, Aldrich) were commercial products. The molar mass of the "phenylpropane unit" of the sulphonated lignin was 247 g mol⁻¹ as indicated by the supplier. The formulas of the three models are the following:

![Image]

Reaction of model compounds
Aqueous solutions of the model compounds were treated at a concentration of 6 mmol l⁻¹ (except for naphthoquinone: 1 mmol l⁻¹). These concentrations were chosen in order to be in the suitable range of absorbance of the spectrophotometer (Unicam UV500, Thermospectronic).

**Ozone treatment**
1.5 mmol (0.25 mmol for naphthoquinone) of the compounds were dissolved into 250 ml of deionized water. This solution was ozonated in a glass flask by injecting directly gaseous ozone at 20°C. This temperature is low enough to favour ozone solubility. The quantity of ozone that was introduced in the solution at a flow rate of 1 l min⁻¹ was measured by an ozone analyzer (BMT 961). The residual gas was directed to a 400 ml trap solution of 20 g 1⁻¹ potassium iodide (Roth) where it was titrated by iodometry. Thus, the exact quantity of ozone consumed by the solutions of the model compounds could be calculated by difference.

**Chlorine dioxide treatment**
1.2 mmol (0.2 mmol for naphthoquinone) of the compounds were dissolved into 100 ml of deionized water. Then, a given quantity of deionized water and of chlorine dioxide was added to reach 200 ml. This solution was maintained in a closed and opaque reactor at 70°C and under agitation during half an hour. Then, it was cooled in an ice bath till its temperature reached 20°C. As chlorine dioxide has a yellow colour which can interfere in the visible spectra, the residual chlorine dioxide was removed by a flow of nitrogen gas injected directly in the solution. The extracted chlorine dioxide was directed into a 350 ml trap solution of 20 g 1⁻¹ potassium iodide where it was titrated by iodometry.

The effects of ozone and chlorine dioxide on the model compounds were followed by UV-Vis spectrophotometry at 457 nm. The advantage is that this wavelength is used for the measurement of the brightness of pulp and paper. An exception was para-benzoquinone for which the analysis was performed at 427 nm since the absorbance at 457 nm was very low. The pH was monitored in all cases.

**RESULTS AND DISCUSSION**
Final bleaching with chlorine dioxide and ozone
The mixed hardwood kraft pulp of 85.1% brightness was treated with chlorine dioxide (D stage) and with ozone (Z stage). The results in Table I clearly show the superiority of the ozone over chlorine dioxide in final bleaching. The reason for such a difference must be related to the nature of the chromophores still present in the pulp before final bleaching.

Even though these chromophores are not precisely known it seems reasonable to assume that they should contain phenolic and quinone groups belonging to residual lignin fragments [2, 3]. Three models were chosen to cover these possibilities: a commercial lignin (lignosulphonate was preferred in order to enhance the solubility in neutral conditions), para-benzoquinone, and naphthoquinone (sulphonated for the same reason). Solutions of the models in water were submitted to D and Z conditions and the colour of the solution was followed by measuring the absorbance at 457 nm or 427 nm. The results are given in Figures 1-3.

Figure 1 shows that the colour of the lignin solution first increased during the treatment. Then colour removal took place. It was interesting to notice that colour was not completely eliminated when ClO₂ was used in large excess, contrary to what happened with O₃ which ultimately led to a colourless solution. In the case of ClO₂ treatment, colour formation may result from the formation of quinones as described in many studies dealing with the ClO₂ oxidation of the phenolic units in lignin [7]. Quinones should not be formed during ozonation. However new carbonyl groups are created which may increase the light absorption of the existing chromophores. Further application of the reagents reduced the colour. Total destruction of the original and new chromophores was possible with O₃ only. Some of them resisted the ClO₂ treatment.

Figure 2 confirms that quinone groups were rather resistant to ClO₂ oxidation but were degraded by O₃. Both Figures 1 and 2 clearly suggest that ozone would be more appropriate to destroy pulp chromophores, which is in accordance with the bleaching results in Table I.
Ozone treatment as final bleaching

The use of ozone in pulp bleaching has been implemented in more than 30 bleaching lines worldwide. The justification of introducing ozone in a bleaching sequence is mainly economical. The fact that in theory one mole of ozone (48 g) can exchange 6 electrons against only 5 for 67 g ClO₂ makes it a cheaper alternative. Moreover ozone reactivity is such that any unsaturated group in lignin readily reacts with ozone, which is not the case with chlorine dioxide.

Ozone operating conditions have been carefully looked at in order to minimize ozone decomposition, favour lignin degradation, and avoid cellulose depolymerization. It is well documented that ozone delignification should most favourably take place at acidic pH (between 2 and 3) and at the lowest temperature possible. When used in final bleaching the level of pH was not found critical [5] and close to neutral conditions gave good results. This may have something to see with the fact that the target of ozone reaction is then some resistant chromophores, rather than lignin, which would require a different chemistry. In this new application the effect of temperature has never been investigated. However this parameter is of interest since the pulp at this stage must be at least around 70°C.

The following figures refer to the influence of temperature in the ozone final bleaching of the hardwood kraft pulp of initial brightness 83.7% ISO.

Figure 3 shows that, contrary to what was expected, brightness development was better at the higher temperatures, despite the fact that ozone stability should have been less. One reason could be that the oxidized chromophores are more soluble at higher temperature. However attempts to obtain the same effect by submitting the pulp treated by ozone at 20°C to a water extraction at 80°C for 30 min. failed. Therefore it is likely that the higher the temperature the better the chemical degradation of the chromophores by the ozone, which remains to be understood.

The better bleaching is obtained at the expense of some cellulose depolymerization (Figure 4). However, the loss in DP was moderate and should not modify the mechanical properties of the hardwood pulp significantly.

Finally, the increase in temperature improved the brightness stability of the pulp (lower PC number) (Figure 5). At low temperature (20°C) some loss in brightness stability accompanied the bleaching effect of ozone. At 80°C brightness stability was the same as the original one before the ozone treatment. Explanation for this effect has not been found yet.

CONCLUSIONS

ECF bleaching sequences are based on the extensive use of chlorine dioxide. No other reagent is necessary in the sequence to obtain fully bleached pulps, provided that sufficient charges of chlorine dioxide are applied, even though some oxygen or hydrogen peroxide are added in the extraction stages to reduce the bleaching cost. However a close examination of the ClO₂ requirements in the successive D stages shows that ClO₂ becomes less and less efficient as the bleaching progresses. In fact, considering the tiny quantities of coloured matters in the pulp before the last bleaching stage, much lower charges of ClO₂ should be required.

This study demonstrates that phenolic lignin fragments may actually develop some new colouration when they react with small quantities of ClO₂. These new chromophores will not be then entirely destroyed with further quantities of reagent. Moreover, this study illustrates the fact that quinones, which are also claimed to be possible residual chromophores, are very reluctant to react with ClO₂. Therefore, reasons for the low efficiency of chlorine dioxide in last bleaching stages could be either the formation of stable chromophores (possibly quinones) when ClO₂ reacts on lignin fragments, or the presence of quinones already in unbleached pulp, which will not readily react with ClO₂.
The behaviour of ozone was shown to be very different. Although new chromophores are also formed when ozone reacts on lignin fragments, those coloured groups will not resist further ozonation. Also, the quinones models used here were easily degraded by the ozone. Those chemical considerations would explain why the potential of ozone in final bleaching was found better than that of chlorine dioxide.

Ozone delignification is known to work better at lower temperature. However, pulp temperature in final bleaching is usually between 70 and 80°C. Contrary to what was expected, ozone bleaching worked much better at 80°C than at 20°C. Several brightness units could be gained only by such an increase in the reaction temperature without substantial consequence on cellulose depolymerization. Moreover, brightness stability was found better after bleaching at 80°C. Therefore ozone final bleaching, which requires neither pH nor pH adjustments, is indeed a very simple and promising process.

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LITERATURE


Résumé: Pour mieux comprendre pourquoi les derniers points de blancher sont si difficiles à obtenir lors du blanchiment des pâtes chimiques, alors que les quantités de chromophores résiduels sont extrêmement faibles, plusieurs composés modèles des structures chimiques vraisemblablement présentes dans les chromophores des pâtes mi-blanchies ont été traités par différentes charges de dioxyde de chlore et d’ozone. Selon le modèle (quinones, fragment de lignine) et le réactif utilisé, des résultats différents ont été obtenus. Lorsqu’il réagit avec des fragments de lignine, ClO2 forme de nouveaux chromophores colorés qui vont résister à une attaque ultérieure. L’ozone O₃ forme également de nouveaux chromophores mais ceux-ci sont entièrement dégradés par un excès de réactif. De plus, les modèles quinoniques se sont avérés très résistants vis-à-vis de ClO₂ alors qu’ils sont facilement dégradés par O₃. Ces résultats peuvent expliquer la moindre efficacité du dioxyde de chlore en fin de blanchiment par rapport à l’ozone.

Les conditions d’utilisation de l’ozone en fin de Blanchiment sont moins critiques que lors d’une délignification. Ainsi il est montré que le stade d’ozonation peut être avantageusement réalisé à haute température (80°C).


Keywords: PULP BLEACHING, CHLORINE DIOXIDE, OZONE, CHROMOPHORES, TEMPERATURE