

Minimizing Viscosity Loss during Totally Chlorine-Free Bleaching of Hardwood Kraft Pulp

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By applying increasing amounts of ozone (Z stage bleaching) on eucalyptus oxygen-delignified pulps, it was observed that both lignin and hexenuronic acids (HexA) are attacked early during the treatment. While the HexA were progressively removed, however, the oxidized lignin tended to stay in the pulp. An acidic stage (A stage) at pH 3 and a temperature of 90 to 95°C removed a high proportion of the HexA, which eventually reduced the ozone requirement. In spite of the negative impact of the A stage on the DP of cellulose, totally chlorine-free sequences containing A led to pulps of higher viscosity. Increasing the temperature in A to 120°C did not seem to have an effect other than increasing the rate of the hydrolysis reactions. A very efficient metal removal was observed when a chelating agent was added in A (A_Q). Some trials showed that splitting the Z stage in a ZEZE-like process (E for alkaline extraction) minimized the impact on pulp viscosity, and that A_QPZE-like sequences can reach a quality comparable to some commercial elemental chlorine free (ECF) pulps.

Keywords: Pulp bleaching; Chlorine-free bleaching sequence; Acid hydrolysis; Ozone; Hydrogen peroxide

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INTRODUCTION

Bleaching hardwood kraft pulp with totally chlorine-free bleaching sequences (TCF) has been the subject of investigation for more than 20 years. In spite of the potential benefits that some TCF sequences may offer in terms of environmental impact, the chlorine-free approach did not develop in the industry, except in some specific cases. The main reason for this indifference is that the resulting viscosity of a fully bleached pulp might be substantially lower for the formerly suggested TCF sequences than for ECF sequences, which is thought to necessarily result in lower paper strength (Rautonen *et al.* 1996; Ek *et al.* 1994; Malinen *et al.* 1994).

The viscosity loss of TCF sequences using ozone is usually attributed to the ozone, as its reaction with lignin generates radicals. Those radicals are highly reactive chemical species that can lead to cellulose depolymerisation (Ragnar *et al.* 1999, 2005). Ozone can also oxidize cellulose, possibly subjecting it to subsequent depolymerisation under alkaline conditions.

The goal of this research was to decrease the viscosity loss during TCF bleaching of hardwood kraft pulp (here exemplified by eucalyptus kraft pulps) to meet the market standards. The limitation of the ozone charge and a better understanding of the ozonation effect on pulp components might be the keys to minimizing this problem.

EXPERIMENTAL

Oxygen-delignified eucalyptus (hybrids between *Eucalyptus grandis* and *Eucalyptus urophylla*) kraft pulps were provided by a Brazilian pulp mill (Table 1).

The conditions used for the different stages composing the sequences are listed below in Table 2. The reagents are given on an oven-dried basis.

Table 1. Pulp Samples

Pulp	DP	Kappa Number	HexA content ($\mu\text{eq/g}$)
Sample #1	1630	9.3	71.7
Sample #2	1660	11	64.5

Table 2. Conditions Used During Bleaching Stages

	pH	Temp ($^{\circ}\text{C}$)	Consistency	Time	Reagents
E	>10	70	10 %	1h	2% NaOH
P	>10	90	10 %	2h	2% NaOH 2% H ₂ O ₂
Z	2.5	25	40 %	N/A	0.6% O ₃
Z (multistage)	2.5	25	40 %	N/A	0.3% O ₃
A	3	90	10 %	3h	H ₂ SO ₄
A _{Q,hot}	3	120	10 %	1h	H ₂ SO ₄ 0.3% EDTA
A _Q	3	90	10 %	3h	H ₂ SO ₄ 0.3% EDTA
Q	5-6	90	10 %	0.5h	0.3% EDTA

Prior to the ozone treatment, the pulp was acidified to pH 2.5 with sulfuric acid, centrifuged to reach a consistency of 40%, and then fluffed. The ozonation was then performed in a rotating spherical reactor. The quantity of ozone is expressed as a percentage of ozone charge on an oven-dried basis.

For the other stages, the temperature was controlled using a thermostated bath, with the reactions taking place in polyethylene bags.

The following procedures were used for pulp characterization: Kappa number (ISO 302-1981), viscosity (ISO 5351/ 1-1981), given here in terms of DP, and brightness (ISO 3688 – 1977). The hexenuronic acid content was measured according to the procedure described by Chai and Zhu (1999). The metal ion content was measured using X-ray fluorescence.

Free phenolic groups in the pulp were measured using a method based on their selective oxidation by chlorine dioxide at 0 $^{\circ}\text{C}$ and on the measure of its consumption by the pulp. This method was developed by Delmas *et al.* (2009), and the results will be referred to here either as the phenol index (Table 4) or as the chlorine dioxide consumption (Fig. 5).

RESULTS AND DISCUSSION

Ozone Effect on Wood Pulp Components

Ozone can react with lignin and polysaccharides in pulp. The reaction can be direct or indirect (through the creation of radicals). Among the polysaccharides, ozone is

said to react heavily with the hexenuronic acids (HexA) (Wennerström 2002). Ozonation also induces the depolymerisation of cellulose. This degradation might mainly be due to radical compounds (Ragnar *et al.* 1999, 2005), which are generated by reactions between ozone and lignin (Magara *et al.* 1996). The cellulose might also be degraded by a direct action of the ozone (Godsay and Pearce 1985; Johansson *et al.* 2000).

According to the literature, ozone reacts faster with HexA than with lignin (Ragnar 2001), and reacts faster with lignin than with cellulose (Eriksson and Gierer 1985). The goal of this study was first to investigate the order of the reactions that occur during ozonation.

Figures 1 through 6 correspond to one of the oxygen-delignified eucalyptus pulps treated with increasing charges of ozone, from 0.15% to 2%, at high consistency (40%). The effect of ozone on the main pulp components was followed by the measure of Kappa number, DP of cellulose, brightness, and HexA content.

Figure 1 shows the efficiency of HexA removal with ozone, as suggested in the literature. All of the HexA was removed at charges of ozone higher than 1% on pulp; however, this does not imply that the HexA were the only targets of the ozone and that other reactions were not taking place simultaneously.

Figures 1 and 2 clearly show the parallel evolution of the Kappa number and the HexA content, suggesting the predominance of the HexA content as a contributor to the Kappa number, as expected from the literature (Costa and Colodette 2007). The halt in the Kappa decrease (beyond 1% ozone on pulp) can be correlated to the total removal of HexA.

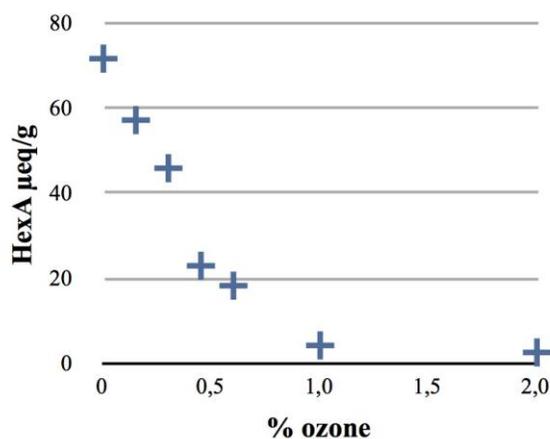


Fig. 1. HexA content against ozone charge for oxygen-treated eucalyptus kraft pulp (sample 1)

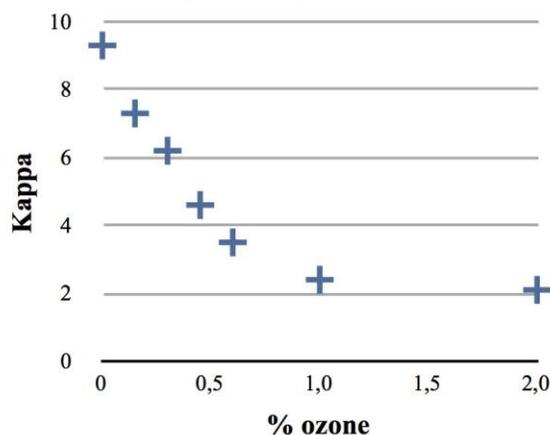


Fig. 2. Kappa against ozone charge for oxygen-treated eucalyptus kraft pulp (sample 1)

The contribution of the HexA to the Kappa number can be found in the literature. Values of the order of 1 Kappa unit per 10 $\mu\text{mol/g}$ HexA were found (Da Silva *et al.* 2002; Vuorinen *et al.* 1996; Li and Gellerstedt 1997). This contribution is measured later in this paper and approaches this value (1 Kappa unit per 9.93 $\mu\text{mol/g}$ HexA).

Figure 3 is obtained by putting together Figs. 1 and 2 and this new value. The lignin contribution was calculated as the difference between the two.

According to this new figure, the lignin contribution to the Kappa number seems to be constant, and the decrease in Kappa number can be explained totally by the HexA removal.

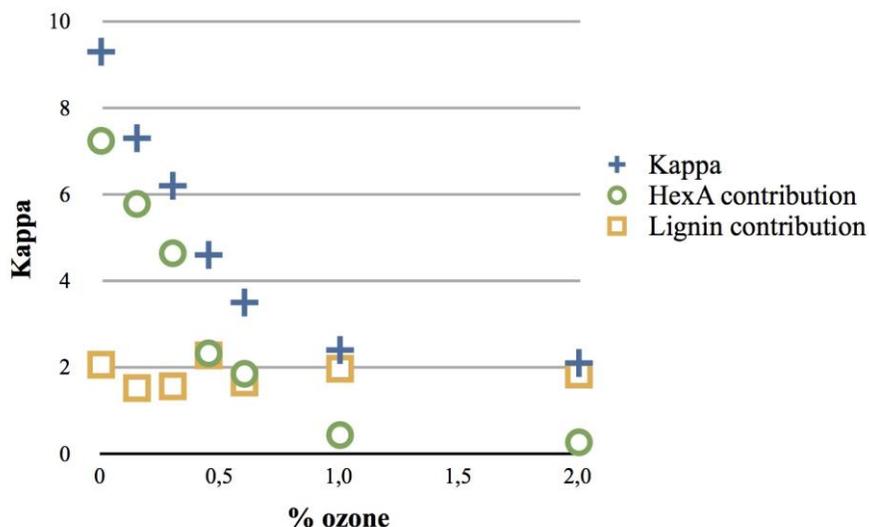


Fig. 3. Kappa, HexA, and lignin contributions to Kappa against ozone charge (sample 1)

The steadiness of the lignin contribution to Kappa does not imply that lignin is not attacked by the ozone. The first clue of modification of the lignin during the ozonation is given in Fig. 4, as the sharp, continuous, and instantaneous increase in brightness can be explained by an oxidation of the lignin chromophores.

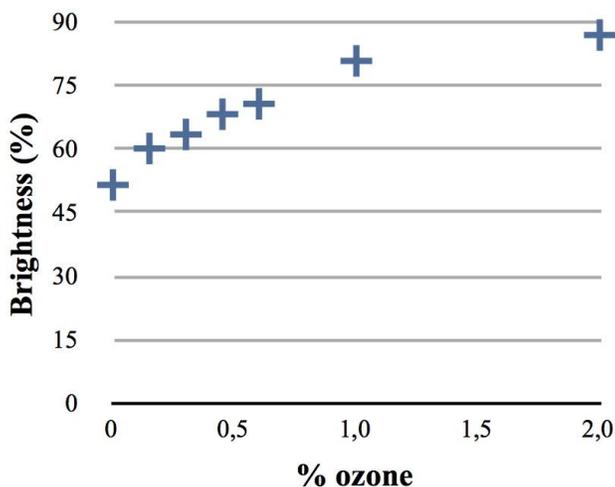


Fig. 4. Brightness against ozone charge for oxygen-treated eucalyptus kraft pulp (sample 1)

A more direct proof of the action of ozone on lignin can be seen in Fig. 5. The method developed by Delmas *et al.* was used to follow the amount of phenolic groups in the pulps. The measure was carried out with chlorine dioxide and under specific conditions in which this reagent is supposed to react mainly with phenolic groups. The higher the reacted reagent, the higher the phenolic content. Figure 5 shows that the amount of phenolic groups gradually decreased during ozonation. This could be explained by a modification of the lignin or by a decrease in the lignin content.

One possible explanation for the constant lignin contribution is that most of the oxidized lignin stays in the pulp after ozonation (Lachenal *et al.* 1994), in spite of extensive washing with water, contributing to the Kappa number to the same extent (Brogdon *et al.* 2002). This result is in accordance with the fact that ozonation creates carboxyl groups on lignin without any substantial depolymerisation (Lachenal *et al.* 1994) and that most of the residual lignin would be linked to carbohydrates (Axelsson *et al.* 2005).

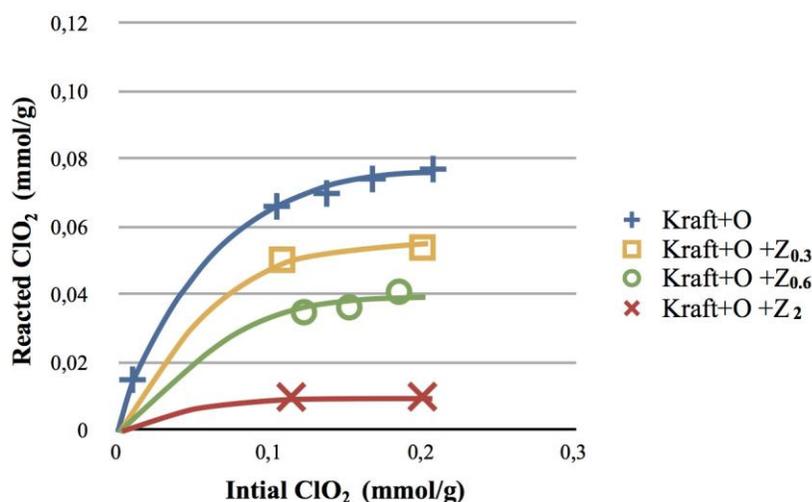


Fig. 5. Chlorine dioxide consumption under specific conditions of non-ozonated kraft+oxygen pulp and ozonated pulps (ozone charges: 0.3, 0.6, and 2%) (sample 2)

Figure 6 shows the evolution of the DP of cellulose during ozonation. The decrease of the DP before 0.5% of ozone is too high to be caused only by the direct action of ozone on cellulose. Since it is known that the reaction of ozone and lignin gives radicals, and that radicals can react with cellulose, the high DP decrease is consistent with an attack of the lignin by the ozone at very low ozone charges.

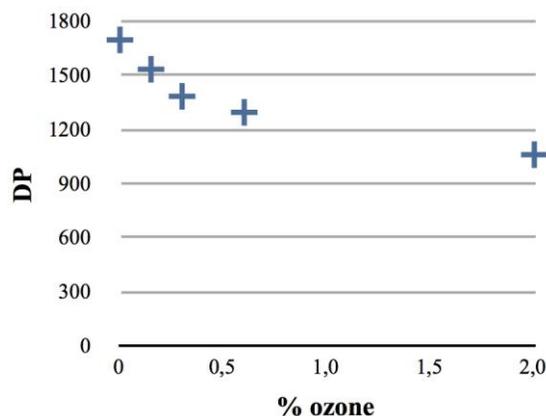


Fig. 6. DP against ozone charge for oxygen-treated eucalyptus kraft pulp (sample 1)

One way to lower this effect is presented in Table 3. The results in Table 3 show that splitting ozone into two stages leads to a higher brightness and a higher DP for a given global ozone charge. Some references have suggested that running ozone as a multistage sequence would yield to such results (the brightening efficiency and DP preservation is mentioned by Allison (1982), the decrease of the ozone requirements by Rothenberg *et al.* (1982), and the higher delignification by Liebergott and Van Lierop (1981)). The removal of some of the partially oxidized lignin in an E stage can be seen as the main explanation if one admits that ozone reactions with the partially oxidized lignin generate radicals. This ozone reaction with the oxidized lignin might also happen early in the ozonation, being a source of ozone loss.

Table 3. Pulp Samples (sample 1)

	Brightness	DP
ZE	64.4	1181
ZEZE	73	1337

A Stage Effects and Improvements

The results obtained above indicate that a substantial part of the ozone is consumed by the HexA. Removing the HexA may contribute to a reduction of the required ozone charge in the bleaching sequence.

Implementation of an A stage (with sulphuric acid as the only reagent) was first proposed in the early 1990's (Maréchal 1993). It was then clearly demonstrated that the effect of A was essentially the removal of the HexA groups located on the xylan chains.

Sulphuric acid reacts with HexA. Some studies suggested, however, that LCC (ligno-carbohydrate complexes) and lignin might be somewhat affected (Bose *et al.* 2011; Uno and Iimori 2006; Clavijo *et al.* 2012; Eriksson and Gierer 1985). The effect of the A stage was revisited in the case of the oxygen-delignified eucalyptus kraft pulp (sample n° 2) for various sets of conditions (pH, temperature, and time).

Figure 7 shows that a high removal of the HexA can be obtained under mild conditions (pH 3, 90°C) if the A stage is long enough. More than 7 hours are required to obtain an extensive removal of the HexA.

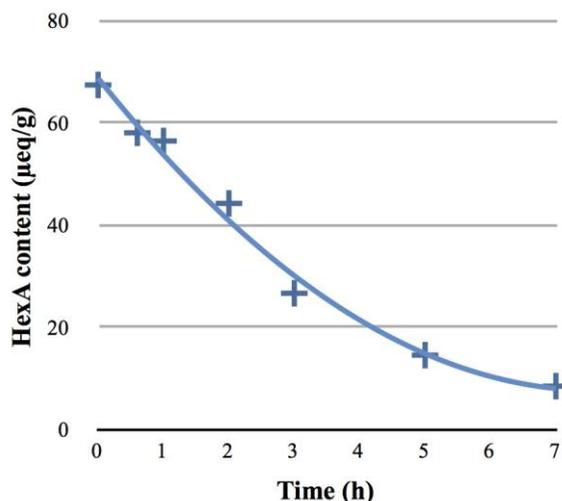


Fig. 7. HexA content against time spent in an A stage (pH of 3, 90°C, pulp sample 2)

The effect of A on lignin used to be considered as null. It is generally admitted that the loss in lignin, if any, should be marginal under typical A conditions. If so, by plotting Kappa against HexA content after A, one can determine the contribution of HexA to the Kappa number. According to Fig. 8, 9.93 $\mu\text{mol/g}$ of HexA contributes to 1 Kappa unit.

Using again the method described by Delmas *et al.* (2009) to obtain the results in Table 4, it can be seen that the A stage slightly reduced the content of phenolic groups (expressed as phenol index) in the pulp. It is concluded that some dissolution of phenolic fragments (possibly lignin fragments) occurred during A.

It was shown in the literature that more lignin could be removed at higher temperatures (Clavijo *et al.* 2012). However, the phenol index obtained in this study for an A stage at a 120°C was the same as that obtained for an A stage a 90°C.

Table 4. Phenol Index Under the Conditions Described by Delmas *et al.* at an initial ClO_2 Charge of 0.2 mmol/g ClO_2 (sample 2)

Pulp	Phenol Index
Kraft+O	0.077
Kraft+O + Z _{0.6}	0.040
Kraft+O + A	0.069
Kraft+O + A _{Q,hot}	0.070

Results in Fig. 8 show that for a given HexA content, the Kappa is roughly the same, regardless of the conditions of the A stage.

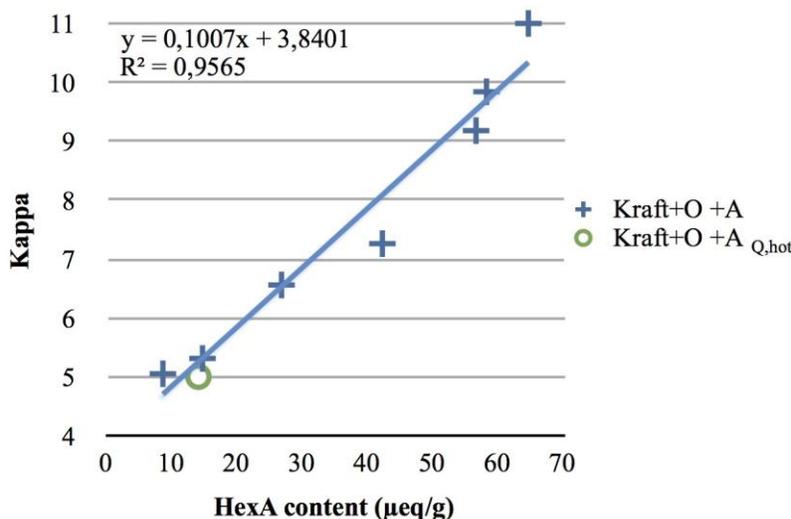


Fig. 8. Kappa against HexA content for conventional A stages (90 to 95°C, pH of 3 to 3.5, 1 to 7 hours) and A stage at higher temperature (A_{Q,hot}, 120°C) (sample 2)

Figure 9 shows that the A stage induces some degradation of the cellulose, and a given decrease of the HexA content seems to invariably lead to a given DP loss under all conditions tested.

As a conclusion, this A stage at higher temperature (120°C) does not seem to be more efficient than a conventional A stage; it is just faster.

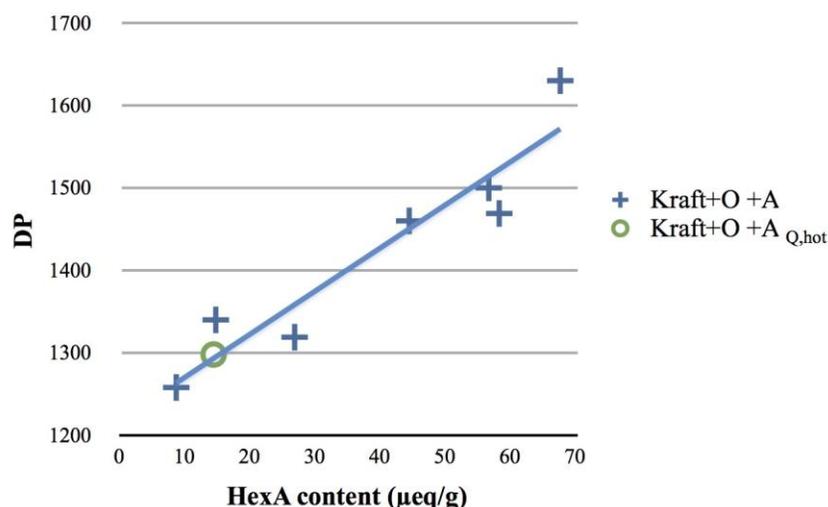


Fig. 9. DP against HexA content for conventional A stages (90 to 95°C, pH of 3 to 3.5, 1 to 7 hours) and A stage at high temperature (sample 2)

In spite of the detrimental effect on the DP, adding an A stage at the beginning of a chlorine-free sequence containing ozone improves the bleaching process dramatically, as shown by the results in Table 5. The A stage is already implemented in ECF sequences in the industry (Bose *et al.* 2011).

Table 5. Sequence Results (sample 1)

	Brightness	DP
Z _{0.6} E	64.4	1181
AZ _{0.6} E	80.9	1197
Z _{0.3} EZ _{0.3} E	73	1337
AZ _{0.3} EZ _{0.3} E	83.9	1254
Z _{0.6} EP	80	757
AZ _{0.6} EP	88.5	838

When using the same chemical charge in Z, E, and P stages, and while the DP loss is of the same magnitude, a higher brightness can be reached with sequences containing an A stage. This higher brightness is evidently due to the fact that more ozone is available for the delignification in the absence of part of the HexA. The positive effect of A on the final DP is quite interesting. One might have expected a lower DP value, since A itself does have a negative impact on the DP and since more ozone would be available to attack the lignin and the cellulose in the absence of at least part of the HexA. The exact mechanisms have yet to be fully understood.

The sequences containing an A stage can be further improved by modifying the A stage. It is well documented that metals in pulps are detrimental during a P stage, even if they are not in the Z stage (Ragnar *et al.* 1999). The catalyzed degradation of peroxide by metals yields the formation of radical compounds (Lachenal *et al.* 1994), inducing a degradation of the cellulose chains. As P is a key stage in a TCF sequence, removing those metals is compulsory to reduce the loss in pulp quality. To remove those metals,

some stages can be used, including chelation stages (Q stages), or A stages, as HexA are metal binding sites (Vuorinen *et al.* 1996).

Table 6. Metal Ion Content after Treatments (sample 2)

Pulp	O	OA	OQ	OA _Q
Fe (ppm)	20	5	<5	<5
Cu (ppm)	5	<5	<5	<5
Mn (ppm)	20	10	<5	<5
* A _Q : A stage with addition of EDTA				

Table 6 shows that the removal of metals can be carried out with a higher efficiency due to the adjunction of a chelating agent in A stages. This A stage with EDTA, A_Q, removes the metals more extensively than A or Q.

Rationalization of the Sequence

The previous results make it possible to rationalize the design of totally chlorine-free sequences, which would minimize the viscosity loss.

The complete removal of the HexA is a necessity since they are said to be directly or indirectly responsible for poor brightness stability (Buchert *et al.* 1997; Cadena *et al.* 2010; Eiras and Colodette 2005). In a TCF sequence the ozone stages are currently the only ones in which the HexA can be removed (O and P (Bergnor-Gidnert *et al.* 1998) stages have no effect). The higher the HexA, the greater the ozone charge required, and therefore the higher the chances of cellulose degradation by direct action of ozone on the cellulose or by indirect action of ozone with lignin and lignin degradation products (possibly generating radicals). As HexA can be removed by acidolysis (Vuorinen *et al.* 1996), the implementation of an A stage to attack at least part of the HexA before the ozone application is justified (Shackford *et al.* 2011). The A stage has to be placed before the ozone stage. A chelating agent is advantageously added (A_Q).

Various stages can be carried out after A_Q, with P and Z being two candidates. As previously seen, the Z stage is likely to react with the free phenolic groups, which are the only lignin structures known to react with peroxide. Additionally, the amount of free phenolic groups after A was proven to be higher than after Z (Table 4). As a consequence, the P stage should come before the ozone stage, as the reactivity of peroxide is likely to be higher after an A stage than after a Z stage.

Two other advantages can be seen in this specific layout. Firstly, the peroxide benefits from the good metal removal of the A_Q stage. Secondly, less lignin is susceptible to react with ozone, leading to a lower amount of radicals (this specific benefit has yet to be quantified).

Consequently, A_QPZE-like sequences were tried, both with and without Z multistage. Results are given in Table 7. Those results show that the rationalization of the sequence led to a promising layout. The pulps of the A_QPZEZE type sequence had almost the same DP and brightness than an ECF_Z sequence. The brightness of this last sequence could be further improved with SO₂ washing, leading to a pulp of comparable quality.

Table 7. New Sequence Results (sample 1)

	Brightness	DP
A _Q PZ _{0.6} E	84.8	1165
A _Q PZ _{0.3} EZ _{0.3} E	89.1	1087
A _Q PZ _{0.3} EZ _{0.3} E + SO ₂ Washing	91	1087
ECF _Z *	91.5	1130

* ECF_Z stands for a commercial pulp bleached by ECF sequences containing an ozone stage

CONCLUSIONS

1. When a Z stage is performed directly on a eucalyptus oxygen-delignified pulp, it is observed that both lignin and HexA are attacked at the beginning of the treatment.
2. While the HexA are progressively removed, the lignin tends to stay in the pulp, even after very high ozone charges (2% on pulp) and even if it is oxidized.
3. Ozone reacts with free phenolic groups. This result leads to a rethinking of the appropriate design of totally chlorine-free bleaching sequences.
4. An A stage can remove a high proportion of the HexA without degrading the pulp substantially. Implementing A in a sequence seems to have a positive impact on the DP, for which the reasons are under investigation.
5. The only difference found so far between a conventional A stage and an A_{hot} stage is the speed of the reactions.
6. A very efficient removal of pulp metals is observed when a chelating agent is added in A, which is essential in a P delignification stage.
7. Some trials showed that A_QPZE-like sequences can reach a quality comparable to some commercial ECF pulps.

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