

HIGH TEMPERATURE CHLORINE DIOXIDE BLEACHING OF HARDWOOD KRAFT PULP

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ABSTRACT

High temperature (95°C) ClO₂ delignification is shown to be more efficient than a conventional D stage performed at lower temperature (45°C). With hardwood kraft pulp, 20% ClO₂ can be saved to reach the same DE kappa number, provided that the time in D is long enough (1.5-4 hrs).

This would be due to the effect of the acid medium, which at 95°C degrades the hexenuronic acids and may also affect the lignin structure. This is confirmed by the fact that a AD sequential treatment where a hot acid stage precedes a conventional D stage gives a similar result.

Another way to achieve the same improvement is to raise the temperature to 90-100°C at the exit of the conventional D stage and to maintain it for several hours.

INTRODUCTION

In most of the kraft mills worldwide, chlorine dioxide has been or will be soon substituted for chlorine. This change makes it possible to meet the regulations on AOX at a moderate investment cost. However, moving to 100% chlorine dioxide substitution represents a costly change since active chlorine in ClO₂ is about 3 times as much expensive as in Cl₂.

Therefore there is a real incentive to minimize the ClO₂ consumption. Several possibilities exist. One is the implementation of a (DZ) stage as described in previous papers (1,2). Several mills are already experiencing this chlorine dioxide - ozone combination (3). An alternative is the reinforcement of the alkaline extraction stages by addition of oxygen, and optionally hydrogen peroxide, coupled with an increase in temperature (4). These modifications lead to substantial savings in ClO₂ and globally to a net decrease in chemical cost. Another possibility is presented in this paper. It is based on the beneficial effect of a hot acid stage on the bleaching of hardwood kraft pulps (5).

EXPERIMENTAL

An oxygen bleached mixed hardwood kraft pulp of kappa number 8.9 was used in this study. The chlorine dioxide stages (D) were performed in polyethylene bags. For D retention time lower than 1 hr, the pulp was preheated before applying ClO₂. For the other cases, ClO₂ was added to the pulp at room temperature.

RESULTS AND DISCUSSION

Effect of a A stage

The effect of a A stage on kappa number was clearly shown in our previous papers (5,6) and in more recent work performed at other places (7,8). Kappa number decreased by several units. However the effect was more pronounced for hardwood than for softwood kraft pulps.

Analysis of A effluent indicated that some products absorbing in the UV region were liberated during the acid treatment (5). Most of them were of carbohydrate origin and were identified as furan derivatives. 2-furancarboxylic acid was by far the most abundant. No lignin degradation products were observed. The kappa number loss was explained by the degradation, during the A treatment, of the hexenuronic groups present in xylans. The conditions under which these groups were selectively and quantitatively attacked were shown to be 2-4 hours at pH 3 or higher and 90-110 °C (5,7).

The fact that no lignin degradation products were produced during a drastic A stage did not mean that residual lignin was left intact. Actually lignin analysis before and after A indicated that some residual β O4 ether linkages were cleaved. This resulted in a slightly higher number of free phenolic groups (6).

Combining ClO₂ and A effects in a D stage.

Whatever the mechanism by which a A stage contributes to easier bleaching, a prerequisite is to apply the acid conditions during at least one hour and preferably several hours at a temperature close to 100°C. The pH of a standard D stage may be easily adjusted to correspond to that of an efficient A stage. Performing the D stage at 90-95°C should then offer the required conditions for A, provided that the time is long enough. This approach differs notably from that described in (9) where ClO₂ was used at high temperature in order to reduce the retention time.

Table 1 shows the effect of increasing the retention time in a D stage performed at 95°C, on the mixed hardwood kraft pulp (oxygen pre-bleached). ClO₂ was entirely consumed after a few minutes, which was expected. Despite that, the kappa number continuously decreased when the time was increased. This clearly showed that the kappa decrease was very likely due to the acid conditions prevailing during the D stage.

Table 1. High temperature (95°C) D stage applied to an oxygen delignified mixed hardwood kraft pulp (initial kappa number 8.9). Effect of time on kappa number after D and DE.

Time, min	15	30	60	90
Final pH	2.3	2.2	2.2	2.3
ClO ₂ consumed, %	100	100	100	100
Kappa number after D	3.8	3.2	3.0	2.4
Brightness after DE, %	72.1	72.3	72.8	73.3
Kappa number after DE	3.4	3.2	2.8	2.2
Viscosity after DE, mPa.s	20.0	20.0	19.5	19.0

D : 1% ClO₂ (chlorine multiple of 0.3), initial pH 3.0 (adjusted with H₂SO₄), 10% consistency, initial pulp viscosity, 21 mPa.s ; E : 1.1% NaOH, 120 minutes, 70°C, 10% pulp consistency

Table 2. Effect of temperature on D stage.

Oxygen delignified mixed hardwood kraft pulp (initial kappa number 8.9).

Temperature, °C	45°C			95°C		
ClO ₂ , %	0.7	1.0	1.3	0.7	1.0	1.3
Final pH	2.5	2.3	2.2	2.4	2.3	2.2
ClO ₂ consumed, %	100	100	97	100	100	100
Kappa n° after D	3.7	2.9	2.5	3.2	2.4	1.8
Brightness after DE, %	73.4	74.8	75.8	70.2	73.3	75.0
Kappa ° after DE	3.4	2.6	2.1	3.0	2.2	1.6
v after DE, mPa.s	20.5	20.5	20.0	19.5	19.0	19.0

Time of D : 90 min. Other conditions as in Table 1.

Table 2 shows the effect of temperature on the efficiency of D on the same pulp as before. Several ClO₂ charges were applied. 95°C gave better results than 45°C. Differences of 15 to 20% were observed on kappa numbers after DE which represented a substantial improvement. However the brightness after DE tended to be adversely affected by the increase in temperature. Pulp viscosity did not suffer from the high temperature. Full bleaching was performed (**Table 3**). 15% of the ClO₂ could be saved by the increase in temperature, despite the lower brightness after DE.

Table 3. Full bleaching of an oxygen delignified mixed hardwood kraft pulp (initial kappa n° 8.9) by D₀ E D₁. Effect of temperature in Do.

Temperature, °C	45°C	95°C	95°C
ClO ₂ in Do, %	1.3	1.0	1.0
initial pH	3.0	3.0	3.0
time, min	90	15	90
ClO ₂ consumed in Do	1.3	1.0	1.0
final pH	2.5	2.3	2.3
Brightness, DoE	75.9	72.1	73.3
Kappa DoE	2.1	3.4	2.2
ClO ₂ in D ₁ , %	0.70	0.70	0.70
ClO ₂ consumed in D ₁ , %	0.67	0.70	0.68
Final brightness, %	89.3	87.1	89.2
Total ClO ₂ consumed, %	1.97	1.70	1.68
viscosity, mPa.s	20.0	20.0	19.0

Other conditions as in Table 1.

Table 4. High temperature (95°C) long retention time D stage. Comparison with AD. Oxygen delignified mixed hardwood kraft pulp (initial kappa n° 8.9)

Temperature, °C	45	95	95	95
Time, h	1.5	1.5	3	2 + 1
	(D)	(D)	(D)	(A)+(D)
ClO ₂ , %	1	1	1	1
ClO ₂ consumed, %	1	1	1	1
final pH	2.5	2.3	2.4	2.3
DE brightness, %	74.8	73.3	72.3	69.9
DE kappa number	2.6	2.2	1.8	1.8
viscosity, mPa.s	20.5	19.0	18	18.5

Other conditions as in Table 1.

A : 10% consistency, initial pH = 3. No washing between A and D.

More important savings were achievable if the retention time was extended to several hours. **Table 4** illustrates this point. It also shows that a 3 hr D stage was equivalent to a 2 hr A stage followed by a 1 hr D stage, confirming that high temperature D could combine A and ClO₂ effects if the time was long enough. In mills having such a high retention system it is estimated that up to 25% ClO₂ can be saved.

Practical Considerations

Implementing a high temperature D stage is not expected to present any serious technical problem. However some potential difficulties have to be considered:

- a temperature of at least 90°C and preferably higher than that seems to be required to maximize the effect of the acid conditions. In this respect the situation may be more favorable after oxygen bleaching where temperature is already close to this level;

- potential yield loss during a hot D stage may be a concern. Actually, close examination of yield data after DE makes it possible to conclude that yield penalty should not be higher than 0.2% (on wood) if any. **Table 5** gives some typical data obtained with the mixed hardwood kraft pulp;
- control of a high temperature D stage could be more difficult. One reason is the non-classic evolution of brightness which actually decreases when the time is extended. How serious this problem could be in some mills is not known. If necessary, the concept developed here can be implemented in another way. **Table 6** shows that the same result is obtained when the D stage is carried out in standard conditions (45°C in this example) and temperature is raised to 95°C after chlorine dioxide consumption and kept at this level for enough time (DA process). In this situation, steam must be added at the exit of the D tower and enough residence time must be given to the pulp in another tower;
- softwood kraft pulp should be less reactive to the hot acidic conditions (5) and consequently the high temperature D process should have less interest. This is still under investigation.

Table 5. Yield of DE bleaching *.

ClO ₂ , %	0.86	0.86
Temperature, °C	45	95
Time, h	1	3
NaOH, %	1.5	1.5
Temperature, °C	70	70
DE yield, %	95.8	95.4
DE kappa number	3.0	2.0

* average of 10 experiments

Table 6. Comparison between high temperature D and DA (D at low temperature).

	D	DA*
ClO ₂ , %	0.86	0.86
Temperature, °C	95	45°C-95°C
Time, h	3	1 + 3
DE kappa number	2.0	1.8
DE Brightness, %	71.8	72.5

*temperature raised to 95°C at the end of D without any other change

CONCLUSION

The beneficial effect of a hot acid stage (A) carried out ahead of a bleaching sequence may be due to dissolution of hexenuronic acids and to modifications to the lignin structure.

High temperature (95°C) ClO₂ treatment represents an attractive way of performing both A and D in the same stage without any need of extra acid except from that already present in a ClO₂ delignification.

Time must be long enough (1.5 to 4 hrs) to see a substantial effect. Compared to conventional practice, the high temperature D process applied on a hardwood kraft pulp reduced the ClO₂ requirement by 15 to 25% for the same final brightness and viscosity.

Another way to achieve the same improvement is to raise the temperature to 90-100°C at the exit of a conventional D stage and to maintain it for several hours.

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