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FUTURE CHALLENGES IN CHEMICAL PULP BLEACHING.

Dominique LACHENAL, Christine CHIRAT and Yahya HAMZEH.

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Resume

Le blanchiment par le dioxyde de chlore est un procédé éprouvé, utilisé partout dans le monde pour blanchir la pâte chimique. Cependant l'examen des performances du procédé fait apparaître que les deux tiers du réactif appliqué sont perdus dans des réactions secondaires sans effet sur le blanchiment. Ce problème pose un défi aux chimistes du blanchiment et aux fournisseurs de technologie. Dans ce papier plusieurs approches ont été étudiées dans le but de minimiser la perte en dioxyde de chlore.

Il est également montré que l'ozone constitue aujourd'hui une alternative sérieuse au dioxyde de chlore. Le remplacement de ce dernier par de l'ozone permet de rendre la délignification et le blanchiment plus efficaces. Des exemples l'illustrent et montrent de plus que l'application de l'ozone est un procédé simple, suggérant que ce dernier pourrait être l'agent de blanchiment du futur.

Summary

Chlorine dioxide bleaching is a well proven technology which is today universally used in the pulp industry. However a close examination of the performance of the process shows that about two thirds of the chlorine dioxide is wasted in useless side reactions. This fact represents one major challenge facing the lignin chemists and the equipment suppliers. Several process modifications are proposed to minimize this problem.

Moreover ozone represents today a serious alternative to chlorine dioxide. For many reasons the replacement of some chlorine dioxide by ozone should be beneficial not only to the delignification rate but also to the brightness development. Some simple ways to introduce ozone in bleaching sequences are described. The interest of the results suggests that ozone could well be the bleaching chemical of the future.

Introduction

In many kraft mills chlorine dioxide (ClO_2) has been substituted for chlorine in the bleaching process. Then the whole bleaching sequence is based on the use of ClO_2 only (DEDED type process) even though some oxygen and hydrogen peroxide are often added to the process to reinforce the extraction stages. Therefore the bleaching chemistry can be summarized by the reaction of ClO_2 on lignin.

Oxidation of lignin with ClO_2 has been the subject of numerous investigations. Despite the occurrence of several side reactions it seems that the main mechanism is the ring opening of the free phenolic groups according to figure 1 (1).

AUTHORS : DOMINIQUE LACHENAL, CHRISTINE CHIRAT AND YAHYA HAMZEH,
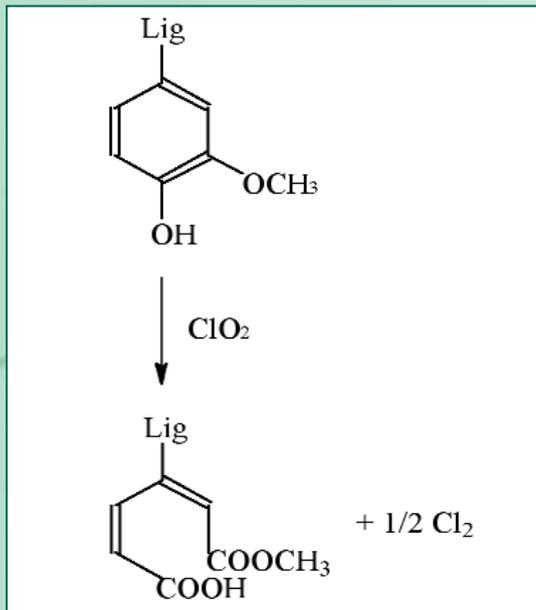*Ecole Française de Papeterie et des Industries Graphiques - France.*

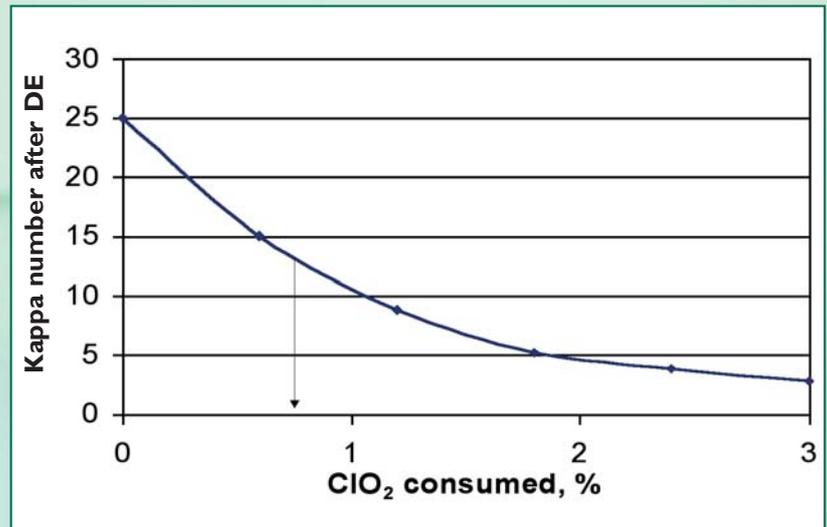Figure 1. Global reaction of ClO_2 with lignin units.

Figure 2. Kappa number loss after DE as a function of the ClO_2 consumed (same pulp sample as in Table 1, D stage: 70°C, 10% consistency for 1h,; E stage: %NaOH = % act.chlorine/2, same conditions as D).

During this reaction some elemental chlorine is generated and is responsible for the formation of AOX. Chlorine would also form new free phenolic groups on the lignin which would assist the ClO_2 reaction on non-phenolic units. The ester group does not resist alkaline extraction and two carboxylate anions are formed.

The creation of carboxyl groups is enough to explain lignin removal in aqueous medium. Then supposing that all the aromatic rings must be opened to make lignin soluble, one mole of ClO_2 (67.5 g) should remove about 200 g of lignin, or 1 g ClO_2 would be required to dissolve 3 g of lignin. Taking a pulp of kappa number 25, which still contains 3.7% lignin, a total charge of 1.2% ClO_2 on pulp should produce a fully bleach pulp. Table 1 shows that this ideal situation is far from been approached, since in the present case 3.5% ClO_2 on pulp had to be applied to reach 86% brightness. This indicates that two thirds of the ClO_2 charge is consumed in useless reactions

Sequence	Total ClO_2 charge/o.d.pulp	D_1	D_2	D_3	Brightness, %
	%	%	%	%	ISO
DEDED	3.5	2.1	0.9	0.5	85.3

ClO_2 stages at 70°C, 10% consistency, during 1h, 2h and 3h for D1, D2 and D3 respectively.

Table 1 : DEDED bleaching of a softwood kraft pulp (kappa number 25).

Another way to look at his problem is to consider the curve representing the kappa number drop against the ClO_2 consumed (Figure 2). As the reaction proceeds ClO_2 becomes less and less efficient, showing that ClO_2 is participating in reactions which do not contribute to delignifica-tion.

These facts suggest that although the ECF bleaching process based on the use of ClO_2 seems to be a well proven technology, something goes wrong in the process and a high potential for cost savings should exist. This represents a challenge for wood chemists and equipment suppliers for the coming years.

This paper will present several developments which were investigated in our group and recently proposed as a way to improve the overall performance of the bleaching process.

1. High temperature ClO_2 delignification

In the case of hardwoods it has been shown that a substantial part of the ClO_2 is consumed by the hexenuronic acids (hexA). However it is thought that ClO_2 reacts more easily with the phenolic groups in lignin than with the hexA, as illustrated by the fact that there is still a significant amount of hexA left in a D_1E-treated hardwood kraft pulp(9). Consequently some ClO_2 is also consumed by these acids in D_2 and D_3 ($D_1 E D_2 E D_3$ sequence). What has been proposed by several groups (2, 3) including ours (4), is to destroy the hexe-nuronic acids by a hot acid hydrolysis pretreatment (typically H_2SO_4, 90-95°C, 2-4 h at pH 3-3.5), prior to the D0 stage. Even though positive results are obtained, carrying out a pretreatment represents some complication. What

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we have recently proposed instead, is to perform a high temperature (95°C) ClO_2 stage for 2 to 3 hours (5). ClO_2 is consumed instantaneously. The acidity of the reaction medium takes care of the hexenuronic acids during the retention time. Table 2 illustrates some of the results obtained on a mixed hardwood kraft pulp. Significant kappa abatement was caused by the combination of high temperature and long retention time. An alternative is to perform the D stage at normal temperature and then to inject some steam at the exit of the D tower (to reach 95°C), and leave the pulp in this hot acidic environment for 2-3 hours. Both alternatives provide

Temperature, °C	45	95	95	95
Time, h	1.5	0.25	1.5	3.0
% ClO_2	1	1	1	1
DE kappa number	2.6	3.4	2.2	1.8
DE viscosity,mPa.s	20.5	20.0	19.0	18.0

Other conditions: D: initial pH 3.0, 10% consistency; E: 1.1% NaOH, 60 min, 70°C, 10% consistency
Initial pulp viscosity: 21mPa.s

Table 2 : High temperature ClO_2 delignification; effect of temperature and time on kappa number; mixed hardwood kraft pulp of kappa number 8.9 (oxygen delignified)

15 to 20% savings in ClO_2.

2. ClO_2 splitting with intermediate alkaline extraction

Examination of ClO_2 consumption during D delignification (Figure 2) shows that it is not proportional to the decrease in kappa number. This indicates that after a certain period of time ClO_2 starts to be consumed in non-useful reactions. One probable hypothesis is that ClO_2 reacts with some products of lignin oxidation. In a first step phenol groups in lignin are converted by ClO_2 into muconic acid derivatives. As it has been demonstrated that ClO_2 reacts with hexenuronic acids, it is most probable that ClO_2 reacts also with muconic acid derivatives, the structure of which presents similarities to that of hexenuronic acids (Figure 4). Figure 3, which shows the consumption of a mixture of model compounds simulating the behaviour of residual lignin in a ClO_2 solution, confirms this hypothesis. Actually the consumption of the muconic acid model remains marginal till about 70% of the phenolic compound has reacted. When all the phenolic and non-phenolic compounds have disappeared, around 50% of the muconic acid derivative has reacted. Consequently, during ClO_2 delignification of a kraft pulp, part of the ClO_2 is very likely consumed by the muconic
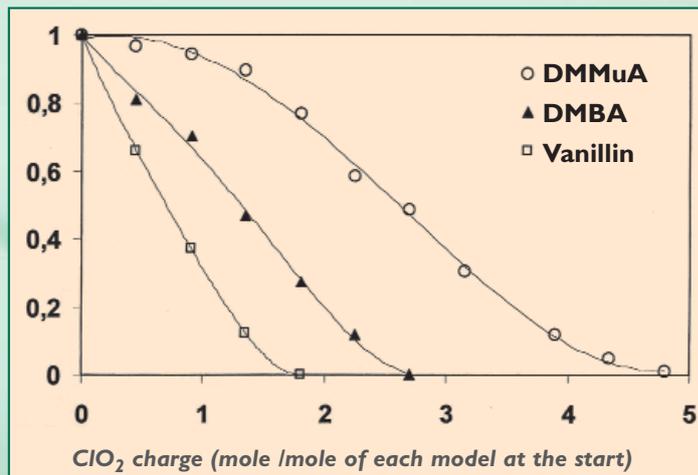

Figure 3. Treatment of an equimolar mixture of 3 model compounds: vanillin (phenolic model), 2, 5-dimethyl muconic acid (DMMuA) and 3, 4-dimethoxy benzilic alcohol (DMBA) (non phenolic) by ClO_2 at 70°C for 30 min. HPLC on a C18 10U ALLTIMA column (inverse phase). Water-CH_3COOH (0.1%)/CH_3CN 90/10 used as solvent. UV detection at 280nm.
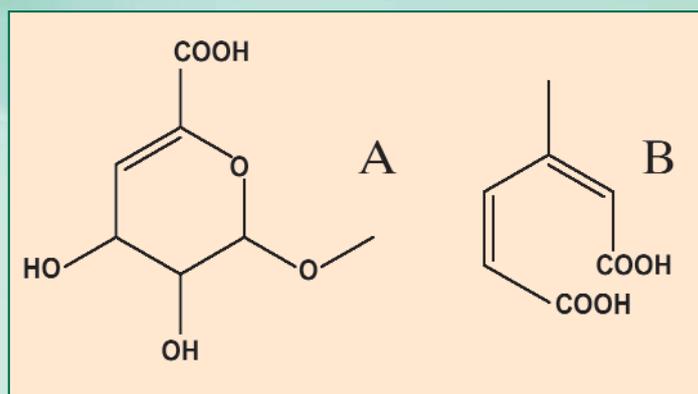

Figure 4. Structure of hexenuronic acid (A) and muconic acid (B) derivatives.

acid derivatives which are continuously formed.
One way to improve ClO_2 delignification would then be to remove the reaction products as often as possible. Ideally the first ClO_2 charge should be limited to values for which the reaction of muconic acid derivatives remains negligible. This principle has been approached by performing the (de)(de)(de)… process (6) where (de) stands for a D step with a low charge of ClO_2 followed by an alkaline extraction phase without any washing between d and e (in order to limit the number of washing stages). Table 3 shows that in this new approach a more efficient delignification is obtained. Full bleaching with (de) (de) (de) D requires about 25% less ClO_2 than with conventional DEDED sequence. Side benefits were observed such as the lower AOX level in the effluent, which may result from the absence of washing between d and e, and thus the occurrence of alkaline hydrolysis of some of the chlorinated

	Total ClO$_2$ charge/o.d.pulp	D$_1$%	D$_2$%	D$_3$%	D$_4$%	Brightness, %ISO
DEDED	3.5	2.1	0.9	0.5	-	85.3
(de)(de)(de)D	2.5	0.6	0.7	0.7	0.5	86.6
(d*e)(de)(de)D	2.5	0.6	0.7	0.7	0.5	86.1

d*: no retention time; other d treatments: 30 min. , 60 min. and 90 min., respectively; last D: 180 min. ;
e treatments: final pH ≥11; all stages at 70°C. Other conditions as in table 2.

Table 3 : ClO$_2$ splitting with intermediate extraction; softwood kraft pulp of kappa number 25.0;

organics (6).
Other details on this process have been published recently (6). Although the investment cost should be higher with this new approach, the difference would be minimized by the possibility of performing the first d step in a mixer and by the absence of any washing between d and e.

3. Final bleaching with ozone

Literature information on the nature of the last chromophores to be removed in a semi-bleached kraft pulp is very poor. One reason must be that it is very difficult to identify chemical groups which are present in minute quantities in the cellulosic matrix. However it is striking to see that the mechanisms described to explain delignification with chlorine, oxygen, chlorine dioxide and hydrogen peroxide mention side routes leading to the formation of quinones. Moreover quinones already exist in the residual lignin of an unbleached kraft pulp. Therefore one may assume that the final chromophores (when the pulp reaches 80-85% ISO brightness) contain quinone groups in their structure. Then the question arises about the suitability of ClO$_2$ to destroy quinones.

A fully bleached pulp was impregnated with p.benzoquinone in order to reach 82.9% ISO brightness. For this purpose a pulp suspension (10%) in 5g/l p.benzoquinone solution was treated at 60°C for 60 min. and then washed with distilled water. Brightness dropped down to 82.9% brightness indicating that some chromophores issued from p.benzoquinone or p.benzoquinone itself had been introduced. This coloured pulp was treated with increasing charges of ClO$_2$ at 80°C for 1 h. Table 4 shows that the initial brightness was difficult to restore. On the contrary, very small ozone charges could destroy the quinone chromophore. Therefore the relevance of the use of ClO$_2$ in final bleaching may be questioned. In this application ozone would be much more efficient (7).

A DEDD bleached hardwood kraft pulp (brightness 83.8%) was impregnated with ozonated water. Ozone concentration in water was 10.5 mg per litre when the ozone gas was dissolved under atmospheric pressure. Concentration went up to 38.4 mg per litre when ozone was pressurized to 4

ClO$_2$, %	-	0.3	0.5	1.0
Brightness, % ISO	82.9	87.0	87.2	87.6
O$_3$, %	-	0.05	0.2	0.5
Brightness, % ISO	82.9	87.6	88.4	89.7

ClO$_2$ conditions : 80°C, 1 h, 10% consistency
O$_3$ conditions : 20°C, pH 3.0, 40% consistency

Table 4 : Bleaching of a fully bleached pulp (89% ISO) impregnated with p.benzoquinone (82.9% ISO)

bars. The ozonated water was mixed with pulp at 3% consistency. Figure 5 shows the effect of time on brightness gain. The ozone dissolved in the 10.5 mg/l solution (0.025% on pulp) was instantaneously consumed which led to an increase in brightness of about 2 units. The same behaviour was observed with a more concentrated solution. 87.5% brightness was obtained in a few seconds with 0.11% ozone on pulp (using the 34.4 mg/l water), which was quite an impressive result.

It is likely that the situation will be less favorable when process water is used instead of pure water, since then impurities could decompose or consume some ozone. In this case it will certainly be more appropriate to apply ozone directly on the pulp under appropriate mixing, thereby minimizing the retention of ozone in the solution surroun-
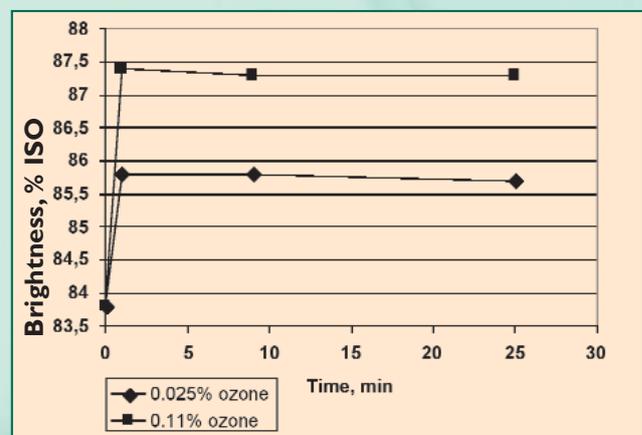

Figure 5. Treatment of a DEDD bleached hardwood kraft pulp with ozonated water (room temperature, neutral pH)

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ding the fibres.

4. Use of ozone in delignification

As mentioned previously, modern ECF sequences rely on the exclusive use of chlorine dioxide. In fact the oxygen stage which is commonly placed ahead the sequence must be seen as a continuation of the kraft cooking. Using a single chemistry to perform the very difficult task of removing all the residual lignin and chromophores of various sorts which may be present in a kraft pulp offers the advantage of simplicity but could be a handicap in terms of efficiency. An example of that was met in the case of final bleaching.

The possibility of applying other chemicals which could assist ClO_2 when it starts to perform less efficiently has been considered. According to what was said before ClO_2 looses its delignination capabilities when it starts to react with the muconic acid derivatives. This would lead to the conclusion that in a D stage the charge of ClO_2 should be limited and the missing oxidation power be brought about by another chemical. For this purpose the best candidate is ozone (Z) for the following reasons.

- on a weight basis ozone is a more powerful oxidant

- ozone reacts well with all the C=C double bonds (contrary to ClO_2)

- ozone, as chlorine dioxide, reacts with the muconic acid derivatives. However ozone cleaves them, which contributes to further delignification

- ozone, contrary to ClO_2 does not form coloured quinone groups when it reacts with lignin

- ozone is very reactive with quinones and, very likely, with most of the chromophores present in kraft pulp .

- ozone does not generate any AOX

- the pH of an ozone stage is compatible with that of a D stage, which facilitates the transition from one chemical to the other.

These considerations open many perspectives which we started to exploit. Replacing D by (DZ) or (ZD) is one alternative (8). Industrial practice showed that 1kg O_3 could replace 1.5-2kg ClO_2. Higher displacement ratios could be contemplated depending on the mill process conditions. Considering the respective cost of the two reagents, some savings in operating cost should be obtained. Washing between Z and D or D and Z is optional.

More generally a Z stage could theoretically be introduced in any ECF bleaching at any place in the sequence. Table 5 compares the delignification power of O_3 and ClO_2 when applied on an unbleached kraft pulp. Ozone treatments were carried out at 20°C and high consistency (35%) in a glass rotating reactor. The chlorine dioxide stages were performed at 70°C in polyethylene bags. In all cases the chemical consumption was almost equivalent to the quantity applied. The results are expressed as kappa number (KN) abatement per kg of chemical applied per ton of pulp. It appears that Z is more powerful than D in delignification, with a displacement ratio of about 1.5 (in weight). This conclusion is certainly valid in

Δ kappa/kg reagent						
Z	D	ZE	DE	Z	D	DE
Δ KN 30-10	Δ KN 30-10	Δ KN 30-10	Δ KN 30-10	Δ KN 30-20	Δ KN 30-20	Δ KN 30-20
1.5	0.95	2.0	1.4	2.0	1.2	1.5

ΔKN represents the investigated delignification range

Table 5 : Average kappa number loss per kg of chemical applied per ton of pulp.

a large range of delignification rate.

Conclusion

In a conventional ECF bleaching process based on the use of chlorine dioxide, at least 50% of ClO_2 would be wasted in side reactions.

One of them is the reaction with the hexenuronic acids present in substantial quantity in unbleached hardwood kraft pulps. In this case 20% of ClO_2 can be saved by running the D0 stage at high temperature (90°C or higher) for several hours.

In the general case it is thought that some ClO_2 is consumed by the degradation products (muconic acid derivatives) of the reaction of ClO_2 with lignin. ClO_2 splitting with intermediate extraction minimizes this side reaction and makes it possible to save 25% ClO_2. However it is clear that the use of the conventional technology makes it difficult to fully develop the previous concept which implies that reaction products must be removed from the system continuously. More appropriate technologies should be looked for.

Applying ClO_2 at the end of the bleaching sequence does not seem to be the best choice in terms of brightness development. The reason would be the slow and incomplete destruction of quinonic chromophores by ClO_2. Ozone offers a much better potential in that respect. Future developments of ECF bleaching processes should include a more extensive use of ozone. For many reasons ozone could advantageously complement chlorine dioxide in DZ or ZD type treatments using low chlorine dioxide charges. Moreover since ozone is a better delignifying reagent than chlorine dioxide (on a weight basis), separate ozone stages could be introduced anywhere in the sequence and give some cost benefit. The validity of these approaches is already supported by the fact that 28

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