Other ways to use ozone in a bleaching sequence

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ABSTRACT

ECF bleaching sequences of the D_1 EOP D_2 E D_3 type (P in EOP and E between D_2 and D_3 being optional) for softwood and hardwood kraft pulps have been modified by total and partial replacement of chlorine dioxide with ozone in D_1 and D_2 to give Z EOP D_2 E D_3, (D_1Z) EOP D_2 E D_3, and (D_1Z) EOP (D_2Z) E D_3. In these sequences, 1 kg of ozone replaced up to 4 kg of chlorine dioxide, depending on the conditions. AOX formation was decreased, and pulp viscosity was generally maintained.

An ozone stage was also added at the end of the TCF and ECF sequences to increase the final brightness. Ozone charges as low as 0.2% were particularly efficient. Acidification was not needed before ozonation. Pulp viscosity and brightness stability were not affected.

Application:

Ozone may be used in combination with chlorine dioxide, (DZ), in replacing D stages as a means to reduce AOX formation and to save bleaching chemicals. Ozone may also be used as a final bleaching stage to rapidly increase the final brightness by 2–3 units.

OZONE IS NOW BEING USED AS A bleaching agent in both elemental chlorine-free (ECF) and totally chlorine-free (TCF) sequences in several mills *(1)*. Its strong delignification ability and rapid reaction rate makes ozone a good candidate to replace chlorine, which is being phased out for environmental and marketing reasons.

Ozone is normally better used in the beginning of a bleaching sequence, where its delignification efficiency is the best and where the degradation of cellulose is retarded by the high amount of lignin still present in the pulp. When ozone is used later in a bleaching sequence, its charge is usually limited to very low amounts (lower than 0.5%); otherwise significant degradation of cellulose can occur.

So far, the main justification of using ozone has been mainly to complement oxygen (and peroxide) delignification either in TCF or ECF sequences. In TCF sequences, fully bleached pulp could then be produced. In ECF sequences, ozone made it possible to further extend the chlorine-free part of the sequence.

In this work, we have been investigating two other possible applications of ozone. The first one consists of replacing part of the chlorine dioxide (D) by ozone (Z) in various ECF sequences. In this respect, the combination of chlorine dioxide and ozone in one stage (DZ) is also considered. The second application deals with the use of ozone as a polishing stage at the end of a bleaching sequence. Indeed, the last points of brightness in a bleaching sequence are sometimes difficult to obtain and usually require residence times greater than 2 hours when hydrogen peroxide (P) or chlorine dioxide (D) stages are used. The high reactivity of ozone could make it a good candidate to be used in a last stage.

RESULTS AND DISCUSSION

Substitution of ozone for chlorine dioxide in various ECF sequences

The replacement of chorine dioxide by ozone was studied in two cases. The first case (see **Table I**) concerns a hardwood kraft pulp bleached by D_1 EOP D_2 D_3, and the second case (see **Table II**) involves a softwood kraft pulp bleached by D_1 EO D_2 E D_3.

Replacing ClO_2 by ozone in the first D_1 stage reduced the amount of AOX considerably. To obtain similar results in final brightness, the replacement ratio of chlorine dioxide by ozone was better for the hardwood pulp than for the softwood pulp. In the case of the softwood pulp (Table II), 1.2% O_3 replaced 1.05% ClO_2, whereas in the case of the hardwood pulp (Table I), 0.6% O_3 replaced 1.31% ClO_2.

The full replacement of the D_1 stage by a Z stage required the use of significant amounts of ozone, which can explain the lower final viscosities. Some experiments, where only a part of the ClO_2 was replaced by O_3, were then carried out. (DZ) stages were performed where D was applied before Z, and no washing was carried out between D and Z. This concept has been previously described by others *(2–4)*. There are several advantages of combining D and Z in one stage. First, one washing step can be avoided. Second, chlorine dioxide stages are acidic; this avoids having to acidify the pulp for the Z stage. Third, ozone has the ability to destroy some AOX that is present in bleaching effluents *(5)*, so one can assume that some of the AOX formed during D may be eliminated by Z. Fourth, the chemistry of ClO_2 and O_3 with residual lignin complement each other *(6)*, which should make (DZ) particularly efficient as a delignifying stage.

Table III presents results for bleaching hardwood pulps using the (DZ) concept. It shows that 0.25% O_3 (consumed) and 1.55% ClO_2 (consumed) in the (DZ) EOP DD sequence

Parameter	SEQUENCE D_1 EOP D_2 D_3	Z EOP D_2 D_3
Chemicals, % o.d.p. (% consumed)		
ClO_2: D_1	1.35 (1.35)	0
D_2	1.00 (0.90)	1.00 (0.99)
D_3	0.25 (0.25)	0.25 (0.25)
Total amount of ClO_2,%	2.65 (2.55)	1.25 (1.24)
O_3, %	0	0.6 (0.56)
DPv (viscosity, mPa·s)	1520 (25.2)	1310 (18.5)
ISO brightness	87.7	87.5
AOX, kg/ton (o.d.p.)	0.80	0.20

*Starting pulp: kappa no. = 14.8, DPv = 1710, viscosity = 33.2 mPa·s. D_1: 50°C, 90 min, 3% consistency. EOP: 70°C, 60 min, 0.3% $MgSO_4 \cdot 7H_2O$, 0.5% H_2O_2, 0.2 MPa O_2, 10% consistency. D_2: 75°C, 90 min, 10% consistency. D_3: 80°C, 180 min, 10% consistency, 0.2% NaOH. Z: 40% pulp consistency, pH = 2.5.

I. Complete substitution of O_3 for ClO_2 in the D_1 stage for the hardwood pulp*

Parameter	SEQUENCE D_1 EO D_2 E D_3	Z EO D_2 E D_3
Chemicals, % o.d.p. (% consumed)		
ClO_2: D_1	2.2 (1.65)	-
D_2	1.5 (1.40)	1.5 (1.50)
D_3	0.5 (0.45)	1.0 (0.95)
Total ClO_2 ,%	4.2 (3.50)	2. 5 (2.45)
O_3,%	0	1.2 (1.17)
ISO brightness	90.8	90.0
DPv	1100	930
Viscosity, mPa·s	13.5	10.5
AOX, kg/ton (o.d.p.)	1.7	0.27

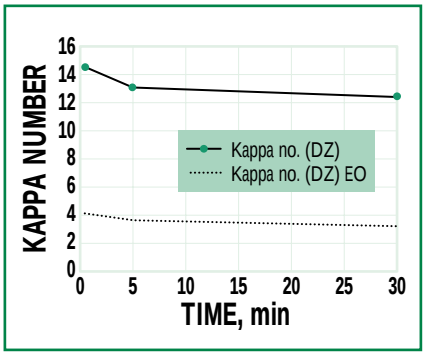
*Starting pulp: kappa no. = 24, DPv = 1480, viscosity = 23.7 mPa·s. D_1: 50°C, 90 min, 3.5% consistency. EO: 3% NaOH, 0.5% $MgSO_4 \cdot 7H_2O$, 0.2 MPa O_2, 70°C, 1 hour, 10% consistency. D_2: 80°C, 120 min, 10% consistency. D_3: 80°C, 180 min, 10% consistency. Z: pH = 2.5, 40% consistency.

II. Complete substitution of O_3 for ClO_2 in the D_1 stage for the softwood pulp*

gave the same brightness as 2.55% ClO_2 in the DEOPDD sequence (Table I). The ClO_2/O_3 replacement ratio is then 4, which is very high. For the higher brightness of 90.2, the replacement ratio was lower (about 2) but still high. Furthermore, since less ozone is needed in (DZ) than in Z, higher viscosities were obtained at a given final brightness of 88. The AOX level with the (DZ)EOPDD sequence was, as expected, higher than with Z EOPDD, as more ClO_2 was used, but the AOX levels were still significantly lower than with the D EOP DD sequence.

Note that the pH of the Z stage in the (DZ) process was 4.3; this is higher than the pH usually recommended in a Z stage *(1).* However, the results were very good.

Table IV shows the effect on bleaching of the pH in Z during the (DZ) process. Adjusting the pH to 2.5 before charging the ozone gave better results in brightness than when the pH was 4.3, but the selectivity (kappa number versus DPv) remained the same.



I. The effect of reaction time of D in the (DZ) process on the kappa number of the softwood kraft pulp after (DZ) and (DZ) EO. (1% ClO_2 in D and 0.35% O_3 consumed in Z, 3.5% consistency, room temperature).

Table V shows the results of bleaching softwood using the (DZ) concept. By comparing these results with those obtained with the DEODE D and ZEODED sequences (Table II), it can be concluded that combining D and Z in (DZ) stages leads to a more efficient bleaching process. With the (DZ)EO(DZ)ED sequence, 2% ClO_2 and 0.6% O_3 gave a similar brightness to the DEODED sequence, where 3.5% ClO_2 was required. Thus, the use of 0.6% O_3 saved 1.5% ClO_2. Using the (DZ)EODED sequence in which all of the ozone was introduced in the first D stage, the replacement ratio was lower but still good: 0.7% O_3 replaced 1.2% ClO_2. As expected, the AOX levels were lower than for the DEODED sequence, and the final viscosities were higher than for the ZEODED-bleached pulp. This is explained by the fact that lower quantities of ozone were used.

Figure 1 shows the effect of the reaction time of D in the (DZ) process on the kappa number of the softwood pulp after (DZ) and (DZ)EO. When the time was increased, the delignification was improved, but after 10–15 min reaction time, there was no further change in the kappa number. This also corresponded to the time when all of the chlorine dioxide was consumed by the pulp. This means that ClO_2 and O_3 are better used if not present in the pulp at the same time.

In a previous study *(6),* it was shown that the residual lignin in the pulp after a D stage is more depolymerized than after a Z stage, at the same lignin content. On the other hand, there are more carboxyl groups formed on lignin during ozonation than during a ClO_2 stage; this explains why the lignin can be easily solubilized during an ozone stage. Ozone is also known to react with almost all types of structures in the lignin, whereas ClO_2 reacts only with the free phenolic groups. ClO_2 must be added first so that it can react with the free phenolic groups before the highly reactive ozone is introduced. The superiority of DZ on ZD has been shown previously *(7).*

The results presented in **Table VI** show that, when a washing is carried out between D and Z, the brightness after DZEOP is slightly better than after (DZ)EOP, but the selectivity is not changed. The improved brightness is due to the fact that the washing step eliminated some dissolved organics that may consume ozone.

The use of ozone in a final bleaching stage (polishing stage)

Ozone is very efficient when used as a delignifying agent. Its high reactivity could be used at the end of a bleaching sequence as well *(8),* where the last points of brightness are usually difficult to obtain and require a long residence time. Final P stages often require 4 hours; this can be reduced to 1–2 hours when these stages are pressurized. Final D stages usually require 2–3 hours. Furthermore, final P or D stages are carried out at high temperature (higher than 70–80°C). **Tables VII and VIII** show the effect of a final Z stage carried out after OQZP and DEDED sequences on a softwood kraft pulp. Acidic, neutral, and alkaline pH conditions in the ozone stage were compared.

It appears that a small charge of ozone increased the brightness by several points, leading to brightness levels higher than 90% ISO. As a small ozone

Parameter	SEQUENCE (D_1Z) EOP D_2 D_3	
(D_1Z)		
% ClO_2	0.8	0.8
% O_3 charge	0.6	1.2
pH after D	4.3	4.3
% O_3 consumed	0.25	0.51
Kappa no.	3.9	2.4
ISO brightness	54.4	59.6
DPv (viscosity, mPa·s)	1440 (22.4)	1330 (18.9)
EOP		
DPv (viscosity, mPa·s)	1400 (21.1)	1310 (18.5)
ISO brightness	69.4	73.3
D_2 (0.75% ClO_2)		
% ClO_2 consumed	0.67	0.65
ISO brightness	86.2	87.9
D_3 (0.15% ClO_2)		
% ClO_2 consumed	0.08	0.07
DPv (viscosity, mPa·s)	1420 (21.8)	1300 (18.2)
ISO brightness	88.9	90.2
ClO_2 charge, %	1.7	1.7
ClO_2 consumed, %	1.55	1.52
AOX, kg/o.d. ton	0.35	0.31

*(D_1Z): pulp consistency 3.0%. First 0.8% ClO_2 during 10 min, 50°C, then O_3 is charged. EOP: same conditions as in Table I.

III. Bleaching hardwood kraft pulp with the (D_1Z) EOP D_2 D_3 sequence*

Parameter	SEQUENCE (DZ) EOP			
(DZ)				
pH before Z	4.3	2.6	4.3	2.6
% O_3 charge	0.6	0.6	1.2	1.2
% O_3 consumed	0.25	0.35	0.51	0.63
DPv	1440	1370	1330	1230
Viscosity, mPa·s	22.4	20.2	18.9	16.5
ISO brightness	54.4	58.6	59.6	65.2
EOP				
DPv	1400	1340	1310	1160
Viscosity, mPa·s	21.5	19.1	18.5	14.8
Kappa no.	1.9	1.4	1.7	1.3
ISO brightness	69.4	75.2	73.3	79.0

*(DZ): see Table III. EOP: same conditions as in Table II.

IV. Effect of the pH in Z in the (DZ) process on the bleaching results after (DZ) EOP for the hardwood kraft pulp*

Parameter	SEQUENCE (D$_1$Z) EO (D$_2$Z) E D$_3$	(D$_1$Z) EO D$_2$ E D$_3$
(D$_1$Z)		
% ClO$_2$	0.5	1.0
% O$_3$ consumed	0.36	0.7
pH before Z	7.9	3.2
EO		
Kappa no.	8.4	2.4
DPv	1480	1340
Viscosity, mPa·s	23.7	19.3
AOX (D$_1$Z) EO, kg/ton	0.15	0.4
(D$_2$Z) or D$_2$	(D$_2$Z)	D$_2$
% ClO$_2$	0.5	1.2
% O$_3$ consumed	0.24	0
pH before Z	2.5	-
ISO brightness	66.9	87.1
E D$_3$		
% ClO$_2$	1	0.5
% ClO$_2$ consumed	0.97	0.46
ISO brightness	91.3	92.2
DPv	1120	1030
Viscosity, mPa·s	13.9	12.1
Total ClO$_2$, %	2	2.7
Total O$_3$, %	0.6	0.7
Total AOX, kg/o.d. ton	0.44	0.49

*(D$_1$Z): 15 min, 50°C, 3.5% consistency, no pH adjustment prior to Z. (D$_2$Z), D$_2$: 5 min, 20°C, 3.5% consistency, pH adjustment to 2.5 before Z. EO, E conditions: see Table II. D$_2$, D$_3$ other conditions: see Table II. In D$_2$, all the ClO$_2$ was consumed.

V. Bleaching softwood kraft pulp using the (DZ) concept*

Species	Softwood		Hardwood	
Stage	(DZ)	DZ	(DZ)	DZ
%ClO$_2$	1	1	0.8	0.8
% O$_3$ consumed	0.33	0.25	0.35	0.36
Initial Z pH	2.5	2.5	2.5	2.5
Stage	EO	EO	EOP	EOP
Kappa no.	3.2	2.8	1.4	1.3
ISO brightness	55.1	57.2	75.2	78.8
DPv	1420	1400	1340	1300
Viscosity, mPa·s	21.7	21.1	19.1	18.2

*D: 30 min, 50°C, 3.5% consistency. Z: 3.5% consistency, pH adjusted at 2.5 before Z. EO: see Table II. EOP: see Table I.

VI. Comparison between D Z EOP and (DZ) EOP bleaching results for softwood and hardwood species*

charge was used, the viscosity of the pulp was only slightly impaired. The difference between the viscosity measured before and after reduction with $NaBH_4$ revealed the formation of carbonyl groups on carbohydrates during ozonation *(9).* Nevertheless, the brightness stability upon heat exposure, known to be sensitive to the presence of carbonyl groups on carbohydrates, was not significantly affected, and the brightness of the ozonated pulps after aging was still much higher than for the starting pulps. The ozone charge was high enough to increase the brightness significantly but sufficiently low to not impair the brightness stability.

Furthermore, ozonation at neutral or alkaline pH gave a similar increase in brightness to that obtained at pH 2.5. The viscosities at neutral pH and at pH 2.5 were equal. A slightly lower viscosity was observed at the alkaline pH. Ozone decomposition in water increases when the pH is higher. According to some authors *(10),* this decomposition is accompanied by the formation of higher amounts of hydroxyl radicals, which are harmful to cellulose. We have shown in a previous study that, at neutral pH, no more hydroxyl radicals were detected from an ozone solution than at a pH of 2.5 *(11).* Therefore, when the pH is increased from 2.5 to 6–7, ozone may decompose more but with no detectable formation of hydroxyl radicals. This finding is consistent with the observation that the cellulose was not further degraded during an ozone stage at neutral pH than at acidic pH. The efficiency of the ozone treatment was only slightly reduced at neutral and alkaline pH, as shown by the brightness levels.

From an industrial point of view, note that an acidification to low pH is not needed.

EXPERIMENTAL

Starting material

The pulps used in this study were a

softwood kraft pulp (kappa no. = 24, DPv = 1480, and viscosity = 23.7 mPa·s) and a hardwood kraft pulp (kappa no. = 14.8, DPv = 1710, and viscosity = 33.2 mPa·s).

Ozone stages

Ozone bleaching at high consistency was performed in a rotating spherical glass reactor at room temperature. Before ozonation, the pulp was brought to the target pH, at a pulp consistency of 1.5%, by adding either sulfuric acid or caustic soda. The pulp was then dewatered to 40% consistency and fluffed. The ozone concentration in oxygen was set at 5.5%.

Ozone bleaching at low consistency was performed at 3.5% pulp consistency. The pH was adjusted by adding sulfuric acid.

(DZ) bleaching was performed at low consistency (3.5%). The D stage was performed either directly in the low-consistency ozonation reactor or in an Erlenmeyer flask for the experiments at 50°C. The reaction time was between 30 seconds and 30 min. The pulp was then ozonated, with or without adjusting the pH to 2.5. No washing was performed between D and Z.

Characterization of the pulp

Kappa number, viscosity, and ISO brightness were determined according to TAPPI Test Methods. DPv was calculated from the viscosity value, *v*, using the following equation *(12)*:

$$DPv = [0.75 \times 954 (\log v) - 325)]^{1.105} \quad (1)$$

If not otherwise indicated, the viscosities were measured after reduction of the pulp with 2% sodium borohydride at room temperature and 5% pulp consistency for 30 min.

Brightness reversion upon heat exposure was performed according to ISO Standard 5630/1: The handsheets were placed in a dry oven at 105°C for 3–24 hours.

Brightness reversion upon light exposure was performed in a Suntest apparatus equipped with an ultraviolet (UV) filter, simulating exposure to sunlight. The handsheets were irradiated for 1 hour.

Parameter	Sequence DEDEDZ			
% O_3*	0	0.2	0.2	0.2
Initial ozonation pH	-	2.8	5.8	10.2
DPv	1280	1240	1230	1190
Viscosity, mPa·s	17.7	16.6	16.4	15.5
DPv before reduction by $NaBH_4$	1280	1060	1060	980
ISO brightness	87.8	91.5	91.2	91.1
Heat aging				
After 3 hours				
ISO brightness	81.2	86.7	87.2	87.2
After 24 hours				
ISO brightness	77.1	82.3	83.2	83.2

*Ozonation carried out at 40% pulp consistency.

VII: Effect of a final Z stage on the DEDED-bleached softwood kraft pulp characteristics

Parameter	Sequence OQZ, PZ_2			
% O_3 in Z_2	0	0.2	0.2	0.2
Initial ozonation pH	-	2.8	7.0	10.7
DPv[b]	920	880	860	800
Viscosity, mPa·s[b]	10.3	9.70	9.40	8.60
ISO brightness	86.0	90.5	90.0	89.8
Heat aging				
After 24 hours				
ISO brightness	79.5	85.1	83.5	83.0
Light aging				
After 1 hour				
ISO brightness	84.7	87.0	87.0	86.6

[a]O: 2% NaOH, 1% $MgSO_4 \cdot 7H_2O$, 1 hour, 100°C, 0.5 MPa O_2. Q: 0.5% EDTA, 30 min, 90°C. Z_1: 40% pulp consistency, 1% O_3, pH = 2.5. P: 2% H_2O_2, 2% NaOH, 0.5% $MgSO_4 \cdot 7H_2O$, 4 hours, 70°C. Z_2: 40% pulp consistency.
[b]Viscosities were measured after reduction with sodium borohydride.

VIII. Effect of a final ozone stage carried out on an OQZ_1P softwood kraft bleached pulp[a]

CONCLUSION

In ECF bleaching sequence AOX can be reduced by replacing part of the chlorine dioxide by ozone. (DZ) stages, in which ozone is added after chlorine dioxide with no washing, were particularly efficient since, in some cases, 1 kg ozone could save up to 4 kg of chlorine dioxide in a full bleaching sequence. Substitution of ozone for chlorine dioxide could then reduce the chemical costs significantly.

Adding a Z stage at the end of a TCF or ECF bleaching sequence appeared to be an efficient way to im-

prove the final brightness. Acidification to pH 2.5, as is usually recommended for ozone stages, was not necessary here; this is of high practical interest. **TJ**

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LITERATURE CITED

1. Liebergott, N., *Proceedings of the Emerging Pulping and Bleaching Technologies Workshop,* TAPPI PRESS, Atlanta, 1995.
2. Lachenal, D., Brevet FR 2 663 348, 1990.
3. Tsai, T. Y., Patent WO 90/13705, Nov. 15, 1990.
4. Bosenius, C., Nilsson, E., and Tibbling, P. (Kamyr Aktiebolag), Brevêt FR 2 656 634, 1990.
5. Hostachy, J. C., Lachenal, D., Coste, C., *et al., Proceedings of the 11th Ozone World Congress,* San Francisco, Vol. I, 1993, p. S10-13. International Ozone Association.
6. Lachenal, D., Fernandes, J. C., and Froment, P., *J. Pulp Paper Sci.* 21(5): J173(1995).
7. Lachenal, D., Taverdet, M. T., and Muguet M., *Nordic Pulp Paper Res. J.* 6: 25(1992).
8. Patrick, K. L. and Young, J. E., *Pulp and Paper* 59(1993). 67(11): 59(1993).
9. Chirat, C. and Lachenal, D., *Proceedings of the 8th International Symposium on Wood and Pulping Chemistry,* Gummerus Kirjapaino Oy, Helsinki, Vol. I, 1995, p. 293.
10. Hoigné, J. and Bader, H., *Water Research,* Vol. 10, Pergammon Press, U.K., 1976, pp. 377–386.
11. Chirat, C. and Lachenal, D., *Proceedings of the 3rd European Workshop on Lignocellulosics and Pulp,* STFI, Stockholm, 1994, p. 260.
12. Sihtola, H., Kyrklund, B., Laamanen, L., *et al., Paperi ja Puu* 45(4a): 225(1963).