Development of an ozone-based TCF sequence for bleaching a hardwood ALCELL® pulp

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ABSTRACT

A fully bleached hardwood ALCELL® pulp of high brightness was produced from a kappa no. 54 pulp in a TCF sequence. The brownstock was first subjected to displacement washing with a 70% ethanol solution. It was then delignified with 2% ozone at high consistency after impregnation with a 30% ethanol solution acidified to pH 2. A subsequent second displacement washing stage with a 70% ethanol solution decreased the kappa number to 10. The resulting pulp had a brightness of 45.9% ISO and a viscosity of 19.0 mPa·s. Further bleaching of this delignified pulp in an Eop1PaEop2 sequence, at a total charge of 1.5% hydrogen peroxide and 0.22% peracetic acid (as H_2O_2), led to the production of a fully bleached pulp having good strength properties and a 92% ISO brightness.

Application:

The solvent-assisted ozone process naturally fits with the ALCELL® technology.

THE ALCELL® PROCESS IS AN ethanol based autocatalyzed solvent pulping technology that was successfully operated by Repap Enterprises Inc. in a demonstration plant located in Miramichi, NB, Canada. The advantages of this novel organosolv pulping, compared to kraft pulping, have been reported (1), and it was concluded that this ethanol based solvent pulping could become an increasingly important alternative pulping process.

Pioneering bleaching of this ethanol based solvent pulp was carried out by Cronlund and Powers *(2)*. They found that by applying a conventional ODED bleaching sequence, the same optical and physical properties can be obtained as for the same furnish kraft pulp bleached by the same sequence. However, inclusion of oxygen delignification in the ethanol based solvent pulping process may pose some concerns. Because the process does not have a recovery boiler, effluent from the O stage needs a secondary treatment. Sodium hydroxide itself is expensive, and discharge into the receiving water could be even more expensive. Therefore, although the ODED bleaching process is technically reliable, it might not fit into the general trend of lower-environmental-impact, lower-effluent-discharge ALCELL mills in the future.

The totally chlorine free (TCF) bleaching sequences OZP and OZPa have been investigated *(2)* for the ethanol based organosolv pulp. It was reported that a typical oxygen bleached pulp of about kappa no. 10 could be bleached to a brightness of 81.1% ISO in an OZP sequence within ozone and hydrogen peroxide charges of 0.5 and 2%, respectively, and to a brightness of 84.1% ISO in an OZPa sequence with ozone and peracetic acid charges of 0.5 and 2%, respectively. The final physical properties were not reported. However, the burst index and breaking length of the OZ pulp were 2.2 kPa·m^2/g and 3.8 km, respectively. These values compare with a burst index of 4.1 kPa·m^2/g and a breaking length of 6.6 km for the ODED-bleached pulp. This suggests that the OZP and OZPa pulps will also be deficient in strength properties.

An earlier study *(3)* showed an excellent ozone to lignin (carbohydrate) selectivity when ethanol was present in the impregnation liquor during ozone bleaching of the ethanol based solvent pulp. The resulting pulp is suitable for final brightening. The objective of this project was to develop final brightening stages using oxygen based chemicals such as hydrogen peroxide and peracetic acid.

EXPERIMENTAL

The pulp samples used in the experiments were obtained from ALCELL Developments Inc. and stored in a cold room at 4°C. The pulp was a mixture of birch, maple, and poplar species. The kappa number and viscosity of the brownstock pulp were 54.0 and 23.8 mPa·s, respectively.

The pulp samples were subjected to a displacement washing (W_e) stage in a stainless steel displacement cell. The pulp was first disintegrated in a stainless steel blender in deionized water for about 20 seconds at 0.5% consistency and poured into the cell while draining. A packed bed of fibers was formed by draining the pulp suspension and was compacted to a 10-cm height. Displacement washing was simulated by pumping two bed volumes of 70 wt.% ethanol–water solution at 65°C through the 10%-consistency pulp bed with a peristatic pump. The flow rate of the ethanol–water solution was about 110 mL/min.

The ozone delignification (Z) stage was performed at 10°C in a specially designed rotating vessel. The washed pulp was first impregnated with a 30% ethanol–water

Process variable	STAGE Eop1	Pa	Eop2
Consistency, %	20	20	20
Time, min	60	120	120
Temp, °C	95	60	95
Oxygen pressure, psi	65	-	65
Chemicals, %	NaOH: 1.5 H_2O_2: 0.5–1.0 $MgSO_4$: 0.1	Pa: 0.5–1.0*	NaOH: 1.0 H_2O_2: 0.5–1.5 $MgSO_4$: 0.1

*Initial pH=8.0–8.5. Final pH=4–5 by $NaHCO_3$ addition.

I. Bleaching conditions

Sample	Brightness, % ISO	Kappa no.	Viscosity, mPa·s
Brownstock	20.9	54.0	23.8
W_e-treated	23.7	32.6	23.4
W_eZ-treated	43.4	11.0	19.9
W_eZW_e-treated	45.9	10.0	19.0

II. Development of pulp properties during the prebleaching stages

solution, which was acidified with sulfuric acid to pH 2. The pulp was pressed to about 40% consistency and fluffed. The ozone delignification took place when the fluffed pulp was contacted with ozone in an air mixture at a flow rate of 4.0 L/min. The ozone-reacted pulp was diluted with the required amount of ethanol–water solution to restore the ethanol concentration of the impregnation liquid to 70% .It was then subjected to the second W_e washing stage, which was performed under conditions similar to those described for the first W_e stage. The only difference was the pumping of two additional bed volumes of distilled water through the packed bed after completion of the displacement washing by the ethanol–water solution.

Oxidative extraction with hydrogen peroxide reinforcement, the Eop stage, was performed under an oxygen atmosphere in a specially designed bomb fitted with a Teflon liner so that the pulp sample did not contact the metal surface. The bomb was placed in a constant temperature oil bath. The process conditions are shown in **Table I.** After the Eop1 stage, the bleached pulp was washed thoroughly with deionized and distilled water and saved for the next operation.

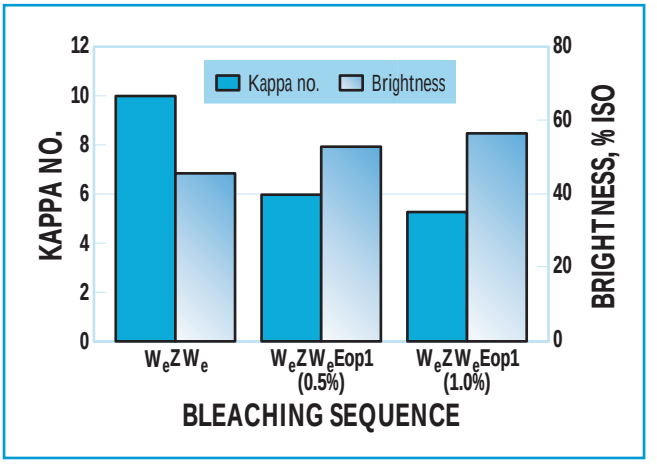
In the peracetic acid (Pa) bleaching stage, the weighed pulp sample was put into a polyethylene bag, and the appropriate quantities of 10-g/L sodium bicarbonate solution and water were added and mixed with the pulp to provide the proper initial pH and 20% consistency. The desired quantity of 30 wt.% peracetic acid was added and rapidly mixed with the pulp. The polyethylene bag was sealed and placed in a constant temperature water bath. The chemical charges and other operating conditions are listed in Table I. After the Pa stage, the pulp slurry was thoroughly washed with deionized and distilled water. Eop2 stage bleaching was performed under conditions similar to the Eopl stage (see Table I). After the Eop2 stage, the pulp was washed thoroughly with tap water and made into handsheets for further analysis. Viscosity, kappa number, brightness, and strength properties were measured using TAPPI test methods.

RESULTS AND DISCUSSION

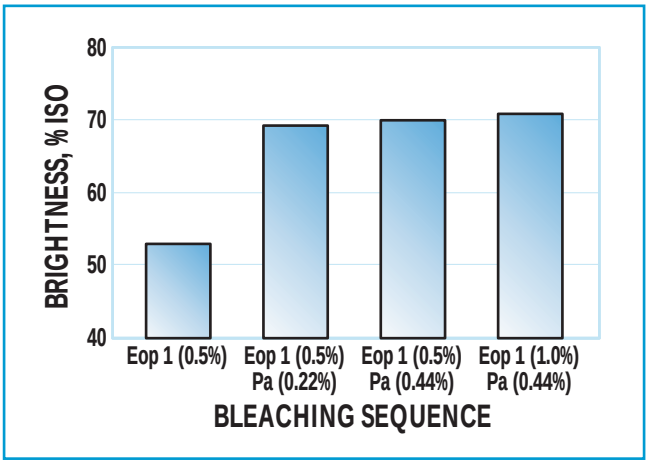
It is known from the literature *(4)* that a significant fraction of the residual lignin in ALCELL brownstock can be removed in a displacement washing stage with an ethanol–water solution. Therefore, before the ozone bleaching stage, the brownstock was first subjected to a displacement washing stage, following the procedure in the "EXPERIMENTAL" section. As a result, the kappa number of the pulp decreased from 54.0 to 32.6, and the brightness increased from 20.9% to 23.7% ISO. In addition, no viscosity loss was observed (see **Table II**).

The washed pulp was subjected to the ethano assisted ozone bleaching with pH 2, 30% ethanol solution as the impregnation liquor. The ozone charge was 2% (on o.d. pulp). The resulting semibleached pulp had a kappa number of 11.0 and a pulp viscosity of 19.9 mPa·s (Table II). Compared with the pulp viscosity of 23.4 mPa·s before ozone treatment, a decrease in viscosity of only 3.5 mPa·s occurred during ozone bleaching. This again confirms the results of a previous study *(3)*, which indicated that carbohydrate degradation is significantly suppressed when ozone bleaching is performed in the presence of ethanol. The brightness of the ozone treated pulp was increased to 43.4% ISO (Table II). A second washing stage, with an ethanol solution, was carried out after the ozonation stage, and the results are listed in Table II. This W_eZW_e-treated pulp was suitable to be fully bleached in later brightening stages.

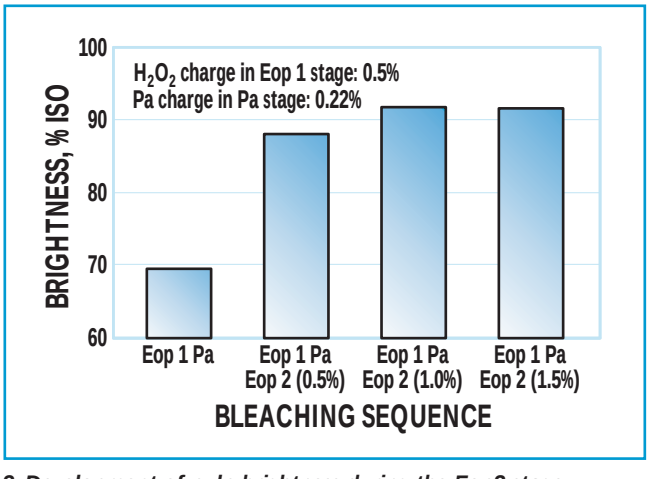
The final brightening sequence consisted of a peroxide reinforced oxidative extraction, Eop1, followed by a peracetic acid stage, Pa, and a second peroxide reinforced oxidative extraction, Eop2. The alkaline Eop1 stage was chosen because, before this stage, the pulp had never been in an alkaline environment, and this treatment was expected to provide effective bleaching conditions. The inclusion of a Pa stage was based on the concept that hydrogen peroxide and peracetic acid can react with different chromophore structures in the residual lignin. It has been reported that the α-carbonyl and quinone structures of the lignin polymer are effectively removed under alkaline hydrogen peroxide conditions *(5)*, but the α,β unsaturated double bonds in the residual



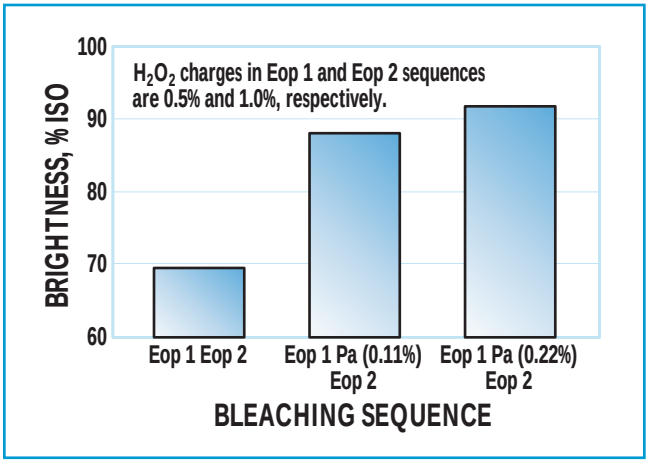
1. Development of pulp properties during the Eop1 stage



2. Development of pulp properties during the Pa stage



3. Development of pulp brightness during the Eop2 stage



4. Effect of Pa charge reduction on brightness in the Eop1PaEop2 sequence

lignin are not only stable, they are also continuously formed during alkaline hydrogen peroxide treatment *(6)*. On the other hand, it has been found *(7)* that these hydrogen peroxide stable double-bond structures are very easily destroyed by a peracetic acid treatment. Finally, a second Eop stage follows immediately after the peracetic acid stage.

The Eop1 stage was performed under the conditions specified in Table I. The resulting brightness and kappa number are shown in **Fig. 1.** The kappa number decreased from 10.0 to 6.0 when 0.5% hydrogen peroxide was charged in the Eop1 stage and decreased to 5.3 when 1.0% hydrogen peroxide was charged. The pulp brightness increased 53.2% and 57.1% ISO, respectively. However, in both cases, the pulp viscosity remained at 19.0 mPa·s. This means that there was virtually no viscosity loss during the Eop1 stage. Note that there is no meta controlling stage prior to the Eop1 stage, and only 0.1% (on o.d. pulp) $MgSO_4$ was added in the Eop1 stage.

The W_eZW_eEop1 pulp was further subjected to a peracetic acid stage. Peracetic acid has received much attention recently as a possible substitute for chlorine as a delignification chemical in the bleaching of chemical pulps *(8, 9)*. However, application of peracetic acid in the final brightening stages has rarely been reported. As indicated earlier, it appears that peracetic acid and hydrogen peroxide complement each other in their reactions with residual lignin structures. The Pa treatment was performed under the conditions shown in Table I.

Brightness attained during the Pa stage is presented in **Fig. 2.** The bar graphs show that a brightness increase of 17% ISO can be achieved with a peracetic acid charge of 0.22% (as H_2O_2). Further increase in the peracetic acid charge proved to be ineffective for bleaching. This is evidenced by the fact that the brightness increased only to 70.5% ISO at a 0.44% Pa charge as opposed to 69.5% ISO at a 0.22% Pa charge. This is further supported in Fig. 2 by the finding that the brightness of the W_eZW_eEop1Pa-treated pulp reached only 71% ISO when 1% hydrogen peroxide and 0.44% peracetic acid respectively, were charged in the Eop1 and Pa stages.

pH profile	Residual Pa, % of original charge	Brightness, % ISO	Viscosity, mPa·s
Initial pH=8.5, final pH=4	65	91.9	18.1
Constant pH=8.5	0	85.8	10.4

*0.5% H_2O_2, 0.22% Pa, and 1% H_2O_2 in the Eop1, Pa, and Eop2 stages, respectively

III. Importance of pH in the Pa stage of the Eop1PaEop2 sequence*

Results	W_eZW_eEop1PaEop2-bleached pulp	ODED-bleached pulp
Burst, kPa·m²/g	4.4±0.2	4.1±0.2
Tear, mN·m²/g	6.3±0.3	6.5±0.3
Tensile, km	7.0±0.3	6.6±0.3

IV. Comparison of strength properties of TCF- and ECF-bleached pulp

In all experimental runs, no viscosity loss was observed during the peracetic acid stage, indicating that carbohydrate degradation caused by peracetic acid is negligible. Therefore, it appears that peracetic acid is not only an effective bleaching chemical but is also selective.

To further increase the brightness level of the W_eZW_eEopPa-treated pulp, a second Eop stage was added under the conditions shown in Table I. The development of brightness during the Eop2 stage as a function of the hydrogen peroxide charge is illustrated in **Fig. 3.** In this case, a hydrogen peroxide charge of 0.5% in the Eop2 stage increased the brightness to 88% ISO, an increase of about 19% ISO. A further increase in the hydrogen peroxide charge to 1.0% leads to a final brightness of 91.7% ISO. Therefore, the Eop2 stage is extremely efficient in increasing brightness. Moreover, we found that carbohydrate degradation is minimal in this stage, as indicated by the pulp viscosity of 18.0 mPa·s at a hydrogen peroxide charge of 1.0%.

As shown in Fig. 2, a brightness increase of about 18% ISO was achieved at a 0.22% peracetic acid charge (as H_2O_2) in the Eop1PaEop2 sequence. The question arises whether a further decrease in peracetic acid would lead to the same final brightness. Therefore, an experiment was performed at a peracetic acid charge of 0.11% (H_2O_2) under otherwise identical conditions. The brightness after the Eop1PaEop2 sequence is shown in **Fig. 4.** Also included is the result obtained without the Pa stage. We observed that the reduction of peracetic acid charge to 0.11% from 0.22% leads to a final brightness of 84.6% ISO compared with 91.7% ISO at the higher charge. Moreover, exclusion of the Pa stage in the Eop1PaEop2 sequence resulted in poor bleaching performance, as indicated by a final brightness of only 75.7% ISO. Therefore, a 0.22% peracetic acid charge is required to achieve a fully bleached pulp with an ISO brightness greater than 90%.

Further studies were conducted to examine the role of the Pa stage in the Eop1PaEop2 sequence. Based on alternating the alkaline/acid condition used in a conventional chlorine bleaching process, one might propose that the peracetic acid treatment could function merely as an acidic stage between two alkaline stages. Therefore, experiments were performed in which an acid treatment at pH 3 was substituted for the Pa stage in the Eop1PaEop2 sequence while other conditions were kept the same. The acidity was achieved by adding sulfuric acid. The resulting pulp had an 80.2% ISO brightness, which compares to 75.7% and 91.7% ISO achieved in the Eop1Eop2 and Eop1PaEop2 sequences, respectively.

Another important observation about the peracetic acid stage is that a proper pH profile is required to achieve good bleaching results, as illustrated in **Table III.** In one experiment, the initial pH was adjusted to 8.5 by adding sodium bicarbonate. The pH fell to about 4 after 2 hours. In another experiment, the pH remained fairly constant at about 8 throughout the course of the reaction. Obviously, the difference in the final brightness is significant (91.9% ISO compared with 85.8% ISO). Moreover, a significant difference in the residual peracetic acid between the two cases is apparent. The lower brightness achieved at the higher pH is caused by the decomposition of peracetic acid, so it was consumed less effectively in bleaching. Table III also shows the carbohydrate degradation. This degradation is indicated by the pulp viscosity, which is substantially lower at a higher pH. This occurs because peracetic acid decomposition leads to the formation of radical species, which are responsible for carbohydrate degradation. Therefore, the proper pH profile in the peracetic acid stage should start at near neutrality and fall gradually to pH 4–5.

It has been recognized *(10, 11)* that the proper management of transition metals is the key to successful hydrogen peroxide bleaching. We found that adding 0.1% of magnesium sulfate in both the Eop1 and Eop2 stages is necessary to maintain good pulp viscosity. This is because the acidic ozone treatment removes most of the metal ions, including magnesium, so that the magnesium content is inadequate in the following hydrogen peroxide stage. This inadequacy is suggested by Henricson *(12)* and, more recently, by Teder and Axegard *(13)*.

KEYWORDS
Bleaching, chlorine free bleaching, ethanol, hardwood pulps, hydrogen peroxide, kappa number, mechanical properties, multistage process, organosolv pulping, ozone, peracetic acid, pH, pretreatment, pulp properties.

We determined the strength properties of W_eZW_eEop1PaEop2-bleached pulp with 2% ozone, 0.5% H_2O_2, 0.22% Pa (as H_2O_2), and 1.0% H_2O_2 charges, respectively, in the Z, Eop1, Pa, and Eop2 stages. The results at 400 mL CSF, obtained with a PFI beater, are listed in **Table IV.** Also included in the table are the strength properties obtained from the same pulp sample but bleached in a conventional ODED sequence. It can be concluded that the fully bleached pulps obtained from the two sequences have comparable strength properties.

An economic evaluation of the W_eZW_eEop1PaEop2 bleaching sequence is shown in **Table V.** The total bleaching chemical cost of the W_eZW_eEop1PaEop2 pulp is approximately US$ 7/o.d. ton pulp higher than that of the ODED pulp.

CONCLUSION

Although the initial kappa number of ALCELL pulp is quite high, the pulp can be delignified to a kappa number of about 10.0 in a W_eZW_e sequence with minimum viscosity loss. The W_eZW_e-treated pulp can be bleached in an Eop1PaEop2 sequence, at a total charge of 1.5% hydrogen peroxide and 0.22% peracetic acid (as H_2O_2), to a full brightness of 92% ISO. A proper pH profile, an initial pH of about 8, and a final pH of 4–5 are required to give the best bleaching results in the Pa stage. Carbohydrate degradation is minimal during the entire bleaching process. The strength properties of the TCF-bleached pulp are comparable to those of an ODED-bleached pulp. TJ

ODED SEQUENCE

Stage	Chemical	Charge, % on o.d. pulp	Unit price, US$/kg	Cost, US$
O	NaOH	4.0	0.30	12.00
	O_2	1.6	0.06	0.93
	$MgSO_4$	0.5	0.53	2.65
E	NaOH	1.5	0.30	4.50
D	ClO_2	1.8	1.24	22.32
Total chemical cost, US$/ton o.d. pulp				42.40

W_eZW_eEop1PaEop2 SEQUENCE

Stage	Chemical	Charge, % on o.d. pulp	Unit price, US$/kg	Cost, US$
Z	O_3	2.0	1.10	22.00
Pa	Peracetic acid	0.5 (as Pa)	1.18*	5.90
Eop	NaOH	2.5	0.30	7.50
	H_2O_2	1.5	0.90	13.50
	$MgSO_4$	0.2	0.53	1.06
Total chemical cost, US$/ton o.d. pulp				49.96

*From Ref. 14; other chemical costs from Ref. 15

V. Comparative chemical costs of the ODED and W_eZW_eEop1PaEop2 sequences

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