THE SECOND GENERATION TCF BLEACHING WITH HC OZONE

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ABSTRACT

There is a growing interest in reduced environmental impact due to strict demands from the authorities in some markets. Therefore Metso will introduce "The Second Generation TCF bleaching", a short sequence that will reach high brightness with low effluent load. In this paper laboratory and simulation results will be presented showing the potential of carrying out TCF bleaching including HC ozone bleaching. Operating and investment costs, environmental load and pulp quality of the TCF bleaching will be compared with standard ECF bleaching and ECF bleaching with HC ozone.

Keywords: AOX, Bleaching, Chlorine dioxide, COD, Color, Eucalyptus, Hydrogen peroxide, Investment cost, Operating cost, Ozone, Pulp Quality

INTRODUCTION

The driving force for the introduction of ozone bleaching has been an ever-increasing concern for the environment and requirements for lower effluent emissions.

Ever since oxygen delignification was commercially introduced in the 1970s, the pulp and paper industry has continuously striven to reduce effluent emissions and meet ever-stricter environmental demands. Furthermore, cost efficiency (in terms of low capital expenditure and low operating costs) and pulp quality have been the measures by which all new developments have been evaluated.

In order to reduce the emissions from bleaching, efforts have been focused on reducing the amount of chemicals containing chlorine. Replacing these chemicals with oxygen, ozone and hydrogen peroxide makes it possible to recover a larger part of the dissolved organic material from bleaching, and in this way reduce the effluent load.

In the year 2008, thirteen pulp mills worldwide will run high consistency ozone bleaching systems delivered by Metso, Table 1. For these mills ozone bleaching has made it possible to produce high quality pulp with reduced bleached plant emissions and lower operating costs compared with standard ECF bleaching.

Table 1. Raw material, bleaching sequence, production and type of product for the different HC ozone installations

Mill	Raw material	Sequence	Production adt/d
IP Franklin	SW Kraft	Z(EO)D	1000
SCA Östrand	SW Kraft	Q(OP)(Zq)(PO)	1250
Wisconsin Rapids	HW Kraft	Z(EO)DD	650
Zellstoff Rosenthal	SW Kraft	Q(OP)(DZ(PO-P))	900
Burgo Ardennes	HW Kraft	DZ(EO)DD	1100
Oji Nichinan	HW Kraft	ZEPD	750
Votorantim Celulose	HW Kraft	(Ze)DP	2100
SCP Ruzomberok	SW/HW Kraft	(Z(EO))(DnD)	1300
Daio Paper	HW Kraft	A(Ze)PD	1600
Sniace, Torrelavega	HW Sulfite	ZEP	240
ITC, Bhadrachalam	HW Kraft	(Ze)(DP)	400
ITC, Bhadrachalam	HW Kraft	(Ze)D(EOP)D	300
Celtejo, S.A. Rodao	SW/HW Kraft	(Ze)DD	720

Market pulps

According to our reflections environmental load, water consumption and energy costs have become more and more important. Previously, Metso has presented that a combination ozone-ECF makes it possible to reduce the effluent load, water consumption and operating costs for the bleach plant with similar pulp properties and better or same paper machine runnability compared with a conventional ECF sequence (1, 2, 3).

However, in some markets there is an interest to reduce the effluent load even further. TCF (Total Chlorine Free) bleaching is then an interesting choice. In this paper we will focus on a combination of high consistency ozone and peroxide bleaching. An advantage of TCF bleaching is that there is a very low amount of chlorides in the filtrates and they can therefore be re-circulated to the recovery area. Furthermore, no investment cost for chlorine dioxide generation is required.

One of Metso's HC ozone installations with TCF bleaching is at SCA Östrand mill in Sweden, Figure 1. The mill has produced TCF-bleached pulp for both softwood and hardwood since the start-up of the new bleach plant 1995. However, since 2002 the production is totally concentrated on softwood pulp.

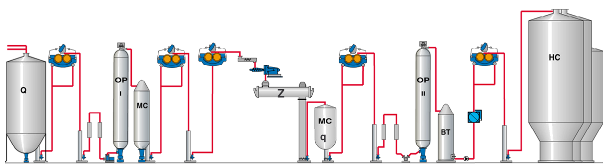

Figure 1. The bleach plant at SCA Graphic Sundsvall AB, Östrand.

The pulp produced at Östrand mill is used in a wide variety of paper products as for example wood free (18%) and wood containing papers (33%), where especially strength is of importance and in tissue (46%), where easy beating, softness and bulk are important properties. SCA Östrand's mill experiences of bleached TCF pulp in comparison with ECF pulp in LWC and SC papers have been presented by Sandström et. al. (4). The conclusion was that the reinforcement properties of the TCF softwood pulp well matched those of different ECF pulps. Furthermore, emissions were drastically reduced in comparison with previous operation, Table 2.

Table 2. Environmental data from 1994 before installation of TCF bleaching and 1996 after installation of TCF bleaching (4). The chemical parameters were measured in bleach plant

	ECF 1994	TCF 1996	Red., %
Production, t/d	1050	1030	-
Flow, m^3/t	36	7	81
COD, kg/t	29	17	41
AOX, kg/t	0.6	0	100

We will take a step further and introduce "The Second Generation TCF bleaching", a short sequence that will reach high brightness with low effluent load. In this paper laboratory and simulation (mass and energy) results will be presented showing the potential of carrying out TCF bleaching including HC ozone bleaching. Operating (bleaching chemicals and energy) and investment costs, environmental load and pulp quality of the TCF bleaching will be compared with standard ECF bleaching and ECF bleaching with HC ozone.

HC OZONE FOR EUCALYPTUS PULP IN TCF AND ECF BLEACHING SEQUENCES

Laboratory investigations were carried out with South American eucalyptus pulps in order to study the potential of TCF bleaching with HC ozone for different eucalyptus pulps.

Chemical consumption and pulp quality

A pulp with good bleachability can reach high brightness with relatively low chemical consumption. Usually a pulp with a high brightness after cooking and oxygen delignification also has a good bleachability.

Three oxygen-delignified eucalyptus pulps were bleached in the laboratory with the TCF sequence (Zq)P, Table 3 and Figure 2. Pulp A and B showed high brightness after the oxygen stage and for these pulps it was possible to reach as high brightness as 91-91.5% ISO with this short sequence.

Table 3. Data of three different oxygen-delignified eucalyptus pulps. Pulp A (E globulus and E nitens), Pulp B (E grandis) and Pulp C (E grandis)

Pulp	Kappa number	Brightness, %ISO
A	8.9	64
B	9.6	61
C	10.6	57

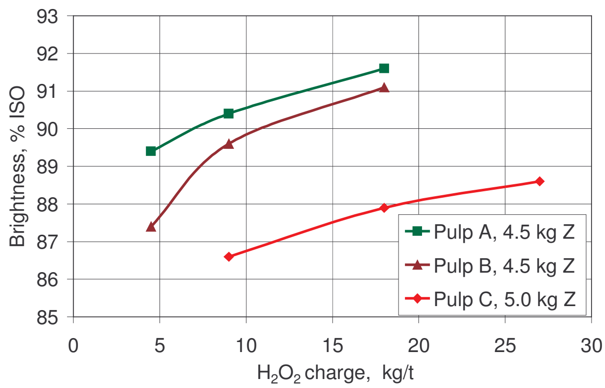

Figure 2. TCF bleaching, (Zq)P, of three eucalyptus pulps.

ECF- and TCF-bleached pulps of pulp A and B were produced for PFI beating and testing of mechanical properties, Table 4. A comparison at 90% ISO showed 60-80 ml/g lower viscosity for the TCF-bleached pulps.

It is customary to evaluate pulp strength as tear index at tensile index 70 or 90 Nm/g. The ECF-bleached pulps required less beating energy compared with the TCF-bleached pulps. Tear index was 5% lower for the TCF-bleached pulps at tensile index 90 Nm/g for pulp A, while there was no differences in tear index at tensile index 70 Nm/g for pulp B.

Table 4 . Bleached pulps produced for testing, pulp A and B. Mechanical properties for bleached pulps at tensile index 70 and 90 Nm/g

Pulp	**A**		**B**	
Sequence	D(EOP)D	(Zq)P	D(EOP)D	(Zq)P
Brightness, %ISO	90	90	90	90
Viscosity, ml/g	810	730	830	770
Tensile index, Nm/g	90	90	70	70
PFI, rev	950	1100	1500	2400
Tear index, mNm^2/g	9.5	9.0	10	10

The studied pulp C showed lower brightness after oxygen delignification and a consequence of this was a lower bleachability, see Table 3 and Figure 2. The maximum brightness reached after (Zq)P for this pulp was only 88.6% ISO.

Therefore, other TCF bleaching sequences have been tested for this pulp with the goal to reach the brightness target 89% ISO. The studied bleaching sequences were (A(Zq))P and P(Zq)P. The idea is to use the HD tower after oxygen delignification for a hot A-stage or a mild peroxide stage, P, to avoid increased investment cost. In Figure 3 a flow sheet showing the sequence (A(Zq))P is shown.

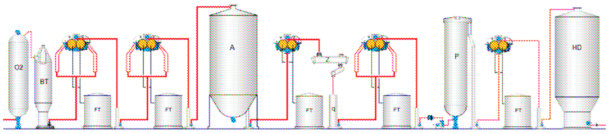

Figure 3. Simplified flow sheet for TCF bleaching sequence (A(Zq))P.

In Table 5 chemical consumption figures are given for the sequences D_{HT}(EOP)D, (Ze)(DD), (A(Zq))P and P(Zq)P. Our intention is that alkaline bleaching filtrates, not containing chlorides, are incorporated in the counter-current washing to post oxygen washing. Oxidized white liquor can then be used as alkali in these alkaline stages.

For the sequence D_{HT}(EOP)D, the chlorine dioxide consumption required to reach 89% ISO was
32 kg active Cl/t. Bleaching to the same brightness with the sequence (Ze)(DD) required 6 kg ozone/t and 18 kg active Cl/t.

The hot A-stage was carried out at 85°C for 180 minutes, which resulted in a kappa number reduction of about 2 units. For the sequence (A(Zq))P 89% ISO was reached with 6 kg ozone/t and 15 kg H_2O_2/t.

A mild P-stage, 3 kg peroxide/t, after oxygen delignification resulted in an increased brightness with about 8% ISO. For the sequence P(Zq)P 89% ISO was reached with 6 kg ozone/t and 21 kg H_2O_2/t.

Table 5. Pulp C bleached for testing. Oxygen delignification and different bleaching sequences. Kappa number of unbleached pulp was 18 and final brightness was 89%ISO

Sequence	D_{HT}(EOP)D	(Ze)(DD)	(A(Zq))P	P(Zq)P
Visc., ml/g	900	770	660	700
ClO_2, kg/t	32	18	-	-
Ozone, kg/t	-	6	6	6
H_2O_2, kg/t	3	-	15	21
NaOH, kg/t	12	5	-	-
OWL, kg/t	16	29	35	38
Oxygen, kg/t	19	16	16	16
EDTA, kg/t	-	-	1	1
H_2SO_4, kg/t	4	12	12	12

Properties for pulp C bleached with different sequences are shown in Table 6. Both TCF-bleached pulps showed lower brightness reversion than the ECF-bleached pulps. The reversion was 1.6 and 2.3% ISO respectively for pulps bleached (A(Zq))P and P(Zq)P. The corresponding figures for pulps bleached (Ze)(DD) and D_{HT}(EOP)D were 2.5 and 2.8% ISO.

In the TCF-bleached pulps, the organic chlorine content in the final bleached pulp was low, <20 g/t. For the ECF pulps the one bleached with ozone showed less than half the OX content, 100 g/t, compared with the pulp bleached with the sequence D_{HT}(EOP)D, 210 g/t.

The content of DCM extractives in bleached pulps was also lowest for the TCF pulps, 0.02-0.04%, compared with 0.11% for pulp bleached D_{HT}(EOP)D.

The AOX content in the bleaching effluent was 0 for the TCF bleaching sequences, 0.1 kg/t for the sequence (Ze)(DD) and 0.3 kg/t for the sequence D_{HT}(EOP)D.

Table 6 also shows the mechanical properties at tensile index 90 Nm/g for pulp C bleached with different sequences. The ozone-bleached pulps required somewhat more beating energy, measured as PFI revolutions, compared with the pulp bleached without ozone. Tear index was lowest for the TCF-bleached pulps for this particular pulp, while there was hardly any or small differences in density, burst index, stiffness and light scattering. However, at the mill it is common to beat the pulp to a certain °SR and there is a difference between ECF- and TCF-bleached pulps as the TCF pulps develop °SR faster than the ECF-bleached pulps.

Table 6. Pulp quality data. Pulp C bleached with different bleaching sequences. Mechanical properties evaluated at tensile index 90 Nm/g

Sequence	D_{HT}(EOP)D	Ze)(DD)	A(Zq))P	P(Zq)P
Brightness, %ISO	89	89	89	89
Viscosity, ml/g	900	770	660	700
Brightness rev., %ISO	2.8	2.5	1.6	2.3
OX, g/t	210	100	<20	<20
DCM extr., %	0.11	0.05	0.04	0.02
AOX , kg/t	0.3	0.1	0	0
At T90				
PFI rev	1100	1400	1400	1200
°SR	24	27	27	26
Density, kg/m^3	770	780	780	780
Tear, mNm^2/g	9.7	9.3	8.4	8.6
Burst, kPam^2/g	5.8	6.1	6.0	6.0
Tensile stiffn. index, mNm/g	4.6	4.6	4.6	4.6
Light scatt. coeff., m^2/kg	29	28	28	28

Environmental load

A bleach plant is a major source of effluent discharge. Filtrate from a conventional ECF sequence, D_{HT}(EOP)D, is difficult to recycle to post oxygen washing due to high chloride level. If the (EOP) filtrate is recycled to the post oxygen washing, the chloride content in the recovery system will be considerably increased and a consequence will be a major risk for plugging and corrosion in the recovery area.

Ozone bleaching gives an opportunity to reduce the effluent volume, the COD discharge and the effluent color compared with the conventional ECF bleaching.

In a bleach plant with a (Ze)(DD) sequence, the alkaline e-filtrate can be recycled to the post oxygen washing and as a consequence the effluent load from the bleach plant will be reduced. According to fiberline simulations, the COD discharge can be reduced by more than 30%. Also the water consumption is reduced significantly.

Still, there is a discharge from the bleach plant that needs to be sent to external effluent treatment. In case the chlorine dioxide in the final bleaching is replaced by hydrogen peroxide there is a potential to eliminate the bleach plant discharge. In the bleaching sequences (A(Zq))P and P(Zq)P, the filtrates from the alkaline P-stages can be recycled to the post oxygen washing. The total discharge volume from these sequences is in the range of 5 m^3/t, which is very low. Since the acid filtrates from A and (Zq) do not contain chlorides, it is possible to evaporate the filtrate and recover the dissolved organic substances in the recovery boiler and thereby totally eliminate the discharge from the bleach plant. A consequence is that this requires additional evaporation capacity. Evaporation of an acid filtrate with low solids content is in operation in a mill since several years.

The simulation results also show that the color of the bleach plant filtrate was highest for the sequence D_{HT}(EOP)D and lowest for P(Zq)P.

Table 7. Results from the fiberline simulations

Sequence	D_{HT}(EOP)D	(Ze)(DD)	(A(Zq))P	P(Zq)P
Water consumption[a], m^3/t	12	10	9	9
Tot. discharge volume, m^3/t	9	7	5	5
Color in discharge, %	100	36	54	33
COD discharge[b] kg/t	23	14	20	15
COD to effluent treatment, kg/t	23	14	0[c]	0[c]

[a]total consumption, including POW and white water
[b]the bleach plant effluents
[c]the acidic filtrates are sent to evaporation

INVESTMENT AND OPERATIONAL COSTS

The total bleach plant investment for each of the sequences has been estimated for the production level 3000 t/d. Table 8 presents the relative investment compared with sequence D_{HT}(EOP)D. The investment for (A(Zq))P is slightly lower than D_{HT}(EOP)D, while (Ze)(DD) is somewhat higher.

Necessity in chemical supply should also be considered on the comparison of the investment cost. Both ozone and chlorine dioxide supply require major investments. From this perspective the TCF sequences have the same benefit as the conventional ECF sequence D_{HT}(EOP)D – only one plant is required. Correspondingly, a drawback of the sequence (Ze)(DD) in a greenfield installation is that two chemical plants are necessary.

If the “zero effluent” alternative is being considered for a TCF sequence, additional capacity is required in the evaporation plant. The evaporation of the acid filtrate increases the flow to evaporation with ca. 50%, which of course affects both investment and operational cost.

The relative estimated bleaching chemical cost for reaching brightness 89% ISO is shown in Table 8 for the four studied bleaching sequences (pulp C). The bleaching chemical cost was lowest for the sequence (Ze)(DD). The TCF sequence (A(Zq))P showed lower cost compared with D_{HT}(EOP)D. The sequence P(Zq)P showed the highest bleaching chemical cost among the tested sequences. In sequences that include ozone bleaching, the ozone stage off-gas is compressed and used in oxygen delignification.

Table 8. Investment and chemical costs for oxygen delignification and bleaching at brightness 89% ISO including the impact of carry-over for pulp C

Sequence	D_{HT}(EOP)D	(Ze)(DD)	(A(Zq))P	P(Zq)P
Investm. bleach plant 3000 t/d	Ref.	Higher	Lower	Lower
ClO_2 plant required	Yes	Yes	No	No
O_3 plant required	No	Yes	Yes	Yes
Steam cost, fiberline	Ref.	Lower	~Ref	Lower
Chemical cost, EUR/t	Ref	- 3.0	- 0.4	+2.9

Except for the chemical cost, the cost for energy must be considered in the total operational cost. In Figure 4, the results from energy balance simulations for the conventional ECF bleaching sequence and the ozone bleaching sequences can be found. As can be seen, the lowest cost for steam was for the sequence (Ze)(DD). The low steam consumption is mainly due to that no bleaching stage is running at high temperature (>75°C) but also because it has been proven to be possible for hardwood pulp to run the high consistency ozone stage at higher temperature without jeopardizing the quality of the pulp (1). A higher temperature in the ozone stage means that the demands of cooling the pulp before the Z-stage and heating before the extraction stage can be reduced significantly.

The cost for steam differs from mill to mill. In this case, the cost for the conventional ECF sequence is estimated at approximately 1-3 EUR/t pulp. The cost for the (A(Zq))P is similar while the steam cost for (Ze)(DD) and P(Zq)P is only about 25% and 60% respectively of the cost for the conventional ECF bleaching.

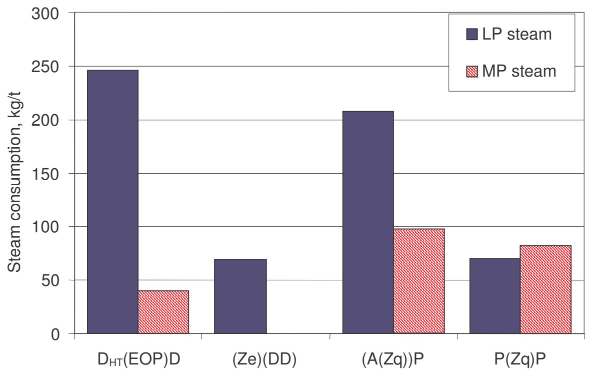

Figure 4. LP and MP steam consumption in bleaching.

DISCUSSION AND CONCLUSIONS

There is a growing interest in reduced environmental impact due to strict demands from the authorities in some markets. TCF bleaching is then an interesting choice.

In this paper we have studied the potential of using TCF bleaching for three South American eucalyptus pulps. One conclusion is that bleachability of the pulps is important for the brightness ceiling and chemical consumption. TCF bleaching of the different pulps showed large variations in bleachability. The studied pulps that were easily bleached reached as high brightness target as
91-91.5% ISO, with a short bleaching TCF sequence, (Zq)P. However, the studied pulp that did not reach as high brightness as the other studied pulps with (Zq)P required a more powerful TCF bleaching sequence. In this paper the sequences (A(Zq))P or P(Zq)P were studied, which increased the brightness from 88.5% ISO to 89.5% ISO without increased investment cost. The idea is to carry out the hot A-stage or soft P-stage after oxygen delignification in the HD tower.

The result of this laboratory study showed that the advantages of TCF bleaching are

- Lower brightness reversion
- Lower OX content and DCM content in pulp
- Lower water consumption
- Lower color and AOX content in the bleach plant discharge
- Potential to fully close the bleach plant and reduce the effluent discharge to zero.
- Lower investment and operating costs

and that the drawback of TCF bleaching is
- Lower tear index for some pulps

For other pulp properties there were only minor differences between ECF- and TCF-bleached pulps.

For mills with strict environmental targets, TCF bleaching gives the opportunity to reduce the effluent load, even to zero discharge. Since the bleach plant filtrate does not contain any chlorides, the bleach plant discharge can be evaporated and the dissolved organic material can be sent to the recovery boiler.

It is important to consider the increased risk for scaling when the bleach plant is closed. This has to be well considered when the fiberline is designed.

EXPERIMENTAL

Three eucalyptus pulps were used in this laboratory study. The pulps were thoroughly washed between the different bleaching stages. D, P, A, q and extraction stages, n and e, were carried out in sealed plastic bags in water bath and (OO)- and (EOP)-stages were carried out in Teflon-lined stainless autoclaves at medium consistency. The HC ozone stage was performed at high pulp consistency (>35%) in a tumbling reactor.

The following chemical costs were used: ClO_2 (act Cl) 0.30 EUR/kg (based on chlorate price 420 EUR/t), NaOH 0.40 EUR/kg, Oxygen (VSA) 0.04 EUR/kg, H_2O_2 0.5 EUR/kg, H_2SO_4 0.08 EUR/kg, DTPA 0.9 EUR/kg, $MgSO_4$ 0.2 EUR/kg, OWL 0.06 EUR/kg, Ozone 0.8 EUR/kg, Electricity 0.04 EUR/kWh. For chemical costs of chlorine dioxide and ozone no investment costs are included.

Analysis methods: AOX ISO 9562, COD ISO 6060, Color ISO 7887, Kappa number ISO 302, Viscosity ISO 5351, Brightness ISO 2470, Brightness reversion Tappi UM 200 (4 hours at 105^{o}C), Organic chlorine in pulp OX SCAN-CM 52:94 and DCM SCAN C 7:62.

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