Eco-Friendly Bleaching With ZeTrac™

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In year 2006 ten pulp mills worldwide will run high consistency ozone bleaching systems delivered by Metso. Ozone bleaching make it possible to produce high quality pulp with reduced bleach plant emissions and lower operating costs compared with standard ECF bleaching. In this paper, experiences will be presented from two mills running high consistency ozone bleaching according to ZeTrac™. Only minor differences can be seen in the standard pulp properties tested before and after the installation of ozone bleaching. The runnability of the paper machine's is in both cases as good as earlier. The effluent load from the bleach plant and the organic chlorine compounds in bleached pulp have been reduced significantly. Bleaching of an Indian hardwood pulp with the sequence (Ze)DP made it possible to reach brightness values over 91% ISO. Comparison of the sequences (Ze)DP and D(EOP)D at 89% ISO showed 25% lower COD, 75% lower AOX and 60% lower OX-content in pulp when bleaching with the sequence (Ze)DP. The bleaching chemical costs were about 20% lower for the sequence (Ze)DP.

INTRODUCTION

When new bleach plants are designed and existing ones are modernized, significant attention is given to bleach plant emissions, pulp quality and operating costs. In order to reduce the emissions from bleaching, the efforts have been focused on reducing the amount of chlorine containing chemicals in bleaching. 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.

Introduction of oxygen delignification makes it possible to reduce the effluent load from bleaching with about 50%. Today this process is used for about 85% of the total bleached pulp capacity, Ref 1.

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Ozone bleaching can further reduce chlorine chemical consumption and effluent load. Ozone gas is produced on site by passing oxygen through an electrical discharge in an ozone generator. Metso's. high consistency ozone bleaching process was introduced in 1992. In year 2006 ten pulp mills will produce more than 4 million tons of bleached softwood and hardwood pulps in ECF and TCF sequences. This amount of pulp corresponds to about 5% of the total bleached pulp capacity worldwide.

In Table 1 the pulp mills utilizing high-consistency ozone are listed. Three of the mills produce softwood pulp, one softwood and hardwood pulps in campaigns and the others produce hardwood pulps. Three mills produce market pulp while the others are integrated pulp and paper mills.

This paper will present results from two pulp mills producing bleached pulp with Metso's ZeTrac high-consistency ozone process and will focus on pulp quality and environmental aspects. The possibility to produce high quality Indian hardwood pulp in a cost-effective way with ZeTrac will also be discussed based on laboratory data.

High Consistency Ozone Bleaching

Ozone bleaching can be carried out at low, medium and high pulp consistency. We see many advantages with high pulp consistency. A higher kappa number reduction can be achieved in one stage and the flexibility for ozone concentration in the feed gas is high. Another very important advantage is that the high-consistency system can be operated in a non- pressurized system and this prevents ozone leakages.

The ZeTrac system is shown in Figure 1. The pulp is acidified and then pressed to high consistency with a TwinRoll press. The main part of the acidic filtrate is recycled in order to dilute the pulp ahead of the acid stage but about 2 m^3/adt is discharged. The pulp is fluffed in a shredder screw on the top of the press

Table 1
Metso HC-Ozone references

Mill	Process	Raw material	Start	Sequence	Production adt/d	Product
IP Franklin	C-Free	SW Kraft	1992	Z(EO)D	1000	Integrated
SCA Ostrand	C-Free	SW Kraft	1995	Q(OP)(Zq)(PO)	1250	Market Pulp
Wisconsin Rabids	C-Free	HW Kraft	1997	Z(EO)DD	650	Integrated
Zellstoff Rosenthal	C-Free	SW Kraft	1999	Q(OP)(DZ(PO-P)	900	Market Pulp
Burgo Ardennes	Ze Tarc	HW Kraft	2000	DZ(EO)DD	1100	Integrated
Oji Nichinan	Ze Trac	HW Kraft	2001	ZEPD	750	Integrated
Votorantim Celulose	Ze Trac	HW Kraft	2002	(Ze)DP	2100	Market Pulp
SCP Ruzomberok	Ze Trac	SW/HW Kraft	2004	(Z(EO))(DnD)	1300	Integrated
Daio Paper	Ze Trac	HW Kraft	2006	A(Ze) PD	1600	Integrated
Sniace, Torrelavega	Ze Trac	HW Sulfite	2006	ZEP	240	Dissolving pulp

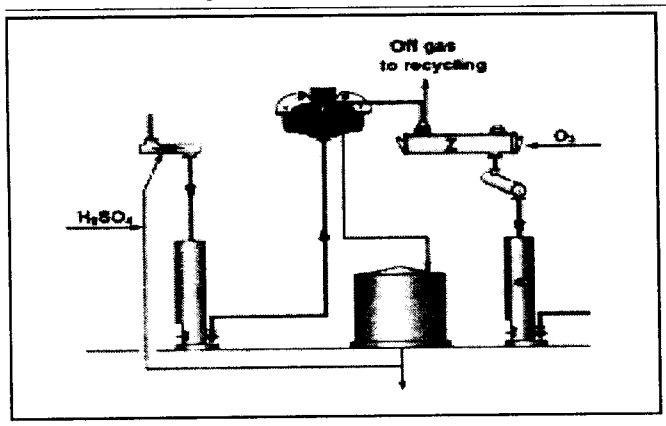

Fig. 1 The ZeTrac system for HC-ozone bleaching

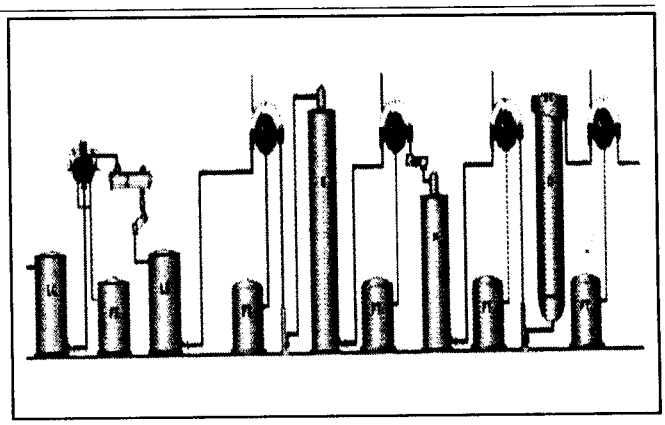

Fig. 2 The Oji Nichinan bleach plant

and then fed into the reactor. Ozone is added to the reactor that is operated at a pressure slightly below atmospheric. After the reactor the pulp is diluted by adding of an alkaline liquor. Pulp is then fed to a short extraction stage (or to an existing longer E- or (EO)-stage (if available) after which it is washed.

The alkaline filtrate from the (Ze)-washer can be used as wash water in post oxygen washing. The system was described more in detail in Ref 2.

TEMPERATURE IN ZeTrac™

The standard temperature in HC-ozone bleaching has so far been 35-45°C. It has been shown that a low temperature is important for bleached softwood pulp quality. However, we have now been able to show both in laboratory and mill scale that for hardwood pulps it is possible to increase the temperature to about 60°C without negative impact on chemical consumption or pulp quality. A higher temperature in the ozone stage means that the demand for cooling the pulp before the ozone stage and for heating before the extraction stage can be reduced significantly.

MILL EXPERIENCES WITH ZeTrac™

Oji Nichinan

In Nichinan mill hardwood kraft pulp is oxygen delignified to a kappa number about 10.5 before bleaching. ECF bleaching with ZeTrac was started up 2002. This was the first high-consistency ozone stage in Japan, Ref

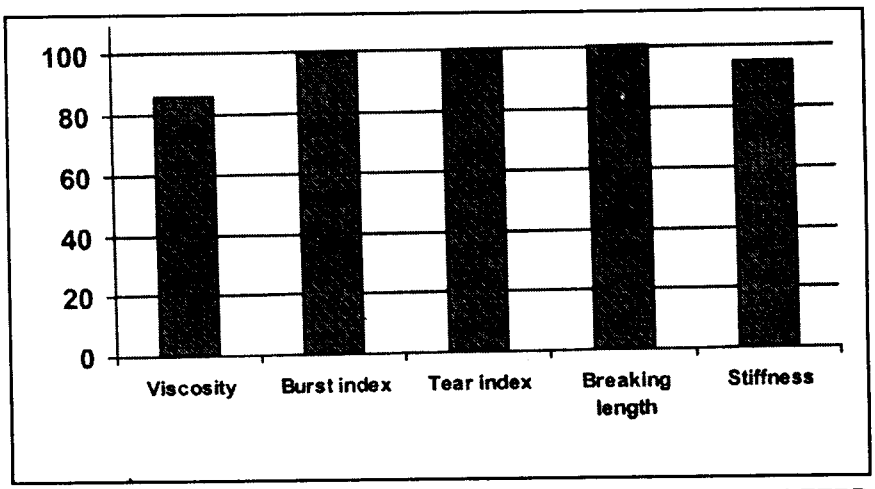

Fig. 3 Relative viscosity and pulp strength for pulp bleached ZEPD compared with CEHD.

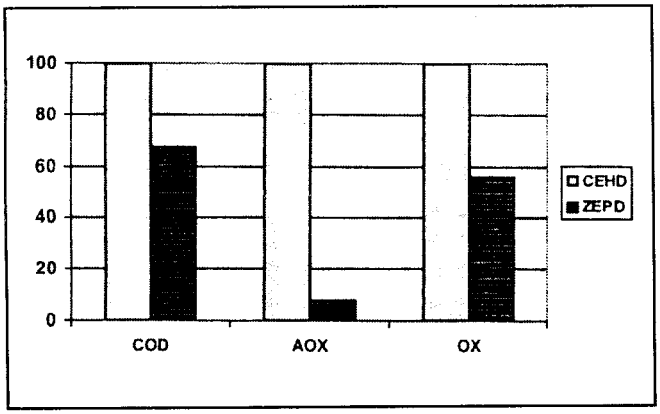

Fig. 4 Bleaching with the sequence ZEPD gives lower COD and AOX discharge and lower OX content in bleached pulp.

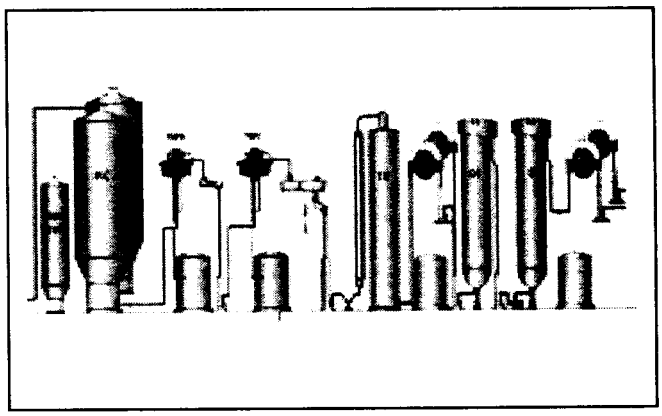

Fig. 5 The SCP Ruzomberok bleach plant.

3. The bleaching sequence CEHD was changed to ZEPD. Figure 2.

Pulp quality was compared for pulp produced before and after installation of ZeTrac, Figure 3. Data for CEHD bleaching was set to 100%. Pulp viscosity is about 14% lower and stiffness about 5% lower with ozone bleaching but burst index, tear index and breaking length show no change compared with the reference. Installation of ozone bleaching did not affect the paper machine runnability.

The effluent load from the bleach plant and the OX-content of bleached pulp have been reduced, Figure 4. The largest effect can be seen for AOX that was reduced by more than 90%.

SCP RUZOMBEROK

In Ruzomberok mill, Slovakia, softwood and hardwood pulp are delignified with OxyTrac™. ECF bleaching with ZeTrac started up in 2004.

The target of the investment was to increase pulp production and to produce high quality pulp without environmental problems. The bleaching sequence D(EOP)DD was rebuilt to (Z(EO))(DnD), Figure 5. The brightness target in this mill is 88% ISO.

In Figure 6 quality is compared for pulps produced before and after installation of ZeTrac. Data for standard ECF bleaching with the sequence D(EOP)DD was set to 100%. There were only minor changes in the pulp properties. An advantage of the ozone bleached pulps is the lower beating demand (10% less PFI revolutions to reach the °SR level aimed at). Burst index, breaking length and tensile index were improved while tear index and stiffness were reduced.

The runnability of the paper machine's using the ozone bleached pulps (hardwood and softwood mixture) is very good. This autumn it was published that a new world record for paper production was achieved on one of the paper machines in this mill, Ref 4.

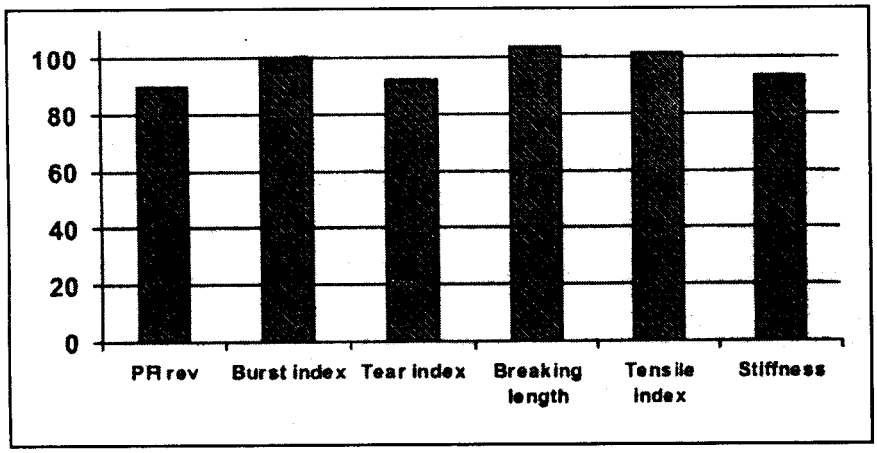

Fig. 6 Relative beatability and pulp strength for pulp bleached (Z(EO))(DnD) compared with D(EOP)DD.

HIGH CONSISTENCY OZONE BLEACHING FOR INDIAN HARDWOOD PULP

A laboratory investigation was carried out in order to study the potential for HC-ozone bleaching for Indian hardwood pulp (mainly eucalyptus). The pulp was cooked by the SuperBatch process in a pilot plant to kappa number 16.7 and then oxygen delignified in two stages to kappa number 10. In Table 2 analysis data are given for unbleached and oxygen delignified pulps.

The oxygen delignified pulp was bleached with the sequences (Ze)DP and D(EOP)D. In the ozone stage 5.5 kg ozone/odt was charged and in the first D-stage the chlorine dioxide charge was 20 kg active Cl/odt. After prebleaching (Ze) and D(EOP) the kappa numbers were 3.6 and 2.5 respectively, Table 3.

Table 2

Properties of SuperBatch pulp produced from Indian hardwoods

Unbleached Pulp	
Kappa number	16.7
Brightness, %ISO	32.8
Viscosity, ml/g	781
Oxygen Delignified Pulp	
Kappa number	10.0
Brightness, %ISO	46.1
Viscosity, ml/g	705

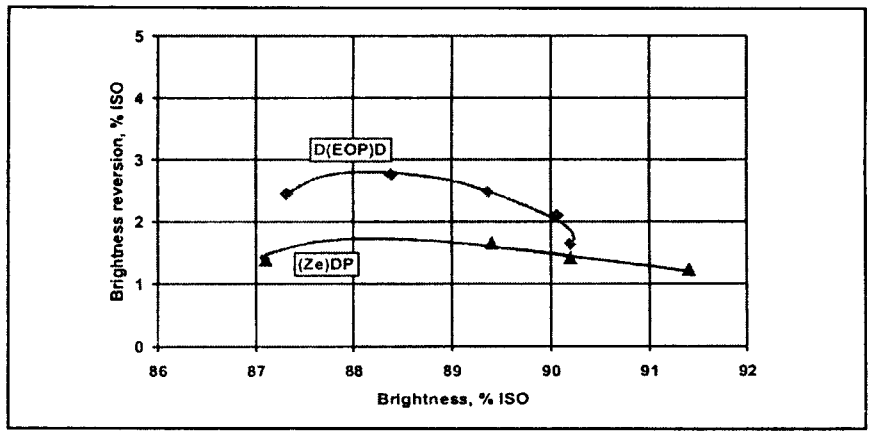

Fig. 8 Brightness reversion for pulps bleached with the sequences (Ze)DP and D(EOP)D.

Table 3

Prebleaching with the sequences (Ze) and D(EOP)

Pulp Properties	(Ze)	D(EOP)
Ozone charge, kg/odt	5.5	-
ClO_2, kg act Cl/odt	-	20
Kappa number	3.6	2.5
Brightness, %ISO	64.9	82.1
Viscosity, ml/g	549	700

When bleaching this pulp with the reference sequence D(EOP)D, the maximum brightness reached was 90.2% ISO, Figure 7. This means that in order to have an acceptable margin, the brightness target should not be set higher than about 89% ISO in the mill. The sequence (Ze)DP is a more powerful sequence. With this sequence the maximum brightness reached was 91.3% ISO meaning that the brightness target in the mill can be about 90% ISO.

Pulp bleached with the sequence (Ze)DP has a more stable brightness than the pulp bleached D(EOP)D, Figure 8. A comparison at 89% ISO shows that the brightness reversion was 1.7% ISO and 2.7% ISO respectively. Both the effective ozone stage and the final peroxide stage contribute to the lower reversion. In some mills this lower brightness reversion means that the target brightness -and the bleaching chemical consumption - can be reduced.

Table 4

Properties of bleached pulps

Sequence	(Ze)DP	D(EOP)D
Brightness, %ISO	88.9	89.0
Brightness rev, %ISO	1.7	2.7
Viscosity, ml/g	525	676

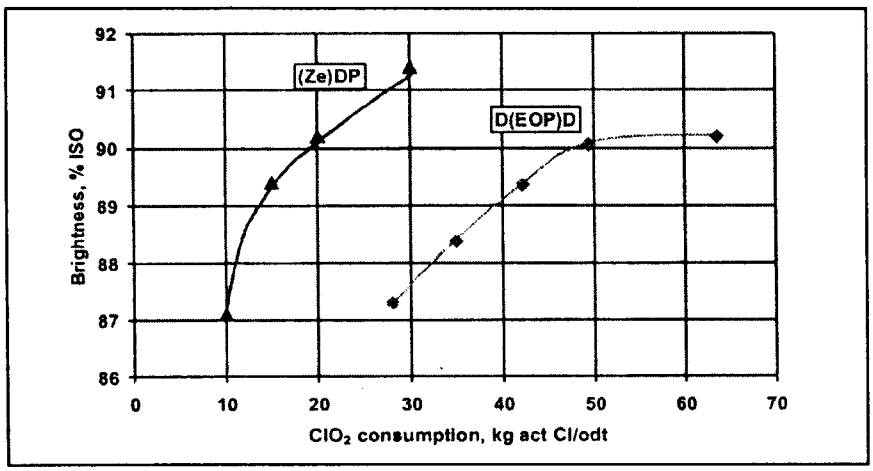

Fig. 7 Bleaching of oxygen delignified Indian HW pulp with the sequences (Ze)DP and D(EOP)D.

Bleached pulps with brightness 89% ISO were produced for testing of mechanical properties. Analysis data for the bleached pulps are presented in Table 4. Data for the pulp bleached D(EOP)D were set to 100 and the relative properties for the pulp bleached (Ze)DP are shown in Figure 9. The evaluation was made at tensile index 80 Nm/g.

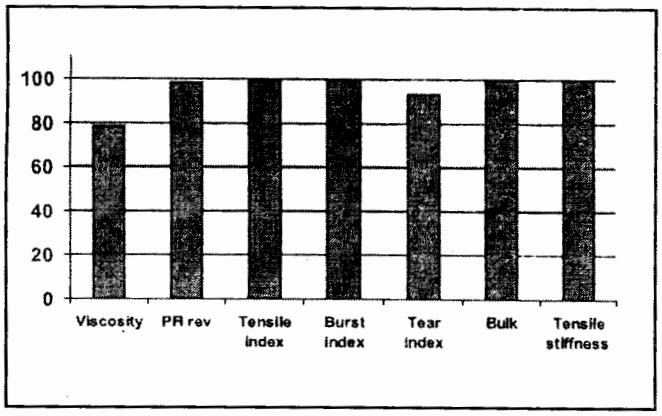

Fig. 9 Relative viscosity, beatability and pulp strength for pulp bleached (Ze)DP compared with D(EOP)D.

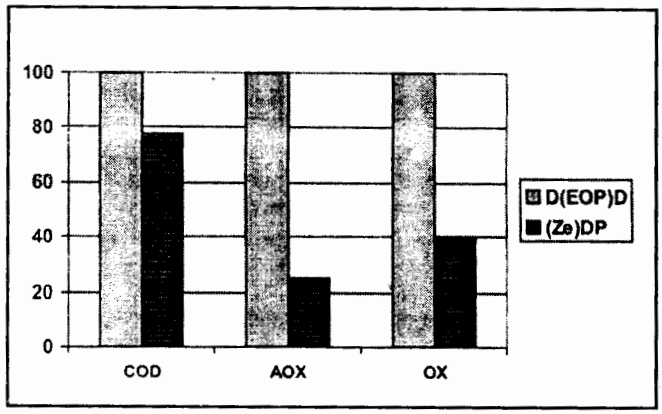

Fig. 10 Bleaching with the sequence (Ze)DP gives lower COD and AOX discharge and lower OX content in bleached pulp.

The viscosity was about 20% lower and the tear index about 6% lower for the ozone bleached pulp. All the other properties were on the same level as for pulp bleached with the sequence D(EOP)D.

The COD and AOX discharge and the OX content in bleached pulp were lower for the sequence (Ze)DP compared with D(EOP)D, Figure 10

OPERATING COSTS WITH ZeTrac™

Based on the laboratory bleaching results presented above in combination with mill experiences we can estimate the bleaching chemical costs for the sequences (Ze)DP and D(EOP)D. When using typical Indian costs for chemicals and electricity the chemical costs are about 20% lower for pulp bleached with ZeTrac to 89% ISO.

In Figure 11 flowsheets are shown for both sequences. The investment cost for machinery, towers and piping is about the same for both sequences.

However, it is important to stress that the sequence (Ze)DP has the potential to produce a pulp with higher brightness and much lower brightness reversion as discussed above. If the target brightness in a mill is 90% ISO the standard ECF sequence alternative is probably D(EOP)DD, with a higher investment cost than (Ze)DP.

For lower brightness targets the storage tower for bleached pulp can be used

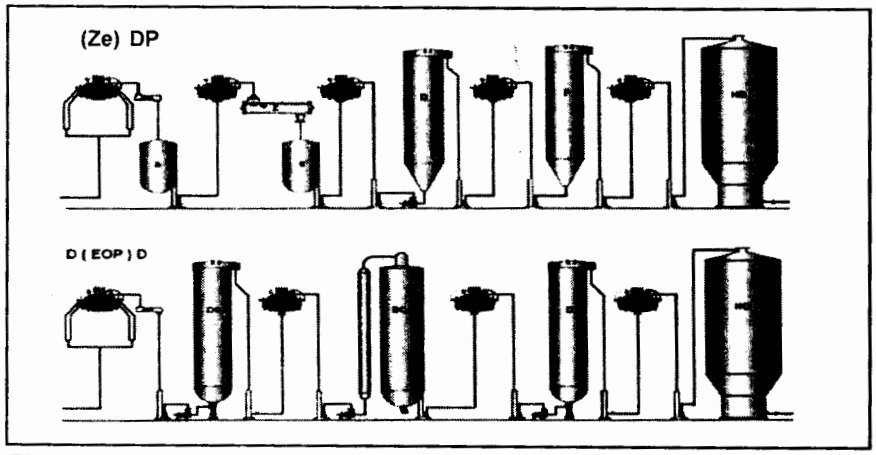

Fig. 11 Flow sheet for bleach plants for the sequences (Ze)DP and D(EOP)D respectively.

for the final peroxide treatment and in that case the investment cost will also be lower for the ozone sequence, Ref 1.

CONCLUSIONS

High-consistency ozone bleaching is today a well-proven technology for environmentally sound bleaching. Compared with standard ECF bleaching the effluent load is lower with ozone. Minor differences in standard pulp properties can be seen. However, from several installations it has been reported that the runnability of the paper machine's is as good as before installation of ozone bleaching.

Indian hardwood pulps can be bleached to high, stable brightness with

Table 5

Oxygen delignification and bleaching sequence (Ze)DP

	(OO)	(Ze)	D	P
Pulp cons, %	12	40	12	12
Temp., °C	82/90	45	75	80
Time, min	30/60	1.5	120	120
Pressure, MPa	1.0/0.5	-	-	-

Table 6 Bleaching sequence D(EOP)D

	D	(EOP)	D
Pulp cons., %	10	12	12
Temp., °C	55	75	75
Time, min	60	120	120
Pressure, MPA	-	0.2	-

the sequence (Ze)DP. Compared with standard ECF bleaching the production costs as well as the effluent load will be lower with the sequence utilizing ozone.

EXPERIMENTAL

The unbleached pulp was cooked by the SuperBatch-K process in a pilotplant. Oxygen delignification and (EOP)-stages were performed in pressurized Teflon lined autoclaves. HC-ozone bleaching in a tumbling reactor and all other stages in sealed plastic bags. Specific conditions are shown in Tables 5 and 6.

Analysis methods

Kappa number	SCAN C 1:00
Viscosity	SCAN CM 15:99
Brightness	ISO 2470:1999
Brightness reversion 4 hours, 105°C	
COD	EN 028142
AOX	EN 1485
OX	SCAN CM 52"94

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