New bleaching processes and fibreline with state-of-the-art technology

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Today many Indian mills are bleaching the pulp with the sequences CEH or CEHH. The effluent from such a bleach plant contains substantial amounts of color, AOX, and COD and the effluent volume is large. Today more and more stringent environmental demands as well as demands for higher efficiency and larger production levels imply that substantial changes in fibreline technology are necessary. Introduction of zone bleaching, according to Metso's ZeTrac™ process and bleaching the pulp in a light ECF sequence, like (Ze) DP or (Ze) DD, or a TCF sequence, like ZQ (PO), will dramatically reduce the effluent load from bleaching. Ozone bleaching is also cost effective compared with other ECF bleaching sequences, like D(EOP)D, as large amounts of chlorine dioxide and/or peroxide can be replaced with moderate amounts of ozone. Bleaching with the sequence (Ze) DP will generate very small amounts of AOX. The usage of ozone will also make it possible to produce a pulp with a very low OX (organic chlorine) content. The OX content has become more and more important to certain paper grades, especially for those used in the food industry. This paper will present results from laboratory bleaching trials of pulps from Indian raw materials.

INTRODUCTION

Fibrelines for annual fibre have looked very much the same for decades. Cooking in rotary type spherical digester or continuous digester, brown stock washing on drum filters, screening on vibratory screens and cleaners and then dewatering on deckers. The washed and screened pulp is then transported on a conveyer band to a HD storage before bleaching. A typical bleaching sequence is CEH.

Today more and more stringent environmental demands as well as demands for higher efficiency and larger production levels imply that substantial changes in fibreline technology are required. At Metso we have for a long time been a major supplier of cooking equipment for production of pulp from annual fibres. We now also intend to become more involved in the rest of the fibreline. Our company has been a pioneer in developing ozone bleaching technology for wood pulp and we also consider ozone bleaching as a very interesting technology for modern annual fibre pulp production.

The annual fibre plant can be converted from using elemental chlorine and hypochlorine to using ozone and chlorine dioxide, or ozone and peroxide. In other words conversion to light ECF or TCF sequences, i.e. according to most modern fibreline standards.

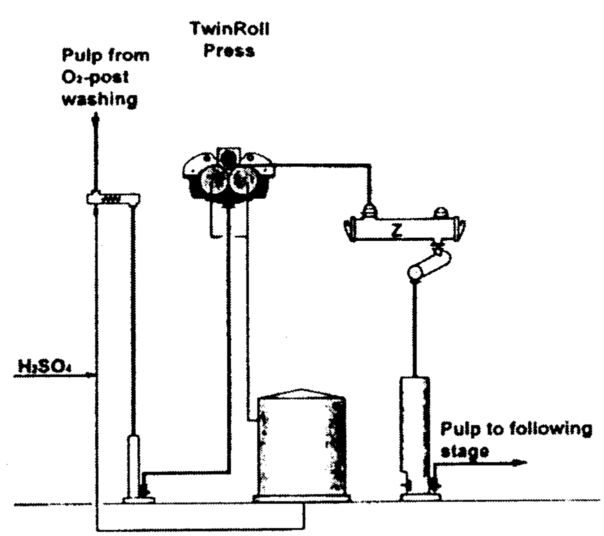

Fig. 1 : The ZeTrac system for HC-ozone bleaching

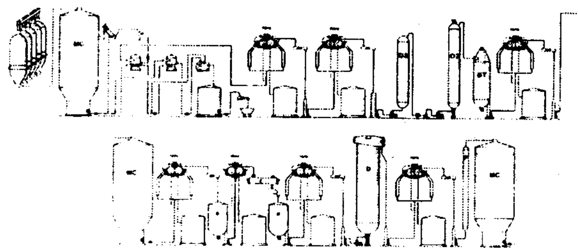

Fig. 2 : A modern fibreline for production of bleached hardwood pulp

Five years ago, at this conference, we presented new bleaching technology for annual fibre pulp mills, ref.1. Since then we have developed our ozone technology further and we now see a great potential for this technique. Last year the evolution of low emission pulp technology for wood pulp was discussed at this conferencee, ref.2.

Ze Trac

Our high consistency ozone system is called Ze Trac. The Ze Trac system consists of a high duty dewatering press, an ozone reactor of paddle conveyor type and a small extraction/receiving tank,

After the extraction tank the pulp is washed on a wash press and then final bleaching is performed. Depending on pulp type, requested final brightness and /or environmental restrictions, the final bleaching can be performed in a single D-stage, or in a D-stage followed by a peroxide stage or, if TCF is required, in a Q-stage followed by a P-or (PO)-stage.

In Fig. 2 a fibreline for bleached hardwood pulp, from SuperBatch cooking to final bleached pulp, is shown. Here the Ze Trac system is located between the last post oxygen washer and the D-stage. The conditions in the ozone reactor are shown in Table 1.

Fig. 3 shows the filtrate arrangement around Ze Trac. Before entering the ozone reactor, the pulp is acidified and the temperature is adjusted. The sulfuric acid is added to the filtrate used for dilution of the pulp going to the press before the ozone reactor. Cooling of the same dilution filtrate controls the temperature. The ozone gas, usually 10-12% concentration, is charged to the discharge end of the reactor. The off-gas from the reactor is led to the fibre scrubber and ozone destruction. The gas is then finally compressed and can be used for example in an oxygen delignification stage.

After the reactor the pulp is diluted to about 12% pulp consistency by addding alkaline dilution liquor. This liquor can also be heated in order to reach the wanted temperature in the short e-stage. The retention time in the e-stage is usually about five minutes.

Table 1 : Ze Trac conditions

Pulp consistency	~40%
Temperature	45-55 °C
pH	2.5-3
Retention time	<1 min

Today we have eight HC-ozone systems in operation, Fig.4. The first installation was made in Union Camp's (now International Paper) mill in Franklin, USA. They changed the bleaching sequence from CEDED to OZED.

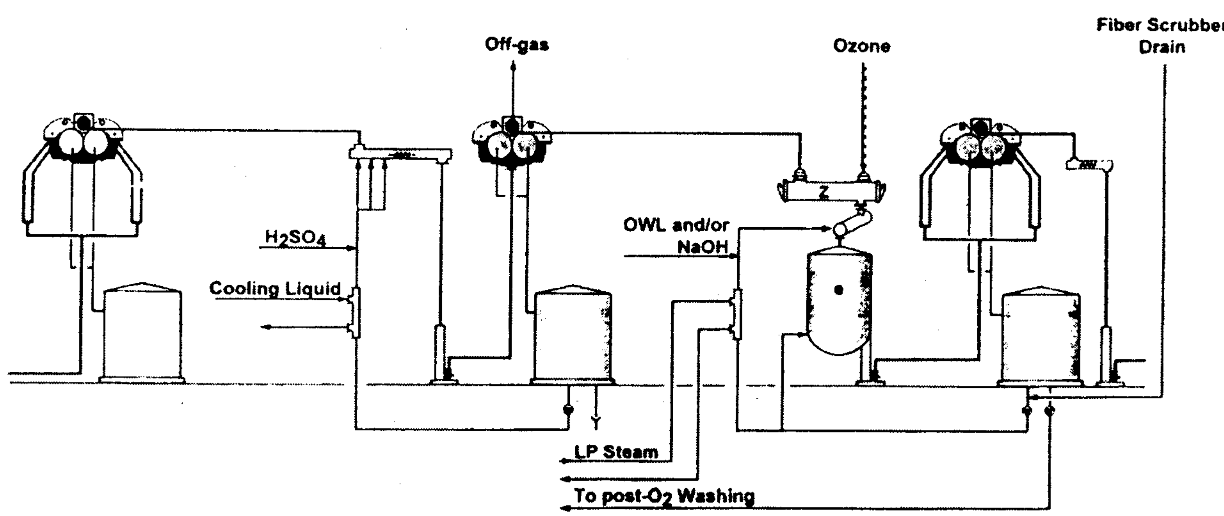

Fig. 3 : Filtrate arrangement in the Ze Trac system

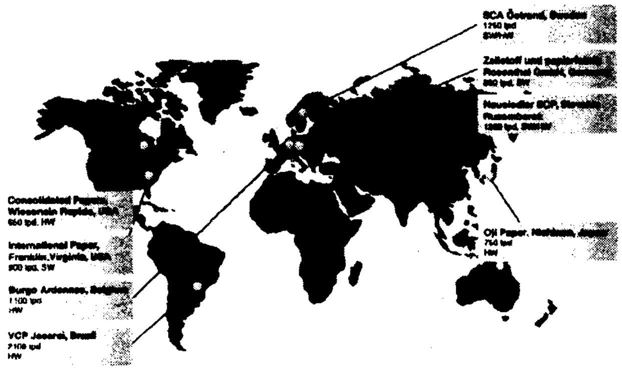

Fig. 4 : Ze Trac references

After this the color of the bleach plant effluent was reduced dramatically down to virtually zero.

In a press based fibreline with Ze Trac it is possible to reach very low effluent flows. Usually the total bleach plant effluent volume is less than 8-9 m^3/adt of pulp and COD is less than 20 kg/adt.

Hardwood fibreline

Ozone is a very interesting chemical for bleaching of hardwoods. In six of our references hardwood pulps are processed. We have mill experience of Scandinavian birch, mixed hardwoods from northern USA, hardwoods from eastern and southern Europe, mixed Japanese hardwoods and Brazilian Eucalyptus grandis. We have also tested many other hardwoods in our laboratory, amongst them a mixed Indian hardwood.

Indian hardwood chips were cooked according to the SuperBatch method in our pilot cooking plant and oxygen delignified according to the OxyTrac concept. Analysis data for this pulp are shown in Table 2.

The pulp was then belached with the reference sequence D(EOP)DD and with Ze Trac followed by chlorine dioxide and peroxide bleaching.

Fig. 5 shows that moderate ozone charge (5kg/odt) can replace a lot of chlorine dioxide. At a final brightness of 90% ISO more than 20kg active Cl/tonne of pulp can be saved with the (Ze) DP compared with a conventional D(EOP)DD sequence.

A small charge of hydrogen peroxide ofter (Ze) D bleaching gives a significant brightness increase. When the peroxide charge is limited to 1.2 kg H_2O_2/odt, bleaching can take place in the storage tower for bleached pulp. The conditions used in the laboratory to simulate this stage, "p", was 120 minutes at 65°C. For higher peroxide charges a separate P-stage has been used 960 minutes, 80°C).

Table 2 : Properties of SuperBatch pulp from Indian hardwoods Wood species: 80% mixed hardwoods (Casuarina, Subabul, Eucalyptus hybrid) and 20% bamboo.

Unbleached pulp	
Kappa number	17.1
Brightness, % ISO	35.0
viscosity, ml/g	920
Oxygen delignified pulp	
Kappa number	9.7
Brightness, % ISO	48.6
Viscosity, ml/g	801

The (Ze) D-bleached pulp was bleached with different conditions in the final peroxide stage, p or P. In Fig. 6 it is shown that a brightness increase for example from 88% ISO after (Ze)D to 90% ISO after (Ze) Dp can be reached with a charge of 2 kg H_2O_2/odt.

Operational cost comparison between the sequences (Ze) Dp and D(EOP)DD is shown in Table 3. The savings with the sequence (Ze) Dp correspond to more than 20% of the total bleaching chemical costs.

From an investment point of view the compact (Ze) Dp bleach plant is less costly than a D(EOP)DD bleach plant. Besides giving lower operational costs, the ozone sequence is also environmentally superior,

If a separate (PO) stage is installed the sequence can easily be changed from O(Ze)D(PO) to OZQ (PO), i.e. from a light ECF sequence to a TCF sequence using the same equipment, Fig. 7. This gives flexibility for future TCF production if regulations or customers will request that.

Fibreline for annual fibres

Ozone is also of great interest to annual fibres. We have tested many different raw materials in our laboratory and as usual, with pulp produced from annual fibres, the results vary much. Depending on type of annual fibre; bagasse, wheat straw, reed, etc., but also the origin of the fibres, how the raw material is pretreated and cooked. Thesefore it is essential to use the very same pulp if different bleaching sequences shall be compared.

A mill cooked bagasse pulp from India has been tested in our laboratory, see Table 5.

Some of the pulp was oxygen delignified in a "Mini-O"-stage. The conditions in the Mini-O-stage and in the

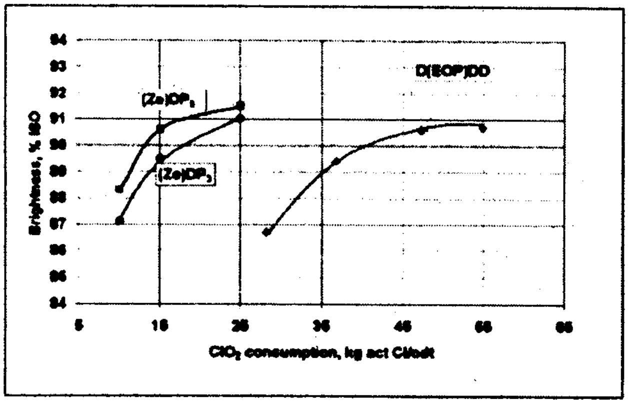

Fig. 5 : Bleaching of oxygen delignified Indian hardwood pulp with the sequences D(EOP) DD and (Ze) DP

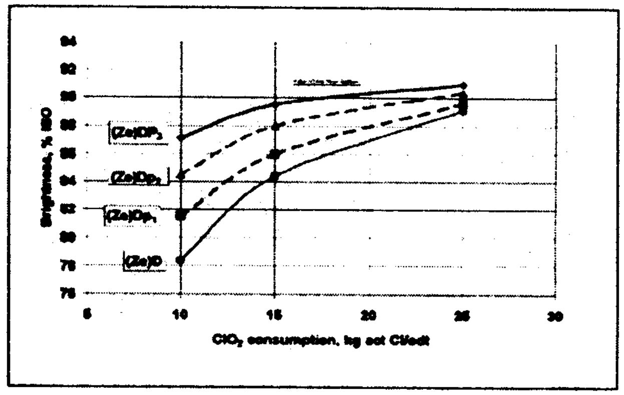

Fig. 6 : Bleaching of oxygen delignified Indian hardwood pulp with the sequences (Ze)D and (Ze) DP

other laboratory bleaching stages are summarized in the Experimental section. The analyses of the pulp after this mild oxygen stage are shown in Table 6.

The delignification was only about 1 kappa number, but the brightness increase was 6% ISO. The pulp was bleached with the sequences D(EO)D and D(OP)D. In the (OP)-stage, 3 kg H_2O_2/odt (Mini-O-delignified pulp) and 5 kg H_2O_2/odt (unbleached pulp) were charged. In Fig. 8 the results are shown.

With the sequence D(EO)D the target brightness 88% ISO was reached but without margin. After introduction of a Mini-O-stage the target brightness was reached with

Table 4 : Effluent load and OX-content in bleached pulp

		D(EOP)DD		(Ze)Dp
Washer		Press	Filter	Press
Effluent volume	m^3/adt	10	15-20	6-7
COD	kg/adt	23	23	18
AOX	kg/adt	0.4	0.4	0.1
OX	kg/adt	150	150	60

Table 3 : Chemical consumption and cost (mill level with carry over)

		OD(EOP) DD		O(Ze)Dp	
Brightness, % ISO		90		90	
Kappa number, unbleached		17		17	
kappa number, O-stage		10		10	
	INR/kg	Kg/odt	INR/odt	Kg/odt	INR/odt
Oxygen stage					
OWL	1.2	18	21	18	21
Oxygen	15	15	225	15	225
Bleaching					
ClO_2(aCl)	22	46	1012	23	506
NaOH	11	15	165	3	33
Oxygen	15	5	75	0	0
H_2O_2	25	3	75	2	50
H_2SO_4	2	13	26	15	30
OWL	1.2	0	0	15	17
Ozone	60	0	0	6	360
Total cost			**1599**		**1242**

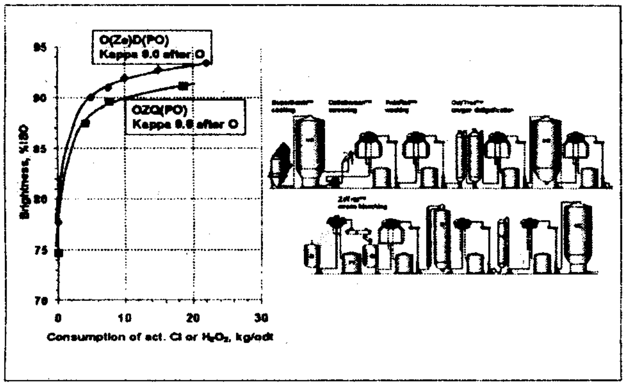

Fig. 7 ; Fibreline for Light ECF and TCF bleaching

a charge of about 35 kg active Cl/odt and with the sequence Mini-O-D(OP)D it was reached with 28 kg active Cl/odt.

By charging 5 kg ozone/odt according to the Ze Trac process, substantial savings in chlorine dioxide were achieved after (Ze)Dp, Fig. 9.

If were start the bleaching with a Mini-O-stage and then continue with Ze Trac and final bleaching Dp we can reach 89-90% ISO brightness, Fig. 10. In the p-stage here only 1 kg H_2O_2/odt was charged.

The bleach plant Mini-O(Ze) Dp is shown in Fig. 11. It is very compact bleach palnt, with only two "bleaching stages". However, In combination with Mini-O and the final p-stage it is still powerful. For example for bagasse pulp it is possible to reach 89% ISO brightness in a most economical way both from an investment and operational cost point of view. Furthermore it gives very low effluent flow and COD values, as it is basically only the D filtrate that is discharged.

EXPERIMENTAL

Both harwood and bagasse pulps were well-washed before laboratory bleaching. OxyTrac-, Mini-O, (EO)-, (EOP)- and (PO)-stages were performed in pressurized Teflon lined autoclaves, HC-ozone bleaching in a

Table 5 : Properties of Soda-cooked unbleached bagasse pulp

Kappa number	9.5
Brightness, %ISO	43.1
Viscosity, ml/g	1065

tumbling reactor and all other stages in sealed plastic bags. Specific bleaching conditions are shown in Table 7-9.

Analysis methods

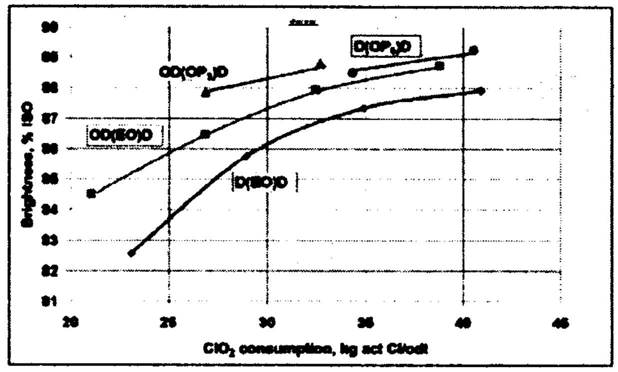

Fig. 8 : Bleaching of bagasse pulp with the sequences D(EO)D, D(OP)D, OD(EO)D and OD(OP)D

Table 6 : Properties of bagasse pulp after Mini-O

Kappa number	8.4
Brightness, %ISO	49.1
Viscisity, ml/g	1042

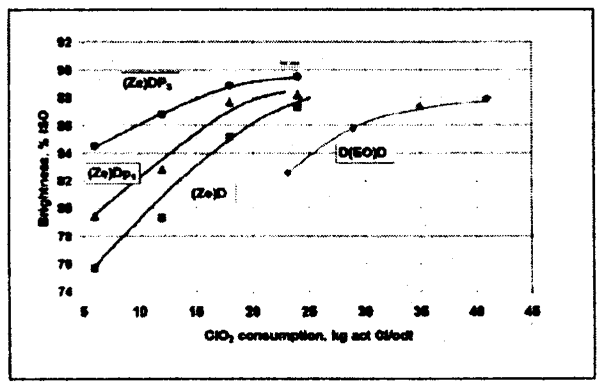

Fig. 9 : Bleaching of bagasse pulp with the sequences D(EO)D, (Ze)D, (Ze)Dp and (Ze)DP

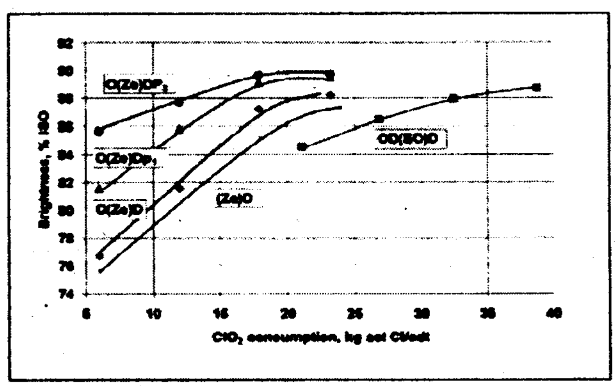

Fig. 10 : Bleaching of bagasse pulp with the sequences Mini-OD(EO)D, (Ze)D, Mini-O(Ze)Dp and Mini-O(Ze)DP

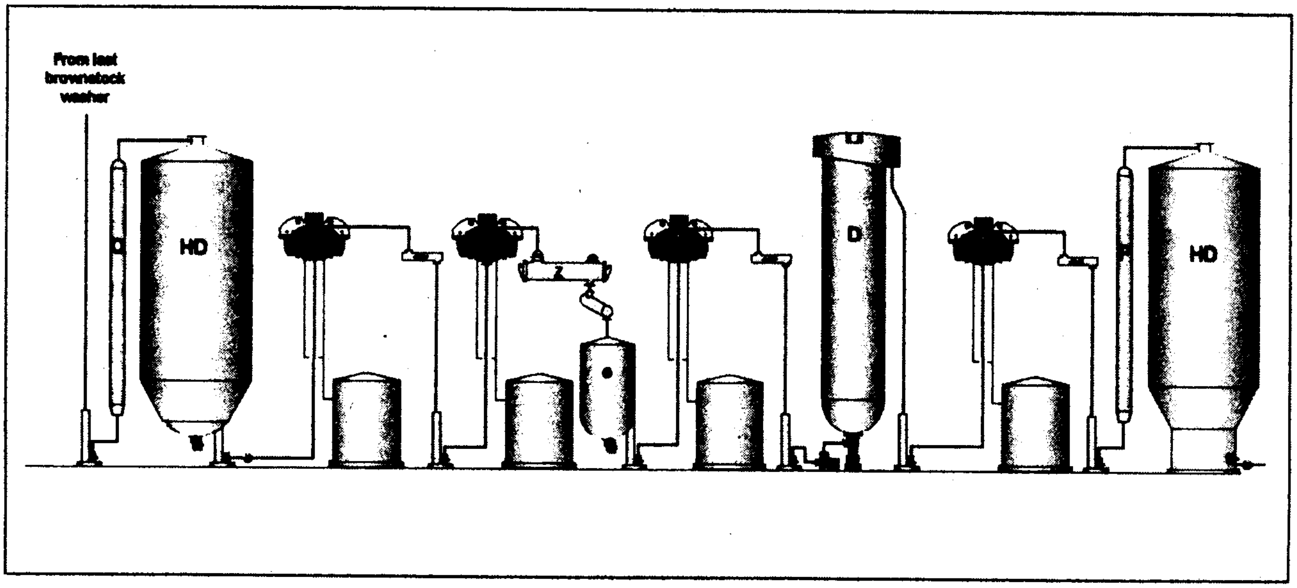

Fig. 11 : Fibreline with Mini-O followed by the bleaching sequences (Ze)Dp

Table 7 : Oxygen delignification

Pulp consistency	%	12	12
Temperature	°C	90/15	90
Time	min	30/60	15
Pressure	bar	10/5	5

Table 8 : Bleaching conditions 1

		D0	(EO)	(EOP)	(OP)	D1	D2
Pulp consistency	%	10	12	12	12	12	12
Temperature	°C	55	80	80	90	70	75
Time	min	60	120	120	60	120	120
Pressure	bar	0	2	2	5	0	0

Table 9 : Bleaching conditions 2

		(Z	e)	D	p	P	Q	(PO)
Pulp consistency	%	42	12	12	12	12	5	12
Temperature	°C	45	55	75	65	80	80	80-100
Time	min	~1	10	120	120	60	20	60-120

The following standard analysis methods were used ;

Kappa number	SCAN C 1: 00
Viscosity	SCAN CM 15 : 99
Brightness sheet preparation	SCAN CM 11 : 95
Brightness measurement	ISO 2470 : 1999
COD	EN 028142
AOX	EN 1485
OX	SCAN CM 52 : 94

ACKNOWLEDGEMENT

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