The ECO-Friendly Bleaching Concept With HC Zone

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ABSTRACT

High-consistency ozone bleaching is today a well-proven technology for environmentally sound bleaching. Today there are fifteen systems for HC ozone bleaching installed or under construction.

High-consistency ozone bleaching is a key factor for controlling the amount and quality of effluent emissions from a bleach plant. Replacing chlorine chemicals with ozone makes it possible to recover a larger part of dissolved organic material from bleaching and reduce the effluent parameters COD, Color and AOX.

In a new bleach plant using the Metso Eco-friendly bleaching concept the effluent volume can be reduced to 8-10 m^3/ton pulp, COD to 16-22 kg/ton, AOX to ~0.1 kg/ton and Color to 7-11 kg Pt/ton.

This paper will also discuss the differences between HC ozone and MC ozone bleaching technology.

Production and handling of ozone gas

Ozone is the most powerful oxidizing agent among the oxygen-based bleaching chemicals. It is an unstable gas that is produced by passing oxygen gas or air through an electrical discharge in the ozone generation system.

Production of 1 kg ozone requires about 10 kWh energy and about 8 kg pure oxygen (1). The product contains 7 kg oxygen and 1 kg ozone (ozone concentration about 12 weight-%).

Precautions for handling of ozone are essentially the same as for chlorine dioxide. Chlorate for chlorine dioxide generation has to be transported to and stored at the mill. Chlorine dioxide is generated on-site but it is then stored as a solution in large quantities.

An advantage of ozone is that it is generated on site and that there is no storage required. If oxygen is produced on site there is no need for transportation of any raw material for ozone generation.

Delignification and bleaching with ozone

Ozone can be used for both delignification and brightening of pulp. It can replace chlorine-based bleaching agents as chlorine and chlorine dioxide. The main by-product of the ozone reaction is oxygen. The use of ozone thus results in an effluent that is free from organochlorine compounds and that can be recirculated to the chemical recovery system.

The position of the ozone stage in a bleaching sequence can vary. The most common position is after oxygen delignification where it primarily acts as a delignifying agent. In this case the ozone charge is 3-8 kg/t. Ozone can also be used for activation of bleaching and as a brightening agent. The location is then later on in the bleaching sequence and the charge of ozone is lower. Ozone can also be used for pulp viscosity control for dissolving pulps.

Ozone reacts very fast with pulp and it is therefore no need for large ozone bleaching reactors. Ozone bleaching can be performed at high or medium pulp consistency. The two bleaching concepts will be compared below, section 5.

Metso HC ozone bleaching, ZeTrac™

The Metso ozone bleaching process is carried out at high pulp consistency, 35-42%. Typical pulp bleaching conditions are shown in **Table 1**.

Figure 1 shows how a typical Ze Trac system looks today. The pulp from post oxygen washing is acidified to pH 2.5-3 and then pressed to a high consistency, >35% with a dewatering press. The main part of the acid filtrate is recycled to dilute the pulp from the press ahead of the acid stage, but 1-3 m^3/adt of the filtrate is discharged to control metal ion concentrations in the system.

The pulp is fluffed in a shredder screw on the top of the press, and is then fed into the Z-reactor. Ozone is added to the reactor, which is operated at a pressure slightly below atmospheric. After the reactor, the pulp is diluted with alkaline filtrate. Pulp is then fed to a short extraction stage e (or to an existing longer E- or (EO)-stage if available) after which it is washed in a wash press. The excess alkaline filtrate from the press can be used as wash water in the post oxygen washing.

After ozone bleaching the spent gas from the reactor is led to a fiber scrubber (gas washer) and an ozone destruction unit. After this treatment the gas, containing primarily oxygen, can be used in other mill processes, for example in the oxygen delignification stage, in (EO)/(EOP)-stages, in white liquor oxidation or in external effluent treatment. However, especially when

Table 1 Typical ZeTrac™ conditions

Pulp consistency, %	35-42
Temperature, °C	45-60 (HW) 35-40 (SW)
pH	2.5-3.5
Pressure, MPa	atmospheric
Reaction time, min	~1
Typical charge, kg ozone/ton pulp	3-8

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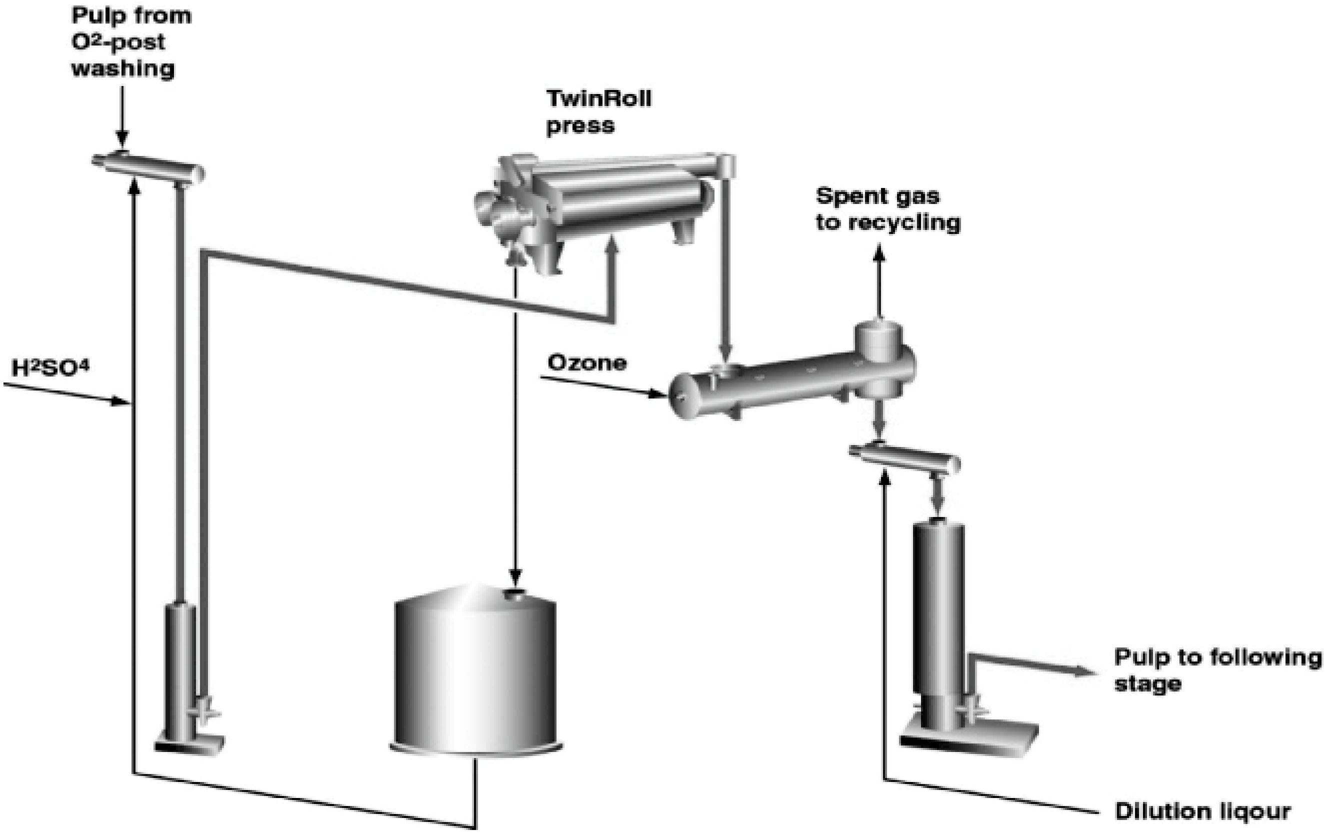

Figure 1 HC ozone bleaching.

high pressure oxygen is required, as in the oxygen delignification stage, the additional investment (compressor unit, piping etc.) has to be considered.

The kappa number reduction achievable in mill application is between 0.8-1.4 kappa/kg ozone and adt pulp in a kappa number interval between 4 to 12 of the pulp entering the ozone stage, **Figure 2**. The kappa number reduction is higher for pulp with higher kappa numbers entering the ozone stage.

ZeTrac HC ozone bleaching can be combined with other bleaching chemicals in many ways. Bleaching sequences used today are for example (Ze)DD, (Ze)DP, (Ze)(DP), (Ze)PP and Q(OP)(Zq)(PO). (DP) denotes a chlorine dioxide and a hydrogen peroxide stage without intermediate washing.

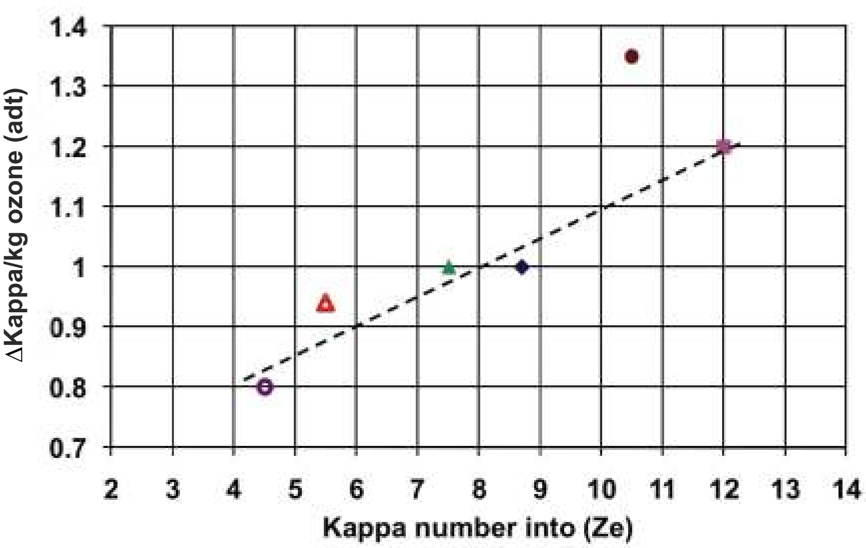

Figure 2 Efficiency of HC ozone bleaching.

Mill results obtained with HC ozone bleaching show only minor differences in standard pulp properties tested before and after the installation of HC ozone bleaching. From several installations it has been reported that the runnability of the paper machine is as good as before the installation of ozone bleaching (2, 3, 4).

Today there are fifteen ZeTrac systems installed or under construction, **Figure 3**. They are spread almost all over the world. These systems are used for production of both softwood and hardwood pulps. The design production varies from 190 t/d to 2100 t/d.

Figure 4 shows capacity during the years for bleached pulp, oxygen-delignified pulp and ozone bleached pulp (HC and MC) (5).

The use of ozone as a bleaching agent was considered for many years until the first industrial applications started about 20 years ago. After this, ozone bleaching has followed the same trend as oxygen delignification in the 70's.

Effluent load

The bleach plant is the major source of discharges to the recipient from a

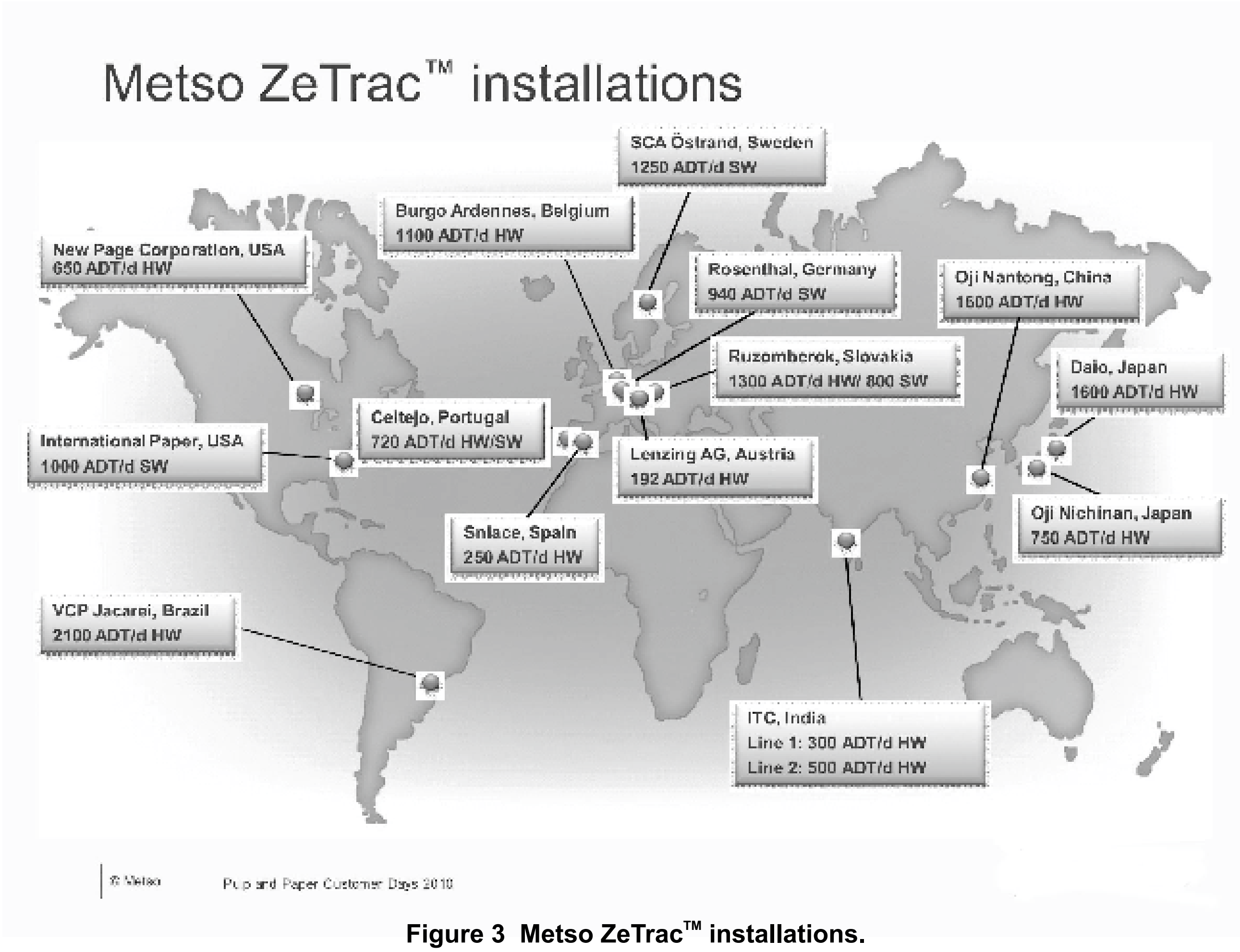

Figure 3 Metso ZeTrac™ installations.

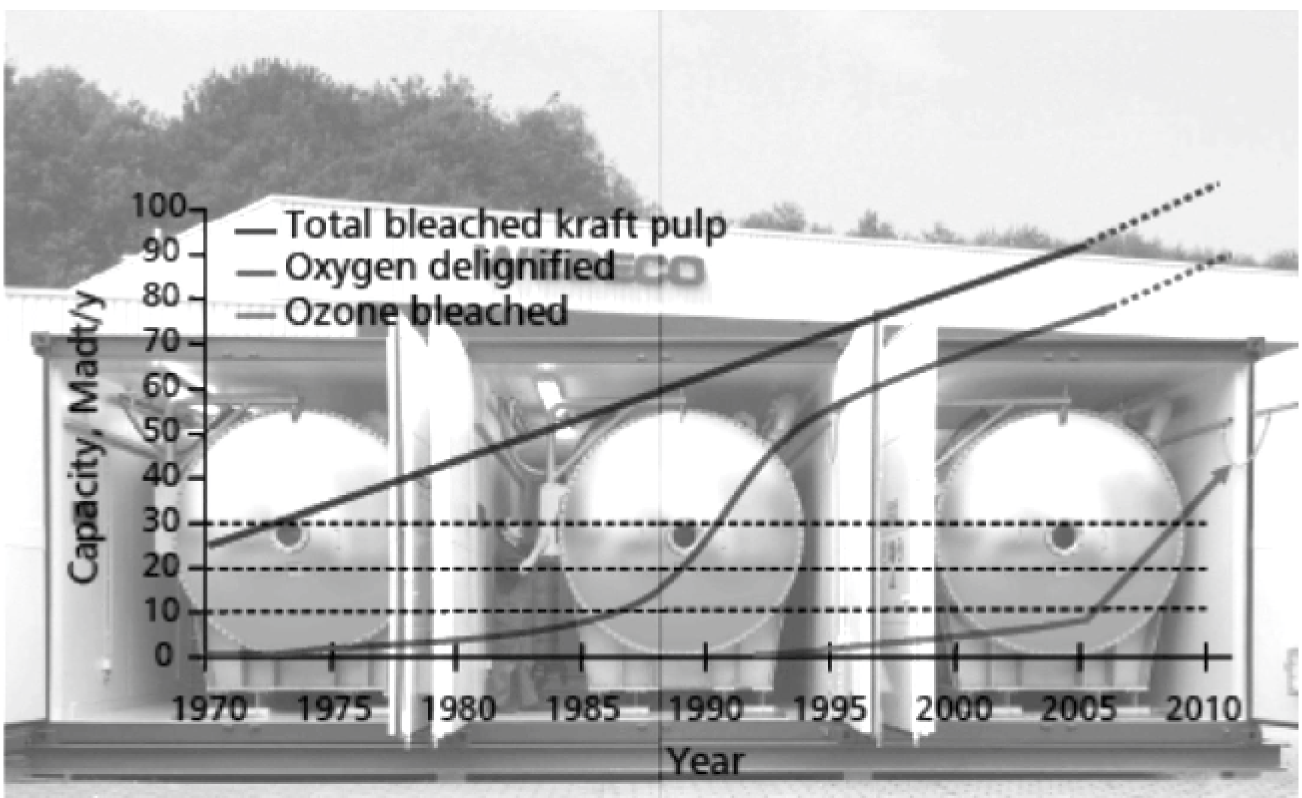

Figure 4 Evaluation of bleached pulp capacity (5).

modern pulp mill. When a conventional ECF sequence is used, for example Dht(EOP)DP, it is difficult to reduce the discharge by closure and recycling of the bleaching filtrates to post oxygen washing. The reason is the high chloride content that can cause plugging and corrosion in the recovery area. This is the case also if only the (EOP) filtrate is recycled.

The effluent load can be decreased by using ZeTrac HC-ozone bleaching, **Table 2**. The (Ze)-filtrate is alkaline and does not contain any chlorides. It can therefore be recycled to the post oxygen washing. Consequently, the COD and color discharge can be reduced. Furthermore, the AOX discharge will be lower for ozone-bleached pulps as the chlorine dioxide consumption is reduced.

When the bleach plant is closed the risk of scaling increases, especially in mills with a high calcium content in wood and mill water. This risk has to be carefully considered when the fiberline is designed.

Comparison of HC and MC Ozone

Ozone bleaching can be carried out at medium, 10-14%, and high, 35-42%, pulp consistencies. In our opinion, high pulp consistency has many advantages, see **Table 3**.

In the HC ozone bleaching systems there is a direct contact between the gas and the pulp. The flexibility of ozone concentration in the feed gas is high and the HC ozone system is operated below atmospheric pressure which prevents ozone leakages.

In the MC ozone systems, a large amount of compressed gas has to be mixed into the pulp suspension in order to get a good contact between ozone and pulp. In order to control the gas volume it is important to use a gas mixture with a high ozone concentration. The high pressure required in the MC system increases the risk of ozone leakages. Furthermore, ozone has a poor solubility in water and the decomposition increases with increasing temperature and partial pressure.

A higher kappa number reduction can be achieved in an HC ozone stage than in an MC ozone stage. **Figure 5** shows a comparison of mill data for MC ozone bleaching and HC ozone bleaching regarding delta kappa/kg of ozone. The ozone efficiency is higher for the HC ozone stage. Delta kappa/kg of ozone is 1.2 for HC ozone compared with 0.5 for

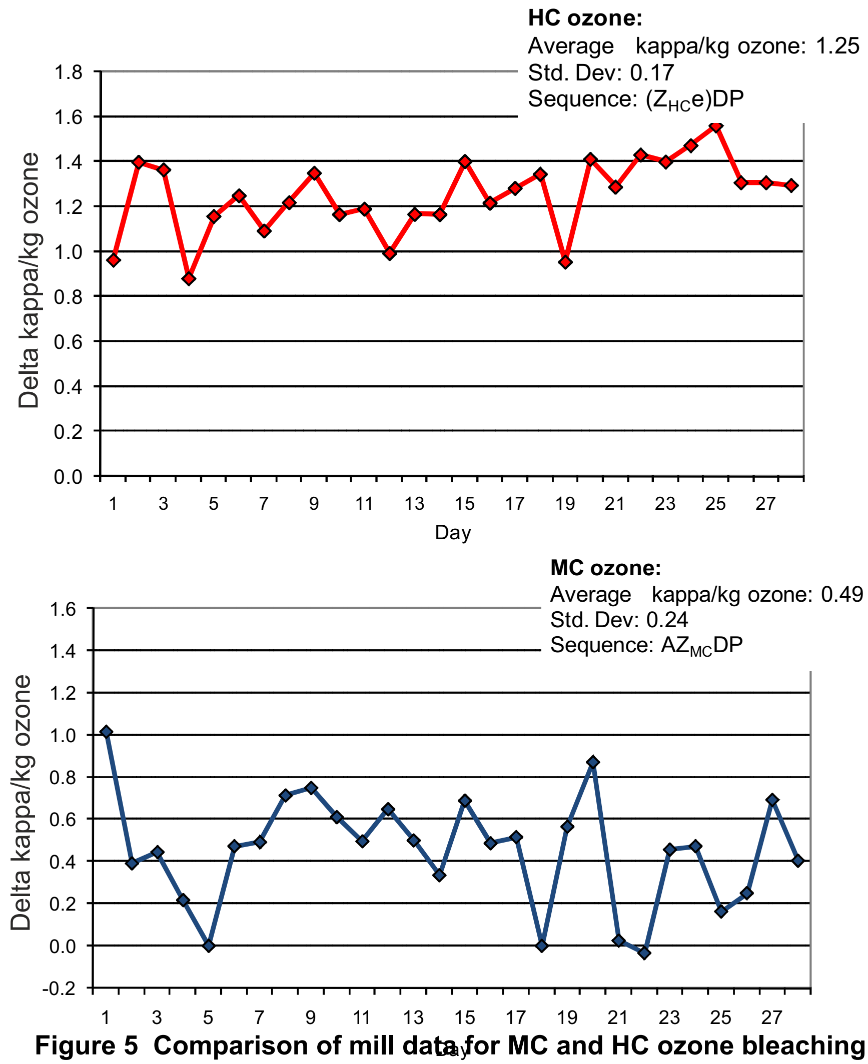

Figure 5 Comparison of mill data for MC and HC ozone bleaching as kappa/kg ozone.

Table 2 Effluent volume and load as a result of mass balance simulation

	D_{HT}(EOP)DD	(Ze)DP
Effluent volume, m^3/odt	11-12	8-10
COD, kg/odt	28	16-22*
AOX, kg/odt	0.4	0.1
Color, kg/odt	13	7-11*

**Variation depends on how much (Ze)-filtrate that is recycled to POW.*

Table 3 Comparison of HC and MC ozone systems

	HC	MC
Efficiency, kappa/kg ozone	+	
Variations in efficiency, brightness and viscosity	+	
Flexibility of ozone concentration	+	
Safety	+	
Investment cost		+
Layout		+
Recirculation of bleaching filtrate	+	
Total "+"	**5+**	**2+**

the MC ozone stage. Furthermore, the variations of delta kappa/kg of ozone are larger for the MC ozone stage.

In **Table 4** we will make the same comparison for brightness and viscosity of the bleached pulps. Again the variations are larger for the MC system. Consequently, the mill needs to bleach the pulp to a higher brightness than the target brightness to be sure of always reaching the target brightness and not too low brightness, which can be expensive.

One reason for the large variations in ozone efficiency, brightness and viscosity shown in Figure 5 and Table 4 can be that it is difficult to mix the large amount of gas with the pulp suspension.

HC ozone references

ITC Bhadrachalam

ITC Bhadrachalam today utilize ZeTrac in both their fiberlines (4). They have experienced many advantages with this process, for example lower production costs (chemicals and energy), improved pulp quality, lower AOX discharge to the recipient and and lower OX-content in the bleached pulp.

The flow sheet in **Figure 6** shows the very short bleaching sequence in ITC, Line 2. The production is 400 odt/d and the raw material is mixed hardwoods. SuperBatch kraft cooking is followed by oxygen delignification according to OxyTrac. The bleach plant consists of ZeTrac followed by washing and then a combined chlorine dioxide and peroxide bleaching stage followed by washing.

The target brightness is 89% ISO. In **Table 5** data from a mill test run performed in ITC mill are shown. The effluent volume in the mill was 10 m^3/ton, the COD discharge was 18 kg/odt and the Color value was 7.7 kg Pt/odt.

Celtejo, Rodau mill

The new Celtejo fiberline in Rodau was started up in 2008. The bleach plant is designed for 720 adt/d and the raw material is Eucalyptus globulus. After kraft cooking the pulp is oxygen-delignified according to OxyTrac.

This bleach plant was built in such a way that it is possible to run alternative ECF bleaching sequences (Ze)DP and (Ze)DD and also the total chlorine free (TCF) sequence (Zq)PP, **Figure 7**. Nowadays the sequence (Ze)DP is used most of the time.

In this mill the target brightness is 89% ISO. In **Table 6** the bleaching chemical consumption and effluent load reported from this mill are shown (6).

A new Chinese mill now under construction is Oji Nantong, **Figure 8**. This new greenfield mill will start the production late 2012. The raw material is a mixture of eucalyptus and acacia and the production rate is 1600 adt/d.

The bleaching sequence is (Ze)DP. The target brightness is 90% ISO. The main reason for choosing ZeTrac in this mill is to keep the effluent load as low as possible. For this production two ozone bleaching reactors in series will be used in order to get a retention time that is long enough.

Table 4 Comparison of mill data for HC and MC ozone bleaching

	HC Z	MC Z
Sequence	(Ze)DP	AZDP
Brightness, % ISO	90.2	89.6
Brightness variations, σ	0.4	1.1
Viscosity, dm^3/kg	743	693
Viscosity variations, σ	27	47

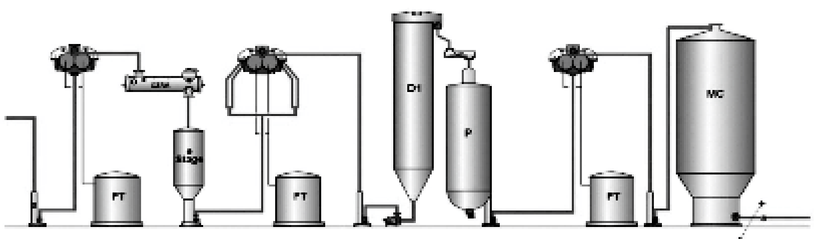

Figure 6 ITC Bhadrachalam bleach plant, Line 2.

Table 5 Effluent load from ITC Bhadrachalam bleach plant, Line 2.

	Mill data
Brightness, % ISO	**89**
Volume, m^3/odt	10
COD, kg/odt	18
Color, kg Pt/odt	7.7

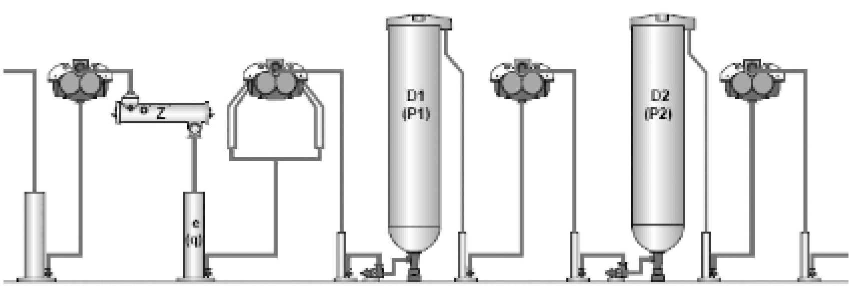

Figure 7 Celtejo bleach plant.

Table 6 Chemical consumption and effluent load from Celtejo bleach plant

	Mill data
Brightness, % ISO	**89**
Chemicals	
ClO_2, kg active Cl/odt	20
Ozone, kg/odt	5-6
H_2O_2, kg/odt	4-5
Effluents	
Volume, m^3/odt	7-9
COD, kg/odt	19

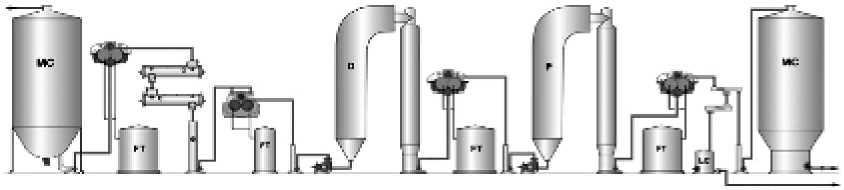

Figure 8 Oji Nantong bleach plant.

Conclusions

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