The Evolution of Low Emission Pulp Mill Technology

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Abstract

The evolution of pulp mill technology focusing on reduced discharge levels of dissolved organic material with bleach plant effluents is discussed. The importance of reaching a low kappa number and recycling dissolved organic material prior to final bleaching in order to minimize pollution is evident. All effluent parameters - COO, BOD, Colour and AOX are decreased as kappa number is decreased. In case of AOX, the reduction is not only depending on decreased kappa number, but also on decreased use of elemental chlorine and chlorine dioxide in the bleaching process.

INTRODUCTION

Ever since Sunds Defibrator (today Metso Paper) together with MoDo and CIL pioneered the development of oxygen delignification technology in the late 60's and early 70's, our basic approach has been to look for processes that increase delignification and increase recycling of dissolved lignin (1,2,3,4).

Parallel to these efforts the pulp industry and research institutions have extensively characterized bleach plant effluents with respect to chemical composition and impact on receiving waters. Some of the effluent effects can be characterized as short term/range and others as long term/range.

The short term/range or acute effects are related to the presence of easily biodegradable material, often represented by the Biological Oxygen Demand (BOD) value of the effluent. This material causes oxygen starvation in the receiving water and can be acute toxic. Such acute effects can be abated in secondary treatment systems.

The long term/range effects are not easily handled in secondary treatment systems. These are related to the persistent character of some effluent components. These materials are more resistant towards biodegradation and have a tendency to bio-accumulate and interfere with the natural processes occurring in aquatic life. For example, the presence of highly chlorinated low molecular mass organic material, like 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF), as well as the total amount of chlorine chemically bound to organic compounds (AOX), originating from the use of chlorine chemicals in bleaching, has been especially focused (5).

There are also other effects associated with the physical properties of the effluent as for example its colour, decreasing light penetration in the water. This property of the effluent is not affected by secondary treatment.

These findings have made us confident in our approach to engage in development of processes that increase delignification, allow recycling of dissolved organic material and minimize the use of chlorine chemicals.

What are the technologies that will give us these benefits?

SuperBatch™ cooking:

• Introduced by Metso (6) in the early 1990's and further developed in recent years (7,8,) has provided a cooking technology that gives you increased flexibility to optimize the complete fibreline for minimum effluent emissions and maximum pulp quality for different wood raw materials.

Oxygen delignification

• Introduced in 1970. Dissolved lignin is recycled to the recovery boiler, decreasing effluent load with up to 40-60%. (5, 9, 10)

Ozone bleaching

• A novel technology by Metso (11, 12, 13), that applies ozone at high pulp consistency and gives additional possibilities to recycle dissolved lignin to the recovery boiler and to produce pulps with very low lignin content.

Hydrogen peroxide bleaching

• A process that was pioneered by EKA Nobel AB (14.15). In combination with oxygen and ozone bleaching, it gives the possibility to produce fully bleached pulps in light ECF bleaching sequences or without the use of any chlorine chemicals in TCF bleaching sequences.

In this paper we will review the evolution of ECF and TCF bleaching technology, made possible by the combination of oxygen, ozone and hydrogen peroxide bleaching stages, and the subsequent impact on effluent emissions.

OxyTrac™ oxygen delignification

Metso's patented two-stage OxyTrac™ bleaching system introduced in 1996 is the third generation of oxygen delignification technology and represents today's state of the art technology.

Oxygen delignification capacity grew moderately during the first fifteen years after the introduction in 1970. From the mid 1980's, after introduction of the second generation oxygen delignification technology, capacity grew significantly faster

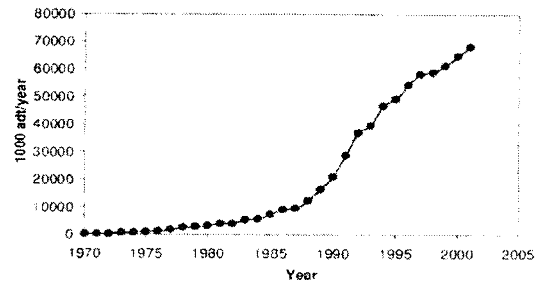
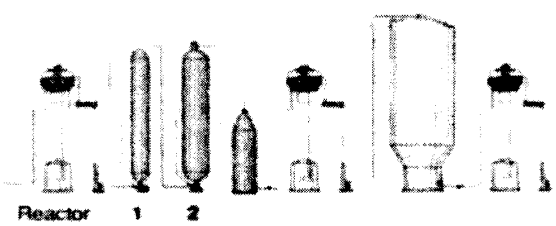


Fig. 1 World wide oxygen delignification capacity

and has today reached about 70 million adt per year, (Fig.1). This corresponds to about 80% of the total production of bleached kraft pulps.

Key features of the OxyTrac system are indicated in Fig. 2.



Reactor	1	2
Time, min	30	60
Pressure top of reactor, bar	8-10	3-5
Temperature, °C	80-85	90-100

Fig. 2. OxyTrac process conditions

In all delignification and bleaching stages there are competing reactions, some of which are positive in terms of delignification and bleaching and some which are negative in terms of creating cellulose and hemicellulose degradation.

By dividing the delignification process into two stages the ratio of lignin degradation to cellulose and hemicellulose degradation can be improved. Beneficial conditions for these two stages are:

• The first stage conditions:

- high concentration of alkali
- high concentration of oxygen (high pressure)
- low temperature

- short retention time
- The second stage conditions:
- lower concentration of alkali
- lower concentration of oxygen. higher temperature.
- longer retention time.

In comparison with one-stage medium consistency oxygen delignification it has been possible with the OxyTrac process to increase degree of delignification for softwoods from about 50% to about 70% and for hardwoods from 30-40% to 40-50%.

Improvements, relative to the one-stage oxygen delignification process, are exemplified in Fig. 3 and 4 for delignification of an eucalyptus kraft

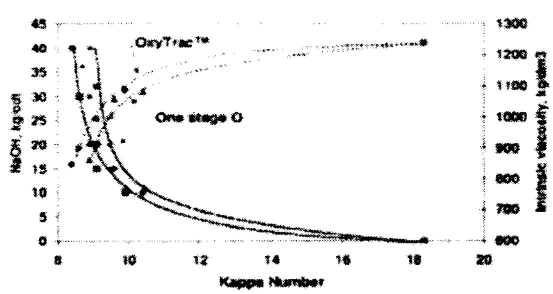


Fig. 3 OxyTrac compared to one-stage oxygen delignification

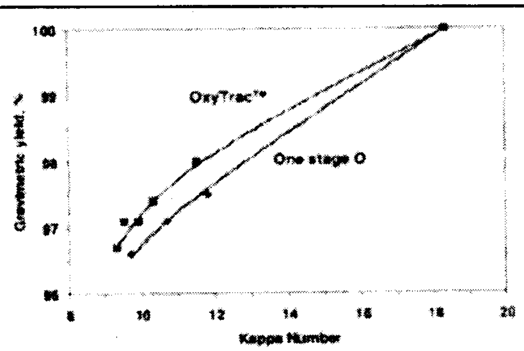
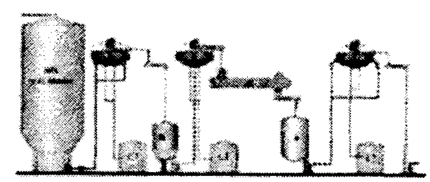


Fig. 4 OxyTrac compared to one-stage oxygen delignification

pulp with kappa number 18.3. The more favourable conditions in the OxyTrac process have resulted in higher yield and viscosity as well as lower caustic consumption for a given kappa number reduction.



	a	Z	e
Pulp cons. %	10	40	12
Temp., C	35-45	35-45	60
Time, min	10	1	10
pH	2-3	2-3	10.5

Fig. 5 ZeTrac conditions

ZeTrac™ Ozone bleaching

Ozone bleaching was commercially introduced in the early 1990's, primarily to cope with increasing demands for pollution abatement in a cost efficient way (12, 13). Basically two technologies were adopted performed at medium (MC) and high (HC) pulp consistency respectively.

Metso's ZeTrac system represents the second generation HC ozone bleaching technology, (Fig.5). The pulp is acidified prior to pressing to high consistency in a TwinRoll press. The acid filtrate is recycled to dilute pulp from the press ahead of the acid stage and part of the filtrate is also put to the sewer.

The pulp is fluffed in a specially designed shredder screw and fed into the reactor. Ozone gas is

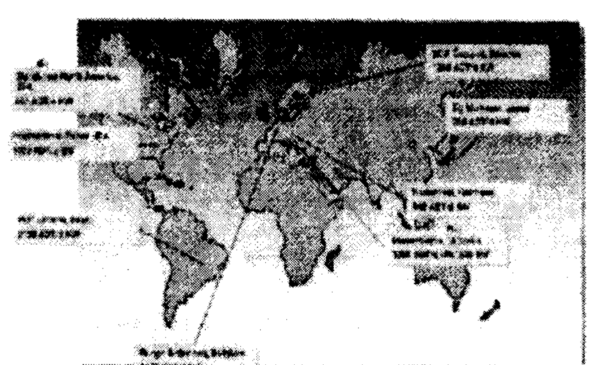


Fig. 6 ZeTrac references

added and gas flow is controlled by two fans, one of which is connected to the shredder hood and the other in the residual gas handling system. Pressure in the reactor is slightly below atmospheric pressure.

By way of a dilution screw pulp is fed to the extraction stage after which it is washed on a TwinRoll press. The alkaline filtrate from the press can be used for counter current washing in the brown stock fibreline. Reference installations are shown in Fig. 6.

Factors influencing the amount and quality of bleach plant emissions

The amount and quality of bleach effluent emissions are dependent on a number of factors. Organic material dissolved in cooking, oxygen delignification and ozone bleaching can to a large extent be recycled to the chemical recovery system.

However, additional bleaching stages are required to produce fully bleached kraft pulps. In the case of chlorine and ECF (elementary chlorine free) bleaching, spent liquors contain inorganic chloride compounds that if recycled to the recovery system would lead to severe corrosion. In the case of TCF (totally chlorine free) bleaching, the equilibrium concentration of certain inorganic and organic salts will increase with increasing degree of closure. At some critical point the concentration of these salts will exceed the solubility limit and various types of deposits may

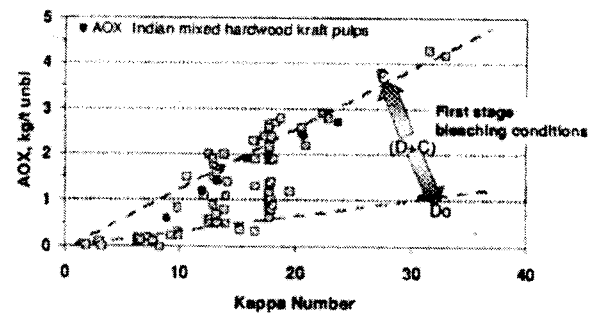


Fig. 8. Chlorinated organic material as kg AOX/t unbleached pulp formed in bleaching

be formed, which negatively affect the operation of the fibreline.

The key factors controlling the amount and quality of effluent emissions from a bleach plant will be lignin content (kappa number) and the amount of Cl_2 and ClO_2 used in bleaching.

This is exemplified in Figs. 7 and 8 showing total dissolved organic material, expressed as COD (chemical oxygen demand), and AOX against kappa number for bleaching of different softwood and hardwood kraft pulps. Results from bleaching of Indian hardwood pulps are included.

From these results it is quite obvious that a lower kappa number decreases the content of COD in the filtrate from bleaching. The scatter in AOX reflects different conditions in the first bleaching stage. A high proportion of chlorine in that stage results in a high AOX formation

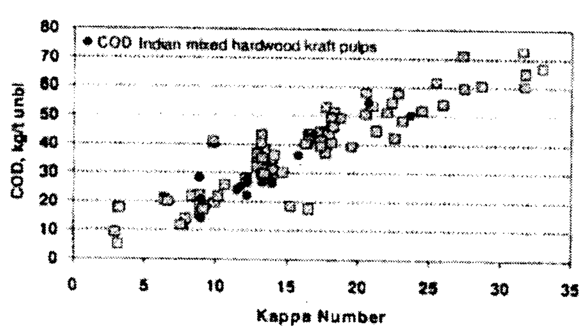


Fig. 7. Dissolved organic material as kg COD/t unbleached pulp formed in bleaching

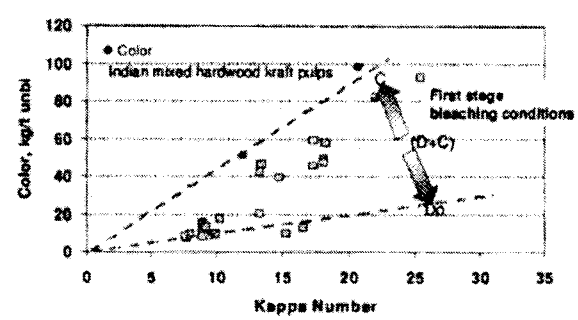


Fig. 9. Coloured material as kg/Pt/t unbleached pulp formed in bleaching.

Table 1 Evolution of pulp bleaching technology for improved environmental performance during the last 20 years.

	Bleaching a seqauences	Focus
1980's	(C+D)(EO)DED, (C+D)(EO)HD, (C+D)(EO)D	BOD
1990's	**ECF:** D(EO)DED, D(EOP)DD, D(EO)D **TCF:** Q(PO), Q(PO)(ZQ)(PO)	Chlorinated organic compound (AOX and dioxins)
2000's	**ECF**: D(PO)(DD), D(EOP)D, D(EO)DD **Light ECF:** Q(PO)DD, Q(PO)(DQ)(PO), (DQ)(PO)D, Z(EO)DD, (Ze)DP, Q(PO)(Dq)(Z(PO) TCF: Q(PO), Q(PO)(ZQ)(PO), Z(PO), Q(PO)(PaaQ)(PO)	Total dissolved organic material, closure, production costs

and vice versa, A low kappa number combined with ECF bleaching results in very low AOX values.

The colour of the effluent is also dependent on kappa number and conditions in the fist bleaching stage, exemplified in Fig. 9.

The total effluent volume will be influenced by the number and type of bleaching stages and the degree of closure of the bleach plant. A modern bleach plant of today will have an effluent volume of less than 10 m^3/adt.

Mill references

Concern for the environment has had a profound impact on the evolution of pulp mill technology, Different aspects of bleach plant emissions have been focused during the last more than 20 years indicated in Table 1.

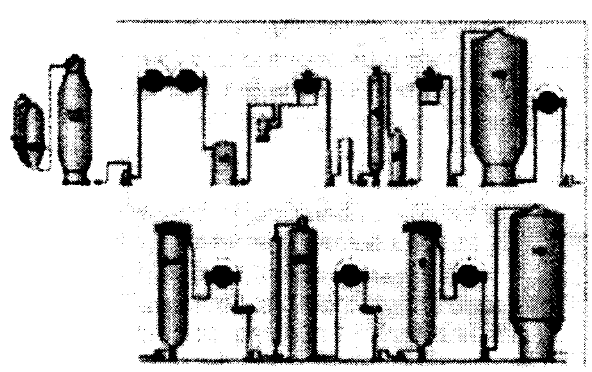


Fig. 10 Schematic outline of the ITC Badrachalam fiberline.

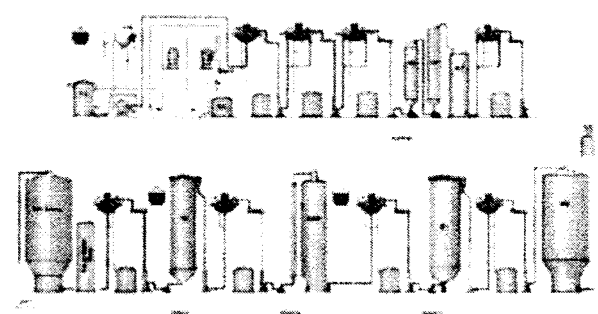


Fig. 11. Schematic outline of the ITC Bhadrachalam fiberline

Today oxygen delignification is standard, Chlorine gas has been abandoned in new installations and is also rapidly replaced with chlorine dioxide in existing installations,

The J,K, Paper Mills, (Fig.10), and ITC Bhadrachalam, (Fig. 11), are good in mill modernization projects prioritizing a reduction of bleach plant emissions, Especially, the ITC Badrachalam represents today's state of the art ECF bleaching technology.

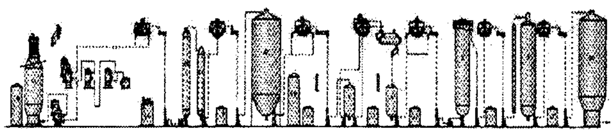


Fig. 12. VCP Jacarei 2100 tpd hardwood fiberline with an Oa(Ze)DP bleach sequence.

There is a growing interest in high consistency ozone bleaching as a cost efficient way to further decrease effluent emissions and to facilitate light ECF and TCF bleaching sequences. The VCP Jacarei fibreline in Brazil, outlined in Fig. 12, takes advantage of a high consistency ozone bleaching stage, ZeTrac™, in order to facilitate a light ECF bleaching sequence.

Today eight mills are using the ZeTrac

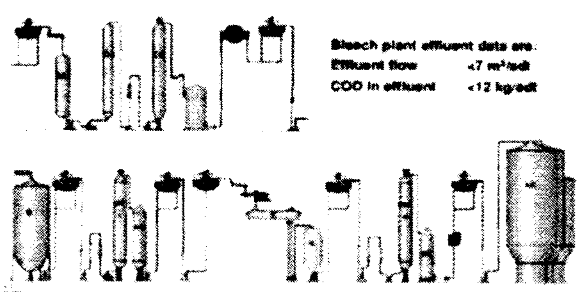


Fig. 13. Schematic outline of the SCA Ostrand TCF bleach plant.

technology, c.f, Table 2. Ruzomberok in Slovakia has made the most recent decision to go with ozone bleaching in order to meet the environmental demands that are put on the mill.

Oji Nichinan in Japan, which has modified its bleach plant for bleaching of hardwood kraft pulp from OCEPD to Oa(Ze)EPD, reports (16) a kappa number reduction form 10.5 after oxygen delignification to 3.1 after the (Ze) stage and a 99% reduction of AOX and chloroform in

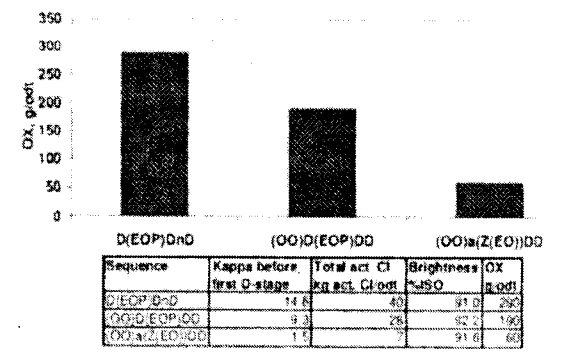


Fig. 14. Chlorinated organic material remaining in pulp after bleaching

their bleach plant effluent.

The SCA Ostrand mill in Sweden referred to above and schematically outlined in fig.13, operates a TCF bleach plant. This mill has reduced

Table 2 ZeTrace™ references

Mill	Country	Pulp	Capacity, adt	Bleaching	Brightness % ISO
IP Franklin	USA	Swd	1000	OaZ (EO) D	83 (%GE)
SCA Ostrand	Sweden	Swd	1250	(OO) Q (OP)a(Zq)(PO)	88
SENA, Wisconsin Rapids	USA	Hwd	650	OaZ(EO)DD	88-5 (%GE)
ZPR Rosenthal	Germany	Swd	900	(OO)Q(OP)D(Z(POP))	90
Burgo Ardennes	Belgium	Hwd	1100	(OO)D(Z(EO))(DD)	89
Oji Nichinan	Japan	Hwd	750	OaZEPD	85
VCP Jacarei	Brasil	Hwd	2100	Oa(Ze)DP	90
Ruzomberok	Slovakia	Swd/Hwd	900/1300	(OO)a(Z(EO))(Dn)D	88

1) Startup 2004

effluent load and discharge of dissolved organic material to less than 7 m³/adt and less than 12 kg COD/adt respectively, Discharge of AOX formed in bleaching is completely eliminated,

The trend towards ECF and light ECF bleaching sequences, utilizing oxygen delignification and ozone bleaching, has also resulted in a significant reduction of chlorinated organic material (AOX) remaining in the pulp after bleaching demonstrated in Fig. 14 for the bleaching of eucalyptus kraft pulp.

The importance of reaching a low kappa number in order to minimize pollution is evident. All effluent parameters-COD, BOD, Color and AOX-are decreased as kappa number is decreased. In case of AOX ther eduction is not only depending on decreased kappa number, but also on decreased use of elemental chlorine and chlorine dioxide in the bleaching process.

CONCLUSION

Although there are very many aspects to consider for the pulp and paper industry in order to reach an environmentally sustainable pulp and paper production, effluents from pulping and bleaching processes represent an important factor. Major steps have been taken in recent years to decrease and abate the harmful effects of such effluents. Still, the industry is constantly looking for better and better technology to further decrease environmental hazards and pulp manufacturing costs.

Metso's approach has been to focus on developing process technology that increases delignification, allows recycling of dissolved organic material and minimizes the use of chlorine chemicals. Extended oxygen delignification and ozone

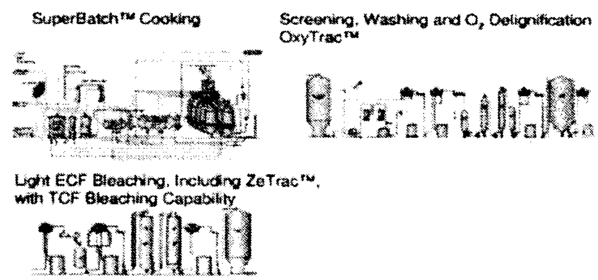


Fig. 15. Fibreline technology beyond the current BAT level.

Table 3. Bleach chemical consumption and costs at 90% ISO reverted brightness. The pulp was produced in the laboratory from Eucalyptus grandis chips in pilot cooking and oxygen delignification equipment.

Sequence Kappa No.		D(EOP)(Dn)D 10.9		a(Ze)(Dn)D 10.9	
Reverted brightness[1], % ISO		90		90	
Brightness before reversion, % ISO		92.3		92	
Est. bleaching yield, %	Chemical cost	96		96	
	USD/unit	kg/bdt	USD/bdt	ka/bdt	USD/bdt
H_2SO_4	0.08	6	0.48	12	0.96
Ox. Wh. Liq. as NaOH	0.06	0	0.00	12	0.72
NaOH	0.25	16.5	4.13	5	1.25
H_2O_2	0.91	3	2.73	0	0.00
O_2	0.07	3	0.21	0	0.00
O_3	1.18	0	0.00	6	7.08
ClO_2, act. Cl	0.38	35.5	13.49	13.5	5.13
Total cost USD/bdt			**121.0**		**15.1**

1) h at 105°C and dry atmosphere

bleaching are good examples that increase recycling of dissolved material and at the same time decrease bleach chemical costs.

In Table 3 it is shown that a substantial bleach chemical cost reduction was achieved when changing from a D(EOP)(Dn)D bleaching to the a(Ze)(Dn)D sequence. The large reduction in chlorine dioxide consumption more than 20 kg/ bdt- and the use of oxidized white liquor in the (Ze) stage instead of fresh caustic are the main factors for this cost reduction.

A fibreline alternative that today would bring the production of bleached kraft pulp beyond what is referred to as current BAT (Best Available Technology) level is exemplified in Fig. 15.

The starting point is SuperBatch cooking combined with extended oxygen delignification and ozone bleaching in order to maximize recycling of dissolved organic material to the recovery boiler. Final bleaching is performed in a light ECF bleaching sequence with TCF bleaching capability.

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