High Consistency Ozone Bleaching-Present Status and Future

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INTRODUCTION

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

Cost efficiency, in terms of low capital expenditure and low operating costs, and pulp quality have been the measures by which this technology has been evaluated.

Metso Paper's development work in the area of ozone bleaching started in 1979. About ten years later a co-operation with Union Camp was initiated resulting in the world's first high consistency ozone bleaching plant starting up in September 1992 at Union camp's Franklin pulp mill. The evolution of this technology to present date is described in this paper.

Environmental concern a driving force for development

Ever since oxygen delignification was commercially introduced in the 1970's, the pulp and paper industry has continuously been striving towards reducing effluent emissions meeting ever-stricter environmental demands. 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. This path of evolution is exemplified in figure 1. While aiming at the utopian target of an effluent free fiberline a number of important new technologies have been introduced to the industry.

During these last 35 years we have seen the introduction of closed pressurized screening and improved washing technology that minimizes the loss of black liquor solids. We have also seen that use of chlorine and sodium hypochlorite has been abandoned in favor of chlorine dioxide, oxygen, hydrogen peroxide and ozone and to some degree PAA (peracetic acid.)

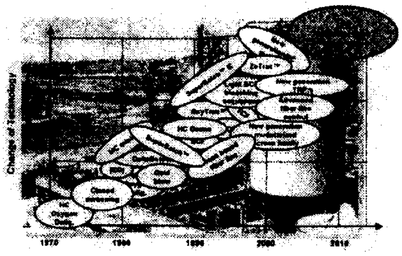

Figure1. Evolution of the chemical pulp fiberline

Kraft cooking has been developed to become more energy efficient and in some cases more selective. Oxygen delignification has reached its 3rd generation with OxyTrac™, which for softwood allows 60-70% kappa number reduction, and for hardwood up to about 50% kappa number reduction (depending on hexeneuronic acid content of unbleached pulp.)

We started in the late 1970's about 25 years ago.

In the late 1970's, oxygen delignification had been around for almost 10 years, though it had not yet become accepted by the industry. There were still doubts whether the quality requirements on pulp were met or not. Today we know better. Oxygen delignification is an industry standard.

The sulfite pulping industry, which often uses magnesium as cooking base chemical, was looking for a delignification technology that would not interfere with the recovery system as a caustic based oxygen delignification system would do.

Metso Paper (at that time Sunds Defibrator) had been investigating HC ozone bleaching in laboratory scale since 1979. We agreed to install a pilot plant for high consistency ozone bleaching of Mg-sulfite pulp at the German pulp and paper company PWA's mill in stockstadt. It was started up in 1982(1). A simplified flow sheet-also from that time-is shown in figure 2.

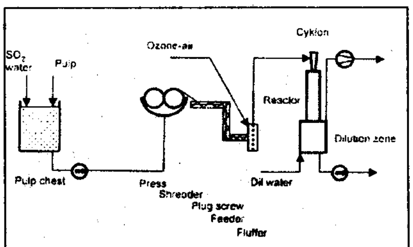

Figure 2. HC ozone pilot plant at PWA's Mg-sulfite mill in Stockstadt, Germany. Capacity 130 kg/h

Although the operation was satisfactory and results in terms of performance and pulp quality met expectations, the customer did not decide to go to full-scale. We shelved the project and for some years we pursued other routes towards low emission pulping and bleaching.

From C-Free® to Zetrac™

The evolution of ozone bleaching resembles that of oxygen delignification. It took 15 to 20 years before oxygen delignification took off and today more than 80% of the production of bleached kraft pulp is processed through oxygen delignification stages. This is illustrated in figure 3.

Ozone bleaching has faced the same challenges as oxygen delignification did more than 30 years back. A key concern within the industry is pulp quality.

One aspect of pulp quality is the impact of the corresponding papermaking furnish on the runnability of the paper machine fed with that furnish. In this way, SCP Ruzomberok demonstrated the high quality of both hardwood and softwood ozone bleached pulps in the autumn of 2005. The mill made a new world-record for paper production on one of their paper machines, using solely ozone bleached hardwood and softwood pulps in their fine-paper furnish (2).

There are today 12 mills that have chosen to install C-freeor ZeTrac high

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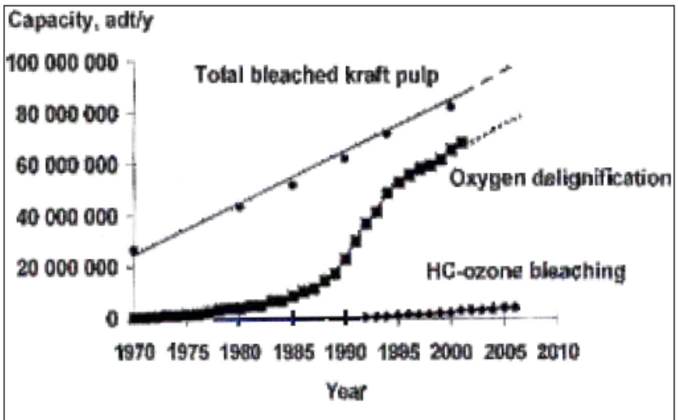


Figure 3 Bleached pulp capacity

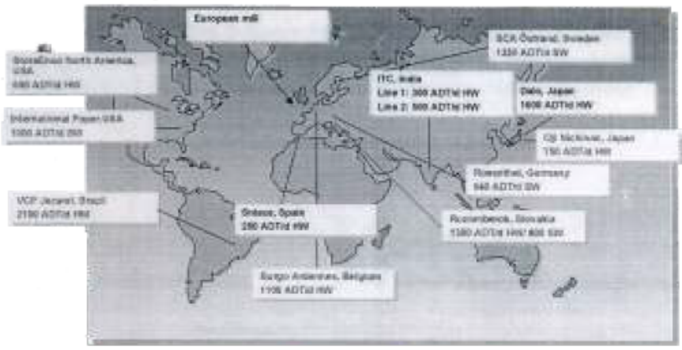


Figure 4. Global Metso HC ozone bleaching installations

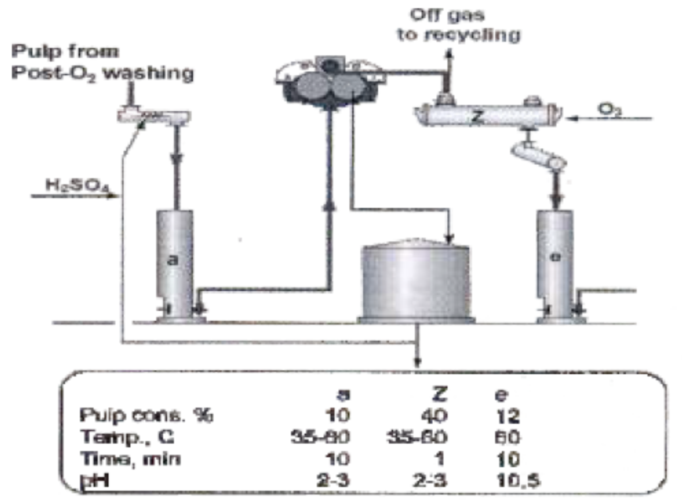


Figure 5. ZeTrac and typical operating conditions

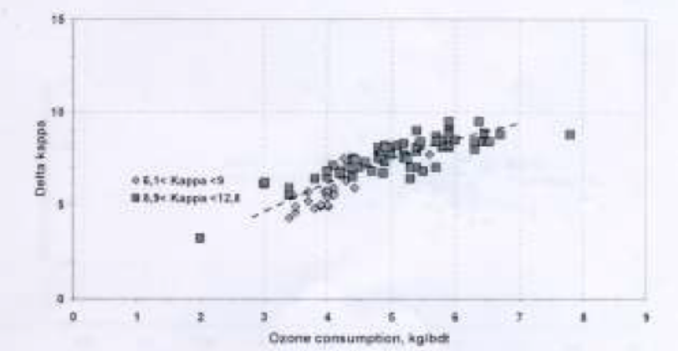


Figure 6. a(Ze) bleaching in the laboratory of hardwood kraft pulps from more than 40 different sources

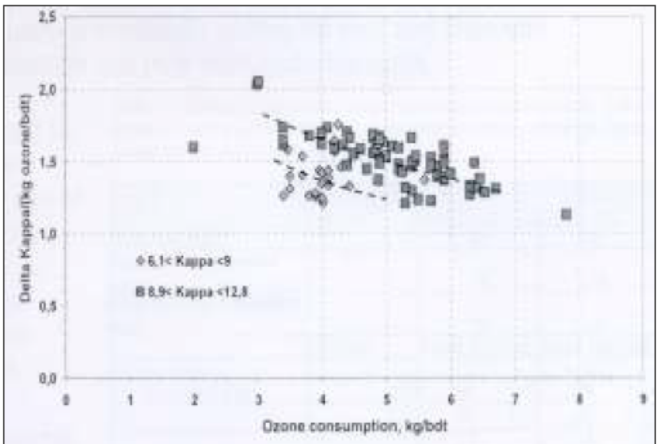


Figure 7. a(Ze) bleaching in the laboratory of hardwood kraft pulps from more than 40 different sources

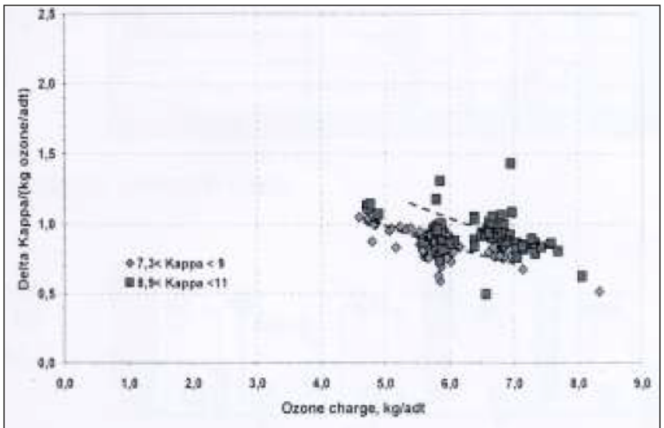


Figure 8. Ozone stage performance of Mill A

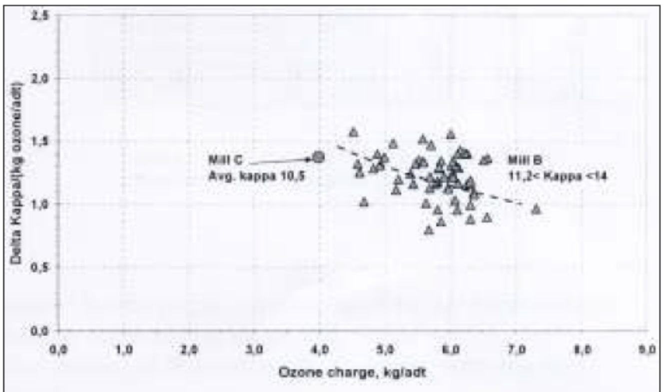


Figure 9. Ozone stage performance of Mill B and C

consistency ozone bleaching technology, corresponding to a production of more than four million tons per year, c.f. Figure 3 and 4. The four first installations were built according to the original C-Free concept, utilizing a plug screw feeder, acting as a gas lock between the reactor and the environment, and a refiner fluffer dispersing the pulp into the reactor's gas atmosphere.

The following nine installations represent the 2nd generation HC technology, i.e. Zetrac -a(Ze)-, schematically shown in figure 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.

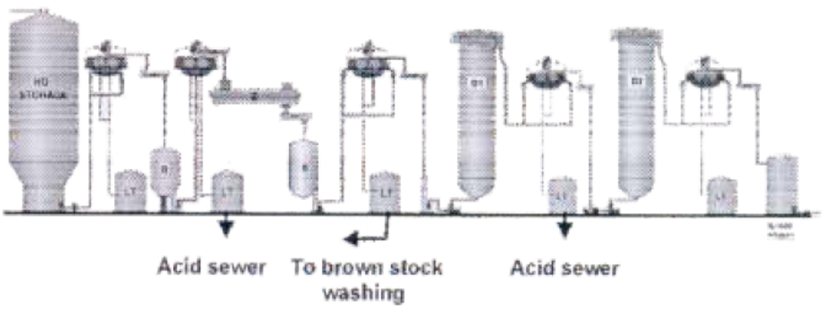
The pulp is fluffed in a specially designed shredder screw and fed into the reactor. Ozone gas is added and gas flow is controlled by two fans; one is connected to the shredder hood and the other to the residual gas handling system Pressure in the rector is slightly below atmospheric pressure.

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 fiber line.

Experiences with hardwood pulps

Table 1 Estimation of mill bleach chemical consumption and costs at 91 %ISO based on cooking and bleaching tests in the laboratory from a mixture of mainly Eucalyptus grandis and globulus chips.

Sequence	Chemical cost	D(EOP)(Dn)D		a(Ze)(Dn)D	
Brighness, %ISO		91		91	
Kappa no of unbleached pulp		18		18	
Kappa of oxygen delignified pulp		10		10	
	USD/unit	kg/adt	USD/adt	kg/adt	USD/adt
Oxygen stage					
Ox. Wh.liq.as NaOH	0,06	20	1,20	20	1,20
O_2	0,07	16	1,12	16	1,12
Bleach plant					
H_2SO_4	0,08	8	0,64	15	1,20
$MgSO_4$	0,18	1	0,18		
Ox. Wh.liq.as NaOH	0,06	0	0,00	14	0,84
NaOH	0,25	15	3,75	4	1,00
H_2O_2	0,91	4	3,64	0	0,00
O_2	0,07	5	0,35	0	0,00
O_3	1,18	0	0,00	6	7,08
ClO_2 act. Cl	0,38	34	12,92	18	6,84
Total cost, USD/adt			23,8		19,3



Kappa number, 10-11	D(EOP)DD	a(Ze)(Dn)D
Total water consumption, m^3/adt	12	10
Total effluent load, m^3/adt	9	7
Total COD discharge, kg/adt	24	14
AOX, kg/adt	0.25-0.4	<0.1

Figure 10. ZeTrac and Light ECF bleaching, a(Ze)(Dn)D of Eucalyptus pulp

Laboratory data

In the laboratory we have bleached hardwood pulps from more than 40 different sources with ozone at high pulp consistency; most of the pulps were oxygen delignified prior to the ozone treatment. Kappa number reduction (Delta kappa) as a function of ozone consumption is shown in figure 6 for these experiments.

Although there is a scatter in the data observed, a higher ozone consumption yields a larger kappa reduction as would be expected. There may be several factors influencing the scatter in kappa number reduction. Earlier we have observed that cooking conditions and wood species influence bleachability in conventional chlorine chemical bleaching sequences of especially hardwood pulps (3). Hexeneuronic acid, formed in cooking and remaining in pulp after oxygen delignification, contributes significantly to the kappa number value (4). Different ratios of hexeneuronic acid/lignin content for different pulps having the same kappa number may be one factor influencing the scatter observed in the data.

Another factor may be the kappa number of the pulp entering the ozone stage. Grouping the data in pulps having a kappa number lower than 9 and pulps with a kappa number from 9 and higher supports this conclusion.

By plotting kappa reduction per kg/bdt of ozone consumed versus ozone consumption this becomes even more evident, c.f. Figure 7.

Further, it appears as if kappa reduction starts to level off at ozone consumption in the upper level of the range studied. Although this is a common feature for bleaching stages, additional experiments would be needed to establish where this level is for high consistency ozone bleaching.

Mill data

Performance of the ozone bleaching stage measured as Delta kappa/(kg ozone charged/adt) for three different mills, A, B and C is shown in figures 8 and 9.

The ozone delignification process behaves in the same way in mill as in laboratory scale. However, two differences need to be kept in mind when comparing figures 7, 8 and 9. Ozone charges have been significantly higher in the mill scale (consider the difference between adt and bdt) and in the mill there is also an influence of carry over of substances to the ozone stage from previous washing stages.

The mill data demonstrates, as did the laboratory data that Delta kappa/kg ozone is higher for a higher incoming kappa number reduction of about 60% has been achieved.

Progress continues

It is obvious that there are many different 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 a main 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 new and improved technologies to further decrease environmental hazards and pulp manufacturing costs.

High consistency ozone bleaching has been around for more than ten years and is now considered a well-established technology. It allows for further reduction of the lignin content of pulp before it is bleached in the open part of the bleach plant. The importance of reaching a low kappa number in order to minimize pollution is evident. Discharge of dissolved organic material, such as COD and AOX, is decreased as kappa number is decreased. In case of AOX the reduction is not only depending on lower lignin content, but also on decreased use of elemental chlorine and chlorine dioxide in the bleaching process.

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. Good examples are extended oxygen delignification and ozone bleaching, which at the same time decrease bleach chemical costs.

This is exemplified in figure 10 and table 1 for bleaching of oxygen delignified eucalyptus kraft pulp. A substantial bleach chemical cost reduction can be achieved when changing from D(EOP)(Dn)D to the A(Ze)(Dn)D sequence.

A large reduction in chlorine dioxide consumption and the use of oxidized white liquor in the (Ze) stage instead of fresh caustic are the main factors for this cost reduction.

ACKNOWLEDGEMENT

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