

PULP & PAPER MILL ENHANCEMENTS FOR GREEN PRODUCTIVITY BENEFITS



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Abstract :

As the Indian Government is striving to improve the environment and reduce the impact of industry on the rivers and air quality, they have introduced ever tighter discharge limits. The pulp industry now has clear guide lines and tight discharge standards that can only be reached through some fundamental changes to the operation of the mill. We will investigate the impact of introducing ozone bleaching to an existing mill, and how through changes in the bleach plant, the mill can reduce effluent and improve effluent quality. We will also review the work on ozone being introduced into the waste water treatment stream to reduce colour, COD and BOD. Ozone is also a pure onsite technology that reduces the overall impact of the mill through reduction in chemical shipping, handling and storage.

INTRODUCTION

The Indian Government in conjunction with the Central Pollution Control Board have embarked on an ambitious campaign to clean up the industrial pollution load and reduce the impact of industry on the environment. This has been done through the implementation of strict effluent discharge standards that challenge industry to find a better way to operate their plants, and improve their effluent treatment plants, with the ultimate goal of a Zero Discharge Process.

For the pulp and paper industry this means that mills need to review their processes to further close their water circuits and improve efficiency of their effluent treatment plants. A green chemical such as ozone, produced onsite from oxygen and green electricity can be used in both the pulp production and the effluent treatment. Especially the use of ozone bleaching allows for:

- Reduction in effluent volume, COD, AOX and colour levels
- Increasing capacity where the capacity chlorine dioxide generator is the bottleneck
- Reducing bleaching costs
- Improving pulp brightness and reverted brightness levels

I. Ozone Bleaching

A hardwood pulp mill is producing 88 ISO brightness bleached pulp, with bleach sequence of O-D-Eop-D-D. The mill is using just 35 kg/adt of chlorine dioxide (as active chlorine) and 3 kg/adt of hydrogen peroxide. This was considered state of the art bleaching, but now the mill is not meeting the new discharge standards.

The mill currently utilises a typical effluent treatment plant using an SBR

(Sequencing Batch Reactor) and discharges effluent into a river. The mill is looking to increase production, whilst reducing its effluent load and improving pulp quality and reducing incremental pulp production costs.

I.1 Impact of Ozone Bleaching on Bleach Plant Discharge

State-of-the-art Z-ECF bleaching sequences are considered to be:

- Ze-D-D or Ze-D-P where the Z stage is high consistency ozone bleaching followed by dilution to medium consistency to allow for a short extraction stage “e” to take place without intermediate washing
- Z/D-EOP-D where Z/D is a medium consistency ozone bleaching stage “Z” followed directly by a chlorine dioxide stage “D” without intermediate washing

With Ze-D-D or Ze-D-P, there is no chloride ions in the liquor recovered

from the first bleaching stage so it can fully be sent back to the recovery circuit. This minimises the COD load sent to the ETP (Effluent Treatment Plant), while improving the colour of the waste water. Valmet has published (1) the below table for comparison of effluent volumes and quality from a conventional DHT-Eop-D-D bleaching sequence with the short Ze-D-P one. As can be seen, there is a 20 to 30 % reduction in both volume and COD values of the effluent coming from the bleach plant when the Z stage effluent is recovered.

With Z/D-Eop-D the effluent from the first bleaching stage can be partially recovered thanks to its lower chloride load. Andritz has published (2) the effluent volumes from the Maryvale plant in Australia, operating a Z/D-Eop-D bleach sequence for Eucalyptus pulp at 90% ISO Brightness.

Table 1: Comparison of effluent parameters for ECF and HC Z ECF bleaching

	D _{HT} -Eop-D-D	Ze-D-P
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

Table 2: Comparison of effluent parameters for ECF and MC Z ECF bleaching

	Z/D-Eop-D
Effluent volume, m ³ /odt	12
COD, kg/odt	22
AOX, kg/odt	<0.15
Color, kg/odt	<5

I.2 Impact of Ozone Bleaching on Bleach Plant Economics

Numerous studies on eucalyptus pulp bleaching have proved that Z-ECF bleaching offers lower overall operating costs than ECF bleaching. Valmet stated as far back as 2003 that “high consistency ozone bleaching has shown to be the most cost efficient way to decrease HexA content of pulp” and published the following table (3).

Table 3: Bleach chemical consumption and costs at 90 %ISO reverted brightness for eucalyptus grandis pulp (3)

Sequence	D-E _{OP} -D-D		D _{Hot} -E _{OP} -D-D		Ze-D-D	
	kg/bdt	USD/bdt	kg/bdt	USD/bdt	kg/bdt	USD/bdt
Kappa no.	10.9		10.9		10.9	
Reverted brightness, %ISO	90		90		90	
Brightness before reversion, %ISO	92.3		92.1		92	
	kg/bdt	USD/bdt	kg/bdt	USD/bdt	kg/bdt	USD/bdt
H ₂ SO ₄	6	0.48	6	0.48	12	0.96
Oxidised white liquor as NaOH	0	0	0	0	12	0.72
NaOH	16.5	4.13	16.5	4.13	5	1.25
H ₂ O ₂	3	2.73	3	2.73	0	0
O ₂	3	0.21	3	0.21	0	0
O ₃	0	0	0	0	6	7.08
ClO ₂ , act. Cl	35.5	13.5	28.5	10.8	13.5	5.13
Total cost, USD/bdt		21.1		18.4		15.1

Lower operating costs of the Z-ECF bleaching sequence are resulting here from:

- The replacement of chlorine dioxide and hydrogen peroxide by ozone
- The use of oxidised white liquor in place of pure caustic soda in the extraction stage

The following calculation details why Z-ECF bleaching is more competitive than ECF bleaching for a fiberline. The calculation is based on the 1.7 theoretical replacement ratio of chlorine dioxide

by ozone (4): every kilogram of ozone replaces 1.7 kilogram of pure chlorine dioxide. Some full-scale installations reported even higher numbers.

Ozone is produced from oxygen at a concentration of 12% by weight using 10 kWh/kgO₃ of power and 8.3 kgO₂/kgO₃ of oxygen, then compressed at 10 bar(g) with 1.5 kWh/kgO₃ of power in MC bleaching. Therefore delivery at the mixing point of 1 kg pressurized ozone requires 11.5 kWh power and 8.3 kg oxygen. Considering an energy price of 0.04 €/kWh and oxygen price of 0.08 €/

kgO₂, 1 kg of pressurized ozone costs 11.5 x 0.04 + 8.3 x 0.08 = 1.124€. But it should be highlighted that oxygen (88% of the gas mixed with the pulp) leaves the ozone bleaching stage unreacted. More than 50% of the mills using ozone bleaching reuse that oxygen in oxygen delignification, Eop-stage or other applications. Therefore, if considering that oxygen is used further, 1 kg of pressurized ozone costs 11.5 x 0.04 + 1 x 0.08 = 0.54€, Ozone is then cheaper than the average 1.5 €/kg price of chlorine dioxide.

Moreover, since every kilogram ozone replaces 1.7 kilogram chlorine dioxide, the use of 5 kgO₃ per ton of pulp allows the mill to earn $5 \times 1.7 \times 1.5 - 5 \times 1.124 = 7.13$ €/adt if or, if reusing oxygen, $5 \times 1.7 \times 1.5 - 5 \times 0.54 = 10.05$ €/adt. Ozone bleaching allows the pulp mill to earn €7-10 million per year! Considering investment costs in ozone generation, ozone compression, ozone mixing as well as automation and civil works, the Return On Investment (ROI) of ozone bleaching can be calculated at between 1.5 and 2.5 years.

I.3 Impact of Ozone Bleaching on Pulp Quality

With more than 8 million tons of pulp being bleached with ozone, and 3 new

mills under construction, ozone has shown to have beneficial effects on the pulp. For dissolving grades, ozone's quick chemistry allows for instantaneous adjustment of viscosity ensuring a stable and controlled bleach stage. This ensures pulp of a high quality.

Ozone helps to reduce the Hex A content of hardwood pulps, ensuring high brightness and a very low brightness loss of pulp. As the figure below shows, tear and tensile strength of the pulp is the same or better than ECF bleached pulps.

Figure 1: Tear and Tensile Comparison on ECF and Light ECF(1)

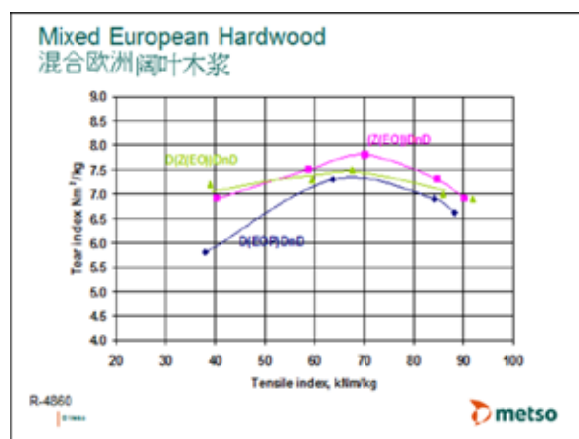
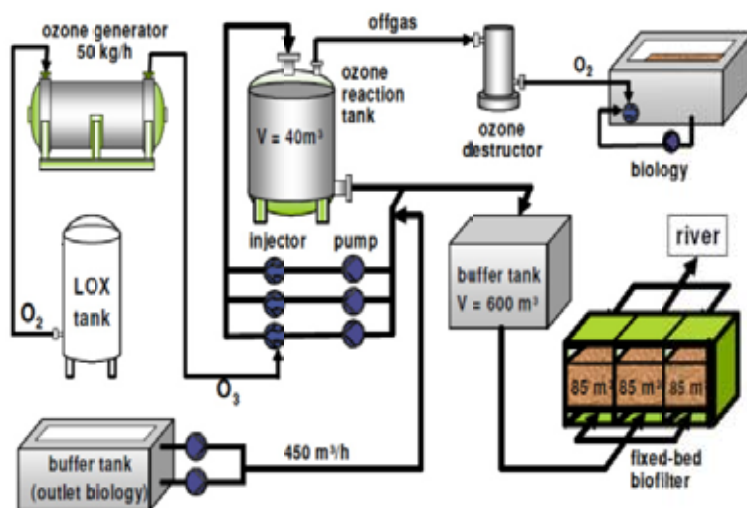


Figure 2: Schematic flow of ozone oxidation combined with biofiltration for COD reduction(5)



In a situation where a mill is looking to increase production, however, the chlorine dioxide generator is running at maximum capacity, then the installation of an ozone stage makes economic sense. The mill can then invest in an ozone generation system, while reducing the consumption of chlorine dioxide. This will allow for increased production utilising the existing equipment while improving pulp quality.

II. Ozone in the ETP

Where a mill is satisfied with their pulp quality and production rate but still needs to reduce its effluent load ozone

can be used to reduce colour and lower COD values in a cost effective manner. Combining the oxidizing power of ozone together with a biological filter has proved to be the most economical and environmentally friendly process, as discussed above.

Ozone is used to partly oxidize the hard COD and transform the COD into more biodegradable matter, BOD. The overall cost of this process depends on the amount of ozone that is needed to produce a significant amount of BOD. The key figures to describe the process are the ratios of ozone dose/COD reduction and BOD/COD before and after oxidation.

An attractive treatment concept for this process can be achieved with 1 to 1.5g ozone/ 1g COD reduced and increased BOD/COD ratios of <0.05 before oxidation to >0.20 after oxidation. Using these figures as a basis to calculate the operational and capital expenses of a full scale plant, the results show advantages in comparison to a solution using chemical flocculation and filtration. The capital expenses of the oxidation solution are higher than for the chemical/flocculation system. However, the lower operational costs for the oxidation solution can result in a payback time of 2 to 3 years for the capital expenses.

The economical attractiveness of the process depends on the following:

- The amount of COD that needs to be removed
- The applied ozone dose that is required to achieve the COD reduction
- The amount of BOD that is formed after ozonation

While the operating cost (OPEX) of the system will be driven by:

- The cost of energy to drive the ozone generator, as well as aeration and pumping of the effluent
- The cost of oxygen

The financial benefit of the system is in the OPEX when compared to a conventional chemical/flocculation/DAF

and filtration process which incurs the following costs:

- Chemical costs
- Sludge handling and disposal costs
- Air supply for DAF
- Power costs for pumping and mixing and backwash.

CONCLUSIONS :

A mill operating a conventional D-Eop-D-D bleach plant that needs to reduce their environmental impact can do so through the addition of an ozone (Z) stage. The most economical bleaching practise is shown to be Light ECF or ECF with ozone. The simplest options for the mill are Ze-D-D or Ze-D-P where ozone bleaching is carried out at high consistency or Z/D-Eop-D where

ozone bleaching is carried out in medium consistency.

The effect of these stages on the mills environmental impact is huge, allowing for:

- Reduced effluent volumes
- Reduced COD loads
- Improved colour levels
- Reduced AOX discharge levels

Where changes in the bleach plant are not possible, ozone can be used to reduce colour and COD levels directly in the EPT, allowing the mill to meet the new discharge norms.

Ozone has been shown to be the greenest chemical for a mill to reduce its environmental impact while improving pulp quality and allowing for an increase in capacity.

LITERATURE

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