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OZONE OXIDATION FOR BRIGHTER PULP & BLUE WATER

*Alexis Métais**

*Sandeep Pahwa **

* alexis.metais@xylem.com,
sandeep.pahwa@xylem.com ;
Xylem Water Solutions India Private Limited,
Plot No. 731 GIDC Savli, Manjusar, Savli Road,
Vadodara-391770, Gujarat, India.*

Abstract:

A chemical can be considered environmentally friendly if its production and use have only very little impact on the environment. Today 2 bleaching chemicals produced in pulp mills clearly meet that definition: oxygen and ozone, both produced from air and green electricity. Ozone is the strongest oxidant available in pulp and paper mills. Made of 3 oxygen atoms, it is formed by a silent electric discharge in an oxygen stream. Its generation is a pure onsite technology: there is neither transport nor storage of hazardous chemical precursors. The authors first review modern ozone generation technology. Then a wide spectrum of applications is introduced with either full-scale, pilot or lab results showing ozone benefits for pulp bleaching, effluent discoloration, COD elimination, process water treatment, NOx elimination in the flue gas and cooling water treatment. It appears ozone can be widely used at different locations to improve mill sustainability and revenue.

Key words: *Ozone, Bleaching, Effluent, Emissions, Green*

Introduction:

Ozone is the strongest oxidant available in the pulp and paper industry. Ozone is produced onsite from oxygen and electricity and is used in pulp and paper mills for pulp bleaching, effluent discoloration, COD elimination, process water treatment, NOx elimination in the flue gas and cooling water treatment. Contrary to chlorine-based chemicals, the use of ozone does not result in the formation of toxic compounds. Moreover, it is most of the time a green chemical since pulp mills produce electricity from biomass.

I. Ozone Generation

Ozone is a molecule consisting in three oxygen atoms. It is an unstable chemical which self decomposes, so it is always produced at site, on demand, just before its implementation. In industrial applications, ozone generation requires oxygen, electricity and cooling water:

- Oxygen (O_2) is the raw material for ozone (O_3) production. Ozone is produced in an oxygen stream typically at 8-12% concentration in weight so the final product is an ozone-oxygen mixture.

- Electricity is used to create an electrical field that breaks some oxygen molecules (O_2) into oxygen atoms (O) that combine further in the form of ozone (O_3)

- Cooling water is required to guarantee the efficient ozone production by removing heat.

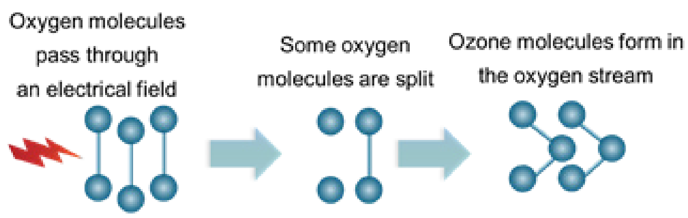

Figure 1: Ozone Generation Principle

Ozone generators are now very flexible and can operate with oxygen purity varying between 90%wt and 99.9%wt. It allows the ozone system to switch from one oxygen quality to another without any prior adjustment. Therefore, an oxygen plant failure does not impact ozone delivery since liquid oxygen is stored in back-up and ozone production is very reliable.

Depending on the ozone demand, oxygen can be either supplied as liquid oxygen (LOX) or produced at site from air through the Vacuum Swing Adsorption (VSA) technology. Production of 1 kg ozone at 12% by weight requires:

- 8.3 kg oxygen
- 10 kWh
- 1-2 m^3/h of cooling water (temperature increase is 5°C).

Until the launch of a new electrode design in 2012, large ozone plants as the ones typically implemented for pulp bleaching required 5-10°C chilled water to be efficiently cooled down. Chillers permitted stable and reliable ozone production but installation of stand-by chilling units was a must to maintain overall availability of the ozone plant. The new technology was specially designed for efficient ozone production with commonly available water temperatures while keeping availability factors above 99%. It allows today for high production outputs that were before possible only in combination with chillers and significantly reduces investment cost and footprint while improving availability of the ozone plant (by getting rid of potential chilling units failure). Modern ozone generators can operate with cooling water temperatures up to 20-30°C.

II. Pulp Bleaching

Ozone bleaching is conducted either at medium or at high pulp consistency. The choice of one process over another depends on several factors - including investment cost, carry-over load, bleaching filtrates recirculation, bleach plant temperature profile, footprint, and others - but has little if any impact on ozone bleaching efficiency itself. However, it does impact the choice of the bleaching sequence.

Ozone bleaching at medium pulp consistency features a pump that feeds the acidified pulp into usually two ozone mixers in series and a standpipe. An ozone compression step is required because of the large amount of gas that needs to be injected so ozone (and oxygen) is compressed to 12 bar(g). Still the pulp suspension contains about 30-40% of gas. The mixers ensure high turbulence intensity and good gas dispersion, so all the reaction takes place primarily in the mixers. Pulp degassing, to avoid pump cavitation, is done in the standpipe to allow for flow stabilization. Ozone bleaching at medium pulp consistency is often combined with the D_0 chlorine dioxide stage in a Z/D combination without intermediate washing between the two stages. Both stages usually take place at acidic pH in the 3-5 range, and it allows the first bleaching step to reach the maximum delignification level at very low chemical cost (Chirat et al., 1996). The D-stage requires only 15-20 minutes and a very small chlorine dioxide charge. Another advantage, from an investment standpoint, is the reduced number of washers needed as per the implementation of the short and efficient bleaching sequence Z/D-Eop-D in operation in numerous mills globally.

Ozone bleaching at high pulp consistency combines the ozone stage with an extraction stage without intermediate washing. Acidified pulp, at pH 2.5-3 is first pressed to 38-42% consistency and shredded. The pulp then falls from the press into the ozone reactor, a horizontal tube equipped with a central rotating shaft with a large number of paddle-type blades to whirl the pulp through the tube. Ozone is fed counter-currently to the pulp flow and the reaction takes place around atmospheric pressure for about one minute. Finally, the high consistency pulp is diluted up to 7-8% consistency with alkaline liquor so the alkali reaches the heart of the fibers without the need for diffusion and quickly solubilizes the oxidized material. Then the press following the e-stage removes solubilized material from the fibers when pressing the pulp. These two aspects - the quick access to the fibers thanks to their high consistency, and the quick removal of the alkali with the press - eliminate the need for long diffusion times and the subsequent need to invest in an extraction tower (in the case of new bleach plants.).

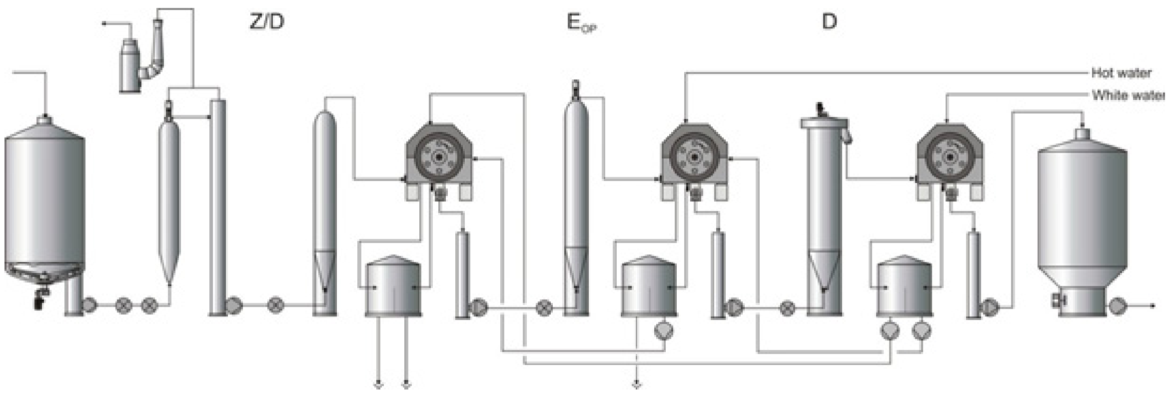

Figure 2: Typical ZD-Eop-D bleach plant from ANDRITZ

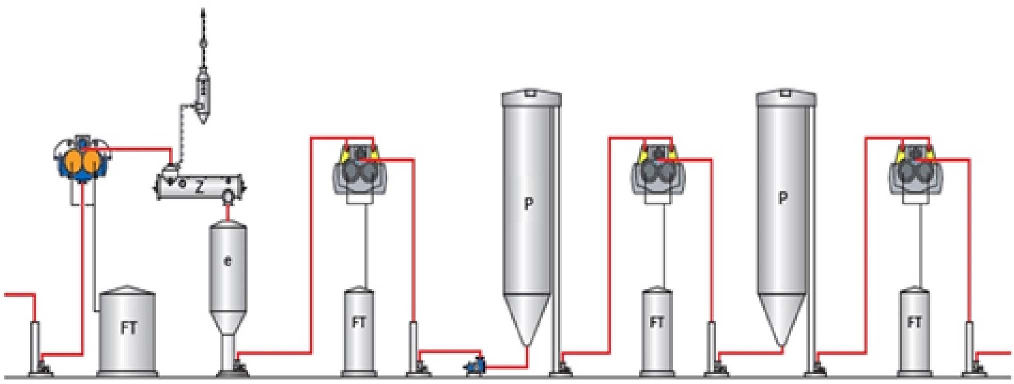

Figure 3: Typical Ze-P-P bleach plant from Valmet©

Ozone bleaching often results in lower pulp viscosity. But that viscosity loss does not translate into a loss in strength (Chirat et al. 2008). Strength properties can be even better for ozone bleached Z-ECF pulps than for standard ECF pulp. For example, Figure 4 shows in the case of hardwood pulp better strength properties with Z-ECF bleaching than with standard ECF bleaching (standard ECF pulp is in blue, Z-ECF pulps are in green and pink).

It is a question of ozone dose and balance between economics and pulp quality: higher is the ozone dose, higher are the economic savings but also higher is the risk to impact the strength properties. Typical bleaching chemical consumptions are shown as example in the table below (*: industrial results from Métais and Germer (2017); ** lab results from Van Wyk (2016))

Ozone bleaching brings several economic, ecological and quality bonuses and especially allows for:

- Lower bleaching chemicals cost
- Similar or better strength properties
- Higher brightness stability
- Lower energy requirements for pulp refining
- Significantly lower extractive content
- Accurate viscosity control in the case of dissolving pulp production
- Up to 60% lower organic halogens (OX) content in the pulp
- Reduction of bleach plant discharge loads by 20-40% for COD, 50-75% for AOX and 40-60% for color
- Lower carbon footprint (Métais, 2023)

III. Effluent Treatment

III.1 Effluent Discoloration

Discoloration is the first noticeable effect when ozonizing final effluent (after secondary clarifier). It is possible to quickly reach color values below 100 Pt-Co. As shown in Figure 5, ozone dose of course depends on the starting point with for example 15 gO_3/m^3 if starting from 168 Pt-Co (Mill C), 75 g/m^3 from 340 Pt-Co (Mill A) and 200 gO_3/m^3 from 453 gO_3/m^3 (Mill B).

Note: Results come from different mills and cannot be directly compared to each other.

III.2 COD Removal

The second phenomenon when ozonizing biological effluent is a decrease of COD.

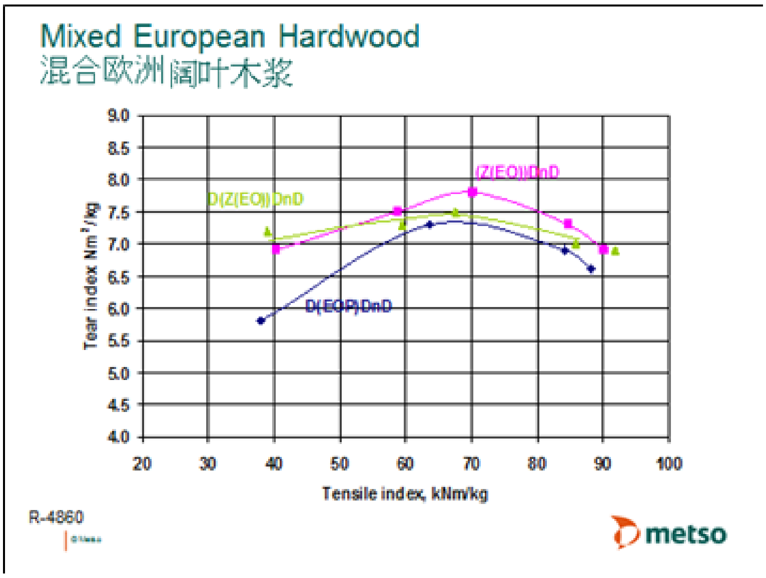

Figure 4: Hardwood Pulp Strength Properties (Feng, 2012)

Table 1: Bleaching Chemicals Consumption for Hardwood Kraft Pulp Bleaching

	Hardwood*		Softwood*		Baga
Bleaching	ECF	TCF	ECF	TCF	TCF
ClO_2, kg/adt	5.7	0	4	0	
O_3, kg/adt	5	6	6	6	5
H_2O_2, kg/adt	3	15	10	20	12
Brightness, %ISO	90	89	89	89	90

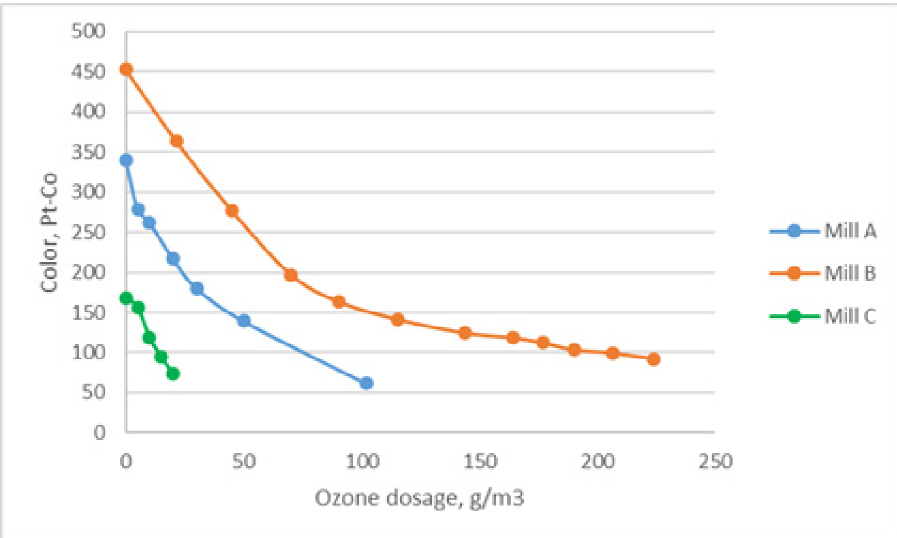

Figure 5: Secondary Clarifier Effluent Discoloration with Ozone (Lab results)

Figure 6: Secondary clarifier Effluent Discoloration with Ozone (Lab results)

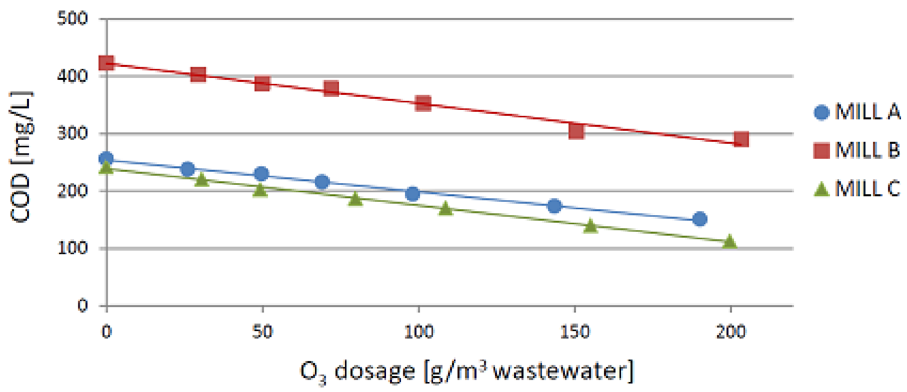

Figure 7: COD Reduction with Ozone (Lab results)

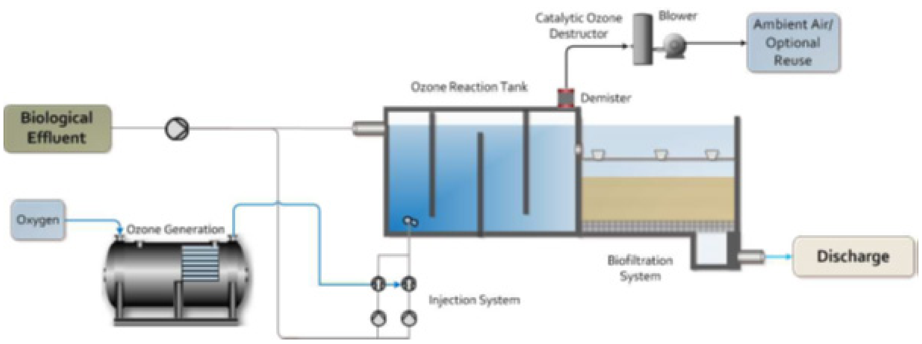

Figure 8: Ozone & Biofiltration for Hard COD Removal

It leads to an increase of the BOD/COD ratio and therefore improved effluent's biodegradability. It is possible to further reduce COD with a biofiltrations stage as per Figure 8. The combination typically requires 1 kg ozone per kg of COD eliminated. The process was installed in 3 integrated pulp and paper mills in Europe.

IV. Process Water Treatment

Ozone can also treat intake water and process water to remove chromophores (colored compounds), chromogenes (uncolored compounds becoming colored over time or in the production process), disinfect water or reduce the COD.

Today 2 paper mills use ozone on intake water.

V. Cooling Water Treatment

Cooling Towers are an important means of ensuring efficient and reliable operation of all industrial plants, like pulp and paper mills. Water is the preferred medium for the extraction of heat from exothermic processes and the cooling of motors. Cooling water circulates in a loop where heat is taken up from the process and then discharged in the cooling tower. In the cooling tower the circulating water is brought into direct contact with air and cooling is achieved through evaporation. The draft caused by the cooling tower draws in dust and other organic material and creates an ideal growth environment for bacteria and algae. This growth leads to slime and scale, lowering the heat transfer efficiency and resulting in corrosion. Chemicals are added to the system to minimize the growth of bacteria and reduce the risk of scale formation. Normal cooling tower water treatment consists of the addition of about 6 different chemicals: biocide, anti-scale chemicals, corrosion inhibitors, defoaming agents, pH control and dispersants. The addition of all these chemicals and the removal of water through evaporation limits the amount of times the cooling water can be circulated before concentration of dissolved solids and chemicals becomes so high that scale can begin to form and become problematic. Therefore some cooling water must be discharged (blowdown) and the basin water diluted with fresh water (makeup water). This blowdown needs to be treated in an effluent treatment plant before it can be discharged to the environment because of all the chemicals it contains.

Ozone can fulfil the role of most of the treatment chemicals. It is a very strong oxidant and biocide. It does not add any organic material to the water, so no defoamers or dispersants are required. If the cooling water is run at high cycles of concentration, then the use of corrosion inhibitors can be limited since the water is already saturated with metal ions. The pH of the ozone treated tower water stabilizes out at around 8 to 8.5, above the corrosion pH, so no pH adjustment is required. Scale does not tend to form in ozone treated water because no colony forming bacteria are present (thanks to the biocide action of ozone), so there is no glue to start the scale process and as a consequence metals reaching their concentration of saturation precipitate into the water body as fine powder. This powder is easily removed in the system sand filters. The cooling water can safely be concentrated to high cycles of concentration.

VI. NOx Treatment

Ozone, hydrogen peroxide or chlorine dioxide oxidize NOx into dinitrogen pentoxide N2O5 which is scrubbed with water and then forms nitric acid as per (for example with ozone):

- $NO + O_3 \rightarrow NO_2 + O_2$
- $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$
- $N_2O_5 + H_2O \rightarrow 2HNO_3$

Ozone is very reactive and no activation energy is needed for ozone and NOx to react. At full scale the ozone treatment is the last flue gas treatment step and is typically carried out below 200°C. Moreover, since ozone reacts in seconds and is an unstable chemical, there is no "ozone slip". NOx oxidation allows for achieving extremely low NOx levels, for example below 5 ppm, in sensitive cases.

That technology is used in several industries globally (oil and gas, steel, microprocessors) including the pulp and paper industry.

Conclusions

Ozone is a green chemical available at competitive cost when compared to other oxidants. It can be used in the process (in pulp bleaching) to reduce operating expenditure but also in other locations of the mill to reduce the environmental impact.

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