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IPPTA AGM & Seminar
February 24, 2024
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Ozone Oxidation for Brighter Pulp & Blue Water

WEDECO
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Introduction

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. It can be used in a wide range of applications to help the Pulp & Paper Industry lowering its impact on the environment.

Ozone

Ozone is a reactive gas:

- Formed by three oxygen atoms
- With a strong oxidizing power
- Unstable, it self decomposes into oxygen and cannot be stored so it shall be produced at site.

Half-life in the air:	3 days at 20°C
	1.5 hrs at 120°C
	1.5 sec at 250°C

Smelly and detected by the human nose at 0.01 ppm concentration (work is allowed during 8 hours at 0.1 ppm concentration)

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Ozone production requires oxygen

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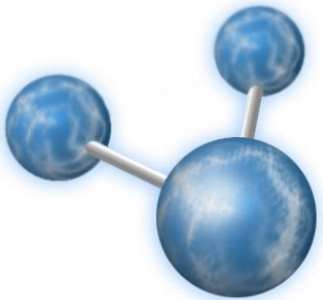
Ozone Production

Ozone can be produced by the following means:

- Electrical discharge
- Electrolysis
- Cold plasma
- Ultraviolet radiation



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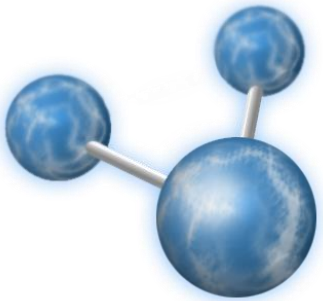

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Ozone production requires electricity

Theory and Reality

Theoretically:

$O_2 \rightarrow \quad 2\ O$	- 5.116 eV
$O + O_2 \rightarrow O_3$	+ 1.084 eV
$1.5\ O_2 \rightarrow O_3$	- 1.474 eV

So, producing 1 kilogram ozone theoretically requires 0.82 kWh.

However industrial figures are 10 times higher. It means approximately 90% of the energy input is converted to heat.

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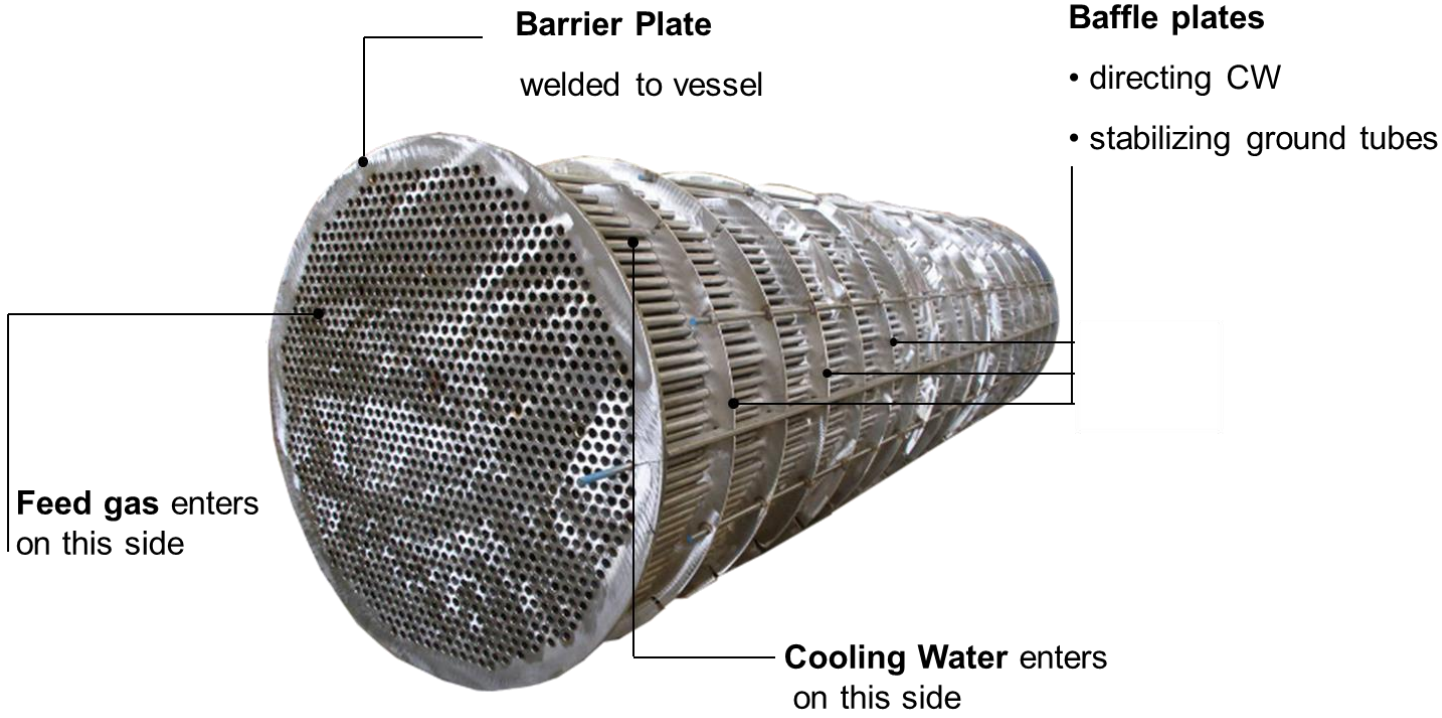
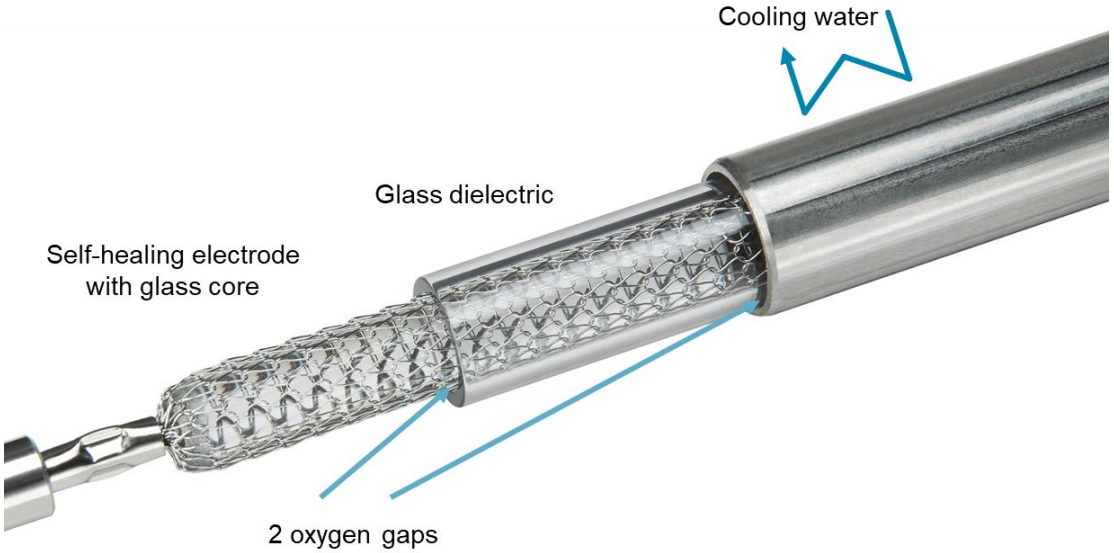
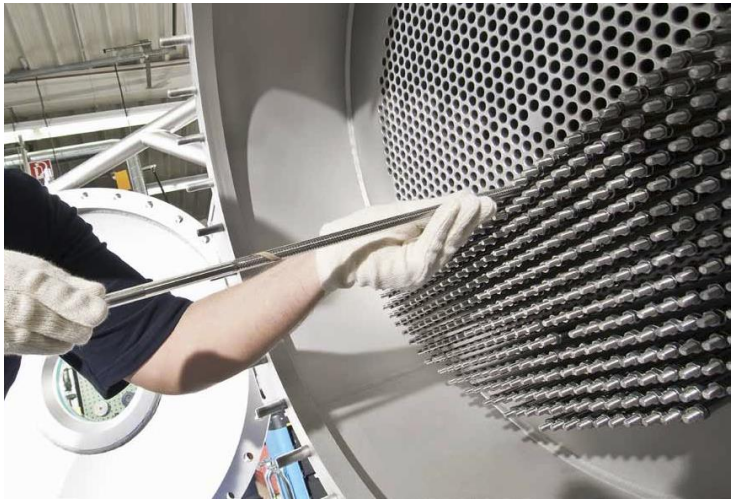
Ozone production requires cooling water

Generator Vessel



Electrode Design





Ozone Production Upgrade

Until 2012 large ozone plants required 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 electrode technology was specially designed for efficient ozone production with commonly available water temperatures (20-30°C) while keeping availability factors above 99%.

It reduces investment cost and footprint while improving availability of the ozone plant (by getting rid of potential chilling units failure)

Modern Ozone Production

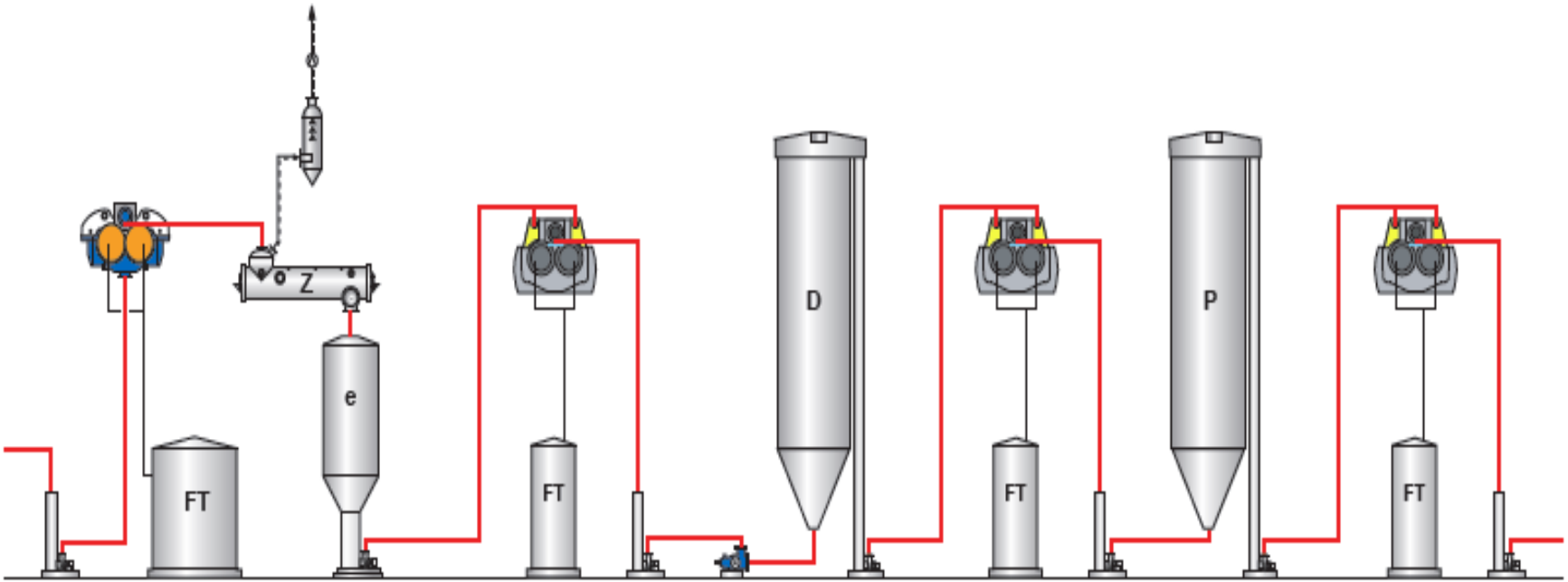
A single generator can produce 200 kgO_3/h. Production of 1 kg ozone at 12%wt requires:

- 8.3 kg oxygen
- 10 kWh
- 2 m^3/h cooling water

Typical energy requirement for production of one kilogram oxygen with a VSA plant is 0.3 kWh. So, one kilogram ozone costs roughly 12.5 kWh.

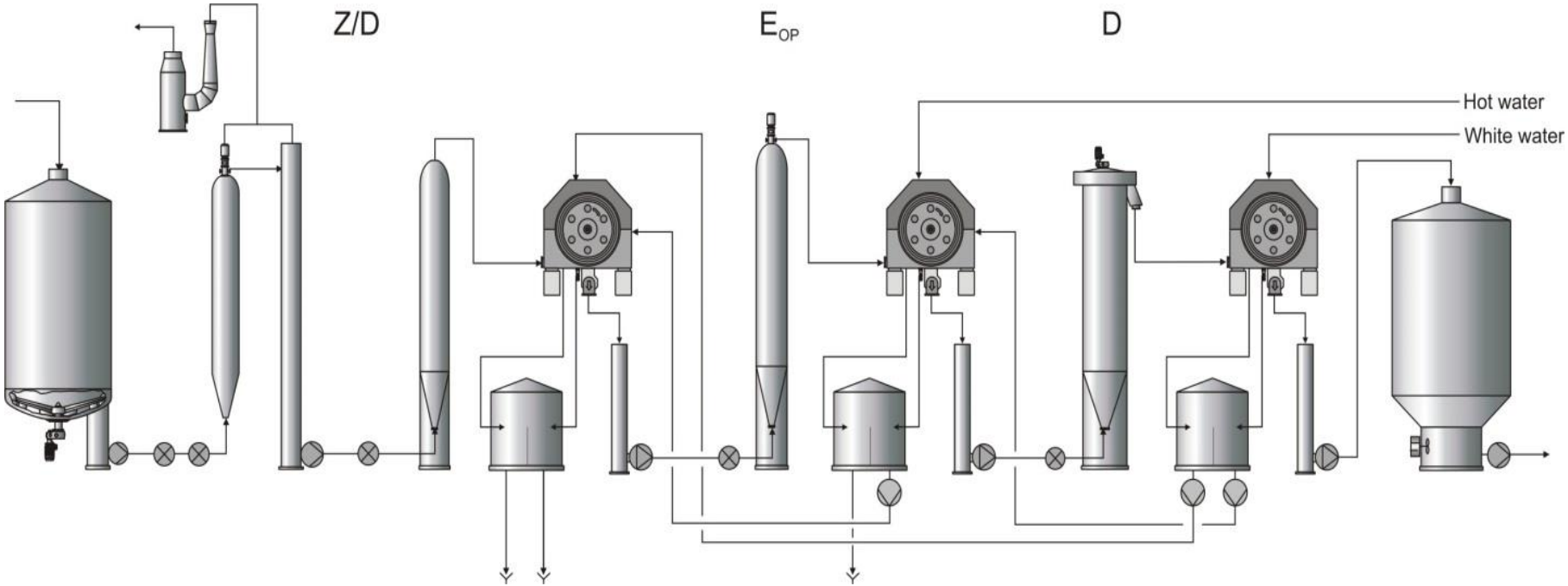
It makes substitution of chlorine dioxide by ozone very attractive from the economic viewpoint.

Standard Ze-D-P Bleach Plant



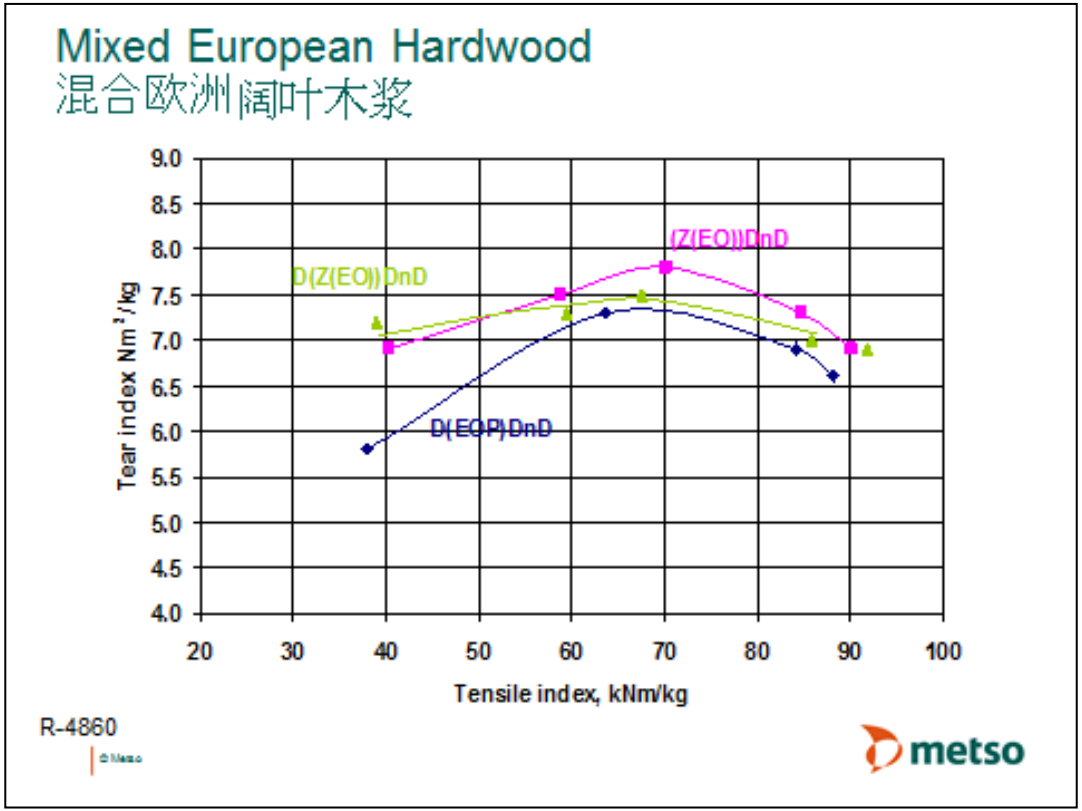
Courtesy of Valmet©

Standard Z/D-Eop-D Bleach Plant



Courtesy of ANDRITZ

Strength Properties



Source: Feng, Y. ZeTrac "Ozone Bleaching – Environmental and Cost Benefits", China Paper, (2012)

Environment

	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	0.05-0.1
Color, kg/odt	13	7-11*

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

Source: Wennerström, M. Norden, S. Jain, N.K. "The Eco-friendly Bleaching Concept with HC-Ozone", IPPTA, (2011)

Bleaching Chemicals Consumption

	Hardwood*		Softwood*		Bagasse**	Wheat Straw**
Bleaching	ECF	TCF	ECF	TCF	TCF	TCF
ClO_2, kg/adt	5.7	0	4	0		
O_3, kg/adt	5	6	6	6	5	5
H_2O_{22}, kg/adt	3	15	10	20	12	10
Brightness, %ISO	90	89	89	89	90	86.4

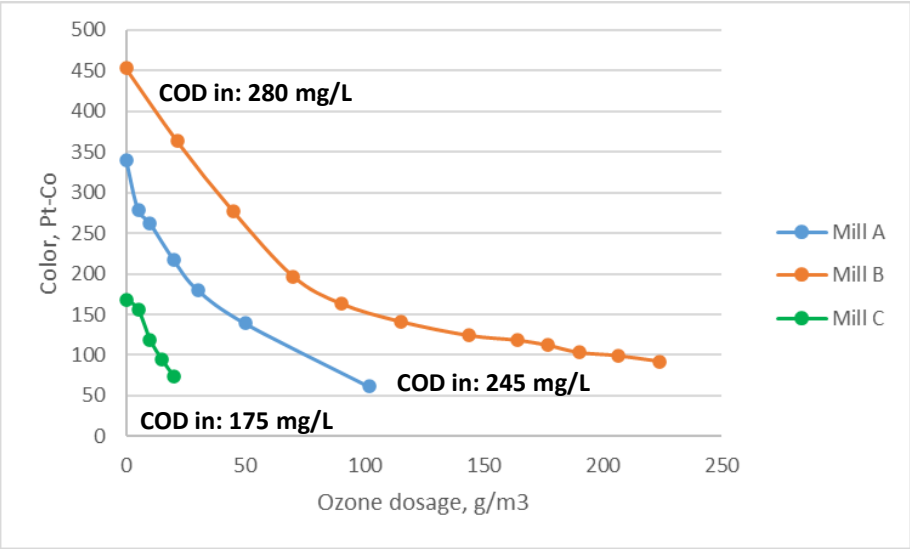
*: industrial results
**: lab results

Ozone Bleaching

Ozone bleaching 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

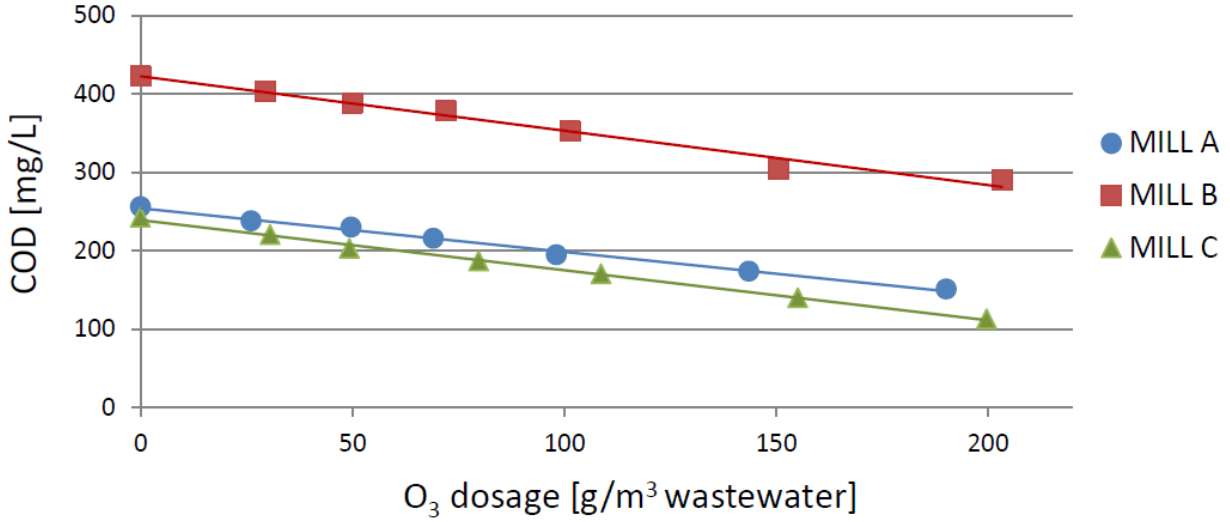
Effluent Discoloration

Discoloration is the first noticeable phenomenon when implementing on biological effluent.



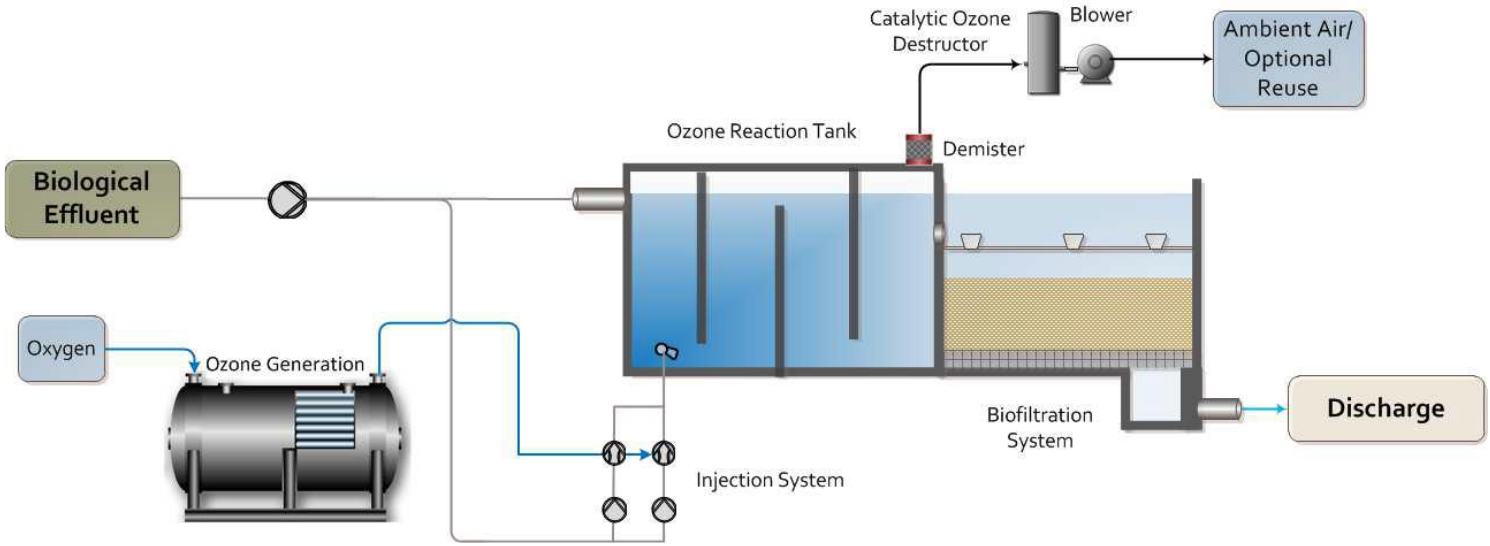
Hard COD Removal

Ozone also reacts with COD. It results in an increase of the BOD/COD ratio and therefore effluent's biodegradability.



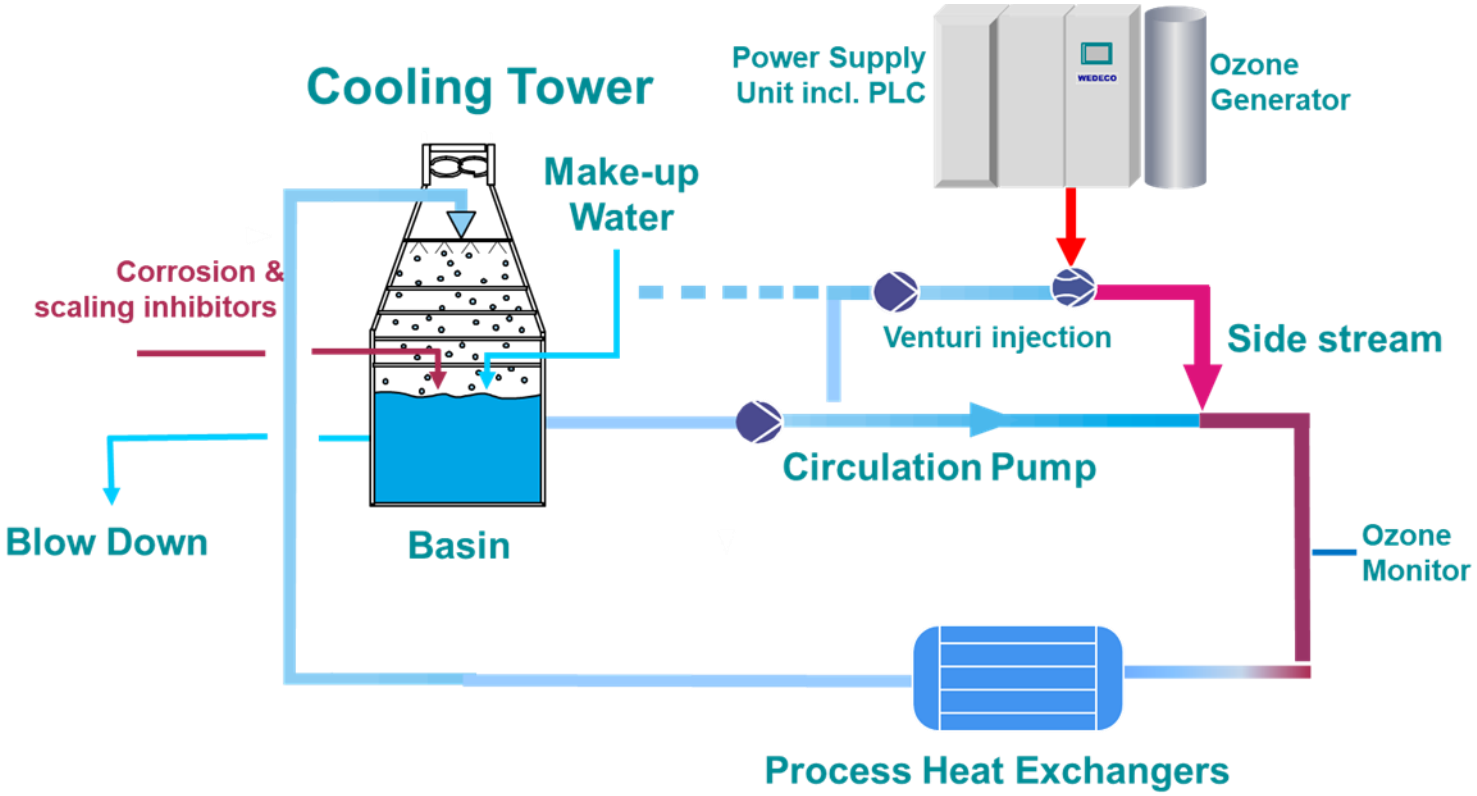
Hard COD Removal

The newly created BOD is then removed in a biofiltration step.



Ozone for Cooling Towers

Before and after ozone treatment



NOx Treatment

Ozone, hydrogen peroxide or chlorine dioxide oxidize NOx into dinitrogen pentoxide N_2O_5 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. 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.

Conclusions

Ozone is a green chemical available at a competitive cost when compared to other oxidants.

It can be used in the process (in pulp bleaching) to reduce production costs but also in other locations of the mill to reduce the environmental impact.

Ozone is a versatile and cost-effective chemical able to solve diverse environmental challenges of the pulp and paper industry.

Thank You
for Your Attention!

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