Ozone in the Pulp & Paper Industry

ECONOMICAL & ECO-FRIENDLY
Ozone in the pulp and paper industry – The ultimate choice for improved productivity and efficiency

Xylem has set a new benchmark in the field of ozone applications within the pulp industry.

With more than 20 pulp mills in operation in various parts of the world, ozone for pulp bleaching is considered as one of the Best Available Technologies (BAT) to meet market demand for:

» Compliance with strict environmental regulations
» Better pulp quality
» Low specific pulp production costs
» High reliability
» Easy and safe operation

The use of ozone as a bleaching agent has been under investigation for many years. The first industrial application started almost 20 years ago, with ozone bleaching following the same growth curve as oxygen delignification in the 70s.

Ozone bleaching marks a clear milestone in the development of pulp bleaching methods. It combines high pulp brightness and strength with the lowest specific pulp production costs – a clever option where eco-friendliness is compatible with quality and production goals. Proven reliable on-site generation of tons of ozone per day with high availability and ease of operation are further reasons why ozone has proved successful.

Xylem, as the outright global leader in ozone supply, has 15 references in operation or close to start-up around the world (Figure 1).

Fig. 1: Xylem’s references

- **Rosenthal**, Germany 1999: 160 kg/h @ 8 wt%
- **Mondi**, Slovakia 2004: 340 kg/h @ 12 wt%
- **Wisaforest**, Finland 1993: 150 kg/h @ 13 wt%
- **2010**: 180 kg/h @ 12 wt%
- **Daio**, Japan 2006: 400 kg/h @ 12 wt%
- **Lenzing**, Austria 2004: 84 kg/h @ 12 wt%
- **2010**: 76 kg/h @ 12 wt%
- **ITC**, India 2008: 200 kg/h @ 12 wt%
- **Marusumi**, Japan 2006: 210 kg/h @ 12 wt%
- **2005**: 220 kg/h @ 12 wt%
- **Nippon Paper Yatsushiro**, Japan 2003: 130 kg/h @ 12 wt%
- **Ceitejo**, Portugal 2008: 180 kg/h @ 12 wt%
- **Sniace**, Spain 2007: 60 kg/h @ 12 wt%
- **Fibria**, Brazil 2003: 500 kg/h @ 12 wt%
- **2012**: 250 kg/h @ 13 wt%
- **Oji Paper Tomioka**, Japan 2005: 220 kg/h @ 12 wt%
Why use ozone?

Ozone is a 3-atom oxygen molecule produced from oxygen. It has the highest oxidation potential among the bleaching chemicals. It reacts very fast (seconds to minutes) with the pulp and limits the need for large equipment with long reaction time.

Ozone, as compared to the other bleaching chemicals, is the true alternative to chlorine in terms of its chemical reactions with the lignin structures. Contrary to chlorine dioxide, ozone does not form coloured by-products but degrades these compounds. This effect is of interest when ozone is used at the end of the bleaching process to improve the final pulp brightness and to reduce the chemical cost.

Finally, as the main by-product of ozone chemistry is oxygen, it is an ideal choice to limit the formation of chlorinated by-products (AOX) formed during conventional bleaching processes.

Bleaching technology

Ozone is currently applied as a bleaching agent on both softwood and hardwood pulps, while its use on non-wood pulps is under investigation.

Pulp bleaching is achieved through a continuous sequence of bleaching steps utilizing different chemicals and operating conditions to remove residual lignin, and destroy chromophoric groups. One possible step in this process is the “Z” stage. Ozone can be used alone in a “Z” stage, or be combined with chlorine dioxide in a “ZD” stage. Depending on the mill requirements and the bleaching technology to be implemented, optimized mixing systems for both High Consistency (HC) and Medium Consistency (MC) are available to introduce ozone into the pulp.

Keeping the same delignification efficiency, ozone is very economical in terms of operating cost since each kg of ozone replaces between 2 to 4 kg of pure chlorine dioxide. Moreover, the filtrates from the Z-stage can be recovered, lowering the effluent load to be treated and fresh water consumption.

Ozone is the ultimate choice of chemical to promote and successfully implement “Green Bleaching” practices!
High consistency (HC) bleaching with ozone

In an HC ozone stage (figure 3), the pulp is acidified before being pressed up to 38-40% pulp consistency and then fed into the ozone reactor. Ozone gas is added counter-currently to the pulp flow. The reactor is operated at a pressure slightly below atmospheric pressure.

The bleached pulp is diluted at the outlet of the reactor and sent to either a short extraction stage or straight to the next bleaching step. The alkaline filtrate from the extraction stage can be circulated back to the brown stock washers of the fibreline.

Fibria Jacarei in Brazil, one of the world’s largest pulp companies, operates two fibrelines using ozone to bleach pulp, one equipped with an HC ozone stage the other with a MC ozone stage. As of 2011, Fibria’s bleaching line is equipped exclusively with Xylem’s WEDECO ozone systems. This is now the largest ozone system in operation worldwide, producing 24 tons of ozone per day. Fibria produces 3600 adt/d of bleached eucalyptus pulp. Line C, with a production capacity of 2400 adt/t incorporates an HC Ozone Bleaching stage in a (Ze)DP bleaching sequence. Applying an ozone charge of 5 kg/ad, it is the biggest ozone plant (3 Z-Compact Systems) in operation with a capacity of 525kg/h.

The (Ze) stage shows a very high efficiency with a Δ kappa/kg ozone of 1.2 and an outlet Kappa around 5.5.

Compared to conventional ECF, the effluent volume and water consumption is reduced by 30% and the COD load by 40%.

Medium consistency (MC) bleaching with ozone

An MC ozone stage (10-14% consistency) is composed of an MC pump, one or two high shear mixers, a small reaction tube and a flow discharger. While keeping the same pulp quality, a mill can achieve savings in chlorine dioxide and a high brightness level. Moreover, its effluent load can be dramatically reduced with only a minimum investment.

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Take a look into the interior of the Z-Compact System for Fibria in Brasil.

Watch the whole movie using the QR Code with your smartphone.
Xylem’s philosophy: Tailormade solutions

Ozone production

Ozone production requires electricity and oxygen, generally generated on-site. Compared to other bleaching chemicals, ozone is a real on-site technology since there are no costs incurred for chemical delivery, logistics and storage. It makes the pulp mill more independent from the chemical market, removing the uncertainty around forecasting chemical availability from the mill. With ozone generated on site, there are no hidden or unpredictable costs!

Off-gas management

The use of ozone in the mill allows for the unique opportunity to use the oxygen molecules twice. Once for the generation of ozone and bleaching, then the vent gases have sufficient oxygen concentration to be used in any application where oxygen may be required in the mill (Eo stage, delignification, white liquor oxidation, lime kiln enrichment etc.).

Ozone compression

For MC ozone bleaching, the ozone feed gas has to be compressed to the operating pressure of the MC ozone mixer (10-12 bar(g)). Xylem has developed a specific expertise to minimize loss of ozone during compression and transportation to the mixing point. Our unique knowledge and experience comes from our continuous follow-up and improvement of our existing MC installations over the past 20 years.

Ozone destruction

Ozone traces present in the vent gas from the Z-stage must be destroyed before being discharging into the atmosphere. Ozone removal from the gas requires special know-how and equipment. Catalytic ozone destruction combined with chemical destruction, a process developed by Xylem, offers the best compromise between safety, operating cost and sustainability for installations where oxygen has to be valorized. Other methods such as thermal ozone destruction are known to be dangerous in terms of safety (fires) and significantly affected by heavy corrosion.

Fig. 5: Bleaching Process

Source: Papermaking Science & Technology - Vol. 6, Chap.4, Page 538
Taking into account the specificity of each project, the objective of Xylem is to provide technical solutions improving the competitiveness of our pulp and paper customers.

With its technical expertise and specific networking, Xylem conducts long-term partnerships with many pulp and paper companies, chemical and equipment suppliers. Among the latest developments entering the industrialization phase, the following can be mentioned:

**Dissolving pulp production**

Many pulp and paper mills are modifying their existing process to generate dissolving pulps. The ability of ozone to control viscosity and to reduce operating cost explains why ozone is becoming a keystone chemical in this particular process. Xylem has been leading the market since 1992, and is recognized as technology leader for installations operating in the production of dissolving pulp.

**Using ozone at the end of the bleaching sequence**

Another interesting development concerns the use of ozone at the end of the bleaching sequence where its high brightening ability is a good complement to the conventional bleaching chemistry mainly based on the use of peroxide or chlorine dioxide.

**Better pulp quality**

Very high brightness can be achieved whereas pulp cleanliness and strength properties are improved.

**Improving the mechanical pulping processes**

Considering the current issues to maintain a sustainable supply of raw materials and to lower the energy consumption for all mechanical pulping processes, Xylem has developed and patented different applications using ozone on TMP/CTMP/PGW processes in order to:

- Decrease the pitch content
- Reduce the energy requirement
- Improve the strength properties

The first industrial application started in February 2008 in collaboration with one of the major pulp & paper producers.
Other ozone applications in P&P mills

Ozone eliminates pollutants as well as colorants and microorganisms until their levels are well below the legal thresholds. Xylem can help to design the most optimized solution for:

» COD elimination to meet discharge limits*
» Improvement of biodegradability ("cracking") in combination with ongoing biological treatment
» Specific elimination of defined pollutant substances (i.e. phenols, nitrites, AOX, toxins, etc.)
» Last "polishing" step to remove odour/colour or disinfection*
» Replacement of biocides (i.e. for cooling water treatment)
» Improvement of the sludge volume index (SVI)
» Reduction of sludge volume

* demonstrated and validated again in pilot tests within AquaFit4Use funded by EU-ENV.2007.3.1.1.1.

For example, in the Lang GmbH paper mill (Ettringen, Germany), ozone oxidizes non-biodegradable organic compounds into biodegradable ones prior to the biological treatment ("cracking"). It is a suitable and cost effective benchmark in order to lower the COD discharge loads.

Ozone helps to reduce fresh water usage in the mill by allowing for treated water to be recycled to the process.
How to produce ozone?

Ozone can be produced in air or oxygen. However, the pulp and paper industry requires ozone concentrations of between 10-14 weight %. These values are only obtained when using oxygen at higher than 90% purity.

WEDECO ozone generators are the overwhelming choice of design engineers and end-users worldwide where reliable and efficient production of large volumes of ozone is required. For applications in the P&P industry, our Z-Compact Systems perfectly meet the market demands by providing ozone production capacities in the range of 15-250 kg/h per generator.

Unique design

Two key features separate WEDECO generators from the rest: the exclusive use of WEDECO Effizon®evo electrode/dielectric technology and the variable frequency technology. These features combined are the basis for an ozone generator with unmatched reliability, production flexibility and low specific power consumptions.

WEDECO EFFIZON® technology

Inside the ozone generator vessel, a specific number of tubes are welded between two fixed tube plates serving as grounded electrodes. The Effizon®evo electrodes, each consisting of a high voltage electrode, a stainless steel mesh and a dielectric glass tube, are placed inside the grounded tubes. Ozone is produced in the gaps between the grounded electrode, the dielectric and the high voltage electrode. Xylem grants a 10 year warranty for the WEDECO Effizon®evo electrodes.

The performance of any ozone generator depends not only on the electrode assembly, but also on optimum power supply to the ozone generator cell. By using frequency to adjust the ozone concentration and production capacity WEDECO Power Supply Units (PSU) allow precise and linear ozone output control as well as a very wide turndown range (up to 100:1). In contrast to variable voltage PSU designs, the voltage is held constant throughout the range. As a result, our variable frequency PSUs maintain a very high power factor (>0.98) throughout their operating range.

Depending on the need for cooling water supply, WEDECO technology for ozone production reaches an energy ratio between 8.5 to 11 kWh/kg ozone.
WEDECO Z-Compact System: An ozone plant designed for the pulp & paper industry

Advantages

» Very limited space requirement (3.5 x 16.5 m)
» Low specific energy consumption
» High operational reliability
» “Plug and play” systems (extremely short start-up time on site)
» Very easy and safe operation
» Robust design for operation under rough ambient conditions
» Certified factory test prior to delivery
» Effective noise reduction

Especially for P&P applications Xylem has developed the Z-Compact-System, which is a sophisticated compact container housing, perfectly adapted to the pulp mill constraints such as space limitation and aggressive ambient air conditions on site.

The Z-Compact-System provides housing for the complete ozone system including the ozone generator vessel, the power supply units and the PLC system. It is insulated, lighted, painted, and equipped with a heating system, an emergency ventilation system and with air conditioning in case of hot climate conditions.

Fig. 13: Standard design of the WEDECO Z-Compact System
References
(excerpt only)

Celtejo, Portugal

» 1 Z-Compact System
» Ozone production: 180 kg ozone per hour
» Start-up: 2008
» Raw material: softwood / hardwood kraft pulp
» Bleaching: (Ze)DD
» Pulp production: 720 adt/d

Mondi, Slovakia

» 4 Z-Compact System
» Ozone production: 1,000 kg ozone per hour
» Start-up: 2002
» Raw material: eucalyptus kraft pulp
» Bleaching: AZDP & ZDP
» Pulp production: 1,200 adt/d & 2,200 adt/d

Fibria, Brazil

» 3 Z-Compact System
» Ozone production: 340 kg ozone per hour
» Start-up: 2004
» Raw material: softwood / hardwood kraft pulp
» Bleaching: (ZE)DP
» Pulp production: 1300 adt/d

ITC, India

» 1 Z-Compact System
» Ozone production: 200 kg ozone per hour
» Start-up: 2007
» Raw material: hardwood kraft pulp
» Bleaching: (Ze)(DP) and (Ze)DEopD
» Pulp production: 400 adt/d and 300 adt/d
Xylem ['zɪəm]

1) The tissue in plants that brings water upward from the roots
2) A leading global water technology company

We’re 12,000 people unified in a common purpose: creating innovative solutions to meet our world’s water needs. Developing new technologies that will improve the way water is used, conserved, and re-used in the future is central to our work. We move, treat, analyze, and return water to the environment, and we help people use water efficiently, in their homes, buildings, factories and farms. In more than 150 countries, we have strong, longstanding relationships with customers who know us for our powerful combination of leading product brands and applications expertise, backed by a legacy of innovation.

For more information on how Xylem can help you, go to xyleminc.com.