

OZONE FOR PULP BLEACHING

MAKE PULP BLEACHING CLEAN

Ozone is considered, from an ecological point of view, to be the best candidate for the bleaching of both hardwood and softwood pulp, in replacement for chlorine, in a combination-competition approach with other bleaching chemicals, such as Chlorine Dioxide, Hydrogen Peroxide and per-Acetic Acid.

Ozone is used, either on High-Consistency pulps (HC), containing 30 to 40% dry solids, or on Medium-Consistency pulp (MC), with 10 to 12% dry solids contents. In each case the process of mixing the gas with the pulp is the key factor.

HC BLEACHING

The pulp is preliminary acidified and pressed until a consistency around 40%. A "drum" mixer is then used to optimize the contact of the gas with the pulp. In these cases, mixers operating at 2 bar are used.

MC BLEACHING

The acidified pulp is directly treated in a mixer. In this case, mixing takes place at 12-13 bar. This assumes controlled compression without destroying the ozone.

In both cases, the oxygen off-gases can be reused in the client's process, either for oxygen delignification, oxidation of white liquor or for the waste water treatment stage, decreasing consequently the ozone variable cost.

EXAMPLES OF USE OF OZONE

Parameters	Eucalyptus pulp		Pinus radiata pulp	
	DEDD	ZDED	DEpDD	ZEpDD
Ozone (%)	0,0	0,8	0,0	0,6
Cl ₂ total (%)	2,40	0,24	2,04	0,50
Final brightness (% ISO)	90,6	91,5	90,3	91,1

→ UP TO 25% SAVINGS COMBINING O, WITH CIO, (CAPEX & OPEX)

DISSOLVING PULP

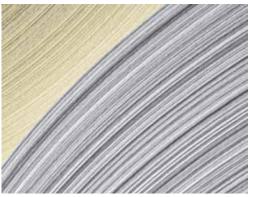
As ozone is very efficient to control the viscosity, the chemical reactions with the pulp are not creating harmful compounds, ligno compounds produced in the cooking process are more easily removed with ozone inducing a cheaper process, ozone is a very good candidate for bleaching of pulps useful for textile.

MECHANICAL PULP

Based on large scale pilot tests, use of ozone allows energy savings of more than 25%, while improving strength properties. Improved run ability on paper machines and better printing results on paper were noted (certainly in relation with the strong pitch removal effect of ozone).



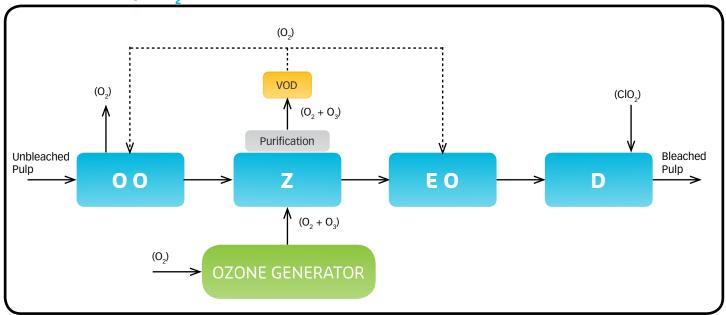






APPLICATION

TYPICAL OZONE/CLO, CHEMICAL PULP BLEACHING DIAGRAM



PAPERMAKING PULP BLEACHED WITH OZONE TOTALLY CHLORINE FREE (TCF)

Since the end of the 80's, much research has demonstrated that, with equally satisfactory results in terms of end product properties (whiteness, mechanical performances of fibres...), ozone could replace Cl_2 , and possibly eliminate all chlorinated bleaching products using the OZP sequence that combines delignification using oxygen (O), ozone treatment (Z) and then hydrogen peroxyde (P) to produce a TCF paper. Furthermore, the use of Ozone for TCF papers, in combination with oxygen and hydrogen proxyde is much cheaper than without Ozone for the same final pulp properties.

ELEMENTARY CHLORINE FREE (ECF)

Even more economical, after oxygen delignification, only an ozone bleaching stage might be retained, followed by a wash - extraction under oxygen atmosphere and a final chlorine dioxide stage. This is the most cost-effective system and, consequently, the most widely used at present for ECF papers.

The OZP line is also used to reduce chlorinated organics products discharge into the effluent by a factor of almost 10. This line also reduces discharged COD.

Most of the bleaching sequences using Ozone are ECF combining $\ensuremath{\mathsf{Z}}$ and $\ensuremath{\mathsf{D}}$ stages.

OZONE BENEFITS

- Beneficial effects on the pulp
- → Mechanical properties are not affected
- Optical properties improved
- → Higher bulk, higher opacity of the paper
- Extractive content strongly reduced
 - → Yellowing is reduced, less brightness reversion
- Reduction of the water retention value
- → Improved drainage, speed on the machine
- No formation of harmful by-products
- → Chromophore compounds
- → Chlorate
- → Dioxins, furans
- → AOX in water effluents, OX in the pulp

APPLICATION: / WASTE WATER TREATMENT

USE OF OZONE FOR TREATING EFFLUENTS FROM PULP AND PAPER INDUSTRY

Pulp bleaching is the largest source of pollution in pulp mills waste waters. Suspended Solids, COD, BOD, AOX and specific toxic compounds are generated. Pulp bleaching (especially when chlorine is used) produces most of theses toxic substances.

Ozone applied as a single treatment step downstream of a conventional biological treatment or combined with a complementary biological treatment can help to solve problems remaining after conventional Pulp & Paper waste water treatment plants.

- If just a polishing treatment is necessary to reach the residual color and COD guidelines, a single ozonation step can be the solution.
 Typically ozone doses between 45 and 450 mg O₃/I lead to 80% color removal and 20-25% COD abatement.
- If hard COD downstream of the biological treatment is still high (> 350 mg/l) a
 solution is to implement downstream the main biological treatment an ozonation
 step followed by another biological treatment (preferably a Biological Membrane
 Reactor). Ozone doses can vary between 0.4 and 1 g O₂/g COD.
- About 100 mg O₃/l leads to about 40% of AOX abatement. A few hundred mg O3/l leads to about 50% of lipophilic wood extractives abatement and 90% of Resin acids abatement
- After ozonation of the effluent, acute toxicity and chronic toxicity decrease is generally observed.
- Finally, ozone can also be used against sludge bulking as well as for activated sludge reduction and improvement of their settleability and dewatering. The vents from the ozone reactors can be reused in the biological treatment.







100% Availability Concept

MAXIMIZE YOUR OPERATION

TECHNICAL ADVANTAGES & HIGHLIGHTS

IGS™ DIELECTRIC TECHNOLOGY

The breakthrough IGSTM Technology is based on the development of a completely new dielectric concept which controls and optimizes barrier discharge intensity along the entire length of the discharge zone where the ozone is produced.

Ozonia's IGSTM Technology assures cost reductions in energy and feed gas consumption establishing ozonation as a technically efficient and environmentally friendly solution for the replacement of chlorine dioxide for pulp bleaching.

In addition, IGS™ Technology reduces:

- Equipment heating
- Equipment redundancy and other infrastructure requirements
- Footprint
- Operation and maintenance requirements
- Utilities consumption

All these advantages reduce the total cost of ozone generator ownership with an overall improvement of ozone system efficiency, reliability and availability.

STATE-OF-THE-ART POWER SUPPLY UNIT (PSU)

The development of the transistor IGBT PSU is a major step forward in semiconductor power technology which is clearly made to replace thyristors aging technologies. In order to keep the leading position with technological development, Ozonia embarked on a development program which has resulted in the top-of-the-line MODIPAC™ modular PSUs.

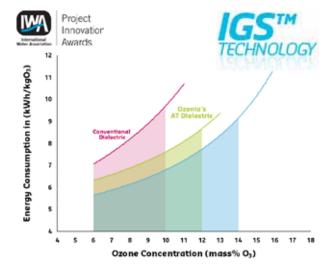
A Modipac PSU consists of several PSU modules. Design is such that nominal ozone production remains in case of a module failure. Replacement of a module is done in a couple of hours.

PRESSURIZED CONTAINERS

The Containerised Ozone Plants (COP) have the same outstanding features as Ozonia's other plants, when it comes to product quality and are capable of producing ozone at very high concentrations from oxygen gas.

The technical features of the systems are exceptional:

- Very compact dimensions
- Integrated controls
- Very simple installation
- High ozone concentrations
- · Robust industrial quality
- High reliability and safety
- Stand alone design
- · Minimal civil works





PRODUCT FOCUS / PERFORMANCES

- > Unbreakable dielectric segments
- > Individual fuses system on dielectric
 - → No shut down if one dielectric fails
- > Multiple power stages
 - → No shut down if one power stage fails
- > IGBT semiconductor technology
- > High power factor of 0.99
- > Low harmonic content
- > Stand-alone plants
- > No corrosion from ambient ai
- > Full protection of the generators & PSU

OPERATE WITH SERENITY

PULP BLEACHING: SPECIFIC TECHNOLOGIES

OZONE COMPRESSION FOR MC-BLEACHING

For MC bleaching processes the ozone gas coming from the ozone generator has to be compressed, usually from about 1 bar(g) to 10-12 bar(g), to the operating pressure of the MC-Mixing equipment. OZONIA developed for this purpose a special ozone compression system to ensure unique compression efficiency by ensuring the highest reliability for P&P clients. The patented process is a combination of a NOx-Scrubber with an appropriate liquid ring compressor. The Scrubber is required to remove Nitrogen oxides which are produced in small concentrations inside the ozone generator. Nitrogen oxides form Nitric acids in the operating water of the compressor could result in very low pH-values. To stabilize the pH-value a special chemical is additionally dosed to the operating water. With the Ozonia compression system the pH value of the operating water is kept in the neutral range which consequently eliminates the risk of corrosion of the compressor.

The advantages of the OZONIA system can be summarized as follow:

- Gentle operation of ozone compressor → no risk of corrosion caused by low pH-value
- No ozone loss caused by high pH-value in the operating water. High pH-value occurs at overdosage of caustic soda (conventional chemical used for stabalisation of pH-value)
- No ozone loss caused by diffusion of ozone in operating water. Dissolved Ozone is recovered by decompression of the water in the scrubber.

UNIQUE KNOW-HOW IN PULP INDUSTRY

- 20 years of experience
- >More than 20 references worldwide
- Unique know-how and experience in ozone compression (MC process)
- Full understanding of vent ozone quality from mixer (unique ozone destruction process and equipment)

OZONE DESTRUCTION

The vent gas coming from the Z-Stage usually still contains small amounts of ozone. Providing the off gas shall not be used for e.g. wastewater treatment, delignification, etc. the ozone in the off gas needs to be destroyed before discharging it to the atmosphere. The treatment of off gas needs special attention and know-how. In principle three ozone destruction methods are available.

- 1) Thermal-Catalytic Ozone destruction systems using a metal-oxide based catalyst to destroy Ozone
- 2) Thermal Ozone destruction systems using temperatures >380 $^{\circ}\mathrm{C}$ to destroy Ozone
- 3) Chemical Ozone destruction

Considering the wide range of wood types and also the different processes, the off gas quality varies from mill to mill. Therefore ozone destruction systems which are extremely flexible in terms of different off gas qualities are required. OZONIA developed especially for the P&P industry an ozone destruction system which is based on thermal ozone destruction. The system combines a gas washer with a thermal ozone destructor.

The thermal Ozone destructor consists essentially of a heater, a reactor (residence time), a heat exchanger for heat recovery, a fan and a control cabinet. The ozone decomposition, and the ozone destruction, is based on the principle of the thermal decomposition. The circumstance is used that ozone decomposes very quickly at increased temperatures (in fractions of a second) into oxygen. In order to optimize the energy consumption, the incoming gas is pre-heated by the outgoing gas in the type RB heat exchanger. Thus about 80% of the heat energy is reused.

The advantages of the OZONIA system can be summarized as follows:

- Operating costs can be forecast (with catalytic VOD not possible)
- Thermal destruction can handle full ozone production capacity with no time limit (catalytic destruction last only up to 5 min.), allowing commissioning even when mixer is not ready!
- Easy operation and maintenance
- Washing and conditioning of the vent gas from Z-Stage
- Possibility to add chemical in the gas washer for a complete destruction of chemicals and ozone (additional back-up to VOD)

SERVICES

FROM 15T THOUGHT ABOUT OZONE UNTIL END OF PLANT LIFE

Process expertise, pulp bleaching and waste water, worldwide recognized experts, lab and piloting capabilities, all to advise you on the best you can get. Below technology supports are based on operator requirements gathered over more than 20 years of experience in pulp mills.

PRIOR TO TAKE OVER

Spare parts management in place

Operation & Maintenance training at site or in Ozonia workshops as required. Set up of a monitoring system for remote data logging.

AFTER TAKE OVER

Technical support for plant operators, during plant lifetime

→ highest possible availability

Data Logging allowing reporting on plant status and maintenance/adjustments to be made by operators

→ Savings on O&M costs.

Possible remote plant control by Ozonia Experts

→ Quick and cost effective trouble shooting

Plant alarms can be automatically forwarded by email / SMS (text)

OZONIA ACADEMIA in Switzerland for training updates

→ Safer and efficient operation

Spare parts management, "wear and tear" & "strategic" follow up

→ highest possible availability

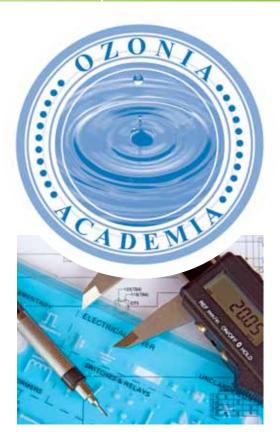
Service agreement, involving local operators and Ozonia engineers

ightharpoonup preventive maintenance, lowest possible running costs

OPERATION & MAINTENANCE

Drawing on its long experience in the field of pulp bleaching using ozone technology, Ozonia can support pulp mill operators in the handling of the Operation & Mainenance. If further assistance is needed, Ozonia can also offer Operation & Maintenance contracts to optimize the operation and availability of the plant.

Flexible O&M duration from months to years is a good way to ensure the highest possible availability and the lowest possible running costs, including spare parts management.











REFERENCES (Excerpt)

Bahia Specialty Cellulose, Brazil

Start up year: 2011 Wood Type: Eucalyptus Consistency: MC

Ozone Production Rate: 60 kg O₃/h

PaperlinX - Maryvale, Australia

Start up year: 2007

Wood Type: Mixed Hardwood

Consistency: MC

Ozone Production Rate: 180 kg O₃/h

SCA - Oestrand (Retrofit), Sweden

Start up year: 2002

Wood Type: Hardwood / Softwood

Consistency: HC

Ozone Production Rate: 231 kg O₃/h

Nippon Paper - Yufutsu, Japan

Start up year: 2000

Wood Type: Mixed Hardwood

Consistency: MC

Ozone Production Rate: 120 kg O₃/h

M-Real (MODO) - Husum, Sweden

Start up year: 1996

Wood Type: Hardwood / Softwood

Consistency: MC

Ozone Production Rate: 250 kg O₃/h

SAPPI - Ngodwana, South Africa

Start up year: 1995

Wood Type: Mixed Hardwood

Consistency: HC

Ozone Production Rate: 270 kg O₃/h

CONTACTS: www.ozonia.com

OZONIA

Stettbachstrasse 1 8600 Dübendorf Switzerland Tel: +41 44 801 85 11, Fax: +41 44 801 85 01 P&P@ozonia.com

