# Ozone bleaching
# - State of the art and new developments -

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## Abstract

Due to the fact that ozone is a highly competitive bleaching chemical, many pulp mills have already chosen ozone in their bleaching process. Reliable on-site generation of tons of ozone per day combined with efficient pulp bleaching systems are the reasons why ozone has become an established technology. This paper presents the state of the art in the use of ozone for pulp bleaching and the latest developments which demonstrate that ozone is indeed the bleaching chemical of the future.

## 1/ Introduction

The use of ozone as a bleaching agent has been considered for many years. But now, more than 12 years after the start-up of the first commercial installations and with 28 ozone bleach plants in operation worldwide (table 1), it is an established technology.

| No. | Mill | Location | Area | Process | kg/h | Supplier | Year |
|---|---|---|---|---|---|---|---|
| 1 | **Lenzing AG** | Lenzing | Austria | MC | 40 | Wedeco | 1992 |
| 2 | **IP** | Franklin (Union C) | USA | HC | 280 | Ozonia | 1992 |
| 3 | **Kymmene** | (Wisaforest) | Finland | | 250 | Wedeco | 1993 |
| 4 | **MoDo** | Husum | Sweden | MC | 200 | Ozonia | 1993 |
| 5 | **Metsä-Botnia** | Kaskinen | Finland | MC | 300 | Ozonia | 1993 |
| 6 | **Peterson** | Säffle | Sweden | MC | 40 | Wedeco | 1994 |
| 7 | **SCA Pulp** | Sundsvall | Sweden | HC | 250 | Ozonia | 1994 |
| 8 | **Bacell** | Salvador / Bahia | Brazil | MC | 65 | Wedeco | 1995 |
| 9 | **Sappi Kraft** | Ngodwana | South Africa | HC | 270 | Ozonia | 1995 |
| 10 | **Stora Enso** | (Consolidated) | WI, USA | HC | 180 | Ozonia | 1995 |
| 11 | **Votorantim** | Jacarei | Brazil | MC | 180 | Ozonia | 1995 |
| 12 | **Votorantim** | Luis Antonio | Brazil | MC | 180 | Ozonia | 1995 |
| 13 | **Metsä-Rauma** | Rauma | Finland | MC | 420 | Wedeco | 1996 |
| 14 | **Klabin** | Telemaco Borba | Brazil | MC | 65 | Wedeco | 1997 |
| 15 | **Domtar EB** | Espanola,ont | Canada | MC | 150 | Ozonia | 1999 |
| 16 | **Rosenthal** | Blankenstein | Germany | HC | 140 | Wedeco | 1999 |
| 17 | **Matussiere** | Turkheim | France | HC | 50 | Ozonia | 1999 |
| 18 | **Burgo** | Burgo Ardennnes | Belgium | HC | 210 | Ozonia | 2000 |
| 19 | **Nippon Paper** | Yufutsu mill | Japan | MC | 120 | Ozonia | 2000 |
| 20 | **OJI Paper** | Nichinan mill | Japan | HC | 180 | Ozonia | 2002 |
| 21 | **Votorantim** | .Jaccarei | Brazil | HC | 500 | Wedeco | 2002 |
| 22 | **Nippon Paper** | Yatsushiro | Japan | MC | 150 | Wedeco | 2003 |
| 23 | **Lenzing** | Lenzing | Austria | MC | 80 | Wedeco | 2003 |
| 24 | **Glatfelter** | | USA | LC | 60 | Wedeco | 2003 |
| 25 | **SCP/Mondi** | Ruzumberock | Slovakia | HC | 340 | Wedeco | 2004 |
| 26 | **OJI Paper** | Tomioka | Japan | MC | 270 | Wedeco | 2005 |
| 27 | **Marusumi** | Mishima | Japan | MC | 210 | Wedeco | 2006 |
| 28 | **DAIO** | Michima | Japan | HC | 400 | Wedeco | 2006 |

*Table 1* – Ozone bleach plants in operation

The evolution of the ozone development follows the same pattern as for oxygen delignification, which had an incubation period of 15 years before taking off (Figure 1). With focus on the pollution abatement and mill closure as well as the trends for market driven pressure to produce light ECF and TCF bleached products, ozone has demonstrated its feasibility as a viable bleaching chemical alternative (1).

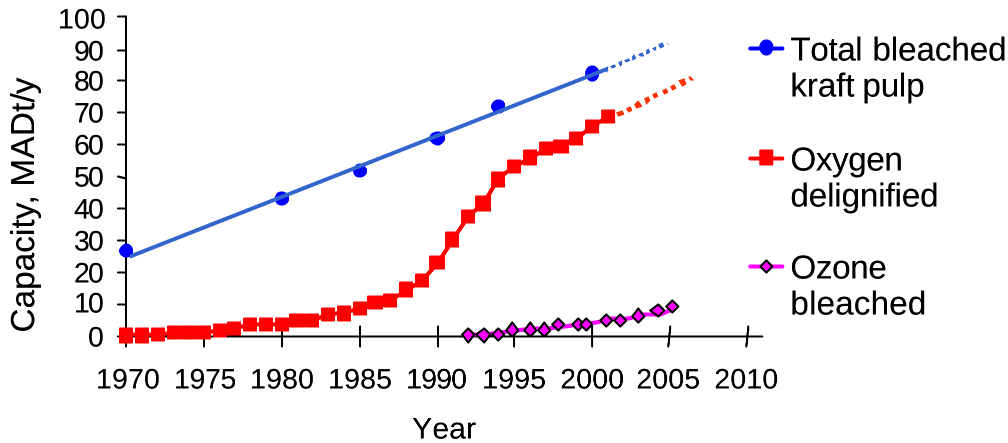


*Figure 1* – Evolution of the ozone bleached pulp

As a complementary delignifying agent after oxygen delignification and in some cases in combination with chlorine dioxide, ozone is known and conventionally applied as an efficient reagent for chemical pulps in the middle of the bleaching sequence. The latest developments show that ozone could also be a good brightening agent when used at the end of a bleaching sequence but can also be applied on high kappa pulps in place of or in combination with oxygen to improve the overall yield in a more efficient way than with oxygen alone.

**2/ Ozone used in the middle of the bleaching sequence – State of the art**

Depending on the bleaching strategy to be implemented, different bleaching technologies are proposed to mix ozone with the pulp. High consistency ozone bleaching systems represents one of the most efficient solutions (figure 2).

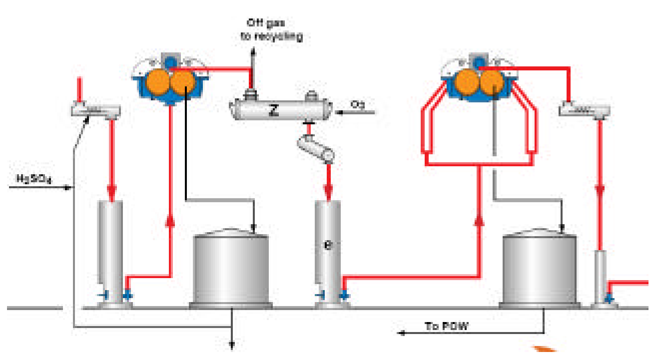


*Figure 2* – High consistency bleaching system using ozone : The ZeTrac$^{TM}$ from Metso

Such high consistency ozone installations have been made for both softwood and hardwood where the ozone charge varies between 2-9 kg ozone/adt for the different installations. One example to show how ozone bleaching is integrated into the fiber line is the VCP Jacarei mill in Brazil (figure 3). In that mill the bleaching sequence is (Ze)DP. The designed production is 2200 adt/d of bleached eucalyptus pulp and the mill is running up to 2500 adt/d (1).

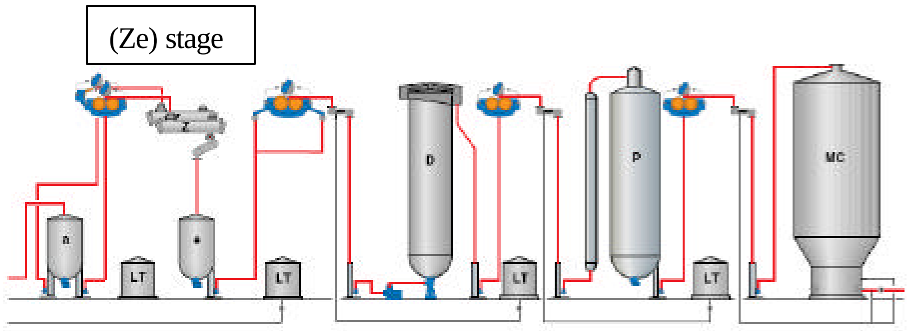


*Figure 3* – VCP Jacarei fibres line ((Ze)DP) – Start-up 2002 – Production 2 500 t/d

The ozone system shows very high efficiency over (Ze) stage since kappa/kg ozone is generally 1.2 with an ozone charge of 5 kg/adt. Figure 4 shows the 500 kg/h ozone production performed by 3 WEDECO ozone containers tested in our manufacturing plant before shipment and installation in the VCP Jacarei mill.

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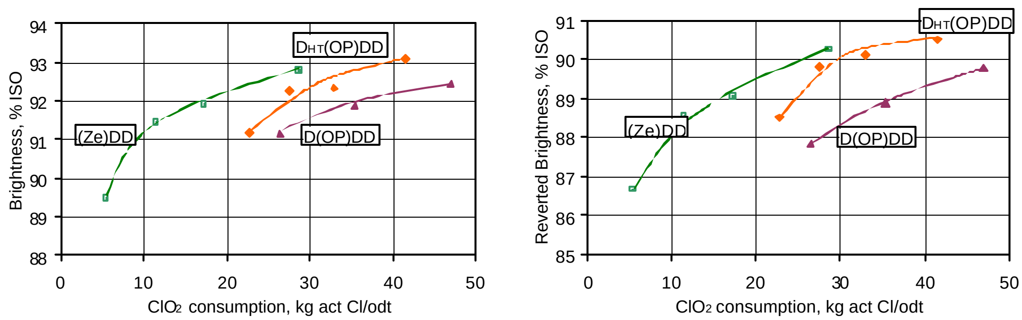
*Figure 4* – Ozone containers from WEDECO installed at the VCP Jacarei mill.

Today, when designing a bleach plant for hardwood pulps or *eucalyptus* pulp, the amount of hexenuronic acids responsible for brightness reversion has to be considered. Ozone bleaching is very effective for removing HexA (2) in a cost-effective way and can be compared to other bleaching alternatives. For example, an ozone bleaching sequence (Ze)DD can be compared with the DHT(OP)DD bleaching sequence including a hot chlorine dioxide stage (DHT), and a reference bleaching sequence D(OP)DD with respect to brightness ceiling & reversion, bleaching chemical cost, mechanical properties and environmental load (1).

**Brightness and Chemical Cost**

The powerful delignification and brightening capability of ozone allows for a significant reduction of total chlorine dioxide use for an ECF bleach plant, e.g. (OO)(Ze)D, (OO)(Ze)DD or (OO)(Ze)DP, and peroxide in a TCF plant, e.g. (OO)(Zq)P or (OO)ZQ(PO). As an example of that, Figure 5 shows that the chlorine dioxide consumption was lowest for the ozone-bleached pulp for reaching a certain brightness and reverted brightness. Furthermore, ozone made it possible to reach higher brightness and reverted brightness targets compared with the reference (1).




*Eucalyptus* pulps cooked (SuperBatch™) and oxygen delignified (OO) before laboratory bleaching

*Figure 5* - Ozone-bleached pulp showed the lowest chlorine dioxide consumption for reaching a certain brightness or reverted brightness.

The relative bleaching chemical costs for reaching brightness and reverted brightness have been calculated in table 2. The use of ozone gave the lowest chemical costs for reaching a certain brightness and reverted brightness.

| | (Ze)DD | $D_{HT}$(OP)DD | D(OP)DD |
|---|---|---|---|
| **Brightness, 92% ISO** | 77 | 86 | 100 |
| **Reverted Brightness, 89% ISO** | 77 | 82 | 100 |

*Table 2* - Relative bleaching chemical cost, %, including the impact of carry over and based on Brazilian chemical costs

**Mechanical Properties and environmental load**

In that example, pulp strength can be well preserved when applying ozone as the first stage in a bleaching sequence. Figure 6 shows the data for the three pulps prepared for PFI beating and tested for strength properties.

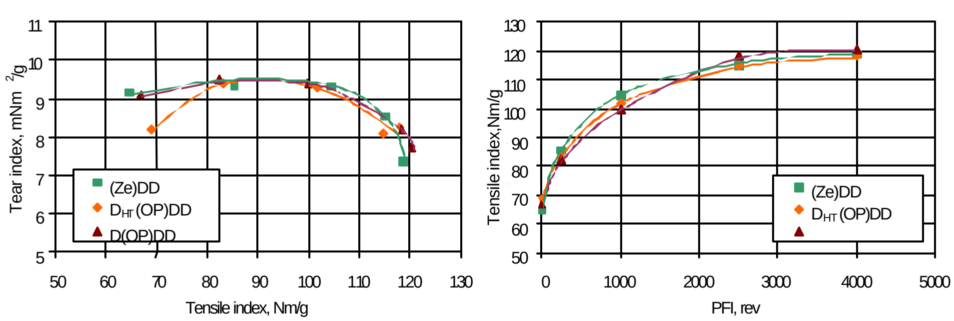





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*Figure 6* - Pulp strength and beatability for the bleached pulps

Ozone sequences also offer the best options for environmentally sound bleaching. By using ozone in a (Ze)DD ECF sequence, the filtrate from the (Ze) stage can be recovered. The washing after ozone bleaching is alkaline as the ozone treatment is followed directly by an alkaline extraction. This makes it possible to recycle the filtrate after ozone bleaching. This is a unique possibility for the HC ozone system, as the dilution with alkali gives a rapid pH change and thereby is precipitation of calcium oxalate avoided. With presses as washers, the total effluent volume will be 7 $m^3$/t including 2 $m^3$/t taken out from the acidification stage ahead of the ozone stage. Comparing the water consumption and effluent load for the light ECF ozone sequence and the $D_{HT}$ bleaching sequence applied on a hardwood pulp, the effluent volume is reduced by 30% and the COD load by 40%. As a consequence of the low effluent volume, also the fresh water consumption is low (1).

### 3/ Ozone as a last bleaching stage

During full bleaching of chemical pulp the last points of brightness are usually difficult to achieve, which is reflected in the relatively high chemical charges needed, and in the rather drastic conditions (temperature and time) required by comparison with those used in the first stages of the bleaching sequence. Moreover, obtaining a constant level of brightness is still an issue in many pulp mills. A new development concerns the use of ozone as a brightening agent applied at the end of a bleaching sequence, where these last points of brightness are usually difficult to gain. As presented in figure 7, 1 to 2 kg ozone per ton of pulp is sufficient to produce an instantaneous bleaching effect, increasing the brightness by several points (3).

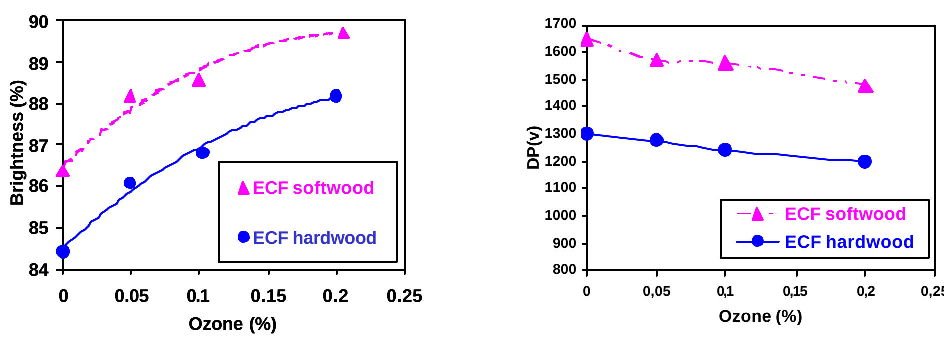


*Figure 7* - Brightness and pulp viscosity versus ozone charges for ECF pulps.

No cellulose degradation takes place under these conditions, and the strength properties of the ozonated pulps are not affected. The process is working equally well at acidic or neutral pH. The efficiency of a last ozone stage depends on the bleaching sequence applied and on the nature of the pulp (wood species…). In terms of chemical saving, the results obtained in the best cases indicated that 1 kg ozone could replace 2 kg hydrogen peroxide or chlorine dioxide.

### Process implementation

Different possibilities have been considered to implement ozone as a last bleaching stage. The first consists to transfer ozone into water before mixing the ozonated water to the pulp. The use of dissolved ozone minimizes the transfer problems and bleaching occurs in a very short time (few seconds) without any significant ozone loss. However, water quality remains the limiting factor for the process implementation. The best ways to apply ozone consist to use conventional bleaching systems where ozone is introduced into low or medium consistency mixers. Industrial validation of the use of ozone as a last bleaching stage is in progress.

**4/ Ozone on high kappa pulps to improve pulp yield**

Several studies have been devoted to the increase in pulp yield to improve the overall economy of the production of kraft pulps. Among those, it was demonstrated that by stopping the cooking at a higher kappa number and then applying oxygen delignification, a higher final pulp yield was observed (4-6). This was explained by the fact that the last phase of a cooking step is less selective than oxygen delignification.
Indeed, ozone is a more efficient delignification agent than oxygen. Moreover the presence of a high quantity of lignin protects cellulose from degradation. First experiments have shown promising results which were confirmed on both softwood and hardwood pulps. As an example, table 3 shows the results obtained with *Eucalyptus* kraft pulps (7).

| **PULP** | **Kappa after Z** | **ClO2 %/Kappa** | **Final brightness, % ISO** | **Total yield, %** |
|---|---|---|---|---|
| **Kappa 17 (Control)** | - | 0.166 | 87 | 42.2 |
| **Kappa 28 + 0.8 % ozone** | 18 | 0.161 | 91 | 44.5 |
| **Kappa 26 + 0.5 % ozone** | 17 | 0.166 | 89 | 44.0 |
| **Kappa 23.5 + 0.5 % ozone** | 15 | 0.176 | 90 | 43.3 |

$D_0ED_1ED_2$ bleaching : a chlorine factor of 0.22 was used in $D_0$, 0.8% and 0.6% pure $ClO_2$ were used in $D_1$ and $D_2$ respectively.

*Table 3* - Bleaching of the control kraft and the high kappa pulps treated by ozone.

Pulps with kappa number ranging from 17 to 28 were prepared. The 17 kappa number pulp was considered as the control. The results show that, as in the ozone treatment applied to the high kappa pulps led to a better overall yield (cooking yield x Z treatment yield) than for the control kraft. For a kappa of 17, the yield gain was 2.3 on wood when applying ozone to the 28 kappa pulp. A better refining ability of the ozonated high kappa pulp vas observed and the strength properties were significantly better especially the tear index (7).

From a practical point of view, the following points are under investigation:

1. From a technological point of view, the feasibility of applying charges of ozone as high as 1 to 2 % on pulp at high temperature still needs to be checked. Potential

recirculation of the acidic effluent of a Z stage back to the recovery boiler should be compared with the conventional O stage.

2. From an economical point of view, oxygen is much cheaper than ozone. However a complete calculation should be done by taking into account the equipment, the gain in yield, the beating ability. Nevertheless it would not be incompatible to apply first a single O stage on a high kappa pulp, and then to apply ozone. There is probably still a yield benefit of applying O(Ze)DED using the ZeTrac™ from Metso over OODEpDED on a high kappa pulps.

Applying ozone on high kappa pulps is an attractive way to increase the pulp yield more extensively than the other known alternatives. The high kappa pulps treated by ozone and then fully bleached by an ECF sequence appeared easier to refine than the control kraft pulp, both for softwood and hardwood. Equal or better strength properties than the control pulps were obtained.

## 5/ Conclusions

Nowadays, ozone is considered as one of the Best Available Technology (BAT) for pulp bleaching. With increasing regulatory pressure and growing market demand for better products, the pulp and paper industry faces many challenges and must find new ways to improve environmental and process performance, and reduce operating costs. By choosing ozone in their bleaching process, many pulp mills in various part of the world have already obtained these benefits. WEDECO, as the largest supplier for ozone equipment in pulp bleaching, will continue to invest and promote new technical developments able to improve competitiveness of our pulp and paper customers.

## References


1. Carre G, Wennerström M. (2005): Ozone bleaching – An established technology, IPBC, Stockholm, Sweden, 144-149
2. Wennerström M (2002): Decreasing brightness reversion with powerful Ozone bleaching, at IPBC, Portland, Oregon, USA, 265
3. Pipon G., Chirat C, Lachenal D. (2005): Final bleaching with ozone – Basic and applied aspects , IPBC, Stockholm, Sweden, 138-143
4. Kleppe, P.J., Chang, H.m., Eckert, R.C.(1972), Delignification of high yield pulp with oxygen and alkali, I, Preliminary studies on southern pines, Pulp and Paper Magazine of Canada, 73 (12), T400-T404.
5. Jamieson, A.G., Fossum, G., (1976), Influence of oxygen delignification on pulp yields, Appita, vol. 29, n°4, 253 – 256

6. Magnotta, V., Kirkman, A., Jameel, H., Gratzl, J. (1998), High kappa pulping and extended oxygen delignification to increase yield, Breaking the Pulp Yield Barrier Symposium, Atlanta, Feb 17-18 1998, Tappi Press, 165-182.
7. Chirat C, Nyangiro D., Struga B., Lachenal D. (2005): The use of ozone on high kappa softwood and hardwood kraft pulps to improve pulp yield, IPBC, Stockholm, Sweden, 74-80.