State-of-the-Art Industrial Ozone Bleaching

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Abstract

The first industrial production of ozone bleached pulp started almost 20 years ago in connection with increasing environmental pressure and the Total Chlorine Free (TCF) wave. Like many other new technologies, ozone bleaching did not immediately reach its optimal efficiency from a technical viewpoint, but had to face several issues during its early years. By improving mixing technology, better understanding ozone chemistry on pulp components and tuning the whole process, the so-called ECF-Light bleaching sequences - including an ozone stage - made it possible to deliver a pulp quality similar or better than is produced by conventional ECF bleaching.

Today the choice of ozone may still be motivated by ecological requirements but it is mostly justified by the economical savings resulting from chemical reduction. Actually, both targets are reached simultaneously when implementing an ozone bleaching stage, whilst pulp quality is either maintained or improved.

Using results from several industrial sites, this article describes process improvements in ozone bleaching since 1992 and shows why ozone should now be considered as the keystone of modern pulp bleaching processes.

Introduction

The first industrial pulp bleaching line including an ozone stage started 19 years ago. Today there are 22 mills worldwide using what is commonly named light-ECF bleaching and they produce almost 7.5 M adt/y. Among those 22 mills, 16 produce solely hardwood pulps, 4 produce both softwood and hardwood pulps while SCA in Östrand (Sweden) and Rosenthal in Blankenstein (Germany) produce exclusively softwood pulp. 13 mills started ozone bleaching in the early years of the 21st century and 2 mills equipped two of their bleaching lines with ozone: Fibria in Jacarei (Brazil) and ITC in Bhadrachalam (India). Fibria in Jacarei selected ozone bleaching in 2002 for its 2,500 a.d. tonnes/day new line C after having operated ozone bleaching as from 1995 on its 900 a.d. tonnes/day line B. This decision clearly shows that ozone bleaching has met all requirements and expectations on line B for 7 years.

Already, four new ozone bleaching stages were contracted since 2010 for:

- a 700,000 a.d. tonnes/year capacity Chinese greenfield mill owned by Oji Paper (the company already uses ozone in its Japanese mills);
- a pulp production capacity increase in Austria at Lenzing;
- a mill converting to dissolving pulp production in South Africa;
- a mill converting to dissolving pulp production in Austria.

Ozone bleaching is efficiently used on hardwood and softwood pulps, on kraft and sulphite pulps dedicated to all kinds of final applications. Pulp producers do not always evaluate the significant ecological advantages of ozone-based bleaching sequences over the traditional ECF bleaching sequence $D_0$,Eop-$D_1$-$D_2$ (or its variants):
the quality of wastewater is drastically improved\(^2,3\) as it is possible to lower bleaching effluents to 4-6\(\text{m}^3\)/a.d. tonne\(^4\). Of course, investors always focus on the return on investment (ROI) and it has now become clear to all ozone users that bleaching costs are reduced by 20-32\% when introducing an ozone stage in an ECF bleaching line\(^3,5,6,7\) and even more in the case of a TCF bleaching\(^8\). The high bleaching efficiency of ozone allows a drastic reduction in the consumption of expensive bleaching chemicals - chlorine dioxide in ECF bleaching and hydrogen peroxide in TCF bleaching as well as sodium hydroxide in both cases – and the implementation of ozone bleaching also results in the reduction of steam requirements during the bleaching process. The ROI in the replacement of a D0-stage by an ozone Z-stage lies between 2 and 4 years\(^1,6\).

Without affecting the pulp strength properties in comparison with conventional ECF sequences, bleaching with an ozone stage additionally gives a wide range of opportunities by:
- making very high brightness levels possible (92-93\% ISO)\(^2,9\)
- decreasing brightness reversion\(^2,8,10\)
- reducing drastically the extractive content\(^10,11\) by 50-75\%\(^8,12\)
- reducing energy requirements during refining by at least 10\%\(^3,13\)
- precisely controlling the viscosity in viscose pulp production.

Nevertheless, arguing that ECF bleaching has already been used in the industry for 30 years, a number of conservative pulp producers still consider the bleaching sequence D0-Eop-D1-D2 - and its variants - as the best alternative today. One should however be aware that within the next twenty years, the pulp & paper industry will have to carry out significant modernisations to retain its competitiveness and, in turn, such a traditional ECF bleaching will then be over 50 years old. This position could be understood if no better technique was available. But considering the very good results and proven stable operation achieved today by a large number of industrial ozone-based light-ECF and TCF bleach plants, such a conservative attitude cannot be justified any longer.

The industrial use of ozone has already undergone a long string of improvements and developments. Like for other new technologies, ozone bleaching did not immediately reach its optimal technical efficiency but faced several issues during its early years. All the same, achievements of ozone bleaching have improved year in year out and it is now a well proven technology. Nevertheless, some pulp producers still keep in mind the difficulties faced in the early years and unfortunately, this still represents a very serious drawback towards the modernisation of their pulp mills. By doing a brief survey of ozone application in pulp bleaching development over the past 20 years, the present article aims to draw specialists’ and investors’ attention to practices and technologies that helped ozone bleaching become the most advanced and promising technology.

### Ozone Generation

Ozone generation is a pure on site technology requiring only energy and oxygen (usually also produced on site from a VPSA plant). Ozone (O\(_3\)) is produced from oxygen (O\(_2\)) in an electrical field at a concentration of 12\% by weight according to Figure 1.

Modern ozone generators are 50\% more efficient than the ones used in the first ozone pulp bleaching applications. Z-Compact-Systems (Figure 2) were specially designed for the pulp and paper industry and they are able to produce up to 250kg O\(_3\)/h (6 tonnes per day) per unit.

Today ozone production only requires 7 to 8 kWh per kg of ozone and as a result, 1kg ozone is now cheaper than 1kg of chlorine dioxide. Based on a “plug and play” principle,
modern ozone generation units are easy to operate and can deliver the full ozone capacity in less than one minute with an availability higher than 99%.

**High Consistency (HC) Ozone Bleaching**

The first commercial HC ozone bleaching started in 1992 at the Union Camp mill in Franklin (Virginia, USA). According to the C-Free® process implemented there, the pulp was pH adjusted, pressed to high consistency (40%), fluffed and transferred to the ozone paddle reactor operating at atmospheric pressure 14. The C-Free® was provided by SundsDefibrator until the late 1990s in the USA, Sweden, South Africa and Germany.

Modern HC ozone bleaching uses the ZeTrac™ technology provided by Metso Paper which is a much simplified version of the C-Free® (Figure 3) 5. The experience gained from the first industrial installations showed that ozone requires very short (around 1 minute) contacting time with the pulp and that a 5-10 minutes extraction stage after the Z-stage is in most cases sufficient. These observations allowed the size of reactors to be reduced, which lowered investment costs. Then the plug screw feeder, the refiner fluffer and the washing stage prior to the extraction stage could all be eliminated. These drastic simplifications led to significant reduction of the capital expenditure, energy requirements, maintenance costs as well as effluent volume 5.

Figure 3 shows the principle of the modern ZeTrac™ system. The pulp is acidified and then pressed to high consistency (38-42%). Such a high consistency is a prerequisite to facilitate the rapid contact between ozone gas and well fluffed pulp and so preserves the reaction efficiency. Once dewatered, the pulp is fluffed in a shredder screw on the top of the press and fed by gravity into the reactor. Ozone is added to the reactor which is operated at a pressure slightly below atmospheric. After the reactor, the pulp is diluted with alkaline liquor.

**Medium Consistency (MC) Ozone Bleaching**

Improvements in MC ozone bleaching consist in fact of alterations to the ozone mixers. This is no wonder since the ozone mixer is the core of the MC Z-stage and the quality of the final pulp depends on its efficiency. It is worth remembering that the very few mills which faced quality issues are those where the first MC ozone bleaching technique was implemented: this was mainly due to a non homogenous mixing and a mixer which mechanically affected the fibres.

Andritz, GL&V and Lenzing Technik are the 3 suppliers of MC ozone mixers and all MC Z-stages are designed according to the same principles. Industrial practice has shown that Andritz technology requires two mixers in series for a 3-6kg/a.d. tonne ozone dose to obtain the optimal bleaching efficiency while Lenzing Technik considers that one single mixer of their own is sufficient for a 4-5kg/a.d. tonne ozone charge.

Because of the larger amount of filtrate around the fibres at 12% pulp consistency, the reaction must take place in a pressurised (7-8bar) reactor and consequently the total gas flow (oxygen + ozone) must be compressed accordingly. A typical MC ozone stage from Andritz (Figure 4) features a MC pump that feeds the pulp to the ozone stage, two ozone mixers in series, a pressurised reaction tube, a flow discharger at the reactor top and a blow tube 11.

It was noticed that the whole reaction process takes place in the mixers while the “reactor” has no effect on the ozone reaction but only guarantees a stable flow to the blow tube 11. It is now possible to decrease the gas pressure from 12bar to 9bar and thus reduce operating costs.

Andritz improved original Ahlström mixer efficiency by reducing the gas bubble size without making any fundamental change in the design of the mixer but only increasing turbulence and mitigating the mechanical action 12. It makes the mixing a lot more homogenous and maintains pulp strength all along ozonation.

Lenzing started a MC ozone mixing system from Kvaerner in 1992 and since then has investigated all
possible improvements in MC ozone bleaching. They have been pioneers in ozone bleaching for almost 20 years and, as a result, LenzingTechnik designed its own ozone MC mixers (called Eccentric Mixers) implementing the revolutionary idea of an asymmetric design to increase both fluidisation of the pulp and retention time.

And this proved to work: Lenzing upgraded its 2 bleaching lines in 2004 with modern Eccentric Mixers and the use of the new mixing technology resulted in a 2.5 ISO brightness points increase for the same ozone dose. Lenzing reduced its bleaching chemical costs by 50% on line 1 and 38% on line B.

**Pulp Quality**

Since the first commercial ozone bleaching installation was started, enhancements to the ozone bleaching process have been conducted jointly by laboratories on the chemical side and by both the industry and equipment suppliers on the operational and technical sides. Improvements in ozone bleaching efficiency were boosted by the development of automatic control systems, mainly as a result of achievements in the accuracy and reliability of electronics. It is now possible to adjust very precisely the ozone dosage, pH, retention time and temperature in
the Z-stage. These improvements now fully guarantee the pulp quality after ozone bleaching.

When ozone bleaching started to develop in the early 1990s, the use of such a powerful oxidant in combination with non-optimised process parameters (the most important issue being the mixing homogeneity) resulted sometimes in uneven pulp delignification and affected the pulp mechanical properties.

Practices improved step by step and opportunities soon replaced difficulties, yet many pulp producers still hold to the cliché that the quality of ozone bleached pulp, especially softwood, is lower than traditional ECF bleached pulp. Since most of the mills using ozone are producing hardwood pulps, some even believe that this evidence sustains the alleged lower strength of softwood ozone bleached pulps. The true explanation instead is rather simple: ozone bleaching is mostly implemented in Europe, Brazil, South Africa, Australia, India and Japan, all countries deficient in softwood resources. Thus, such an argument does not stand considering that 25% of the mills using ozone are producing softwood pulps. This proportion is not lower than the ratio of softwood/hardwood bleached pulps produced in those countries.

One could argue for a long time about the few myths hampering the most advanced bleaching technology in the pulp industry. The truth is that no significant difference could objectively be observed on the paper machine run except the saving in refining power requirement which is obviously lower for ozone bleached pulps.

On the other hand, numerous studies carried out during the 1990s and in the more recent years have shown that the selectivity of ozone against lignin is very high. It is now established that the reaction kinetic of ozone with typical lignin structures is 10 to 1,000 times higher than with carbohydrates (Figure 5) 17.

This means that as long as there is some remaining lignin (even only 0.5-1.5%) a well-operated ozone bleaching process does not impact the cellulose more than any other bleaching stage (a chlorine dioxide one for example). In fact, according to the best wood chemistry specialists 15,17, the reaction kinetic of ozone with lignin is 1,000 times higher than the kinetic of cellulose oxidation or depolymerisation by ozone. Those scientific results are confirmed by the following industrial experience of ozone bleaching.

In 1998, Domtar mill in Espanola (Canada) switched from the ECF O-A-D-DnD sequence to the light-ECF O-A-Z-D-E-DnD sequence for bleaching pulp up to 93% ISO brightness. Comparing the 2 sequences Domtar noticed “ozone has no impact on viscosity or PFI strength properties and in paper machine performance” 9.

Mondi mill in Ruzomberok (Slovakia) produces hardwood and softwood pulps at 89% ISO brightness and switched in 2004 from a D-Eop-D-E-D bleaching to a Z-Eo-DnD one. It should first be noticed that there was only one washing stage (after ZEo) in the new process. Mondi compared hardwood and softwood pulp strength parameters of the new pulps with the ones of the former pulps set as the reference (100%); only minor differences could be seen in standard pulp properties (Table 1) 18.

<table>
<thead>
<tr>
<th></th>
<th>Hardwood</th>
<th>Softwood</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFI rev</td>
<td>89</td>
<td>90</td>
</tr>
<tr>
<td>Burst Index</td>
<td>100</td>
<td>97</td>
</tr>
<tr>
<td>Tear Index</td>
<td>92</td>
<td>90</td>
</tr>
<tr>
<td>Breaking Length</td>
<td>104</td>
<td>102</td>
</tr>
<tr>
<td>Tensile Index</td>
<td>102</td>
<td>102</td>
</tr>
<tr>
<td>Stiffness</td>
<td>93</td>
<td>94</td>
</tr>
</tbody>
</table>

Concerning hardwood pulp, energy requirements for refining dropped by 11%, burst was maintained, breaking length and tensile index increased while tear and stiffness decreased. Meanwhile, for softwood pulp, refining energy was again reduced significantly, tensile properties increased marginally while burst, tear and stiffness showed some reduction.

At this stage it is worth remembering that generally, the tensile index is increased by refining while the tear index follows the opposite trend and it is impossible to increase both of them at the same time. Nevertheless the mill reported that the paper machine runnability was not
impacted and the final paper properties were even better than expected (stiffness) 13. Hardwood pulp properties were particularly excellent and the hardwood proportion in the paper machine furnish was increased over 90% 13. In 2005 Mondi Ruzomberok set up a new world record for copy paper production at 1,500 m/min 13,18. Of course, these two achievements would not have been possible with a lower pulp quality than before.

Moreover, Mondi Ruzomberok has kept improving the Z-stage operation and its bleaching process by installing a pressurised (PO) stage in place of the last D stage in August 2008. Current pulp strength properties shown under Figure 6 are excellent and would make most pulp mills envious.

Actually, ozone bleaching process improvements never stopped. ITC mill in Bhadrachalam (India) started ozone bleaching in 2007 after 5 years of ECF bleaching operation. Their statement is pretty clear 19:

- the breaking length increased by 5.5%
- the burst factor increased by 10%
- the tear factor increased by 6%
- the bleaching chemicals cost decreased by about US$10/a.d. tonne

### Operating Parameters

Pulp temperature is one important operating parameter that has been tuned. Ozonation was initially carried out at 40°C in the 1990s and such a low temperature was not very convenient as the Z-stage is located right after the 85-95°C oxygen delignification and before an alkaline extraction or a chlorine dioxide stage (after a few MC ozone stages) generally carried out at around 60-80°C. It is therefore necessary to cool down the pulp before heating it back.

It was thought that a higher temperature would lower the Z-stage efficiency, speed up the ozone decomposition, increase the negative impact of transition metals and ultimately decrease the pulp quality. Slowly, throughout industrial trials, it appeared that such fears were totally unfounded. Several results have demonstrated that for hardwood pulp the Z-stage temperature could be increased up to 60°C and sometimes even higher without any negative impact on pulp strength and brightness 9,13,18.

For example data from Mondi mill in Ruzomberok show that an increase of the Z-stage temperature from 43°C to 61°C gives a higher brightness (+1.8% ISO), a lower brightness reversion, a higher stiffness and a better ozone delignification efficiency, with all other properties (PFI rev, Burst Index, Tear Index, Tensile Index and Bulk) unaltered (Table 2) 13,20.

<table>
<thead>
<tr>
<th>Temp in Z</th>
<th>43°C</th>
<th>43°C</th>
<th>58°C</th>
<th>61°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kapp number after Z(EO)</td>
<td>4.1</td>
<td>4.0</td>
<td>4.0</td>
<td>3.8</td>
</tr>
<tr>
<td>ClO2 charge, kg/adt (DCS data)</td>
<td>24.5</td>
<td>23.5</td>
<td>24.7</td>
<td>24.4</td>
</tr>
<tr>
<td>Brightness, % ISO</td>
<td>85.9</td>
<td>85.2</td>
<td>86.6</td>
<td>87.7</td>
</tr>
<tr>
<td>Reverted Brightness, % ISO</td>
<td>81.8</td>
<td>82.2</td>
<td>83.9</td>
<td>85.9</td>
</tr>
</tbody>
</table>

Domtar mill in Espanola first operated the Z-stage at 55°C. When they decided to increase the ozone stage temperature to 60°C, they increased delignification by 5-10% and gained 1 point ISO brightness. Today, they are operating the ozone stage at 70°C 9.

All HW pulp mills which set up an ozone stage in the past 5-6 years are running the Z stage at a 55°C minimum. This also resulted in significant steam savings. For example Mondi Ruzomberok reduced its steam requirements by 75% by running the Z-stage at 58-61°C 13.

Metso Paper has shown industrially that steam requirements for light-ECF bleaching are only 25% of steam requirements for conventional ECF bleaching in
the case of HW pulp. While the bleaching sequence DHT-Eop-D requires 249kg/t of LP steam and 40kg/t of MP steam, 65kg/t of LP steam only are necessary for the Ze-DD bleaching sequence.

As an example, implementation of the ozone stage at ITC Bhadrachalam led to a 50% drop in steam consumption in comparison to the former D-Eop-D bleaching sequence.

Steam savings are of course the highest in the case of hardwood pulp bleaching where usually a first A-stage (acidic) or DHT-stage (D-stage at hot temperature) is implemented. Such A or DHT stages have 2 targets:

- removing hexenuronic acids which are responsible for parasite chlorine dioxide consumption and brightness reversion
- cleaning the pulp from transition metals which are known to decompose \( \text{H}_2\text{O}_2 \) and responsible for weakening of the cellulose during peroxide bleaching

By removing transition metals, the A-stage effectively replaces the use of a chelating agent. Acidic stages were built prior to the ozone stage in the 1990s at the UPM mill in Pietarsaari (Finland), at the Sateri mill in Bahia (Brazil), at the Fibria mill in Jacarei and at the Domtar mill in Espanola (Canada). But today there is no doubt that the implementation of an A-stage reduces both pulp strength properties and pulp yield.

Of course, there is no such problem of hexenuronic acids in the case of softwood pulp bleaching. But the issue of transition metals remains and in the 1990s Swedish mills SCA Östrand and the German Rosenthal mill in Blankenstein chose to start their bleaching sequence with a Q-stage (chelation).

Such A-stages or Q-stages are costly because they require a tower (with 2-3 hours retention time for the latter) and the use of expensive chemicals. Yet industrial light-ECF and ozone based TCF experiences have shown that the installation of Q-stages should be avoided while the use of A-stages depends on the hexenuronic acids amount.

The hexenuronic acids content is reduced by at least 60% in the ozone stage. This makes the ozone stage even more efficient than any A-stage and it partly explains why ozone bleached pulps have a lower brightness reversion than other pulps.

Actually, removal of transition metals is efficiently carried out during the ozone stage where the pH is acidic (usually 2.5-3). Awareness of this fact avoids investing in any acid or chelating stage when ozone is applied, and results in operating cost savings. As a result, only 2 of the 16 pulp bleaching lines having started since 2000 use an A-stage and none of them use chelating agents.

**Bleaching Sequences**

The proven economical, technical and environmental advantages, the development of oxygen delignification as well as improvements in ozone bleaching and in the whole pulping process over the last 20 years, have allowed the bleaching sequence to be shortened by one, two or even three stages, while simultaneously increasing the brightness ceiling with 2-3 points compared to what was possible.

In the nineties it was common to fully bleach the pulp with 6 or even 7 bleaching stages as in the following sequences:

- A-Z-D-Eop-Z-D-Ep in Pietarsaari (Finland)
- Q-OP-D-Z-PO-P in Blankenstein (Germany)
- A-Z-D-E-DnD in Espanola (Canada)

Bleaching sequences built in the last decade for both hardwood and softwood pulps usually have only 3 or 4 stages and vary little from one another:

- Z-D-Ep-D at Nippon Paper Yufutsu (Japan)
- ZEop-D-P at Mondi Ruzomberok (Slovakia)
- ZD-E-D at Nippon Paper Maryvale (Australia)
- Z(EOP)-(PO) at Sniace (Spain, sulphite pulp for dissolving grades)
- Ze-D-P at Celtejo (Portugal)

These bleaching sequences reflect the continuous and impressive developments of ozone application in light-ECF bleaching process and clearly show the worldwide interest of pulp makers in ozone bleaching.

**Perspectives**

Having improved pulp mixing technology and better understood pulp quality impact resulting from the rationalisation in the ozone dosage, the advantages using ozone have been clearly demonstrated at industrial scale. However, the story is not completely finished.

The coming step is the implementation of “Green bleaching” where the usage of chlorine chemicals such as chlorine dioxide usage is minimised or even completely eliminated. As explained before, when hardwood pulp bleaching is concerned and for Eucalyptus pulp in particular, it is known that ozone is considered as an efficient HexA removal agent. However for economical reasons, a significant part of the job can
be efficiently done by an A-stage. In that case, the use of ozone could be mainly focused on both finalising pulp delignification and starting final pulp brightening. One can argue that high temperature could remain a limiting factor in the ozone application especially when located after an A-stage generally performed at high temperature. However, it has been shown that high temperature (80°C) in the ozone stage is not a limitation but, on the contrary, is beneficial since it increases sensitivity of the coloured groups (chromophores) remaining into the pulp toward ozone oxidation [25].

The final goal is to definitively eliminate chlorine chemistry and to implement a bleaching chemistry only based on oxygen, peroxide and ozone. Bleaching options such as A-Ep-ZP or A-Ze-P are currently under investigation. The expected advantages of that such “Green Bleaching” alternative will be:

- Low operating cost since bleaching efficiency of ozone is at least 3 times higher than chlorine dioxide when ozone is used in the middle/end of the bleaching sequence 6
- Low carbon footprint emission since the main chemicals are produced on site (oxygen & ozone) limiting transportation, storage of chemical precursors 24
- No risk of hazardous by-products formation such as Dioxins & Furans which could be potentially generated during modern chlorine dioxide generation technology 26. On the contrary, the single by-product of ozone is oxygen that can be further valorised.
- Possibility of high level of water closure and limited water usage if needed
- Equivalent pulp quality when compared to ECF

Conclusions

1. Ozone bleaching has already been industrially implemented, experienced and improved for 18 years.
   - It is a well proven and safe process, currently used by some reference pulp mills among the most modern in the world.
   - Its advantages in terms of bleaching cost savings, effluent load reduction and usage simplicity are no longer questionable.
   - It is applicable to all kind of pulps and has no negative impact on their mechanical properties.

2. The Z-stage takes place in just one minute and both HC and MC technologies are recognised as fully reliable, safe and stable processes.

3. HC ozone bleaching is performed at atmospheric pressure. Behind the ozone reactor, it requires only a 5-10 minutes long extraction stage and no intermediate washing is necessary. This solution allows the E filtrate to be recycled back to the brown stock or post oxygen washing and further to the recovery boiler, and so the total bleaching effluent can drop to 4-6m³/a.d. tonne.

4. As a result of continuous improvements of the equipment and process automation, as well as tuning of the operating conditions over a period of almost 20 years, modern ozone bleaching is recognised today as a state of the art technology for both hardwood and softwood pulps.

Today there is neither technical nor economical reason to stick to a 30 years old conventional ECF process. The use of a light-ECF bleaching sequence can by itself decrease bleaching costs by more than 20% and lead to the same pulp strengths with better optical properties and refining ability. Ozone Bleaching is by far the most valuable solution not only for forerunners but for all pulp mills.

References


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