Theory and Practice of Ozone Bleaching

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Abstract
Ozone bleaching began on an industrial scale in 1992 in connection with increasing environmental pressure and customers’ demand for Elemental Chlorine Free (ECF) and Total Chlorine Free (TCF) bleached pulps. 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, ozone bleaching sequences made it possible to produce a pulp quality similar to or better than conventional ECF would do. They mark a clear milestone in the development of environmentally sound bleaching methods. Today the choice of ozone may still be motivated by ecological requirements but it is mostly justified by the economical savings resulting from chemical cost reduction. They allow combining high brightness and strength with cost efficiency. Ozone bleaching is conducted either at medium or high pulp consistency, depending on ozone bleaching process suppliers. The choice of one process over another depends on a number of factors – including investment costs, carry-over load, bleaching filtrates recirculation and bleach plant temperature profile and others.

Keywords : ozone bleaching, ECF, TCF

1. Introduction
The history of ozone bleaching is old and dates back to 120 years ago when the first patent of ozone bleaching of cotton fibers was issued. Ozone has a powerful oxidation potential to react with any type of lignin compounds and can thoroughly replace chlorine gas in bleaching pulps to high brightness. Containing little amount of chloride ion, the filtrate of ozone bleaching can be used counter-currently to wash unbleached pulp and recovered. Some portion of effluent from ozone bleaching should be discharged to purge metal ions and calcium ions to prevent calcium-based scale troubles. The first full-scale ozone bleaching installations were started at Lenzing (Austria) and Union Camp (USA) in 1992, and have been in continuous operation since then. About 50% of new ozone bleaching plants implemented after the year of 2,000 is owned by Japanese paper companies.

2. Manufacture and Characteristics of Ozone
Ozone generation is a pure on site technology requiring only energy and oxygen usually also produced on site from a PSA (Pressure Swing Adsorption) plant. Ozone is produced from oxygen in an electrical field at a concentration of 12% by weight according to Fig. 1. Modern ozone generators are 50% more efficient than the ones used in the first ozone pulp bleaching applica-
tions. They are especially designed for the pulp and paper industry and are able to produce 250 kg O₃/h (6 tons per day per unit). Today ozone production requires only 7 kWh/kg O₃ and as a result, 1 kg ozone is now cheaper than 1 kg chlorine dioxide.

Ozone has a very high electronegative oxidation potential, 2.07 eV, second only to that of fluorine (2.87 eV). This high oxidation potential has made ozone both a good bactericide for air and water and a potent oxidant in chemical pulp bleaching. Ozone is a toxic, irritating gas with good odor-warning properties (the odor threshold is 0.01-0.015 ppm). Ozone should be monitored continuously and, if critical levels be exceeded, the system should be shut down. Ozone, unlike chlorine dioxide, cannot be stored and is produced only when power is applied. Theoretically 1 kg ozone replaces 1.7 kg chlorine dioxide or 2.1 kg hydrogen peroxide. Delignification efficiency of ozone (ΔKN/kg O₃) defined as the Kappa number reduction per 1 kg ozone application is usually about one.

3. Reaction of Ozone with Pulp

It is preferable to place the ozone stage at the beginning of the bleaching sequence to remove most of the residual lignin. This is based on the much faster reaction of ozone with lignin than with polysaccharides: the rate constant of ozone with lignin is 1,000 times higher than that of ozone with carbohydrates (Fig. 2). So lignin should be considered and used as a protection for polysaccharides. Another important reason to use ozone in the first bleaching stage is that the higher the lignin content, the higher is ozone’s selectivity expressed as the Kappa number reduction per added ozone unit (ΔKN/kg O₃). If mills use ozone in the middle of the bleaching sequence or at the end, then the high oxidation potential can definitely impact bleached pulp strength. The cellulose viscosity decreases with the increase of ozone charge. But the viscosity loss due to the introduction of ozone in the ECF sequence does not translate into a similar loss in strength. The maximum charge of ozone should be controlled at 8 kg/AD.pulp.ton in high consistency ozone bleaching and 5 kg/AD.pulp.ton in medium consistency ozone bleaching.

The key to efficient bleaching is efficient delignification; interestingly, it has only been 10 or 15 years since cooking conditions have been stabilized. Fundamentals of modified cooking conditions were developed at full-scale in the early 1980s to extend delignification during cooking and limit bleaching reagents consumption. The Lo-Solids™ cooking was first applied at commercial scale in 1993 and the compact cooking G1 in 1997, the Downflow Lo-Solids™ in 1998 and the Compact Cooking G2 in 2003. Kappa number after cooking should usually be in the 25-30 range for softwood pups and 14-18 for hardwood pulps. This allows mills to maintain mechanical strength while reducing bleaching chemicals, thanks to oxygen delignification before supplying the bleach plant with a 9-11 Kappa number pulp. The Kappa number can be reduced by 40% on hardwood pulps with a single stage oxygen stage, and by 60-70% on softwood pulps with a double oxygen stage. A double oxygen stage is often implemented on hardwood pulps as well, but benefits of such an approach are still a matter of discussion.

An important concern in hardwood kraft pulping is the formation of hexenuronic acids (HexA), since keeping them in the pulp results in later important brightness reversion. It is interesting that ozone reacts with HexA while chlorine dioxide does not – only chlorine produced during the chlorine dioxide stage does. This explains why brightness reversion is lower for ozone-bleached pulp. In the specific case of pulps with high HexA content such as eucalyptus pulp, it is beneficial to
start the bleaching sequence with an A–Z combination. However, the use of acid hydrolysis should be restricted only to specific high HexA content hardwood pulps since its harsh condition (two hours at 85–90°C and pH 2.5–3.5) impacts pulp quality and increases steam costs. The HexA 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.

Apart from the proven economical, technical and environmental advantages, the development of oxygen delignification as well as improvements in ozone bleaching in the whole pulping process over the last 20 years, amazingly permitted to shorten the bleaching sequences by one, two, or even three steps, and at the same time to increase the brightness ceiling with 2–3 points compared to what is used to be. In the nineties it was common to fully bleach the pulp with 6 or even 7 bleaching stages as in the following sequences.

- Pietarsaari (Finland) A–ZD–Eop–ZD–Ep
- Blankenstein (Germany) Q–OP–D–Z–PO–P
- Espanola (Canada) A–ZD–Eo–DnD

Bleaching sequences built in the last decades for both hardwood and softwood pulps usually have only 3 or 4 stages and do not much vary from one another:

- Nippon Paper Yufutsu (Japan) ZD–Eop–D
- Mondi Ruzonberok (Slovakia) ZEop–D–P
- Nippon Paper Maryvale (Australia) ZD–E–D
- ITC Bhadrachalam (India) Ze–DP
- Sniace (Spain, sulfite pulp for dissolving grades) Z(EOP)–(PO)
- Celtejo (Portugal) Ze–D–P

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

4. Medium Consistency Ozone Bleaching

Improvements in medium consistency (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 fibers. Industrial practice has shown that Andritz technology requires two mixers in series for 3–6 kg O₃/AD.pulp. ton dosage to get the optimal bleaching efficiency (Fig. 3).

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

MC ozone bleaching is placed as ZD in the first bleaching sequence. ZD does not need a washer between Z and D, and removes residual lignin at the maximum efficiency with the minimum cost. Ozone charge should
not exceed 5 kg/AD.pulp.ton in MC ozone bleaching. Ozonization was initially carried out at 40 °C in the 90s and such a low temperature was not very convenient as the Z-stage is located after the 85-95°C oxygen delignification and before an alkaline extraction generally carried out at 60-80 °C. It is therefore necessary to cool down the pulp before heating it up. Several results have demonstrated that for hardwood pulp MC ozone bleaching, Z-stage temperature can be increased up to 60°C and sometimes even higher without any negative impact on pulp strength and brightness.

5. High Consistency Ozone Bleaching

The first commercial high consistency (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 adjusted by pH, pressed to high consistency (40%), fluffed and transferred to the ozone paddle reactor operating at atmospheric pressure. The C-Free® was provided by Sunds Defibrator until the late 1990’s in the USA, Sweden, South Africa and Germany (Fig. 4).

Modern HC ozone bleaching uses the ZeTrac™ technology provided by Valmet which is a much-simplified version of the C-Free®. The experience gained for the first industrial installations has shown that ozone requires very short contacting time with the pulp for around one minute and that a 5-10 minutes extraction stage after the Z-stage without intermediate washing is in most cases sufficient. Experience has shown that a 5-10 minutes e-stage at 11-12 percent pulp consistency, following the ozone treatment at high consistency produces results similar to those of a 60-90 minutes conventional extraction stage. The pulp at 38-42 percent consistency is diluted directly with alkali, so the alkali reaches the heart of the fibers without the need of diffusion and quickly solubilizes the oxidized material. Then the press following the e-stage removes solubilized material from the fibers when pressing the pulp. These two aspects — the quick access to the fibers thanks to their high consistency, and the quick removal of the alkali with the press — eliminate the need for long diffusion times in an extraction tower (in the case of new bleach plants). These observations permitted to reduce the size of reactors and to lower the investment costs. 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 a significant reduction of the capital expenditure, energy requirement, maintenance costs as well as effluent volume.

A new green field mill owned by Oji in Nantong, China started the production late 2012 (Fig. 5). The raw material is a mixture of eucalyptus and acacia and the production rate is 1,600 AD.ton/day. The bleaching sequence is (Ze)DP. The target brightness is 90% ISO. The main reason for choosing ZeTrac™ in this mill is to keep the effluent load as low as possible. For this production two ozone bleaching reactors in series are used to
get a retention time that is long enough.

6. Conclusion

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).
- decreasing brightness reversion.
- reducing drastically the extractive content by 50–75%.
- reducing energy requirements in the refining by at least 10%.
- precisely controlling the viscosity in viscose pulp production.

References
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