# TCF Pulp Bleaching for Viscose Pulp Production

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**Abstract**
Viscose pulp production has been growing at a quick pace over the last years and several new projects are foreseen. Indeed the growing market demand for man-made fibers and increased environmental constraints that limit the ability of oil-based fibers to capture the growth has resulted in an increased demand for viscose. However, the opportunity will be sustainable only by improving the environmental impact of dissolving pulp production and the viscose process. This paper addresses issues associated with the dissolving pulp process and looks especially at TCF bleaching of viscose pulp with ozone and hydrogen peroxide. Starting with a review of chemical reactions involved in TCF bleaching, different bleaching approaches will be discussed along with industrial examples to propose sustainable bleaching sequences for viscose pulp production.

## INTRODUCTION

Ozone bleaching has been implemented globally at about ten dissolving pulp mills and is considered a key process step. Three leading dissolving pulp producers operate ozone bleaching in two different facilities each, thus confirming its benefits. Ozone is very reactive towards lignin and leads to extremely low lignin content in final pulp, high brightness and high brightness stability. In the specific case of dissolving pulp production, ozone bleaching is mainly implemented for precisely adjusting final viscosity while maintaining pulp yield.

## OZONE IN VISCOSE PULP BLEACHING

Viscose pulp should have a very low content of organic impurities with a maximum hemicellulose content of 5%wt, extractives content of 0.2%wt and lignin content of 0.3 expressed as Kappa number. These low values are reached during the bleaching which involves mainly four bleaching chemicals - chlorine dioxide, oxygen, ozone and hydrogen peroxide. Hypochlorite remains in use in some dissolving pulp mills to adjust pulp viscosity and chlorine has almost disappeared from bleach plants. These six chemicals have different reaction abilities and react with lignin exclusively as shown in Table I.

Table I: Classification of the Bleaching Chemicals Based on Their Reactivity Towards Lignin Structures [1]

| Phenolic groups and C=C | Free phenolic groups (and C=C) | Carbonyl groups including quinones |
|---|---|---|
| $Cl_2$ | $ClO_2$ | ClOH |
| $O_3$ | $O_2$ | $H_2O_2$ |

Lignin structures including conjugated double bonds such as carbonyl groups (C=O), ethylenic groups (C=C) and aromatic rings are the main chromophores. Considering the above table, it appears a bleaching sequence combining ozone and hydrogen peroxide can remove more chromophores than using chlorine dioxide only or chlorine dioxide and hydrogen peroxide. Ozone bleaching theoretically allows for the highest brightness and the lowest lignin content.

Ozone has also proved to be very effective on extractives in bleaching of paper grades. For example:
- Pikka and Vehmaa [2] reported a pitch reduction from 0.1-0.3% down to 0.05% after start-up of the ozone bleaching stage at the Espanola mill in Canada
- Stål and Wennerström [3] presented lab results with a DCM extractive content after a $D_{HT}$-Eop-D of 0.27% and 0.16% after Ze-DD
- Chirat et. al [4] compared D-E-D-D and ZD-E-D and found an ozone dose of 0.4% led to a reduction in the total extractive content of 40%

A similar effect of ozone can be expected in dissolving pulp bleaching. Indeed in 1998 Peter and Lima [5] reported about operations at Bacell: "the extractive content of our pulp is extremely low and so far we have not observed in our production line any scaling or deposits caused by pitch."
The main task of the ozone stage in the dissolving pulp process is to control pulp viscosity. It is done easily by implementing an ozone dosing model designed empirically for every different pulp where outlet viscosity is related to a mix of parameters measured online. In general, every dose of one kilogram ozone per ton of pulp reduces pulp viscosity by 40-80 mL/g. Depending on some online measurements, the control system automatically calculates the right ozone dosage. Viscosity is accurately controlled thanks to the ozone generators' ability to adjust production within seconds; thus reacting to process variations almost instantaneously.
The conventional solution for adjusting pulp viscosity is the use of pressurized alkaline stages at high temperatures. However these severe conditions may have a negative effect on pulp yield and adjustment requires more time than with ozone bleaching.

**INDUSTRIAL EXAMPLES**

Sulfite Pulp

An Austrian pulp mill upgraded in 1992 its EOP-H-P bleach plant to EOP-Z-P and stood as the first company to use ozone at commercial scale for pulp bleaching, and a fortiori for dissolving pulp bleaching. The mill has been producing beech dissolving pulp with the magnesium bisulfite process and reported in 1995 bleaching chemicals consumption as per table II for final pulp quality of 90% ISO brightness and 550 mL/g viscosity [6]. In their case, the main targets of ozone bleaching are pulp brightening and Kappa reduction but not viscosity control. Indeed bleaching happens in only two stages (Z-P) since the Eop stage plays the role of oxygen delignification by removing the bulk of the remaining lignin prior to the bleaching itself. Moreover, that EOP-stage is used as an alkaline hydrolysis step, to remove hemicelluloses as specifically required in the case of dissolving pulp production.

Table II: Bleaching Parameters for Sulfite Pulp (1995)

| Bleaching sequence | EOP-Z-P |
|---|---|
| NaOH, kg/adt | 44 |
| $O_3$, kg/adt | 2 |
| $H_2O_2$, kg/adt | 11 |

In 1999-2003 the sulfite pulp producer Sniace studied with Metso potential bleaching sequences to replace C-E-H. Considering lab assessments presented in table III, Sniace implemented in 2007 the Z/EOP-PO bleaching sequence.

Table III: Bleaching Chemicals Consumption for Sulfite Pulp (lab assessments) [7]

| Bleaching sequence | C-E-H | Z-E-P | PO-E-P |
|---|---|---|---|
| NaOH, kg/adt | 55 | 55 | 85 |
| $Cl_2$, kg/adt | 17 | | |
| ClOH, kg/adt | 130 | | |
| $O_3$, kg/adt | | 4.5 | |
| $H_2O_2$, kg/adt | | 10 | 30 |

Lower caustic consumption in EOP-Z-P (table 2) than in Z-E-P (table 3) is explained by the fact milder conditions are used in EOP as a first stage than in E as a second stage. In one case EOP removes mainly lignin while in the other case E has to remove hemicelluloses after delignification was mostly done by ozone in the preceding stage. Since 2007, two other sulfite pulp mills converted to dissolving pulp production and both of them chose the EOP-Z-P bleaching sequence. So the 4 sulfite pulp mills operating an ozone stage operate Z-TCF bleaching sequences.

Kraft Pulp

Seven pulp mills are currently able to produce pre-hydrolyzed kraft dissolving pulp with ozone. The oldest bleach plant operates an A-Z-P sequence with a Z-stage at medium consistency. Kappa number is first reduced in oxygen delignification from 9-10 to 2.5-3 and then dosages of only 3 kg/adt ozone and 8 kg/adt hydrogen peroxide allows producing high quality viscose pulp [5]. The A-stage operates around 60°C during one hour for removing transition metals and allows for high efficiency of hydrogen peroxide bleaching in the last stage. Implementation of that short TCF bleach plant has been very competitive versus the newer and longer ECF one D-(Eop)-D-D located at the same mill and designed for acetate grades. Actually TCF is a very attractive alternative for pulp mills aiming to produce exclusively viscose pulp thanks to low investment and operating costs. A two-washer bleach plant such as Z/Q-P appears as the simplest alternative [8].

Two mills operate high consistency ozone bleaching: in D-Z/Eop-D and D-Z/e-(PO). Both bleach plants are flexible and capable of producing ECF and TCF dissolving pulp, as well as paper grades. For example the D-Z/Eop-D bleaching sequence can be turned on demand into an $A_{Hot}$-Z/Eop-P to produce TCF BEKP (bleached eucalyptus kraft pulp). However such bleach plants could be limited in production of softwood paper grades: a high ozone charge in the middle of the bleaching may lead to lower pulp strengths since not enough lignin would remain to protect the fibers [9].

Four mills run a Z/D-Eop-D bleaching sequence with a Z-stage at medium consistency. Authors consider Z/D-Eop-D as more flexible bleach plants as it allows for production of dissolving pulp as well as both hardwood and softwood paper grades. Table IV shows lab results comparing bleaching sequences of oxygen delignified pre-hydrolyzed eucalyptus Kraft pulp.

Table IV: Lab Bleaching of Oxygen Delignified Pre-hydrolyzed Eucalyptus Kraft Pulp [8]

| Bleaching sequence | Z/Q-P | Z/D-Eop-D | D-Eop-D-P |
|---|---|---|---|
| NaOH, kg/adt | 11.7 | 8 | 14 |
| DTPA, kg/adt | 1.5 | 0 | 0 |
| $ClO_2$, kg/adt | 0 | 3 | 6.5 |
| $O_3$, kg/adt | 4 | 5 | 0 |
| $H_2O_2$, kg/adt | 7 | 3.3 | 5 |

| | | | |
|---|---|---|---|
| Brightness, % ISO | 92 | 94 | 92 |

## CONCLUSIONS

Ozone bleaching allows for delivering viscose pulp with:
- Low lignin content
- Excellent cleanliness with especially low extractives content
- High brightness and brightness stability
- Stable viscosity range

Sustainable bleaching sequences for viscose pulp production are:
- Z/D-Eop-D and Ze-D-P for swing kraft pulp mills producing alternatively viscose and paper grades
- A-Z-P for kraft pulp mills producing viscose grades and BEKP
- Z/Q-P for kraft pulp mills producing only viscose grades
- Eop-Z-P for sulfite pulp (without prior oxygen delignification in the case of hardwood)

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# TCF Pulp Bleaching for Viscose Pulp

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# Introduction

- **First industrial production of TCF dissolving pulp started in 1992 at Lenzing in Austria.**

- **TCF bleaching combines ozone, hydrogen peroxide and oxygen and allows for improving effluents quality and better closing water loops when compared to conventional ECF bleaching.**

- **Today at least 5 bleach plants continuously produce TCF viscose pulp with ozone.**

# TCF Bleaching

**TCF bleaching allows for removing most of the chromophores:**

| Phenolic groups and C=C | Free phenolic groups (and C=C) | Carbonyl groups including quinones |
|---|---|---|
| $Cl_2$ | $ClO_2$ | ClOH |
| $O_3$ | $O_2$ | $H_2O_2$ |

**Table I: Classification of the Bleaching Chemicals Based on Their Reactivity Towards Lignin Structures**

Source: Lachenal, D. Muguet, M. "Degradation of Residual Lignin in Kraft Pulp with Ozone application to Bleaching", 1991, ISWPC

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# Ozone Bleaching

- **Ozone is usually used at the beginning of TCF bleaching sequences. Depending on the cooking process, it is used for bleaching in the case of sulfite pulp or all at once bleaching and controlling viscosity in the case of kraft pulp.**

- **Ozone also improves pulp cleanliness by readily reacting with extractives. For example Peter and Lima reported about an OO-A-ZQ-P bleach plant producing PHK pulp: "the extractive content of our pulp is extremely low and so far we have not observed in our production line any scaling or deposits caused by pitch."**

**Source: Peter, W., Lima, A., Bacell's Solucell – A New Dissolving Pulp for High Quality Requirements, Lenzinger Berichte 78/98, pp. 28-32, (1998).**

# Viscosity Control

- **The main task of the ozone stage in the dissolving pulp process is to control pulp viscosity.**
- **It is done easily by implementing an ozone dosing model designed empirically for every different pulp where outlet viscosity is related to a mix of parameters measured online.**
- **Depending on some online measurements, the control system automatically calculates the right ozone dosage.**
- **Viscosity is accurately controlled thanks to the ozone generators' ability to adjust production within seconds; thus reacting to process variations almost instantaneously.**



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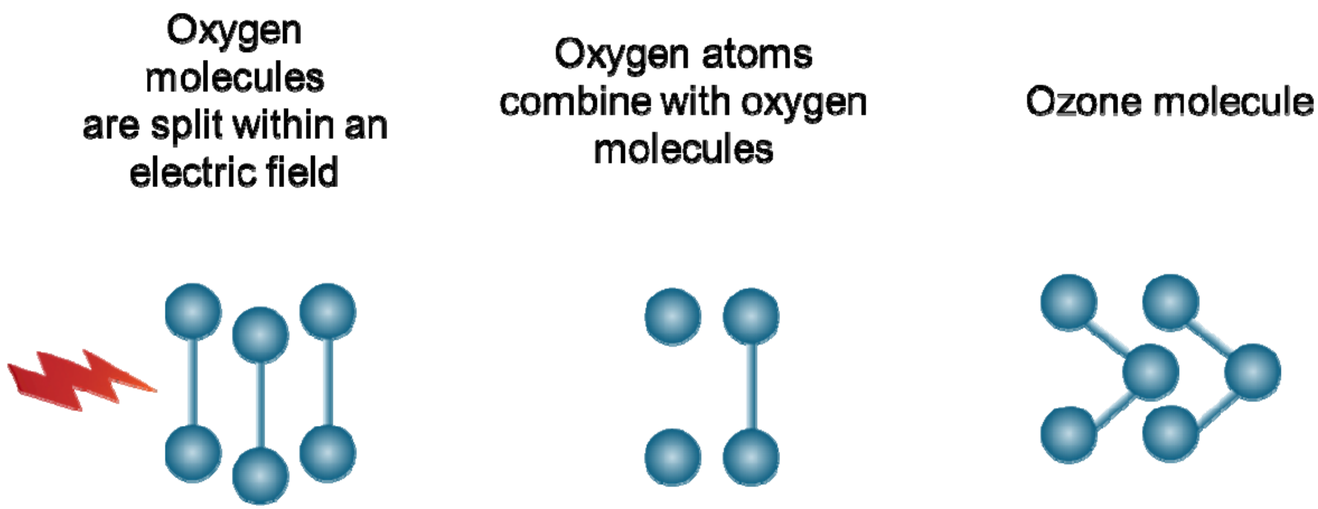
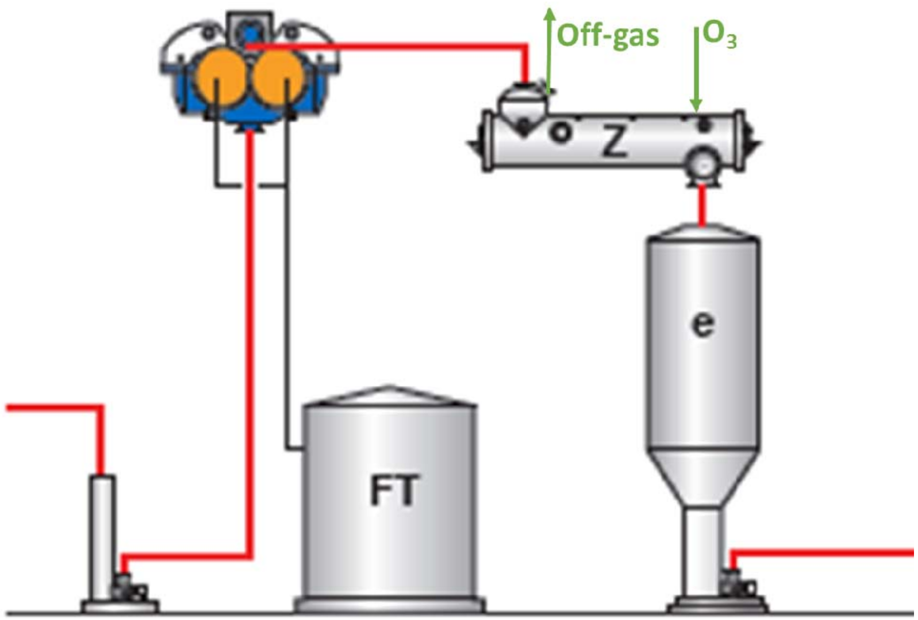
# Ozone Generation

- **Ozone production at 12% by weight requires 10 kWh and 8.3 kg oxygen per kg ozone.**



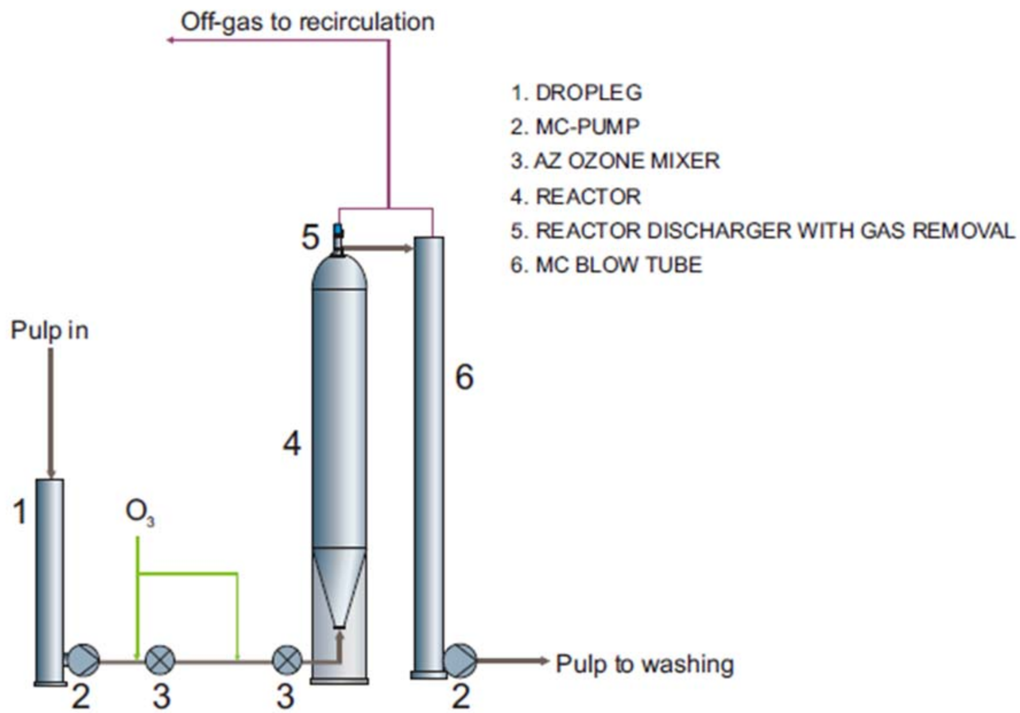

- **Production of 1 kg oxygen with a VSA needs 0.3 kWh so 1 kg ozone costs roughly 12.5 kWh.**

# High Consistency Ozone Bleaching




Courtesy of Valmet©

# Medium Consistency Ozone Bleaching




Courtesy of ANDRITZ

# Sulfite Pulp Bleaching (Industrial Results)

| Bleaching sequence | EOP-Z-P |
|---|---|
| NaOH, kg/adt | 44 |
| $O_3$, kg/adt | 2 |
| $H_2O_2$, kg/adt | 11 |
| Brightness, %ISO | 90 |
| Viscosity, mL/g | 550 |

**Source: Krotscheck, A.W., Sixta, H., Peter, W., Gerzer, T., The Effects of Bleach Plant Closure: Laboratory Bleaching Plus Computer Simulation Versus Mill Data, Proceedings from International Non-Chlorine Bleaching Conference, pp. 1-6, Orlando, FL, USA, (1995).**

# Sulfite Pulp Bleaching (Lab Results)

| Bleaching sequence | C-E-H | Z-E-P | PO-E-P |
|---|---|---|---|
| NaOH, kg/adt | 55 | 55 | 85 |
| Cl2, kg/adt | 17 | | |
| ClOH, kg/adt | 130 | | |
| $O_3$, kg/adt | | 4.5 | |
| $H_2O_2$, kg/adt | | 10 | 30 |

Source: Blanco, A. Introducción al Proyecto, Proceedings from Encuentro Hispana-Luso-Brasileño sobre madera, pulpeado y blanqueo - Workshop - estrategias a corto y medio plazo en el campo de la madera, pulpeado y blanqueo en el campo de la madera, pulpeado y blanqueo, Sevilla, Spain, (2008).

# Kraft Pulp Bleaching (Industrial Results)

| | O | O | A | Z | Q | P |
|---|---|---|---|---|---|---|
| Time (min) | 15 | 60 | 50 | 2 | 40 | 360 |
| Temperature (° C) | 105 | 110 | 60 | 55 | 60 | 80 |
| Consistency (%) | 11 | 11 | 5 | 10 | 9 | 11 |
| pH | 11 | 10,5 | 2,5 | 2,2 | 5 | 10,5 |
| Chem. Dosage (%) | 2,2 $O_2$ | | 1,8 $H_2SO_4$ | 0,3 $O_3$ | 0,1 EDTA | 0,8 $H_2O_2$ |
| | 2,0 NaOH (as oxidized white liquor) | | | 0,5 $H_2SO_4$ | | 0,9 NaOH |

| | |
|---|---|
| **brightness:** | 88 - 90,5 % ISO |
| **viscosity:** | 400 - 550 ml/g |
| **alpha cellulose content:** | > 94,5 |
| **R 18:** | > 96,5% |
| **R 10:** | > 92,0% |
| **kappa number:** | < 0,5 |
| **extractives(DCM):** | < 0,1% |
| **ash:** | < 0,12% including sodium oxide |
| **metals:** | Fe < 10ppm |
| | Ca < 100 ppm |
| | $SiO_2$ < 80pPM |
| | Mn: < 0,5ppm |
| | Mg: < 80ppm |
| | Cu: < 1,5ppm |
| | Na: < 300ppm |
| | dirt: < 5mm²/m² |

Source: Peter, W., Lima, A., Bacell's Solucell – A New Dissolving Pulp for High Quality Requirements, Lenzinger Berichte 78/98, pp. 28-32, (1998).

# Kraft Pulp Bleaching (Lab Results)

| Bleaching sequence | Z/Q-P | D-Eop-D-P | Z/D-Eop-D |
|---|---|---|---|
| Inlet Kappa | 2.8 | 2.8 | 2.8 |
| NaOH, kg/adt | 11.7 | 14 | 8 |
| DTPA, kg/adt | 1.5 | 0 | 0 |
| $ClO_2$, kg/adt | 0 | 6.5 | 3 |
| $O_3$, kg/adt | 4 | 0 | 5 |
| $H_2O_2$, kg/adt | 7 | 5 | 3.3 |
| Brightness, % ISO | 92 | 92 | 94 |

Source: Ramark, H. Vehmaa, J., Manufacturing of Dissolving Pulp with Continuous Cooking and Novel Fiberline Technology, Proceedings from the ABTCP Conference, Sao Paulo, Brazil, (2013).

# Bleach Plant Flexibility

- Longer bleaching sequences, either TCF or ECF, allows for production of dissolving and paper grades in the same bleach plant.

- Two mills operate high consistency ozone bleaching: in D-Z/Eop-D and D-Z/e-(PO). Both bleach plants are flexible and capable of producing ECF and TCF dissolving pulp, as well as paper grades. For example the D-Z/Eop-D bleaching sequence can be turned on demand into an $A_{Hot}$-Z/Eop-P to produce TCF BEKP (bleached eucalyptus kraft pulp).

- Four mills run a Z/D-Eop-D bleaching sequence with a Z-stage at medium consistency. Authors consider Z/D-Eop-D as more flexible bleach plants as it allows for production of dissolving pulp as well as both hardwood and softwood paper grades.



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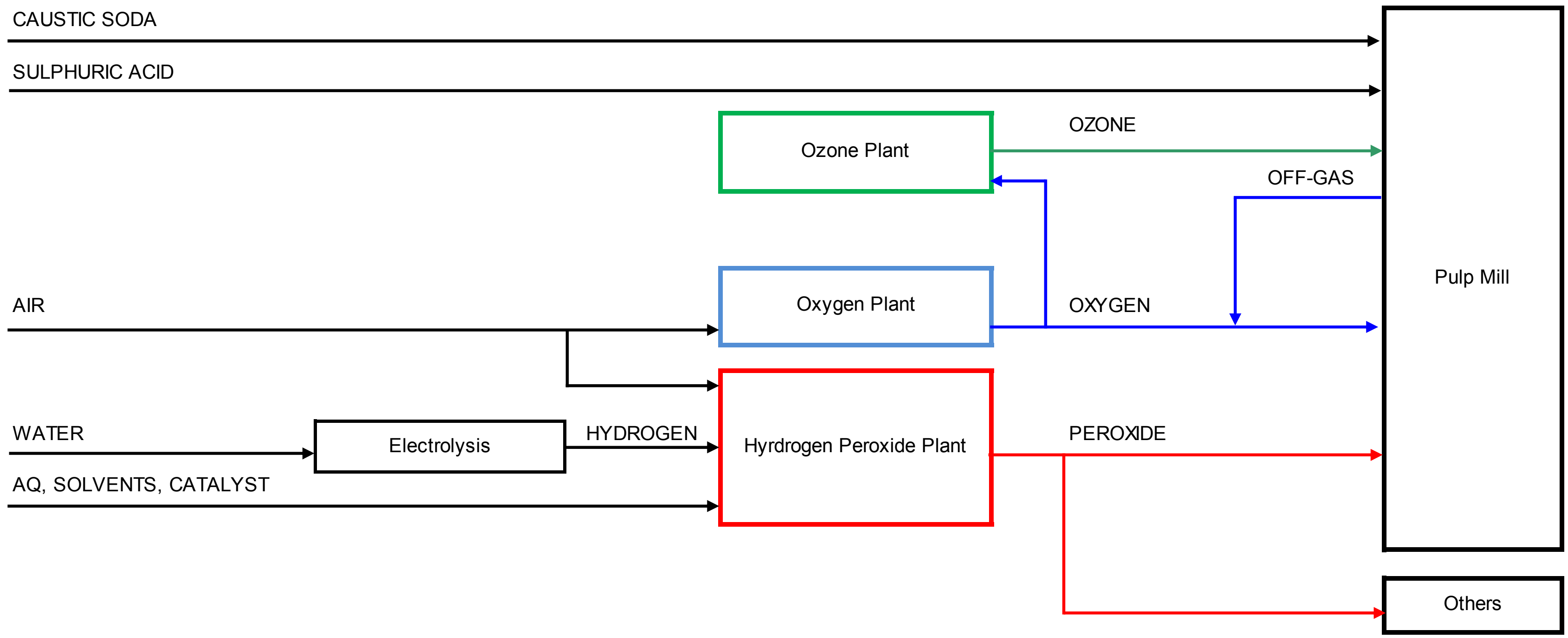
# Environment

- **AOX and COD loads are significantly reduced.**
- **No OX in the final viscose product.**
- **Theoretically a Green Chemical Island can be implemented.**

# Green Chemical Island




Source: Métais, A. Hostachy, J.-C. Larnicol, P. Blanc , J. Verkoeyen, G. Smeets, F. Green Technology for Bleaching. Paper360°, November/December issue, (2014).

# Conclusions

- **TCF bleaching with ozone and hydrogen peroxide has proved successful technically and economically.**

- **It allows for:**

- **Excellent pulp quality stability**
- **Excellent pulp cleanliness**
- **High pulp yield**
- **Low bleaching chemical costs**
- **High brightness**
- **Significant reduction in COD, AOX color discharge**

# Conclusions

**Sustainable bleaching sequences for viscose pulp production are:**

- **- Z/D-Eop-D and Ze-D-P for swing kraft pulp mills producing alternatively viscose and paper grades**
- **- A-Z-P for kraft pulp mills producing viscose grades and BEKP**
- **- Z/Q-P for kraft pulp mills producing only viscose grades**
- **- Eop-Z-P for sulfite pulp (without prior oxygen delignification in the case of hardwood)**

# Thank You!

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