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Alexis Métais

Energy Demand and Carbon Footprint of Bleaching Chemicals

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Introduction

Energy prices have been strongly increasing in 2022 and may not stabilize quickly. It leads to additional challenges in meeting all at once competitive pulp bleaching and global targets on reduction of GHG emissions.

The present paper intends reviewing energy demand for production of the main chemicals involved in bleaching of chemical pulp such as oxygen, ozone, chlorine dioxide and hydrogen peroxide as well the chemical precursors needed.

Once done in a first part, carbon footprint will be assessed considering the influence of different national grids to help pulp producers and the local regulation authorities.

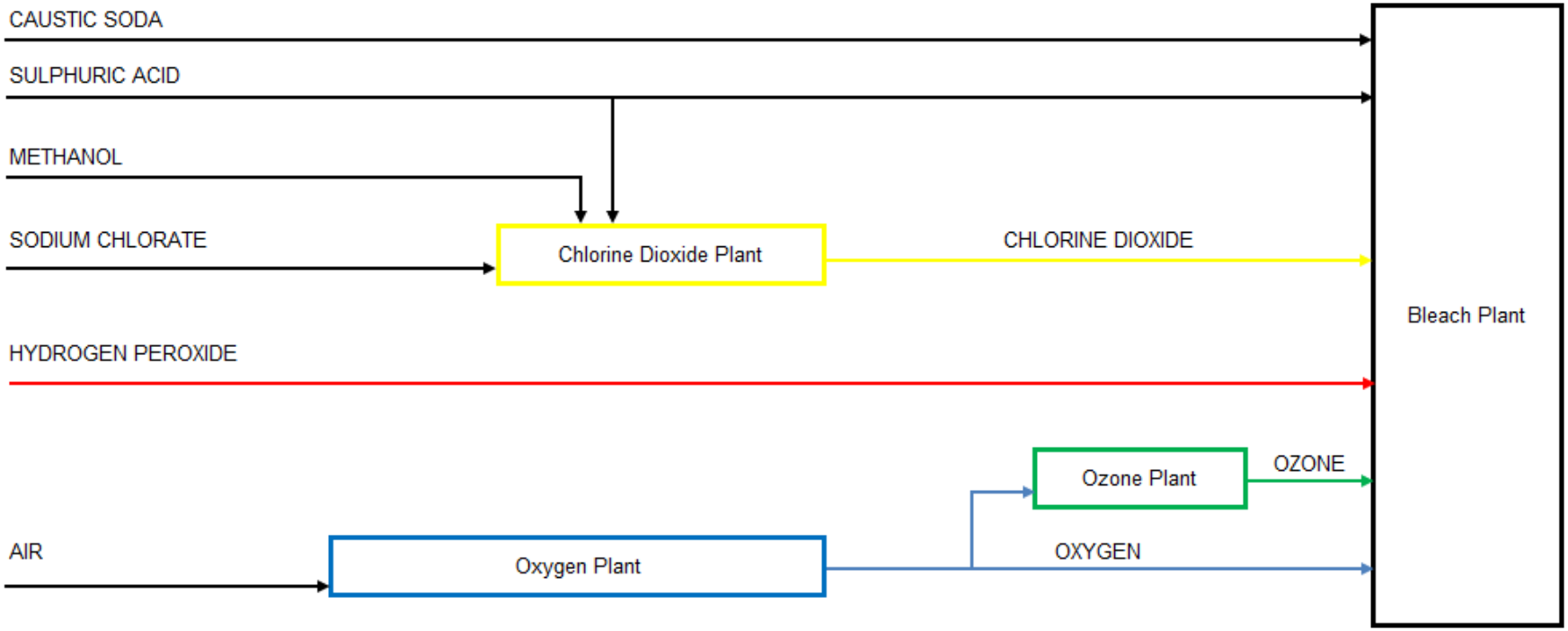
Bleaching Chemicals

Different bleaching chemicals are involved in modern pulp bleaching, each one reacting specifically with some lignin compounds.

I Active on any phenolic group and C=C	II Active on free phenolic groups and some C=C	III Active on C=O
Cl_2	ClO_2	ClOH
O_3	O_2	H_2O_2

Source: Lachenal, D. Muguet, M. “Degradation of Residual Lignin in Kraft Pulp with Ozone Application to Bleaching”, ISWPC, (1991)

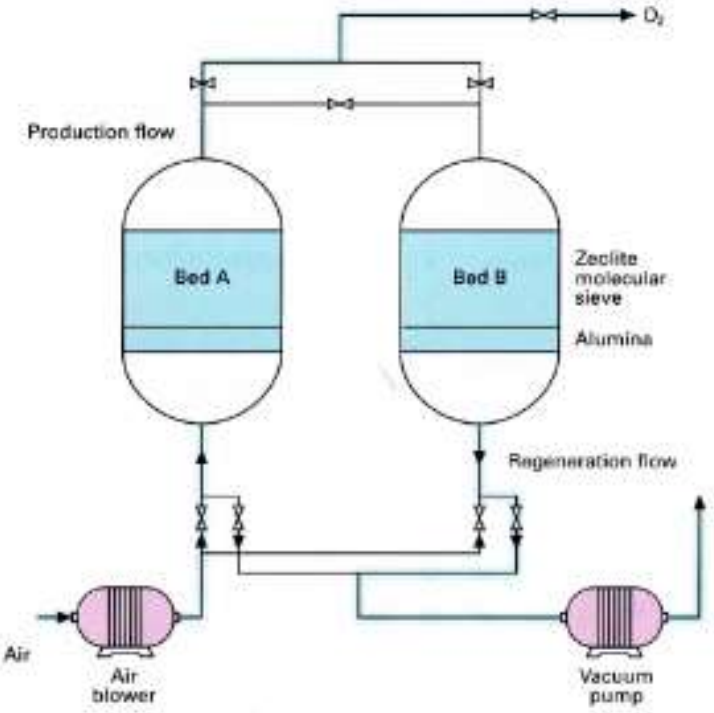
Bleaching Chemicals Supply



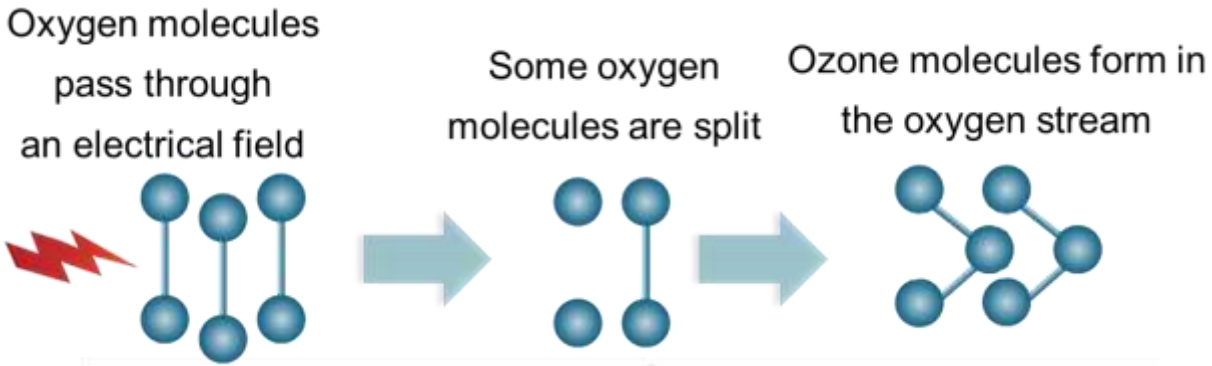
Oxygen

Oxygen is produced at site with the VSA (Vacuum Swing Adsorption) process. Air is compressed and then goes through a molecular sieve vessel where nitrogen is adsorbed so that typically a 93% pure oxygen stream is obtained. When the molecular sieve is saturated with nitrogen, air flows to a second vessel while a vacuum pump pulls nitrogen out of the first vessel.

Production of 1 kg oxygen requires 0.3 kWh and air.



Ozone


Oxygen molecules pass through an electrical field
Some oxygen molecules are split
Ozone molecules form in the oxygen stream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Ozone

Ozone production is a pure onsite technology: there is neither transport nor storage of hazardous chemical precursors.

Production of 1 kg ozone at 12% by weight requires:

- 8.3 kg oxygen
- 10 kWh

Oxygen is usually produced at site with the VSA process. Production of 1 kg oxygen requires 0.3 kWh and air.

So, production of 1 kg ozone requires 12.5 kWh.

Chlorine Dioxide

Chlorine dioxide, like ozone, is an unstable chemical and is produced at site. The dominant approach is to manufacture chlorine dioxide from sodium chlorate ($NaClO_3$) and a reducing agent (mainly methanol, sometimes hydrogen peroxide).

Production of 1 kg chlorine dioxide requires*:

- 1.65 kg$NaClO_3$/kgClO_2
- 0.17 kgCH_3OH
- 1 kgH_2SO_4/kgClO_2
- 0.13 kWh/kgClO_2

Chemical precursors such as sodium chlorate, methanol and hydrochloric acid are purchased outside of the mill.

*: Pelin, K. "Using a Benchmarling Perspective to Ensure Chlorine Dioxide Availability and Competitiveness", IPBC, Portland, OR, USA, (2011)

Chlorine Dioxide

Sodium chlorate generation consists in three main steps:

- Sodium chloride (NaCl) is dissolved in water and purified.
- Then brine is electrolyzed at near neutral pH and minimum 70°C temperature. Sodium hydroxide, hydrochloric acid and catalytic amounts of sodium dichromate are used during electrolysis.
- The third and final step consists in sodium chlorate crystallization.

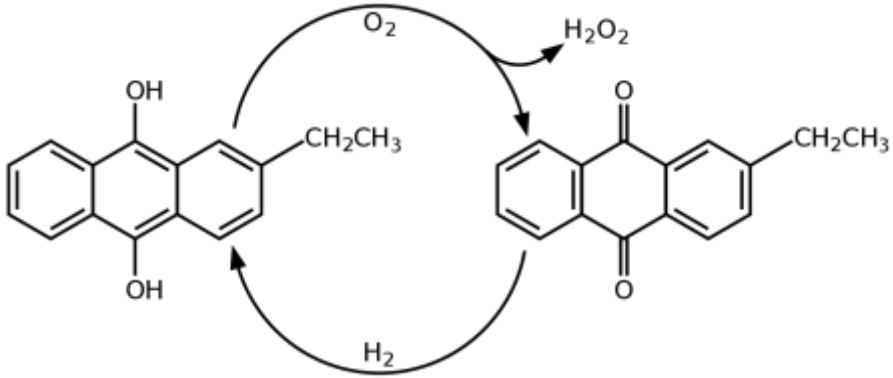
The overall reaction is $NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$ and requires* 5.2 kWh per kg of sodium chlorate.

Overall production of 1 kg ClO_2 requires 1.65 $kgNaClO_3$ x 5.2 $kWh/kgNaClO_3$ = 8.6 kWh of outsourced electricity.

*: St. Pierre, M. “Sodium Chlorate Plant, Brandon, Manitoba”, Chemtrade, (2018)

Hydrogen Peroxide

Hydrogen peroxide is produced through the alkylanthraquinone oxidation process. Alkylanthraquinone is first hydrogenated and then oxidized with oxygen, from air, to yield hydrogen peroxide and alkylanthraquinone back.



Production of 1 kg hydrogen peroxide requires (almost) only 1 kWh, hydrogen and deionized water.

Hydrogen Peroxide

Hydrogen is produced at 76% from natural gas, 22% from coal and at 2% through water electrolysis. The dominant process is steam methane reforming where methane reacts with steam under 20-30 bar and at 800-900°C.

Overall reaction is $CH_4 + 2H_2O$ (+heat) $\rightarrow CO_2 + 4H_2$.

Methane is both a fuel (at 30-40%) and a feedstock (at 60-70%).

Source: IEA, “The Future of Hydrogen”, (2019)

Hardwood Kraft Pulp Bleaching

Standard bleaching sequences for hardwood bleaching are Z/D-Eop-D and D-Eop-D-D. The following table shows typical bleaching chemicals consumptions.

Bleaching sequence	Z/D-Eop-D	D-Eop-D-D
ClO_2, kg/adt	7.2	14
O_3, kg/adt	4	0
H_2O_2, kg/adt	3	3

Source: Métais, A. Germer, E. “Ozone Bleaching Economics”, PaperWeek, Montréal, Canada, (2019)

Green Electricity from Black Liquor

Onsite electricity consumption is obtained considering bleaching chemicals consumption (page 12) and electricity demand for O_3 and ClO_2 production (pages 7 and 8).

Bleaching sequence	Z/D-Eop-D	D-Eop-D-D
ClO_2, kWh/adt	0.9	1.8
O_3, kWh/adt	50	0
H_2O_2, kWh/adt	0	0

Outsourced Electricity Consumption

Outsourced electricity consumption is obtained considering bleaching chemicals consumption (page 12) and electricity demand for $NaClO_3$ and H_2O_2 production (page 9 and 10).

Bleaching sequence	Z/D-Eop-D	D-Eop-D-D
ClO_2, kWh/adt	61.9	120.4
O_3, kWh/adt	0	0
H_2O_2, kWh/adt	3	3

Lower Energy Demand for Z-ECF

Overall electricity consumption is in the same range, though 7% lower for Z-ECF than for conventional ECF.

The gap would become more important if considering mining, producing, shipping and storing chemical precursors (such as sodium chloride, sodium chlorate, methanol, etc.).

It is no surprise but only a confirmation as energy convert into costs: it confirms the numerous results showing lower bleaching chemicals cost for Z-ECF than for conventional ECF*.

*For example:

Lindström, L.-Å, Larsson, P.-E., “Fiberlines for Bleached Eucalyptus Kraft Pulps”, ICEP, Viçosa, Brazil, (2003)

Stål, C. M. Wennerström, M. “ZeTrac Technology”, Estrategias a Corto y Medio Plazo en el Campo de la Madera, Pulpeado y Blanqueo, Sevilla, Spain, (2008)

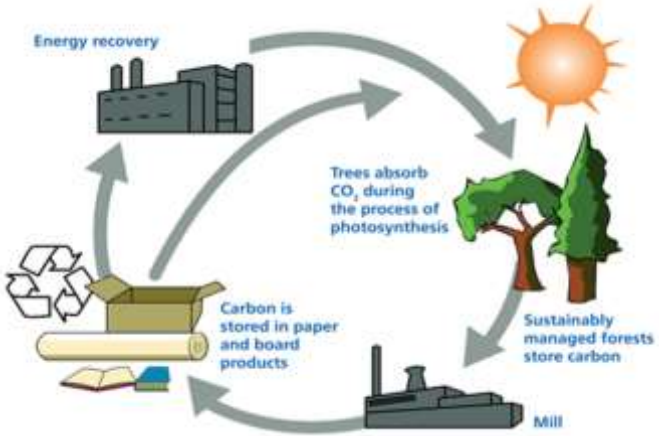
Métais, A. Germer, E. “Ozone Bleaching Economics”, PaperWeek, Montréal, Canada, (2019)

Guzev, D., Sovremennaya Tendentsiya Razvitiya Tekhnologiy Proizvodstva Belonoy Tsellyulozy, Webinar «Sovremennoye Sostoyaniye i Perspektivy TsBP», (2021)

Carbon Footprint

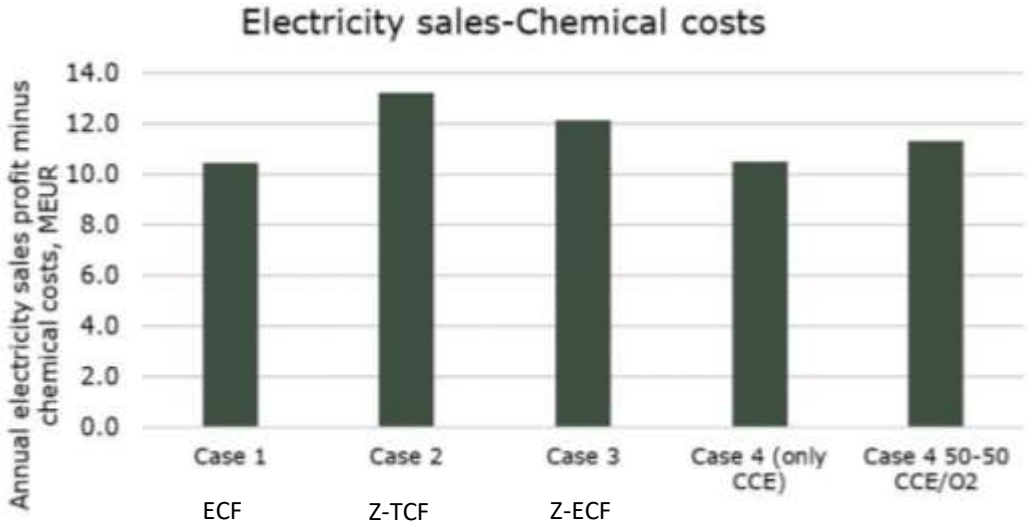
Bleached pulp mills harvest carbon stored in the trees to produce pulp and energy from a single raw material. Electricity produced from sustainably managed forests can be considered as green electricity with 0 carbon footprint.

Modern pulp mills produce two times more electricity than needed at site and electricity sales account for significant amounts of their revenues. Would selling electricity erase cost benefits of Z-ECF bleaching?



Lower OPEX Including Electricity Sale

In a limited OPEX review, the profits from annual electricity sales were subtracted by direct chemical costs to demonstrate the effect of both on-site chemical production as well as the cost of purchased chemicals (Figure 2). The TCF bleaching in Case 2 resulted in the most profit, whereas the lowest profit from electricity sales was associated with Case 1 (and Case 4 in CCE production).



Source: https://afry.com/en/insight/assessing-industrial-production-different-prehydrolysis-kraft-dissolving-pulp-grades

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Overall reaction is $CH_4 + 2H_2O$ (+heat) $\rightarrow CO_2 + 4H_2$.

Methane is both a fuel (at 30-40%) and a feedstock (at 60-70%).

In average 10* tons of carbon dioxide are emitted per ton of hydrogen produced from natural gas.

So, using 1 kg of H_2O_2 emits a minimum of 600 gCO_2 if considering only natural gas.

*: carbon capture has been discussed lately but is far to be widespread and results in 50% price increases for the cheapest H_2 producers.

Source: IEA, “The Future of Hydrogen”, (2019)

2021 GHG Emissions of Electricity Generation

Canada[1]: 110 gCO_2e/kWh

China[2]: 549 gCO_2e/kWh

France[3]: 67 gCO_2e/kWh

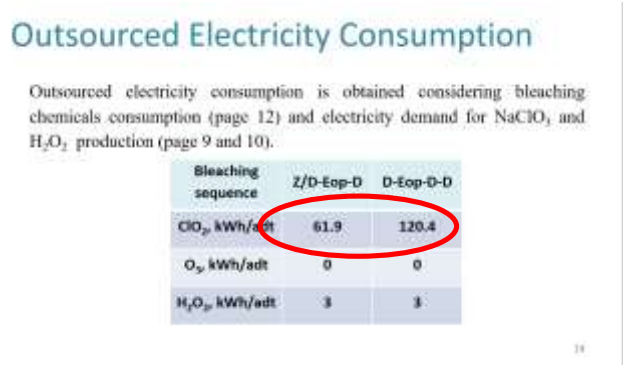
Germany[3]: 402 gCO_2e/kWh

India[2]: 663 gCO_2e/kWh

USA[4]: 387 gCO_2e/kWh

1. https://www.cer-rec.gc.ca/en/data-analysis/energy-markets/provincial-territorial-energy-profiles/provincial-territorial-energy-profiles-canada.html
2. https://ember-climate.org/insights/research/global-electricity-review-2022/
3. https://www.eea.europa.eu/data-and-maps/daviz/co2-emission-intensity-12/#tab-chart_2
4. https://www.eia.gov/tools/faqs/faq.php?id=74&t=11#:~:text=In%202020%2C%20total%20U.S.%20electricity,CO2%20emissions%20per%20kWh

Carbon Footprint of Z-ECF and ECF



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ClO_2, kWh/adt	61.9	120.4
O_2, kWh/adt	0	0
H_2O_2, kWh/adt	3	3

It's 120.4 - 61.9 = 58.5 kWh that are outsourced to external electricity producers.

	Canada	China	France	Germany	India	USA
Z-ECF	ref	ref	ref	ref	ref	ref
ECF, gCO_2e/adt	+6,435	+32,116	+3,919	+23,517	+38,785	+22,639

Carbon Footprint of Z-ECF and ECF

Choice of the bleaching sequence strongly impacts carbon footprint of bleached pulp production.

Z-ECF proves to limit the overall climate change impact of bleached pulp production already with a limited study not addressing shipments and storage of sodium chlorate as well as other aspects of bleaching chemicals sourcing.

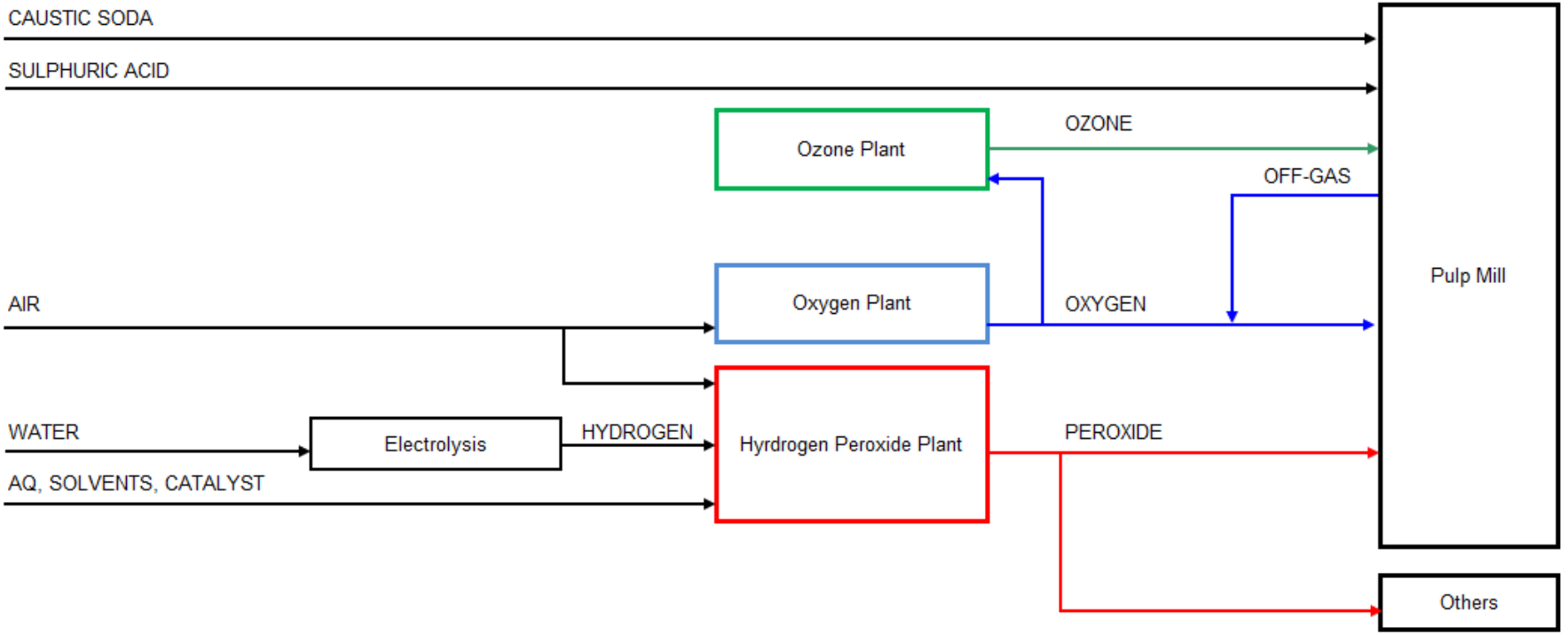
It is more or less important depending on the national grid, adding for example 3.9 $kgCO_2e/adt$ in France, 22.6 $kgCO_2e/adt$ in the USA and 38.8 $kgCO_2e/adt$ in India.

Conclusions

Pulp mills produce more green electricity than they consume internally. The choice of Z-ECF bleaching allows for all at once:

- reducing carbon footprint of bleached pulp production
- increasing profits obtained from pulp and electricity sales
- operating more independently from market variations
- benefiting of well-known environmental benefits of ozone bleaching with lower effluent flow, COD, AOX and color loads

In the Future?



Thank You
for Your Attention!

alexis.metais@xylem.com