BAGASSE PULP BLEACHING WITH OZONE
"It's Time to Implement *Green Bleaching* Practices"

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About the Author

Dr. Hostachy has done his PhD in Pulp and Paper Engineering from the French Pulp and Paper Engineer School in 1994. He has occupied several positions in companies supplying bleaching chemicals such as ozone, peroxide and chlorine dioxide. After obtaining an Executive MBA from the Management School at Lyon, he joined ITT Water and Wastewater and is currently Director of the P&P department.

KEYWORDS

Green bleaching, Ozone, Non-wood fibers, *Bagasse*, Environmental impact, Strength properties, Economic aspects.

APPLICATION STATEMENT

Results obtained in this study show that ***Green bleaching*** of *Bagasse* pulp is certainly the right combination between environmental constraints, pulp quality and cost efficiency.

ABSTRACT

With increasing regulatory pressure and growing market demand, the pulp and paper industry faces many challenges and must find new ways to improve product quality, environmental and process performance. By choosing ozone in their bleaching process, many pulp mills in various part of the world, producing softwood and hardwood bleached pulps, have already obtained these benefits. Concerning non-wood fibers, *Bagasse* or wheat straw represents a sustainable source of raw materials for bleached pulp production keeping a significant growth potential. After a short introduction about the use of ozone for pulp bleaching, this paper summarizes some results obtained on *Bagasse* pulp where conventional pulp bleaching is compared with ***Green bleaching*** which is an evolution of TCF bleaching including optimization of chemicals usage and on-site implementation. Special attention is given to the technical aspects like pulp bleachability, brightness reversion and strength properties. The practical consequences of the integration of this concept are also discussed in terms of investment and variable cost. The objective is to show why ***Green bleaching*** should be considered as the new BAT (Best Available Technology).

INTRODUCTION

As one of the fastest growing economies in the world having a large number of new pulp and paper projects, India has the opportunity to implement the most advanced technologies and to become a leading reference for the whole world. There are currently more than 500 paper and board mills in India where the access to raw material and the transport infrastructure limit the mill size to between 100,000 and 300,000 tons per year. Only about 20 % of India's surface area is forest, and a lot of India's natural forest has been severely depleted.

Less than one third of the fibre used in paper and board production is from timber; the majority of which comes from eucalyptus plantings established on State owned and private land. Considering fibre availability for the long-term, the importance of *Bamboo* and annual plants such as wheat straw and *Bagasse* from sugarcane waste is growing year after year. As renewable raw materials, the use of *Bagasse* for pulp and paper production is also a very good choice to reduce carbon footprint and to decrease pressure on the natural forest. Consequently, the challenge is to define the best solution for the mills to invest in the state-of-the-art technology, as well as commitment to sustainable development.

The first fibrelines producing ozone bleached pulp are mainly coming from the emergence of Total Chlorine Free bleaching (TCF) during the 90s. That decade really boosted the arrival of new bleaching practices based on the use of oxygen, ozone and peroxide. During that period, discussion about ECF (Elemental Chlorine Free), TCF bleaching and ozone was really passionate. Whereas a lot of people claimed that ozone bleaching was not ready for continuous operation, others explained that it would become a major chemical for pulp bleaching technology in the coming years. In 1996, when the TCF "wave" stopped and ECF bleaching mainly based on chlorine dioxide became the Best Available Technology (BAT), ozone started to be integrated into conventional ECF bleaching to significantly reduce the operating cost of the bleaching sequence to create the ECF-light bleaching concept [1].

Since the start-up of the first ozone pulp bleaching installations, a lot of alterations have been carried out to improve all the components of the ozone bleaching systems (pulp mixing, ozone generation technology). Today, ozone bleaching is fully adapted to the bleaching of hardwood and softwood pulps [2]. In most cases, ozone is used to reduce the chemical cost and to improve the environmental impact. It is generally applied just after oxygen delignification to finalize lignin removal before the final bleaching phases [3]. The ozone charge is generally in the range of 5 kg per ton of pulp. Depending on the mill expectations and equipment supplier, the ozone stage can be supplied at high (HC) or medium (MC) pulp consistency.

No.	Mill	Location	Area	Process	Pulp type	Year
1	**Lenzing AG**	Lenzing	Austria	MC	Birch	1992
2	**IP**	Franklin (Union C)	USA	HC	Mixed Hard.	1992
3	**Kymmene**	(Wisaforest)	Finland	MC	Hard./Softwood	1993
4	**MoDo**	Husum	Sweden	MC	Hard./Softwood	1993
5	**Metsä-Botnia**	Kaskinen	Finland	MC	Softwood	1993
6	**Peterson**	Säffle	Sweden	MC	Hard./Softwood	1994
7	**SCA Pulp**	Sundsvall	Sweden	HC	Hard./Softwood	1994
8	**Bacell**	Salvador / Bahia	Brazil	MC	Eucalyptus	1995
9	**Sappi Kraft**	Ngodwana	South Africa	HC	Mixed Hard.	1995
10	**Stora Enso**	(Consolidated)	WI, USA	HC	Hard./Softwood	1995
11	**Votorantim**	Jacarei	Brazil	MC	Eucalyptus	1995
12	**Votorantim**	Luis Antonio	Brazil	MC	Eucalyptus	1995
13	**Domtar EB**	Espanola,ont	Canada	MC	Mixed Hard.	1999
14	**Rosenthal**	Blankenstein	Germany	HC	Hard./Softwood	1999
15	**Burgo**	Ardennnes	Belgium	HC	Mixed Hard.	2000
16	**Nippon Paper**	Yufutsu mill	Japan	MC	Mixed Hard.	2000
17	**OJI Paper**	Nichinan mill	Japan	HC	Mixed Hard.	2002
18	**Votorantim**	,Jaccarei	Brazil	HC	Eucalyptus	2002
19	**Nippon Paper**	Yatsushiro	Japan	MC	Mixed Hard.	2003
20	**Lenzing**	Lenzing	Austria	MC	Birch	2003
21	**SCP/Mondi**	Ruzumberock	Slovakia	HC	Hard./Softwood	2004
22	**OJI Paper**	Tomioka	Japan	MC	Mixed Hard.	2005
23	**Marusumi**	Mishima	Japan	MC	Mixed Hard.	2006
24	**Daio**	Mishima	Japan	HC	Mixed Hard.	2006
25	**SNIACE**	Cantabria	Spain	HC	Eucalyptus	2007
26	**Paperlinx**	Maryvale	Australia	MC	Mixed Hard.	2007
27	**ITC**	Hyderabad	India	HC	Eucalyptus	2008
28	**Celtejo**	Vila Velha de Rodao	Portugal	HC	Eucalyp / Pine	2008

Table 1 – Pulp mills having ozone bleaching in operation in their fibreline

As shown in table 1, most pulp mills have mainly chosen ozone to produce bleached pulps at high brightness levels. Keeping a low bleaching chemical cost, extended ozone delignification offers the possibility to reduce the effluent reject to be treated since the filtrate from the ozone (Z) stage and further alkaline stages can be circulating back to the recovery boiler [3]. Such environmental benefit is a strong argument in the decision process. Finally, whether it concerns greenfield mills, new fibrelines (capacity expansion) or retrofit options, ozone is frequently investigated at the initial phase of the project giving the mill the opportunity to adopt an efficient bleaching process. Several mills in various part of the world have already successfully implemented ozone and chlorine dioxide stages in the same bleaching sequences [1, 2]. An example is given by one of the latest references in India where ozone is efficiently applied on *Eucalyptus* pulp at high pulp consistency.

For *Bagasse* pulp production, there is not yet any reference where ozone is used at industrial scale. In fact, in the specific case of small production facilities, many pulp mills are still using chlorine and/or hypo in their bleaching process. Generally, the mills are combining the modification of the bleaching fibreline with an increase in the production capacity. Concerning bleaching itself, the first change will be to invest in oxygen delignification, and to finally choose between chlorine dioxide or ozone generation plants but not in both units at the same time. The possibility to implement a bleaching sequence where ozone and chlorine dioxide can be combined in the same bleaching sequence (ECF-Light) is quite limited for a pulp mill still using chlorine, especially from investment point of view.

Another aspect to be taken into account is the ***Green bleaching*** concept itself being perceived as a "risky" technical challenge for the mill. It is not easy "to cross the bridge" directly toward ***Green bleaching***. In general, many questions about pulp quality, process efficiency and safety margins are coming on the table. This is why the challenge in this work is not only to show that this option is a viable alternative to replace conventional bleaching based on chlorine or chlorine dioxide, but the most optimized in terms operating and investment cost, pulp quality, environment and on-site implementation.

EXPERIMENTAL

Pulp samples

An unbleached *Bagasse* pulp is collected from a pulp mill after cooking. The pulp sampled has a Kappa number of 12.5, a viscosity of 980 ml/g and a brightness of 46.9% ISO, and is bleached with different bleaching sequences.

Reagents and bleaching stages

The current sequence in the mill is a conventional CEpHp. The pulp is bleached in the lab using the beaching conditions provided by the mill. C, H, and P stages are performed in plastic bags and the pulp is washed between the bleaching stages.

Before ECF or ***Green bleaching***, the unbleached pulp is previously delignified with oxygen. Depending on the charge of sodium hydroxide, oxygen reaction is optimized to achieve at least a 40% pulp delignification. Ozone is produced in a laboratory ozone generator from pure oxygen. Chlorine dioxide is also produced in the laboratory from the reaction between sulphuric acid and sodium chlorite. The stages based on the use of oxygen and peroxide are carried out in Teflon-lined stainless steel autoclaves. Table 2 summarizes the operating conditions used in the different bleaching phases. A stage is carried out to remove metal ions before ozone and (PO) stages. For practical reasons the Z stages are carried out at high pulp consistency in a rotating spherical glass reactor. Ozone charges expressed as kg per oven dried ton of pulp (kg/odt), vary from 4 to 6 kg/t.

	A	**(Z+q)**	**(PO)**	**D**	**(EOP)**	**D**
Pulp consistency, %	3	(40 + 10)	10	10	10	10
Temp., °C	50	(40 + 60)	100	60	80	75
Duration, minutes	30	(4-6 + 30)	120	60	120	120

Table 2 - Bleaching conditions for the sequence A(Zq)(PO) and D(EOP)D.

To obtain brightness development, different charges of peroxide in (PO) stage and chlorine dioxide in the final D stage are tested.

After bleaching, pulp beating is performed in a PFI mill and the analysis of brightness, viscosity and physical properties (bulk, tensile & tear resistance) are measured using ISO standards. Prior to viscosity measurement the pulp is reduced with 2% NaBH4 and 1% Na2CO3 at 10% consistency and room temperature for 30 min. Regarding optical properties, brightness loss of the bleached pulps is the brightness difference before and after aging at 105°C for 2h, 24 h and 48h.

RESULTS & DISCUSSION

Brightness and pulp quality

Taking into account the specific constraints of *Bagasse* pulp bleaching, a promising approach consists in investigating short bleaching sequences after oxygen delignification and to compare the results obtained regarding brightness development and stability, pulp quality and economical aspects.

Among the main factors affecting the performance of ***Green bleaching*** of *Bagasse* pulp it can be mentioned:

- Pulp preparation:
  - Kappa after Cooking phase
  - Efficiency of the oxygen delignification stage (kappa versus viscosity)
  - Acidic stage to control metal ions profile
- Ozone dosage to finalize pulp delignication before bleaching without impairing pulp quality. In this work, 4, 5 and 6 kg ozone per ton of pulp are respectively tested in the OA(Z4q)(PO), OA(Z5q)(PO) and OA(Z6q)(PO) bleaching sequences.

Chemical consumption figures, brightness, viscosity, mechanical and optical properties are measured in order to characterise the effect of ***Green bleaching*** compared with the conventional options. The main results obtained for brightness development versus viscosity (selectivity curves) are introduced below in Figure 1.

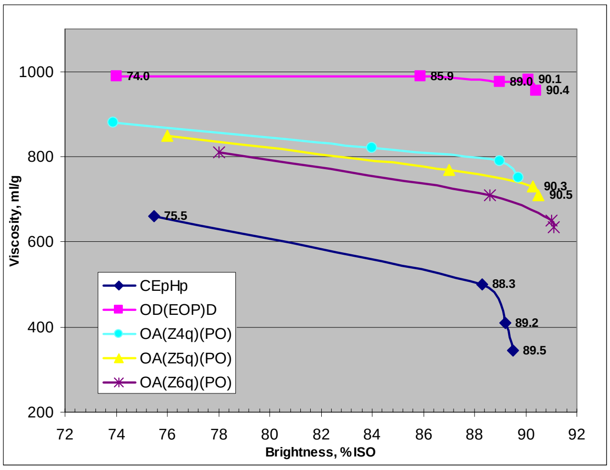

Figure 1- Pulp viscosity versus brightness development

Figure 1 shows that the viscosity of the ozone bleached pulp drops of about 150 units after the ozone stage when compared with the ECF bleaching sequence. Concerning the effect of ozone charge on brightness development, an ozone dosage of 5 kg/t is necessary to finalize lignin removal and to achieve a brightness of 90+ after the (PO) stage. It can be observed that viscosity starts to drop with the increase of the peroxide dosage. This confirms that pulp acidification to remove metal ions (mainly Iron and Manganese) before the ozone stage is always a good approach to maximizing the efficiency of peroxide bleaching. One of the main characteristics used by the pulp producer to quantify pulp quality is strength properties which is analysed on the final bleached pulps presented in table 3.

Sequence	**CEpHp Mill pulp**	**CEpHp**	**OA(Zq)(PO)**	**OD(EOP)D**
Ozone, kg/t	-	-	5	-
Act. Cl. , kg/t	-	52	-	32.6
H_2O_2, kg/t	-	17.5	12	5
Brightness, %ISO	87	88.3	90.3	90.1
Viscosity, mg/l	440	540	770	980

Table 3 - Chemicals consumption, brightness and viscosity

To conclude about the impact of ***Green bleaching*** on pulp quality, the analysis of bulk, strength and optical properties are performed and the results are presented on figures 3, 4, and 5.

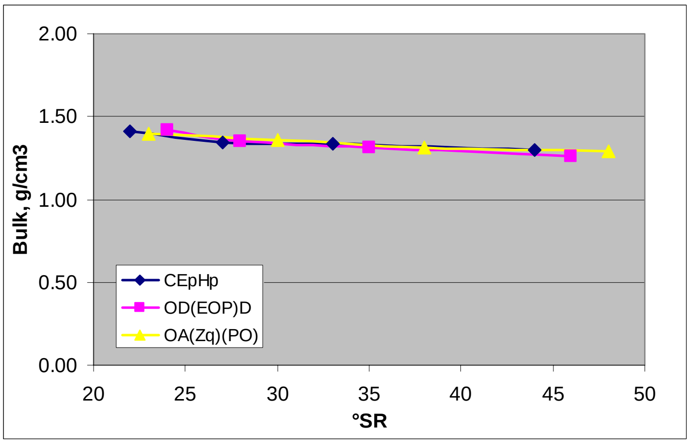

Figure 3 - Bulk versus beating

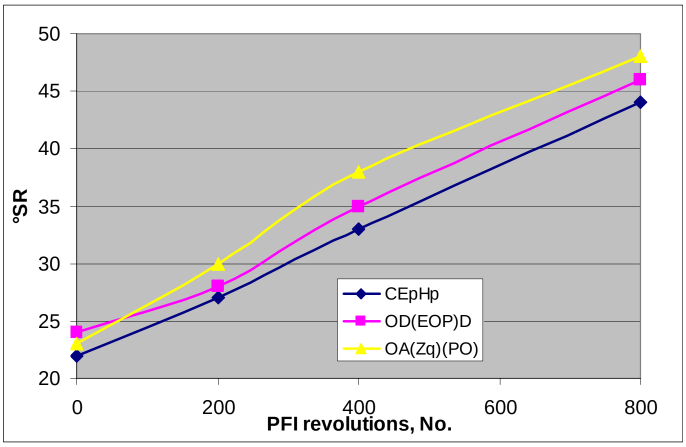

Figure 4 - Beatability

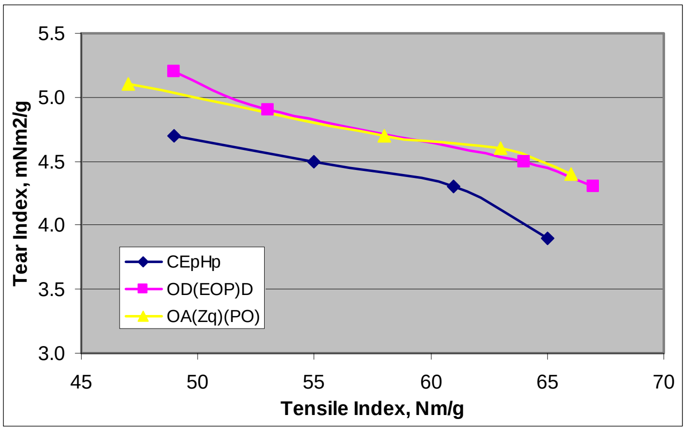

Figure 5 - Tensile versus tear index

As appears in figure 3, no effect on the bulk could be observed. Concerning beatability of the pulp, figure 4 shows that at least 15 % of the energy can be saved using ***Green bleaching***. This can be explained by the softening action of ozone already observed on other pulp type (Hardwood species & *Eucalyptus*) [6,7]. The tensile versus tearing strength, as shown in figure 5, are equivalent for the ECF and ***Green bleaching*** sequences and improved when compared with the conventional CEpHp. Therefore, a lower pulp viscosity after ozone does not mean necessarily lower pulp strength, although it is admitted that pulp viscosity is generally correlated to the strength properties of the pulp [4,5]. This observation is in accordance with publications found in literature and many industrial feed-backs showing that viscosity is not a correct indicator of pulp strength especially when ozone bleaching is concerned [6,7]. To complete the pulp quality assessment, optical properties such as brightness stability upon heat exposure are performed on the bleached pulps. It can be observed in figure 6 that ozone treatment improves brightness stability significantly.

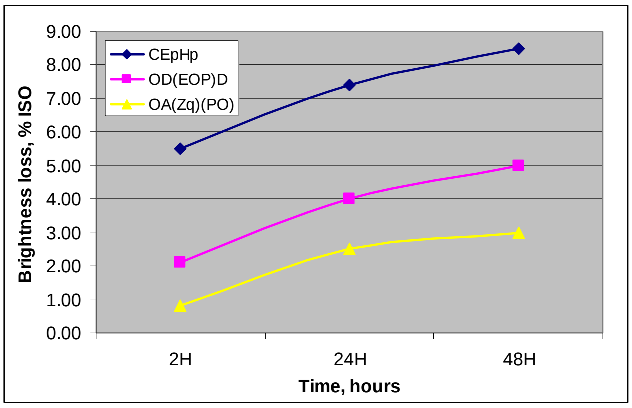

Figure 6 – Brightness stability upon heat exposure

These results are in accordance with the latest publications [7, 8] showing that the behaviour of ozone regarding brightness stability was shown to be significantly better compared with chlorine dioxide. One explanation could be that ozone has selectively eliminated substances or precursors remaining into the *Bagasse* fully bleached pulp having a negative impact on brightness stability which can not be removed by a bleaching chemistry only based on chlorine, chlorine dioxide or peroxide [9]. Contrary to chlorine dioxide, ozone does not form coloured by-products as quinones into the pulp [8].

Economic assessment

To highlight the potential interest of using ozone on *Bagasse* pulp in terms of economic and environment aspects, a detailed assessment is performed using the results previously obtained, and some data (chemicals cost) collected from some pulp mills in India.

Green bleaching

Form the environment point of view, table 4 gives a brief overview and perspectives of the two bleaching options regarding several environmental indicators.

	Green Bleaching	ECF Standard
AOX emission	0	Yes
OX remaining into the pulp and final paper	0	Yes
COD reject	Lower	Higher
Effluent volume to be treated	Lower	Higher
Water consumption	Lower	Higher

Table 4 - Environmental indicators

It is shown that, by adopting a ***Green bleaching*** sequence, the mill is in a better position to gradually upgrade its sequence to meet evolving effluent standards, to reduce water usage, to develop new products without any residual chlorinated by-products (food-contacting papers for example), while finally minimizing the risks of making soon-obsolete investments.

Green and economical at the same time

In the same level as environment, the assessment of the investment and operating cost soon becomes a critical issue, and getting reliable information about those costs is fundamental in the decision making process. To assess the difference in the use of ***Green bleaching*** compared with ECF standard, the calculation must integrate a realistic idea about the investment and operating cost.

A first point to be clarified is the capital expenditures for the different bleaching alternatives. Normally, a detailed calculation about investment cost for bleaching equipment (bleaching towers, mixers, presses, washers,…) is required in a "real" project before building any conclusions. However, in this study a general comparison is performed to point out major differences between ***Green*** and chlorine based bleaching.

Due to efficient mixing and fast chemical reaction, the reaction time of ozone is between few seconds to minutes depending on the mixing equipment. Two ozone mixing systems are available today on the market. Ozone can be introduced into the pulp at medium pulp consistency (MC ozone stage) or high pulp consistency (HC ozone stage). Basically, although MC ozone requires a MC-pump, a mixer unit and a blower to separate the gas phase from the pulp, HC ozone needs a press in front of the ozone reactor to reach high pulp consistency. The pulp at the outlet of the ozone stage is washed and sent to the final (PO) stage. The operating cost of the bleaching fibreline includes energy requirement for the operation of the different bleaching stages. Tables 5 gives a short summary to highlight the difference of the two ozone options when compared with the ECF bleaching OD(EOP)D.

	OA(ZHCq)(PO)	OA(ZMCq)(PO)
Capital cost	Higher	Equivalent
Variable cost (Pumping, Heating, Pulp Mixing, …)	Lower	Equivalent
Process flexibility	Higher	Equivalent

Table 5 – Comparison of ECF bleaching with Green bleaching including an ozone stage performed at high or medium pulp consistency.

Despite some variations, the different bleaching options are close in terms of investment cost. Whereas ECF bleaching will require longer retention time and more heat in the different bleaching phases, ***Green bleaching*** with ozone will be compact especially with the MC option, and will be more flexible and easier for water management with HC ozone. Anyway, the final process design always answers to a specific situation.

Ozone or chlorine dioxide

The generation of ozone and chlorine dioxide both requires a dedicated unit to be purchased for on-site production. The operating cost of chlorine dioxide is mainly linked to the purchasing cost of chemical precursors such as sodium chlorate, a reductive agent & sulfuric acid, and to the technology used for the on-site generation. Moreover, to build a correct comparison with ozone, it is also necessary to include the operation and maintenance expenses of the chlorine dioxide plant and those related to the purchase, delivery and storage of the chemicals on site. In comparison, ozone production is simple to investigate since only three main components have to be considered:

- Oxygen requirement from V(P)SA or LOX (Liquid oxygen) production facility
- Local energy for ozone generation
- Operation & maintenance

For pulp bleaching, ozone is generated at a concentration of about 12% by weight in oxygen to reach the optimal figure between investment and variable costs (oxygen & energy). To generate ozone in such conditions, 1 kg ozone requires 8.3 kg of oxygen and 10 Kw/h energy. Figure 7 describes the principle of ozone generation.

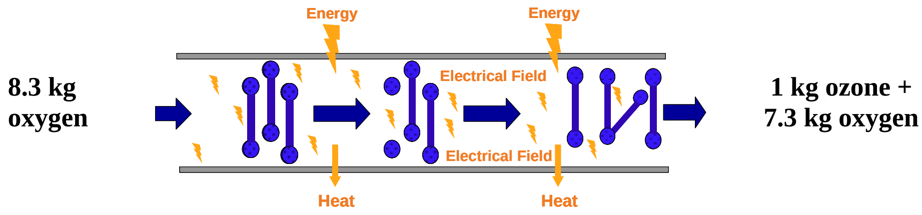

Figure 7 - Ozone formation in an electric field

Contrary to chlorine dioxide production requiring a chemical plant, integrated solutions for on-site ozone generation have been developed specifically for pulp and paper applications. An example is given by the *Z-*

Compact-System presented in figure 8 which is a compact ozone plant adapted to the pulp mill's constraints such as space limitation and aggressive ambient air conditions. Such a system is supplied as a turnkey "plug & play" solution. Depending on process requirement, the ozone generator meets the demands by providing ozone production capacities up to 6 tons per day per *Z-Compact-System* unit. Figure 7 shows 3 *Z-Compact-System* installed in a pulp mill in Europe.

Figure 8 - Z-Compact-Systems delivering ozone to a bleaching fiberline

For a pulp mill producing 300 ADT per day of *Bagasse* pulp bleached with 5 kg/t ozone, the oxygen requirement reaches 12.5 tons per day for the ozone generation of 1.5 ton of ozone per day. The off-gases vented from the Z-stage containing oxygen can be re-used in the oxygen consuming applications of the bleaching fibreline such as oxygen delignification, (PO) stage and other applications (wastewater treatment). It is the case for two thirds of the 28 ozone bleaching systems in operation in the world. A typical layout of an ozone system including oxygen reuse and designed in the case of ***Green bleaching*** of *Bagasse* pulp is presented in figure 8.

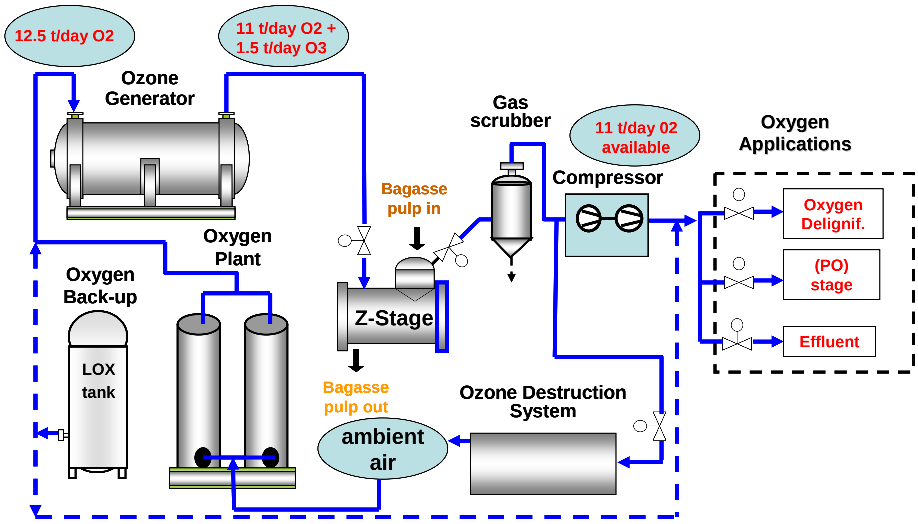

Figure 8 - Ozone and oxygen production including oxygen reuse from the Z-stage of a pulp mill producing 300 ADT/ day Bagasse bleached pulp.

Recycling oxygen should be viewed as a clever means to "save" oxygen and to reduce the cost of ozone, but this possibility has to be balanced with additional investment (compressor unit, piping …) especially when high pressure is required for applications such as oxygen delignification. Defining the most optimized solution for oxygen reuse is done in connection with the local conditions and constraints of the pulp mill.

In the case 300 ADT of pulp per day, the on-site chemical production of ozone and chlorine dioxide is respectively 1.5 and 3.6 tons per day. The investment in ozone production including equipment for the oxygen reuse will have the same order of magnitude than a complete new chlorine dioxide plant.

To conclude about bleaching cost, other chemicals such as oxygen, peroxide, sodium hydroxide, sulfuric acid, EDTA, ozone and chlorine dioxide are taken into account in the calculation. The operating cost of ECF bleaching sequence OD(Eop)D is then compared with OA(Zq)(PO) including oxygen reuse at a given brightness target of 90% ISO.

	Brightness % ISO	ClO2 kg/t	NaOH kg/t	EDTA kg/t	O2 kg/t	O3 kg/t	H2O2 kg/t	H2SO4 kg/t	Chemical costs
		75 Rs/kg	20 Rs/kg	20 Rs/kg	7 Rs/kg	88 Rs/kg	40 Rs/kg	3.5 Rs/kg	Rs / ton of pulp
OD(EOP)D	*90+*	*12*	*10*	*0*	*20*	*0*	*5*	*6*	**1461.0**
O(AZq)(PO)	90+	0	16	*1*	*0*	5	12	12	**1302.0**

Table 6 – Bleaching chemicals cost in Rs per ton of pulp (Based an Energy cots of 3 Rs/Kwh)

As indicated in Table 6, the bleaching chemicals cost is 10 % lower with the ***Green bleaching*** concept. This is additional saving and safety margin regarding variable costs for pulp production. Of course, the result highly depends on the local cost for energy and bleaching chemicals, but also on factors such as the location and size of the pulp mill.

CONCLUSION

When it comes to developing *Bagasse* as sustainable source of fibre for pulp and papermaking, it is shown that adopting a ***Green bleaching*** process enables increased environmental compliance, greater operational efficiency and more cost-effective production. This work demonstrates that pulp and paper producers using sugarcane waste have the opportunity to implement the most advanced bleaching technologies.

Among the other reasons favouring this concept, it can be mentioned that, contrary to the chemistry based on chlorine or chlorine dioxide, ozone generation is “real” on-site technology requiring limited space, reducing ecological footprint, and giving the mill greater independence from the chemicals market since the main variable cost will be finally local energy when oxygen is also produced on-site.

Of course, risk and cost remain the main criteria of the decision making process, but when these factors have to be balanced with long-term vision and guided by principles of environmental responsibility, “crossing the bridge” opens possibilities to produce new pulp and paper grades and create opportunities in a changing market.

The time to implement ***Green bleaching*** practices is now on, and our pioneering effort will continue to develop processes that help minimize water and chemicals usage, conserve resources and finally protect biodiversity.

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