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# ***THE COST OF OZONE-BASED ECF AND TCF BLEACHING***

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***Abstract*** **:**
*Thanks to recent advances in oxygen and ozone production technology, the cost of ozone as applicable to a 1000 ODMT/day bleach line has decreased to levels of about USD 1.10-1.30 per kilogram, all expenses included. At equal bleaching power, and taking generator investment into account in both cases, ozone is 1.5 times less costly than chlorine dioxide. Analysis of representative bleaching sequences shows that ozone-based options are today economically the most competitive, not only for TCF-, but also for ECF bleaching.*

## 1. INTRODUCTION

When the previous Ozone Symposium was held in Helsingör in September 1993, eight pulp mills worldwide had made the decision to implement ozone on industrial scale. At the time of writing, this number has doubled to a total of sixteen. Fourteen lines, listed in table 1, are in operation or under construction, while two others, Votorantim's mills at Jacarei and at Luis Antonio, Brazil, should install ozone bleaching equipment in the near future [1].

| COMPANY | LOCATION | O3 CAPACITY (kg/h) | S/UP | PRODUCT |
|---|---|---|---|---|
| LENZING | LENZING, Austria | 40* | 1992 | TCF SULFITE (DISS) |
| *UNION CAMP* | *FRANKLIN, Va., USA* | *280* | *1992* | *ECF KRAFT* |
| SÖDRA CELL | MÖNSTERAS, Sweden | 210 | 1992 | TCF KRAFT |
| *STORA BILLERUD* | *SKOGHALL, Sweden* | *40** | *1992* | *ECF/TCF KRAFT* |
| *MODO PAPER* | *HUSUM, Sweden* | *200** | *1993* | *ECF/TCF KRAFT* |
| KYMMENE | PIETARSAARI, Finland | 100/100* | 93/94 | ECF/TCF KRAFT |
| *METSÄ-BOTNIA* | *KASKINEN, Finland* | *300** | *1993* | *ECF/TCF KRAFT* |
| PETERSON SEFFLE | SÄFFLE, Sweden | 30* | 1994 | TCF SULFITE |
| *S C A* | *OSTRAND, Sweden* | *>> 100** | *1995* | *TCF KRAFT* |
| *SAPPI* | *NGODWANA, South Africa* | *270** | *1995* | *ECF KRAFT* |
| *PONDEROSA* | *MEMPHIS, Tenn., USA* | *70** | *1995* | *RECYCLED MKT PULP* |
| BACEL | CAMACARAI, Brasil | 70* | 1995 | TCF PH KRAFT |
| METSÄ-RAUMA | RAUMA, Finland | 420* | 1996 | TCF KRAFT |
| *CONSOLIDATED* | *WISC.RAPIDS, WI, USA* | | *1996* | *ECF KRAFT* |

*Table 1 : Industrial ozone bleach plants in operation or under construction as of August 1995.*
*The asteriks (*) denote ³ 10% W/W ozone concentrations. Italics indicate sites equipped with Ozonia systems.*

Industrial references now exist for a wide variety of ozone-based pulp bleaching processes : the list of table 1 includes both sulfite- and kraft mills, ECF- as well as TCF bleaching, dissolving grades as well as pulp for paper- and board manufacturing, virgin pulp and recycled fibers, integrated mills as well as market pulp mills, hardwood and softwood bleach plants.

When compared with the industrial development of oxygen delignification, which was initiated more than twenty-five years ago, the implementation of ozone for pulp bleaching has grown quite rapidly (see fig.1). The main reason underlying this evolution is the necessity to respond to growing environmental awareness, reflected both in regulatory constrains and market demands.

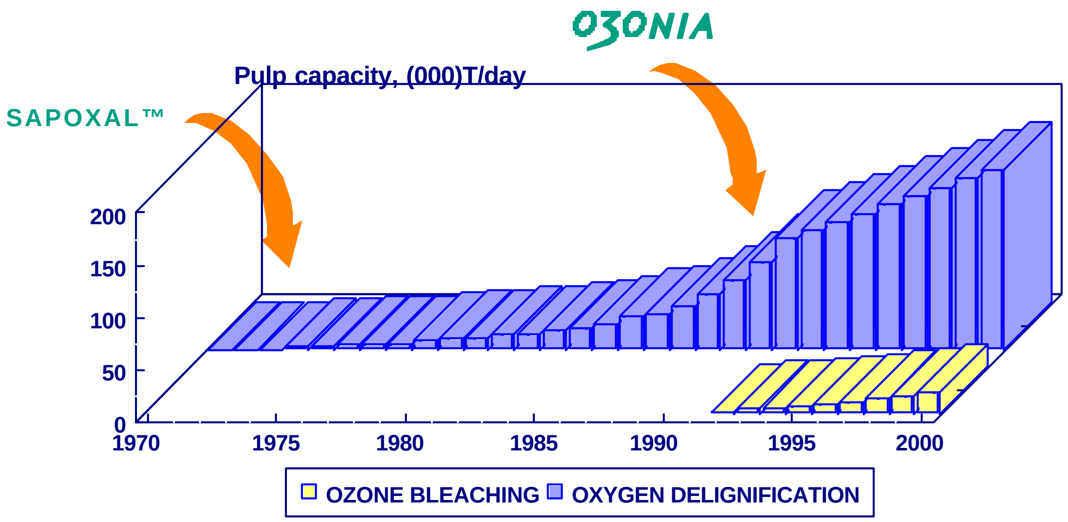


*Figure 1 : Evolution of oxygen delignification and ozone bleaching as measured by the daily pulp tonnage employing these processes worldwide.*

The fact that ozone is finding growing acceptance as a bleaching chemical compatible with these requirements results from a combination of advances with regard to the bleaching process and associated equipment on the one hand, and ozone production and- handling on the other. Several of these issues are addressed in papers and round-tables at this Symposium, as is the question of pulp quality. The present contribution focuses on the question of <u>cost</u>. Recent advances in ozone generation, and in particular the development of Ozonia's AT95 technology [2], as well as the lowering of oxygen cost by means of on-site production, have established ozone as a highly competitive bleaching chemical. While it may come as no surprise that TCF sequences combining ozone and hydrogen peroxide are significantly less costly than those employing hydrogen peroxide only, it should be stressed that ECF sequences that combine ozone with chlorine dioxide are more cost-effective than ECF sequences using only chlorine dioxide. When compared on the basis of the same costing structure, i.e. allowing for operating expenses and investment costs in both cases, and at equal bleaching power, ozone is today about 1.5 times <u>less</u> expensive than chlorine dioxide.

## 2. COST OF OXYGEN + OZONE SUPPLY ALTERNATIVES

Many combinations can be considered when optimizing an integrated oxygen + ozone supply system. Both once-through and long-loop systems, schematically illustrated in fig.2, are now in industrial operation. Ozone can be generated economically at concentrations ranging from 6 or 7% to 14% by weight or more, with 10% to 12% being the most common choice.

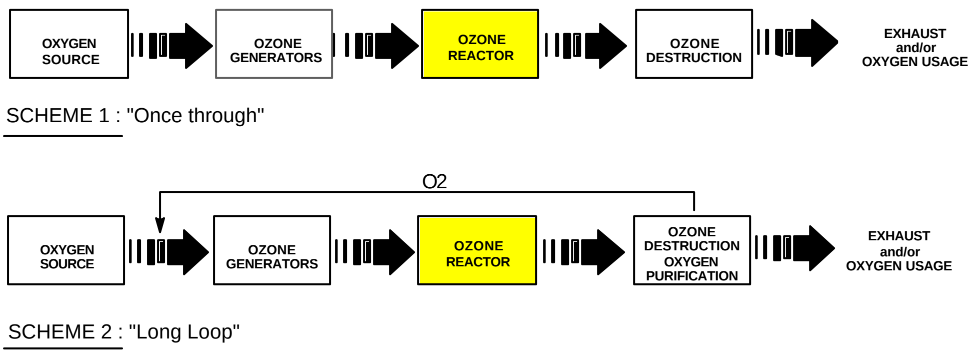


*Figure 2 : Schematic representation of once-through and long-loop oxygen + ozone supply systems*

The oxygen sources employed at the mills listed in table 1 include liquid oxygen ("LOX") transported from merchant air separation plants as well as oxygen produced on-site by means of cryogenic distillation, or by vacuum-swing adsorption ("VSA") technology. The configuration that best suits a given mill is site specific, and depends, among other factors, on the relative amounts of oxygen and ozone used by the mill (and their foreseeable evolution) and the consistency at which ozone bleaching is carried out. High consistency bleaching is rather flexible in regard to ozone concentration and employs ozone at near-atmospheric pressure ; medium consistency favors higher ozone concentrations and pressures, to improve mixing efficiency.

To evaluate the cost of ozone on a "per kilogram" basis, we consider the case of a 1000 ODMT/day bleach line requiring 23T/day of oxygen for delignification and Eo, and 6 T/day of ozone (250 kg/h). We shall leave open the question whether ozone bleaching is carried out at medium- or high consistency and for the sake of comparison consider that ozone is supplied at near-atmospheric pressure. To illustrate the many different supply options, we have chosen three of the most pertinent alternatives, in each case employing Ozonia's new AT 95 ozone generators [2] :

a) Ozone generated at 6% by weight in oxygen, obtained by evaporating LOX. The oxygen-rich exhaust gas from the bleaching stage is treated by a residual ozone destruct unit and a long loop system to be recycled to the ozone generators. The gas purge from the loop is matched to the 23 T/day requirement for delignification and Eo and compressed at 10 barg. If we conservatively assume that all the 6 T/day ozone supplied to the pulp is consumed without liberating oxygen, the LOX make-up requirement is 23 + 6 = 29 T/day (this assumption is conservative in the sense that it overestimates overall oxygen consumption : typically the bleaching reaction will return under the form of oxygen between 1/2 and 2/3 of the ozone weight consumed).

b) Ozone generated at 10% by weight in oxygen from a VSA on-site unit operating at 93% V/V oxygen content with an oxygen mass flow of 60 T/day. The system operates in the once-through mode. Again assuming that all the ozone is consumed in the bleaching reactor without conversion to oxygen, 60 - 6 = 54 T/day of oxygen is recovered after the residual-ozone destruct unit. Of this, 23 T/day is compressed to 10 barg for delignification and Eo, leaving 31 T/day available for other oxygen applications in the mill : white- or black liquor oxidation, wastewater treatment, or lime kiln enrichment, for instance.

c) A scheme analogous to b), but with ozone produced at 14% by weight. The VSA is now sized at 43T/day of oxygen ; at least 43 - 6 = 37 T/day of oxygen is recovered of which 23T/day is used for delignification and Eo, leaving an excess of 14 T/day available for other mill applications.

Note that it is assumed that the loop purge of alternative a) or the off-oxygen recovered after bleaching in alternatives b) or c) is of sufficient purity to be used in delignification. This requires verification on a case-by-case basis. Delignification systems can be designed to operate with oxygen purities as low as 85%. Some existing systems may require oxygen purities of $\geq$ 90%, however. One should therefore pay attention to the modification of the oxygen purity by air entrainment and reaction products from the bleaching process, and choose the oxygen source so as to ensure that recovered off-oxygen will be of sufficient purity.

The economic comparison of the above oxygen + ozone supply alternatives requires taking into consideration investment costs and operating expenses. To do so, we have added investment costs, including the ozone generation equipment, residual ozone destruct unit, recycle loop in the case of alternative a), oxygen compressor for the delignification and Eo supply, as well as estimated civil works costs on the one hand, and four years of expenses covering maintenance, electrical power and oxygen supply on the other hand. Cooling water, assumed to be available at 15°C, is not included. The total has been divided by four to yield a yearly cost for meeting the assumed requirement of 6 T/day of ozone and 23T/day of oxygen on a 350 days/year basis. In the case of alternatives b) et c), the excess oxygen representing 31 and 14 T/day, respectively, is available at no additional charge at battery limits, as its cost is integrated in that of the stated ozone and oxygen requirements.

The results of this evaluation are illustrated in figure 3. The cost of power was assumed to be 0.036 USD/kWh, while those of oxygen were based on figures intermediate between those representative of the North American and Scandinavian markets.

It will be recognized that the supply solutions of figure 3 integrate both the oxygen and ozone requirements, so that dividing the yearly expense between these two gases is somewhat arbitrary. In most cases, the mill would use oxygen for delignification and Eo regardless of ozone being implemented in the bleaching sequence or not. The most logical approach is then to attribute to oxygen the cost that would be incurred if only this 23 T/day LOX requirement would have to be met. The corresponding expense represents a "credit" that allows one to establish the expenditure assigned to ozone, as illustrated in the right-hand columns of figure 3. One thus obtains the costs for one kg of ozone as indicated at the bottom of the figure. The currency conversion is based on an exchange rate of 1 USD = 7.30 SEK.

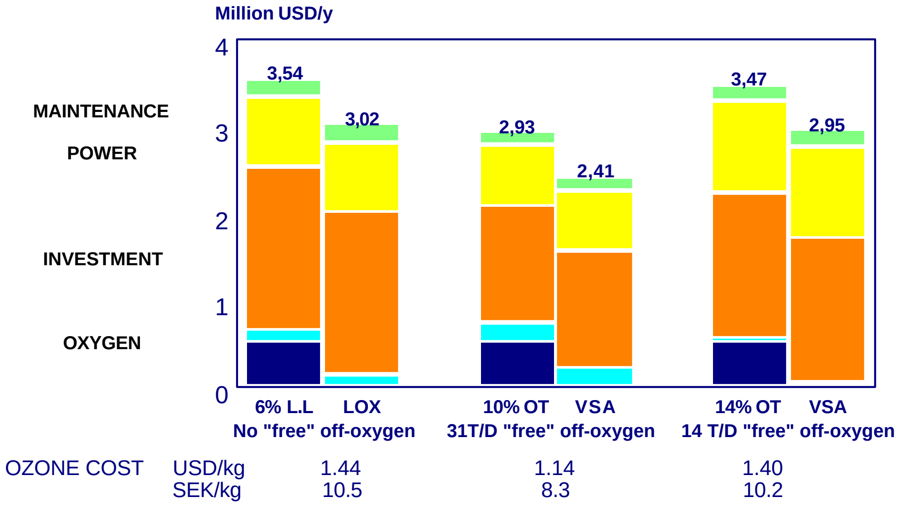


*Figure 3 : Indicative figures for the total yearly cost for 6 T/day (250 kg/h) ozone at near-atmospheric pressure + 23 T/day oxygen (10 barg), defined as one fourth of turnkey investment, including civil works + 4 years of maintenance, power and oxygen supply. Electrical power was valued at 0.036 USD/kWh ; oxygen costs are based on representative figures for the North-American and Scandinavian markets. The right- hand columns allow for a credit represented by delignification + Eo oxygen requirements, yielding the cost per kg of ozone indicated in the bottom of the figure (1 USD = 7.30 SEK).*

The ozone costs indicated in figure 3 are lower than the equivalent figures reported two years ago [3, 4] by about 20 to 30%. Even the 14% once-through option is today more economical than the 10% solution evaluated at that time. These improved economics and the ability to reach higher ozone concentrations are the result of significant progress in the design and construction of large-capacity generators employing second-generation advanced dielectrics. Ozonia's pioneering work in this area is outlined in the paper presented by Norbert Wiegart at this Symposium [2].

The fact that the off-oxygen from the ozone bleaching stage is re-used for delignification and Eo results in oxygen representing a relatively small contribution to the cost assigned to ozone. Recycling oxygen to the ozone generators should, in general, not be viewed as a means to "save" oxygen. Opting for a once-through solution with a larger on-site oxygen plant will in most cases be more economical than choosing a lower oxygen capacity but increasing investment- and operating costs by the addition of a recycle loop.

Recycle loops will be most appropriate when site-specific situations make it preferable to maintain the existing oxygen supply solution when installing the ozone system, for instance, or in cases where the mill consumes little or no oxygen as such. A once-through option is more simple, more flexible, and takes up less space. It also makes available substantial quantities of off-oxygen that can be put to use at minimal cost, since all expenses in figure 3 have been charged to the established 6 T/day ozone and 23 T/day oxygen requirements. Any credit assigned to such additional applications (lime kiln enrichment, black- or white liquor oxidation, etc.) will make ozone even more competitive as compared to the data of figure 3.

As seen in figure 3, capital expenditures represent the largest single contribution to the cost of ozone. It is therefore important to tailor the ozone generation system to the mill's present and foreseeable requirements with particular care. By integrating, in association with its daughter company Ozonia, all relevant know-how related to oxygen- and ozone production and handling, Air Liquide is in the unique position to be able to examine each case on an individual basis, whether ozone bleaching is carried out at medium- or high consistency, without any bias as to the choice of ozone concentration, the type of oxygen supply, the incorporation of recycle loops or not.

Production of ozone at concentrations well above 10% is now industrially proven and economically realistic. As shown in figure 3, opting for 14% rather than 10% concentration in a once-through system increases the ozone cost by about 20% with the present assumptions. This additional expense has to be evaluated against the possible benefit of improving mixing efficiency in the case of medium-consistency ozone bleaching, and the additional flexibility in regard to ozone production capacity : a system designed to produce 250 kg/h of ozone at 14% can produce up to 40% more ozone if the concentration requirement is relaxed to 10% [2].

Regardless of the technical choice of supply scheme, two options are proposed to our customers in regard to contractual arrangements : purchase of the ozone generation system with a separate oxygen supply contract, or an integrated oxygen + ozone service agreement. In the latter case, Air Liquide owns, operates and maintains the oxygen and ozone production facilities, located within or adjacent to the pulp mill, and ensures that oxygen and ozone are permanently available at the flowrate, pressure and composition required by the mill. This "over the fence" solution enables the customer to have the benefit of the most appropriate oxygen + ozone supply option without detracting capital- and human resources from the mill's core business. It also establishes a long-term relationship that gives the customer access to our Group's substantial R&D efforts relating to the Pulp and Paper Industry. These concern industrial gases, including ozone, as well as hydrogen peroxide and its derivatives.

From a financial point of view, outsourcing the supply of ozone or not does not significantly modify the cost analysis summarized in figure 3. When comparing an "over-the-fence" solution with an equipment purchase option, the mill's economic evaluation should in the latter case incorporate the "lost opportunity cost" corresponding to additional profits that could be made by investing process equipment rather than purchasing a gas generation system. As return-on-capital requirements in the Pulp and Paper Industry are similar, if not higher than those in the Industrial Gases Industry, such an analysis will show little difference between the "over-the-fence" and generator purchase options. In the former case, however, the ozone equipment will not burden the mill's balance sheet, and mill personnel will be freed of the task of operating and maintaining the gas supply system. In either case, the analysis summarized in figure 3 gives a realistic indication of the cost of ozone under the conditions considered.

# 3. ECONOMICS OF OZONE-BASED ECF AND TCF SEQUENCES

## 3.1. Relative costs of ozone and chlorine dioxide

Ozone can be combined with chlorine dioxide or with hydrogen peroxide in cost-effective ECF or TCF sequences. Several representative examples are considered below to illustrate this point.

To account for the cost of chlorine dioxide, we have adopted an approach analogous to that used in the analysis of the cost of ozone. Investment costs was added to four years' of operating expenses and the sum was divided by four to yield a total yearly amount. From this, the full cost of chlorine dioxide per tonne was obtained assuming 350 days/year operation. Table 2 shows the relevant numbers for a 40 T/day R8 chlorine dioxide generator. The analysis is based on data from ref. [5].

| **$ClO_2$ PRODUCTION COSTS (R8, 40 T/day)** | | | |
|---|---|---|---|
| FEED REQUIREMENTS | | | USD /Tonne $ClO_2$ |
| | Usage per Tonne $ClO_2$ | Unit Cost USD | |
| $Na_2ClO_3$ | 1.64 T | 435/T | 713 |
| $H_2SO_4$ | 1.05 T | 60/T | 63 |
| $CH_3OH$ | 0.15 T | 500/T | 75 |
| NaOH | 0.21 T | 275/T | 58 |
| Steam | 5 T | 8/T | 40 |
| Power | 100 kWh | 0.036/kWh | 4 |
| CHEMICALS AND UTILITIES | | | 953 |
| $Na_2SO_4$ credit | | | - 130 |
| Maintenance + Operation (4% of inv./year) | | | 46 |
| Royalty | | | 40 |
| NET OPERATING COST | | | 909 |
| CAPITAL COST (amort. + ROI on 16 MM USD Investment) | | | 285 |
| FULL COST PER TONNE $ClO_2$ | | | 1194 |

*Table 2 : Cost analysis for production of 40 T/day $ClO_2$ by means of an R8 generator. The saltcake credit assumes that its recovery allows savings of 35 T/day of sulfur valued at USD 100/T and 28 T/day of sulfuric acid valued at USD 60/T.*

The full cost of chlorine dioxide is thus found to be USD 1.19/kg, a figure similar to the USD 1.14/kg cost of ozone of figure 3.

The bleaching power of one kg of ozone is, however, significantly higher than that of one kg of chlorine dioxide. In terms of theoretical oxidative bleaching ability, one kg of ozone represents 125 oxidation equivalents (OXE, see references [6]and [7]), while for chlorine the number is 74.12 OXE/kg. This implies a theoretical bleaching ability per kg that is about 1.7 times higher for ozone than for chlorine dioxide. In practice, industrial-scale comparison of ECF bleaching using only chlorine dioxide on the one hand, and a combination of ozone and chlorine dioxide on the other [8], has shown the application of one kg of ozone to be equivalent to about 1.5 kg of chlorine dioxide [9]. One concludes that with the full cost of ozone and chlorine dioxide being very similar on a per kg basis, ozone is at equal bleaching ability about 1.5 times more economical than chlorine dioxide.

The argument that ozone is an "expensive" bleaching chemical is to-day no longer sustainable. On the contrary. Even mills that are equipped with sufficient chlorine dioxide capacity could achieve savings in ECF bleaching costs by introducing ozone in their sequences : if the -potentially misleading- hypothesis is made that the chlorine dioxide investment should no longer be taken into consideration because that expenditure has already been made, while ozone should be evaluated at full cost, including generator capital, typical numbers will be USD 0.91/kg for chlorine dioxide (the net operating cost in table 2) and USD 1.14/kg for ozone (figure 3). Allowing for a 1.5 bleaching efficiency ratio, ozone, even in such a comparison, is still more economical by a factor 1.2.

### 3.2. Chemicals costs of ECF and TCF Bleaching Sequences

To illustrate the competitiveness of ozone-based ECF and TCF bleaching, we have examined a selection of sequences documented in the recent literature. In a first step, expenditures are examined without taking into account the capital required for installing process equipment. The data are summarized in table 3. Ozone and chlorine dioxide are valued at the representative full costs of USD 1.14 and 1.19 per kg, respectively. In the cases where ozone bleaching is carried out at medium consistency, we have added an expenditure of USD 0.16/kg $O_3$, representing the full cost of ozone compression including capital- and operating expenses. The right-hand entries in the last column of table 3 pertain to situations where availability of sufficient chlorine dioxide generation equipment would justify taking only chlorine dioxide operating cost into consideration (USD 0.91/kg $ClO_2$).

| | Chemical : | | $ClO_2$ | NaOH | $O_2$ | $O_3$ | $H_2O_2$ | $H_2SO_4$ | EDTA | $MgSO_4$ | Bleaching Chemicals USD/ODMT | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Unit cost USD/kg | | 1.19 (0.91) | 0.38 | 0.065 | 1.14 (1.30) | 0.90 | 0.06 | 1.0 | 0.5 | | |
| Sequence | Ref. | Kappa after 0 | Charge kg/tonne pulp | | | | | | | | $ClO_2$ full cost | $ClO_2$ operat. cost |
| ① DEopDED | [10] | (30.8) | 36.7 | 33.3 | 7.8 | - | 6.7 | - | - | - | 62.8 | 52.5 |
| ② ODEopDED | [11] | 18 | 24 | 41 | 23 | - | 6.5 | 8 | - | 2 | 53.0 | 46.2 |
| ③ ODEopDED | [8] | 15 | 23 | 45 | 23 | - | 3 | - | - | 2 | 49.7 | 43.2 |
| ④ OAZEopDED | [8] | 12 | 13 | 45 | 23 | 4.5 | 3 | 10 | - | 2 | 44.2 | 40.6 |
| ⑤ OAZQEopP | [8] | 11 | - | 45 | 23 | 5 | 30 | 15 | 3 | 2 | 57.0 | |
| ⑥ OQPpZPp | [12] | 8.2 | - | 45 | 15 | 7.8 | 25 | 10 | 4 | 4 | 57.3 | |
| ⑦ OQEop(ZQ)(PO) | [13] | 12.1 | - | 47 | 23 | 4 | 18 | 10 | 2 | 2.5 | 44.6 | |
| ⑧ O(QZ)Q(PO) | [14] | 8 | - | 35 | 20 | 6 | 15 | 20 | 4 | 2.5 | 42.4 | |
| ⑨ OQ Eop Q (PO) | [15] | 14 | - | 45 | 23 | - | 45 | - | 4 | 5 | 65.6 | |

*Table 3 : Representative costs of bleaching chemicals for a 1000 ODMT/day C/D bleach line with oxygen delignification, retrofitted to ECF or TCF bleaching. Sequence ① represents, as a reference, the D100 option without oxygen delignification. The two sets of figures in the last column correspond to cases where chlorine dioxide cost is evaluated including and excluding generator capital charge, respectively. In sequence ⑧, ozone bleaching is carried out at high consistency (ozone = USD 1.14/kg), in the others at medium consistency (ozone = USD 1.30/kg). The applied chemicals charges are those indicated in the references cited or our own estimates based on the data provided therein. The bleach line produces SW kraft at about 89% ISO brightness, except for sequence ⑨ where 84-85% ISO is obtained.*

The costs of delignification- and bleaching chemicals listed in table 3 are representative figures that need to be verified on a case-by-case basis, and depend in their details on local market conditions and site-specific supply configurations. Several conclusions can be drawn, however, that apply quite generally :

- Mills that have installed oxygen delignification benefit from the most competitive bleaching costs. An ECF sequence with oxygen delignification saves up to 20% in bleaching chemicals expenses. In addition, these mills achieve higher wood yields because less losses are incurred in reaching a given kappa number by combining cooking and oxygen delignification than by cooking alone [23]. It should also be mentioned that the NaOH charges of table 3 include 15 kg/ODMT for the oxygen stage. If oxidized white liquor is used instead, the chemicals costs for the sequences with oxygen delignification will be lowered by about USD 2.8/ODMT.

- ECF sequences that combine ozone and chlorine dioxide are more economical than those using only chlorine dioxide. Savings are of the order of 10% when full dioxide cost is taken into account, and about 5% if only operating costs of chlorine dioxide are taken into consideration. New ECF bleaching lines will be most competitive when combining ozone and chlorine dioxide. Mills wishing to abandon molecular chlorine in existing bleach plants in favor of ECF sequences, or that plan on increasing ECF capacity, should take into consideration that introducing ozone will most probably lower their bleaching costs, even if available chlorine dioxide capacity is sufficient or can be extended with little investment.

- The most competitive TCF sequences that combine ozone and pressurized hydrogen peroxide are less costly in regard to bleaching chemicals than ECF sequences using only chlorine dioxide. They are similar in bleaching cost to ozone-based ECF solutions, if not slightly more competitive.

- In addition to achieving higher brigthness, ozone-based TCF bleaching is significantly more economical than when only hydrogen peroxide is employed. The difference is on the order of USD 20/ODMT.

### 3.3. Full costs of ECF and TCF bleaching sequences

Greenfield mills, or mills installing new bleach lines, are in the most favorable position to take advantage of the economic competitiveness of ozone-based ECF or TCF sequences. Significantly, the new Metsa-Rauma mill under construction in Finland will produce 1600 T/day fully bleached ozone-based TCF softwood pulp with a production cost no higher than ECF pulp ; investment expenses are lower than for a comparable ECF mill [16].

How do the bleaching sequences of table 3 compare in the less advantageous situation where their implementation would require retrofitting an existing C/D bleach line ? The estimated capital expenditures for much modifications are summarized in table 4. The corresponding yearly capital charges (amortization + ROI) were evaluated at 20% of the investment value, as compared to the 25% used for the ozone- and chlorine dioxide cost calculations, assuming that the mill would assign a longer amortization period and/or lower ROI to core-equipment than to auxiliaries.

Capital charges per tonne of pulp were obtained assuming 350 days/year production at 1000 ODMT/day.

| OXYGEN, OZONE, PEROXIDE PROCESS EQUIPMENT ADDITIONS | Investment Million USD | Yearly capital charge 000 USD | Capital charge USD/ODMT |
|---|---|---|---|
| Additional Eop stage at atmosph. pressure (20 to 30% delignification) | 2 | 400 | 1.14 |
| Mini oxygen delig., 6 barg (25 to 30% delignification) | 4 | 800 | 2.29 |
| Oxygen delig. (45%+) with recovery boiler modifications | 32.5 | 6500 | 18.6 |
| Ozone bleaching stage | | | |
| M.C. Pump + mixer + upflow tower | 4.7 | 940 | 2.69 |
| M.C.mixer + tower + washing [17] | 13 | 2600 | 7.43 |
| HC reactor [17] | 24 | 4800 | 13.7 |
| Peroxide storage, dilution pumps, metering equipment for existing Eo stage | 2 | 400 | 1.14 |
| Pressurized peroxide with washing | 10 | 2000 | 5.71 |

*Table 4: Estimates of process equipment investments and corresponding capital charges (amortization + ROI) for upgrading an existing 1000 ODMT/day C/D bleach line. Some of the data were obtained from ref. [17].*

The results for mills that have already installed oxygen delignification are shown in table 5. For the two ECF sequences employing chlorine dioxide only, we took bleaching chemicals cost values intermediate between those of table 3 : USD 49.6 and 46.5 per tonne of pulp for sequences ② and ③ , respectively, assuming that part of the necessary chlorine dioxide capacity would already be available. For ECF sequence ④, we used the value of 40.6 USD per tonne of pulp, corresponding to a situation where the mill would have sufficient chlorine dioxide capacity when complementing it with ozone. In all cases account was take of capital requirements to add peroxide to the existing Eo stage.

| Sequence | Ref. | Bleaching Chemicals Cost | Capit.Charge Peroxide storage, etc... | Capit.Charge Ozone Stage | Capit.Charge Press. Peroxide | Full Bleaching Cost |
|---|---|---|---|---|---|---|
| ② ODEopDED | [11] | 49.6 | 1.14 | - | - | 50.7 |
| ③ ODEopDED | [8] | 46.5 | 1.14 | - | - | 47.6 |
| ④ OAZEopDED | [8] | 40.6 | 1.14 | 7.43 | - | 49.2 |
| ⑤ OAZEopP | [8] | 57.0 | 1.14 | 7.43 | - | 65.6 |
| ⑥ OQPpZPp | [12] | 57.3 | 1.14 | 7.43 | 2 x 5.71 | 77.3 |
| ⑦ OQEop(ZQ)(PO) | [13] | 44.6 | 1.14 | 7.43 | 5.71 | 58.9 |
| ⑧ O(QZ)Q(PO) | [14] | 42.4 | 1.14 | 13.7 | 5.71 | 63.0 |
| ⑨ OQ Eop Q(PO) | [15] | 65.6 | 1.14 | - | 5.71 | 72.5 |

*Table 5 : Full bleaching costs, including capital charge on process equipment for a 1000 ODMT/day C/D bleach line with oxygen delignification retrofitted to ECF or TCF bleaching. All costs are expressed in USD/ODMT.*

Introducing an ozone stage is an existing C/D bleach line is economically attractive even if the investment for installing ozone mixing is taken into consideration : the full costs of the three ECF sequences in table 5 are very similar. Mills that can re-use their existing C/D washer after the medium-consistency ozone stage will have full costs for ozone-based sequences that are lower than those in table 5 by (7.43-2.57) = 4.9 USD per tonne (cf. table 4). In those cases, the full cost of ozone-based ECF bleaching is about 10% lower than that of the option using only chlorine dioxide.

The solution combining ozone and chlorine dioxide has a number of significant advantages :

- ozone can be purchased on an over-the-fence basis, avoiding capital expenditure for additional chlorine dioxide generation equipment. This option also has the benefit of improved cost predictability, as it reduces exposure to fluctuations in chlorine dioxide raw materials costs, sodium chlorate and methanol in particular ;

- OZED sequences have significantly lower levels of AOX and COD in the effluent, and can therefore more easily comply with increasing environmental demands. To illustrate this point, table 6 shows effluent characteristics before the aerated lagoon measured by Stora's Skoghall mill [8]. Potential savings by avoiding modifications or expansion of effluent treatment facilities are in many cases comparable if not more substantial that the cost of new ozone process equipment. The environmental benefits of combining ozone and chlorine dioxide were among the main motivations for Union Camp's extensive development work that lead to the first industrial implementation of an ECF bleaching plant employing a high consistency ozone stage [19].

- Incorporating ozone in its ECF sequences positions the mill on a pathway to cost-effective TCF, or, more importantly, TEF bleaching. While significant progress is being made towards (near) closure of chlorine dioxide-based ECF plants [18], lowering the amount of dioxide in the bleaching sequence can only facilitate such an undertaking.

| Sequence | AOX | Chlorate | COD | $BOD_7$ | N | P |
|---|---|---|---|---|---|---|
| ECF ③ | 0.83 | 6.8 | 32.6 | 6.7 | 0.48 | 0.005 |
| Z - ECF ④ | 0.45 | 3.3 | 29.8 | 6.4 | 0.31 | 0.02 |
| Z - TCF ⑤ | 0 | 0 | 24.5 | 6.3 | 0.31 | 0.05 |

*Table 6 - Effluent characteristics, expressed in kg per tonne of pulp, before the aerated lagoon at Stora's Skoghall mill. The sequence references are those of table 2. Data from ref. [8].*

Mills with oxygen delignification that are planning TCF bleaching for part or the totality of their production will have a substantial competitive advantage when incorporating ozone in their sequences. Retrofitting to TCF bleaching combining ozone and a single pressurized hydrogen peroxide stage will limit the increase in full bleaching costs, capital for process equipment included, to about 10 or 15 USD per tonne of pulp. A solution based on pressurized peroxide only will be more costly by an additional USD 10 to 15 per tonne pulp as compared to ZP solutions. This difference will become even more pronounced as market conditions re-establish peroxide price levels compatible with the capital requirements for capacity expansions.

Peroxyacids, Caro's acid (Caa) and peracetic acid (Paa) in particular, have recently received considerable attention. They make it possible to reach brightness levels that cannot be achieved with hydrogen peroxide alone, and are comparable to ozone in that respect. Bleaching selectivity is reported to be better than with ozone, and as a result the peroxyacids are being considered as a possible alternative to ozone, in particular for bleaching softwood fibers to high brightness. From an economic point of view, experience is too limited to make a reliable assessment of their competitiveness. Most likely, bleaching costs of sequences combining peroxyacids and hydrogen peroxide will be even higher than those using only peroxide. In our opinion, the benefits of peroxyacids will most probably find their industrial application in sequences using ozone and hydrogen peroxide as their main constituents.

What about mills that do not have oxygen delignification and that are considering retrofitting to ECF bleaching or modifying ECF lines to improve effluent characteristics, rather than adding end-of-pipe treatments ? Installation of full-fletched oxygen delignification will carry the burden of a capital expense typically estimated at USD 32.5 million. In these cases, it may be attractive to adopt a stepwise development, taking advantage of "mini-delig" or "wise man's delig" solutions to optimize competitiveness while incorporating flexibility to meet increasing effluent constrains.

The relevant cost data are summarized in table 7 for bleaching chemicals, and in table 8 for full sequence costs. Capital expenses were incorporated according to the guidelines set forth earlier. In these tables, the D/Z and Z stages were assumed to operate at medium consistency. For a full Z stage, the added flexibility of high consistency may offset its higher expenditure for process equipment (table 4).

| | Chemical | $ClO_2$ | NaOH | $O_2$ | $O_3$ | $H_2O_2$ | $H_2SO_4$ | EDTA | $MgSO_4$ | Bleaching Chemicals USD/ODMT | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Unit cost USD/kg | 1.19 (0.91) | 0.38 | 0.065 | 1.30 | 0.90 | 0.06 | 1.0 | 0.5 | | |
| Sequence | Kappa after cooking | Charge kg/tonne pulp | | | | | | | | $ClO_2$ full cost | $ClO_2$ operat. cost |
| D Eop DED (ref) | 30 | 36.7 | 33.3 | 7.8 | - | 6.7 | - | - | - | 62.8 | 52.5 |
| Eop D Eop DED | 22 | 26 | 35 | 18 | - | 6 | - | - | 2 | 51.8 | 44.5 |
| Eop D/Z Eop DED (atmosph.) | 23 | 18 | 40 | 20 | 5 | 6 | - | - | 2 | 50.8 | 45.8 |
| Eop D/Z Eop DED (pressure) | 22 | 16 | 35 | 18 | 5 | 6 | - | - | 2 | 46.4 | 41.9 |
| EopAZ Eop DED | 22 | 14 | 35 | 18 | 6 | 6 | 10 | - | 2 | 45.9 | 42.0 |
| OAZ Eop DEpD | 25 | 10 | 39 | 22 | 6 | 8 | 10 | - | 3 | 45.3 | 42.5 |
| OQ Eop (ZQ) (PO) | 18 | - | 45 | 27 | 6 | 20 | 10 | 3 | 4 | 50.3 | |

*Table 7 : Representative costs of bleaching chemicals for a sequence development retrofitting a 1000 ODMT/day C/D bleach line without oxygen delignification. The last two columns correspond to cases where chlorine dioxide cost is evaluated including and excluding generator capital charge, respectively. Ozone bleaching is assumed to be carried out at medium consistency, and the cost of ozone of USD 1.30/kg therefore includes compression. The bleach line produces 1000 ODMT/day SW kraft at about 89% ISO brightness..*

As shown in table 7, the introduction of a "mini-delignification" stage lowers the chemicals cost of a D100 sequence by about 17%. Combining ozone and chlorine dioxide can yield a further 10% decrease in chemicals expenses, and is particularly attractive when this enables the mill to avoid investing in additional chlorine dioxide capacity. Many bleach lines in North America have dual mixer arrangements for the addition of $Cl_2$ and $ClO_2$. In theses cases, the use of a combined D/Z stage without intermediate washing [20] will be a very attractive solution.

| Sequence | Bleaching Chemicals Cost | Capit.Charge Oxygen Delig. | Capit.Charge Peroxide Storage etc. | Capit.Charge Ozone Stage(s) | Capit.Charge Pressurised Peroxide | Full Bleaching Cost | Expected AOX (kg/ODMT) |
|---|---|---|---|---|---|---|---|
| D Eop DED (ref.) | 57.7 | - | 1.14 | - | - | 58.8 | 0.6 |
| Eop DEop DED | 48.2 | 2.29 | 1.14 | - | - | 51.6 | 0.4 |
| Eop D/Z Eop DED atmosph. | 45.8 | 1.14 | 1.14 | 0.69 | - | 48.8 | 0.3 |
| Eop D/Z Eop DED pressure | 41.9 | 2.29 | 1.14 | 0.69 | - | 46.0 | 0.3 |
| Eop AZ Eop DED | 42.0 | 2.29 | 1.14 | 7.43 | - | 52.9 | 0.25 |
| OAZ Eop DEpD | 42.5 | 18.57 | 1.14 | 7.43 | - | 69.6 | 0.15 |
| OQ Eop (ZQ) (PO) | 50.3 | 18.57 | 1.14 | 7.43 | 5.71 | 83.2 | 0 |

*Table 8 : Representative full sequence costs (in USD/ODMT) including process equipment capital charge, corresponding to the sequence development summarized in table 7. For the first two sequences, the chemicals cost was taken as the average of the corresponding entries in table 7, assuming that part of the necessary dioxide generation capacity would already be available. In the other cases, chlorine dioxide operating cost only was considered, which would be justified if no new dioxide generator investments were needed. The last column lists expected AOX levels after effluent treatment, assuming 40% abatement.*

The competitiveness of D/Z ECF sequences is further illustrated in table 8, which gives full costs including capital charges for process equipment. For the first two sequences, the chemicals costs were taken as the average of the corresponding values in table 7, assuming that part of the required $ClO_2$ capacity would be available. In the other cases, existing dioxide capacity was assumed to be sufficient, and $ClO_2$ operating cost only was considered. The two D/Z sequences require little capital expenditures and are highly cost-effective. The possibility to apply medium-consistency ozone bleaching using a mixer without up-flow tower was demonstrated by the Peterson Seffle mill in Sweden [21].By using the existing C/D washer after the D/Z stage, the ozone process equipment can then be limited to a ~USD 1.2. Million pump + mixer arrangement, corresponding to a capital charge of USD 0.69/ODMT. For the full Z stage an upflow tower has been added.

The last column in table 8 illustrates expected AOX levels assuming 40% abatement by effluent treatment. It is seen that values of the order of 0.3 kg AOX/tonne pulp can be achieved using D/Z bleaching, for a full sequence cost, process equipment included, as low as USD 46/ODMT. This is more than 20% less expensive than the reference D100 sequence, which yields AOX levels that are twice as high. The introduction of a full-fledged Z stage after "wise-man's delignification" provides for further lowering of the AOX load, at a full bleaching cost that remains 10% below that of the reference D100 option.

Finally, should market conditions or regulatory constrains require this, the mill could follow-up on this sequence development by the introduction of a complete oxygen delignification stage, and, ultimately, pressurized peroxide.

## 4. CONCLUSION

Ozone is being used by a growing number of mills to produce fully bleached hardwood- and softwood pulps that have mechanical properties compatible with most paper making applications. Significant progress has been made in the optimization of both ECF and TCF sequences, as will be discussed in several presentations at this Symposium. Industrial experience concerning brightness and pulp quality was also examined in references [19] and [24, 25], for instance.

From an economics point of view, ozone is a highly competitive bleaching chemical which, when compared at equal bleaching power, is typically 1.2 to 1.5 times less costly than chlorine dioxide. It can be purchased on an "over-the-fence" basis, enabling the mill to benefit from the most appropriate oxygen + ozone supply solution without detracting capital- and human resources from its core activities.

ECF sequences combining ozone and chlorine dioxide are economically competitive with sequences using chlorine dioxide only, even when capital expenses for modifying process equipment are taken into consideration. They have the advantage of improved performance and added flexibility in regard to effluent characteristics, and position the mill on the pathway to (nearly) effluent-free bleaching.

In combination with (pressurized) hydrogen peroxide, ozone makes it possible to produce fully bleached TCF pulp while maintaining expenditures in bleaching chemicals at levels that are comparable, if not lower, than those pertaining to ECF bleaching. Bleaching lines equipped with oxygen delignification can be retrofitted to ozone-based TCF production with a full bleaching cost, including capital charges on process equipment, only about 10 USD higher than that for ECF sequences. Mills that are considering modifying or expanding their effluent treatment facilities may well find that opting for TCF bleaching instead is economically more advantageous [22].

Bleaching plants that do yet have oxygen delignification can achieve AOX levels of the order of 0.3 kg/tonne pulp after effluent treatment by combining "wise man's" delignification with D/Z-based ECF bleaching. The cost of such sequences, capital charges for process equipment included, is comparable or lower than that of standard ECF solutions whose AOX levels are nearly twice as high. By adopting D/Z-based bleaching, the mill will be in a position to gradually upgrade its sequence to meet evolving effluent standards or market demands, while minimizing the risks of making soon-obsolete investments.

Whether it concerns greenfield mills, new bleach lines or retrofit projects, whether the mill wishes to adopt ECF or TCF sequences, oxygen and ozone are today the most cost-effective bleaching chemicals available to the Pulp and Paper Industry.

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