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LOW ENVIRONMENTAL IMPACT BLEACHING SEQUENCES FOR ATTAINING HIGH BRIGHTNESS LEVEL WITH EUCALYPTUS SPP PULP

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Abstract - The alternatives used for minimizing the usage of chlorine dioxide in bleaching sequences included a hot acid hydrolysis (A_{hot}) stage, the use of hot chlorine dioxide (D_{hot}) and ozone stages at medium consistency and high consistency (Z_{mc} and Z_{hc}), in addition to stages with atmospheric hydrogen peroxide (P) and pressurized hydrogen peroxide (PO). The results were interpreted based on the cost of the chemical products, bleaching process yields and on minimizing the environmental impact of the bleaching process. In spite of some process restrictions, high ISO brightness levels were kept around 90 % brightness. Additionally, the inclusion of stages like acid hydrolysis, pressurized peroxide and ozone in the bleaching sequences provided an increase in operating flexibility, aimed at reducing environmental impact (ECF Light). The D_{hot}(EOP)D(PO) sequence presented lower operating cost for ISO brightness above 92 %. However, this kind of sequence was not allowed for closing the wastewater circuit, even partially. For ISO brightness level around 91%, the $A_{hot}Z_{hc}$DP sequence presented a lower operating cost than the others.
Keywords: High Brightness Eucalyptus Pulp; Low Environmental Impact; ECF-Light Sequences; Partial Bleach Plant Closure; Operating Cost.

INTRODUCTION

The high brightness bleached pulp market has signaled the need to raise the currently practiced brightness levels (88-90% ISO) to higher values, somewhere around 92% ISO. The reason for such demand has been the high price of optical bleaches in paper mills and relative environmental risks in the excessive use of such additives. Obtaining a 92% ISO brightness level is often possible by using the already existing bleaching technologies implemented at mills; however, the cost of chemical reagents can be steep. In some cases, obtaining brightness at such levels is not possible because the supply of oxidizers is insufficient and/or the bleaching mill does not have the capacity to receive new oxidizers and/or raise dosages.

Works carried out with Kraft-O_2 eucalyptus pulp point to the D(EOP)D(EP)D sequence as the main option for obtaining 92% ISO and recommend the usage of high dosages of ClO_2 in the D_0 and D_1 stages, efficient washing and normal time and

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temperature conditions in the different bleaching stages (Suess et al., 2000; Colodette et al., 1993). The authors also advocate the D(EOP)DP sequence as an option for a 92% ISO brightness level or 90^+ %ISO, but in this case they indicate the need of even higher dosages of ClO_2 in the D_0 and D_1 stages.

However, using only chlorine dioxide as the main bleaching agent hampers obtaining high brightness levels, especially if there is no additional chlorine dioxide production capacity. The quickest way to overcome this need has been to use hydrogen peroxide and ozone to replace the additional dioxide that would be necessary for raising final pulp brightness levels.

Ozone has increasingly gained importance at several bleaching plants, for both ECF and TCF. Being a potential replacement for molecular chlorine and chlorine dioxide, the usage of ozone minimizes the problem of OX (organochlorine content on pulp) and AOX (absorbable organochlorine content on pulp) generation in the bleaching plant without necessarily impacting on the operating cost of bleaching (Diliner et al., 1991). Additionally, great reduction of hexenuronic compounds is achieved during ozone bleaching (Roncero, 2001; Da Silva et al., 2003). Also, ozone adapts well to the ECF bleaching process (Lachenal et al., 1991), which makes it attractive within the current scenario of the bleached pulp industry as a choice for the bleaching process.

For the case of hydrogen peroxide, despite being easy to use, the cost-benefit relationship has limited its usage to loads of somewhere around 3 to 5 $kg.odt^{-1}$ (over dry ton) in extraction stages, resulting in slight increases in brightness level. However, the demand for ECF pulp and even TCF pulp has required greater peroxide effectiveness in order to reduce the operating cost of using it in bleaching.

Several authors (Colodette et al., 1993; Colodette et al., 1995; Stronberg and Szopinski, 1994) have suggested new usage conditions for peroxide. Concepts are based on Arrhenius principles, where reaction speed is proportional to temperature (Colodette, 1994). Studies have shown that pressure and the type of pressurizing gas is another important factor in increasing peroxide usage efficiency, with oxygen mainly being used (Stronberg and Szopinski, 1994). In the literature it is reported that, theoretically, high pressures delay side reactions, making peroxide more efficient. Other authors suggest that increasing pressure provides better diffusion of the peroxide solution in fibers (Colodette, 1994). These two proposed methods, increasing pressure and increasing temperature, produce gains in the reaction time with peroxide, improving plant flexibility, although they do not show significant differences regarding peroxide consumption.

Another fundamental factor for avoiding hydrogen peroxide decomposition and/or stage selectivity loss is the removal of pulp heavy metals like iron, copper and manganese, which have high efficiency in certain unfavorable reactions. Thus, removing metals as a pretreatment is essential for hydrogen peroxide stages (Colodette et al., 1993). Cost-effective pulp metals removal could be done under acidic conditions instead of Q-stage (Chelate), which has a high operational cost as well as high environmental impact related to the significant impact on the toxicity levels of the bleaching effluents. However, acidic conditions associated with high temperature, like D_{hot} or A_{hot} stages, could achieve low levels of metals in the pulp and also produce additional reduction in the hexenuronic acid and residual lignin content (Vuorinen et al., 1996; Ratnieks et al., 1997; Daniel et al., 2003; Lachenal and Chirat, 1998; Santos et al., 2001).

In this study, a comparative analysis between D(EOP)DP (reference) and alternative sequences was made. The aim of this work was to obtain pulps with high brightness levels, 90^+ % ISO, from industrial Kraft-O_2 eucalyptus pulp, with low environmental impact and low operating cost of bleaching chemicals. Such ECF-light options cover the usage of hot acid hydrolysis (A_{hot}) and bleaching with ozone at medium consistency and high consistency (Z_{mc} and Z_{hc}) and with pressurized peroxide. According to this, a comparative analysis of bleaching options is made aiming to increase the flexibility of the bleaching sequence to produce pulps with a high brightness level.

METHODS AND MATERIALS

A sample of industrial Kraft-O_2 eucalyptus pulp of kappa number 8.9, viscosity of $19.2 \cdot 10^{-3}$ Pa·s, brightness of 58.6 % ISO, HexA´s content of 47.7 10^{-3} $mol \cdot kg^{-1}$ and COD of 6.6 $kgO_2 \cdot odt^{-1}$ was used throughout this work. Except where otherwise stated, the standard analytical methods from Tappi Standard Methods (2000), Standard Methods for the examination of Water and Wastewater (20^{th} ed., 1998) and Scandinavian Pulp, Paper and Board Testing Committee (SCAN W9:1989) were used. All of the analyses were carried out in duplicate.

The bleaching simulation procedures were standardized, having initiated the first stage of the bleaching sequences with samples of 300 g of over dry pulp. After each bleaching stage, the pulps were washed by a standardized procedure, using a specific volume of 7 $m^3 \cdot odt^{-1}$ of distilled water. In order to evaluate the washing carry-over effects of the laboratory bleaching stages, the reference sequence was also tested by washing after each bleaching stage with an excessive volume of distilled water, in this case with the specific volume standardized at 67 $m^3 \cdot odt^{-1}$. The atmospheric bleaching stages with dioxide (D or D_{hot}) and peroxide (P) were carried out in polyethylene sacks. The following stages were carried out in the Mark V reactor (Quantum Technologies Inc.): hot acid (A_{hot}), oxidative extraction (EOP) and pressurized peroxide (PO) stages.

Bleaching with high consistency ozone was carried out in a glass reactor by sending a gas flow of a known concentration of ozone through a previously disaggregated pulp bed under constant mixing. Bleaching with medium consistency ozone was carried out in a Quantum-Mark V reactor/mixer coupled to an Ozone Cart. Residual ozone was collected in a 5% KI solution and certified by iodometry. Ozone consumption was calculated by the difference between the ozone used and residual ozone.

Brightness reversion tests were made after putting the sheets for 4 h in an acclimatized room heated at 105 ºC for 4 h with 0% relative humidity. Thus, the difference between initial brightness (AD - air dry) and final brightness (OD – over dry) after this above treatment was called brightness reversion. Bleached pulp yields were estimated precisely by the technique of determining total organic carbon (TOC) content in the bleaching filtrates generated in each sequence, which show good correlation with pulp degradation and yield (Costa et al., 2002; Lanna et al., 2002)**.**

In this study, an 0.26 kappa factor, based on the industrial kappa for Kraft-O_2 pulp, was used. As optimized in previous work (Costa et al., 2003a; Costa et al., 2003b), in the (EOP) stage an H_2O_2 load of 3.0 $kg \cdot odt^{-1}$ for pulp was fixed, in the ozonolysis stage (O_3) a load of 4.0 $kg \cdot odt^{-1}$ was fixed, in the P or (PO) stage loads of 3.0 $kg \cdot odt^{-1}$ were fixed and only in the D_1 stage were different dosages of chlorine dioxide (ClO_2) tested, with the aim of obtaining pulps with high brightness levels.

In this work, technological changes were evaluated against the D(EOP)DP reference sequence. These technological changes consisted of inserting an ozonolysis stage at medium consistency or high consistency, a hot acid hydrolysis stage, a stage with or without chlorine dioxide (D_{hot} or A_{hot}), and the washing carry over effect on bleaching capacity after the bleaching stages of the reference sequence. The following bleaching options were tested: D(EOP)DP (reference), D(EOP)D(PO), D_{hot}(EOP)DP, D_{hot}(EOP)D(PO), A_{hot}(EOP)DP, A_{hot}D(EOP)DP, A_{hot}(Z_{hc}D)(EOP)DP, A_{hot}(EOP)(Z_{hc}D)P, $A_{hot}Z_{hc}$DP, (Z_{mc}D)(EOP)DP, Z_{mc}D(EOP)DP, Z_{hc}D(EOP)DP. The main operating conditions of the bleaching stages are given in Table 1.

RESULTS AND DISCUSSION

Washing Carry Over Effect Between Bleaching Stages

A summary of the main bleaching results of each bleaching alternative sequence is given in Table 2. Concretely, the results for AD- and OD-brightness levels in relation to $ClO_2.odt^{-1}$ pulp consumption in the second chlorine dioxide stage of the D(EOP)DP sequence (reference with standard washing) and D(EOP)DP sequence (reference with excessive washing) are presented in Figure 1.

A kappa factor of 0.26 in the first stage was standardized for all tests, as well as the dosage of all other main reagents. This was adopted for all results presented below. The dosage of hydrogen peroxide was also standardized, varying only in the dosage of chlorine dioxide for obtaining pulps with high brightness levels (90% to 93% ISO). In the reference pulp, 7 $m^3 \cdot odt^{-1}$ water was used for standard washing and 67 $m^3 \cdot odt^{-1}$ for excessive washing.

It is known that poorly washed pulp entrains part of the organic material dissolved in the reactions of the previous stage (carry over). In turn, this material consumes chemical reagents in order to be neutralized, resulting in an increase of total chemical consumption in bleaching. For a 92% brightness level, the carry over effect resulted in an increase of 2.5 kg $ClO_2 \cdot odt^{-1}$ in relation to excessively washed pulp.

Brightness level reversion, shown by the OD brightness level in Figure 1, was not strongly influenced by carry over, especially for a brightness level above 90% ISO. From Table 2 it can be observed that carry over did not significantly impact on the viscosity value to reach a determined brightness level. Total yield results were evaluated by estimation using the total organic carbon (TOC) technique. For the bleaching sequences evaluated, this parameter was not significantly influenced by washing excessively each bleaching stage as illustrated in Table 2.

Table 1: Main conditions of bleaching stages

Parameters	D_{hot}/A_{hot}	D	Z_{hc}	Z_{mc}	(EOP)	D_1	P	(PO)
Consistency (%)	10	10	40	10	10	10	10	10
Temperature (^oC)	90	75	25	50	80	75	80 - 90	90
Time (min)	100	40	2	3	15+67	172	150 - 60	60
Pressure (kPa)	-	-	-	-	250	-	-	400
Final pH (± 0.2)	3.0	2.9	2.5	3.0	10.8	3.8-4.5	10.8	10.8
O_3 ($kg \cdot odt^{-1}$)			4.0	4.0	-	-	-	-
ClO_2 (kappa factor)	0.26	0.26	-	-	-	-	-	-
H_2O_2 ($kg \cdot odt^{-1}$)	-	-	-	-	3.0	-	3.0	3.0
$MgSO_4$ ($kg*odt^{-1}$)	-	-	-	-	-	-	-	0.5

Table 2: Summary of the main bleaching results of each alternative sequences

Alternative Sequences	Specific values $kg \cdot odt^{-1}$										Bleached Pulp Quality			
	Mg	ClO_2 [a]	H_2O_2	O_3	TAC [b]	O_2	NaOH	H_2SO_4	TOC [c]	US $	AD, %ISO	OD, %ISO	AD-OD, %ISO [d]	Viscosity, mPa*s
D(EOP)DP		26.6	6		39.1	5	13	3.2	5.1	17.8	90	88.4	1.6	13.6
D(EOP)DP		31.6	6		44.1	5	13	1.	8.0	19.2	92	90.7	1.3	12
D(EOP)DP (washing)		29.1	6		41.6	5	13	2.4	8.7	18.5	92	90.7	1.3	11.5
D(EOP)D(PO)	0.5	26.6	6		39.1	13	13.5	3	7.8	18.7	92	90.7	1.3	13
D_{hot}(EOP)DP		23.1	6		35.6	5	13	3.7	6.1	16.8	90	88.8	1.2	13.2
D_{hot}(EOP)DP		31.6	6		44.1	5	10	1.2	9.4	18.1	92	90.1	1.9	10.9
D_{hot}(EOP)D(PO)	0.5	29.6	6		42.1	13	14.7	2.7	9.1	20.0	92	90.2	1.8	13.3
A_{hot}(EOP)DP		35.0	6		47.5	5	19	7.5	9.7	22.7	89.4	87.5	1.9	10.7
A_{hot}D(EOP)DP		27.3	6		39.8	5	17	8.5	10.3	19.8	92	90.6	1.4	12.4
A_{hot}(Z_{hc}D)(EOP)DP		24.1	6	4	46.6	5	17.2	13	10.4	25.3	93	91.5	1.5	10.3
A_{hot}(EOP)(Z_{hc}D)P		25.0	6	4	47.5	5	20.5	15.5	9.1	26.9	93	91	2.0	10.3
$A_{hot}Z_{hc}$DP		35.0	3	4	51.3		12	10	7.1	23.8	92	90	2.0	10.6
(Z_{mc}D)(EOP)DP		27.1	6	4	49.6	5	19	11	8.4	26.6	93	91.4	1.6	10.8
Z_{mc}D(EOP)DP		25.1	6	4	47.6	5	16.5	11	8.5	25.2	93.1	91.6	1.5	10.1
Z_{hc}D(EOP)DP		24.1	6	4	46.6	5	18.5	10.5	7.9	25.5	93	91.5	1.5	10.6

[a]Chlorine dioxide charge expressed as active Cl_2
[b]Total active chlorine calculated as active chlorine – TAC, kg $Cl_2 \cdot odt^{-1}$ = ClO_2 (as active Cl_2) + $H_2O_2 \cdot 2.09$ + $O_3 \cdot 2.5$.
[c]Total Organic Carbon - TOC, kg $C \cdot odt^{-1}$
[d]Bleached pulp reversion is the difference between air dry (AD) and over dry (OD) brightness obtained after treatment on the oven (4h at 105 ºC with 0% relative humidity)

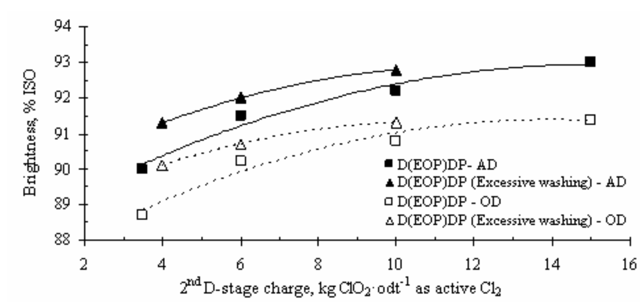

Figure 1: Excessive washing effect between bleaching stages on the AD and OD brightness levels of the D(EOP)DP sequence in relation to chlorine dioxide charge in the second D-stage.

Effect of the (PO) Stage on D(EOP)DP and D_{hot}(EOP)DP Type Squences

In Figure 2, AD and OD brightness level results are shown in relation to chlorine dioxide dosage, in kg of active chlorine.odt^{-1} of pulp, employed in the second D-stage of the [D(EOP)DP (reference) vs D(EOP)D(PO)] sequence.

The results indicate that inclusion of the pressurized hydrogen peroxide (PO) stage produced an increase in the brightness level threshold using lower chlorine dioxide dosages in relation to the reference sequence. For a 92% ISO brightness level, inclusion of the (PO) stage resulted in a savings of 5.0 $kg \cdot ClO_2 \cdot odt^{-1}$, expressed as active chlorine, in relation to the [D(EOP)DP vs D(EOP)D(PO)] reference sequence. The results also indicate that, similarly to the reference sequence, in pulps with higher brightness levels there was a tendency toward greater loss of the OD brightness level.

However, pulp viscosity in the sequence with the (PO) stage showed better results, being one unit higher than the reference pulp, as given in Table 2. The better performance of the D(EOP)D(PO) sequence can also be explained by the employment of 0.5 kg $MgSO_4 \cdot odt^{-1}$ in the (PO)-stage, which minimized hydrogen peroxide decomposition, preserving the oxidative potential of this reagent and protecting yield and viscosity. Yield results, given in Table 2 expressed by TOC profile, showed a trend of slightly better results for pulp using a (PO) stage.

Figure 3 shows the effects of including a pressurized peroxide (PO) stage to replace the last stage of the sequences initiated with hot chlorine dioxide and compares D_{hot}(EOP)DP vs D_{hot}(EOP)D(PO) sequences through AD and OD brightness level results for different chlorine dioxide charges at the second D-stage.

For a 92% ISO brightness level, the inclusion of the pressurized peroxide (PO)-stage permitted a savings of 2.0 kg $ClO_2 \cdot odt^{-1}$ to be obtained, expressed as active chlorine, in addition to a tendency toward a higher brightness level ceiling. This savings in chlorine dioxide was lower than that for the pressurized stage ending the previous sequence initiated with the conventional D_0-stage. However, it indicated a tendency toward a higher brightness level threshold, somewhere around 0.5% ISO higher (see Figure 2 vs Figure 3). However, it was also found that, in these pulps with higher brightness levels, there were also greater reversions values, about 1.8% to 2.5% ISO for the D_{hot}(EOP)D(PO) sequence (Figure 3), as compared to D(EOP)D(PO), somewhere around 1.3% to 1.5% ISO (Figure 2), *i.e.*, the gain in higher brightness level threshold is lost in the form of greater reversion, mainly for final brightness levels above 93% ISO.

Viscosity and yield results estimated by the TOC technique are given in Table 2. Bleached pulp viscosity for the sequence ending with (PO)-stage was 2.4 units higher than pulp obtained by the [D_{hot}(EOP)DP] option. Similarly to the previous sequence, the better performance of the sequence can also be attributed to the use of 0.5 kg $MgSO_4 \cdot odt^{-1}$ in the (PO)-stage, which minimized hydrogen peroxide decomposition, preserving the oxidative potential of this reagent. Moreover, the TOC generation results were slightly lower for the sequence with the (PO)-stage, indicating a slightly high yield, similar to the previous sequence. In both cases, there is the possibility of optimizing the operating conditions of the atmospheric P-stage, in order to preserve viscosity and also yield by adding Mg ions at the hydrogen peroxide stage.

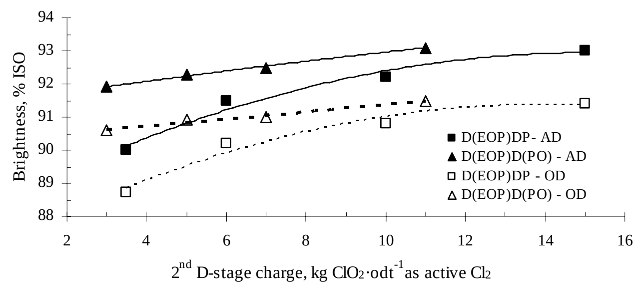

Figure 2: Effect of inserting the (PO)-stage for AD and OD brightness levels in relation to chlorine dioxide charge in the second D-stage of D(EOP)DP vs. D(EOP)D(PO) sequence.

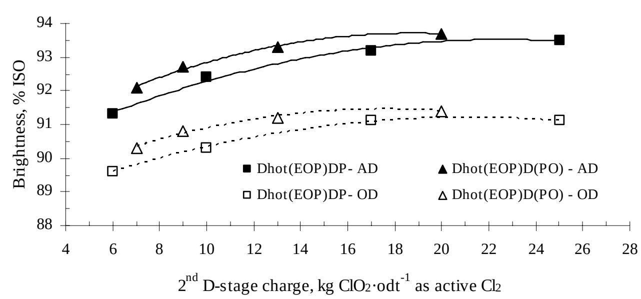

Figure 3: Effect of inserting the (PO)-stage for AD and OD brightness levels in relation to chlorine dioxide charge in the second D-stage of D_{hot}(EOP)DP vs. D_{hot}(EOP)D(PO) sequences.

Effect of D_{hot} Stage in D(EOP)DP and D(EOP)D(PO) Type Sequences

Figure 4 shows AD and OD brightness level results in relation to the kg $ClO_2{\cdot}odt^{-1}$ pulp consumption used in the second D-stage, aiming at obtaining high brightness level pulps, *i.e.*, the D(EOP)DP vs D_{hot}(EOP)DP sequences, and standardizing the dosage of the other chemical oxidants.

In this evaluation, for a 92% ISO brightness level, inserting the D_{hot}-stage did not result in any significant reduction in the chlorine dioxide load. For a 90% ISO brightness level, the inclusion of the D_{hot}-stage resulted in a savings of merely 1.0 kg $ClO_2{\cdot}odt^{-1}$ as active chlorine. It was also found that, for higher brightness level pulps, there was a greater loss in the OD brightness level. The D_{hot}(EOP)DP option presented a reversion of 0.6% ISO over the reference pulp (1.3% ISO) at 90 %ISO and, as shown in Figure 4, the OD curve of the D_{hot}(EOP)DP sequence stayed below that of D(EOP)DP. It could be explained by the optimized kappa factor used at the D_0-stage (Costa et al. 2003a; Costa et al., 2003b). As shown in this previous work, the effect of the D_{hot}-stage on the HexA's (hexenuronic acid) content was somewhat the same as a D_0-stage if the comparison was done at the optimized kappa factor. As a consequence of using the ideal amount of chlorine dioxide charge at the D_0-stage, there is an exact formation of Cl_2 *in situ* that selectively removes HexA compounds.

The results for including the D_{hot}-stage in the (PO) sequence, given in Figure 5, indicate that, for brightness levels between 92% and 93% ISO, inserting the D_{hot}-stage did not significantly affect the required dosage of chlorine dioxide in the second D-stage. The sequence with this stage, however, showed a slightly larger brightness level reversion, *i.e.*, lower OD brightness level. For higher brightness levels, the results indicate a tendency toward similarity to the sequence without the D_{hot}-stage.

Results for total active chlorine (TAC), yield according to TOC and viscosity are shown in Table 2. A greater advantage with the D_{hot}(EOP)DP option was expected, compared to the reference sequence, in relation to dioxide dosage in the second D-stage, or even through chemical charge consumption, since the D_{hot}-stage is typically effective both in pulp delignification and in HexA's removal, producing as a result a reduction in the consumption of bleaching chemicals. On the other hand, this sequence was the one that presented a tendency toward higher yield over the others, as shown by the TOC profile (Table 2).

The D_{hot}(EOP)DP sequence presented the lowest TAC, which will undoubtedly benefit the operating cost of this sequence. Consequently, low TAC charge viscosity results were higher for this sequence. However, enhanced viscosity is due to the use of magnesium sulfate in the (PO) stage, which improved selectivity. Yield results according to the TOC profile were practically to the same as those of the reference sequence.

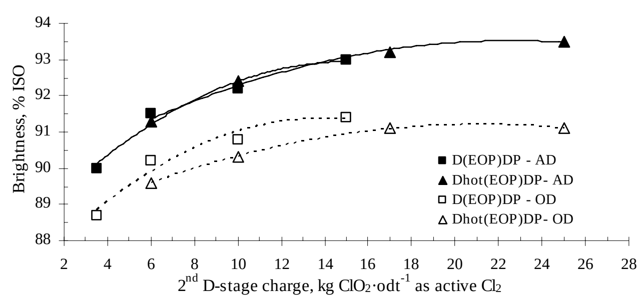

Figure 4: Effect of inserting the D_{hot}-stage in AD and OD brightness levels in relation to the chlorine dioxide charge at the second D-stage of D(EOP)DP vs. D_{hot}(EOP)DP sequences.

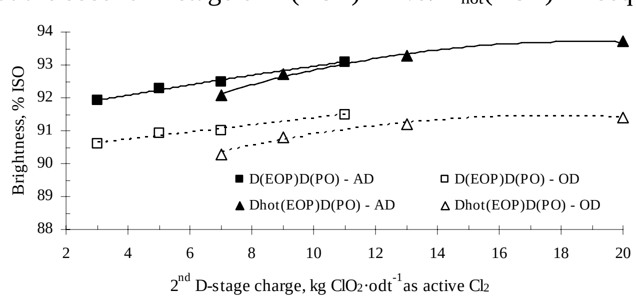

Figure 5: Effect of inserting the D_{hot}-stage in AD and OD brightness levels in relation to the chlorine dioxide charge at the second D-stage of D(EOP)D(PO) vs. D_{hot}(EOP)D(PO) sequences.

Effect of Removing Chlorine Dioxide in the First Stage

One the most important advantages of running a D_{hot}-stage is connected to higher bleaching flexibility, i.e., depending on the bleach plant operation approach, it is possible to get different products at different costs. Figure 6 shows the AD and OD brightness level results in relation to chlorine dioxide charge consumed in the second D-stage for obtaining high brightness level pulps. The objective was to evaluate the effect of replacing the D_{hot}-stage by a hot acid hydrolysis A_{hot}-stage in chlorine dioxide consumption.

The implementation of an A_{hot}-stage impaired the sequence's performance, since this stage does not have the same capacity for removing lignin as the D_{hot} stage does. The kappa number after the A_{hot}(EOP) stages was 5.5 as compared to 2.3 for the sequence with D_{hot}(EOP). Thus, the A_{hot}(EOP)DP sequence did not let the brightness level objective be reached, and the maximum brightness level obtained was 89.4% ISO. Results for viscosity and yield according to TOC profile were not compared due to the different brightness levels (Table 2). However, the replacement of the D_{hot}- stage by a A_{hot}-stage allowed partial bleach plant closure. So in this case, low environmental impact could be achieved and part of the sodium hydroxide make up could be avoided as well, with positive impact on the operation bleach cost.

Effect of Including Additional Washer (5 Stages)

In order to develop a sequence with partial bleach plant closure, the idea of adding a new washer between the A_{hot}- and D-stage was tested. Figure 7 presents the effect of inserting an additional washer on AD and OD brightness level in relation to chlorine dioxide charge at the second D-stage. In this case, the comparison was made between the D_{hot}(EOP)DP and A_{hot}D(EOP)DP sequences.

For a 92% ISO brightness level, inserting an additional washing element [D_{hot}(EOP)DP vs A_{hot}D(EOP)DP] resulted in an improvement in performance of the sequence, producing an specific savings of 4 kg $ClO_2 \cdot odt^{-1}$, expressed as active chlorine. In addition to reducing chlorine dioxide consumption and providing pulps with a ceiling over 93% ISO brightness level, the washer after the hot acid stage also worked as an option for partially closing the wastewater circuit, in this case considering the filtrate return from the washer to the recausticizing plant (Costa et al., 2006). It was also found that, for pulps with higher brightness levels, there is a greater loss of OD brightness level, but remaining at levels above the reference level, when compared at the same final brightness level.

Results for total active chlorine (TAC), yields according to TOC profile and viscosities are given in Table 2. The A_{hot}D(EOP)DP sequence showed slightly higher viscosity than the pulp of the D_{hot}(EOP)DP sequence. TOC generation was somewhere around 1 kg $C.odt^{-1}$ higher than the D_{hot}(EOP)DP sequence, which consequently indicates a slight negative impact on bleaching yield. As this sequence required a smaller dosage of reagents (TAC), the higher TOC values can be explained by the lower selectivity of the acid hydrolysis stage.

Effects of Including a Z-Stage in the D(EOP)DP Sequence

The effect of inserting a Z-stage at medium consistency in the reference sequence, both with and without washing [D(EOP)DP vs (Z_{mc}D)(EOP)DP vs Z_{mc}D(EOP)DP], on the AD and OD brightness level can be seen at Figure 8.

For a 93% ISO brightness level, the Z_{mc}D(EOP)DP sequence resulted in a savings of 2.0 kg $ClO_2 \cdot odt^{-1}$, indicating that the carry over present in the pulp consumes a part of the ozone in oxidation reactions of organic matter. Comparison against the D(EOP)DP reference sequence indicates significant benefits for including the medium consistency ozone stage and, for brightness levels of somewhere around 93% ISO, the savings was about 6 kg $ClO_2 \cdot odt^{-1}$, expressed as active chlorine, without washing after the Z-stage. When washing was done after the Z-stage, this savings rose to 8 kg $ClO_2.odt^{-1}$. In general, for both Z-ECF sequences, adding 4 kg $O_3.odt^{-1}$ resulted in a higher brightness ceiling level (up to 94% ISO) and, consequently, partial displacement of chlorine dioxide charge as mentioned above. There was also a higher OD brightness ceiling level, up to 92% ISO.

Results for total active chlorine (TAC), TOC generation and bleached pulp viscosity are given in Table 2. TAC was higher for sequences with ozone, by including hydrogen peroxide and ozone in equivalent active chlorine. TOC results were somewhat higher, indicating a tendency toward smaller yields. As expected, viscosity results were also slightly lower.

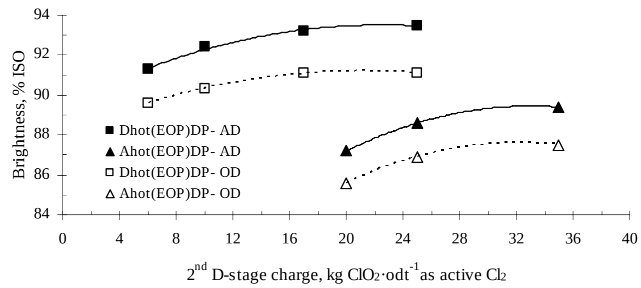

Figure 6: Effect of replacing the D_{hot}- to A_{hot}-stage in AD and OD brightness levels in the last D-stage of the D_{hot}(EOP)DP and A_{hot}(EOP)DP sequence.

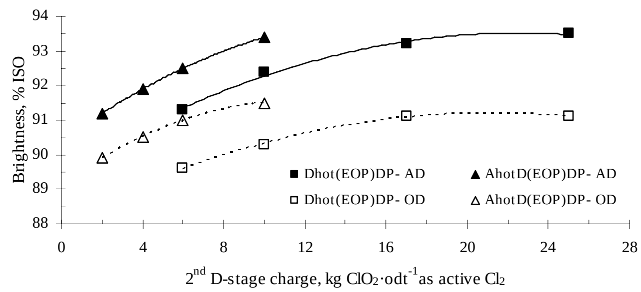

Figure 7: Effect of inserting an additional wash on AD and OD brightness level results in relation to chlorine dioxide charge at the second D-stage of the D_{hot}(EOP)DP and A_{hot}D(EOP)DP sequences.

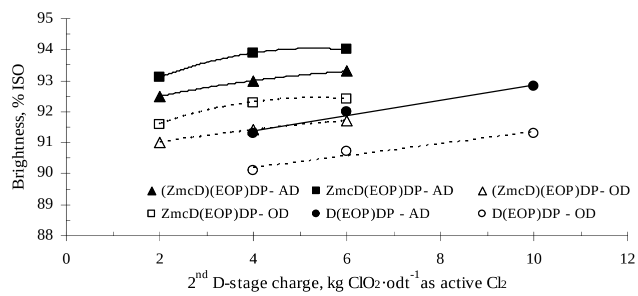

Figure 8: Effect of inserting a Z-stage as a first stage of the reference sequence both with and without washing [D(EOP)DP vs (Z_{mc}D)(EOP)DP vs Z_{mc}D(EOP)DP] on the AD and OD brightness level results in relation to chlorine dioxide charge at second D-stage.

Effect of Z-Stage Consistency

Figure 9 shows the effect of Z-stage consistency on AD and OD brightness level in relation to chlorine dioxide charge used in the second D-stage of the Z_{hc}D(EOP)DP vs Z_{mc}D(EOP)DP sequences to obtain high brightness level pulps. The aim was to evaluate the effect of ozonolysis stage consistency and evaluate the impact on the pulp's bleaching capacity.

For a 93% ISO brightness level, the sequence with a high consistency ozonolysis resulted in a savings of 1.0 kg $ClO_2 \cdot odt^{-1}$, expressed as active chlorine, when compared against a similar sequence using medium consistency [Z_{hc}D(EOP)DP vs Z_{mc}D(EOP)DP]. This fact was mainly due to a reduction of the carry over present in Kraft-O_2 pulp when higher consistencies were used. For both sequences, a brightness level threshold of up to 94% ISO was obtained with similar dosages of chlorine dioxide in the second D-stage. This savings of chemical (1.0 kg $ClO_2 \cdot odt^{-1}$) would hardly justify the extra investment of operating with high consistency vs medium consistency due to the additional equipment involved.

Results for total active chlorine (TAC), yields according to TOC profile and viscosity are given in Table 2. TAC and TOC presented a tendency toward slightly lower values for the Z-stage with high consistency, while viscosity results were similar.

ECF-Light Bleaching Technology Adapted to Partial Bleach Plant Closure

Nowadays, besides high brightness levels, the bleaching sequence should have low environmental impact. The Figure 10 shows the results for the alternate sequences that were adapted to partial bleach plant closure while attaining a high brightness level. The ceilings of AD and OD brightness are also shown in relation to chlorine dioxide charge used in the second D-stage of the $A_{hot}Z_{hc}DP$ and $A_{hot}(EOP)(Z_{hc}D)P$ sequence.

The $A_{hot}(EOP)DP$ sequence could be an alternative sequence adapted to partial bleach plant closure. However, it did not attain a brightness level result higher than 90% ISO (Figure 6). In fact, it reached its brightness level threshold slightly below this value and thus cannot be evaluated by comparison against the other sequences. The $A_{hot}Z_{hc}DP$ and $A_{hot}(EOP)(Z_{hc}D)P$ sequences attained brightness levels of somewhere around 92% to 93% ISO, respectively, and are technology adapted to partial bleach plant closure. The slightly higher performance of the $A_{hot}(EOP)(Z_{hc}D)P$ sequence was due to the Z–stage position, which in this case happens after the second bleaching stage. It should be noted that both Z-ECF sequences have the same number of stages and consequently the same number of washings.

In terms of dosage of reagents, expressed here as active chlorine, the $A_{hot}(EOP)(Z_{hc}D)P$ sequence would produce a savings of somewhere around 13 kg active chlorine·odt^{-1} to attain a brightness level of 92% ISO when compared against the $A_{hot}Z_{hc}DP$ sequence, which is explained by its higher brightness level threshold provided by oxidative extraction. Brightness level reversions were similar between the sequences that were evaluated, being somewhere around 2% ISO, with a slight increment for the highest brightness levels.

Results for total active chlorine (TAC), yields according to TOC and viscosities are given in Table 2. Compared with the $A_{hot}(EOP)(Z_{hc}D)P$ sequence, the $A_{hot}Z_{hc}DP$ sequence required a higher dosage of reagents to attain higher brightness level values. However, this sequence presented significantly lower TOC generation, thus indicating higher yield. Viscosity results were similar for both sequences.

In relation to partially closing the wastewater circuit, these two sequences, $A_{hot}Z_{hc}DP$ and $A_{hot}(EOP)(Z_{hc}D)P$, produced a return through the brown wash of filtrates from the first two bleaching stages. This return of filtrates and the recycling points should be well studied to avoid incrustation in bleaching, mainly with carbonates and oxalates, since pH and temperature “shocks” could occur.

The decision on the best sequence for circuit closing should also take into account the operating cost of each sequence and, to this effect, a focus on operating costs with chemical reagents is covered in the next topic of this work.

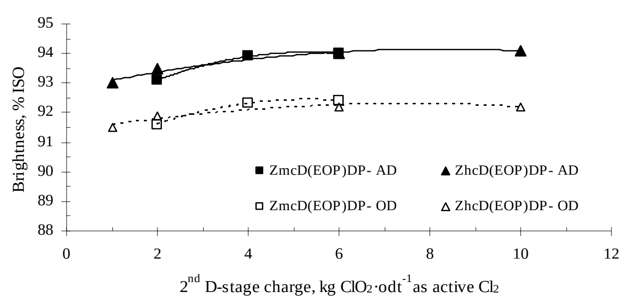

Figure 9: Effect of Z-stage consistency on AD and OD brightness level results in relation to chlorine dioxide charge at the second D-stage of the $Z_{hc}D(EOP)DP$ vs. $Z_{mc}D(EOP)DP$ sequences.

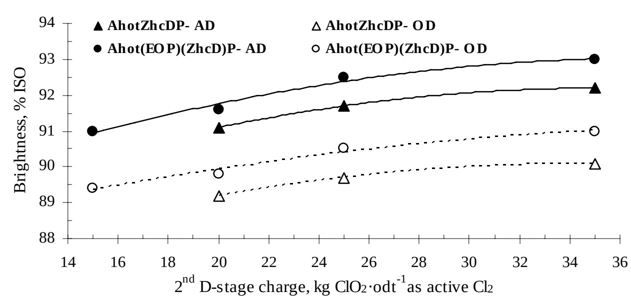

Figure 10: Ceiling of AD and OD brightness in relation to chlorine dioxide charge used in the D-stage of the $A_{hot}Z_{hc}DP$ and $A_{hot}(EOP)(Z_{hc}D)P$ sequence.

Specific Bleaching Operating Cost

Table 3 shows the specific operating costs of main bleaching chemicals used in each alternative sequence evaluated for different AD brightness levels. All the cost values were calculated for consumption estimated according to laboratory test results. The following bleaching chemicals values were used as a basis of operating cost calculation: US$ 0.342/kg NaOH; US$ 0.8/kg ClO_2, US$ 0.08/kg H_2SO_4; US$ 0.75/kg H_2O_2; US$ 0.1/kg O_2; US$ 1.5/kg O_3; US$ 0.23/kg $MgSO_4$.

A comparison of costs for bleaching reagents in the reference sequence D(EOP)DP using standard washing vs excessive washing impacted positively on operating costs, somewhere around US$ 1·odt^{-1} to US$ 1.5·odt^{-1}, representing a reduction of approximately 4% due to the lower consumption of reagents already discussed above. This lower operating cost indicates that a more efficient wash can have financial returns and should be analyzed case by case.

Considering brightness levels in the range of 92% to 93.5% ISO, the sequence that obtained the lowest operating cost for chemicals in bleaching was the D_{hot}(EOP)D(PO) sequence, with a bleaching operating cost of somewhere around US$ 19 ·odt^{-1} to US$ 21·odt^{-1}, under the conditions of the sequences that were evaluated and costs of reagents considered.

A comparison of the costs of the reference sequence, D(EOP)DP, against the D_{hot}(EOP)DP sequence indicated that adding a hot chlorine dioxide, D_{hot}, stage produced a significant reduction in operating costs, from US$ 27·odt^{-1} to US$ 19,70·odt^{-1}, about 30% in relation to reference costs for a 92% ISO brightness level.

On the other hand, comparing the D_{hot}(EOP)DP sequence against the D_{hot}(EOP)D(PO) sequence indicated an insignificant reduction in operating costs, going from US$ 19.70·odt^{-1} to somewhere around US$ 19.01·odt^{-1}, *i.e.*, adding the (PO)-stage produced an additional reduction of only 3% for a brightness level of 92% ISO. When higher brightness levels are considered, the effect of the pressurized peroxide (PO) stage became significant; for example, at a brightness level of 93.5% ISO, the operating cost was reduced from somewhere around US$ 25·odt^{-1} to approximately US$ 21·odt^{-1}, indicating a 16% reduction in costs that can be assigned to the (PO)-stage.

Another cost reduction for chemicals that stood out was the sequence that included an acid hydrolysis stage, A_{hot}D(EOP)DP. The inclusion of the A_{hot}-stage significantly reduced costs with chemical reagents by the already familiar reduction in hexenuronic acid content and ensuing savings in chlorine dioxide charge. Cost reduction for reagents was somewhere around 27%, from about US$ 27.15·odt^{-1} to US$ 19.80·odt^{-1}, which is significant; however it should be taken into account that this effect was obtained considering a complete stage that included an additional washer, *i.e.*, comparing a 5 stage sequence against a 4 stage one. Any eventual yield loss due to acid hydrolysis should also be considered.

Some of the sequences with ozone produced a significant rise in the brightness threshold level. In the case of (Z_{mc}D)(EOP)DP, however, operating costs stayed in the range of US$ 24·odt^{-1} to US$ 26·odt^{-1}, approximately 15% more than for the D_{hot}(EOP)D(PO) sequence for brightness levels of somewhere around 93% ISO. However, these sequences can be interesting when high brightness levels are required.

Table 3: Specific operating costs of main bleaching chemicals used in each alternative sequence evaluated for different AD brightness levels

Alternative sequences	**Bleaching Chemical Cost, US$·odt^{-1}**				
AD Brightness, % ISO	**91**	**92**	**93**	**93.5**	**94**
D(EOP)DP (reference)	26.01	27.15	28.97		
D(EOP)DP (excessive washing)	25.41	25.99	28.06		
D(EOP)D(PO)	20.51	22.49			
D_{hot}(EOP)DP		19.72	22.16	25.04	
D_{hot}(EOP)D(PO)		19.01	20.41	20.92	
A_{hot}D(EOP)DP	19.25	19.78	20.95	21.48	
A_{hot}(Z_{hc}D)(EOP)DP			25.25	26.05	26.61
A_{hot}(EOP)(Z_{hc}D)P	23.30	26.86	28.19		
$A_{hot}Z_{hc}$DP	17.63	23.80			
(Z_{mc}D)(EOP)DP			24.50	26.40	27.05
Z_{mc}D(EOP)DP			25.16	25.42	26.30
D(EOP)Z_{hc}P	27.17				
D(EOP)(Z_{hc}D)P		21.50	23.40		

A sequence with ozone that stood out was $A_{hot}Z_{hc}DP$, which presented a lower operating cost than the others, approximately US$ 17.63·odt^{-1} for a brightness level of 91% ISO, but increased to US$ 23.80·odt^{-1}, somewhere around 25%, for a brightness level of 92% ISO. This sequence can be interesting as an alternative when bleaching technology adapted to partial bleach plant closure was required due to environmental concerns. As mentioned in the literature (Costa et al., 2006), if this operation mode was running another additional gain should be on balances such as energy savings and sodium hydroxide make-up, as well as water and effluent treatment costs.

CONCLUSIONS

The main conclusions obtained from this work with alternative bleaching sequences on a lab scale were:

- All of the sequences evaluated have the potential to be used as technologies for producing bleached pulp with a high brightness level (90^{+}% ISO), except for the A_{hot}(EOP)DP sequence, which did not attain the desired brightness levels. On the other hand, the D_{hot}(EOP)D(PO) sequence presents a lower operating cost for brightness above 92 % ISO. However, this kind of sequence does not allow for closing the wastewater circuit, not even partially.
- For brightness level around 91% ISO, the $A_{hot}Z_{hc}DP$ sequence presented a lower operating cost than the others. This alternative sequence should be evaluated when partial bleach plant closure is desirable and consequently could achieve low environmental impact.
- Considering a brightness level above 92% ISO among the evaluated sequences, the one with the best performance in terms of dosage of chemical reagents and respective operating cost was the D_{hot}(EOP)D(PO) sequence.
- The D_{hot}(EOP)DP sequence in relation to the reference sequence, D(EOP)DP, indicates that adding a hot chlorine dioxide, D_{hot}, stage produces a significant improvement in bleaching performance and significant reduction in operating costs for a brightness level of somewhere around 92% ISO.
- The D_{hot}(EOP)D(PO) sequence compared against the D_{hot}(EOP)DP sequence indicates that adding a pressurized peroxide (PO) stage produces an additional reduction of only 3% for a brightness level of 92% ISO. When higher brightness levels are considered, the effect of this (PO)-stage becomes significant.
- A comparison between Z-stage at high and medium consistency indicates a savings of somewhere around 1 kg active Cl_2.odt^{-1}, which could not justify any additional investment for a bleaching Z-stage with high consistency.
- In general, Z-ECF sequences showed a higher brightness level threshold; these sequences could be interesting when high brightness levels are required coupled with bleach plant closure.
- For a brightness level of 92% ISO, washing affects the pulp's bleaching capacity. The D(EOP)DP sequence (reference with excessive washing) required less chlorine dioxide than the D(EOP)DP sequence (reference), which produced a reduction of somewhere around 4% in costs with reagents.

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