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Optimal Conditions for Bleaching Eucalyptus Kraft Pulp with Three Stage Sequence

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Abstract

In December 2003 Suzano Papel & Celulose S/A company implemented a three stage sequence to produce fully bleached (88-90% brightness) eucalyptus kraft pulp at the Suzano mill. In order to guarantee a smooth operation, a thorough optimization study of the bleaching process was previously undertaken in the laboratory and the most significant results are reported in this paper. Also, some significant results of the successful mill operation are given. An oxygen delignified eucalyptus kraft pulp of kappa 10.5, viscosity 21.2 mPa.s and brightness 52.3% ISO was used throughout the study. The laboratory study involved the optimization of the most significant variables of the D_{HT}(PO)D sequence, including D_{HT}-stage temperature, kappa factor and pH, (PO)-stage temperature, pH, magnesium sulfate charge and oxygen charge, and D-stage chlorine dioxide charge and pH. It was concluded that optimum D_{HT} stage conditions include a temperature of 80-85 °C, kappa factor of 0.25 and pH 3.0. Extremely high temperatures penalize pulp viscosity and yield. Increasing D_{HT} stage temperature over 85 °C results in significant kappa number decrease but causes pulp darkening and, as a result, no significant brightness improvement is achieved at the end of bleaching. Decreasing D_{HT} stage pH under 3.0 also results in significant kappa drop but causes pulp darkening and significant viscosity loss. Increasing (PO) stage temperature from 80 to 95°C penalizes process efficiency and selectivity and the use of oxygen in this stage is completely unnecessary. The final D-stage of the D_{HT}(PO)D sequence is much more efficient when run at pH 5.5, contrary to the common belief that this stage should be run in the range of pH 3.5-4.0. For a brightness of 89% ISO, the bleach plant optimized according to the findings above presented very low chemical consumptions (9.7 kg/adt ClO₂, 4.5 kg/adt H₂O₂, 8.6 kg/adt NaOH). The results of the laboratory study have been successfully verified under mill operation for about 12 months. After the implementation of the new bleach plant the chlorine dioxide, hydrogen peroxide and sodium hydroxide consumptions at the mill decreased by about 21, 58 and 18%, respectively.

Introduction

Eucalyptus kraft pulp bleaching to full brightness with a three-stage sequence became standard practice in Brazil after the wide adoption of hot chlorine dioxide bleaching technology [1-8]. The slight decrease chlorine dioxide demand [4] and slight increase in pulp brightness stability [9] provided by this technology has made possible the elimination of the fourth bleaching stage commonly installed in the older bleach plants. However, a three stage bleaching sequence requires careful optimization to deliver full brightness even when it contains a D_{HT} stage. The proper pH, temperature and kappa factor required to run the D_{HT} stage are still a matter of debate, particularly in regard to yield losses and effluent load. In addition, the impact of this stage on the operation of the subsequent (PO) and final D stages is not entirely clear. Considering that the kappa number of the pulp leaving the D_{HT} stage is rather low and comprised largely of HexA's, the use of oxygen in the (PO) stage is questionable, but the use of Mg in this stage may be important given that D_{HT} stage causes significant viscosity loss. Furthermore, the ideal pH in the final D stage may not be the usual (3.5-4.0) for pulps treated with the

D_{HT} stage. The brightening capability of chlorine dioxide is higher in the 4.5-5.5 pH range, particularly when pulp arriving at this stage contains very little residual lignin. Thus, the ideal pH of the final D-stage depends upon the efficiency of the previous stages. Proper choice of operating conditions for each bleaching stage allows for meeting the brightness target at the lowest chemical cost. The choice of conditions must also take into account the potential yield losses derived from hot stages and implications with regard to pulp quality and environmental load.

The objective of this study was to optimize the main operating conditions of each stage of the $D_{HT}(PO)D$ sequence in order to produce high quality bleached eucalyptus kraft pulp at the lowest chemical costs and environmental impact.

Material and Methods

An oxygen delignified eucalyptus kraft pulp (kappa 10.5, viscosity 21.2 mPa.s and ISO brightness 52.3%) derived from a brown pulp (kappa 19.6; HexA's 56.8 mmol/kg; viscosity 36.9 mPa.s, ISO brightness 29.1%, 1.2 ppm Cu, 16.7 ppm Mn, 23.7 ppm Fe, 712 ppm Ca and 117 ppm Mn) was used throughout the study. Oxygen delignification (O) was optimized and the following conditions were used in the O-stage: 10% consistency, 46 min, 100°C, 500 kPa final pressure, 27 kg/adt NaOH applied as oxidized white liquor, 18 kg/adt O_2 and 1.5 kg/adt $MgSO_4$. The most significant variables of the $D_{HT}(PO)D$ sequence were optimized, including: hot chlorine dioxide stage (D_{HT}) temperature (70, 80, 90 and 95°C for 120 min), kappa factor (0.15, 0.20, 0.25 and 0.30) and pH (2.5, 3.0, 3.5 and 4.0); oxygen/peroxide pressurized extraction stage (PO) temperature (80, 85 e 95°C for 60 min), anhydrous magnesium sulfate charge (0 and 3.0 kg/t); oxygen dose (0 and 4.0 kg/t) and end pH (10.0 and 11.0); final chlorine dioxide stage (D) chlorine dioxide charge (2.0, 4.0 and 6.0 kg/odt) and pH (3.5, 4.5 and 5.5). The O, D_{HT} and (PO) stages were carried out in a model Mark V mixer/reactor (Quantum Technologies Inc.) whereas final D stage was carried out in polyethylene bags. The required doses of acid or base required to adjust pH were in all cases determined in preliminary experiments using the trial and error technique. After each bleaching stage, run in duplicate, the samples were washed with the equivalent to 9 m³ of distilled water per oven dried ton (odt) of pulp. Reagent doses are expressed in kg/odt (oven dried tons) of pulp. Chlorine dioxide doses are expressed as such.

Pulp kappa number, viscosity, brightness and brightness stability values were measured according to Tappi procedures. Pulp xylans contents was determined through HPLC - RID (model LC-10AD VP – Shimadzu). Pulp OX and filtrate AOX values were measured in an absorbable organic halogen analyzer (ECS 1600 – Euroglas), according to SCAN procedures. Filtrate total organic carbon (TOC) values were measured directly in a Shimadzu model 5000A TOC analyzer. Overall bleaching yield was determined indirectly by analyzing TOC in the bleaching filtrates and converting carbon loss into yield loss through proper calibration equations.

Results and Discussion

Hot Chlorine Dioxide Stage (D_{HT}) Optimization

Table 1 shows that kappa # and viscosity, measured after the (PO) stage, decrease with increasing D_{HT} stage kappa factor and temperature. Brightness, on the other hand, increases with kappa factor but tends to decrease with increasing temperature above 80 °C. The negative impact of temperature on brightness is explained by the brightness reversion reactions caused by maintaining the pulp at high temperature over a long period of time in the complete absence of chlorine dioxide [4]. The hot acid treatment induces formation of new lignin phenolic hydroxyl groups, which may give rise to new chromophores [10]. However, the brightness loss caused by increasing D_{HT} stage temperature is recovered in the second (PO) and third (D) bleaching stages. For a fixed total active chlorine dose,

maximum final brightness was actually obtained when the D_{HT} stage was run at 95°C, a result of the lower post extraction kappa number at this temperature (Table 1).

To produce fully bleached pulp with a three-stage sequence the kappa number after the second stage must be in the range of 2. The results in Table 1 indicate that this number is not achieved with kappa factors lower than 0.25 and temperature lower than 90 °C in the D_{HT} stage. Raising the temperature over 90°C has no significant effect on kappa # at kappa factors equal to or above 0.25. These results indicate that a kappa factor of 0.25 and temperature of 90 °C are appropriate for the D_{HT} stage with the pulp evaluated. However, it is worth noting that at 90 °C or above the pulp viscosity is significantly penalized at the higher kappa factors (0.25 and 0.30), suggesting that pulps of low viscosity may require temperatures lower than 90 °C in the D_{HT} stage, likely in the range of 80-85°C, in order to maintain pulp quality. In other words, the ideal temperature to run the D_{HT} stage depends upon the viscosity loss that can be accepted in this stage.

Increasing D_{HT} stage pH from 2.5 to 4.5 increased the kappa number measured after extraction (Fig 1A). Brightness also increased with increasing pH up to 3.5 and then decreased (Fig 1B). The most significant brightness increase occurred when pH was raised from 2.5 to 3.0. Considering that the post extraction kappa number of 2.0 was achieved at pH 3.0 with the chosen 0.25 kappa factor, this pH was considered ideal because of the higher brightness (Fig 1B) and viscosity (Fig 1C) and the lower demand of acid for pH adjustment.

The superior delignification efficiency obtained at pH 2.5 is explained by the larger presence of elemental chlorine in the system at this pH in relation to the higher pH values. This also explains the lower brightnesses, given that elemental chlorine is not effective as a brightening agent and can harm viscosity particularly at the high temperature used in the D_{HT} stage (90 °C). The decrease in brightness and viscosity as pH increased above 4 may be explained by the increase of hypochlorous acid concentration in the reaction media.

Table 1. Optimization of D_{HT} stage temperature for an eucalyptus kraft-O₂ pulp¹

D _{HT} Stage ²			(PO)-stage ³				D-Stage ⁴			
Temp, °C	ISO Bright, %	Yield, %	ISO Bright, %	Kappa No.	Visc, mPa.s	Yield, %	ISO Bright., %	Reversion % ISO	Visc, mPa.s	Yield, %
70	70.9	98.6	86.1	3.0	18.2	99.0	89.8	2.2	16.2	99.7
80	71.3	98.7	85.7	2.7	17.0	98.9	90.2	2.0	15.0	99.6
90	69.6	98.3	85.5	2.0	13.8	98.7	90.0	1.9	12.3	99.7
95	69.1	98.3	85.4	1.9	12.5	98.6	90.7	2.1	11.5	99.7

¹Kappa 10.5; viscosity 21.2, ISO brightness 52.3% ISO; ²10.5% consistency, 120 min, pH 2.9-3.1, KF 0.25;

³11.5% consistency, 85°C, 60 min, 400 kPa; 5 kg/odt H₂O₂; 11 kg/odt NaOH, pH 11.3-11.4; ⁴11.2% consistency, 85°C, 150 min, 5.7 kg ClO₂/odt, pH 4.1-4.4.

Pressurized Peroxide Stage (PO) Optimization

For the optimization of the (PO) stage a large quantity of pulp was prepared in the D_{HT} stage run under optimized conditions (pH 3.0, KF 0.25, temperature 80 °C and 120 min reaction time). The (PO) stage was optimized to a kappa target around 2.5 and viscosity about 20mPa.s, through the evaluation of pH, temperature and oxygen and magnesium doses. The results shown in Figures 2A indicate that an end pH of 10 is adequate for the (PO) stage run at the temperature of 80 °C. An increase in pH to 11 has very little impact on kappa number viscosity and brightness. On the other hand, the increase in temperature from 80 to 95°C causes a drop in pulp viscosity and brightness, but an increase in kappa number (Fig. 2B). The use of oxygen in the (PO) stage is unnecessary. In fact, oxygen causes a slight drop in pulp brightness (Fig. 2C). The use of magnesium has a positive effect both on brightness and viscosity (Fig 2D).

Ending the (PO) stage at the lowest feasible pH is always good practice to minimize sodium hydroxide consumption and dissolution of hemicelluloses. On the other hand, too low a pH in the (PO) stage may be risky in three stage bleaching sequences because insufficient extraction may leave materials in the pulp such as carbonyl groups derived from carbohydrates or lignin that can cause pulp brightness reversion. Longer sequences containing at least two extraction stages are more tolerant to lower pH values in the extraction stages. The results of this study showed however that an end pH of 10 is sufficient to produce satisfactory results with the $D_{HT}(PO)D$ sequence.

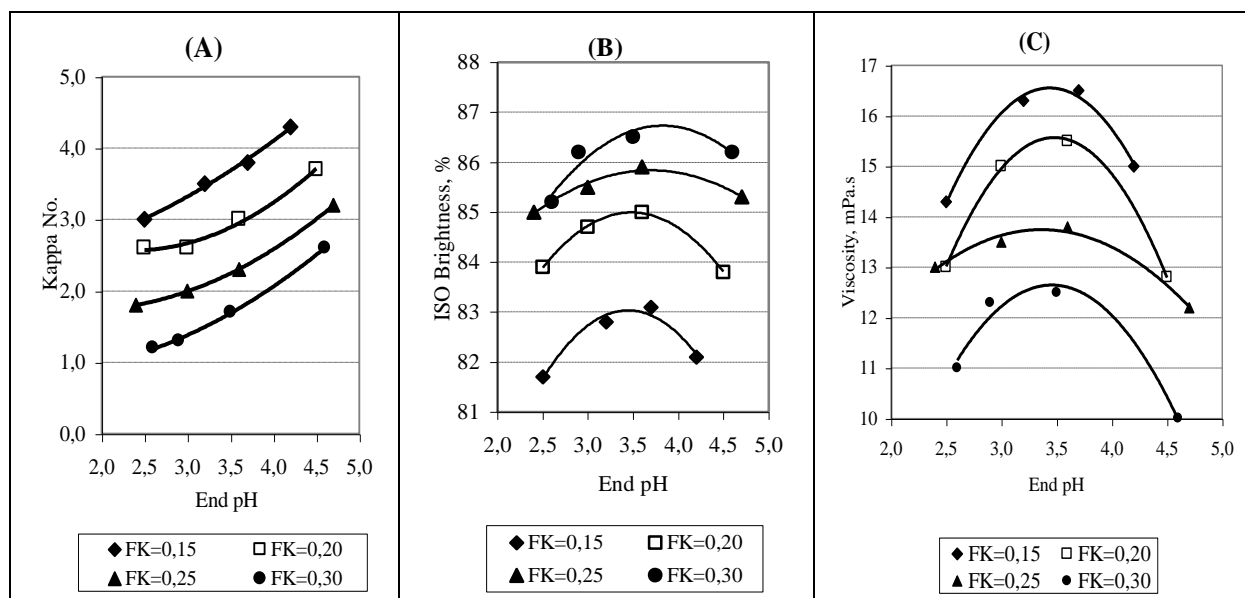
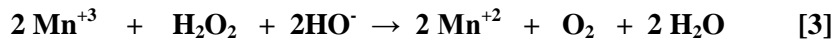
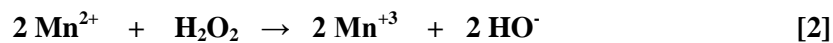


Fig. 1. Effect of D_{HT} stage pH and kappa factor on pulp kappa (A), brightness (B) and viscosity (C) measured after the (PO) stage (90 °C temperature and 120 min in D_{HT}).

For bleaching sequences starting with a hot chlorine dioxide stage (D_{HT}) it is interesting to run the (PO) stage at higher temperatures to take advantage of the hot pulp. Thus, the choice of temperature in the (PO) stage is no longer limited by steam demand but rather by the stage performance. The results of Figure 2B show that too high a temperature in the (PO) stage (95°C) is harmful. The high temperature results in total consumption of the applied hydrogen peroxide, likely caused by heat induced peroxide decomposition. At the lower temperature (80°C), some peroxide left over at the end of the reaction, indicating lower peroxide losses by decomposition. Consequently, a better (PO) stage performance obtained at this temperature.

Oxygen decreases the (PO) stage performance. Thus, it is suggested that oxygen be eliminated from (PO) or (EPO) stages for bleaching or eucalyptus kraft pulp in modern sequences starting with a hot chlorine dioxide stage (D_{HT}). Oxygen is a very helpful delignifying agent when applied in the extraction stages of softwood bleach lines. Softwood pulp contains a sizeable kappa number (4-6 units), largely comprised of lignin, when it reaches the first extraction stage. On the other hand, eucalyptus pulp enters the first extraction stage with very low kappa numbers (1.5-3.0), which are largely comprised of hexenuronic acids. Since oxygen does not react with hexenuronic acids [11] it has very little role when applied in the first extraction stage. The slight negative impact of oxygen on (PO) stage performance may be explained according to Wekeza & Ni's [12] proposal of acceleration of peroxide decomposition by oxygen through the redox mechanism shown below (reactions 1-3). The production of Mn^{3+} by oxygen complicates peroxide stabilization by Mg^{2+} , which is more effective in stabilizing peroxide against Mn^{2+} but not so effective against Mn^{3+} . Considering that the pulp studied contained a significant amount of manganese (10.8 ppm) it is not unlikely that oxygen accelerated the manganese induced peroxide decomposition, thus decreasing (PO) stage performance. In fact, peroxide consumption tended to be higher in the experiments using oxygen, which corroborates the

theory that oxygen can enhance peroxide decomposition. Since oxygen had no lignin to oxidize, its negative impact on peroxide stability resulted in overall loss of performance of the (PO) stage.



The use of magnesium sulfate in the (PO) stage improves its performance (Fig. 4D). According to Lidén & Öhman [13] this should be expected given that magnesium precipitates (hydroxides, carbonates) are effective in counteracting the negative impact on peroxide stability of manganese present in the pulp, particularly in the form of Mn^{2+} . Magnesium present in precipitates formed under the alkaline conditions of peroxide bleaching is replaced isomorphically by Mn^{2+} . In fact, higher peroxide residuals were observed in the experiments having magnesium as an additive.

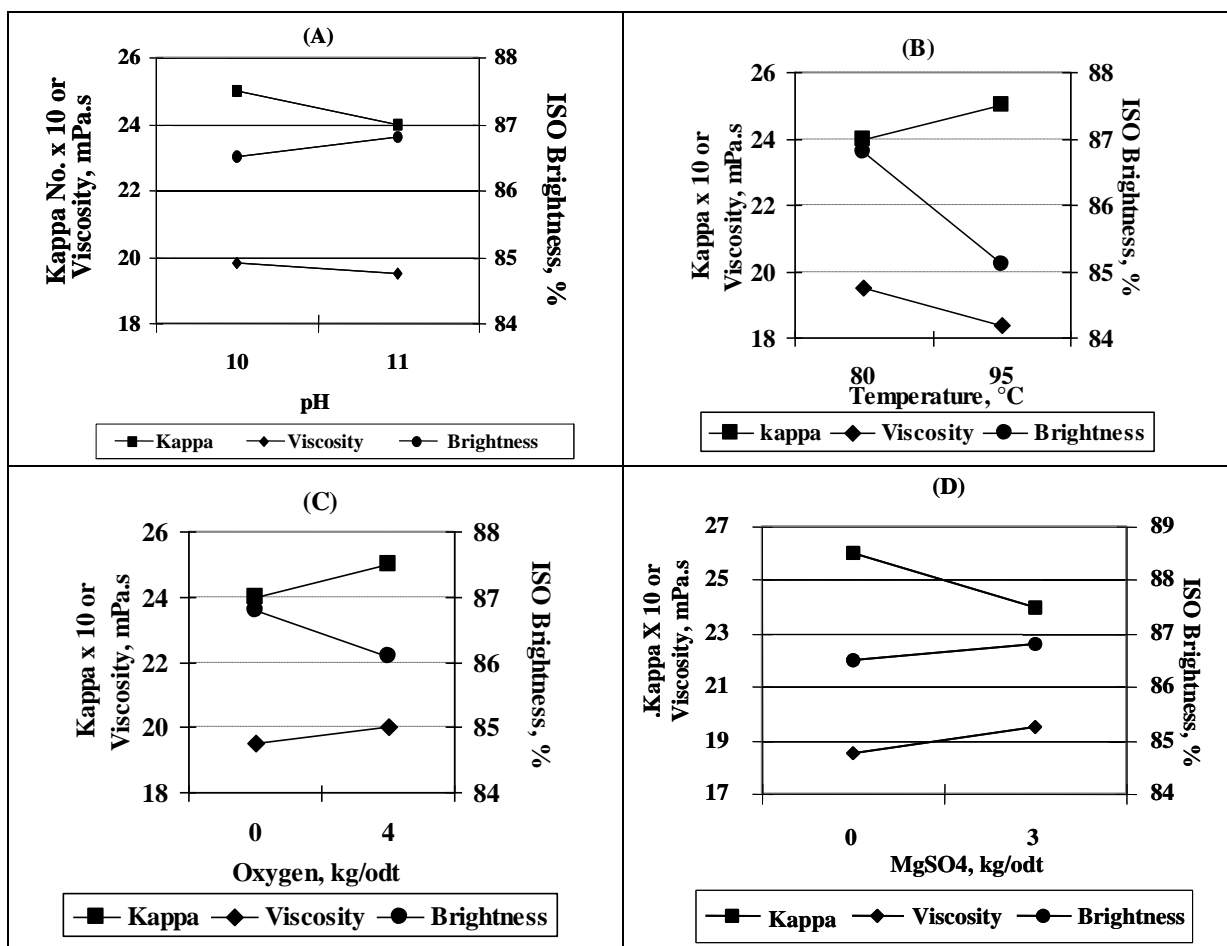


Fig 2. Effect of (PO) stage pH (A), temperature (B), oxygen charge(C) and magnesium charge (D) on pulp kappa, viscosity and brightness. Pulp previously treated with KF 0.25, pH 3.0 and 80 °C in D_{HT} -stage.

Chlorine Dioxide Stage (D) Optimization

For optimization of the final D stage a large quantity of pulp was prepared in the (PO) stage run under optimized conditions (end pH 3.0, 5 kg/odt H₂O₂, 3 kg/odt MgSO₄, no oxygen, temperature 80 °C and 120 min reaction time). The final stage was optimized to 89 and 90 % ISO brightness targets through the evaluation of end pH and chlorine dioxide doses in this stage. The results shown in Figure 3A indicate that final brightness increases with increasing pH in the range of 3.5 to 5.5, different from results reported elsewhere [14]. For the 90% ISO brightness target the ClO₂ requirement at end pH 5.5 is only 2.0 kg/odt whereas at pH 4.5 and 3.5 the requirements are 6 and 5 kg/odt of ClO₂, respectively. Note that brightening efficiency is higher at pH 5.5 despite the fact that more chlorine dioxide is converted into chlorite at this pH value (Fig 3B). The content of OX in the pulp bleached to 90% ISO brightness also decreases with increasing end pH as should be expected (Fig 3C). Pulp viscosity tends to decrease with increasing D-stage pH from 3.5 to 5.5 (Fig 3D), a fact that can be explained by the higher concentration of hypochlorous acid in the system at the higher pH values. Pulp viscosity also decreases with increasing chlorine dioxide dose (Fig 3D). It is worth noting that pH 5.5 still renders the highest viscosity for a 90% ISO target brightness since at this pH the ClO₂ demand is much lower.

Table 2 shows the chemical demand and the pulp characteristics obtained at optimum conditions for 89 and 90% ISO brightness. It is seen that the D_{HT}(PO)D sequence can produce 89-90% brightness pulp with a rather low chemical demand but such demand would raise sharply for a brightness target of 91% ISO (Fig. 3A). For brightness targets in the range of 91-92% an additional P- or D-stage at the end is suggested, making a four-stage sequence.

Mill Results

The new bleach plant has been operating successfully for 12 months. Table 2 compares the performance of the old bleach plant (data gathered in 2003) with the new bleach plant (data gathered in 2004). After implementation of the new bleach plant, chlorine dioxide, hydrogen peroxide and sodium hydroxide consumptions at the mill decreased by about 21, 58 and 18%, respectively (Table 2). A significant part of this chemical savings derived from better pulp washing with the new presses. Other savings originated from optimized hot chlorine dioxide bleaching in the first stage and from raising D-stage pH from 3.5 to 4.5. Further increase in D-stage pH to 5.5 is planned for the near future. Elimination of oxygen from the (PO) will also be implemented at the mill. The chemical and physical pulp characteristics have not changed to any significant extent since start up of the new bleach plant (Table 2). The slight changes in some of the pulp physical properties were likely caused by fiber morphology alterations derived from variations in wood supply between 2003 and 2004.

It is worth noting that laboratory study results are being successfully verified under mill operation for the new bleach plant. In general, the optimized chemical consumptions and pulp characteristics obtained in the laboratory matched those achieved at the mill.

Conclusion

The optimum conditions to run the D_{HT}(PO)D sequence at Suzano mill are: 80-85°C for all stages, D_{HT} stage with kappa factor of 0.25 and pH 3.0, (PO) stage at final pH 10 in the presence of magnesium and absence of oxygen and final D-stage at pH 5.5.

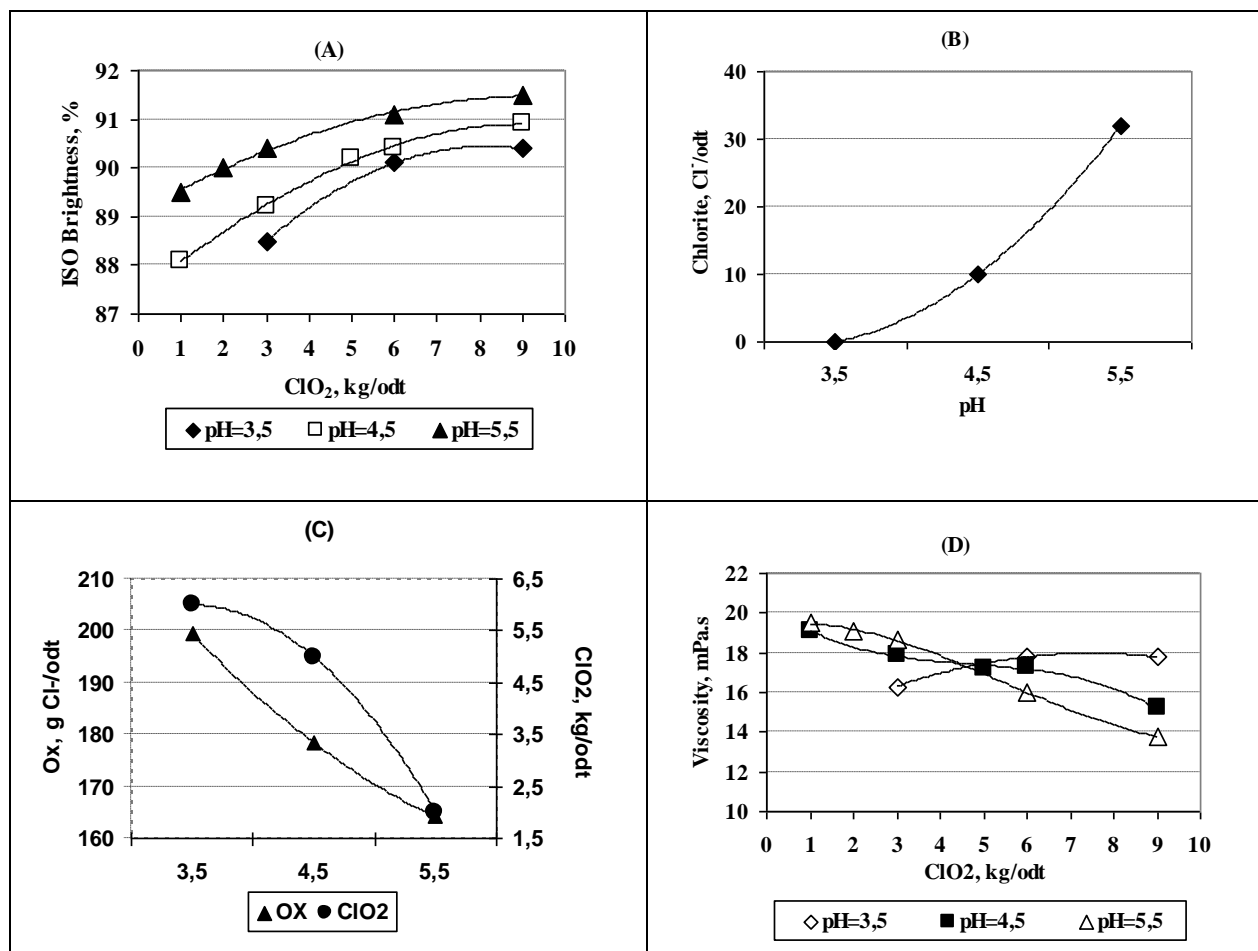


Figure 3. Effect of final D-stage pH and chlorine dioxide charge on pulp brightness (A) and viscosity (D) and effect of D-stage pH on pulp OX (C) and filtrate chlorite concentration (B). Pulp previously treated with KF 0.25, pH 3.0 and 80 °C in D_{HT} -stage and with 5 kg/odt H_2O_2 , pH 10, 85°C, 1.5 kg /odt Mg and no oxygen in (PO)- stage.

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Table 2. Optimized laboratory and old and new bleach plant results for 89 and 90% ISO brightness

Parameter	Old Bleaching Plant		New Bleaching Plant		Optimized Lab Results
ClO ₂ , kg/odt	14.0		11.1 (13.4)*		10.8 (11.9)*
H ₂ O ₂ , kg/odt	9.4		3.9 (5.2)		5.0 (5.0)
NaOH, kg/odt	13.7		11.2 (11.4)		9.5 (9.7)
Viscosity, mPa.s	16.6		18.1		19.7 (19.1)
Kappa #	1.8		1.4		0.9 (0.9)
Bleaching Yield, %	-		-		94.9(94.9)**
Coarseness (mg/100 m)	8.3		7.1		-
Fiber length (mm)	0.80		0.79		-
Fines (%)	10.7		10.1		-
Fiber /gram (n° x 10 ⁶)	19.1		22.5		-
PFI mill revolutions, #	0	3000	0	3000	
Shopper-Riegler, (°SR)	16.6	39.3	16.6	35.2	-
Air Resistance, s/100mL	2.21	45.1	1.91	38.0	-
Stiffness Taber (gf/cm)	1.49	1.09	1.49	1.15	-
Tear Index, (Nm ² /kg)	6.87	8.54	5.81	9.53	-
Burst Index, (kPa m ² /g)	1.84	5.40	1.51	5.19	-
Tensile Index, (Nm/g)	34.8	76.2	39.0	74.2	-
Stretch, (%)	1.70	2.99	1.60	3.14	-
Opacity (%)	78.7	70.3	78.4	70.8	-
Bulk, (cm ³ /g)	2.10	1.41	2.16	1.48	-
Capillary rise Klemm, (mm/10min)	100.2	25.0	107.7	29.4	-

* Numbers within brackets are for 90% ISO brightness. **Includes yield loss in the O-stage.