

The Effect of D₀-Stage Temperature, pH and Kappa Factor on Chlorine Dioxide Decomposition and D-(EP)-D Bleaching Performance for Eucalypt pulp

Umit S. Sezgi: GL&V USA, Inc., Nashua, USA, Umit.Sezgi@glv.com
Janaina Resende: Msc, UFV, Viçosa, Brazil, jana_resendes@hotmail.com
Lewis Shackford: GL&V USA, Inc., Nashua, USA, Umit.Sezgi@glv.com
Jorge Colodette: Full Professor, UFV, Brazil, colodett@ufv.br

Abstract

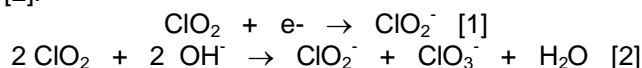
Eucalyptus kraft pulp bleaching has been done largely with chlorine dioxide, using well established technologies. However, significant variation in chlorine dioxide demand to reach full brightness (90⁺) has been observed among different mills. While modern mills reach this brightness target with ClO₂ dosages as low as 8 kg/adt, it is not unusual to find mills operating with over 20 kg ClO₂/adt pulp. These large differences in ClO₂ consumption among mills derive from many factors, with the differences in pulp incoming carryover loads and hexenuronic acid contents (HexA) as well as the level of chlorate formation across bleaching being the most significant ones. Handling of pulp high HexA content and of ClO₂ losses to chlorate can be minimized by proper operation of the chlorine dioxide stages across the bleach plant. A kappa 10-12 oxygen delignified eucalyptus kraft pulp contains only 4-6 units actually derived from lignin. This scarce amount of lignin (0.6-0.9%) is not able to consume high ClO₂ doses and, as a consequence, the excess ClO₂ applied may end up being converted into chlorate. Hence, a proper optimization of chlorine dioxide bleaching stages may save significant amounts of this oxidant. This study focused on optimizing chlorine dioxide bleaching for a typical oxygen delignified eucalyptus kraft pulp of kappa number 11.7. ECF bleaching was carried out with the D-(EP)-D sequence, and the following conditions were varied in the D₀-stage: Temperature: 50; 60; 70; 80 and 90°C; end pH: 2.5; 3.5; 4.5; 5.5; 6.5 and 7.5; kappa factor in D₀-stage: 0.10; 0.14; 0.18; 0.22; 0.26; 0.30. The bleached pulps were evaluated for their kappa number, viscosity, brightness and brightness stability. The profiles of pulp kappa number, viscosity and brightness were determined across the sequence. Also determined were the residuals oxidants, the end pH and the contents of chlorite, chlorate and chloride in the filtrates from the D₀, (EP) and D₁ bleaching stages. The results indicated that maximum chlorine dioxide bleaching efficiency is achieved when minimum chlorate is formed, especially when chlorine dioxide bleaching is adjusted in such way that residual active chlorine is maintained to a bare minimum. The most significant variable affecting chlorate formation is pH but chlorine dioxide doses (ClO₂ concentration) also play a very important role. Chlorate formation is more intense in the D₁- stage in relation to D₀-stage. Optimum conditions to run the D₀-stage were 90°C, pH 4.5 and kappa factor of 0.22.

Keywords: eucalypt, kraft pulp, bleaching, chlorine dioxide, D₀-stage, chlorate, HexA

Introduction

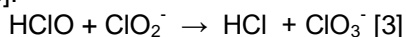
A significant amount of the chlorine dioxide applied in pulp bleaching is lost in decomposition reactions (chlorate and chlorite), resulting increased bleaching costs and undesirable effluent load. The extent of such reactions is influenced by many factors including the pulp type (kraft sulfite, SWD, HWD etc.), pulp kappa number, hexenuronic acid content and washing degree, D-stage location in the sequence, and D-stage operating conditions such as temperature, residence time, pH and ClO₂ concentration (kappa factor and consistency).

The rate of ClO₂ decomposition reaction is slow in neutral pH conditions [1]. Under normal ClO₂ bleaching pH conditions (pH 3-5) the rate of ClO₂ conversion into other species such as perchlorate, chlorate, chlorine and chloride is low as long as the concentration of hypochlorous acid in the system is maintained at low levels. However, in the presence of significant amounts of hypochlorous acid, ClO₂ oxidation into chlorate occurs very fast [2;3]. In neutral aqueous solution, ClO₂ is largely converted to chlorite ions through reactions [1] and [2].



ClO₂ decomposition accelerates under alkaline pH conditions [4]. This reaction [2] leads to chlorite and chlorate [3;5]. High reaction pH tends to severely increase formation of chlorite in the reaction system and,

as a consequence, leads to formation of hypochlorous acid [6]. Acidic conditions also promote ClO_2 decomposition, resulting in chlorate formation [4;7]. The main reaction involves combination of hypochlorous acid with chlorite as shown in reaction [3].



In addition to reaction pH other important variables such as temperature and chloride concentration also affect ClO_2 decomposition [4;8]. It has been suggested (5) that UV light also enhances ClO_2 decomposition into chlorate and established that carbonate negatively affects ClO_2 stability (9). Reducing agents such as hydrogen peroxide and sulfurous acid can convert ClO_2 into chlorite [10], and oxidizing agents such as ozone may oxidize ClO_2 into a Cl_2O_6 [9].

ClO_2 decomposition produces more chlorite when reacting at alkaline pH and more chlorate when reacting at acid pH [3; 5]. Chlorate formation is more harmful since it is inactive towards pulp bleaching. Chlorite can regenerate ClO_2 in the course of the bleaching reaction. It has been claimed [3;11] that minimum formation of chlorite and chlorate is achieved at pH around 3.8 in softwood pulp bleaching with ClO_2 .

During pulp bleaching, chlorine dioxide is reduced through a series of reactions involving different intermediates in different oxidations states [3; 12; 13]. The first ClO_2 reaction with the pulp results formation of chlorite through the abstraction by ClO_2 of a hydrogen from lignin free phenolic structures. Chlorite is not reactive towards lignin but it can be converted into chlorous acid under acidic conditions, which is active towards lignin. Chlorine dioxide also reacts with lignin/HexA giving rise to hypochlorous acid, and the latter is partially converted into chlorine gas. Both hypochlorous acid and chlorine gas are effective in reacting with lignin/HexA, being converted into chloride and chlorinated organic compounds. The hypochlorous acid also reacts with chlorite giving rise to chlorate. Under acidic conditions chlorite decomposes into chlorine dioxide and chloride and also reacts with chlorine regenerating chlorine dioxide [3;13].

At pH above 7, ClO_2 reacts with lignin to form chlorite preferentially. The by-products of this reaction may cause harm to cellulose chains, thus decreasing the pulp viscosity. The chlorous acid produced from chlorite ($\text{ClO}_2^- + \text{H}^+ \leftrightarrow \text{HClO}_2$) is highly reactive towards free phenolic hydroxyl groups in lignin and it also gives rise to formation of hypochlorous acid as a by-product. Hypochlorous acids may attack cellulose chains [13].

The largest losses of ClO_2 oxidizing power occurs when it is converted into chlorate, which is inactive in pulp bleaching [11]. Thus, it is relevant to minimize chlorate formation in favor of more lignin oxidation [14].

The formation of chlorinated organic compounds in chlorine dioxide bleaching increases with increasing *in situ* formation of hypochlorous acid and chlorine gas [13;15]. In general, acid conditions are necessary in chlorine dioxide bleaching in order to consume the chlorite formed, however such acid conditions can give rise to more chlorate, which is unfavorable to bleaching [13]. It has been proposed that a pH of about 3,5 is the most suitable for bleaching with ClO_2 both in the D_0 and D_1/D_2 stages of a bleach sequence [6]. The strict pH control is more relevant in the D_1/D_2 stages where pulp contains small amounts of lignin/HexA of low reactivity, favoring ClO_2 side reactions that lead to chlorate formation. Thus, investigations on ClO_2 conversion during bleaching are quite relevant, especially for optimization of proper reaction conditions that mitigate chlorate formation.

The objective of this study was evaluating the effect of first D-stage temperature, pH and kappa factor on chlorine dioxide bleaching performance with the D-(EP)-D sequence and on chlorine dioxide conversion into chlorite, chlorate and chloride in all three bleaching stages of the sequence. ECF bleaching was carried out with the D-(EP)-D sequence, and the following conditions were varied in the D_0 -stage pH, temperature and kappa factor were optimized. The profiles of pulp kappa number, viscosity and brightness were determined across the sequence. The contents of chlorite, chlorate and chloride in the filtrates from the D_0 , (EP) and D_1 bleaching stages were also measured for the various D_0 -stage operating conditions.

Experimental

A sample of oxygen delignified eucalypt kraft pulp was obtained from a Brazilian mill. The main pulp characteristics are presented in Table 1.

Table 1. Main characteristics of the oxygen delignified eucalypt kraft pulp

Characteristics	Oxygen delignified eucalypt kraft pulp
Kappa N ^o	11.7
Viscosity, dm ³ /kg	1092
ISO Brightness, %	48.2
COD, kg O ₂ /odt	8.4
HexA, mmoles/kg	58

The chlorine dioxide delignification stage (D₀) was carried out with a 280 g o.d. pulp sample in polyethylene bags under the conditions presented in the Table 2. The pulp sample was mixed with hot water at proper temperature and the desired amount of chlorine dioxide and sulfuric acid was added and thoroughly mixed. At this point the temperature dropped to the desired value. Following, the initial pH was measured and the bag was airtight sealed and placed in a heating bath at the desired temperature. After completion of the desired reaction time, a 300 mL sample of liquor was squeezed out from the pulp for pH, active chlorine residuals and chloride, chlorite and chlorate analyses. Following that, the pulp was washed with distilled warm water equivalent to 9 m³ per ton of pulp. These experiments were run in duplicate.

The same procedure above was followed for the (EP) and D₁ bleaching stages, except that they were run with 260 and 240 g o.d. pulp sample. The conditions used in these stages are also shown in Table 2.

Table 2. General Bleaching Conditions

Bleaching Condition	Bleaching Stage		
	D ₀	(EP)	D ₁
Consistency, %	10	10	10
Time, min	120	120	180
Temperature, °C	50-90	70	85
End pH	2.5±0.1- 7.5±0.1	-	5±0.1
Kappa Factor	0.10-0.30	-	-
ClO ₂ , kg Cl ₂ /odt	11.7-35.1	-	6.9-30.3
H ₂ O ₂ , kg/odt	-	3	-
NaOH, kg/odt	*	10	*
H ₂ SO ₄ , kg/odt	*	-	-

* Sufficient to achieve desired end pH.

Pulp and residual liquors were analyzed according to Tappi, Scan or other methods, as described in Table 3.

Table 3. Analytical procedures used for pulp and residual liquor analyses

Parameter	Procedure
Kappa Number	Tappi T 236 cm-85
Viscosity	Tappi T230 om-94
Hand sheets for reflectance tests	Tappi T 218 sp-97
Hexenuronic acids	Tenkanen, M., Gellerstedt, G., Vuorinen, T., et. al., J. Pulp Paper Sci. 25(9): 306(1999). Acid hydrolysis/UV method
Pulp Brightness	Tappi T525 om-92
Pulp Brightness Reversion	Tappi UM 200: 4 hour at 105±3°C and 0% RU, after acclimation of hand sheets for 12 hours in temperature and humidity controlled room (50±2% UR e 23±1 °C).
Analysis of ClO ₂ and H ₂ O ₂ in solutions and residuals	Kraft, P., In: Pulp & Paper Manufacture, Vol.1, McDonald, R.G. (editor), 2nd ed., McGraw-hill Book Company, New York, 1967, p. 628-725 [12]
Chloride, Chlorate, and Chlorite	Anion Chromatography after filtration of effluents in membranes (47 mm diameter, 45 µm porosity) in equipment <i>Dionex ICS-3000</i> . Calibration curves were done with pure solutions of NaCl, NaClO ₂ and NaClO ₃ . An analytical column <i>ionpac</i> was used for separation of the three different ions.

Results and Discussion

Effect of D₀-stage End pH

The effect of D₀-stage (at 10% consistency, 120 min, kappa factor 0.18, temperature 70 °C) end pH on the performance of the D-(EP)-D bleaching sequence and on the chlorine dioxide conversion into chlorite, chloride and chlorate anions is presented in Table 4.

The pulp brightness measured after the D₀-stage increased with increasing D₀-stage end pH in the range from 2.5 to 6.5, from 66.4 to 72.3 % ISO, respectively. Raising the pH to 7.5 decreased the brightness because a significant amount of the applied ClO₂ was not consumed (40% residual) within the time and temperature used (Table 4). The positive effect of raising pH on brightness delivery is explained by the slow consumption of chlorine dioxide in the course of reaction. By increasing D₀-stage pH a significant part of the chlorine dioxide is converted into chlorite, which is not effective in bleaching the pulp. However, as the reaction proceeds, the formed chlorite is slowly converted into chlorous acid, which reacts fast with lignin resulting in formation of hypochlorous acid that further reacts with lignin. Thus, in the higher pH range, the consumption of ClO₂ occurs in a slow rate and the slightly acidic to neutral conditions prevent ClO₂ losses to chlorate. The positive effect of increasing D₀-stage end pH on brightness was also visible after the alkaline extraction stage. After the extraction, brightness values of 82.5 and 84.4 %ISO were obtained for the D₀-stage end pH values of 2.5 and 6.5, respectively. However, the (EP)-stage kappa number increased linearly with increasing D₀-stage end pH. (EP)-kappa number values of 3.5 and 4.4 were obtained for D₀-stage pH of 2.5 and 6.5, respectively. The negative impact of increasing D₀-stage pH on the kappa number is explained two folds: (1) At the lower pH range more chlorine gas is produced from hypochlorous acid and chlorine is known to be highly effective in reacting with both lignin and HexA and (2) the efficiency of HexA removal from pulp by acid hydrolysis is higher at lower pH values.

Final pulp brightness after the whole bleaching sequence (D-EP-D) increased with increasing D₀-stage end pH in the range of 2.5 to 4.5, where brightness in the range of 90-91% ISO were achieved (Table 4). Above end pH 5.5 the final brightness decreased drastically reaching values of about 89% for the D₀-stage pH range of 6.5-7.5. The positive effect of increasing D₀-stage pH in the 2-5-4.5 range is explained by significant enhancement in pulp brightness, as measured after the (EP)-stage, but raising the pH over 4.5 had too large an impact on (EP)-stage kappa number that hampered final brightness. The kappa number values of the fully bleached pulps varied in the range of 1.4-2.0, with the lower values obtained for the low D₀-stage end pH values. These final kappa numbers were consistent with those reported for the (EP)-stage. The brightness reversion of the fully bleached pulp varied in the range of 1.5-2.3% ISO, and increased with increasing D₀-stage end pH, reflecting the trend observed for the final kappa numbers of these pulps. The higher contents of HexA present in the final bleached pulps treated at the higher D₀-stage end pH explain the higher brightness reversion values. Final bleached pulp viscosity was negatively affected by increasing D₀-

stage pH in the range of 2.5-7.5. The maximum and minimum values were 793 and 768 dm³/kg for the 2.5 and 7.5 end pH, respectively. The negative impact of pH on viscosity is explained by the ClO₂ conversion during bleaching. At the higher pH range, particularly above 5.5, the formation of hypochlorous acid increases and this oxidant is known to attack the cellulose chains, thus reducing viscosity.

Although the D₀-stage end pH of 4.5 resulted the highest final brightness (91.1 % ISO), this high pH may lead to severe oxalate scaling in the bleach plant equipment. There have been studies indicating that the ideal D₀-stage to minimize oxalate scaling is in the range of 2.5-2.8, although at this pH barium sulfate type scales may appear [16]. Since the benefits of increasing D₀-stage pH from 3.5 to 4.5 was not very significant regarding bleaching performance, the 3.5 value was chosen for the subsequent bleaching optimization since the risk of oxalate scaling is largely enhanced at pH 4.5. In addition, the pH 4.5 produced bleached pulp with higher brightness reversion. Eucalypts pulp mills have successfully run D₀-stage at pH 3.5, without oxalate scaling problems. Regarding bleaching efficiency, there are great differences between softwood and eucalypt pulps. It is true that softwood mills run D₀-stage at pH 2.5 almost as a rule of thumb. The reason is not only scaling; softwood pulps are highly dependent on the formation of chlorine gas during the D₀-stage so that the condensed lignin can be oxidized. The only way to make chlorine from chlorine dioxide is lowering the pH to 2.5 or less in order to convert hypochlorous acid into chlorine. In the case of eucalypt pulps, the small amounts of lignin left (~6 kappa units) can be easily handled with a chemistry that does not require chlorine gas. Eucalypt residual lignin is not condensed because they are mostly syringyl type lignin. Therefore, pH conditions that minimize chlorate formation (3.5-4.5) are more favorable for eucalypt D₀-stage performance, but the risk of scaling does exist.

The end pH of the D₀-stage showed significant impact on ClO₂ conversion (Table 4). The formation of chlorite increased exponentially with increasing pH above 4.5, reaching 6.8 kg Cl₂/odt at pH 7.5. The increased chlorite formation at the high pH values is explained by the slow conversion of chlorite into chlorous acid when lacks acidity in the reaction system. Chlorous acid is consumed by lignin and HexA but is not formed in significant amounts when the pH is around neutral. Chlorate formation decreased with increasing D₀-stage end pH; values of 5.65 and 2.57 kg Cl₂/odt were obtained for pH values of 2.5 and 7.5, respectively. The large formation of chlorate when ClO₂ reacts with pulps under acidic conditions has been shown by many other workers [3; 4; 6; 13], and explained by the reaction of chlorite with hypochlorous acid, a reaction that is favored at low pH values. Chloride concentration in D₀-stage filtrates also decreased with increasing pH, achieving values of 2.53 and 1.29 kg Cl₂/odt for end pH values of 2.5 and 7.5, respectively. The decrease in chloride concentration at high pH values is explained by the high ClO₂ residuals that were observed in the high pH range. At the high pH the ClO₂ residual remain in the form of chlorite and never reacts with the pulp to form chloride. The ClO₂ conversion in the (EP)-stage filtrates followed somewhat the same pattern as in the D₀-stage filtrates, except that the magnitudes of values were much lower. In the D₁-stage filtrates, the formation of chlorite increased with increasing D₀-stage pH but the values were quite low; these values were likely influenced by the higher kappa (EP) kappa number of the pulps obtained with higher D₀-stage pH values. In order to form chlorite, ClO₂ must be reduced by lignin/HexA. The lower chloride formation at the higher pH values reflects the higher chlorite formation. The amount of chlorate in D₁-stage filtrate were quite high but were not influenced by D₀-stage end pH.

The results in Table 4 also illustrate the levels of chlorite, chlorate and chloride formation in the different bleaching stages of the D-(EP)-D bleaching sequence. It is obvious that more chlorate is produced in the D₁-stage than in the D₀-stage for a similar ClO₂ charge application. However there are no large differences in chloride and chlorite formation in the D₀ and D₁ stages. The (EP)-stage filtrate contained unusually high amounts of chlorite, considering that no ClO₂ was added to this stage. The reaction of residual ClO₂ carried over from the D₀-stage into the (EP)-stage with hydrogen peroxide could explain such phenomena as shown in reaction [5]. However, residual ClO₂ were found only at the D₀-stage end pH of 5.5 or over.

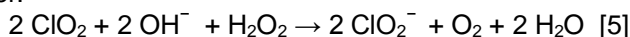


Table 4. Effect of D₀-stage end pH on D-(EP)-D bleaching results for an oxygen delignified eucalypt kraft pulp of kappa number 11.7.

D-(EP)-D Sequence	Evaluation Parameters	D ₀ -stage End pH					
		2.5	3.5	4.5	5.5	6.5	7.5
D₀-stage (10% cst, 70 °C, 120 min, Kappa Factor 0.18)	ClO ₂ applied, kg Cl ₂ /odt	21	21	21	21	21	21
	ClO ₂ Consumed, %	100	100	100	89	78	60
	Brightness, % ISO	66.4	67.6	70.4	72.1	72.3	71.2
	Chlorite, kg Cl ₂ /odt	0.02	0.21	0.26	0.95	3.45	6.82
	Chloride, kg Cl ₂ /odt	2.53	2.43	2.31	2.13	1.47	1.29
	Chlorate, kg Cl ₂ /odt	5.65	4.67	2.13	1.62	2.05	2.57
(EP)-stage 10% cst, 70 °C, 120 min, 10 kg NaOH/odt, 3 kg H ₂ O ₂ /odt)	Final pH	11.1	11.3	11.4	11.5	11.6	11.7
	H ₂ O ₂ applied, kg/odt	3	3	3	3	3	3
	H ₂ O ₂ Consumed,%	100	100	100	100	100	100
	Kappa No.	3.5	3.8	4.1	4.2	4.4	4.6
	Viscosity, dm ³ /kg	891	889	887	882	880	875
	Brightness, % ISO	82.5	83	83.8	84.2	84.4	84
	Chlorite, kg Cl ₂ /odt	1.62	1.7	1.83	1.95	2.1	2.28
	Chloride, kg Cl ₂ /odt	0.35	0.27	0.31	0.25	0.22	0.17
Chlorate, kg Cl ₂ /odt	0.37	0.32	0.24	0.18	0.15	0.1	
D₁-stage (10% cst, 85 °C, 180 min, pH 5.0, 21 kg Cl ₂ /odt)	ClO ₂ applied, kg Cl ₂ /odt	21	21	21	21	21	21
	ClO ₂ Consumed,%	100	100	100	100	100	100
	Kappa No.	1.4	1.6	1.7	1.8	1.9	2
	Viscosity, dm ³ /kg	793	789	781	776	771	768
	Brightness, % ISO	90	90.7	91.1	90.9	89.1	88.8
	Reversion, % ISO	1.5	1.7	1.9	2	2.2	2.3
	Chlorite, kg Cl ₂ /odt	0.32	0.41	0.47	0.52	0.67	0.82
	Chloride, kg Cl ₂ /odt	2.22	2.48	2.48	1.63	1.41	1.37
	Chlorate, kg Cl ₂ /odt	7.72	7.54	7.39	7.35	7.29	7.11

Effect of D₀-stage Kappa Factor

The effect of D₀-stage (at 10% consistency, 120 min, temperature 70°C and pH 3.5) kappa factor on the performance of the D-(EP)-D bleaching sequence and on the chlorine dioxide conversion into chlorite, chloride and chlorate anions is presented in Table 5.

In order to evaluate the impact of D₀-stage kappa factor on D-(EP)-D bleaching performance, six values were selected, covering a range that is mostly used commercially for pulp bleaching, including extreme situations. A fair comparison required that the total amount of oxidants used in the sequence was constant, regardless of the kappa factor used. The initial pulp kappa number was 11.7, which multiplied by the kappa factors of 0.10, 0.14, 0.18, 0.22, 0.26 and 0.30 resulted ClO₂ charges of 11.7, 16.4, 21.0, 25.7, 30.4 and 35.1 kg Cl₂/odt pulp in the D₀-stage, respectively. Therefore, in order to complete the total 42 kg Cl₂/odt pulp charge, previously established for the whole sequence (D₀ + D₁), the ClO₂ charges applied to the

D1-stage were 30.3, 25.6, 21.0, 16.3, 11.6 and 6.9 kg Cl₂/odt, respectively (Table 5). In all cases, the H₂O₂ charge in the (EP)-stage was kept constant and equal to 3 kg/odt pulp. Therefore, all six cases scenarios were compared using the same amounts of oxidants.

As anticipated, the D₀-stage and (EP)-stage pulp brightnesses increased with increasing kappa factor. However, the increase in D₀-stage and (EP)-stage brightness was quite insignificant above the 0.22 kappa factor, although the (EP)-stage kappa number decreased almost linearly with increasing kappa factor. The D₀- and (EP)-stage insignificant brightness increase at excess ClO₂ charges is explained by the lack of lignin in the pulp to be oxidized. The original pulp had kappa number 11.7 and 58 mmols HexA/kg of pulp. This much HexA represent about 6 kappa units [17]. Therefore, the amount of lignin present in the original pulp was about 6 kappa units. This amount of lignin does not demand the high ClO₂ charges applied with the kappa factors of 0.26-0.30. Since only lignin affects brightness, no changes in the latter occurs when adding ClO₂ to a pulp almost depleted of lignin and containing a lignin highly chlorinated (low reactivity), unless the pulp goes through an extraction stage to get activated again. At the high kappa factor, HexA continues to be removed and that effect appears in the continuous decrease of (EP)-kappa values with increasing kappa factors (Table 5).

Final pulp brightness after D-(EP)-D bleaching reached to a maximum value at the kappa factor of 0.22 at which a brightness value of 91.3% ISO was achieved. At the lowest (0.10) and highest (0.30) kappa factors, brightness values of 89.4 and 89.9% ISO were achieved. It is worth noting that no ClO₂ residuals were observed either in D₀ or D₁ stages, regardless of the kappa factor used. This result calls the attention for proper distribution of ClO₂ between D₀ and D₁ stages. In this particular case, the maximum brightness value was achieved with the application of 25.7 and 16.3 kg Cl₂/odt pulp at D₀ and D₁ stages, respectively. This represents 61% and 39% distribution between D₀ and D₁ stages. The fully bleached pulp kappa number varied in the range of 1.2-3.2 and reflected the (EP)-kappa values, with the lower values for the higher kappa factors. Brightness reversion varied in the range of 1.5-2.2 and tended to be lower for the lower kappa factor. In other words, reversion had an inverse tendency in comparison to the fully bleached kappa values. This result is contradictory and hard to explain. One possible explanation is that at the lower kappa factors, the dosage of ClO₂ applied to the D₁-stage is higher since the total ClO₂ dosed in the sequence was kept constant. High doses of ClO₂ in the D₁-stage means high production and high availability of hypochlorous acid, since at this stage there is not much kappa number left in the pulp to consume hypochlorous acid. This excess hypochlorous acid may have attacked the residual HexA present in the pulp, which is known to be the major cause of brightness reversion of eucalypt pulp [13; 18; 19]. The effectiveness of hypochlorous acid to attack HexA has been proven elsewhere [20; 21; 22]. The viscosity the fully bleached pulps varied in the range of 775- 826 dm³/kg, with the minimum and maximum values obtained for the lowest and highest kappa factors, respectively. Since the total amount to ClO₂ applied in bleaching was kept constant, it is evident that the ClO₂ distribution between D₀ and D₁ stages affects viscosity. Apparently, the use of higher ClO₂ charges in D₁ stage has a negative impact on viscosity because the pH used in the D₁ stage (5.0) was higher than that of the D₀ stage (3.5.), thus increasing the pulp exposition to hypochlorous acid, which is known to affect pulp viscosity negatively.

The kappa factor applied to the D₀-stage had significant impact on the ClO₂ conversion in all three bleaching stages of the D-(EP)-D sequence (Table 5). As anticipated, the concentrations of chloride and chlorate in the D₀-stage filtrates increased sharply with increasing D₀-stage kappa factor. However, the chlorite concentration remained very low for all kappa factors because the reactions were run at end pH of 3.5. At this pH, formation of chlorite is well known to be low. In the (EP)-stage filtrate only chlorite was found in sizeable amounts, but its concentration was not much affected by kappa factor, except above the value of 0.22. The D₁-stage filtrate presented large concentrations of chlorate and chloride and their amounts decreased sharply with increasing D₀-stage kappa factor. Because the total amount of ClO₂ used in the sequence was constant, the ClO₂ charges applied to D₁ decreased with increasing D₀-stage kappa factor and so were the concentrations of chlorate and chloride. A certain quantity of chlorite ion was found at the low kappa factors where large charges of ClO₂ were applied at D₁-stage. The D₁ stage was run at pH 5 and is therefore expected to produce some chlorite.

The results on Table 5 also show that more chlorate is produced in the D₁-stage than in the D₀-stage for a given ClO₂ charge application. For example, at kappa factor 0.18, where the ClO₂ charge to D₀ and D₁-stage were equal (~21 kg Cl₂/odt pulp), the amounts of chlorate present in the D₀ and D₁ stage filtrates were 4.67 and 7.54 kg Cl₂/odt, respectively. Such result is explained by the large consumption of hypochlorous acid (the source of chlorate) by organic reactions in the D₀- stage whereas in the D₁- stage a significant part of the hypochlorous acid is consumed in inorganic reactions that gives rise to chlorate, because of the low amounts of oxidizable organic substrate present in the pulp at this stage (low kappa). Because of the lower

pH used in the D₀-stage (3.5) there was a large formation of chlorides in such stage in comparison with the D₁-stage. Formation of chlorite was quite low both in D₀ and D₁ stages, with slightly higher values for the later stage. The (EP)-stage filtrates showed very small amounts of chloride and chlorate (< 0.6 kg Cl₂/odt pulp), but a sizeable amount of chlorite anions (1.6-2.0 kg Cl₂/odt pulp), with the higher values occurring for the higher kappa factors. Currently, there is no clear explanation as to why chlorite appears in sizeable concentrations in the (EP)-stage filtrates.

Effect of D₀-stage temperature

The effect of D₀-stage (at 10% consistency, 120 min, kappa factor 0.18, and end pH 3.5±0.1) temperature on the performance of the D-(EP)-D bleaching sequence and on the chlorine dioxide conversion into chlorite, chloride and chlorate anions for each bleaching stage is presented in Table 6.

The results in Table 6 indicate that D₀-stage pulp brightness decreased with increasing D₀-stage temperature, particularly above 70 °C. This trend has been observed by other workers [18] and explained on the basis of pulp darkening that occurs at high D₀-stage temperatures, in the absence of chlorine dioxide residuals. At the high temperatures, ClO₂ is consumed rapidly and then the pulp darkens due to the final long retention time. The negative effect of D₀-stage temperature on brightness was also visible after the alkaline extraction stage (EP-stage); in other words, the negative impact on brightness caused by the high temperature was not mitigated in the (EP)-stage. However, pulp kappa number after (EP)-stage decreased with increasing D₀-stage temperature and the effect was more significant above 70 °C. At high temperatures, the removal of pulp HexA by simple acid hydrolysis is significant and that explain the lower kappa numbers obtained at the higher temperatures. Regarding lignin removal, the effect of temperature is not so relevant since ClO₂ reacts rather fast and efficiently with phenolic lignin substances.

Table 5. Effect of D₀-stage kappa factor on D-(EP)-D bleaching results, for an oxygen delignified eucalypt kraft pulp of kappa number 11.7.

D-(EP)-D Sequence	Evaluation Parameters	D ₀ -stage Kappa Factor					
		0.1	0.14	0.18	0.22	0.26	0.3
D₀-stage (10% cst, 70 °C, 120 min, pH 3.5)	ClO ₂ applied, kg Cl ₂ /odt	11.7	16.4	21	25.7	30.4	35.1
	ClO ₂ Consumed, %	100	100	100	100	100	100
	Brightness, % ISO	62.2	65.1	67.6	70.4	71.8	72.3
	Chlorite, kg Cl ₂ /odt	0.15	0.19	0.21	0.23	0.25	0.28
	Chloride, kg Cl ₂ /odt	1.58	2.04	2.43	3.42	4.14	4.73
	Chlorate, kg Cl ₂ /odt	2.72	3.88	4.67	5.26	6.53	7.32
(EP)-stage (10% cst, 70 °C, 120 min, 10 kg NaOH/odt, 3 kg H ₂ O ₂ /odt)	Final pH	11.4	11.4	11.3	11.2	11.1	11
	H ₂ O ₂ applied, kg/odt	3	3	3	3	3	3
	H ₂ O ₂ Consumed, %	100	100	100	100	100	100
	Kappa No.	5.5	4.3	3.8	3.2	2.8	2.2
	Viscosity, dm ³ /kg	906	897	889	875	867	854
	Brightness, % ISO	80.6	81.8	83	83.8	84	84.2
	Chlorite, kg Cl ₂ /odt	1.58	1.68	1.7	1.84	1.97	1.98
	Chloride, kg Cl ₂ /odt	0.22	0.24	0.27	0.38	0.37	0.47
Chlorate, kg Cl ₂ /odt	0.15	0.21	0.32	0.45	0.43	0.63	
D₁-stage (10% cst, 85 °C, 180 min, 10 kg NaOH/odt, 7-30 kg Cl ₂ /odt)	ClO ₂ applied, kg Cl ₂ /odt	30.3	25.6	21	16.3	11.6	6.9
	ClO ₂ Consumed, %	100	100	100	100	100	100
	Kappa No.	3.2	2.4	1.6	1.4	1.3	1.2
	Viscosity, dm ³ /kg	775	786	789	802	816	826
	Brightness, % ISO	89.4	90.4	90.7	91.3	90.5	89.9
	Reversion, % ISO	1.5	1.6	1.7	1.8	2	2.2
	Chlorite, kg Cl ₂ /odt	0.97	0.77	0.41	0.37	0.29	0.19
	Chloride, kg Cl ₂ /odt	3.42	3.21	2.48	1.92	1.24	0.8
	Chlorate, kg Cl ₂ /odt	11.5	9.41	7.54	6.02	4.16	1.59

Final pulp brightness after the whole bleaching sequence (D-EP-D) increased with increasing D₀-stage temperature in the range of 50 to 90 °C (Table 6). Although brightnesses over 90% ISO were achieved for all D₀-stage temperatures, the maximum (91.2% ISO) and the minimum (90.2% ISO) values were obtained at the temperatures of 90 and 50 °C, respectively. The positive effect of increasing D₀-stage temperature reflects the decreased kappa number values achieved after the (EP)-stage. It is evident that (EP)-stage kappa number is more relevant to predict final pulp brightness than (EP)-stage brightness, for example. The kappa number values of the fully bleached pulps were low, in the range of 1.1-2.0, with the maximum and minimum values obtained at the D₀-stage temperatures of 90 and 50 °C, respectively. These final kappa numbers were consistent with those reported for the (EP)-stage. It is worth noting that the residual kappa number values present in the bleached pulp are largely comprised of hexenuronic acid as reported elsewhere [23]. The brightness reversion of the fully bleached pulps decreased with increasing D₀-stage

temperature, reflecting the trend observed for the final kappa numbers of these pulps. The higher contents of HexA in the final bleached pulp treated at the lower D₀-stage temperatures explain the higher brightness reversion values. The negative impact of pulp HexA content on pulp brightness stability has been shown by several workers [19; 24; 25]. Final bleached pulp viscosity was negatively affected by increasing D₀-stage temperature in the range of 50-90 °C. Although the viscosity values achieved for all pulps are acceptable for most applications of eucalypt pulps, regardless of D₀-stage temperature, the maximum and minimum values were 810 and 761 dm³/kg for the 50 and 90 °C D₀-stage temperatures, respectively. The negative impact of temperature on viscosity is explained by the ClO₂ explained by the chlorine species formed from decomposition of ClO₂ during bleaching. During chlorine dioxide bleaching, a small but significant part of ClO₂ is converted to hypochlorous acid and thereby into chlorine gas [6]. Such species are known to attack cellulose chains, particularly at very high temperatures. To minimize the negative impact on pulp viscosity, full hypochlorous acid (H) and chlorine (C) stages are usually run at temperatures in the range of 40-50 °C, but such temperatures are too low for running D₀-stages. In order to get the full benefits of a D₀-stage for eucalypt pulp a high temperature (~90 °C) is recommended for removing maximum amounts of lignin and HexA, but a slight penalty on pulp viscosity shall be expected.

Regarding ClO₂ conversion it was observed that D₀-stage temperature had only a slight effect on the concentrations of chloride, chlorite and chlorate in the filtrates of the D₀-, (EP)- and D₁-stages (Table 6). The only significant result was the formation of chlorate in the D₁-stage filtrate, which decreased with increasing D₀-stage temperature. In this case, the variation was from 8.76 kg Cl₂/odt at 50°C to 6.88 kg Cl₂/odt at 90 °C temperature. The only possible explanation for this trend was the difference in (EP)-stage kappa number for the pulps produced at different D₀-stage temperatures. Because of the lower (EP)-kappa numbers obtained with the higher D₀-stage temperatures, less hypochlorous acid was formed and it is known [3; 14] that formation of chlorate is directly related to the concentration of the former.

The results in Table 6 also illustrate the levels of chlorite, chlorate and chloride formation in the different bleaching stages of the D-(EP)-D bleaching sequence. While the levels of chloride for the D₀ and D₁-stage filtrates are somewhat similar for the same charge of ClO₂ (21 kg/odt) applied to both stages, the levels of chlorate are quite different, with much more chlorate being produced in the D₁-stage. This result is also explained by differences in hypochlorous concentration levels in the reaction media in the D₀ and D₁ stages. In the D₀-stage, the pulp is quite rich in lignin/HexA and most of the hypochlorous acid produced is consumed by these organic materials, with little of it remaining available to react with chlorite giving rise to chlorate [4]. On the other hand, the availability of lignin/HexA in the D₁-stage is scarce with the hypochlorous acid formed largely participating in inorganic reactions that leads to chlorate. The ClO₂ conversion in the (EP)-filtrate is a consequence of the amount of chlorine species that are carried over with the pulp from the D₀-stage. The amounts of chloride and chlorate were not affected by the D₀-stage temperature and the values were quite low as should be expected since no ClO₂ was added to the (EP)-stage. However, the amounts of chlorite present in the (EP)-filtrates were significant and tended to increase with increasing D₀-stage temperature. The significant formation of chlorite in the extraction stage is not so easy to explain. Under the (EP)-stage alkaline conditions, ClO₂ residuals carried over from the D₀-stage would be converted into chlorite, but no residuals were observed in the D₀-stage (Table 6).

Table 6. Effect of D₀-stage temperature on D-(EP)-D bleaching results for an oxygen delignified eucalypt kraft pulp of kappa number 11.7.

D-(EP)-D Sequence	Evaluation Parameter	D ₀ -stage Temperature, °C				
		50	60	70	80	90
D₀-stage (10% cst, 120 min, pH 3.5, Kappa Factor 0.18)	ClO ₂ applied, kg Cl ₂ /odt	21	21	21	21	21
	ClO ₂ Consumed, %	100	100	100	100	100
	Brightness, % ISO	68.8	68.3	67.6	66.1	65.6
	Chlorite, kg Cl ₂ /odt	0.21	0.22	0.21	0.25	0.26
	Chloride, kg Cl ₂ /odt	2.43	2.58	2.43	2.69	2.78
	Chlorate, kg Cl ₂ /odt	4.68	4.59	4.67	4.61	4.64
(EP)-stage 10% cst, 70 °C, 120 min, 10 kg NaOH/odt, 3 kg H ₂ O ₂ /odt)	Final pH	11.2	11.2	11.3	11.4	11.5
	H ₂ O ₂ applied, kg/odt	3	3	3	3	3
	H ₂ O ₂ Consumed,%	100	100	100	100	100
	Kappa No.	4.2	4	3.8	3.2	2.6
	Viscosity, dm ³ /kg	910	902	889	875	861
	Brightness, % ISO	83.6	83.2	83	82.8	82.6
	Chlorite, kg Cl ₂ /odt	1.55	1.6	1.7	1.81	2.16
	Chloride, kg Cl ₂ /odt	0.28	0.24	0.27	0.26	0.28
	Chlorate, kg Cl ₂ /odt	0.28	0.24	0.32	0.29	0.31
D₁-stage (10% cst, 85 °C, 180 min, pH 5.0, 21 kg Cl ₂ /odt)	ClO ₂ applied, kg Cl ₂ /odt	21	21	21	21	21
	ClO ₂ Consumed,%	100	100	100	100	100
	Kappa No.	2	1.8	1.6	1.4	1.1
	Viscosity, dm ³ /kg	810	802	789	775	761
	Brightness, % ISO	90.2	90.4	90.7	91	91.2
	Reversion, % ISO	2	1.9	1.7	1.5	1.3
	Chlorite, kg Cl ₂ /odt	0.38	0.37	0.41	0.39	0.41
	Chloride, kg Cl ₂ /odt	2.64	2.51	2.48	2.53	2.5
	Chlorate, kg Cl ₂ /odt	8.76	8.42	7.54	7.02	6.88

Conclusions

- For a given charge of ClO₂ (42 kg Cl₂/odt pulp), maximum final pulp brightness is achieved when D₀-stage is run at pH 4.5, in the range of 2.5-7.5, where D₀- and D₁-stage chlorate plus chlorite levels minimize; the risks of oxalate formation at end pH 4.5 is high.

- Maximum final pulp brightness (91.3 % ISO) is achieved at kappa factor 0.22, in the range of 0.10-0.30 keeping brightness stability and viscosity at high levels. Chlorate formation in D₀-stage and D₁-stage filtrate increases and decreases with increasing kappa factor, respectively, for a fixed total ClO₂ charge (42 kg Cl₂/odt pulp). Chlorite formation is low and only slightly affected by kappa factor.

• In the bleaching of eucalypt kraft pulp with the sequence D-(EP)-D, Increasing D₀-stage temperature in the range of 50-90 °C results pulps of increased brightness and brightness stability and decreased kappa and viscosity. Increasing D₀-stage temperature slightly decreases chlorate formation in D₁-stage filtrate.

References

1. VON HEIJNE, G.; TEDER, A. Kinetics of the decomposition of aqueous chlorine dioxide solutions. *Acta Chem. Scand.*, v. 27, p. 4018-4019, 1973.
2. DODGEN, H.; TAUBE, H. The exchange of chlorine dioxide with chlorite ion and with chlorine in other oxidation states. *J. Am. Chem. Soc.*, v. 71, n. 7, p. 2501-2504, 1949.
3. REEVE, D. W. Chlorine Dioxide in Bleaching Stages. In: DENCE, C.W.; REEVE, D. W. (Eds.). *Pulp Bleaching – Principles and Practice*, Tappi Press, 2006b, p. 379-394.
4. BRAY, W. Einige Reaktionen des Chlordioxyds und der chlorigen Säure. *Z. Anorg. Chem.*, v. 48, p. 217-250, 1996.
5. LEE, Y.; KIM, H.; LEE, V. Formation of chlorite and chlorate from chlorine dioxide with ham river water. *Korean J. Chem. Eng.* v. 21, n. 3, p. 647-653, 2004.
6. SIXTA, H.; SÜSS, H.; POTTHAST, A.; SCHWANNINGER, M.; KROTSCHKE, A. W.; ANDREAS, W. Pulp bleaching. In: SIXTA, H. (Ed.). *Handbook of pulp*. Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA, 2006. p. 609-893
7. REEVE, D. W.; WEISHAR, K. M. Chlorine dioxide delignification- Process variables. *Tappi Journal*, v. 74, n. 6, p. 164-167, 1991.
8. REEVE, D. W. Chlorine dioxide in delignification. In: DENCE, C.W.; REEVE, D. W. (Eds.). *Pulp Bleaching – Principles and Practice*, Tappi Press, 2006a, p. 261-290.
9. GORDON, G.; KIEFFER, R. G.; ROSENBLATT, D. H. The chemistry of chlorine dioxide. *Prog. Inorg. Chem.*, v. 15, p. 201-286, 1972.
10. HALPERIN, J.; TAUBE, H. The transfer of oxygen atoms in oxidation-reduction reactions. III. The reaction of halogenates with sulfite in aqueous solution. *J. Am. Chem. Soc.*, v. 74, p. 375-380, 1952.
11. HART, P.; CONNELL, D. Improving chlorine dioxide bleaching efficiency by selecting the optimum pH targets. *Tappi Journal*, v. 7, n. 7, p. 3-11, 2008.
12. LEHTIMAA, T.; TARVO, V.; KUITUNEN, S.; JÄÄSKELÄINEN, A.; VUORINEN, T. The effect of process variables in chlorine dioxide pre-bleaching of birch kraft pulp. Part 1. Inorganic chlorine compounds, kappa number, lignin, and hexenuronic acid content. *Journal of Wood Chemistry and Technology*, v. 30, n. 1, p. 19-30, 2010a.
13. SUESS, H. S. Bleaching of chemical pulp. In: SUESS, H. S. (Ed.). *Pulp bleaching today*. Berlin/New York: Walter de Gruyter GmbH & Co. KG, 2010, p. 16-20.
14. SVENSON, D. R.; JAMEEL, H.; CHANG, H.; KADLA, J. F. Inorganic reactions in chlorine dioxide bleaching of softwood kraft pulp. *Journal of Wood Chemistry and Technology*, v. 26, n. 3, p. 201-214, 2006
15. LEHTIMAA, T.; TARVO, V.; KUITUNEN, S.; JÄÄSKELÄINEN, A.; VUORINEN, T. The effect of process variables in chlorine dioxide pre-bleaching of birch kraft pulp. Part 2. AOX and OX formation. *Journal of Wood Chemistry and Technology*, v. 30, n. 1, p. 1-18, 2010b.
16. HART, P. W.; RUDIE, A.W. Mineral scale management: part I – case studies. *Tappi Journal*, v. 5, n. 5, p. 22-27, 2005.
17. VUORINEN, T.; BUCHERT, J.; TELEMANN, A. et al. Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps. In: *INTL. PULP BLEACHING CONF.*, 1996, Atlanta. Proceedings... Atlanta: Tappi Press, 1996. p. 43-51.
18. EIRAS, K. M. M.; COLODETTE, J. L. Eucalyptus kraft pulp bleaching with chlorine dioxide at high temperature. *Journal Pulp and Paper Science*, Montreal, v. 29, n. 2, p. 64-69, 2003
19. BUCHERT, J.; BERGNOR, E.; LINDBLAD, G.; VIIKARI, L.; EK, M. Significance of xylan and glucomannan in the brightness reversion of kraft pulps. *Tappi Journal*, v. 80, p. 15-171, 1997.
20. VUORINEN, T.; JÄÄSKELÄINEN, A.-S.; LEHTIMAA, T.; TOIKKA, K. and ZHOU, Z., *Fundamentals and Characteristics of Modern Hardwood Pulp Bleaching*, ABTCP-PI 2005: 38th Pulp and Paper International Congress and Exhibition, Sao Paulo, Brazil, October 17–20, CD-ROM (2005).
21. IMMANUEL, A.; JÄÄSKELÄINEN, A.-S., ZHOU, Z. and VUORINEN, T., *Synthesis and Application of the HexA Model methyl 4-deoxy-β-L-threo-hex-4-enopyranosiduronic Acid*, 9th European Workshop on

- Lignocellulosics and Pulp, Vienna, Austria, August 27-30, Advances in Chemistry and Processing of Lignocellulosics, 138-141 (2006).
22. Zhou , Z., Jääskäläinen, A-S, Vuorinen, T., Reversible Equilibrium of Hypochlorous Acid and its Correlation with ClO₂ Bleaching of Pulp. 2008 Intl Pulp Bleaching Conference, Quebec City, Canada, June 2-5, 2008
 23. COLODETTE, J.L, GOMES, C.M., RABELO, M.S., EIRAS, K.M.M., GOMES, A.F., OLIVEIRA, K.D., Eucalyptus kraft pulp bleaching: state-of-the-art and new developments. TAPPI JOURNAL Online. February 2008. p. 18A-18M.
 24. COLODETTE, J. L.; HENRICSON, K. O. The hot acid stage for hexenuronic acid removal. In: HART, P. W.; RUDIE, A. W. (Ed.). The bleaching of pulp. 5th edition. Tappi Press, 2012, p. 103-146.
 25. COSTA, M. M.; COLODETTE, J. L. The impact of kappa number composition on eucalyptus kraft pulp bleachability. Brazil. J. Chem. Eng., v. 24, n. 1, p. 61-71, 2007.

Acknowledgements

The authors wish to thank CAPES, CNPq and Fapemig for partially sponsoring this research.