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The Effect of Process Variables in Chlorine Dioxide Prebleaching of Birch Kraft Pulp. Part 1. Inorganic Chlorine Compounds, Kappa Number, Lignin, and Hexenuronic Acid Content

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Abstract: This study investigated the effects of temperature, chlorine dioxide dosage, and filtrate circulation on various filtrate and pulp properties in chlorine dioxide prebleaching of birch kraft pulp. Also the effect of a preceding A-stage was examined. Kappa number, delignification, and hexenuronic acid removal were unaffected by the used dilution media and temperature. Increasing ClO₂ charge resulted in a lower kappa number, increased hexenuronic acid removal, and more efficient delignification. With a preceding A-stage the kappa number was lower throughout the D₀-stage, but the kappa number reduction and the removal of hexenuronic acid were slightly decreased. Chlorine dioxide consumption was practically independent of the tested variables; only dosage had an effect. The formation of chlorate and chloride was increased with higher dosages of ClO₂, but the stoichiometry remained unchanged. The concentration of chlorite + chlorous acid during bleaching depended on temperature, used dilution medium, and the presence of an A-stage.

Keywords: chlorine dioxide, chlorite, chlorate, chloride, hexenuronic acid, kappa

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INTRODUCTION

The identification of chemical reactions and their kinetics taking place in chlorine dioxide prebleaching is vital when attempting to understand and model bleaching chemistry. In literature, plenty of studies illustrate pulp characteristics before and after a chlorine dioxide stage performed under certain conditions. However, only a limited amount of studies have reported the changes in important reactive species, such as lignin and inorganic chlorine compounds during chlorine dioxide bleaching.^[1–5] This article is the first one to present this kind of results for hardwood kraft pulp and to include the changes in hexenuronic acid content.

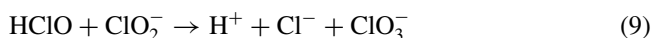
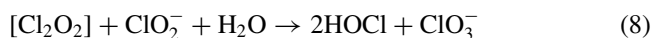
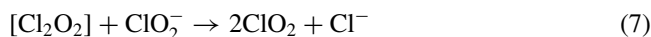
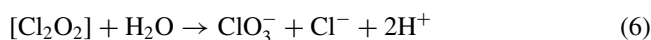
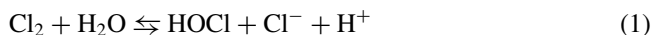
Chlorine dioxide bleaching process is a complex combination of organic and inorganic reactions. Lignin reactions are initiated by a fast reaction between chlorine dioxide (ClO_2) and phenolic lignin structures,^[6,7] which results in a rapid kappa number decrease at the beginning of bleaching.^[1,8,9] This initial phase is only slightly faster at elevated temperatures and it consumes almost all available chlorine dioxide.^[2,3,9]

The rapid initial kappa number decrease is followed by a phase where kappa number reduction and chlorine dioxide consumption are much slower.^[1,8,9] Toward the end of the slower phase the kappa number approaches asymptotically a non-zero limit^[9]. This limit is lower when high temperature^[1,9] or elevated ClO_2 charge is applied.^[10,11] It is noteworthy that ClO_2 concentration does not affect the stoichiometry of bleaching (i.e., the ratio between ClO_2 consumption and kappa number reduction is the same regardless of the chemical charge).^[11] However, the contribution of hexenuronic acid (HexA) in kappa number was not identified in these studies. It has been documented that while chlorine dioxide reacts only very slowly with hexenuronic acid, other intermediate chlorine species react with hexenuronic acid, which contributes to kappa number reduction.^[12,13]

It has been shown that the best delignification is achieved within a final pH interval of 1 to 4.5 and the delignification rate is rather unaffected by changes in pH.^[9,10,14] However, according to Germgård^[1] the consumption of chlorine dioxide increases as the pH is increased above pH 2. Since chlorine dioxide is known to be stable below pH 6^[15] there must be other reactions in bleaching besides delignification that consume chlorine dioxide.

Inorganic chlorine species have major importance in chlorine dioxide bleaching. When chlorine dioxide reacts with phenolic lignin, chlorite (ClO_2^-) and hypochlorous acid (HOCl) are formed in 1:1 molar ratio.^[2] Hypochlorous acid is in equilibrium with chlorine (Cl_2) as shown in Eq. (1), and chlorite (ClO_2^-) is in equilibrium with chlorous acid (HClO_2) (Eq. (2)). Chlorite and chlorous acid will later in the article be referred to as Cl(III) according to their oxidation state. In acidic conditions, chlorous acid can decompose and form hypochlorous acid and chlorate (ClO_3^-) according to Eqs. (3) and (4).^[16]

On the other hand, chlorous acid can react very rapidly with hypochlorous acid forming an intermediate Cl_2O_2 , which reacts further forming chlorate and chlorine dioxide (Eqs. (5)–(9)).^[16–19]



Since chlorite and hypochlorous acid are formed in the initial reaction between chlorine dioxide and phenolic lignin their amounts increase rapidly in the beginning of bleaching. However, HOCl reacts fast with many inorganic and organic compounds^[20,21] and therefore it is consumed almost instantaneously. Cl(III), on the other hand, is consumed more slowly^[5] and its consumption is pH dependent; at pH above 3.5 Cl(III) is not entirely consumed^[2,14] while at lower pH only trace amounts can be measured at the end of bleaching.^[2,5]

In a typical chlorine dioxide prebleaching (D_0), all active chlorine (i.e., chlorine dioxide, Cl(III), hypochlorous acid, and chlorine) is consumed. Because only a small portion of chlorine is bound to organic substances, it is obvious (Eqs. (3)–(9)) that chloride and chlorate are the main final products of chlorine dioxide. Chloride is formed through several organic and inorganic reactions in chlorine dioxide bleaching, such as those presented in Eqs. (5)–(9). On the other hand, chlorate has been proposed to originate mainly from the reaction between chlorite and hypochlorous acid (Eq. (9)).^[22] The concentration of both chloride and chlorate increases throughout the bleaching^[5] and a high ClO_2 dosage results in high residual chlorate concentration.^[10]

This article shows the impact of temperature and chlorine dioxide charge on organic and inorganic reactions during chlorine dioxide prebleaching. The concentration of lignin, hexenuronic acid, and inorganic chlorine compounds were followed as a function of time. In addition, the impact of hexenuronic acid removal and carry-over in the bleaching filtrate on the kinetics of the reactions was studied. As a consequence, this article gives a summary of the essential chemistry taking place in chlorine dioxide prebleaching.

EXPERIMENTAL

Titration stock solution for iodometric titration (0.1 mol/l) was prepared from sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, FF-Chemicals, min 99.5%) and its concentration was verified by titrating with potassium iodate (KIO_3 , MERCK, min 99.5%). Commercial ortho-boric acid (H_3BO_3 , Merck, min 99.8%), sodium hydroxide (NaOH , EKA, min 98%), potassium iodide (KI , VWR, 99.9%), and sulfuric acid (H_2SO_4 , VWR, 98%) were used without additional purification.

Chlorine dioxide (ClO_2) was prepared from calcium chlorate ($\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$, Merck, p.a.) and oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$, VWR, rechapur). Reagents were heated to 60°C and the formed ClO_2 was flushed from the reactor with clean air to the receiver where chlorine dioxide was bound to chilled distilled water. The composition of ClO_2 -water was measured using iodometric titration according to Juurikas^[23] and it was found not to contain chlorine or chlorite, only chlorine dioxide and occasionally traces of chlorate.

Oxygen-delignified birch kraft pulp was obtained from a Finnish pulp mill and mill filtrate was obtained from the last washer before D_0 -stage of the same mill. Prior to the experiments, the pulp was washed with de-ionized water and homogenized.

Chlorine dioxide bleaching was performed using seven different experimental conditions (Table 1). In all the conditions, separate bleaching batches with 1, 5, 10, 20, and 30 minute retention times were conducted. Bleaching was performed using 40 g o.d. pulp in a plastic bag at 10% consistency. pH was not adjusted but it was measured from the filtrate in the beginning and at the end of bleaching. Pulp mixing was done by squeezing the plastic bag for the first minute after ClO_2 addition and then after every 10 minutes. When analyzing the results it should be kept in mind that this method does not result in ideal mixing, and this may cause deviation in some of the fastest reactions taking place in bleaching. After the desired reaction time, pulp was placed to an ice water bath to stop the reactions. The samples for filtrate analysis were separated from the pulp immediately with the aid of a wirepouch.

Table 1. Experimental conditions for hardwood pulp

No.	Temperature °C	ClO_2 charge (kg act. Cl/ADt)	Other remarks
1	45	20	
2	55	20	
3	65	20	
4	45	15	
5	45	30	
6	45	30	Mill filtrate
7	45	20	A-stage

In series 6 mill filtrate was used instead of distilled water to dilute the pulp to reach the 10% consistency.

In series 7 an acidic treatment (A-stage) was conducted for the pulp prior to chlorine dioxide bleaching. A-stage was performed in a plastic bag at 90°C, pH 2.5, and 11% consistency for three hours. The pH was set with sulfuric acid. After the three hour reaction time, pulp was cooled down by placing the plastic bag in an ice bath after adjusting the pH to 7–8 with NaOH. The pulp was not washed before chlorine dioxide stage to simulate the carryover of the reaction products from the A-stage to D₀-stage. Otherwise the chlorine dioxide stage was conducted as described earlier.

The concentrations of chlorine dioxide, chlorite + chlorous acid (Cl(III)) and chlorate in the filtrate were determined with iodometric titration according to Wartiovaara.^[24] Filtrate samples for instant iodometric titration were pipetted to vessels containing KI and boric buffer. The amount of chloride was measured with ion chromatography (Dionex ICS-1500) according to SFS-EN ISO 10304-4. Samples for IC analyses were dosed to vessels, which were in ice bath and contained the chemicals needed for their pretreatment. The samples for pH measurements were cooled to 21°C prior to measurement.

After bleaching, the pulp was washed with de-ionized water and homogenized. Kappa number was determined according to standard SCAN-C 1:00. Aromatic lignin and hexenuronic acid (HexA) contents were determined with UV resonance Raman (UVR) spectroscopic method by Jääskeläinen et al.^[25] The UVR method detects only aromatic lignin structures, not the oxidized structures which contribute to other types of lignin measurements and kappa number. The phenolic content of the pulp was measured according to Warsta et al.^[26] All samples were stored in a refrigerator.

RESULTS AND DISCUSSION

Our results are generally in line with previous literature. Kappa number decreased rapidly in the beginning, followed by a slower phase.^[1,8,9] The chlorine dioxide consumption followed a similar trend.^[2] Also the hexenuronic acid and lignin removal behaved alike: A fast first minute followed by a slower decay.

During the first minute an average of 57% of the total kappa removal was observed. For aromatic lignin (measured with UVR) the removal during the first minute was on an average 84% of the total removal during 30 minutes while for HexA the corresponding number was 68%. The percentage for kappa number decrease is lower than for the removal of aromatic lignin or HexA because kappa number also includes other oxidizable structures besides aromatic lignin and HexA. From this it can be concluded that this other matter is not removed from the pulp as efficiently as aromatic lignin or HexA during the first minute. Of course this can also be a result of ring opening reactions that decrease the amount of aromatic lignin. These reactions increase the amount

of other lignin structures (such as quinones and muconic acids) that contribute to the kappa number and also consume ClO_2 in following reactions.

Hypochlorous acid is produced in the reaction between phenolic lignin and chlorine dioxide.^[2,3] Previous attempts to monitor HOCl content during bleaching have failed due to very low concentrations.^[3] HOCl reacts rapidly with HexA ($k(25^\circ\text{C}) = 400 \text{ M}^{-1}\text{s}^{-1[21]}$), lignin ($k(25^\circ\text{C}) = 40 \text{ M}^{-1}\text{s}^{-1[21]}$) and chlorous acid (Eq. (5), $k(12^\circ\text{C}) = 406 \text{ M}^{-1}\text{s}^{-1[27]}$). Due to its fast reactions, HOCl should not be present in measurable quantities during bleaching and therefore it was not analyzed.

The amount of Cl(III) (chlorite + chlorous acid) increased in the beginning of bleaching and then slowly decreased. This behavior has been known for a long time^[2,5]. According to the results of Svenson et al.^[5] half of all chlorate and chloride is formed already during the first 5 minutes. This was observed also in our experiments. Ni et al.^[3] reported that in their experiments 10–18% of ClO_2 was turned into chlorate and 63–75% into chloride. In our experiments an average of 12% and 48% of ClO_2 was turned into chlorate and chloride, respectively. The results are comparable, when taking into account the different experimental conditions used.

pH

pH development followed the trend of chlorine dioxide consumption. The pH drop was most extensive during the first minute, the pH dropped from the initial 7–8 to 3.7–4.2. After 5 minutes the pH was 3.5–3.9 in all the series. The pH seemed to level off after this; the measured values after 10, 20, and 30 minutes were 2.7–3.9. Changes in temperature did not affect the final pH nor did the preceding A-stage. Higher chlorine dioxide charges resulted in lower pH, but the differences were not substantial. They seemed to derive only from the acidity of the implemented chlorine dioxide solution. The used mill filtrate had a pH of 9.8. This mild alkalinity was able to keep the final pH at a slightly higher level, at an average 0.33 units higher than with water.

Dosage

It is known that increasing ClO_2 charge results in a lower kappa number.^[10,11] This was expectedly seen also in our experiments (Figure 1). However, it was surprising to notice that increasing chlorine dioxide dosage enhanced also the fast initial kappa reduction. Assuming that this reaction is due to ClO_2 and phenolic lignin, the amount of chlorine dioxide should not affect the extent of the reaction, yet there was 1 unit difference in the kappa number after one minute with the 15 and 30 kg dosages. This can be a result of more extensive removal of HexA by the intermediately formed HOCl. The higher ClO_2 dosage resulted

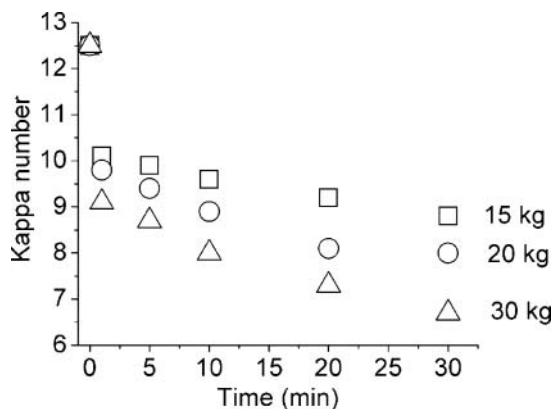


Figure 1. The development of kappa number with different dosages of active chlorine, 15 kg act. Cl/Adt (□), 20 kg act. Cl/Adt (○), and 30 kg act. Cl/Adt (△) as a function of time in 45°C.

also in a bigger kappa decrease during the slower part of the bleaching. This was due to the higher concentration of ClO_2 available to oxidize different organic structures. Also the removal of aromatic lignin was expectedly increased with higher dosages of chlorine dioxide (40% with 15 kg, 49% with 20 kg, and 52% with 30 kg of ClO_2). This is illustrated in Figure 2 where the UVRR spectra of the 30 minute bleached pulps with different chlorine dioxide dosages are presented. When more chlorine dioxide was added the heights of the aromatic lignin band (1605 cm^{-1}) and the HexA band (1655 cm^{-1}) were reduced.

Higher amounts of chlorine dioxide increased hexenuronic acid removal (Figures 2 and 3). This is consistent with the amount of ClO_2 consumed. The more ClO_2 is consumed, the more HOCl is formed to react with HexA. The effect was not that pronounced with the 30 kg dosage, which most likely is due to the fact that all ClO_2 was not consumed with this largest dosage and thus no excess HOCl was formed.

Chlorine dioxide dosage did not have a clear influence on chlorine dioxide consumption (Figure 4). With 20 and 30 kg act. Cl/Adt the same amount of chlorine dioxide was consumed during the first minute (10.7 and 10.8 mmol/l, respectively). This constant consumption implies that this was the amount of ClO_2 needed to oxidize all available phenols and therefore the consumption was not higher with the 30 kg dosage. With 15 kg act. Cl/Adt the consumption of chlorine dioxide was reduced to 8.0 mmol/l, which indicates that this smallest dosage was too low to be able to oxidize all phenolic structures in the pulp.

The phenol content of residual lignin was 0.79 mol/kg lignin. Using the obtained total lignin content of the pulp, the phenol content of the pulp was calculated to be 10.26 mmol/kg pulp. According to a widely presented reaction scheme^[2,6,28] two ClO_2 equivalents would be consumed in the initial reaction

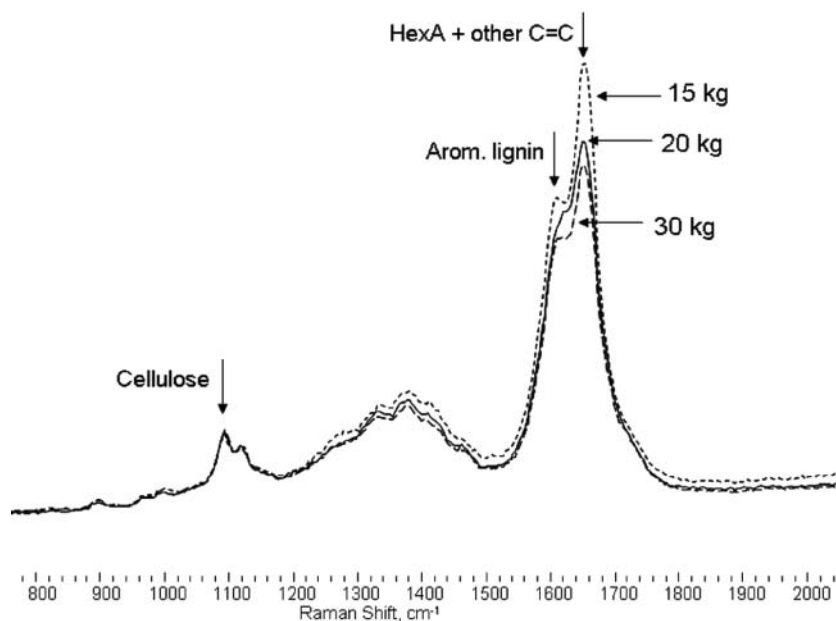


Figure 2. UVR spectra of D₀ pulps (45°C, 30 minutes) with different dosages of active chlorine, 15 kg act. Cl/Adt, 20 kg act. Cl/Adt and 30 kg act. Cl/Adt. The height of the spectra were normalized to the cellulose band at 1094 cm⁻¹.

with a phenolic structure. This would correspond in our consistency to 2.3 mmol/l consumption of ClO₂ in the beginning. Yet the observed amount was four times that. This is merely an indication that the primary reaction products are oxidized further by chlorine dioxide as has been discussed before.^[29] It has

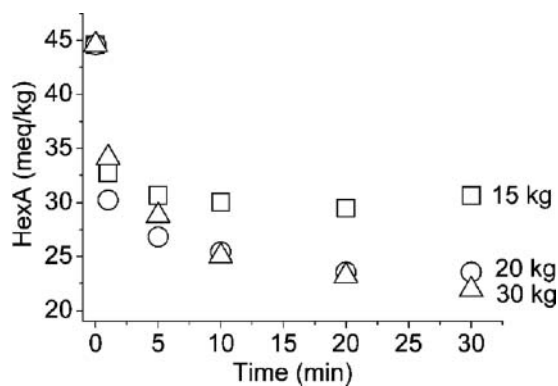


Figure 3. The removal of hexenuronic acid with different dosages of active chlorine, 15 kg act. Cl/Adt (□), 20 kg act. Cl/Adt (o), and 30 kg act. Cl/Adt (Δ) as a function of time in 45°C.

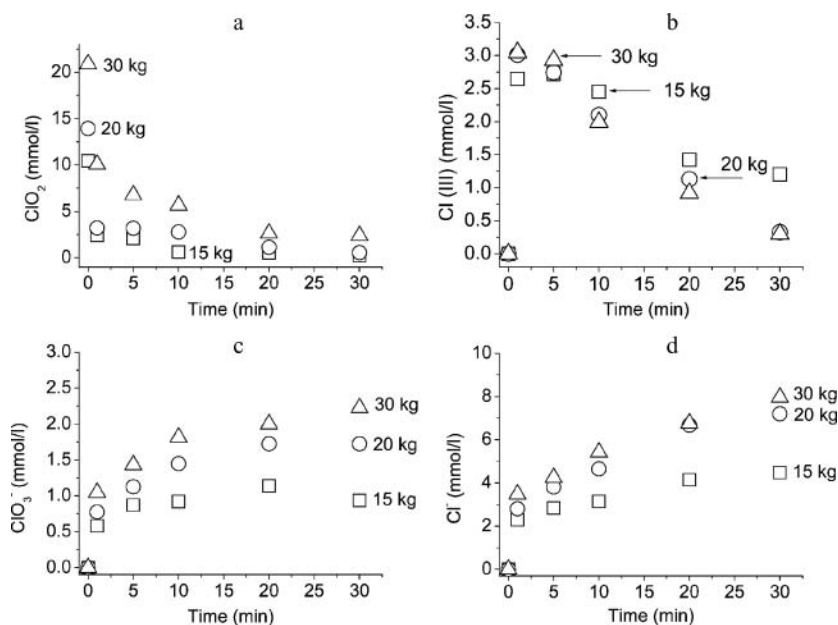


Figure 4. The effect of different dosages of active chlorine, 15 kg act. Cl/Adt (◻), 20 kg act. Cl/Adt (○), and 30 kg act. Cl/Adt (Δ) to a) chlorine dioxide, b) Cl(III) (= chlorite + chlorous acid), c) chlorate, and d) chloride as a function of time in 45°C.

also been suggested that there would be multiple fundamental parallel reactions occurring during the ClO_2 oxidation of phenols.^[30] Also other reactions, such as reactions with extractives^[31,32] and reactions with new phenolic groups formed by the action of HOCl ,^[8,33] can contribute to the consumption of ClO_2 .

After the initial step the consumption was similar for the 15 and 20 kg dosages, while an increased consumption was observed with the 30 kg dosage. In the end of bleaching practically all ClO_2 was consumed with 15 and 20 kg act. Cl/Adt, while with the 30 kg dosage a 2.4 mmol/l residual remained in the filtrate. This suggests that the 30 kg dosage was slightly high. It has been claimed that the ClO_2 concentration does not affect the ratio between ClO_2 consumption and kappa decrease.^[1] This was verified in our experiments, with all dosages 1 kg/Adt of consumed chlorine dioxide removed 0.22–0.25 kappa units.

An equal amount of Cl(III) was formed with 20 and 30 kg act. Cl/Adt. This is consistent with the fact that the same amount of ClO_2 was consumed whether the charge was 20 or 30 kg. With the 15 kg dosage less Cl(III) was formed, but the ratio was similar to the larger dosages. The amount of Cl(III) formed was approximately one third of the consumed ClO_2 . It is known that ClO_2 should be converted into chlorite (ClO_2^-) and hypochlorous acid (HOCl) in this initial reaction in 1:1 molar ratio.^[2] This means that roughly 5.3 mmol/l of

Cl(III) should be formed when 10.7 mmol/l of ClO₂ is consumed. However, the amount was only 3.0 mmol/l. This is due to chlorous acid reacting partly with the formed HOCl very rapidly. A clear indication of this is the fast chlorate and chloride formation (Eqs. (3), (6)–(9)). After the first minute Cl(III) disappeared more slowly with the 15 kg dosage than with 20 or 30 kg and the level remained higher at the end. The slower decay is a result from small pH deviations. As it was stated before, the acidity of the implemented ClO₂ caused slight changes in the end pH. With a lower dosage the end pH remained higher: 30 kg pH 3.1, 20 kg pH 3.3, and 15 kg pH 3.7. At higher pH the reactions of chlorous acid (decomposition and reaction with HOCl, Eqs. (3)–(5) are slower.^[18]

Similar to what Gunnarsson and Ljunggren^[10] have observed, higher ClO₂ dosages increased the formation of chlorate and chloride, which are the final products in ClO₂ bleaching. However, the proportion of chlorine dioxide converted to ClO₃⁻ and Cl⁻ stayed constant even though the dosage was varied.

Temperature

Earlier studies have indicated that the final kappa number would depend on reaction temperature.^[1,9,34] However, in our studies no clear correlation was found. This can be due to the rather small changes in the temperature (10°C) that were used in this experimental series. Barroca et al.^[9] stated that the initial kappa decrease depends slightly on temperature; at higher temperature the kappa number decrease is faster. This was seen to some extent also in our experiments; with the highest temperature (65°C) the kappa reduction in the first minute seemed to be increased by half a unit. This result was anticipated as higher temperatures increase reaction rates.

Temperature had no effect on the removal of hexenuronic acid. It seems that the conditions used were too mild to cause acid hydrolysis of HexA. Therefore the only reactions consuming HexA were the ones with HOCl and/or Cl₂. Because the ClO₂ consumption was constant regardless of the temperature it can be assumed that also equal amounts of HOCl were formed capable of reacting with HexA.

Temperature had no effect on chlorine dioxide consumption or on chlorate formation (Figure 5). Barroca et al.^[9,34] have previously suggested that temperature would increase the fast initial consumption of ClO₂. This is contrary to our results. This is most likely because ClO₂ reacts mainly with phenolic lignin structures during this fast initial stage.^[6,7] Even though this reaction is faster at higher temperature ($E_a = 52 \text{ kJ/mol}$ for 4-cresol^[7]), this impact was not seen. This is because the reaction is so fast even in lower temperatures that it occurs within the first minute ($k(23^\circ\text{C}) = 5.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ for 4-cresol, $k(23^\circ\text{C}) = 1.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ for 4-tert butylphenol^[7]).

The amount of Cl(III) grew rapidly and uniformly in all the temperatures during the first minute. Since Cl(III) is mainly consumed in a reaction with

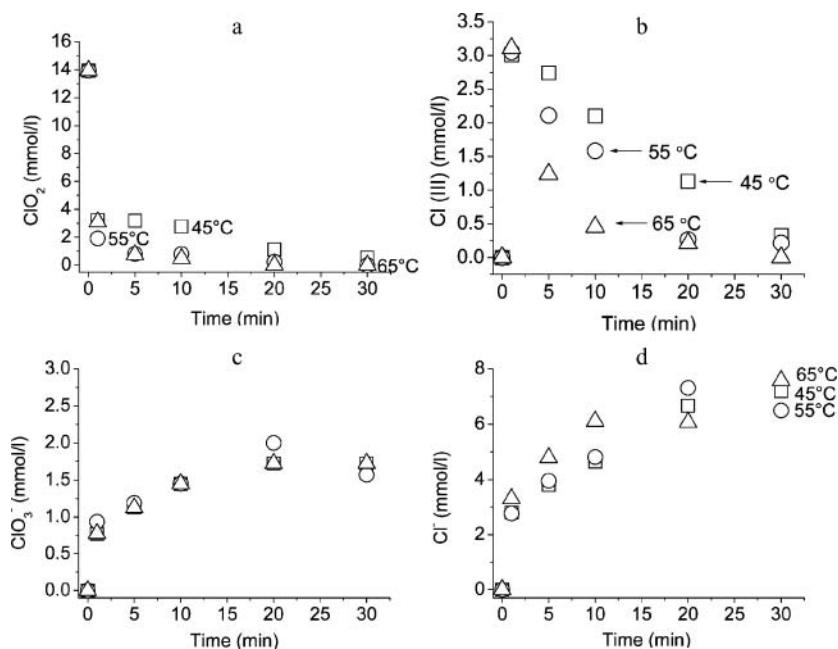


Figure 5. The development of a) chlorine dioxide, b) Cl(III) (= chlorite + chlorous acid), c) chlorate, and d) chloride in different temperatures, 45°C (□), 55°C (○), and 65°C (△) as a function of time with 20 kg act. Cl/Adt.

HOCl (Eq. (5)) in the beginning of bleaching, these similar concentrations might be an indication of comparable activation energies for the reactions of HOCl with chlorous acid and organic compounds. Another possibility is that the reactions between HOCl and organic compounds are diffusion controlled leading to an unchanged amount of HOCl reacting with chlorous acid. After the first minute the amount of Cl(III) decreased with a rate that was dependent on the temperature. This was simply due to the higher temperature speeding up the Cl(III) consuming reactions (Eqs. (3)–(5)). It also seems that the formation of chloride was slightly enhanced in higher temperature. This can be a consequence of the increased reaction rate between chlorous acid and hypochlorous acid (Eqs. (5)–(8)) where chloride is one of the reaction products.

A-Stage

The benefits of including an acidic A-stage in the beginning of a bleaching sequence have been described by Vuorinen et al.^[35] In acidic conditions hexenuronic acid can be removed from the pulp rather selectively. This saves bleaching chemicals.^[35]

Approximately 45% (20 meq/kg) of the hexenuronic acid in the pulp was removed during the A-stage (Table 2). HexA removal in the following chlorine

Table 2. The decrease of kappa number, hexenuronic acid content, and percentage of removed aromatic lignin in a D₀-stage with and without a preceding A-stage with 20 kg act. Cl/Adt as a function of time in 45°C

	Time, min	Kappa number	Δ Kappa	HexA, meq/kg	Δ HexA, meq/kg	Δ arom. lignin
D ₀	0	12.5	0	44.6	0	0
	1	9.8	2.7	30.2	14.4	43%
	5	9.4	3.1	26.8	17.8	48%
	10	8.9	3.6	25.4	19.2	47%
	20	8.1	4.4	23.6	21.0	48%
	30	8	4.5	23.6	21.0	49%
A + D ₀	0	8.6	0	25.0	0	17%
	1	6.6	2.0	18.2	6.8	50%
	5	5.9	2.7	16.8	8.2	53%
	10	5.2	3.4	16.0	9.0	54%
	20	4.8	3.8	14.4	8.9	53%
	30	4.5	4.1	11.5	10.6	56%

dioxide stage was smaller than without the A-stage (Table 2, Δ HexA). The conventional D₀-stage removed 24 meq/kg of HexA while only 12 meq/kg was removed in the D₀-stage following an A-stage. Yet the final amount of hexenuronic acid in the pulp was almost double after the conventional D₀-stage compared to the A + D₀ system. The slower removal of hexenuronic acid due to the preceding A-stage can be explained with two factors. First, the starting concentration of hexenuronic acid is already smaller and thus they will be removed more slowly and second, part of the hypochlorous acid might be consumed in reactions with the reaction products of the A-stage.

In the A-stage the kappa number was reduced by four units. According to Li and Gellerstedt^[36] 10 μmol of hexenuronic acid in 1 g of pulp correspond to 0.84–0.86 kappa units meaning that only 1.7 kappa units was removed due to the removal of HexA. The rest of the kappa decrease (2.3 units) must be due to altered lignin structures. This was supported by the observed lower amount of aromatic lignin (Table 2, Δ arom. lignin). This effect has been examined by Furtado et al.^[37] in more detail and they noticed that an A-stage removes also small amounts of lignin from the pulp. After the D₀-stage the kappa number of the acid treated pulp was 3.2 kappa units lower than with the untreated pulp. When comparing the kappa reduction (Table 2, Δ kappa) between the A + D₀ and the D₀-stage, it was seen that with the preceding A-stage the kappa reduction was slightly smaller. This was a result of the slower HexA removal and the lower residual aromatic lignin content with the preceding A-stage.

Chlorine dioxide consumption was not altered by the A-stage (Figure 6). This is in agreement with the fact that chlorine dioxide itself reacts only very slowly with hexenuronic acid.^[12,13] It reacts primarily with phenolic lignin

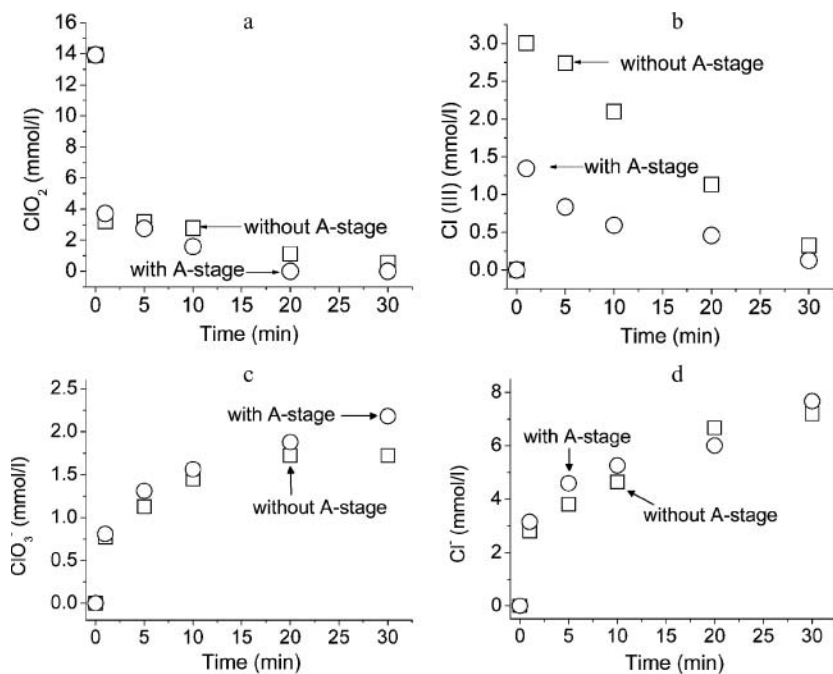


Figure 6. The development of a) chlorine dioxide, b) Cl(III) (= chlorite + chlorous acid), c) chlorate, and d) chloride in a D_0 -stage with (o) and without (\square), a preceding A-stage as a function of time with 20 kg act. Cl/Adt in 45°C .

structures, which are unaffected by the A-stage. The only inorganic chlorine compound that was really affected was Cl(III). After an A-stage the amount of Cl(III) formed was halved in the following D_0 -stage. This is logical, since after the A-stage the pulp contains less hexenuronic acid which reacts with HOCl. This “left over” HOCl is free to react with chlorous acid more extensively according to Eq. (5), lowering the amount of observed Cl(III). Another contributing factor is that one of the A-stage reaction products is 5-formyl-2-furoic acid.^[38] Since this structure is an aldehyde, it can react with chlorite, reducing its amount.^[39,40] The major hydrolysis product of HexA, furoic acid, is not reactive with Cl(III) and does not affect the consumption of Cl(III).

Mill Filtrate

When mill filtrate was used for pulp dilution, kappa number remained higher in the beginning of bleaching (Figure 7). The differences leveled out toward the end of bleaching so that the final kappa was independent of the used dilution medium. This is in agreement with a previous study by Barroca et al.^[34] They reported that higher COD values in the pulp either have no effect or a small negative effect on kappa number. The presence of mill filtrate did not affect

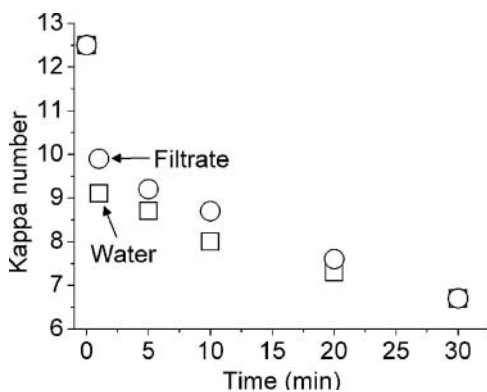


Figure 7. The development of kappa number when using water (□) and mill filtrate (○) for the dilution of pulp as a function of time in 45°C with a chlorine dioxide charge 30 kg act. Cl/Adt.

the removal of aromatic lignin and had no clear effect on the removal of HexA (Figure 8).

The use of mill filtrate for pulp dilution had no effect on chlorine dioxide consumption (Figure 9). The first minute point in the filtrate experiment seems to be flawed; therefore it should not be taken into account when considering the results. Previously Barroca et al.^[9,34] have suggested that the amount of COD would increase the fast initial consumption of ClO_2 . In our experiments this was not observed. This result must be due to the fact that the filtrate used in this study did not possess a high carry over and did not contain substances that would react fast with ClO_2 . Differences in the filtrate properties could

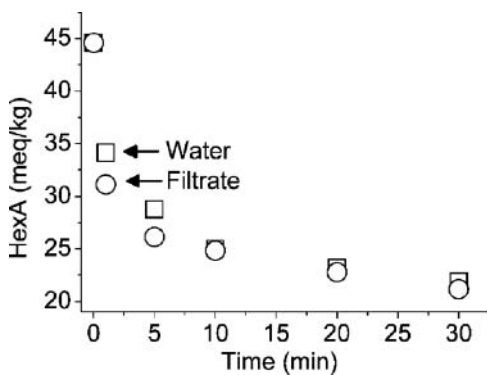


Figure 8. The removal of hexenuronic acid when using water (□) and mill filtrate (○) for the dilution of pulp as a function of time in 45°C with a chlorine dioxide charge 30 kg act. Cl/Adt.

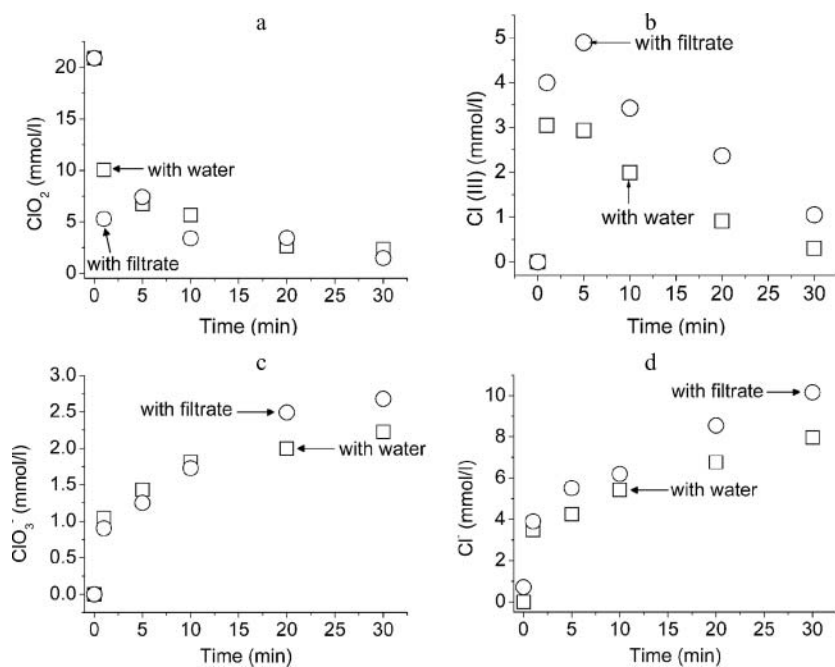


Figure 9. The development of a) chlorine dioxide, b) Cl(III) (= chlorite + chlorous acid), c) chlorate, and d) chloride when using water (\square) and mill filtrate (o) for the dilution of pulp as a function of time with 30 kg act. Cl/Adt in 45°C.

affect these results, especially if a filtrate with a higher carry over was used the outcome would most likely be different.

The use of mill filtrate increased the amount of Cl(III). This is likely to result from more extensive HOCl consumption in reactions with organic matter in mill filtrate, especially during the first minute. This would cause less HOCl to react with chlorous acid. Chloride formation was slightly increased when using mill filtrate. The used mill filtrate contained originally 0.7 mmol/l of chloride ions, thus the increase of chloride is noticeable only after 20 minutes. In our results the differences in chlorate formation due to the presence of mill filtrate were rather ambiguous, perhaps a slight increase was observed in the end of bleaching similar to chloride ions. The higher amounts of ClO_3^- and Cl^- in the end of bleaching can be explained by the different reaction route of Cl(III). As was discussed above, HOCl most likely reacts partly with organic compounds in the filtrate instead of Cl(III) leading to a higher concentration of Cl(III). This residue will react slowly further by chlorous acid dismutation (Eqs. (3)–(4)) and possibly in a reaction with aldehydes^[39,40] producing the additional amounts of ClO_3^- and Cl^- .

CONCLUSIONS

The fast initial reduction in kappa number is mainly due to the fast reaction of chlorine dioxide with lignin. The hypochlorous acid formed in this reaction also contributes to the fast initial stage by oxidizing lignin, HexA, and other organic structures. The slower decay of kappa number toward the end of bleaching is due to the reactions of different chlorine compounds with lignin and hexenuronic acid.

Kappa number and the removal of aromatic lignin and of hexenuronic acid were practically unaffected by the used dilution media or temperature. Increasing ClO_2 charge resulted in a lower kappa number, increased hexenuronic acid removal and more efficient removal of aromatic lignin. With an implemented A-stage the kappa number was lower throughout the D_0 -stage, but the kappa number reduction was slightly decreased as well as the removal of HexA.

The consumption of chlorine dioxide was practically independent of all the tested parameters. The only factor that had some effect was the dosage. With higher dosages the consumption was increased as was also the formation of chlorate and chloride, but the stoichiometry remained the same. In our experiments an average of 12% and 48% of the ClO_2 was turned into chlorate and chloride, respectively, and half of the chlorate and chloride was formed already during the first 5 minutes of bleaching.

Cl(III) (chlorite + chlorous acid) had significant differences in its decomposition rates. In all experiments the amount of Cl(III) first increased in the beginning of bleaching and then slowly disappeared. It seems that the different decomposition rates in different experiments were mainly due to the reaction of chlorous acid with HOCl. The amount of HOCl that is available to react with chlorous acid is dependent on the organic reactions consuming HOCl. Therefore, when using mill filtrate, where more organic matter that can react with HOCl is present, the amount of Cl(III) was increased. After an A-stage less HexA was present to react with HOCl and thus more HOCl would have reacted with chlorous acid, leading to lower amounts of observed Cl(III).

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