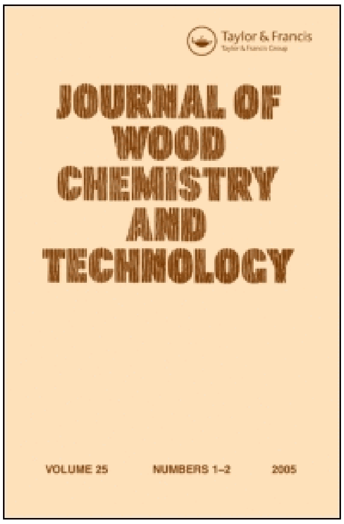

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The Effect of Process Variables in Chlorine Dioxide Prebleaching of Birch Kraft Pulp. Part 2. AOX and OX Formation

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Abstract: Chlorine dioxide prebleaching (D_0-stage) is known to produce some chlorinated organic compounds. This article presents the development of AOX and OX as a function of time under various prebleaching conditions for oxygen delignified hardwood pulp. It was observed that OX is formed more rapidly than AOX and its amount was less affected by a preceding A-stage. Temperature had little effect on chlorination. Using mill filtrate instead of water for dilution increased the amount of AOX formed while the amount of OX remained unchanged. Higher charges of chlorine dioxide expectedly increased chlorination during a D_0-stage.

Keywords: AOX, chlorination, chlorine dioxide, OX, hardwood pulp

INTRODUCTION

Chlorinated organic compounds are formed in chlorine dioxide bleaching when intermediately formed hypochlorous acid (HOCl) and chlorine (Cl_2) react with organic structures present in the filtrate or fibers.[1,2] Hypochlorous acid, which is formed in the reaction between chlorine dioxide and phenols, is in equilibrium

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with molecular chlorine (Cl_2) according to Eq. (1).[3,4]

$$Cl_2 + H_2O \rightleftarrows HOCl + Cl^- + H^+ \quad (1)$$

Both HOCl and Cl_2 react rapidly with lignin and hexenuronic acid.[5,6] Both of them also chlorinate various structures in pulp.[2,4,7–10] Most of the AOX (Adsorbable organic halogens) is formed in the first minutes of bleaching.[11–13] After this the amount of AOX seems to stay rather constant.[13] Also, organic chlorine in the fibers is formed rapidly at the beginning.[12] After the initial phase OX (organically bound halogens) formation is stopped and part of the OX may decompose in further reactions.[12] It has been reported that after the first D stage, 16–21 mol-% of the chlorine dioxide charge was found as chlorine bound to organic substances, either as AOX or OX.[14]

The amount of AOX can be reduced by raising temperature[15] or lowering the chlorine dioxide dosage.[16] In the experiments of Ljunggren et al.[16] AOX was decreased by about 50% when the ClO_2 charge was reduced by 36% but only a slight or no change was observed in OX formation. Ragnar and Törngren[17] have stated that OX is formed in relation to the chlorine dioxide charge, but the amount is significantly reduced after a subsequent alkaline extraction stage.

More AOX and OX is known to be formed at lower pH.[2,9,13,15,18] At low pH chloride ions promote the formation of chlorine and thereby also AOX formation.[13] However, if the pH is increased to 3, chloride ion concentration does not affect the AOX formation.[13] This is due to the equilibrium between HOCl and Cl_2 (Eq. (1)) that is dependent both on pH and chloride ion concentration.

A portion of AOX originates from hexenuronic acid (HexA).[19–21] The portion has been proposed to be anything between 27% up to even 80% of the total amount of AOX.[14,19,20] The addition of an acidic A-stage in the beginning of a bleaching sequence removes hexenuronic acid selectively from the pulp. This saves bleaching chemicals and reduces the amount of formed AOX.[21,22] On the other hand, it has been stated that the chlorination products of HexA would be unstable and therefore an A-stage would have only a minor effect on the amount of stable AOX.[14] Björklund et al.[14] have suggested that chlorinated lignin structures would be the major contributors to the OX in the pulp and to stable AOX in the filtrate. Also, Ragnar and Törngren[17] found that most OX seems to be attached to lignin, pure fractions of carbohydrates did not contain OX. They concluded that HexA or other carbohydrates are not sources of OX, only AOX.

Several studies report AOX and OX results after chlorine dioxide bleaching. However, it seems that the development of AOX and OX as a function of time when bleaching hardwood pulp or O_2-delignified softwood pulp has not been studied. Results have only been published for softwood kraft pulp that has not been O_2-delignified.[9,11–13] In addition information is lacking on how the development of AOX and OX is affected by changes in chlorine dioxide dosage, removal of hexenuronic acid or the purity of the pulp filtrate. This work was performed to fulfill this gap for oxygen-delignified hardwood kraft pulp.

EXPERIMENTAL

The methods for chlorine dioxide manufacturing, pulp bleaching and sampling were described in "Part 1. Inorganic chlorine compounds, kappa number, lignin, and hexenuronic acid content." Filtrate samples for AOX analysis were dosed to vessels containing sodium sulfite to stop the reactions. The amount of organically bound chlorine in the filtrate (AOX) and in fibers (OX) was measured with an AOX-analyzer (Thermo Electron, Dextar) as described in standards SFS-EN 1485 and SCAN-CM 52:94, respectively. The chlorination degree of lignin was calculated assuming an average molecular weight of 200 g/mol for lignin and by utilizing Eq. (2) adopted from Saariaho et al.[23] in calculating the lignin content of the pulp. The kappa number and HexA results were presented in Part 1. The correlation factor 0.15 that is used in Eq. (2) between total lignin content and kappa number has been shown to be accurate also for oxygen delignified pulp.[24] However, it is unknown how this correlation factor is affected by chlorine dioxide bleaching and presumably it should be different for different samples. Here the calculated lignin content is used only as a tool to assess the chlorination degree of lignin and the limitations were considered when the results were analyzed.

$$\mathrm{L}(w - \%) = (\mathrm{kappa} - 0.086 \times \mathrm{HexA}(mmol/kg)) \times 0.15 \qquad (2)$$

All the sample points were conducted as separate bleaching experiments and are thus unique, even though they were always performed analogously. This led to some variations in the results. Another source of error was chlorine dioxide vaporization. Since the experiments were carried out in plastic bags, as is quite often done,[9,25] chlorine dioxide losses were inevitable. An average of 22 mol-% of chlorine was lost (according to chlorine balance calculations).

RESULTS AND DISCUSSION

The chlorination of organic compounds was observed to be very fast at the beginning of a D_0-stage, but the rate decreased as the bleaching continued (Figures 1–4). This is in agreement with previous studies.[11–13] This fast initial phase was more pronounced with OX than with AOX. Hypochlorous acid is produced in the reactions of chlorine dioxide.[3,11] Since the consumption of chlorine dioxide is known to be very fast in the beginning of bleaching[3] relatively high amounts of HOCl (and Cl_2) are present during this initial stage. This leads to the observed rapid chlorination.[3]

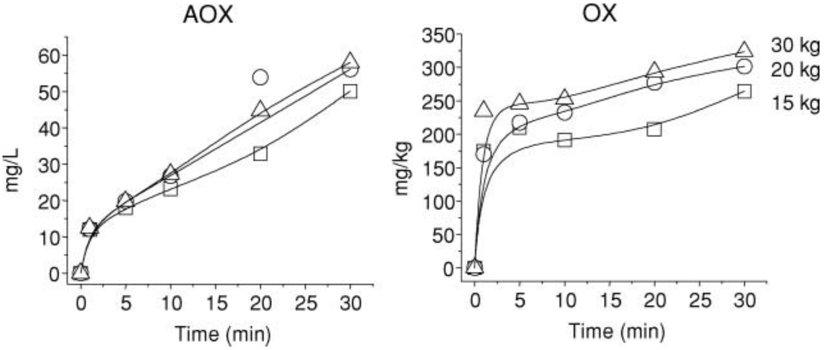

Figure 1. The formation of AOX and OX with different dosages of active chlorine, 15 kg act. Cl/Adt (□) 20 kg act. Cl/Adt (o) and 30 kg act. Cl/Adt (Δ) as a function of time in 45°C.

The trend of OX formation was different in our experiments than observed before.[11,12] In the previous experiments OX formation stopped after the initial step and some OX was even decomposed in further reactions, while in our experiments the amount of OX grew steadily but slowly toward the end. Ni and van Heiningen[12] monitored the reaction for several hours, so it is possible that the amount of OX would have decreased also in our experiments during a longer reaction time. Ni and van Heiningen[12] concluded that this observed decrease in OX can be due to dissolution of OX. Another contributing issue can be the oxidation of chlorinated structures by ClO_2.[18,26]

AOX formation, although being rather rapid during the initial phase, was much more moderate than OX formation. Of AOX, 20–50% was formed during

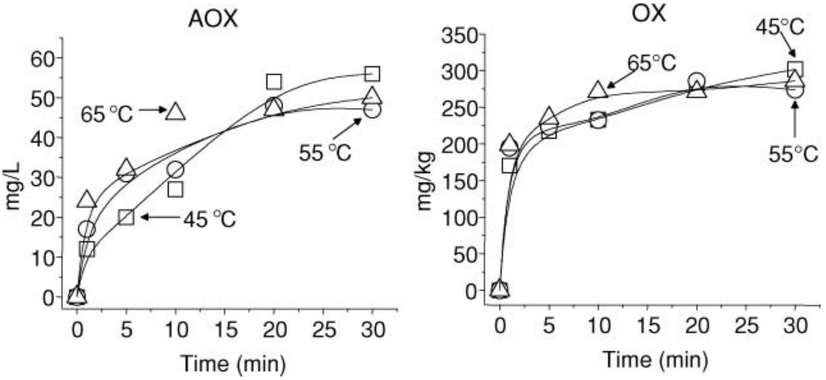

Figure 2. The formation of AOX and OX at different temperatures 45°C (□), 55°C (o) and 65°C (Δ) as a function of time with a 20 kg act. Cl/Adt dosage of chlorine dioxide.

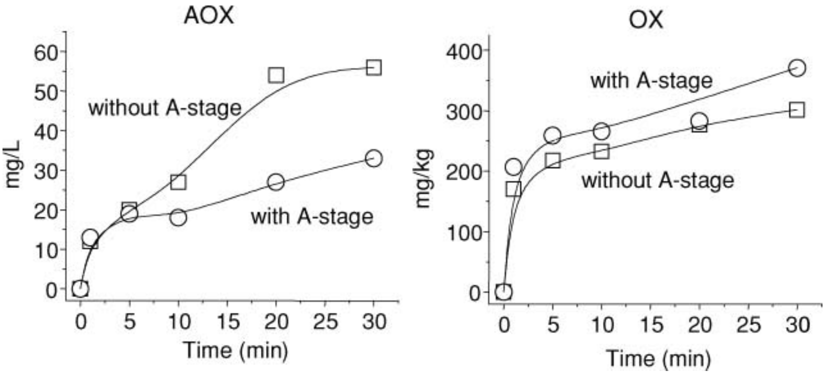

Figure 3. The formation of AOX and OX with (o) and without (□) acid treatment as a function of time in 45°C.

the first minute. This result is in agreement with earlier publications, where 30–50% of AOX was formed in the beginning of a D_0-stage.[9,11–13] AOX is usually considered to be formed as organic compounds in the filtrate are chlorinated, but part of the AOX can be derived from the dissolution of OX as mentioned earlier.[12]

After D_0-stage 14–21 mol-% of chlorine dioxide had ended up as AOX or OX (Table 1). This is consistent with the results of Björklund et al.,[14] who reported that after bleaching O_2-delignified birch 16–21 mol-% of the chlorine dioxide charged was either as AOX or OX. For Ni et al.[11] this figure was only ~7% when bleaching softwood kraft pulp.

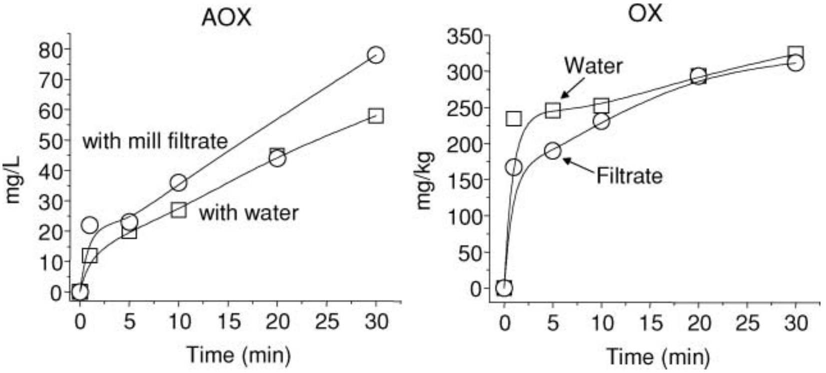

Figure 4. The formation of AOX and OX with water (□) and mill filtrate (o) used as the dilution liquid as a function of time at 45°C with a 30 kg act. Cl/Adt dosage of active chlorine.

Table 1. The percentage of consumed ClO_2 as organic chlorine

Temp (°C)	ClO_2 (kg/Adt)	1 min	5 min	10 min	20 min	30 min
45	15	10%	13%	12%	15%	21%
45	20	8%	11%	13%	18%	18%
45	30	9%	9%	10%	11%	14%
55	20	8%	11%	12%	16%	15%
65	20	12%	12%	15%	15%	16%
45[1]	20[1]	9%	11%	10%	11%	14%
45[2]	30[2]	7%	9%	9%	12%	16%

[1] The D_0-stage was preceded by an A-stage.

[2] Pulp was diluted with mill filtrate.

Dosage

AOX formation in the beginning was identical with different chlorine dioxide charges (Figure 1). When the bleaching continued, the amount of AOX formed was somewhat lower with the 15 kg dosage. No differences were observed between 20 and 30 kg dosages. This can be due to overdosing, for not all ClO_2 was consumed during bleaching with the 30 kg dosage. Previously it has been shown that higher chlorine dioxide dosages led to increased AOX formation.[13,16,18] The unexpectedly small differences of AOX formation in our results can be explained by the rather high consistency, 10%, that was used in the experiments. Reeve et al.[13] stated that at higher consistencies the amount of AOX is less affected by the dosage. They indicated that above 12% consistency, the increase in AOX concentration was not as significant.

Higher chlorine dioxide dosages produced more OX (Figure 1). The differences were noticeable already during the first minute and stayed rather constant throughout the bleaching. This is in agreement with the results of Ragnar and Törngren,[17] who stated that OX is formed in relation to the chlorine dioxide charge. Others[16,18] have claimed that only a slight or no increase of OX was observed when changing the chlorine dioxide charge.

Surprisingly, the fraction of Cl-atoms bound to organic compounds was lower with bigger chlorine dioxide dosages (Table 1). The total amount of organic chlorine (AOX+OX) was only slightly higher with the bigger dosages. It seems that instead of chlorinating, the additional ClO_2 was mainly consumed in inorganic reactions and ended up as chloride or chlorate, as stated in Part 1. When studying chlorination of natural organic matter with chlorine, Gallard and von Gunten[27,28] observed a rapid initial phase after which the amount of chlorinated compounds increased more slowly. They accounted the fast initial phase to reactions of HOCl with dihydroxybenzenes and the slower phase to reactions between monohydroxybenzenes and HOCl. The same phenomenon could partly explain our results; structures that are susceptible to chlorination

Table 2. Second order rate constants ($M^{-1}s^{-1}$) at 23°C for the reactions of chlorine dioxide,[27] hypochlorous acid,[25] and chlorine with phenol and phenoxide[25]

Reactant	ClO_2	HOCl	Cl_2
phenol	0.4	0.36	2.5×10^{2a}
phenoxide	4.9×10^7	2.2×10^4	
4-methylphenol	50	0.09	1.7×10^{3a}
4-methylphenoxide	5.2×10^8	2.7×10^4	

[a]The rate constants were reported for acid-catalyzed hypochlorous acid reaction instead of chlorine. It should be corrected with [Cl^-] to obtain the accurate rate constant for chlorine.

would react fast with $HOCl/Cl_2$ in the initial phase and structures that are chlorinated more slowly would dominate the reactions in the slower phase. In that case the extent of chlorination would be mostly dependent on the amount of reactive structures in the pulp. However, the presence of polyphenolic compounds in the pulp, especially after O_2-delignification, is highly improbable and thus some other structure should be responsible for the rapid chlorination.

When comparing the reaction rate of phenol and 4-methylphenol with chlorine dioxide and hypochlorous acid (Table 2), it is obvious that the reaction rates are smaller with HOCl. In addition, the amount of HOCl is always very small during chlorine dioxide bleaching, while ClO_2 is usually present in excess. Also, the reaction rate of ClO_2 with the dissociated phenols is approximately 10^7 times faster than with the undissociated form. Even though ClO_2 bleaching takes place in acidic medium, there is a portion of phenols in their dissociated form (e.g., 2-methoxyphenol with pKa 9.9,[29] 0.0001% is dissociated at pH 4). Therefore it seems that almost all of the available phenols present in the pulp would react with ClO_2 and the reaction of HOCl with phenols is unlikely responsible for the chlorination.

Larson and Rockwell[30] have shown that HOCl chlorinates certain carboxylic acid structures. The reaction rates of carboxylic acids with HOCl seem to be much faster[31] than with chlorine dioxide.[29] However, carboxylic acids are found so abundantly in chlorine dioxide bleaching (e.g., hexenuronic acid, muconic and maleic acids) that they can not be a restricting factor for chlorination.

The reaction rates of phenol and 4-methylphenol with chlorine are several orders of magnitude faster than with chlorine dioxide or hypochlorous acid (Table 2). As discussed previously, the amount of phenols restrains the amount of chlorine dioxide consumed, leading to a practically unchanged formation of $HOCl/Cl_2$. Thus the available amount of the chlorinating compounds $HOCl/Cl_2$ might be the limiting factor for chlorination and the almost constant amount of chlorination would be due to the unchanged chlorine dioxide consumption.

Table 3. Calculated chlorination degree of lignin

Temp (°C)	ClO_2 (kg/Adt)	1 min	5 min	10 min	20 min	30 min
45	15	9%	11%	10%	12%	16%
45	20	9%	12%	13%	17%	19%
45	30	14%	15%	16%	21%	25%
55	20	10%	12%	13%	19%	18%
65	20	11%	14%	18%	17%	21%
45[1]	20[1]	16%	22%	26%	31%	41%
45[2]	30[2]	9%	10%	13%	20%	24%

[1]The D_0-stage was preceded by an A-stage.

[2]Pulp was diluted with mill filtrate.

Whether chlorination is mostly dependent on the composition of pulp or the $HOCl/Cl_2$ formation or both, cannot be concluded here.

The chlorination degree of lignin in the pulp was calculated (Table 3). It was found to increase as the ClO_2 charge increased. This is suggested to be mostly due to the different amounts of lignin removed from the pulp.

Temperature

Bleaching temperature had a diverse effect on AOX formation (Figure 2). At higher temperature the formation was more rapid and more AOX was formed during the first minute. The final amount appeared to be higher at the lowest temperature, 45°C, while at 55 and 65°C the final level was equal. In most previous results AOX formation has not been influenced by temperature (25–45°C).[11, 12, 16] At higher temperature (70–95°C at pH 2.5) it has been observed that the amount of AOX can be reduced by raising temperature.[32] Their conditions, however, were harsh enough for acid hydrolysis of hexenuronic acid and thus cannot be compared to our results.

The rate of OX formation showed no clear temperature dependency (Figure 2). The formation was slightly faster at 65°C, but this effect was not seen at 45 or 55°C. The final amount of OX remained unchanged in all the temperatures. This result is in agreement with the results of Ni et al.[11] and Ni and van Heiningen.[12] They reported that temperatures between 25–45°C had no influence on chlorination. This has also been verified in experiments with a lignin model compound, where same amounts of different reaction products were obtained regardless of the temperature between 20–40°C.[2] Also, the calculated chlorination degree of lignin remained unchanged in different temperatures (Table 3, 45, 55 and 65°C) throughout the bleaching.

The amount of chlorine dioxide converted into organic chlorine seems to be higher at elevated temperature in the beginning of bleaching (Table 1).

However, this difference is leveled out during 20 minutes and by the end of bleaching the proportion of ClO_2 turned into organic chlorine was the same irrespective of temperature.

A-Stage

AOX originating from a D_0-stage consists partly of chlorination products of HexA.[14,19–21] When HexA was removed from the pulp with a hot acidic treatment (A-stage) before a D_0-stage, the final amount of AOX decreased drastically, approximately by 40% (Figure 3). The proportion of AOX originating from HexA has been suggested to be anything between 27% up to even 80% of the total amount of AOX.[14,19,20] The initial rate of AOX formation was unaffected by the A-stage. This implies that the majority of AOX formation in the beginning is due to chlorination of dissolved lignin, not HexA.

The amount of OX formed augmented slightly when the pulp was subjected to an acidic treatment prior to the D_0-stage. Similar behavior has been denoted by Björklund et al.[14] It has been found that most OX appears to be attached to lignin, HexA is not a source of OX.[14,17] Thus the elevated amount of OX formed is due to more extensive chlorination of lignin. This is supported also by the higher chlorination degree of lignin (Table 3). The more extensive chlorination arises from the higher amount of $HOCl/Cl_2$ present. Since after an A-stage they are not consumed to same extent in reactions with HexA, they instead cause more chlorination of lignin.

The proportion of chlorine dioxide turned into organic chlorine was the same in the beginning of bleaching regardless of the A-stage but at the end of bleaching the level was substantially lower with the A-stage (Table 1, D and A+D). This difference is due to the lower amount of AOX after the A-stage.

Mill Filtrate

In one bleaching series the pulp was diluted with mill filtrate instead of water. Mill filtrates typically contain varying amounts of impurities, for example, inorganic salts and organic compounds dissolved from the pulp. These impurities may affect the reactions taking place in chlorine dioxide bleaching. A larger amount of AOX was formed in the beginning of bleaching when mill filtrate was used (Figure 4). This was most likely due to faster reactions of $HOCl/Cl_2$ with organic matter present in the filtrate compared to the fiber bound organics. This was supported by the fact that OX formation was retarded after the mill filtrate addition. The amount of AOX remained at a higher level throughout the bleaching, indicating that the organic compounds in the filtrate induced more chlorination. The final amount of OX, however, remained unchanged. This supports the suggestion that the extent of chlorination would be more affected by the presence of structures susceptible to chlorination instead of the amount of $HOCl/Cl_2$. The presence of chloride (0–0.1 mol/l) has been reported to increase the formation of OX.[18] The chloride concentration in the used mill filtrate was rather low, 0.71 mmol/l, and did not affect the final OX level. The calculated chlorination degree of lignin (Table 3) was a little lower after the first minute when using mill filtrate but the difference vanished by the end of bleaching.

The proportion of chlorine dioxide converted into organic chlorine was practically the same regardless of the dilution medium in the beginning of bleaching (Table 1, water and filtrate). At the end of bleaching the amount of chlorination was slightly higher when mill filtrate was used. This seems to be due to the presence of more dissolved organics in the filtrate producing higher AOX amounts.

CONCLUSIONS

The chlorination of organic matter was very fast in the beginning of a D_0-stage, but the rate decreased when bleaching continued. Of AOX, 20–50% was formed within the first minute, after which AOX was formed quite steadily along the bleaching as long as some active chlorine was present. The slow growth in the amount of AOX can also be due to OX dissolution. OX was formed more rapidly than AOX; 54–72% of OX was formed during the first minute. Increased chlorine dioxide charges increased the amount of OX, but had only a small effect on AOX. The amount of OX formed was less affected by a preceding A-stage than AOX. Temperature had little effect on chlorination. Addition of mill filtrate increased the amount of AOX while OX formation remained unchanged. It was concluded that there is something restricting the amount of chlorination. Whether the limiting factor was the composition of the pulp, the $HOCl/Cl_2$ formation, or both, could not be concluded here.

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