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Inorganic Reactions in Chlorine Dioxide Bleaching of Softwood Kraft Pulp

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Abstract: A softwood kraft pulp (27 kappa) was bleached with chlorine dioxide to various end pH values. The formation of chlorite, chlorate, and chloride was measured to quantify the amount of chlorine dioxide wasted as a function of pH during a D₀ (pre-bleaching) stage. Chlorate formation increased with a decrease in final pH. Conversely, residual chlorite increased with an increase in the final pH. After 120 min of bleaching the total residual chlorite and chlorate showed that no substantial increase in residual oxidant occurs when bleaching to an end pH below 3.4. As a result, the brightness and permanganate numbers for low pH chlorine dioxide bleached pulps did not differ when bleaching to an end pH between 3.4 and 1.8. However, decreasing the pH below 3.4 did result in increased organic chloride formation. The results are contrary to previous studies where the maximum bleaching efficiency for a D₁ stage was reported to occur when the end pH was between 3 and 4.

Keywords: Bleaching, chlorine dioxide, lignin, chlorite, chlorate, inorganic reactions

INTRODUCTION

Due to environmental concerns, elemental chlorine is being replaced with chlorine dioxide (ClO₂) for the bleaching of wood pulps. Chlorine dioxide is a very selective bleaching reagent, preferentially oxidizing lignin in the

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presence of carbohydrates, thereby preserving pulp quality. In addition, ClO_2 generates less chlorinated organics or adsorbable organic halides (AOX) compared to chlorine, increasing the attractiveness of chlorine dioxide as a bleaching reagent. However, there are issues surrounding the utilization of chlorine dioxide. Based on oxidation equivalents it is more expensive than elemental chlorine. Furthermore, the formation of chlorate and chlorite decrease its oxidation efficiency, further increasing the cost of bleaching.

One of the keys to optimizing a chlorine dioxide bleaching stage is to minimize the formation of chlorate and chlorite. In the past, chlorine dioxide bleaching studies on chlorine pre-bleached pulps have shown that the optimal usage of chemical (minimum chlorate and chlorite residues) requires that the end pH be around 3.8.^[1] However, this may not be true for chlorine dioxide pre-bleaching because residual kraft lignin components most likely differ from the residual lignin in a chlorine pre-bleached pulp. It has been shown that lignin structure, particularly phenolic lignin content, directly influences the bleachability of wood pulps.^[2,3] Therefore, pre-bleaching with chlorine dioxide may require different reaction conditions to minimize chlorite and chlorate formation. In this article we report the effect of end pH on the formation of inorganic chlorine species during chlorine dioxide pre-bleaching of a softwood kraft pulp.

EXPERIMENTAL

Materials

3,4-Dimethoxyacetophenone, sodium borohydride (NaBH_4), *p*-dibromobenzene, biphenyl, and all solvents were purchased from Aldrich Chemicals and used as received. Chlorine dioxide was produced by reacting 80% stabilized sodium chlorite (ACROS) with 1.5 equivalents of potassium persulfate (Fluka) in distilled water at room temperature. The resulting solution was stripped with UHP-nitrogen. Nitrogen gas containing stripped chlorine dioxide was passed through a column of sodium chlorite (Aldrich), then scrubbed in cold HPLC water.

Methylveratryl alcohol (MVA) was prepared by reacting 3,4-dimethoxyacetophenone with 2 equivalents of NaBH_4 . The reaction mixture was refluxed in 3:1 MeOH:H₂O for 3 h, neutralized with carbon dioxide, and extracted with 1,2-dichloroethane. Quantitative conversion of the acetophenone was obtained. MS *m/z* (rel. int.) 182(M+, 59), 167(87), 153(47), 139(100), 124(32), 108(21), 93(50), 77(21), 65(25), 51(11), 43(41). ¹H-NMR δ 1.48(d,3H), 3.90(d,6H), 4.83(q,1H), 6.84(q,1H), 6.86(q,1H), 6.93(d,1H).

Kraft Pulp Production

Loblolly pine chips were pulped in a M & K digester with external liquor circulation and electric heating. The cooking schedule and H-factor (1600

H-factor) were controlled by a process computer. The chip charge was 1000 g (OD), at 19.5% AA (active alkali), and a liquor-to-wood ratio of 4:1. White liquor was made from stock solutions of NaOH and Na₂S. Cooked chips were disintegrated in an agitated tank and screened on a flat screen with 0.006 inch slots. The screen accepts were collected and washed repeatedly. The lignin content (kappa number = 27) was measured on the accepted pulp according to TAPPI UM 246.

Chlorine Dioxide Reactions with Pulp

The 27 kappa softwood kraft pulp (12 g OD) was prebleached with chlorine dioxide using a 0.2 kappa factor. The bleaching was carried out at 10% consistency at 50°C for 2 h. The initial pH of the pulp was adjusted using aqueous sodium hydroxide (5 wt%) or sulfuric acid (5 wt%) to achieve a desired final pH. HPLC grade water (Aldrich) was used as the makeup water. Polyethylene bags fastened with rubber septa were used for bleaching. Samples for inorganic ion analysis were prepared by injecting 20 μL effluent samples into a 7 mL vial and evacuating for 45 s, a 1 mL aliquot of HPLC water was then added to the sample, followed by the addition of a sodium fluoride internal standard. Effluent samples were taken periodically during the 2 h bleach. Ions were analyzed using an ion-exchange column (Dionex AS9/AG9 guard column) with 2.5 mM sodium borate eluent. The eluent flow rate was 1.75 mL/min. Chemical detection was done by suppressed conductivity using a Dionex CD20 conductivity detector. Chlorine dioxide concentrations were determined by iodometric titration. The quantity of hypochlorous acid in the reaction medium was determined by trapping with aqueous solutions of dimethylsulfoxide (DMSO). Samples (100 μL) of the reaction mixture were injected into 0.5 mL of cold aqueous solutions containing excess DMSO (0.25 M, pH adjusted to 8). Trapped samples were quenched after 15 s with a saturated sodium thiosulfate solution. The resulting dimethylsulfone content was determined by GC using cyclohexanol as an internal standard.

Chlorine Dioxide Reactions with MVA

MVA reactions were run at $25 \pm 1^\circ\text{C}$ in an oil bath as previously reported.^[4] The pH of the chlorine dioxide reaction was kept constant by using a pH control feedback loop. Reactions were run in a 100 mL, 4-necked flask. An OmegaTM pH controller (model PHCN-37) was connected to a Milton-Roy micro-chemical metering pump (model A771-155S). A sodium hydroxide solution (0.8 M) was delivered to the reaction vessel from a burette via Nalgene[®] PVC tubing. The alkali addition did not exceed 1% of the total reaction volume. The reaction mixture was stirred magnetically with a

Teflon coated bar. The pH of the water and chlorine dioxide were adjusted using aqueous sodium hydroxide (5 wt%) or sulfuric acid (5 wt%) to achieve the desired final pH and mixed for one minute prior to injection of an aqueous solution of MVA. Samples of the reaction were taken with a syringe through a rubber septum. In the kinetic experiments sampling was done until all MVA or chlorine dioxide was consumed.

Organic compound concentrations were determined by gas chromatography. Twenty μL samples of the reaction mixture were quenched either by adding 0.5 mL of 0.4 M ascorbic acid or 0.5 mL of a saturated aqueous sodium thiosulfate solution. The quenched samples were extracted with 0.5 mL of ethyl acetate containing 0.6 mg/L *p*-dibromobenzene or biphenyl as an internal standard. Thereafter, the samples were dried over anhydrous sodium sulfate and made up to 2 mL with ethyl acetate prior to GC analysis.

GC analyses were performed on an HP 5890 (splitless injection) instrument equipped with a flame ionization detector, using He as the carrier gas. Injector and detector temperatures were 240°C and 280°C, respectively. Separations were achieved on a J&W DB-5 fused silica capillary column (30 m \times 0.32 mm \times 0.25 μm). Typical temperature programs were from 45°C to 250°C at a rate of 10°C/min with an initial time delay of 1 min, and from 100°C to 270°C at 10–20°C/min. In quantitative studies, *p*-dibromobenzene or biphenyl was used as an internal standard and the relative peak areas and corresponding response factors were used to calculate concentrations.

All GCMS analyses were conducted using the GC analysis conditions on a HP 5985B GCMS equipped with a DB-5 capillary column. In the EI mode, the electron energy used was 70 eV.

$^1\text{H-NMR}$ spectra were determined on a GE 300 MHz instrument. Samples were dissolved in CDCl_3 . Chemical shifts are given in ppm downfield from TMS (tetramethylsilane).

RESULTS AND DISCUSSION

A 27 kappa softwood kraft pulp was bleached with chlorine dioxide (ClO_2) to various end pH values. The quantity of chlorite (ClO_2^-), chlorate (ClO_3^-), and chloride (Cl^-) were determined as a function of reaction time and are shown in Figures 1 and 2.

During high pH bleaching (pH 11.2), chlorite formed rapidly. The first sample point (3 min) for the pH 11.2 reaction shows that approximately 70% of the chlorine dioxide had been converted to chlorite. At this pH the chlorite concentration did not change significantly (Figure 1A). However, as the end pH dropped, chlorite degradation began to occur (Figure 1B–1D). The rate of chlorite consumption appeared to increase with a decrease in bleaching pH. As a result, less residual chlorite was measured after 120 min of bleaching with decreasing end pH. By contrast, chlorate and chloride

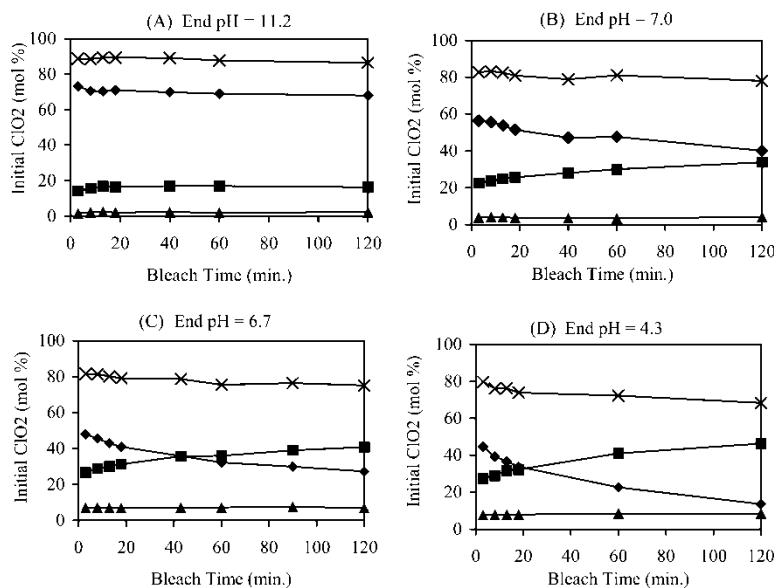


Figure 1. Inorganic species present during chlorine dioxide bleaching of a 27 kappa softwood kraft pulp at 50°C, 0.2 kappa factor, 120 min: \blacklozenge - Chlorite; \blacktriangle - Chlorate; \blacksquare - Chloride; \times - Sum. A) starting pH = 12.2, end pH = 11.2; B) starting pH = 12.0, end pH = 7.0; C) starting pH = 11.9, end pH = 6.7; D) starting pH = 11.8, end pH = 4.3.

formation increased with decreasing end pH. Bleaching to a pH below 3.4 did not increase chlorate levels substantially, maintaining levels between 10–15% of the initial chlorine dioxide (Figure 2). Chloride formation reached a maximum of $\sim 50\%$ based on the initial chlorine dioxide applied, at an end pH = 3.4. Increasing or decreasing the end pH from 3.4 resulted in a decrease in chloride content (Figure 3). Figure 3 shows the effect of end pH on the levels of inorganic chlorine compounds present after 120 min of reaction with chlorine dioxide. It can be seen that the sum of chlorite + chlorate, expressed as mole % initial chlorine dioxide, decreased as a function of pH until an end-pH of about 3.4. At pH values less than 3.4, the chlorite + chlorate levels did not change significantly.

Analysis of Ion Formation

Studies with lignin model compounds and isolated kraft lignin have been helpful in understanding bleaching efficiency and the inorganic reactions in chlorine dioxide bleaching. It is well known that chlorine dioxide initially reacts with phenolic and non-phenolic compounds by a one-electron transfer reaction that results in the formation of chlorite and a radical

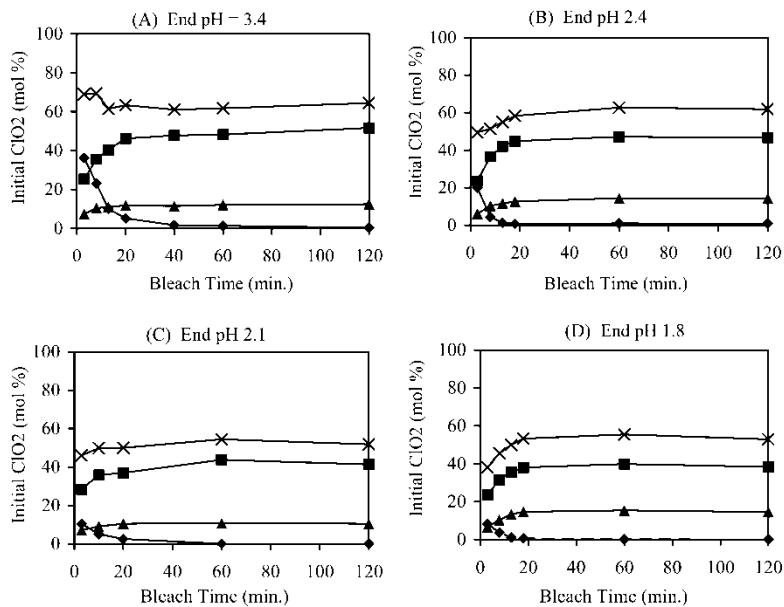


Figure 2. Inorganic species present during chlorine dioxide bleaching of a 27 kappa softwood kraft pulp at 50°C, 0.2 kappa factor, 120 min; \blacklozenge - Chlorite; \blacktriangle - Chlorate; \blacksquare - Chloride; \times - Sum. A) starting pH = 11.7, end pH = 3.4; B) starting pH = 11.4, end pH = 2.4; C) starting pH = 10.1, end pH = 2.1; D) starting pH = 3.1, end pH = 1.8.

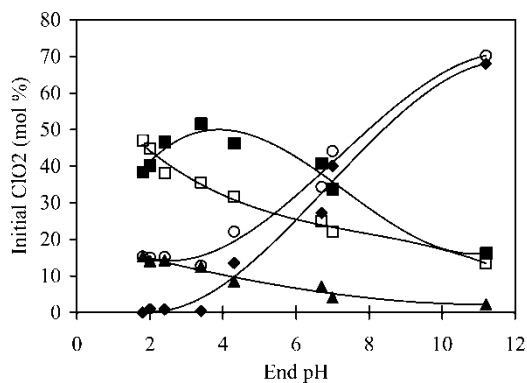
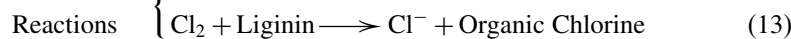
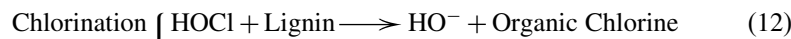
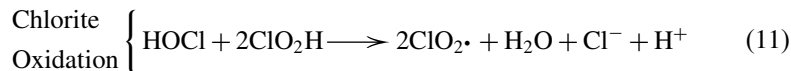
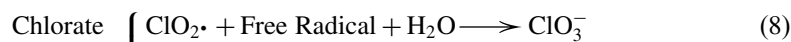
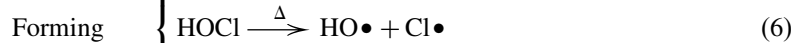
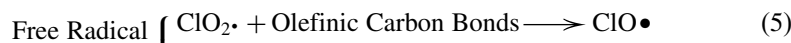
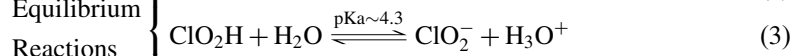
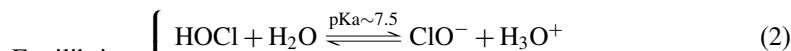
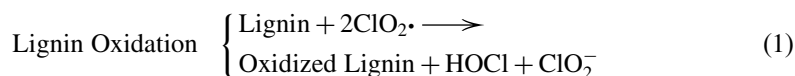


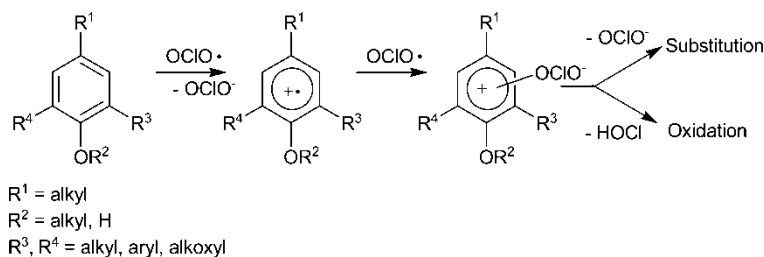
Figure 3. Inorganic species present after chlorine dioxide bleaching (0.2 kappa factor) of a 27 kappa softwood kraft pulp at 50°C for 120 min; \blacklozenge - Chlorite; \blacktriangle - Chlorate; \blacksquare - Chloride; \circ - Chlorite + Chlorate; \square - Organic chlorine (Data points labeled as end pH; Organic chlorine calculated by difference).

phenolic or non-phenolic intermediate (Scheme 1).^[5] The radical intermediate is further oxidized by chlorine dioxide to form a variety of oxidation products and hypochlorous acid (HOCl). The initial reaction with the phenolic lignin forms both chlorite and hypochlorous acid, whereas reactions with non-phenolic lignin models preferentially form only chlorite at high pH.^[4] Another important difference is that phenolic lignin compounds react with chlorine dioxide at rates that are roughly 10^5 times faster than non-phenolic compounds.^[6] Assuming that residual lignin behaves similarly to lignin models, the quantity of inorganic species formed during chlorine dioxide bleaching will be related to the lignin composition.

The chlorite and hypochlorous acid formed during the initial reaction with lignin are involved in several side reactions.^[7-10] Some of these reactions are listed in Equations (2) through (12). The efficiency of the inorganic side reactions is highly dependent on pH and concentration. Because the quantity of inorganic species formed during chlorine dioxide bleaching is directly related to the lignin structure and pH during bleaching, the overall efficiency of bleaching with chlorine dioxide becomes a complex function of lignin composition and bleaching pH.



A stepwise explanation can simplify the observed results in Figures 1 and 2. For example, during high pH bleaching, chlorite and chloride formation is a function of lignin oxidation (Equation [1]) and chlorite oxidation (Equation [11]). Because it is known that phenolic lignin structures



Scheme 1. Reaction mechanism of ClO_2 with phenolic and nonphenolic lignin moieties.

react much faster than non-phenolic lignin with chlorine dioxide, the phenolic lignin will be oxidized first. The initial phenolic oxidation generates chlorite and hypochlorous acid (Equation [1]). Hypochlorous acid then reacts further with either lignin to form organic chlorine, or with chlorite to regenerate chlorine dioxide (Equations [11] and [12]). The oxidation of chlorite by hypochlorous acid (Equation [11]) is the only known reaction, during chlorine dioxide bleaching, which can generate chloride. Therefore, the chloride formation observed in these reactions comes directly through this oxidation pathway. Assuming that chlorite and hypochlorous acid generated from the initial oxidation of the phenolic lignin results in a one to one molar ratio, there will be a surplus of hypochlorous acid, based on the stoichiometry in Equation (11). This surplus in hypochlorous acid results in the chlorination of lignin to form organic chlorides (Equation [12]). Therefore, just from the initial oxidation of phenolic lignin, the chlorite is formed via Equation (1), the chloride and the regenerated chlorine dioxide via Equation (11), and the organic chlorine via Equation (12).

The next step involves the oxidation of the non-phenolic lignin structures. Studies have shown that chlorine dioxide reactions with non-phenolic lignin models that contain an α -hydroxy side chain result only in the formation of chlorite at high pH.^[4] This can be seen experimentally in Figure 4, where two moles of chlorite form for every mole of non-phenolic lignin model (MVA) oxidized. Following the rapid oxidation of phenolic lignin structures, chlorine dioxide preferentially forms chlorite through the oxidation of the non-phenolic lignin structures. This would explain the results observed at high pH in Figure 1A, where nearly 70% of the chlorine dioxide is converted to chlorite. Because the oxidation of the non-phenolic lignin results in no more hypochlorous acid being formed, chlorine dioxide can not be regenerated (Equation [11]) to propagate the oxidation of lignin. Therefore, chlorite residue is high, resulting in very inefficient bleaching.

During low pH bleaching, chlorite and chloride formation are quite different. For example, bleaching to an end-pH of <3.4 results in a greater consumption of chlorite and higher chloride formation (Figure 2). Similar to high pH chlorine dioxide bleaching, phenolic lignin oxidizes first due to its

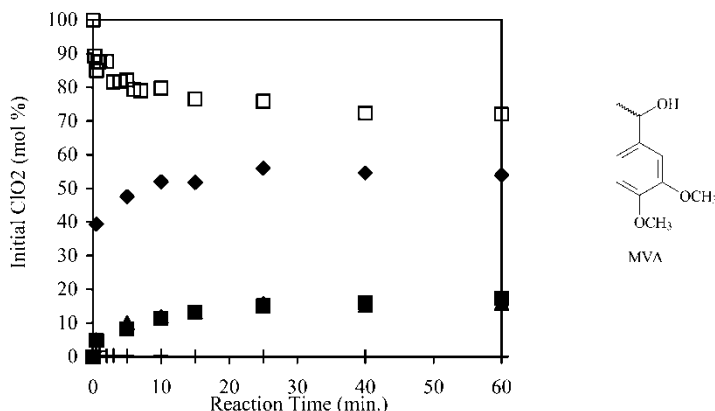


Figure 4. Chlorine dioxide reaction with Methylveratryl alcohol (MVA). 1 : 1 Mole ratio MVA:chlorine dioxide, $T = 25^{\circ}\text{C}$, $[\text{MVA}]_0 = 37.5 \text{ mM}$, $\text{pH} = 8$ with pH control. (◆- Chlorite; ▲- Chlorate; ■- Chloride; +-Hypochlorous acid; □- MVA).

high reaction rate relative to non-phenolic lignin. However, at low pH the oxidation of the non-phenolic lignin begins to generate both chlorite and hypochlorous acid, rather than just chlorite, which can be seen experimentally in Figure 5. The oxidation of the non-phenolic model compound does not generate hypochlorous acid until the pH drops into the acidic range. During bleaching, this results in a stepwise sequence where the oxidation of non-phenolic lignin forms hypochlorous acid and chlorite. The hypochlorous acid competes for the oxidation of chlorite to regenerate chlorine dioxide, and the chlorination of lignin. As previously discussed, chloride can only be formed by chlorite oxidation as shown in Equation (11). Therefore, the

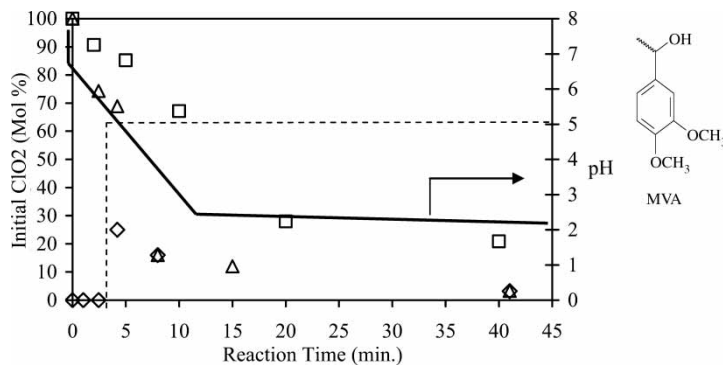


Figure 5. Chlorine dioxide reaction with Methylveratryl alcohol (MVA). 1 : 1 Mole ratio MVA:chlorine dioxide, $T = 25 \text{ C}$, $[\text{MVA}]_0 = 37.5 \text{ mM}$, initial $\text{pH} = 8$, no pH control. (Δ Chlorine Dioxide; \diamond Hypochlorous acid; \square MVA; —pH).

maximum chloride formation in the pH 3.4 reaction indicates that the most efficient consumption of chlorite occurs at this pH.

The formation of chlorate results in the loss of oxidizing power. Chlorate formation can occur by many oxidation pathways (Equations [8], [9], and [10]). Although chlorate can form through alkaline decomposition of chlorine dioxide (Equation [9]), Figure 1A suggests that alkaline decomposition of chlorine dioxide is not a major factor. The formation of chlorate is nearly complete before the first sample point at three minutes, whereas oxidation still continues. This is noted by the degradation of chlorite and the formation of chloride, which must be coming from chlorite oxidation. Therefore, chlorine dioxide reactions are taking place while conditions for alkaline decomposition of chlorine dioxide are prevalent, yet no chlorate is formed, therefore it is unlikely that the reaction in Equation (9) is very active in this reaction system.

Another mechanism for the formation of chlorate is through the quenching of free radicals by chlorine dioxide (Equation [8]). In terms of pulp strength this is a favorable reaction as eliminating free radicals lowers the amount of potential damage that can be done to the carbohydrates. However, it also results in the loss of ClO_2 oxidation efficiency through the formation of chlorate per Equation (8). This is likely the mechanism for chlorate formation at high pH.

A decrease in the end pH from pH 6 to pH 2 increases the amount of chlorate formed during the bleaching reactions with chlorine dioxide. One explanation is the disproportionation of chlorous acid as per Equation (10). The main requirement for this reaction to occur is the protonation of chlorite (Equation [3]), which under these acidic conditions is favorable. Thus, the formation of chlorate in Figure 2A–D is most likely attributable to this reaction.

A maximum in chloride formation occurred during bleaching to an end pH of 3.4 (Figure 6). Chloride arises from the oxidation of chlorite (Equation [11]). The formation of chloride is an indication that the hypochlorous acid formed did not react with an organic compound to produce organic chlorine. As a result, full utilization of the oxidizing power has been achieved. When bleaching to a pH lower than 3.4, chloride content begins to decrease, as illustrated in Figure 6. Because residual chlorite levels are negligible and no significant increases in chlorate are observed, the decrease in chloride at low pH is an indication that more organic chlorine is being formed due to the reaction of hypochlorous acid with lignin (Equation [12]). An approximate 34% increase in organic chlorine was calculated when the end pH was decreased from 3.4 to 1.8. This is one drawback of bleaching at low pH. However, the increased chlorination may help in subsequent bleaching stages as hydroxylation of lignin occurs in a hot alkaline extraction by displacement of the organic chlorine, which should promote bleaching based on the initial discussion covering the reactivity of phenolic lignin.

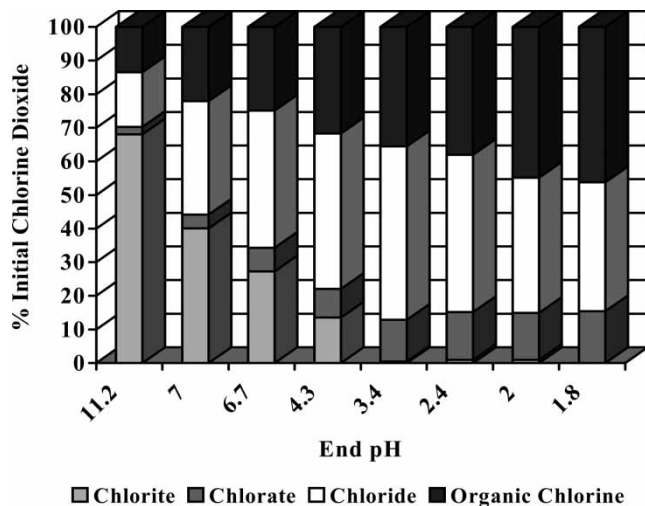


Figure 6. Inorganic ions present after Chlorine Dioxide bleaching of a 27 kappa softwood kraft pulp at 50°C, 0.2 kappa factor, 120 min.

Bleaching Efficiency

Final analysis of inorganic compounds in the bleach effluent shows that bleaching to an end pH of less than 3.4 results in the most efficient usage of chemicals. As shown in Figure 3 the amount of residual chlorite + chlorate decreases with end pH until about 3.4. Below an end pH of 3.4, the quantity of residual chlorite + chlorate levels out. This observation is different than that reported by Chollet et al.,^[11] who found that bleaching a chlorine prebleached pulp (Kappa no. 5) with chlorine dioxide gave the minimum chlorate + chlorite levels at an end pH of between 3 and 4. In addition, the maximum pulp brightness was attained around an end pH of 3.8. In Chollet's study the quantity of chlorine dioxide lost to chlorate was shown to increase dramatically with decreasing pH below 3. Under acidic conditions chlorate is formed according to Equation (10). Under our conditions, the amount of chlorite that is available to participate in this reaction is likely lower than that in Chollet's system due to the higher lignin content of our pulp. The higher lignin content corresponds to a larger amount of phenolic moieties (the phenolic hydroxy content of a 30 kappa softwood kraft pulp is approximately between 20 to 30% of the residual lignin^[12,13]), resulting in a much lower concentration of chlorite available to participate in Equation (10).

Brightness and permanganate number trends appear to correlate with the amount of residual chlorite + chlorate. Figure 7 shows that decreasing end pH below 3.4 did not have a significant effect on the brightness or the permanganate number after an extraction stage; however, the organic chlorine level

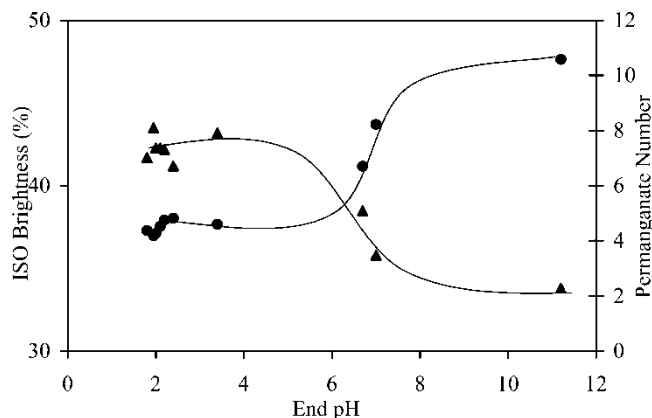


Figure 7. Post-Alkaline extraction ISO brightness and permanganate number of chlorine dioxide bleached softwood kraft pulp. Bleaching conditions: Initial kappa = 27, 100% chlorine dioxide at 50°C, 0.2 kappa factor, 120 min, 10% consistency, varied end pH. Extraction conditions: 10% consistency, 70 C, initial pH = 12.0, 30 min.

increases. Therefore, unlike chlorine pre-bleached pulps, it appears that there is more flexibility with end pH when pre-bleaching with chlorine dioxide with the optimum pH ~ 3.4 (same efficiency but less organic chlorine).

CONCLUSIONS

Pre-bleaching a 27 kappa softwood kraft pulp with chlorine dioxide was performed to various end pH levels. During high pH bleaching, the majority of the bleaching chemicals were lost to chlorite formation. The rapid oxidation of the phenolic lignin results in the formation of chlorite and hypochlorous acid, but the oxidation of non-phenolic lignin at high pH forms only chlorite. Without the presence of the hypochlorous acid formed from the reaction with the non-phenolic lignin moieties, chlorine dioxide is not regenerated and further reaction with lignin and the residual chlorite does not occur. Further, chlorite is ionized at high pH, which prevents it from undergoing disproportionation. Therefore, at high pH chlorite remains fairly stable, resulting in a loss in oxidation efficiency.

Decreasing end pH (<6) resulted in a greater amount of chlorite degradation. At low pH the reaction of chlorine dioxide with non-phenolic lignin moieties formed both chlorite and hypochlorous acid. The hypochlorous acid then reacts with chlorite to regenerate chlorine dioxide or reacts with lignin to form organic chlorine. Lignin oxidation by chlorine dioxide followed by chlorine dioxide regeneration by hypochlorous acid continued

until all of the chlorite was consumed. As a result, residual chlorite did not contribute to losses in chlorine dioxide oxidation efficiency at low pH.

Chlorate formation increased with decreasing end pH during chlorine dioxide bleaching. At high pH, chlorate formed through radical quenching by chlorine dioxide. At low pH, chlorate formation resulted from chlorous acid disproportionation. No significant chlorate levels were measured at end pH values below 3.4.

Brightness and permanganate number trends correlate with the amount of residual chlorite + chlorate; leveling off at end pH values of ≤ 3.4 . This is contrary to what has been observed for the chlorine dioxide bleaching of low kappa pulps, where a minimum residual chlorite + chlorate is typically observed at an end pH around 3.8. Thus, pre-bleaching with chlorine dioxide provides more flexibility in end pH (3.5–1.5) as compared to a D₁ bleaching stage. However, decreasing end pH from 3.4 to 1.8 did result in an approximate 34% increase in organic chlorine.

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