Mechanism of Chlorate Formation During Bleaching of Kraft Pulp with Chlorine Dioxide

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Possible reaction routes which have been proposed for chlorate formation during ClO_2 bleaching are: (1) ClO_2 disproportionation; (2) acid-catalyzed decomposition of chlorite; and (3) regeneration of ClO_2 from reaction between chlorite and hypochlorous acid. In the present study, it is shown that the third route is responsible for essentially all chlorate formed during ClO_2 bleaching of kraft pulp. The effect of operating variables on chlorate formation can be predicted with a ClO_2 regeneration reaction mechanism, which explains why more chlorate is formed with hypochlorous acid rather than with chlorine as reactant. Based on the present theory, it follows that chlorate formation can be minimized by recycling the acidic filtrate, charging chlorine first, delaying the addition of chlorine in a DC sequence until the chlorite concentration is substantially decreased, and by increasing the consistency.

INTRODUCTION

During the bleaching of pulp with chlorine dioxide (or its mixtures with chlorine), part of the chlorine dioxide is converted into chlorate. Since chlorate is known [1,2] to be an ineffective delignification chemical, its formation represents a waste of the oxidizing power of chlorine dioxide. Moreover, it was reported [3] that chlorate is harmful to the environment when discharged to recipient waters. For example, it was found that the bladder wrack population in the sea near a kraft mill was destroyed by chlorate in the effluent [4]. Thus, with the present trend of increasing chlorine dioxide substitution in the prebleaching stage, there is both an economic and environmental incentive to understand the mechanism of chlorate formation.

Three studies [3,5,6] have been published concerning the formation of chlorate during chlorine dioxide bleaching (with or without the presence of chlorine). These studies focused on the amount of chlorate formed as a function of process variables such as pH, chloride concentration, charging sequence and timing of chlorine and chloride dioxide addition, consistency and kappa number of the unbleached pulp. However, the fundamental questions of how chlorate is formed, and why the amount of chlorate formed is different when the operating conditions are changed are still unanswered.

The purpose of the present paper is to answer these questions, and discuss practical possibilities to decrease or even eliminate chlorate formation during chlorine dioxide bleaching.

RESULTS AND DISCUSSION

The chlorate formation during pure chlorine dioxide bleaching was studied in a continuously stirred batch reactor. The chlorate concentration was followed by ion chromatographic (IC) analysis. A 28.7 kappa number kraft black spruce pulp was used. Details of the experimental procedures and techniques are given in reference [14]. The development of chlorate formation at 25°C and 45°C is shown in Fig. 1. It can be seen that initially the formation of chlorate is very fast, and that after 2.5 h at 45°C about one fifth of chlorine dioxide is converted into chlorate. This is in agreement with values reported in literature for pure chlorine dioxide prebleaching [3,5,7,8].

It is difficult to envisage a reaction whereby chlorate is directly formed by oxidation of ClO_2 with lignin. A more likely formation route is that chlorate is the reaction product of different inorganic species in the bleach effluent such as chlorite, chloride, chlorine dioxide and hypochlorous acid.

The following three reaction routes have been proposed for chlorate formation [9]:

(1) Disproportionation of ClO_2

$$2\ ClO_2 + 2OH^- \longrightarrow H_2O + ClO_2^- + ClO_3 \qquad (1)$$

(2) Acid-catalyzed decomposition of chlorite

$$4\ ClO_2^- + 2\ H^+ \longrightarrow Cl^- + 2\ ClO_2 + ClO_3^- + H_2O \qquad (2)$$

(3) Reaction between chlorite and hypochlorous acid.

$$HClO + ClO_2^- \longrightarrow H^+ + Cl^- + ClO_3^- \qquad (3)$$

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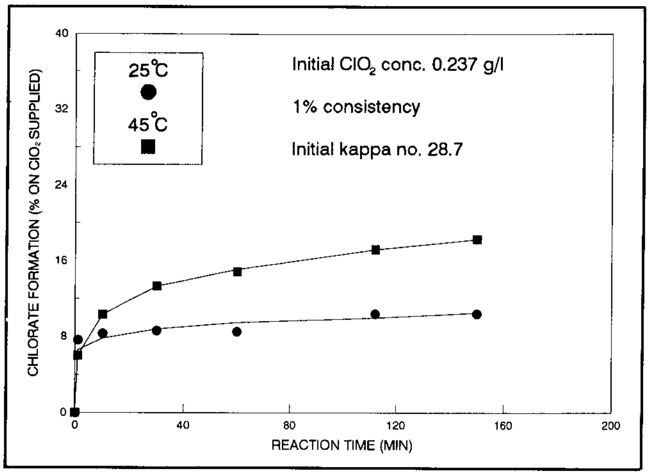

Fig. 1. Comparison of chlorate formation during ClO_2 treatment of kraft pulp at 25 and 45°C.

TABLE I
CHLORATE FORMATION DURING ClO_2 TREATMENT OF FULLY BLEACHED PULP

	Composition (% of atomic chlorine)		
Time (min)	**ClO_2^-**	**ClO_2**	**ClO_3^-**
0	0	100	0
1	2.8	98.0	NI
10	3.2	97.5	NI
30	3.7	97.0	NI
60	4.4	96.3	NI
112	4.8	95.1	NI
150	5.5	93.5	NI

NI: IC peak too small to be integrated (<0.2 ppm).
1% consistency, initial ClO_2 concentration 0.237 g/L, 45°C, pH after 45 min: 3.6.

TABLE II
CHLORATE FORMATION BY ACID-CATALYZED DECOMPOSITION OF CHLORITE

	Composition (% of atomic chlorine)				
Time (min)	***Cl^-**	**ClO_2^-**	**ClO_2**	**ClO_3^-**	**Chlorine Balance**
0	0	100	0	0	100
1	0.1	98.4	1.2	NI	99.7
10	1.1	87.3	10.8	NI	99.2
30	5.9	71.8	19.5	NI	97.2
60	7.3	61.8	27.4	NI	96.5
112	14.2	49.5	32.4	NI	96.1
150	16.7	44.0	34.2	NI	94.9

NI: IC peak to small to be integrated (<0.2 ppm).
45°C, Initial chlorite conc. 0.24 g/L, initial pH 2.57.
*Corrected for chloride in technical-grade sodium chlorite of 20.7% atomic chlorine based on chlorite being 100%.

because it has been shown [14,15] that hypochlorous acid is an important reaction intermediate formed during the bleaching of kraft pulp with ClO_2. No chlorate is formed when chlorite reacts with chlorine (which is in equilibrium with hypochlorous acid), as

$$2\,ClO_2^- + Cl_2 \longrightarrow 2\,Cl^- + 2\,ClO_2 \qquad (4)$$

In the following sections, the contribution of each of the above reactions to the overall chlorate formation during ClO_2 bleaching will be determined.

To test the contribution of reaction 1 to the chlorate formation, fully bleached pulp was subjected to chlorine dioxide treatment. The conditions of the experiment were the same as those used for the unbleached pulp shown in Fig. 1, i.e., 1% consistency, 45°C, and an initial ClO_2 concentration of 0.237 g/L. The development of the inorganic chlorine-containing species is shown in Table I.

The results show that the amount of chlorate formed is insignificant under these conditions. The consumption of chlorine dioxide can be explained by reduction of chlorine dioxide to chlorite with concurrent oxidation of the pulp, and/or by decomposition of chlorine dioxide to chlorite and oxygen [10]. Since the experimental conditions were the same as those shown for unbleached pulp in Fig. 1, it can be concluded that chlorate formation by disproportionation of ClO_2 can be neglected during chlorine dioxide treatment of unbleached pulp. This is in agreement with the result of Germgard et al. [3], who concluded that the disproportionation reaction accounts for only about 2% of the total chlorate formation during ClO_2 bleaching. Gordon et al. [9] also reported that the ClO_2 disproportionation reaction rate becomes appreciable only under alkaline conditions.

The rate of chlorine dioxide decomposition increases with increasing temperature [11]. However, the activation energy for the decomposition reaction (45 kJ/mol [11]) is lower that that of chlorine dioxide bleaching reactions (about 60 kJ/mol [12]). Therefore, the relative importance of the chlorine dioxide decomposition reaction decreases with increasing temperature.

The contribution of reaction 2 to the chlorate formation was investigated by following the development of inorganic chlorine species in a solution of 0.24 g/L technical-grade sodium chlorite at 45°C without the presence of pulp. The sodium chlorite content of the technical grade was 83.1% by weight as determined by titration. IC analysis showed that chloride was the only other chlorine-containing species besides chlorite. This is equivalent to a chlorite molar ratio of 0.207. The initial pH of 2.57 was obtained by addition of sulphuric acid. The development of the content of chloride, chlorite, chlorine dioxide and chlorate, as determined by IC analysis, is summarized in Table II. Hypochlorous acid was not detected.

Clearly, the main products of the acid-catalyzed decomposition reaction of chlorite are chlorine dioxide and chloride. No measurable amount of chlorate is formed. Even if one assumes that chlorate accounts for the small deviation of a closed chlorine mass balance (last column in Table II), the results show that the potential chlorate formation via acid decomposition of chlorite is still very small. This is surprising if one considers the stoichiometry of reaction 2. However, it was reported by Kieffer and Gordon [13] that the presence of chloride can alter the stoichiometry of the acid-catalyzed decomposition of chlorite. They found that, at high chloride ion concentrations, the chlorite decomposition is better approximated by reaction 5.

$$5\,ClO_2^- + 4\,H^+ \longrightarrow 4ClO_2 + Cl^- + 2\,H_2O \qquad (5)$$

whereby no chlorate is formed. Therefore the presence of chloride in technical-grade sodium chlorite may explain why no detectable amount of chlorate was found in the present experiments. Since, in actual ClO_2 bleaching, the molar ratio of chloride to chlorite is much higher [14], it appears that chlorate formation by acid-catalyzed decomposition of chlorite can also be neglected.

Table II shows that the stoichiometry of the reaction products of the acid decomposition of chlorite, Cl^- and ClO_2, varies from about one tenth to one half. Since this is not consistent with either reactions 2 or 5, other reactions may be involved. For example, the reaction reported [9] to take place to a limited extent during acid-catalyzed decomposition of chlorite:

$$\mathrm{ClO_2^-} \longrightarrow \mathrm{Cl^- + O_2} \tag{6}$$

might explain the present large variation in the ratio of Cl^- formed to ClO_2 formed.

Chlorite and hypochlorous acid are reaction intermediates formed during pulp bleaching with ClO_2 [14]. They could combine to form chlorate, as shown in reaction 3. To identify the importance of this reaction for the overall chlorate formation during ClO_2 bleaching, an experiment was performed with the effective removal of the HOCl generated in situ. This can be achieved by the addition of sulphamic acid, a very effective scavenger of hypochlorous acid [15]. The results in Fig. 2 show that the formation of chlorate is virtually eliminated when hypochlorous acid is captured by sulphamic acid. Thus, it can be concluded that hypochlorous acid is involved in the chlorate formation during ClO_2 treatment of unbleached pulp, and that it is most likely generated from chlorite and hypochlorous acid via reaction 3. Also, this result is further evidence that chlorate formation by ClO_2 disproportionation and acid decomposition of chlorite are negligible since these two reactions are not affected by the capture of hypochlorous acid. The final pH values, with and without sulphamic acid addition, of the experiments in Fig. 2 were 2.3 and 3.6, respectively.

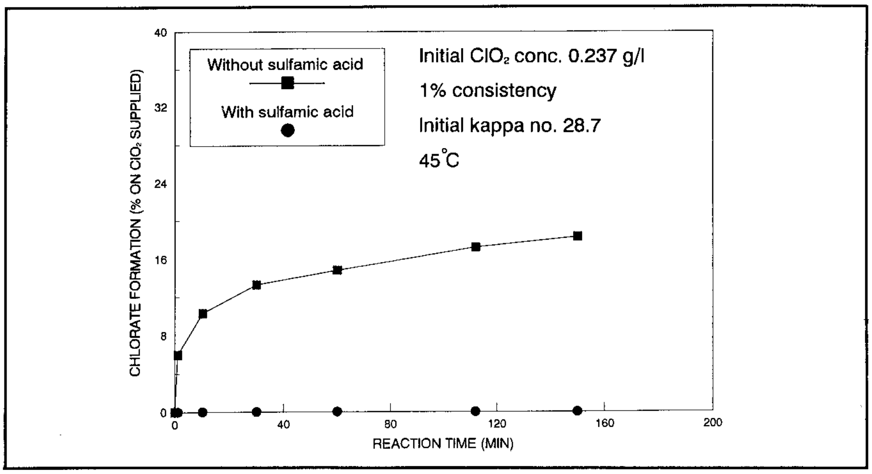

Fig. 2. Development of chlorate formation during ClO_2 treatment of kraft pulp with or without the presence of sulphamic acid.

TABLE III
EFFECT OF pH ON CHLORATE FORMATION DURING ClO_2/Cl_2 PREBLEACHING [19]

pH before D	2.8	3.0	4.0	5.1	6.6
pH after D	2.5	2.8	2.8	2.8	3.5
Chlorate (kg/adt)	1.33	1.50	1.53	1.60	1.91

Initial kappa number: 31.0, kappa factor: 0.19, 30°C.
ClO_2 substitution: 50%, DC sequence, Cl_2 added at zero ClO_2 residual.

Reaction Mechanism

It was found by Taube and Dodgen [16] that the stoichiometry of the reaction between chlorite and hypochlorous acid (or chlorine which is in equilibrium with hypochlorous acid) changes with pH and initial concentrations of the reactants. They proposed a reaction mechanism for the overall reactions 3 and 4, which was later expanded by Emmenegger and Gordon [17] to:

$$\mathrm{Cl_2 + ClO_2^-} \xrightarrow{k_1} \left[\mathrm{Cl-Cl-Cl} <^{\mathrm{O}}_{\mathrm{O}}\right]^- \tag{7}$$

$$\mathrm{HOCl + ClO_2^-} \xrightarrow{k_2} \left[\mathrm{HO-Cl-Cl} <^{\mathrm{O}}_{\mathrm{O}}\right]^- \tag{8}$$

$$\left[\mathrm{Cl-Cl-Cl} <^{\mathrm{O}}_{\mathrm{O}}\right]^- \xrightarrow{k_3} \left[\mathrm{Cl-Cl} <^{\mathrm{O}}_{\mathrm{O}}\right] + \mathrm{Cl^-} \tag{9}$$

$$\left[\mathrm{HO-Cl-Cl} <^{\mathrm{O}}_{\mathrm{O}}\right]^- \xrightarrow{k_4} \left[\mathrm{Cl-Cl} <^{\mathrm{O}}_{\mathrm{O}}\right] + \mathrm{OH^-} \tag{10}$$

$$2\left[\mathrm{Cl-Cl} <^{\mathrm{O}}_{\mathrm{O}}\right] \xrightarrow{k_5} \mathrm{Cl_2 + 2\,ClO_2} \tag{11}$$

$$\left[\mathrm{Cl-Cl} <^{\mathrm{O}}_{\mathrm{O}}\right] + \mathrm{H_2O} \xrightarrow{k_6} \mathrm{Cl^- + ClO_3^- + 2H^+} \tag{12}$$

In this reaction scheme, an intermediate, Cl_2O_2, is produced by reaction of both Cl_2 and HOCl with chlorite in consecutive reactions 7 and 9, and 8 and 10, respectively. Cl_2O_2 then reacts further to form ClO_2 or ClO_3^- via, respectively, reactions 11 and 12. Since reaction 11 is a second-order reaction while reaction 12 is first order, a high concentration of $[Cl_2O_2]$ favours the formation of ClO_2 relative to ClO_3^-. Since k_1 is larger than k_2, a high concentration of Cl_2 relative to HOCl leads to a relatively higher concentration of $[Cl_2O_2]$, favouring the formation of chlorine dioxide (reaction 11) over chlorate (reaction 12). In other words, in the mechanism given by reactions 7 to 12, chlorine favours the formation of ClO_2, while hypochlorous acid results in the formation of relatively more chlorate.

Explanation of the Effect of Operating Variables on Chlorate Formation

Influence of pH

Recently, Reeve and Weishar [18] and Histed et al. [19] have reported that a lower pH results in less chlorate formation during ClO_2 prebleaching. In Table III, the experimental data of Histed et al. are reproduced. They show that the chlorate formation decreases with increasing acidity. Chlorine and hypochlorous acid in solution are in equilibrium according to the well-known reaction:

$$\mathrm{Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^-} \tag{13}$$

With the equilibrium constant, K,

$$K = \frac{[\mathrm{H^+}]\,[\mathrm{Cl^-}]\,[\mathrm{HClO}]}{[\mathrm{Cl_2}]} \tag{14}$$

the chlorine/hypochlorous acid molar ratio can be writen as

$$\frac{[\mathrm{Cl_2}]}{[\mathrm{HClO}]} = \frac{[\mathrm{H^+}]\,[\mathrm{Cl^-}]}{K} \tag{15}$$

Thus, with increasing acidity, relatively more molecular chlorine is available and, according to the present theory, the regeneration of chlorine dioxide is favoured over the formation of chlorate.

In earlier studies [3,6,20], it was reported that the amount of chlorate formed in D_1 and D_2 stages decreases with decreasing acidity. The explanation for this apparent contradiction with the present theory is that in these cases an increasing amount of chlorite remains with increasing pH. However, if all the chlorite had been consumed, then the chlorate formation would have been higher with increasing pH. The reason for the larger amount of chlorite remaining at higher pH is that the chlorite consumption by both acid decomposition and reaction with hypochlorous acid decreases with increasing pH [9]. This explanation is supported by the finding of Germgard et al. [3] that the chlorate formation increases with increasing pH for mixture of chlorine dioxide and chlorine, whereas in the absence of chlorine the chlorate formation decreases with increasing pH. In the latter case, an increasing amount of chlorite remains, while in the former chlorite is converted into chlorate and chlorine dioxide. Therefore, a fair comparison of chlorate formation can be made only when all chlorite has been consumed.

The chlorate formation characteristics of the prebleaching and brightening stages are different. For example, more chlorate is formed per chlorine dioxide consumed in the brightening stages than in the prebleaching stage [6]. Also, the chlorate formation increases linearly with the chlorine dioxide consumption in the brightening stage, while the increase is stronger than linear in the prebleaching stage [3]. These differences can also be explained by the mechanism we propose for chlorate formation when the intensity of the reaction between lignin and chlorine (hypochlorous acid) in the different stages is considered. It was argued by Ni et al. [14] that hypochlorous acid formed in situ is consumed in competing reactions with lignin and chlorite. The reaction between chlorine (hypochlorous acid) and lignin is more intensive in the prebleaching stage than in the brightening stages. Therefore, less hypochlorous acid is converted into chlorate in the prebleaching stage. The lower pH in the prebleaching stage compared to the brightening stages also contributes to the relatively lower chlorate formation in the former stage. The chlorate formation is relatively small in the initial phase of the prebleaching stage. This can be explained by the rapid consumption of hypochlorous acid by reactive lignin in kraft pulp. However, after consumption of the reactive lignin, the chlorate formation behaviour in the later phase of the prebleaching stage becomes more similar to that of the brightening stages. This explains the non-linear relationship between chlorate formation and chlorine dioxide consumption in the prebleaching stage.

Influence of Chloride Concentration

It was reported [3,18] that the presence of chloride ions decreases the chlorate formation for a given chlorine dioxide consumption. For example the data from Reeve and Weishar [18], reproduced in Table IV, show that the chlorate formation is lower at all three consistencies when chloride is present. The explanation for this effect is that the increased chloride concentration shifts the equilibrium of reaction 13 towards chlorine, which favours the regeneration of ClO_2 rather than chlorate formation.

Rapson and Anderson [21] found that the chlorate formation in the D_1 and D_2 stages was only slightly decreased by an increased chloride ion concentration. The difference from the data of Germgard et al. [3] and Reeve and Weishar [18] for the prebleaching stage can be explained by a decreased chlorine/hypochlorous acid concentration ratio in the D_1 and D_2 bleaching stages as a result of the lower acidity and ClO_2 charge in these stages. Therefore, the addition of a very large amount of chloride is needed for a significant shift in the equilibrium between chlorine and hypochlorous acid.

Influence of Order of Addition of Cl_2 and ClO_2

The fraction of ClO_2 converted into chlorate was reported [5,20] to depend on the charging sequence of Cl_2 and ClO_2. At the same total active chlorine charge and ClO_2 substitution ratio, the least amount of chlorate was produced with chlorine dioxide charged first (DC mode), while simultaneous charging (D + C mode) or chlorine charged first (CD mode) produced roughly the same amount of chlorate. The difference in chlorate formation becomes progressively smaller when the ClO_2 substitution ratio increases. The explanation is that in the DC mode some chlorite is consumed via the acid decomposition reaction (reaction 5), which does not produce any chlorate. In the CD and (C + D) modes, on the other hand, the acid-catalyzed decomposition of chlorite is insignificant because chlorite is immediately consumed by reaction with chlorine (hypochlorous acid).

Influence of Delay Time Between Addition of Cl_2 and ClO_2 in a DC Sequence

Very recently, Histed et al. [19] found that delaying the chlorine charge in a DC sequence will result in less chlorate formation. The relevant data, reproduced in Table V, show that the chlorate formation is reduced by a factor 2 when the delay time is extended from 10 to 120 s.

The same explanation as for the effect of the order of Cl_2 and ClO_2 addition is valid in this case. Thus, with further delay of the chlorine charge, more of the formed chlorite will be consumed in the acid-catalyzed chlorite decomposition reaction. As a result, a continuously decreasing chlorite concentration will be available for formation of chlorate when chlorine is charged in the DC sequence.

Influence of Consistency

Reeve and Weishar [18] found that the chlorate formation decreased moderately when the prebleaching consistency was increased from 4% to 12% (see Table IV). This finding can be explained by the kinetics of the reaction mechanism represented by reactions 7 to 12, and the fact that the concentrations are higher at higher consistencies. Since the chlorine dioxide formation reaction 11 is second order, while the chlorate formation reaction 12 is first order, it follows that regeneration of ClO_2 is favoured over chlorate formation at higher consistencies.

Influence of Initial Kappa Number

Germgard et al. [3] found that the chlorate formation at a given chlorine dioxide consumption decreases with increasing kappa number of the unbleached kraft pulp. This behaviour can be attributed to two factors: (1) at the same consistency and charge factor, the chlorine dioxide concentration increases with increasing kappa number, which favours regeneration of ClO_2 over chlorate formation; (2) similarly, the higher concentrations result in a lower final pH which also reduces the relative formation of chlorate. Of course, because the chlorine dioxide consumption increases with increasing kappa number of the unbleached pulp, the absolute amount of chlorate formed is larger with the higher kappa number pulp.

TABLE IV
EFFECT OF CHLORIDE ADDITION ON CHLORATE FORMATION DURING ClO_2 BLEACHING [18]

Initial chloride Concentration	Chlorate formation (as % of ClO_2 on pulp)		
	4% cons.	8% cons.	12 cons.
5 g/L	0.31	0.24	0.25
0	0.41	0.36	0.35

Charge factor: 0.22, hardwood kraft pulp, kappa no: 10, 60°C, 1.5 h, initial pH adjusted to 2 with H_2SO_4.

TABLE V
EFFECT OF DELAY TIME BETWEEN ADDITION OF Cl_2 and ClO_2 ON THE CHLORATE FORMATION IN A DC SEQUENCE [19]

Delay time of Cl_2 addition (s)	10	30	120
Chlorate formed (kg/adt)	2.97	2.44	1.50

Experimental conditions: Same as Table III.

PRACTICAL IMPLICATIONS

Chlorate formation represents a loss of ClO_2 bleaching power as well as an environmental load. Based on the present theory, chlorate formation can be minimized when the pH of the pulp suspension is about 2 so that the presence of chlorine instead of hypochlorous acid is favoured. In practice this is done by recycling the acidic filtrate. An additional advantage of recycling the filtrate is that the increased chloride concentration also leads to less chlorate formation.

The chlorate formation in the preferred DC sequence can be further reduced when the delay time for chlorine addition is increased to the point where the residual chlorite concentration in the bleach liquor is reduced to a negligible value. In practice, this can be achieved within 10 min for a chlorine dioxide charge of 1.20% when the initial pH is adjusted to 2 and the temperature is kept at 45°C or higher [22]. Finally, the highest consistency should be used since this leads to higher chemical concentrations, which in turn favour ClO_2 regeneration over chlorate formation.

Complete elimination of chlorate formation can be achieved by preventing the reaction between chlorite and hypochlorous acid. This can be done, in principle, by capturing the produced hypochlorous acid with a scavenger such as sulphamic acid. It should be noted that, even though hypochlorous acid is captured, the regeneration of ClO_2 from chlorite is still accomplished via the chlorite acid decomposition reaction. Based on the hypochlorous acid formation [14], the required sulphamic acid addition should be about 60% of the molar ClO_2 charge. Another advantage of the sulphamic acid addition besides elimination of chlorate formation is a 45% reduction in AOX formation [14]. A disadvantage is the small reduction of about 10% in delignification due to the capture of hypochlorous acid [22]. However, only an economical and environmental analysis can establish whether the addition of sulphamic acid is practical.

CONCLUSIONS

Chlorate is formed mainly by the reaction of two intermediates generated during chlorine dioxide bleaching: chlorite and hypochlorous acid. A theory is presented which can explain the influence of process variables such as pH, chloride concentration, delay time between the addition of chlorine and chlorine dioxide in a DC sequence, order of addition of chlorine and chlorine dioxide, and pulp consistency on the chlorate formation.

In practice, the chlorate formation can be minimized by recycling the acidic filtrate, charging chlorine dioxide first, delaying the addition of chlorine in a DC sequence until the chlorite concentration is substantially decreased, and by increasing the consistency. Chlorate formation can be eliminated, in principle, if a hypochlorous acid scavenger such as sulphamic acid is added to the pulp suspension before ClO_2 addition.

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ABSTRACT: Possible reaction routes which have been proposed for chlorate formation during ClO_2 bleaching are: (1) ClO_2 disproportionation; (2) acid-catalyzed decomposition of chlorite; and (3) regeneration of ClO_2 from reaction between chlorite and hypochlorous acid. In the present study, it is shown that the third route is responsible for essentially all chlorate formed during ClO_2 bleaching of kraft pulp. The effect of operating variables on chlorate formation can be predicted with a ClO_2 regeneration reaction mechanism, which explains why more chlorate is formed with hypochlorous acid rather than with chlorine as reactant. Based on the present theory, it follows that chlorate formation can be minimized by recycling the acidic filtrate, charging chlorine first, delaying the addition of chlorine in a DC sequence until the chlorite concentration is substantially decreased, and by increasing the consistency.

RÉSUMÉ: Les voies de réaction qui ont été proposées pour expliquer la formation du chlorate durant le blanchiment au ClO_2, (1) la disproportionation du ClO_2 (2) la décomposition du chlorite par l'acide catalysé, et (3) la régénération du ClO_2 à partir des réactions entre le chlorite et l'acide hypochloreux ou le chlore. Dans notre article, nous démontrons que la troisième voie de réaction est responsable de la presque totalité du chlorate qui se forme durant le blanchiment au ClO_2 de la pâte kraft. Les effets des variables du processus sur la formation du chlorate peuvent être prédits à l'aide du mécanisme de la réaction régénératrice du ClO_2, lequel explique pourquoi une plus grande quantité de chlorate est formée avec l'acide hypochloreux qu'avec le chlore agissant comme corps en réaction. Selon cette théorie, il s'ensuit que la formation de chlorate peut être minimisée par le recyclage du filtrat à caractère acide, le chargement du chlore en premier lieu, le délai dans l'addition du chlore au niveau de la séquence DC jusqu'à la diminution substantielle de la concentration de chlorite, et l'augmentation de la consistance.

KEYWORDS: CHLORATES, REACTION MECHANISMS, CHLORINE DIOXIDE, BLEACHING, DISPROPORTIONATION, PROCESS VARIABLES, THEORIES, SEQUENCES, REACTION KINETICS, HYPOCHLOROUS ACID.

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Characterization of Fibre-Fibre Bond Strength from Out-Of-Plane Paper Mechanical Properties

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The techniques of out-of-plane elastic stiffness and Z-toughness as measures of fibre-fibre bond strength were compared for an unbleached kraft pulp beaten to several freenesses and classified. The sensitivity of each technique to the effects of refining, wet pressing, and polymetic strength aid are described. The separate contributions to strength by pulp fines and by fibrillation are evaluated.

INTRODUCTION

Authors using the term "bond strength" have defined it in a variety of ways. In the present work the term is given the meaning of "the force required to cause the failure of a single fibre-fibre bond divided by the bond area of that bond".

Having put forth this definition, one is immediately required to select a direction in which to apply the force to the nonsymmetrical bond. This is because it is likely that the stress concentrations in the fibre-fibre bond will be different depending upon whether the force is applied a) in shear in the plane of the bond, or b) in tension normal to the bond. Thus, the bond-breaking force in these two experimental geometries will probably be different, and there is some experimental evidence that this may be so. Measurements of the bond strength in shear of single fibre-fibre bonds [1 and references cited therein] produce a value of 3-4 MPa. In contrast, Hieta and coworkers [2] found values of less than 1.5 MPa when the force was applied in the direction normal to the bond. Unfortunately, both shear and normal force experiments have not been performed on fibre-fibre bonds from the same set for a direct comparison of the effects of geometry. Waterhouse [3] has measured the in-plane shear strength (MD) of sheets with non-random fibre orientation and found it to be about four times the z-direction strength of the same sheet. Apparently, the different stress concentrations in the in-plane shear and the z-direction geometries produce about a 3- to 4-fold difference in the measured strengths.

In addition to the direction of the force, in order to calculate a fibre-fibre bond strength, one must also specify the bond area. This is inherently difficult because of the three-dimensional aspect of the bond. Fibres have rough surfaces including pits and defects. Refining further roughens the surface by producing external fibrillation and loss of wall material. The resulting fibre-fibre bonds must necessarily be three-dimensional as graphically shown in the recent work of Nanko and coworkers [4,5]. The only absolute method available to date to determine the bond area is the gas adsorption technique developed by Haselton [6]. This method requires measurements on a set of completely nonbonded fibres as well as on the bonded sheet and is not practical for single fibre-fibre bonds. The most common choice for determining the single fibre-fibre bond area is the light-scattering technique [7]. Alternatively, some of the authors cited in [1] have used the simple geometric overlap area of the fibre-fibre bond. The validity of the value obtained from light scattering has been debated since it was first advanced, but it remains the best readily measurable estimate of the bond area.

Measurement of the bond strength (shear or z-direction) of individual fibre-fibre bonds is extremely tedious and includes large standard deviations [1] because of individual fibre variability. It would be better to derive a measure of the bond strength from a large number of bonds simultaneously, but there is at

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