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A FUNDAMENTAL STUDY OF CHLORINE DIOXIDE BLEACHING OF KRAFT PULP

by

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A Thesis Submitted to the Faculty of Graduate Studies
and Research in Partial Fulfilment of the
Requirements for the Degree of
Doctor of Philosophy

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TABLE OF CONTENTS

ABSTRACT

The fundamentals of chlorine dioxide bleaching of softwood kraft pulp are studied by measuring the development of the inorganic chlorine species: chloride, hypochlorous acid, chlorite, chlorine dioxide and chlorate, as well as organically bound chlorine in the pulp and bleach solution. The pulp delignification is characterized by determining the development of the concentration of methanol and methoxyl group containing material in the bleach liquor and that of the functional groups in the residual lignin.

A complete chlorine mass balance was obtained throughout the bleaching reaction. Based on the development of the chlorine containing species, a series of reactions are formulated which give a complete description of the transformation of atomic chlorine during ClO_2 bleaching. It is found that all organic chlorine, defined as the sum of AOX in the spent bleach liquor and the organically bound chlorine in the chlorinated pulp, is formed within the first 10 minutes of reaction. Subsequently, the increase in AOX in solution is matched by an equivalent decrease of organically bound chlorine in the pulp. The organic chlorine during ClO_2 bleaching is mainly formed from the reaction between lignin and hypochlorous acid. It is also shown that chlorate is mainly formed by the reaction of two intermediates generated during chlorine dioxide bleaching, chlorite and hypochlorous acid. A theory is presented which explains the effect of operating variables on chlorate formation. The methoxyl group loss from softwood kraft pulp during chlorine dioxide treatment can be accounted for by the methanol produced and the methoxyl content of dissolved organic material in the bleach filtrate. It was found that ClO_2 rather than the in-situ generated hypochlorous acid is mainly responsible for the methanol formation. The experimental evidence suggests that demethylation and delignification

are closely related during ClO_2 treatment of softwood kraft pulp. Based on the present experimental evidence the ClO_2 delignification mechanism presented earlier by Gierer and others is modified.

Finally, two techniques are evaluated to decrease the AOX formation in a bleach plant based on respectively the removal of hypochlorous acid by reaction with chlorite, and on decreasing the dissolved lignin concentration. The former can be achieved either by mixing chlorite with pulp prior to the addition of chlorine dioxide, or by converting part of chlorine dioxide to chlorite with hydrogen peroxide. The latter is accomplished by introducing a washing step between the D and C stages of a DC bleach sequence.

RESUME

Les fondamentals du blanchissement de chlore dioxidé de bois tendre à pâte Kraft sont étudiés en mesurant le développement des spécimens chlore inorganique: chloride, acide hypochlorous, chlorite, chlore dioxidé et chlorate, aussi bien que la chlore liée organiquement dans la solution de blanchissement et de pâte. La délignification de pâte est charactérisée en déterminant le développement de la concentration du groupe de méthanole et méthoxyle qui contient du matériel dans le liquide de blanchissement et de celui des groups fonctionnels dans le lignine résiduel.

Une balance complète de masse chlore a été obtenue à travers la réaction du blanchissement. Baser sur le développement des spécimens contenus de chlore, une série de réactions sont formulées qui donne une description complète de la transformation de chlore atomique pendant le blanchissement ClO_2. Il a été découvert que toute chlore organique, décrit comme la somme de AOX dans le liquide de blanchissement utilisé et la chlore liée organiquement dans la pâte chlorinée est formé pendant les 10 premières minutes de la réaction. C'est alors que l'augmentation dans la solution AOX est égale par une diminution équivalente de chlore liée organiquement dans la pâte. La chlore organique pendant le blanchissement ClO_2 est formée principalement par la réaction entre lignine et l'acide hypochlorous. Il est aussi démontré que la chlorate est formée principlaement par la réaction des deux intermédiaires générés pendant le blanchissement de chlore dioxidé, chlorite et d'acide hypochlorous. Une théorie est présenté qui explique l'effet sur l'opération des variables sur la formation chlorate. La perte du groupe méthoxyl du bois tendre à pâte Kraft pendant le traitement de chlore dioxidé

peut être justifié par le méthanol produit et le contenu du méthoxyl de matériel organique dessoudu dans le filtre blanchit. Il a été découvert que $Cl0_2$ au plus tôt que le in-situ généré d'acide hypochlorous est principalement responsable pour la formation de méthanol. Les preuves expérimentales suggères que la déméthylation et délignification sont prochement reliés pendant le traitement ClO_2 du bois tendre à pâte Kraft. Baser sur la présente preuve expérimentale du ClO_2 délignification mécanisme présenter auparavant par Gierer et d'autres est modifié.

Finalement, deux techniques sont évaluées pour diminuer la formation AOX dans une plante à blanchissement baser respectivement sur l'enlèvement d'acide hypochlorous par réaction avec chlorite, et sur la diminution de la concentration de lignine dissoudu. Le précédent peut être accomplit soit par mélanger chlorite avec la pâte avant l'addition de chlore dioxidé, ou par convertir une partie de la chlore dioxidé avec hydrogen peroxyde. Le dernier est accomplit par introduire une étape de lavage entre les stages D et C d'une séquence de blanchissement DC.

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LIST OF TABLES

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

CHAPTER 8

LIST OF FIGURES

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

CHAPTER 8

GLOSSARY

AOX:	Adsorbable Organic Halogen
BOD:	Biochemical Oxygen Demand
C:	Chlorine Treatment
Charge Factor:	The chlorine charge in percentage divided by the kappa number of the pulp
COD:	Chemical Oxygen Demand
D:	Chlorine Dioxide Treatment
DC:	A bleach sequence consisting of chlorine dioxide treatment followed by chlorine treatment
E:	Sodium Hydroxide Treatment
Eo:	Oxygen enforced sodium hydroxide treatment
Eop:	Oxygen and hydrogen peroxide enforced sodium hydroxide treatment
GAC:	Granular Activated Carbon
Kappa Number:	Test of lignin content in pulp. The number of millilitres of 0.02 M potassium permanganate consumed by one gram of pulp corrected to an assumed 50% consumption using an empirical correction factor.
Klason Lignin:	Lignin insoluble in 72% sulfuric acid
TCDD:	Tetra-chloro-dibenzo-dioxin
TCDF:	Tetra-chloro-dibenzo-furan
UV Lignin:	Lignin soluble in 72% sulfuric acid and determined by UV absorption spectroscopy

CHAPTER 1

INTRODUCTION

BACKGROUND

In principle, pulp bleaching consists of two steps: (1) to remove the residual lignin, (2) to whiten and brighten the pulp without severe degradation of the carbohydrate fraction. In a conventional bleaching sequence, the first two stages, respectively "chlorination" and caustic extraction are considered as the first step, while the remaining stages are considered the second step.

Chlorine has been the dominant chemical used in a bleaching plant for removing the residual lignin, because it is cheap and reacts preferentially with lignin rather than the carbohydrates. However, delignification by chlorine is also accompanied by formation of relatively large quantities of organically bound chlorine, both in the effluent and bleached pulp [1]. Recent concern regarding the environmental impact of these chlorinated organic compounds has lead to the rapid introduction of operational practices which reduce the formation of chlorinated organics during pulp bleaching. These include (1) lowering the lignin content of pulp prior to entering the bleachery by extended delignification [2] and/or oxygen delignification [3], (2) modifying the bleaching process by partial or complete substitution of chlorine with chlorine dioxide [4], and adoption of an alkali oxidative extraction stage (Eo) or a peroxide enforced Eo stage (Eop)[5], (3) treating the bleach plant effluent in aerated lagoons [6], (4) introduction of total chlorine free bleaching sequences [7].

Substitution to various degrees of Cl_2 by ClO_2 in the chlorination stage has proven to be very effective for reduction of the organic chlorine formation and is now common practice in the industry. The practical effects of chlorine dioxide substitution on parameters such as degree of delignification, consumption of chemicals and effluent properties have been reported extensively in literature. For example, it was found that partial replacement of chlorine by chlorine dioxide increases pulp yield and viscosity, decreases the kappa number after an Eo stage, and reduces colour, BOD, COD and toxicity of the bleach plant effluent.

However, only a few publications in literature deal with the reaction mechanism of chlorine dioxide bleaching. Although some of the lignin model compounds studies done in the sixties have contributed significantly to the understanding of chlorine dioxide bleaching, the delignification reactions in actual pulp are still not firmly established. Similarly the formation pattern of the several inorganic chlorine containing species, as well as their relationship with the overall delignification process is not completely understood. Considering that substitution of chlorine by chlorine dioxide is one of the most practical alternatives for the industry to reduce the emission of organically bound chlorine, a fundamental understanding of the delignification process by chlorine dioxide is desirable in order to identify further improvements in its environmental impact.

OBJECTIVES

The general objective of the present project is to characterize the behaviour of chlorine dioxide bleaching of kraft pulp. More specifically the objectives are:

(1) to establish an atomic chlorine mass balance during ClO_2 bleaching by determining the development of the various inorganic chlorine species as well as the organically bound chlorine content of both filtrate and treated pulp.

(2) to explain how organically bound chlorine is formed.

(3) to explain why all lignin cannot be removed in single chlorine dioxide treatment stage.

(4) to propose a detailed reaction pattern of kraft pulp delignification by chlorine dioxide.

(5) to identify process conditions which will reduce the formation of chloro-organics during chlorine dioxide bleaching.

OUTLINE OF THE THESIS

This thesis is a fundamental investigation of the chlorine dioxide treatment of kraft pulp with a chemical mechanistic and a mass balance approach.

The relevant literature on chlorine dioxide bleaching is discussed in Chapter 2

Details of the experimental set-up and techniques are described in Chapter 3.

In Chapter 4, the distribution of atomic chlorine, originally supplied in the form of chlorine dioxide, among the various chlorine containing species during ClO_2 bleaching is presented. In this chapter the reaction intermediate hypochlorous acid is also identified as being mainly responsible for the formation of organically bound chlorine when pure chlorine dioxide is applied to pulp.

In Chapter 5, the mechanism of chlorate formation during chlorine dioxide bleaching is given. The present mechanism is also used to explain the effects of various operating variables on chlorate formation.

The demethylation during chlorine dioxide bleaching is characterized and compared to delignification in Chapter 6. It is found that demethylation and delignification are closely linked.

The mechanism of delignification by chlorine dioxide is presented in Chapter 7.

In Chapter 8, a few novel techniques are evaluated of reducing organic chlorine formation during bleaching with chlorine dioxide with or without the addition of chlorine.

Chapter 9 summarizes the contributions to knowledge as a result of this study.

The work described in Chapters 4, 5, 6, 7 and 8 have been written as self-contained papers suitable for publication with little or no further modifications. Thus each chapter has its own abstract and references. As far as possible, uniform and standard symbols are used throughout the thesis. The major content of several chapters has been presented at technical conferences or published in journals. Specifically:

Chapter 4: presented at the 1991 International Pulp Bleaching Conf., Stockholm, Sweden, June 11-14, 1991. The refereed paper will be published in Nordic Pulp & Paper

Chapter 5: presented at the 78th CPPA Annual Meeting, Montreal, Canada, Jan. 1992. The refereed paper will be published in JPPS.

Chapter 6: presented at the 1991 Tappi Pulping Conf., Orlando, USA, Nov. 3-7, 1991

Chapter 7: accepted for the Second European Workshop on Lignocellulosics and Pulp, Grenoble, France, Sept. 2-4, 1992.

Chapter 8: submitted to the 79th CPPA Annual Meeting, Montreal, Canada, Jan. 1993.

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CHAPTER 2

LITERATURE REVIEW

INTRODUCTION

Bleaching of chemical pulp is a multi-stage process, with each stage having pumps, mixers, a washer and a retention tower. A typical bleach plant consists of five stages giving a total retention time of about 10 hours. A typical configuration for a modern bleach plant in North America is presently (DC)EopDED sequence, where D symbolizes a stage with chlorine dioxide (D) as bleaching chemical, D_C is the so called prebleaching stage whereby most of the bleaching chemical is first charged as chlorine dioxide and is subsequently followed by a smaller charge of chlorine (C), and E_{OP} and E stand for a caustic extraction (E) stage respectively with or without reinforcement with oxygen (O) and peroxide (P). Most of the residual lignin is removed in the first two stages ((DC)Eop), while brightening of the pulp is accomplished in the remaining stages. For a comprehensive description of the pulp bleaching technology one is referred to a recent review by Reeve (Chapters XIV, XV and XVI in Pulp and Paper Manufacture, Vol. 5, "Alkaline Pulping") Since the present investigation deals with the fundamentals of pulp bleaching with chlorine dioxide, the following review focuses on the literature relevant to the use of chlorine dioxide in the prebleaching stage.

CHLORINE DIOXIDE IN PREBLEACHING STAGE

Chlorine dioxide substitution

The term chlorine dioxide "substitution" is used to describe addition of ClO_2 to the chlorination stage with an equivalent reduction in chlorine dosage. Since both chemicals behave as oxidizing agents, it is normally assumed that one weight unit of ClO_2 is equivalent to 2.63 weight units of Cl_2 because, on a weight basis, ClO_2 can accept 2.63 times as many electrons as Cl_2. Therefore, the "total active chlorine", T is referred to as:

$$T = C + 2.63*D$$

and the chlorine dioxide substitution ratio, S, is:

$$S = 2.63D/(C + 2.63D)$$

where C and D are respectively the weight charges of chlorine and chlorine dioxide to pulp.

At constant total active chlorine charge, the efficiency of lignin removal after caustic extraction depends on the degree of ClO_2 substitution, and the order of addition of Cl_2 and ClO_2. It is generally found [1,2,3,4,5] that the kappa number after chlorination and extraction (CE) decreases as the ClO_2 substitution increases up to about 60%. Further increase in substitution again causes an increase in CE kappa number. At a given consumption of total active chlorine, the lowest CE kappa number is obtained when chlorine dioxide is charged before chlorine, as denoted by (DC) rather than when chlorine is charged first, i.e. a (CD) charging sequence. Simultaneous addition of chlorine and chlorine dioxide, (C + D) gives an intermediate result. Even though this is accepted knowledge, until now no adequate explanation has been given for this behaviour.

Chlorine dioxide prebleaching

Chlorine dioxide prebleaching of pulp is characterized by a fast initial reaction with substantial delignification, followed by a slower phase with limited delignification [6]. This reaction pattern is similar to that found when pulp is bleached with chlorine. However, the residual lignin content after pure chlorine dioxide prebleaching is higher than that obtained for chlorine at the same amount of charged equivalent oxidant (7). The formation of organically bound chlorine is also much less compared to that of pure treatment with chlorine.

The rate of chlorine dioxide prebleaching increases with increasing chlorine dioxide concentration, temperature, and chloride ion concentration (8), while the delignification efficiency improves with increasing chloride ion concentration and decreasing pH [6]. Germgärd et al have modelled the kinetics of chlorine dioxide consumption on the lignin-chloride dioxide stoichiometry when prebleaching with pure chlorine dioxide (D) [6,8], and with chlorine dioxide mixed with small amounts of chlorine (D + C) [9,10,11,12], as well as with sequential chlorine dioxide/chlorine (D/(C+D)) prebleaching [7].

Formation of organically bound chlorine

When elemental chlorine is charged in a bleaching plant to delignify pulp, some of the applied chlorine ends up as covalently bound chlorine in the lignin structure, either before or after dissolution of the lignin. On average 6 kg of organically bound chlorine is discharged per tonne of conventionally delignified softwood kraft pulp bleached by a CE prebleaching sequence [17]. The organically bound chlorine is measured as AOX, an environmental control parameter for effluents which stands for Adsorbable Organic Halogen. Most of the chlorinated organic compounds are toxic and some are bio-accumulative. However, recent research undertaken at Paprican [28] has shown that there was no significant correlation between the amount of organically bound chlorine produced in the bleach plant per ton of pulp and the toxicity of the effluent. Notwithstanding these findings, public demand will most likely lead to additional process changes which will lead to further reduction and even complete elimination of organic chlorine in bleach effluents and paper products.

Several processes are available to decrease the organic chlorine discharge. Decreasing the lignin content of the pulp entering the bleach plant will lower the requirements of the pulp for chlorine containing bleach chemicals. Biological treatment of effluents can also eliminate some 35% of the chlorinated organic matter. Finally large or even complete substitution of chlorine by chlorine dioxide becomes more and more the standard practice in the industry in order to meet the environmental regulations and market demand.

Part of the chlorine supplied during bleaching is converted to organochlorine. Axegard [14] reported that about 10% of chlorine in Cl_2 and ClO_2 consumed by the pulp ends up as AOX, irrespectively whether it originates from Cl_2 or ClO_2. Because the weight of atomic chlorine applied to pulp as chlorine dioxide is five times smaller than the weight of atomic chlorine supplied as molecular chlorine at the same total active chlorine charge, the amount of AOX in the chlorination effluent is strongly influenced by the percentage of chlorine dioxide substitution [13,14,15,16].

CHLORINE DIOXIDE CHEMISTRY

Disproportionation reactions of ClO_2

Chlorine dioxide undergoes a rapid electron exchange with chlorite in an aqueous solution. The disproportionation reaction was described [22] as

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

Taube and Dodgen [19] reported that a value of 36 for the chlorine dioxide disproportionation equilibrium constant:$[ClO_2]^2/[H^+]^2[ClO_2^-][ClO_3^-]$ at a temperature of 25°C. Thus at equilibrium in a neutral solution, chlorine dioxide is almost completely disproportionated, and even in a fairly acidic solution, the disproportionation will largely go to completion. However, the reaction is slow. The rate of disproportionation of ClO_2 according to Gordon and Feldman (20) is:

$$-\frac{d\,[ClO_2]}{dt} = [ClO_2]\ \{5\ x\ 10^5 + 1.6\ x\ 10^7\ x\ [OH^-]\}\ x\ \ e^{-\,(14600/RT)}$$
$$+ [ClO_2]^2\ [2.6\ x\ 10^9]\ x\ \ e^{-\,(14600/RT}$$
$$+ 7.3\ x\ 10^6\ [OH^-]\ x\ \ e^{-\,(7700/RT)}$$

where the concentrations are in mol/liter and time, t, in seconds.

Another possible ClO_2 disproportionation reaction was reported [21] as:

$$6\ ClO_2 + 3\ H_2O \text{———}> 5\ HClO_3 + HCl \qquad \textbf{(2)}$$

Hydrogen ions and chloride ions, but not chlorate ions, were said to accelerate this reaction. The rate of this reaction was reported to be only appreciable at high acidities and high temperatures.

With 10% of the active chlorine present as chlorine, it has been reported [22] that at $pH<7$ the following decomposition reaction also accounts for about 5% of the disappearance of ClO_2

$$2ClO_2 \text{———}> Cl_2 + 2O_2 \qquad \textbf{(3)}$$

The presence of chlorine accelerates the disproportionation ClO_2 into mainly chlorine [22].

Formation of chlorine dioxide from chlorite

Unlike the inactive bleaching product chlorate, chlorite is able to regenerate chlorine dioxide by reacting with chlorine according to

$$2\ Cl_2 + 3\ ClO_2^- + H_2O \text{———}> 4\ Cl^- + 2\ ClO_2 + ClO_3^- + 2H^+ \qquad \textbf{(4)}$$

The reaction is rapid in an acidic or neutral solution.

High hydrogen ion and chlorite ion concentrations can produce more chlorine dioxide, simultaneously suppressing the formation of chlorate. This was explained by Emmenegger and Gordon [21] by the following reaction mechanism:

$$Cl_2 + ClO_2^- \xrightarrow{k1} [Cl-Cl-Cl <^{O}_{O}]^- \xrightarrow{k3} [Cl-Cl <^{O}_{O}] + Cl^- \qquad (5)$$

or

$$HOCl + ClO_2^- \xrightarrow{k2} [HO-Cl-Cl <^{O}_{O}]^- \xrightarrow{k4} [Cl-Cl <^{O}_{O}] + OH^- \qquad (6)$$

$$2\ [Cl-Cl <^{O}_{O}] \rightarrow Cl_2 + 2\ ClO_2 \qquad (7)$$

$$[Cl-Cl <^{O}_{O}] + H_2O \rightarrow Cl^- + ClO_3^- + 2\ H^+ \qquad (8)$$

For this reaction scheme, and intermediate Cl_2O_2, is produced by reaction of both Cl_2 and HOCl with chlorite in reactions (5) and (6) respectively. Cl_2O_2 then reacts further to form ClO_2 or ClO_3^- via respectively reactions (7) and (8). Since reaction (7) is a second order reaction while reaction (8) is first order a high concentration of Cl_2O_2 favours the formation of ClO_2 relative to ClO_3^-. Since k1 is greater than k2, a high concentration of chlorine relative to hypochlorous acid leads to a relatively higher concentration of Cl_2O_2, which in turn favours the formation of ClO_2 (reaction (7)) over chlorate (reaction (8)). In other words in the mechanism given by reactions (5) to (8) process conditions which increase the chlorine concentration favour the formation of ClO_2, while hypochlorous acid results in the formation of relatively more chlorate. It was reported that a large excess of chlorine and acidic conditions are needed to produce only chlorine dioxide and no chlorate.

A possible consecutive reaction in the HOCl + ClO_2^- system was proposed [23] as:

$$2\ ClO_2 + HOCl + H_2O \rightleftarrows 2\ HClO_3 + HCl \qquad (9)$$

where the produced ClO_2 reacts with excess hypochlorous acid, forming more chlorate and chloride. It was claimed by White and co-workers [23] that the above reaction occurs rather fast in an acidic solution. However, Emmenegger and Gordon [21] reported that under acidic conditions, the chlorine dioxide formed from reaction of chlorine with chlorite does not disappear with time, even with hypochlorous acid in excess, indicating that the reaction between hypochlorous acid and chlorine dioxide is negligible. They observed that the ratio of chlorine dioxide formed to chlorite consumed by hypochlorous acid can vary from 0.3 to 0.7, depending on the reaction conditions. They also reported that the ratio of hypochlorous acid consumed to chlorite consumed remains constant during the reaction and is always less than 1. All this evidence supports that the reaction between hypochlorous and newly formed chlorine dioxide is negligible. It should be noticed that the reverse reaction (9) describes the overall reaction for the commercial chlorine dioxide generation from sodium chlorate in a very strong acidic milieu. Of course at these acidic conditions Cl_2 rather than HOCl is the product formed besides ClO_2.

Another reaction whereby chlorine dioxide could be produced from chlorite is by the so called acid catalyzed disproportionation reaction [24].

$$ClO_2^- \longrightarrow xCl^- + yClO_2 + zClO_3^- \qquad \textbf{(10)}$$

The stoichiometry of the reaction depends on the reaction conditions. It was suggested [24] that hypochlorous acid is an intermediate in this reaction.

Reactions of chlorine with chlorine dioxide

In practice, the chlorine dioxide produced is always contaminated with chlorine. Also, in a number of mills, chlorine and chorine dioxide are used simultaneously for pulp bleaching. Therefore, it is of interest to consider possible reactions between chlorine and chlorine dioxide.

Many investigators have recognized the existence of the following reaction:

$$2\ ClO_2 + Cl_2 + 2\ H_2O \rightleftarrows 2\ ClO_3^- + 2\ Cl^- + 4\ H^+ \qquad (11)$$

According to Hong and Rapson [25], the equilibrium constant for reaction (11) at 25°C is $K = 2.95 * 10^8$.

It was observed [34] that in an acidic solution, chlorine and chlorine dioxide react, producing chlorate and hypochlorous acid in a ratio of approximately 1. At higher chlorine dioxide concentrations, this ratio increases somewhat possibly because of the reaction:

$$6\ ClO_2 + 3\ H_2O \longrightarrow 5\ HClO_3 + HCl \qquad (12)$$

Reaction (11) is very slow in an acidic solution even though the corresponding equilibrium constant is very large. However, under neutral conditions, where chlorine is present as chloride and hypochlorous acid, the oxidation of chlorine dioxide to chlorate ion proceeds much faster as:

$$2\ ClO_2 + HOCl + H_2O \longrightarrow 2\ ClO_3^- + Cl^- + 3\ H^+ \qquad (13)$$

Still the disappearance of chlorine dioxide is relatively slow at conditions which favour the presence of hypochlorous acid [22].

DELIGNIFICATION MECHANISM BY CHLORINE DIOXIDE

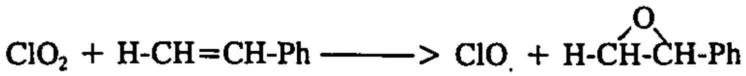
Progress has been made towards the understanding of the pulp delignification reactions during chlorine dioxide treatment by studying the behaviour of lignin model compounds. For example, Sarkanen et al [26] found that ring opening between carbon 3 and 4 of the aromatic ring of vanillin occurs during chorine dioxide treatment, since muconic acid monomethyl ester is formed in a quantity less than 30% of the original model compound. They also suggested that other reactions such as oxidation to *p*-quinones and their derivatives are responsible for the consumption of ClO_2 and the model compound. This was confirmed by Dence et al [27] in a follow-up paper on the reaction of vanillyl alcohol with ClO_2 and sodium chlorite. They suggested that at least two distinct reaction paths are involved in the oxidation of guaiacyl type compounds by chlorine dioxide:

(a) oxidative ring opening resulting in the formation of derivatives of muconic acid monomethyl ester

(b) oxidation to chlorine-substituted *p*-benzoquinones.

In practice, the latter reaction path is significant for lignin degradation because it leads to the cleavage of the side chain para to the free phenolic hydroxyl group. Other oxidation reactions may also contribute significantly to the overall breakdown of vanillyl alcohol, since the combined yield of the products resulting from these two reaction paths account only for 28% of the original model compound. Further degradation of monomethyl muconic acid ester derivatives and substituted *p*-benzoquinones seems unlikely since Dence et al [27] found that both type of compounds are reasonably inert towards chlorine dioxide. It is interesting to note that only non-chlorinated muconic acid derivatives were isolated. On the other hand the identification of chlorinated quinones and other chlorinated compounds let Dence et al [27] suggest that during oxidation of the model compound and/or sodium chlorite are reduced to elemental chlorine. The formation of organically bound chlorine during pulp bleaching with ClO_2 could then be explained by the in-situ generation of chlorine. When syringyl alcohol was oxidized with sodium chlorite only substituted *p*-benzoquinones and no muconic ester derivatives were isolated.

Kolar and Lindgren [28] used styrene as lignin model compound to study the mechanism of pulp bleaching by chlorine dioxide. They found that the reaction between styrene and chlorine dioxide proceeds via an epoxide whereby chlorine dioxide is reduced to monochlorine monoxide. The latter is unstable and very reactive and reacts with chlorine dioxide to chlorate and hypochlorous acid. A small amount of chlorite was observed at pH 6, but not at pH 2 or pH 4. Therefore, the following reaction pattern was proposed:



$$ClO_2 + H\text{-}CH{=}CH\text{-}Ph \longrightarrow ClO_{\cdot} + H\text{-}\overset{O}{\overbrace{CH\text{-}CH}}\text{-}Ph \qquad (14)$$

$$ClO^{\cdot} + ClO_2 + H_2O \longrightarrow HClO + ClO_3^- + H^+ \qquad (15)$$

This route transforms two molecules of chlorine dioxide into one molecule of chlorate and hypochlorous acid. There is, however, some question whether styrene is representative for the guaiacyl structures in lignin.

Lindgren [29] studied the reaction between chlorine dioxide and lignin related phenols, such as creosol, vanillin and proposed a reaction mechanism described in Figure 1. It shows that phenolic group is first oxidized by a one-electron oxidation to a phenoxyl radical (step 1). Chlorine dioxide is thereby reduced to chlorite. The phenoxyl radical is then oxidized by a three-electron oxidation reaction (steps 2 + 3b) to the monomethyl ester of the muconic acid derivative or by a one-electron oxidation (steps 2 + 3a) to an ortho-quinone.

In a follow-up paper, Kolar et al [30] measured how much hypochlorous acid is formed as an intermediate during chlorine dioxide bleaching of an oxygen-prebleached softwood kraft pulp. This was done experimentally by capturing this intermediate with sulfamic acid and titrating the resulting N-chlorosulfamic acid iodometrically in a neutral solution. It was found that the amount of hypochlorous acid captured was larger than the amount of chlorite formed. Since steps 1,2 and 3b in Figure 1 give equimolar amounts of hypochlorous acid and chlorite, while steps 1,2 and 3a produce only chlorite, part of

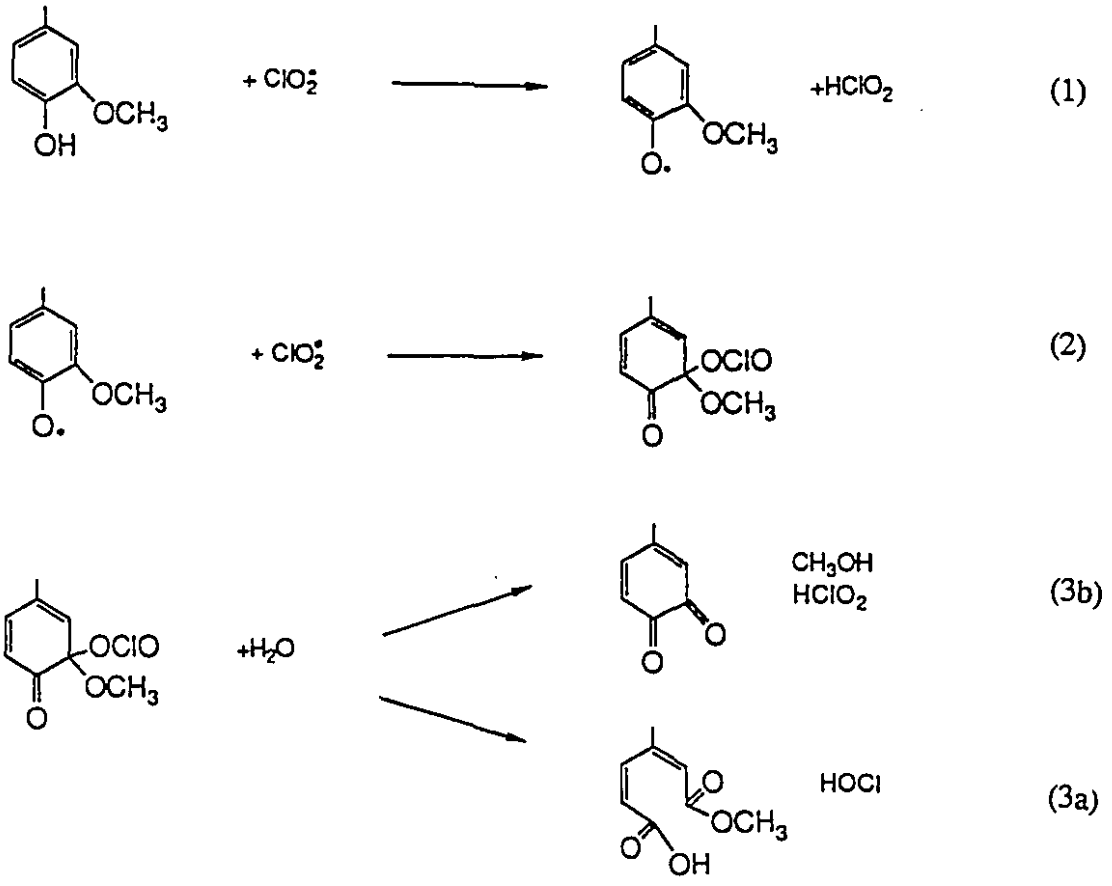
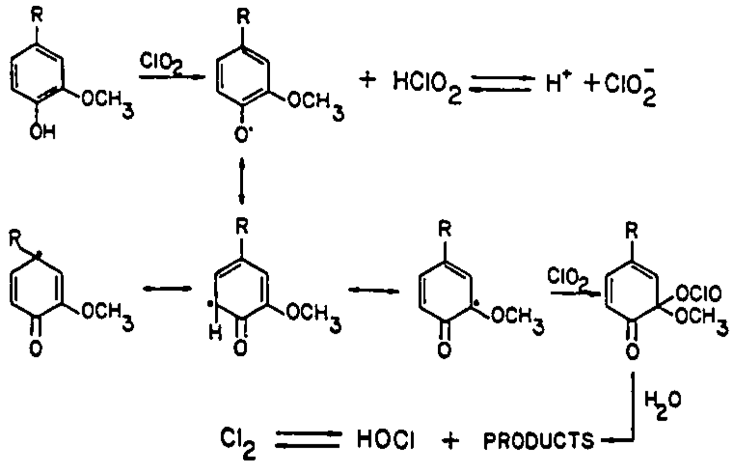


Figure 1. The suggested route for the ClO_2 oxidation of guaiacyl derivatives by Lindgren [29]

the hypochlorous acid must be formed by other routes than given in Figure 1. Kolar et al argue therefore that part of the hypochlorous acid (or chlorine) is formed by the two-electron transfer process with ClO formation given by reactions (14) and (15). This would also explain the formation of chlorate during pulp bleaching with ClO_2. It is further assumed that the proportion of the one-electron reduction to chlorite and the two-electron reduction to monochlorine monoxide depends on the properties of the residual lignin in the pulp. For example, in unbleached kraft pulp with lignin containing many phenolic groups, chlorine dioxide attacks mostly by the one-electron mechanism. During the bleaching of this type of pulp 5 - 20% (depending on the pH) of the consumed chlorine dioxide is transformed into chlorate. In prebleached pulp, the active groups may consist, to a large extent, of groups which chlorine dioxide attacks by the two-electron reaction, so that a larger proportion of ClO_2 is transformed into chlorate, 25 - 50% according to Germgard et al [31].

Strumila and Rapson [32] proposed that chlorine dioxide oxidation of lignin takes place through a chain mechanism, which is initiated by abstracting a hydrogen atom from the phenolic hydroxyl group, producing chlorous acid. Then, the reactive phenoxy free radical intermediate reacts again with ClO_2 to form a hypochlorite ester which is rapidly hydrolysed with the liberation of hypochlorous acid. ClO_2 attacks the phenoxy free radical preferentially at the methoxyl substituted carbon since this is the site of the greatest electron density. Hypochlorous acid and chlorous acid or chlorite react rapidly to regenerate chlorine dioxide as well as chloride. This reaction scheme is shown in Figure 2. The model compound studies of Strumila and Rapson [32] clearly show that ClO_2 is regenerated with guaiacyl derivatives when the pH is 3.5 or 4.5. However, chlorine dioxide is not regenerated when the pH is raised to 6.0. The initial reaction rate



$$Cl_2 + 2\ HClO_2 \longrightarrow 2\ ClO_2 + 2\ HCl$$

Figure 2. The proposed mechanism of reaction between ClO_2 and phenolic lignin models by Strumila and Rapson [32]

of phenolic compounds is much less than that of the guaiacyl derivatives and also do not show clear evidence of regeneration of ClO_2. Strumila and Rapson [32] compared the consumption profile of chlorine dioxide by guaiacyl structures with that of syringyl compounds and found that the introduction of the second methoxyl group decreases the overall consumption of chlorine dioxide considerably. They also found that methylation of the hydroxyl group in guaiacyl and syringyl compounds renders them virtually inert to chlorine dioxide.

DEMETHYLATION DURING ClO_2 BLEACHING

Only one publication is available in literature on this subject. Dence et al [27] studied chlorine dioxide treatment of lignin model compounds, isolated kraft lignin and wood meal and classified the fate of the methoxyl groups during chlorine dioxide treatment into two groups.

(a) Indirect cleavage: The methoxyl groups are still attached to degraded lignin or lignin model compounds such as monomethyl muconic acid ether or methoxyl-*p*-benzoquinone obtained after reaction with chlorine dioxide, but these relatively stable products are hydrolysed under methanol formation during subsequent alkaline or hot water treatment.

(b) Direct cleavage: The methoxyl groups are attacked and liberated as methanol during treatment with chlorine dioxide.

The quantity of the methoxyl groups associated with these two classes was crudely determined by measuring the methanol content of the distillate of the reaction product obtained by regular and vacuum distillation, i.e. representative respectively of the direct and indirect cleavage . The amount of methanol produced by both classes of methoxyl groups after a two-hour ClO_2 treatment of vanillyl alcohol and vanillin amounted to 85-

100% of the theoretical value. However, for guaiacol only 52% was recovered. With kraft lignin and Norway spruce wood meal the percentages of methanol recovered are respectively 75% and 39% of the theoretical value. Since in all cases approximately ⅔ to ¾ of the total amount of recovered methanol was obtained by the direct cleavage reaction path, it follows that a considerable portion of demethylation occurs by direct action of chlorine dioxide or its reaction intermediate, hypochlorous acid (or chlorine). Dence et al [27] point out that based on this data it is not possible to draw any conclusion as to whether a hydrolytic or oxidative mechanism is involved in the direct cleavage reaction path. They conclude that demethylation is only restricted to lignin units which possess a free phenolic hydroxyl group, while etherified units remain intact when contacted with chlorine dioxide. As to the effective demethylation reagent, they stated that it is entirely possible that demethylation may take place as a consequence of the action of hypochlorous acid (or chlorine) generated in the reaction mixture.

SUMMARY

The development of the concentrations of chlorine dioxide, chlorite and chlorate formed during chlorine dioxide bleaching has been studied. However, in none of these studies was the development of chloride or organic chlorine measured, thus making it difficult to obtain a complete picture of all the transformation of atomic chlorine. Most of the literature available concerning the AOX formation deals with practical aspects of how to decrease the discharge of AOX to the environment. Fundamental investigations regarding the formation process are, however, rather limited. Even though it was proposed that organic chlorine is formed by reaction between lignin and in-situ generated chlorine as hypochlorous acid, no evidence was ever provided in terms of the development of organic chlorine. Studies, so far, concerning the formation chlorate during ClO_2 bleaching focused on the amount of chlorate formed as function of process variables such as Ph, chloride concentration, charging sequence, 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 characteristics of demethylation during chlorine dioxide treatment of kraft pulp has hardly been studied. No attempt has been made to relate demethylation with delignification during chlorine dioxide treatment. Progress towards the understanding of delignification during pulp chlorine dioxide bleaching was mostly obtained through studies with lignin model compounds. Experimental confirmation of the results obtained from lignin model compounds for actual ClO_2 treatment of kraft pulp is very difficult because of the complexity of the reaction system. Of the numerous publications on ClO_2 bleaching only a few have tried to establish the delignification mechanism based on measurements with actual pulp.

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CHAPTER 3

EXPERIMENTAL SET-UP AND TECHNIQUES

GENERAL

Conventional kraft pulps from black spruce wood were prepared at Paprican's chemical pulping pilot plant. Pulp samples at a consistency of about 35% were stored in a refrigerator throughout the study. Handsheets were made 24 to 48 hours prior to the start of an experiment since the moisture content of the air dried handsheets can easily be determined. The pulp bleaching experiments with chlorine dioxide were performed in a stirred batch reactor. More details regarding the experimental set-up and its operation will be given later in this chapter.

EXPERIMENTAL PROCEDURES

Reactant Preparation

Chlorine water

A four-litre carboy was filled with distilled water. Chlorine gas from a gas cylinder was bubbled through the distilled water by means of a glass tube equipped with a fritted glass tip for good dispersion. When the desired chlorine concentration was reached, the chlorine gas flow was terminated.

Chlorine dioxide solution

Chlorine dioxide was prepared by passing chlorine gas diluted with nitrogen through 4 columns filled with solid sodium chlorite, and collecting the evolving chlorine dioxide gas in cold deionized water. It should be pointed out that the chlorine gas concentration in the nitrogen was less than 2% in order to avoid a too high chlorine dioxide concentration after passage through the chlorite columns. A high ClO_2 concentration, noticeable by a dark orange colour of the gas, should be avoided because chlorine dioxide gas at high concentration is potentially explosive. Chlorine dioxide solutions were made one day before a bleaching experiment.

Bleaching Experiments

Experimental set-up

The bleaching experiments were performed in a stirred batch reactor shown in Figure 1. Controlled agitation is achieved by a variable speed electric stirrer.

Chlorine dioxide treatment

The three neck glass reactor was filled with the required volume of pulp suspension and then submerged in a constant temperature bath for 10 to 15 minutes while stirring to obtain a uniform and known temperature. Before the required amount of freshly made chlorine dioxide was added to the pulp suspension by a pipette, the stirrer was turned off. As soon as the charging of chlorine dioxide solution was finished, timing and mixing were started immediately. For the experiments with the addition of sulfamic acid, the required amount of sulfamic acid was first mixed with pulp suspension and then chlorine dioxide was added while stirring. After certain reaction times liquor samples were taken for analysis of chlorine containing species by ion chromatograph (IC), for the determination of the methanol content by gas chromatograph (GC) and for AOX content by the Dohrmann DX-20 analyser. When the reaction was terminated by addition of KI, the pulp slurry was transferred to a specially designed buchner funnel, and then thoroughly washed with water.

Chlorine treatment

Chlorination was performed in the same reactor. First a specified amount of chlorine water was introduced by a pipette into the reactor. In order to facilitate this procedure, excess gas inside the reactor was allowed to escape by opening a glass valve in the third neck of the reactor. The required amount of pulp in the form of air dried handsheets was soaked in deionized water for about one half hour. The concentrated

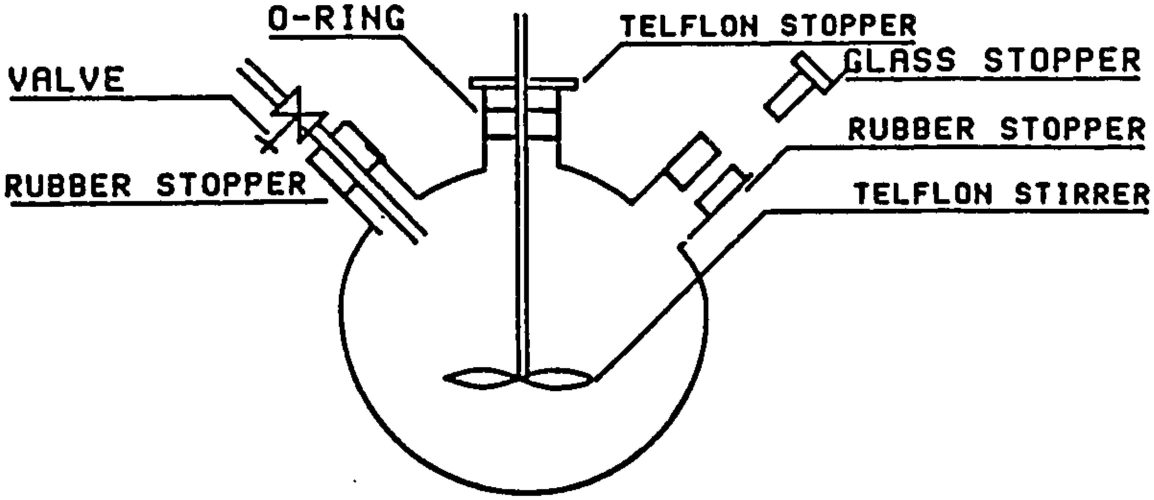

Figure 1. Reactor used for bleaching

pulp suspension was put in a 50 ml syringe. Before the pulp was injected into the reactor, the chlorine concentration was determined, and chlorine water and deionized water were added so that the desired chlorine concentration and consistency would be obtained. Thereafter, the pulp sample was injected into the flask with the syringe by opening the rubber stopper. The stopper was immediately replaced and agitation was started. At different specified times, a small amount of bleach liquor was separated from the pulp suspension for further analysis. The pulp was saved for further treatment such as washing and caustic extraction.

Pulp Washing

Pulp obtained after the chlorine dioxide or chlorine treatment was washed with large amounts of tap water and then transferred to a British handsheet making machine, diluted and drained three times with tap water and finally 4 litres of distilled water. The pulp sample was then saved in the form of an air dried handsheet for further treatment or analysis.

Alkali Extraction

A conventional extraction was performed at a consistency of 10%, 70°C for the duration of 1 hour in a polyethylene bag after mixing the required amount of sodium hydroxide with the pulp suspension to achieve the required caustic charge. The mixture was kneaded every 20 minutes. After one hour of reaction the liquor was separated from the pulp for further analysis. The extracted pulp was washed as described earlier and air dried handsheets were prepared for further analysis.

ANALYTICAL TECHNIQUES

Cl^-, ClO^-, ClO_2^-, ClO_2 and ClO_3^- Determination by Ion Chromatography

The five inorganic chlorine containing species, Cl^-, ClO^-, ClO_2^-, ClO_2 and ClO_3^-

were determined ion chromatographically (Dionex model 2000i) by two separate injections. One of the two 1 ml samples was diluted to 25 ml with a 2mM $NaCO_3$ solution and subsequently subjected to a nitrogen purge for 15 minutes in order to remove any remaining chlorine dioxide. A fritted glass sparger was used and the flask was shaken continuously in an ice bath. The presence of sodium carbonate makes sure that all the chlorine is converted to ClO^-.

ClO^- was determined by direct injection of a 7 to 8 ml sample into the electrochemical detector (ECD). The preferred concentration of OCl^- is 1 to 10 ppm. The experimental conditions are:

Detector: platinum type ECD, with applied potential of -0.2 volts
Flow Rate: 1.4 ml/min
Eluent: 2mM Na_2CO_3
Diluent: 2mM Na_2CO_3

The solution of ClO^- in 2mM Na_2CO_3 is reasonable stable at room temperature as can be inferred from a concentration decrease of only about 6% for a repeat analysis done 100 minutes later. Because the present solution was kept in ice and analyzed within 15 minutes, it is estimated that the loss of ClO^- is negligible.

No OnGuard-P cartridge (for dissolved lignin removal) was used, because its presence reduced the ECD response to OCl^-. Also, it appears that the cartridge filling polyvinylpyrrolidone, converts ClO_2 to chlorite, because the OnGuard-P cartridge completely eliminated the very large ECD response to ClO_2. The presence of the cartridge might also explain why Easty et al [1] found that chlorine dioxide is not detected by ECD. Finally, it emphasized the need for complete removal of chlorine dioxide when analysing ClO^- with the ECD.

After passing through the ECD, the sample was analyzed for its Cl^-, ClO_2^- and ClO_3^- content with the conductivity detector. The conditions are:

Column:	Dionex AS3 and AG3 guard column
Eluent:	2mM Na_2CO_3
Diluent:	2mM Na_2CO_3
Flow Rate:	1.4 ml/min

The retention times for ClO_2^-, Cl^- and ClO_3^- are 2.74, 4.58 and 14.53 minutes, respectively. Typical chromatogram is shown in Figure 2.

The same analysis (ClO_2^-, Cl^- and ClO_3^-) was repeated for the second 1 ml sample which was also diluted in 2 mM sodium carbonate, but not subjected to a nitrogen purge. Since chlorine dioxide is analyzed as chlorite, the chlorine dioxide content can be obtained by difference from the samples with and without nitrogen purge.

It was suggested [2] that potassium iodide must be used for complete conversion of ClO_2 to chlorite. However, the present results showed that KI is not required when working within the range of 1 to 10 ppm chlorine dioxide. Also, because KI can reduce ClO^- and ClO_2^- to chloride, it was decided not to use KI.

For the experiments whereby sulfamic acid was present, the analysis of the chlorine containing inorganic species was modified because sulfamic acid has almost the same retention time as chlorite when analyzed by IC. Sulfamic acid reacts with hypochlorous acid according to:

$$HClO + H_2NSO_3^- \longrightarrow HClNSO_3^- + H_2O \qquad (1)$$

Therefore, the concentrations of chlorite and the reaction product of hypochlorous acid and sulfamic acid (reaction 1) were determined by iodometric titration, according to the following reactions:

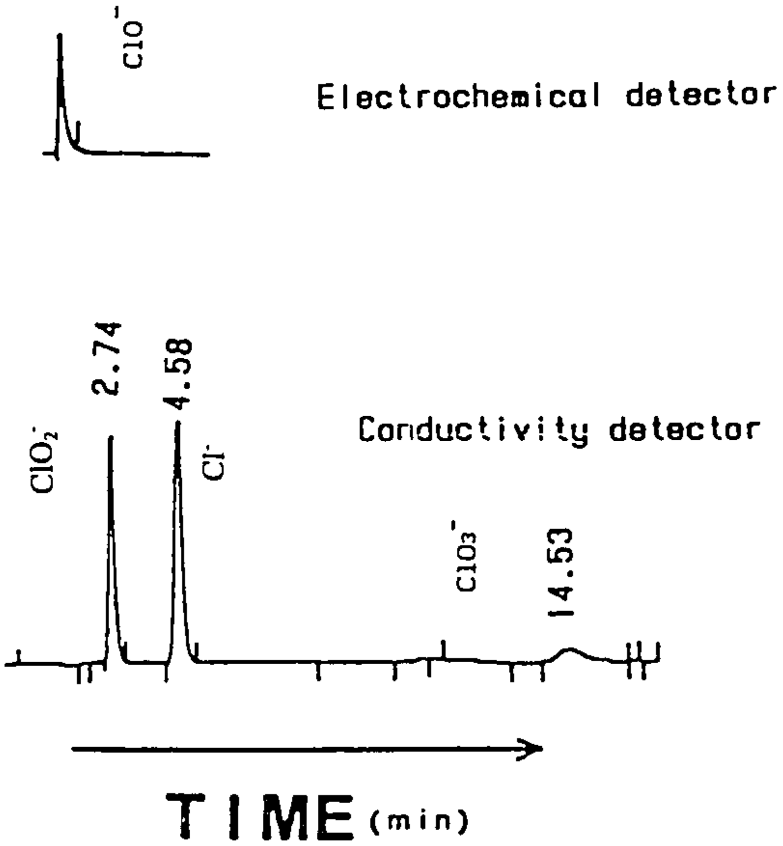

Figure 2. Typical ion chromatogram for the inorganic chlorine containing species

$$HClNSO_3^- + 2I^- + H^+ \longrightarrow I_2 + Cl^- + H_2NSO_3^- \quad (2)$$

$$ClO_2^- + 4I^- + 4H^+ \longrightarrow 2I_2 + Cl^- + 2H_2O \quad (3)$$

$$I_2 + 2S_2O_3^{2-} — 2I^- + S_4O_6^{2-} \quad (4)$$

Reaction (2) occurs at pH 7, while reaction (3) only takes place at pH 2. Since ClO_2 also reacts with potassium iodide, any residual ClO_2 was removed with a nitrogen gas purge before titration. To make sure that the pH is above 7, sufficient sodium bicarbonate is added to the solution. 25 ml of sample is then immediately titrated with 0.01N $Na_2S_2O_3$ consumed. The calculation of the amount of HClO captured by sulfamic acid expressed as chloride is:

$$\frac{A \ x \ N}{2 \ x \ v} \ x \ 35.5 \ (g/l)$$

or twice this value when expressed as molecular chlorine concentration. The ClO_2 concentration expressed as chloride is:

$$\frac{(B-A) \ x \ N}{4 \ x \ v} \ x \ 35.5 \ (g/l)$$

where N is the $Na_2S_2O_3$ normality and v is the sample size (ml).

The method was checked with a mixture of chlorite and chlorine captured by sulfamic acid. Duplicate analyses were performed for a mixture of $HClNSO_3^-$ (with excess sulfamic acid) and chlorite with concentrations of 1.55 and 1.86 g/l respectively. Both analyses gave 1.53 g/l and 1.83 g/l, respectively, showing that the method is accurate.

Phenolic Hydroxyl Group Determination

The determination of phenolic hydroxyl group content in lignin was first attempted by methylating the pulp with diazomethane [5]. The method is based on the conversion of phenolic hydroxyl groups to methoxyl groups, and subsequent analysis of the increase in methoxyl content of the treated pulp. However, the results of this method turned out to be unrealistically high for ClO_2 treated pulp samples, presumably because carboxyl groups are introduced during chlorine dioxide treatment and diazomethane can easily methylate the carboxyl groups. Therefore, this method was dismissed as unsuitable for the present pulps.

The periodate oxidation method was subsequently employed for the determination of the phenolic hydroxyl group content of pulp. This method is based on the fact that methoxyl groups in the ortho positions to a free phenolic hydroxyl group are split off as methanol by the action of periodate, while methoxyl groups in the side chain and etherified aromatic methoxyl groups are stable towards periodate. When using this method, Adler and Hernestan [3] distilled off the methanol liberated by oxidation, purified it, and determined the amount of methanol colorimetrically with chromotropic acid. Owing to the large number of steps involved, some small losses of methanol are difficult to avoid. Gierer et al [4] later used gas chromatography to determine the methanol released by periodate treatment of isolated lignin samples. Glacial acetic acid was used for dissolving the lignin sample. The drawback of this procedure is that part of the methanol is esterified by the acetic acid, and also, all acetic acid has to be removed from the column before the next run GC analysis can be done.

In the present study, the periodate oxidation method was used to estimate the phenolic hydroxyl group content of the unbleached and chlorinated pulp samples. A large excess or periodate was used since the cellulose, the main constituent of the pulp, is also oxidized by periodate. The following procedure was used: 0.46 gram sodium metaperiodate ($NaIO_4$) and 1 ml of 4N sulfuric acid were mixed, followed by the addition of 2.8 ml water. The sodium metaperiodate solution was cooled to 4°C before 0.20 gram of o.d. pulp sample was charged to the solution. The reaction mixture was maintained at 4°C inside a refrigerator for 3 days, and mixed periodically. The filtrate was then separated from the pulp and the excess amount of periodate was destroyed with sodium thiosulfate. The amount of methanol in the sample was subsequently determined by GC analysis. Application of the above method to a sample of guaiacol gave a methanol recovery of 93.2% of the theoretical amount of methoxyl groups. On the other hand, only 4.3% of the methoxyl groups in a veratrol sample were converted to methanol by periodate oxidation. This confirms the validity of the technique to measure the quantity of free phenolic hydroxyl groups which have a methoxyl group in the ortho position.

Methanol Determination by GC

The methanol concentration in the liquor samples was determined by gas chromatography. The analytical conditions are:

Column: Chromosorb 102, mesh size 80/100, 6 ft long, 0.125 in o.d.
Injection Temperature (°C) : 150
Oven Temperature (°C): 105
Detector Temperature (°C): 200
Helium Flow Rate (ml/min): 50
Hydrogen Flow Rate (ml/min): 22
Air Flow Rate (ml/min): 250
Sample Size (ul): 1.0

A typical chromatogram is shown in Figure 3. The retention time for methanol is 1.61 minutes.

AOX Determination

The AOX technique which quantifies the organically bound chlorine content in

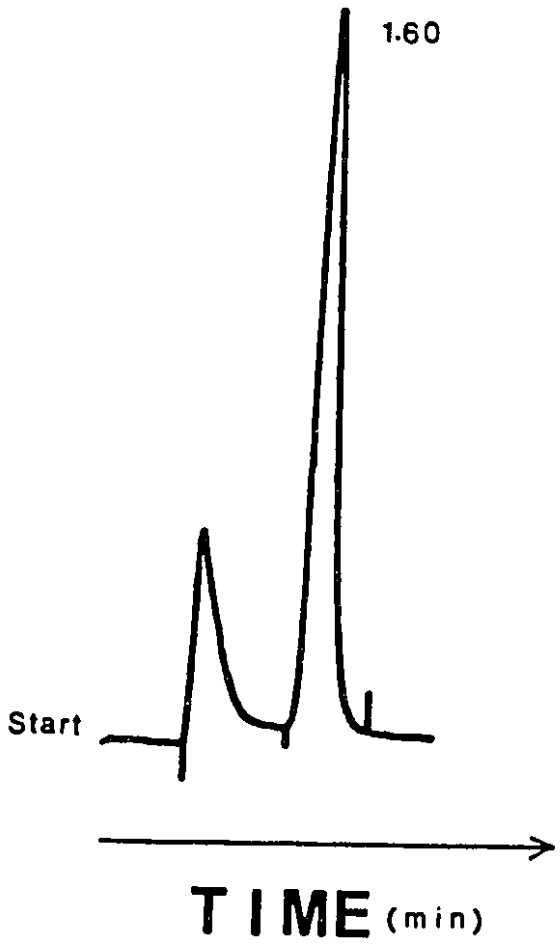

Figure 3. Typical gas chromatogram for methanol determination

the filtrate, consists of adsorption on activated carbon, combustion of the loaded carbon and microcoulometric titration of the chloride as illustrated in Figure 4.

A black liquor sample was diluted to about 6 - 8 ppm, of organic chloride concentration. In most cases, the samples were analyzed immediately , however, on some occasions the diluted samples were kept in a refrigerator until analysis the next day. A few ml of 0.01 N sodium thiosulfate were added to the sample to destroy any residual chlorine dioxide or chlorine just before adsorption on the granular activated carbon (GAC). 100 ml of the diluted bleach liquor were passed through two GAC columns in series (each column containing approximately 40 mg of GAC). Then the GAC, together with the adsorbed material were subjected to a washing step by elution of 2 ml of a 5 g/l sodium nitrate solution through the two packed columns. This step is needed becasue any adsorbed or ion exchanged inorganic chlorine would not completely be removed from the GAC after the adsorption stage. Subsequently, the activated carbon and the absorbed materials were transferred to the combustion module of the Dohrmann DX-20 analyser and burned in oxygen in a closed container at a temperature of around 850°C so that all organic chlorine is converted to hydrochloric acid gas.

Organically Bound Chlorine in Pulp

The organic chlorine content of the pulp was determined by modifying the AOX testing method. Instead of activated carbon, about 20 mg of ClO_2 treated pulp was packed in a glass column and washed with a 5 g/l sodium nitrate solution at a flow rate of about 1 ml/min for 10 minutes. The $NaNO_3$ washed pulp is subsequently combusted in the Dohrmann AOX analyzer and the chloride produced was determined by microcoulometric titration.

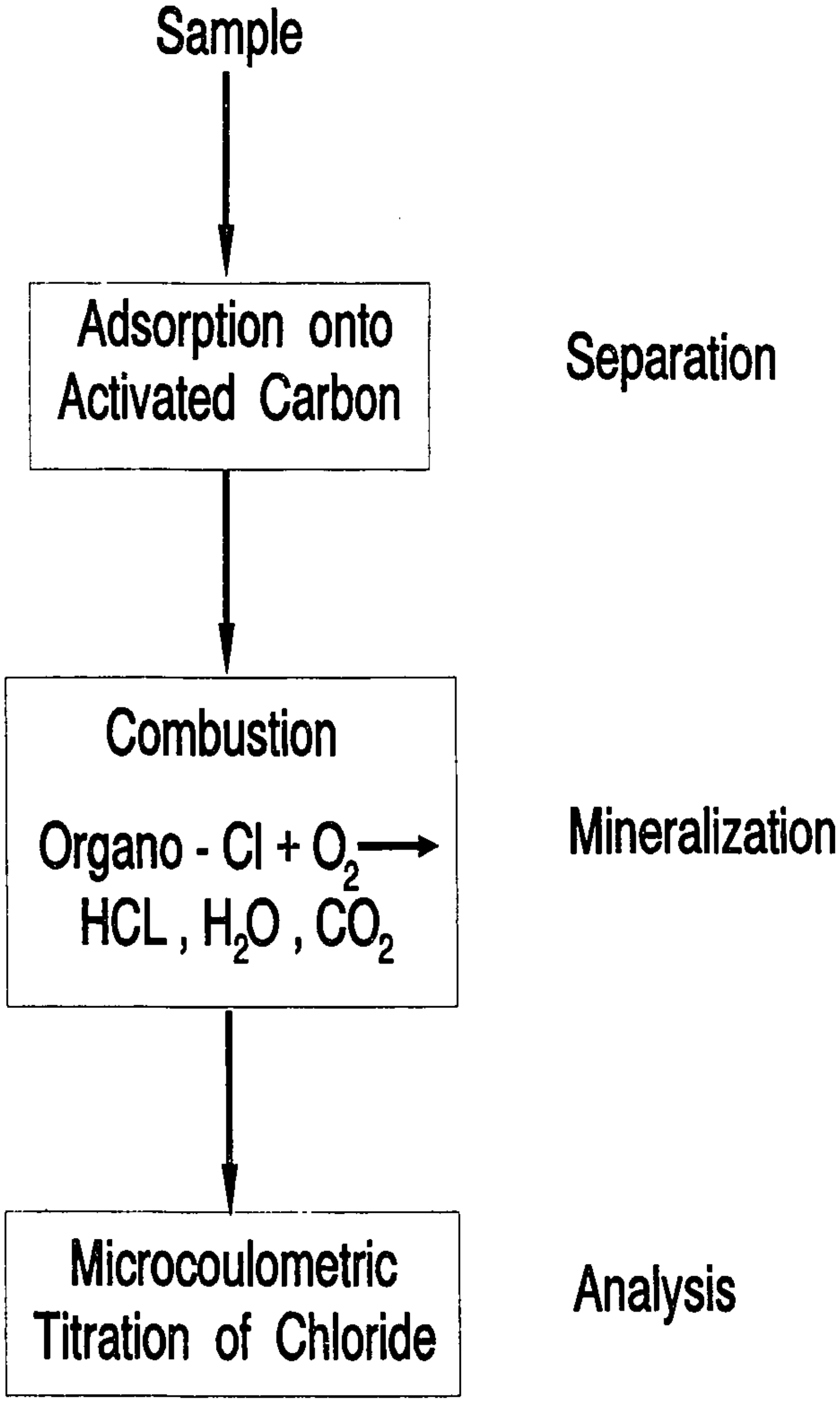

Figure 4. Schematic of AOX determination

Methoxyl Group Content

The methoxyl group content in the pulp samples was measured according to Tappi standard T209. The modification made to the apparatus is the replacement of the ground socket joint by a spherical O-ring joint so that leakage is prevented and the use of lubricating oil can be avoided.

The methoxyl content of the dissolved organic material in the ClO_2 bleach filtrate was determined by passing a certain amount of filtrate through the two columns packed with GAC used for the AOX analysis (see AOX determination). Then the methoxyl content of the absorbed material together with the GAC was performed following the T209 Tappi standard.

Other Analyses Used

The kappa number and klason lignin were measured according to CPPA standard methods G18 and G9 respectively. Pulp viscosity was determined by Tappi standard T230 om-82. UV lignin was analyzed by Paprican's chemical analysis group.

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CHAPTER 4

RATE PROCESSES OF AOX FORMATION AND CHLORINE SPECIES DISTRIBUTION DURING CLO$_2$ PREBLEACHING OF KRAFT PULP

ABSTRACT

The distribution of atomic chlorine over all chlorine containing species such as chloride, chlorine (hypochlorous acid), chlorite, chlorine dioxide and chlorate as well as organically bound chlorine in the pulp and bleach solution, was measured during ClO_2 prebleaching of kraft pulp.

The chlorine mass balance was satisfied throughout the bleaching reaction. Based on the development of the chlorine containing species, a series of reactions are given which explains the path of atomic chlorine during ClO_2 bleaching. It was found that all organic chlorine, defined as the sum of AOX in the spent ClO_2 solution and the organically bound chlorine in the chlorinated pulp, is formed within the first 10 minutes of reaction. Subsequently, the increase in AOX in solution is matched by an equivalent decrease of organically bound chlorine in the pulp. The organic chlorine during ClO_2 bleaching is mainly formed from the reaction between lignin and hypochlorous acid.

Keywords Chlorine Dioxide, AOX Formation, Mechanism, Rate Processes, Chlorine Mass Balance, Kraft Pulp

INTRODUCTION

When contacted with unbleached pulp, chlorine dioxide is reduced to chlorite, hypochlorous acid (chlorine) and chloride, and is oxidized to chlorate. Some of the atomic chlorine also ends up as organic chlorine. The understanding of this complex reaction system would improve if the development of all chlorine containing species is known, and a complete chlorine mass balance is obtained.

The development of the concentrations of chlorine dioxide, chlorite and chlorate formed during chlorine dioxide bleaching of kraft pulp has been the subject of several studies [1,2,3,4,5,10]. However, in none of these studies was the development of chloride or organic chlorine measured, thus making it difficult to obtain a complete picture of all the transformations of atomic chlorine.

Numerous publications are available concerning the AOX formation during Cl_2/ClO_2 bleaching. Most of these deal with practical aspects of how to decrease the discharge of AOX to the environment [6,7,8]. Fundamental investigations regarding the formation process are, however, rather limited. A key study is that of Kolar et al [5], who found that about 50% of the supplied chlorine dioxide is converted to hypochlorous acid. In a schematic model of the chlorine transformation reactions, it was indicated by Kolar et al [5] that organic chlorine is formed by reaction between lignin and in-situ generated chlorine or hypochlorous acid. However, no evidence was provided in terms of the development of organic chlorine.

The objective of the present study is to establish an atomic chlorine mass balance during ClO_2 bleaching of kraft pulp by determining the development of various inorganic chlorine species as well as the organically bound chlorine content of both the filtrate and treated pulp. This information will then be used to explain the formation path of the different species. The second part of this study deals with the formation path of organically bound chlorine in the treated pulp and bleach effluent.

EXPERIMENTAL

A 28.7 kappa number kraft black spruce pulp was used. The ClO_2 experiments were performed in a 3-neck round bottom flask. A chlorine dioxide solution was added to 4 grams of pulp, which was well dispersed in deionized water by mechanical stirring. A high ClO_2 concentration was used, so that the addition of the ClO_2 solution could be completed in about 5 seconds. The final pulp consistency was 1%.

Two liquor samples of 1 ml volume each were taken at 1 min., 10 min., 30 min., 1 hr., 1 hr. 52 min. and 2.5 hrs. for Cl^-, ClO^-, ClO_2^-, ClO_2, and ClO_3^- determination. The total amount of liquid removed with the samples represented 3% of the initial reaction volume. Both liquor samples were diluted to 25 ml with an ice-cold solution of 2mM $NaCO_3$ (same as the eluent used for ion chromatograph (IC) analysis). One of the samples was sparged with nitrogen to remove the residual ClO_2. The nitrogen purge was performed in an ice-bath to minimize further reactions. For details of the analytical techniques, see Chapter 3.

In the first set of experiments a pulp sample was only collected after 2.5 hours when the reaction was stopped. Therefore, the experiment was repeated, but now the reaction was stopped at each sampling time, allowing analysis of both the liquor and pulp samples. The results reported for the liquor composition are the average of the corresponding samples of the two sets of experiments.

The AOX content of the filtrate was measured with a Dohrmann DX20 analyzer. The organically bound chlorine content in the chlorine dioxide treated pulp was determined using the following modified AOX method. Instead of activated carbon, about 20 mg of the pulp was packed in a capillary column and washed with a 5 g/l sodium nitrate solution at a flow rate of about 1 ml/min for 10 minutes. The $NaNO_3$ washed pulp was subsequently combusted in the Dohrmann AOX analyzer and the chloride produced was determined by coulometric titration. The kappa number was determined according to the CPPA standard method.

RESULTS AND DISCUSSION

ClO_2 treatment of fully bleached pulp

It is known [9] that chlorine dioxide can disproportionate to chloride, chlorite and chlorate as

$$ClO_2 \longrightarrow x\,Cl^- + y\,ClO_2^- + z\,ClO_3^- \qquad (1)$$

The importance of this reaction during actual ClO_2 treatment of kraft pulp was determined from a reference experiment with fully bleached pulp. The conditions of the experiment were the same as those of the experiments with unbleached pulp i.e. 1% consistency, 45°C, and an initial ClO_2 concentration of 0.237 g/l.

The chlorine species development during this experiment is shown in Table 1. It shows that ClO_2 is quite stable, with 93.5% ClO_2 still present after 2.5 hours. This is in agreement with the knowledge [9] that ClO_2 disproportionation proceeds only appreciably in alkaline conditions, but is very slow in an acid solution. Table 1 also shows that no significant amount of chlorate is formed during the entire experiment. Therefore, it can be concluded that the contribution of the ClO_2 disproportionation reaction to the disappearance of ClO_2 and to the chlorate formation is very small during ClO_2 treatment of unbleached kraft pulp.

ClO_2 treatment of unbleached kraft pulp

The unbleached pulp was treated with ClO_2 at an initial concentration of 0.237

Time (min)	Composition (% of atomic chlorine)					Chlorine Balance
	Cl^-	ClO^-	ClO_2^-	ClO_2	ClO_3^-	
0	0	0	0	100.0	0	100
1	0	0	2.8	98.0	NI	100.8
10	0	0	3.2	97.5	NI	100.7
30	0	0	3.7	97.0	NI	100.7
60	0	0	4.4	96.3	NI	100.7
112	0	0	4.8	95.1	NI	99.9
150	0	0	5.5	93.5	NI	99.0

NI: IC peak is too small to be integrated (< 1.6%)
1% consistency, initial ClO_2 concentration 0.237 g/l, 45°C

Table 1. Development of liquor composition during ClO_2 treatment of fully bleached pulp at 45°C

g/l, 1% consistency and 25°C. The equivalent chlorine charge factor was 0.22. The distribution of chlorine over the species in the liquor and in the ClO_2 treated pulp are listed in Table 2.

Time (min)	Composition (% of atomic chlorine)							Chlorine Balance
	Cl^-	ClO^-	ClO_2^-	ClO_2	ClO_3^-	AOX	Pulp	
0	0	0	0	100.0	0	0	0	100
1	30.3	0	19.3	37.5	7.6	1.8	3.7	100.2
10	40.8	0	24.6	21.4	8.3	2.7	4.4	102.2
30	45.9	0	26.5	13.1	8.6	2.9	3.5	100.5
60	51.3	0	25.7	8.7	8.5	3.4	4.1	101.7
112	55.0	0	23.5	6.4	10.4	3.6	3.2	102.1
150	63.0	0	21.4	0	10.4	3.7	3.2	101.7

25°C, 1% consistency, initial ClO_2 concentration 0.237 g/l

Table 2. Development of liquor composition and organic chlorine content during ClO_2 treatment of kraft pulp at 25°C

The results show that the chloride content of the liquor increases rapidly, and that most of the ClO_2 is converted to chloride at the end of the reaction. The chlorite concentration reaches a maximum after about 30 minutes. The formation of chlorate is small, but significant. No measurable amount of chlorine or hypochlorous acid was detected, even though it is known [5] that these chlorine species are formed. The explanation for this apparent discrepancy is that chlorine or hypochlorous acid are immediately consumed in rapid consecutive reactions with chlorite or lignin. The nature of these reactions will be discussed later. The total amount of organic chlorine (the sum of AOX and the organically bound chlorine in the pulp) accounts only for about 7% of the atomic chlorine charged, throughout most of the experiment. The accuracy of the present analyses is supported by the well closed chlorine mass balance at all reaction times. It should be noted that this is the first time that a complete chlorine mass balance has been reported in literature for ClO_2 bleaching of kraft pulp.

In order to establish the influence of temperature, the experiment was repeated at 45°C, a more common level for chlorine dioxide bleaching. The development of the distribution of atomic chlorine for this experiment is given in Table 3.

A comparison of the results in Tables 2 and 3 shows that the chlorine dioxide consumption rate is higher and that the chlorite concentration is always lower at 45°C. Also, the maximum chlorite concentration occurs earlier, and essentially no chlorite is remaining at the end of the experiment performed at 45°C . This suggests that both the rate of conversion of chlorine dioxide in chlorite as well as the rate of consumption of chlorite increase with temperature. The same behaviour has been reported earlier for different types of pulp, such as unbleached kraft pulp [10], prebleached pulp [2] and oxygen delignified kraft pulp [6].

Time (min)	Composition (% of atomic chlorine)							Chlorine Balance
	Cl^-	ClO^-	ClO_2^-	ClO_2	ClO_3^-	AOX	Pulp	
0	0	0	0	100.0	0	0	0	100
1	29.3	0	15.5	41.5	6.0	1.4	3.9	97.6
10	51.3	0	20.0	11.4	10.3	2.6	4.1	99.6
30	56.8	0	15.4	5.8	13.3	2.7	3.6	97.6
60	66.9	0	10.9	0	14.8	3.1	3.6	99.3
112	72.6	0	1.6	0	17.2	3.8	3.2	98.4
150	75.2	0	0.9	0	18.3	4.1	3.2	101.7

45°C, 1% consistency, initial ClO_2 concentration 0.237 g/l

Table 3. Development of liquor composition and organic chlorine content during ClO_2 treatment of kraft pulp at 45°C

Since chloride and chlorate are both unreactive, their concentrations are generally higher at the higher temperature. Thus after two and half hours at 45°C, the active bleaching chemicals, ClO_2 and chlorite, are almost completely converted into chloride (75.2%), chlorate (18.3%) and organic chlorine (7.3%). The formation of about 18% chlorate is in agreement with values reported in literature for pure ClO_2 prebleaching [3,4,11]. The development of all the inorganic chlorine containing species during the course of the bleaching experiment at 45°C is more clearly seen in Figure 1.

The development of the total organic chlorine, measured as AOX in solution and organically bound chlorine in pulp, is almost identical at the two different temperatures. In both cases, the total organic chlorine content reaches the same constant level within the first 10 minutes of reaction. Thereafter, the increase in AOX is compensated by an equivalent decrease in the organically bound chlorine content of the pulp.

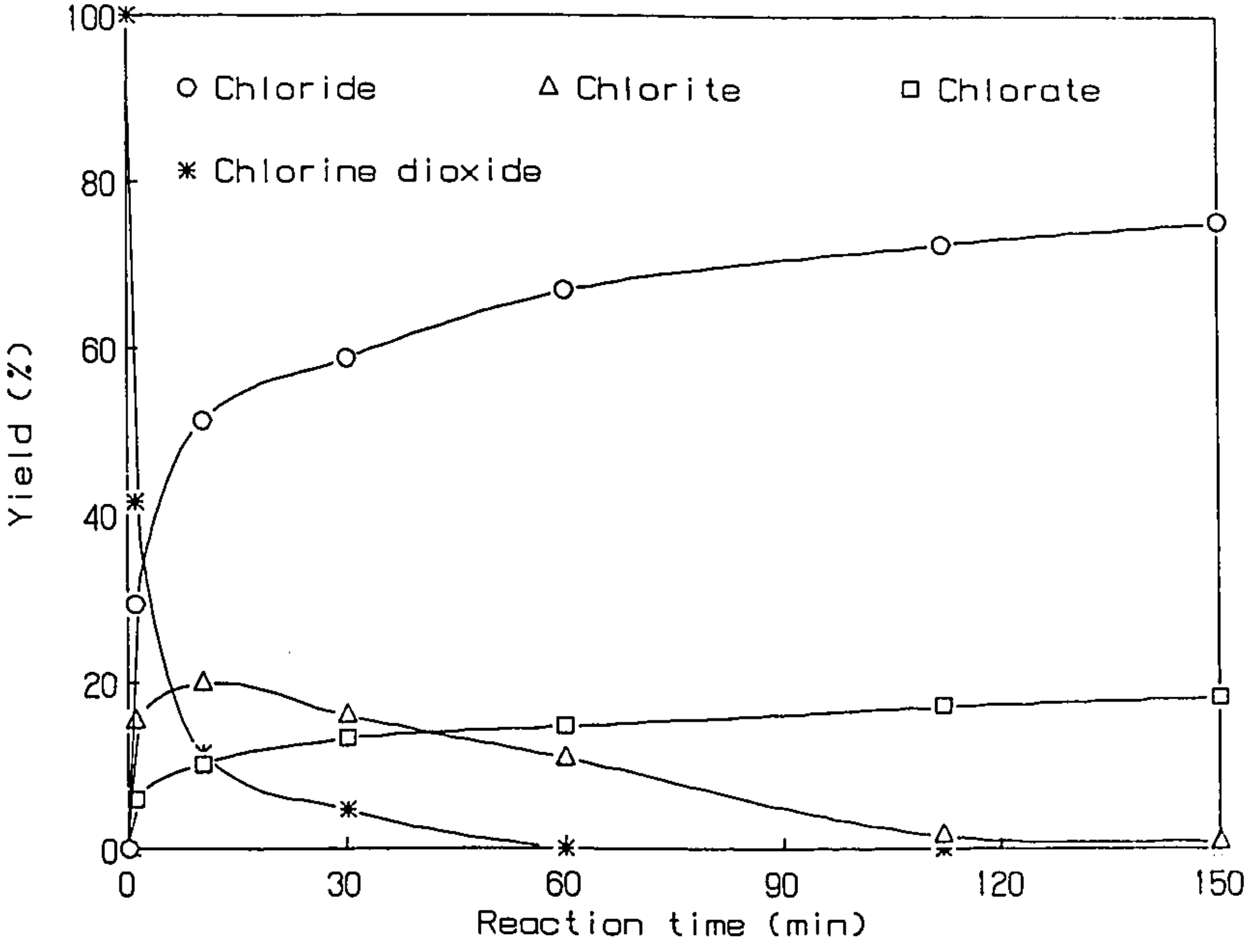

Figure 1. Development of the inorganic chlorine containing species during ClO_2 bleaching of kraft pulp at 45°C

Since chlorite reacts only to a limited extent directly with lignin [5], the most likely explanation for the consumption of chlorite is the following two overall reactions:

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

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

It was reported [12] that the above reactions are very rapid under acidic conditions. Since chlorine is in equilibrium with hypochlorous acid, the amount of chloride and chlorate associated with the regeneration of ClO_2 depends on the reaction conditions. The reaction kinetics proposed in the literature [12] also explain why higher concentrations favor the regeneration of chlorine dioxide, while lower concentrations produce more chlorate. These rapid reactions also explain why never any chlorine or hypochlorous acid was detected.

As mentioned earlier, no chloride was found when fully bleached pulp was treated with chlorine dioxide. Therefore, it is certain that chloride is produced in the reactions involving lignin or products of the reaction between ClO_2 and lignin. Since hypochlorous acid is a reaction intermediate, and it was found [13] that about 85% of chlorine ends up as chloride during chlorine bleaching of kraft pulp, some of the chloride formed during ClO_2 treatment of kraft pulp most likely also originates from the reaction between chlorine and lignin.

ClO_2 treatment of kraft pulp in the presence of sulfamic acid

The complexity of chlorine dioxide bleaching of kraft pulp would be greatly reduced when reactions 2 and 3 are eliminated by effective removal of hypochlorous acid (chlorine) from the reaction system. Kolar et al [5] found that sulfamic acid (H_2NSO_3H) was an effective chlorine scavenger by the reaction:

$$HClO + H_2NSO_3^- \longrightarrow HClNSO_3^- + H_2O \qquad (4)$$

Therefore, it was decided to study the development of the different chlorine containing species during ClO_2 bleaching in the presence of sulfamic acid.

For these experiments the analysis of the chlorine containing inorganic species was modified because sulfamic acid has almost the same retention time as chlorite when analyzed by IC. Therefore, chlorite and $HClNSO_3^-$, the product of reaction 4, were determined by titration, while chloride and chlorate were still analyzed by IC. ClO_2 was not determined. A complete description of the titration procedure is given in Chapter 3.

First, however, a number of experiments were done to verify that sulfamic acid preferentially reacts with Cl_2 or hypochlorous acid and not with ClO_2. The latter was established by adding sulfamic acid to a ClO_2 solution. Based on the total reaction volume the concentrations of chlorine dioxide and sulfamic acid are 0.237 g/l and 10.5 mmol/l, respectively. It can be seen in Table 4 that ClO_2 disappears slowly, with more than 90% remaining after 2.5 hours. Considering that some of the disappearance of ClO_2 is due to the disproportionation reaction 1 (see Table 1), these results show that the reaction between ClO_2 and sulfamic acid is very slow.

Time (min)	ClO_2 conc. (g/l)	ClO_2 remaining (%)
0	0.237	100
9	0.230	97.0
60	0.220	92.8
150	0.214	91.7

45°C, final pH 1.53

Table 4. Disappearance of ClO_2 in the presence of sulfamic acid

In another set of experiments, the prevalence of reaction 4 over 2 or 3 was established by addition of chlorine water to an aqueous mixture of chlorite and sulfamic acid. The experimental conditions were similar to those during the actual ClO_2 treatment of kraft pulp in the presence of sulfamic acid. Thus, the concentrations of chlorite and sulfamic acid were 0.072 g/l (1.07 mmol/l) and 10.5 mmol/l, respectively, based on the total volume after the chlorine water addition. The chlorine concentration based on the total reaction volume was 0.127 g/l (or 1.8 mmol/l). Immediately after mixing, the concentrations of chlorite and the reaction product of the sulfamic acid and chlorine were determined as 0.0694 g/l and 0.124 g/l respectively. These results confirm that the reaction between chlorine and sulfamic acid is much faster than the reaction between chlorine and chlorite. This is further supported by the absence of chlorate formation, which is characteristic of the reaction between chlorine and chlorite, as will be shown later.

In the experiment with kraft pulp, sulfamic acid was thoroughly mixed with the pulp suspension before the addition of ClO_2. The sulfamic acid concentration was 10.5 mmol/l based on the total reaction volume. The development of the chlorine containing species in Table 5 shows that the initial formation of hypochlorous acid is very rapid, but then its formation slows down considerably. At the end of the experiment, 58.4% of the atomic chlorine is captured by sulfamic acid. This is comparable to a value of about 50% measured by Kolar et al [5].

Reaction 4 shows that hypochlorous acid is captured by sulfamic acid. However, chlorine and hypochlorous acid are in equilibrium via the well known reaction:

$$Cl_2 + H_2O \longleftrightarrow HCl + HClO \qquad (5)$$

Time (min)	Composition (% of atomic chlorine)							Chlorine Balance
	Cl^-	HClO	ClO_2^-	ClO_2	ClO_3^-	AOX	Pulp	
0	0	0	0	100.0	0	0	0	100
1	31.9	28.1	24.7	ND	NI	0.9	2.2	87.8
10	26.3	41.5	22.0	ND	NI	1.0	2.1	92.9
30	27.0	51.1	17.5	ND	NI	1.4	1.9	98.9
60	28.3	57.3	11.8	ND	NI	1.6	1.6	100.6
150	30.3	58.4	6.5	ND	NI	2.2	1.5	98.9

NI: IC peak too small to be integrated (<1.6%)
ND: not determined
1% consistency, 45°C, initial ClO_2 conc. 0.237 g/l
sulfamic acid: 10.5 m mol/l

Table 5. Development of liquor composition and organic chlorine content during ClO_2 treatment of kraft pulp in the presence of sulfamic acid

Although it is rather obvious from a mechanistic point of view that hypochlorous acid and not chlorine is formed, this has not been confirmed experimentally. If chlorine is the intermediate, then HCl should be present in at least equimolar amounts with HClO since reaction 5 will completely proceed to the right. However, it is clear from Table 5 that this is not the case. Furthermore, if chlorine was the intermediate, then the reaction with sulfamic acid is

$$Cl_2 + H_2NSO_3^- \longrightarrow HClNSO_3^- + HCl \qquad (6)$$

and the amount of elemental chlorine determined by titration of $HClNSO_3^-$ would be twice as large. This would obviously lead to violation of the chlorine mass balance for the present results.

A very interesting result in Table 5 is that almost no chlorate is formed when sulfamic acid is present. This compares to 18% chlorate formation at the end of the same experiment without addition of sulfamic acid (Table 3). Therefore, the important conclusion can be drawn that chlorate must be predominantly formed by a reaction involving hypochlorous acid. In a recent paper [20], it is shown that reaction 3 is the main reaction responsible for the production of chlorate during ClO_2 bleaching of kraft pulp.

Comparison of Table 3 and Table 5 shows that less chloride is formed when sulfamic acid is present. The difference can be explained by the elimination of reactions 2 and 3 between chlorite and chlorine or hypochlorous acid, respectively. However, with the presence of sulfamic acid, still a rather large fraction of ClO_2 is converted into chloride within the first minute of reaction. Thereafter, the chloride concentration increases only slightly. It was found that no chloride is produced by ClO_2 disproportionation (Table 1) and later it will be shown that the rate of formation of chloride by acid catalyzed decomposition of chlorite is also small. Therefore, the initial chloride formation in Table 5 most likely originates from reactions between chlorine and highly reactive lignin or other pulp components. The rate of these reactions should at least be comparable to that of chlorine and sulfamic acid. Indirect evidence for these reactions is the formation of organic chlorine despite the presence of sulfamic acid. Comparison of Table 5 and 3 shows that the total organic chlorine content is reduced by approximately 50% when sulfamic acid is present. Finally, the fact that the chloride content is the same (approximately 30%) after 1 minute of ClO_2 irrespective of the temperature (Tables 2 and 3) or presence of sulfamic acid (Table 5), is consistent with chloride being formed by an "instantaneous" irreversible reaction.

Chlorine dioxide was the only chlorine containing species which was not determined in the experiment with sulfamic acid present. However, the chlorine mass balance in Table 5 is still closed within about 1% after 60 minutes of reaction. Thus, after this point essentially all ClO_2 must have disappeared. This is in agreement with the expectation that all ClO_2 is consumed at the end of the experiment. Conversely, at short reaction times, the ClO_2 concentration might be calculated from the difference between 100% and the chlorine mass balance. This calculation gives 12.2 and 7.1% ClO_2 after 1 and 10 minutes of reaction, respectively. Comparison of these values with those in Table 3 indicates that ClO_2 disappears significantly faster when sulfamic acid is present. This can be explained by the absence of regeneration of chlorine dioxide from chlorite by reaction with hypochlorous acid as a result of the capture of hypochlorous acid by sulfamic acid.

The results in Table 5 show that after rapid initial formation, the chlorite concentration decreases continuously. This slow decrease cannot be caused by reactions 2 and 3, because it was shown earlier that hypochlorous acid is captured by sulfamic acid. Therefore, these results suggest that chlorite is consumed in another slow reaction, presumably by decomposition in an acid solution.

Acid catalyzed decomposition of chlorite

It was reported [9] that sodium chlorite is decomposed in an acid solution by the following reaction:

$$4\ ClO_2^- + 2\ H^+ \longrightarrow Cl^- + 2\ ClO_2 + ClO_3^- + H_2O \qquad (7)$$

It is known [9] that reaction 7 is strongly pH dependent. Therefore, the decomposition of chlorite was studied at two different pH levels and an initial concentration of 0.24 g/l at 45°C. Technical grade sodium chlorite was used. Its sodium chlorite content was determined by titration as 83.1% by weight. IC analysis showed that chloride was the only other chlorine containing species besides chlorite. The chloride to chlorite molar ratio was 0.207. The initial pH was adjusted by addition of sulfuric acid. The development of the liquor composition at an initial pH of 3.57 and 2.57 are summarized in Tables 6 and 7 respectively, the latter more closely simulating actual ClO_2 bleaching.

Time (min)	Composition (% of atomic chlorine)					Chlorine Balance
	* Cl^-	ClO^-	ClO_2^-	ClO_2	ClO_3^-	
0	0	0	100	0	0	100
1	-0.3	0	97.9	0.2	NI	97.8
10	1.5	0	92.8	4.3	NI	98.6
30	4.8	0	82.4	9.4	NI	96.6
60	6.3	0	76.0	12.7	NI	95.0
112	9.3	0	70.8	14.0	NI	94.1
150	11.3	0	69.4	16.8	NI	97.5

NI: IC peak too small to be integrated (<1.6%)
45°C, Initial chlorite conc. 0.24 g/l, Initial pH 3.57
* corrected for chloride in technical grade sodium chlorite of 20.7% atomic chlorine based on chlorite being 100%

Table 6. Acid catalyzed decomposition of chlorite at pH 3.57

The results in both tables show that chlorine dioxide and chloride are the main products, and that the decomposition rate is faster at lower pH. Some of the deviation of the chlorine mass balance from 100% could be explained by the presence of chlorate, which remains below the detection limit of the IC analysis. Assuming that the acid catalyzed decomposition of chlorite proceeds according to reaction 7, it is quite surprising that only a very small amount of chlorate is formed. However, it was reported [9] that the presence of chloride can alter the reaction stoichiometry. Gordon et al [9] found that at high chloride ion concentrations the chlorite decomposition is better approximated by

$$5\ ClO_2^- + 4\ H^+ \longrightarrow 4\ ClO_2 + Cl^- + 2\ H_2O \qquad (8)$$

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

NI: IC peak too small to be integrated
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%

Table 7. Acid catalyzed decomposition of chlorite at pH 2.57

whereby no chlorate is formed. The presence of chloride in technical grade sodium chlorite may explain why no significant amount of chlorate was formed in the present experiments. The results also suggest that the slow disappearance of chlorite in Table 5 is caused by acid catalyzed decomposition. This is further confirmed by the slow increase in chloride concentration.

It should be noted that in both Table 6 and 7 the valency of chlorine is not balanced, i.e. too much chloride is formed compared to chlorine dioxide. This suggests yet another reaction which reduces chlorite may be involved. For example, the reaction reported [9] to take place to a limited extent during chlorite acid decomposition

$$ClO_2^- \longrightarrow Cl^- + O_2 \qquad (9)$$

may account for the measured imbalance between chloride and chlorine dioxide.

Mechanism of AOX formation during ClO_2 bleaching

The formation of organic chlorine during chlorine dioxide bleaching of kraft pulp presented in the previous tables will be further analyzed in this section. To facilitate comparison, the formation of organic chlorine will be expressed in the more customary units of kg per ton of o.d. pulp.

Shown in Table 8 are the organic chlorine formation previously presented in Table 2, and the kappa number of the ClO_2 treated (but not caustic extracted) pulp. The last column shows the Cl/C_9 molar ratio of the lignin in the pulp. It is calculated assuming that the lignin content is equal to the kappa number times 0.15, and that the molecular weight of a lignin monomer unit is 185 [14]. It shows that the molar ratio of chlorine to lignin monomer unit is constant. This strengthens the previous claim that the total amount of organic chlorine is formed in the initial stages of chlorine dioxide bleaching. It also suggests that the increase in AOX in the bleaching liquor during

Time (min)	Organic chlorine (kg/ton o.d.pulp)			Kappa no.	Cl/C_9 molar ratio
	Pulp	Liquor	Total		
0	0	0	0	28.7	--
1	0.45	0.22	0.67	16.2	0.10
10	0.50	0.34	0.84	15.3	0.11
30	0.45	0.37	0.82	14.4	0.11
60	0.44	0.42	0.86	13.3	0.11
112	0.40	0.44	0.84	12.8	0.11
150	0.39	0.46	0.85	12.4	0.11

1% Consistency, Initial ClO_2: 0.237 g/l, 25°C

Table 8. Organic chlorine formation during ClO_2 treatment of kraft pulp at 25°C

chlorine dioxide treatment is due to increased solubility of organically bound chlorine in the pulp.

The results for the equivalent experiment at 45°C are shown in Table 9. The development of organic chlorine formation is very similar to that at 25°C, except for a small increase in the Cl/C_9 molar ratio as bleaching progresses.

Time (min)	Organic chlorine (kg/ton o.d. pulp)			Kappa no.	Cl/C_9 molar ratio
	Pulp	Liquor	Total		
0	0	0	0	28.7	--
1	0.48	0.17	0.65	15.9	0.10
10	0.50	0.31	0.81	13.9	0.12
30	0.44	0.32	0.76	12.3	0.13
60	0.44	0.36	0.80	10.7	0.14
112	0.43	0.47	0.90	10.6	0.14
150	0.43	0.49	0.92	10.4	0.14

1% Consistency, Initial ClO_2: 0.237 g/l, 45°C

Table 9. Organic chlorine formation during ClO_2 treatment of kraft pulp at 45°C

The organic chlorine formation and kappa number development during ClO_2 bleaching at 45°C in the presence of sulfamic acid are shown in Table 10. The behaviour is very similar to that presented in Tables 8 and 9, except that now the level of organic chlorine is reduced by about 50%. Another difference with Table 9 is that now the Cl/C_9 molar ratio remains constant when sulfamic acid is present. However, since sulfamic acid is supposed to eliminate hypochlorous acid as soon as it is formed, the question arises of how the remaining 50% of organic chlorine is formed. As suggested earlier to explain the initial chloride formation in Table 5, it might be that the reaction rate between lignin and chlorine (or hypochlorous acid) is comparable to that between sulfamic acid and hypochlorous acid. Other possibilities are that $HClNSO_3^-$ still reacts with lignin to form organic chlorine, or that chlorinated organics are produced by addition of hydrochloric acid to compounds containing unsaturated bonds.

Time (min)	Organic chlorine (kg/ton o.d. pulp)			Kappa no.	Cl/C_9 molar ratio
	Pulp	Liquor	Total		
0	0	0	0	28.7	--
1	0.28	0.11	0.39	17.1	0.06
10	0.26	0.13	0.39	15.1	0.06
30	0.24	0.18	0.42	14.9	0.06
60	0.24	0.20	0.44	13.3	0.06
150	0.22	0.26	0.48	12.8	0.06

1% Consistency, Initial ClO_2: 0.237 g/l, 45°C
Sulfamic acid: 10.5 m mol/l

Table 10. Organic chlorine formation during ClO_2 bleaching of kraft pulp in the presence of sulfamic acid

Further experiments were done to investigate these possibilities. The hypothesis of further reaction between $HClNSO_3^-$ and lignin was tested by adding chlorine water to a solution of sulfamic acid. This mixture was then added to a suspension of the unbleached pulp according to the hypochlorous acid (chlorine) formation profile in Table 5. The other conditions were exactly the same as Table 5. The measured organic chlorine content of the filtrate and treated pulp after the 2.5 hours was 0.16 and 0.19 kg/ton o.d. pulp, respectively. The kappa number was slightly reduced from 28.7 to 26.2. After 1 minute of reaction, with an available chlorine charge of only about half of that at 2.5 hours, the AOX in the filtrate and organic chlorine in the pulp was 0.1 kg and 0.11 kg per ton of pulp, respectively. (The unbleached kraft pulp was found to contain 0.07 kg/ton of organic chlorine). Comparison of this data with that in Table 10, shows that approximately 73% of the organic chlorine formed after 2.5 hours of reaction in the presence of sulfamic acid can be explained by further reaction of $HClNSO_3^-$ with organic material in the pulp. The nature of the reaction with $HClNSO_3^-$ is unknown, but it has been reported [23] that $HClNSO_3^-$ reacts with lignin groups such as stilbenes. However, this still leaves about 23% of the total organic chlorine unaccounted for at the end of the experiment in Table 10. It should be noted that these results show that 86% of the total organic chlorine formation in normal chlorine dioxide bleaching (Table 9) is associated with in-situ generated hypochlorous acid.

Muconic acid derivatives and quinones are formed during ClO_2 treatment of lignin model compounds [15,16,17.18]. Presumably, similar products are also generated during ClO_2 bleaching of pulp. Two experiments were done to test whether organic chlorine can be produced from addition of hydrochloric acid to these typical unsaturated structures. In the first experiment muconic acid was dissolved in 6 ml methanol and then diluted with water to 200 ml. Hydrochloric acid was added until a concentration of 0.15 g/l and a pH of 1.36. The muconic acid concentration was 0.21 g/l. After 2½ hours at 45°C, the AOX was determined as 0.83 mg/g of muconic acid. If it is assumed that all the dissolved lignin associated with the kappa number decrease from 28.7 to 10.6 is in the form of muconic acid, then the AOX formation is 0.0163 kg/ton. This is only 4.2% of the total AOX generated during ClO_2 bleaching.

The second experiment was performed with 1,4-quinone in an aqueous hydrochloric acid solution. The concentrations of 1,4-quinone and chloride were 0.16

and 0.15 g/l respectively and the pH was 1.40. After 2½ hours at 45°C, an AOX of 1.04 mg/g quinone was measured. This corresponds to 5.2% of the total AOX formation during chlorine dioxide bleaching, calculated using the same assumptions as above. Therefore, it is likely that the contribution of the addition reaction of hypochlorous acid to the total AOX production is negligible during chlorine dioxide bleaching.

Finally, it is worth noting that other components in pulp besides lignin might contribute to the organic chlorine formation, because it was found that the present black spruce pulp still contained 0.31 kg organic chlorine per ton of pulp or organic chlorine after being fully bleached (CEDED) It was also reported [19] that the organic chlorine content in fully bleached pulp depends on the pulp source.

SUMMARY

The experimental results of chlorine dioxide bleaching of kraft pulp can be summarized by the following reactions of the chlorine containing species. A major part of chlorine dioxide is rapidly converted to chlorite and hypochlorous acid when contacted with unbleached pulp. After the initial fast reaction, hypochlorous acid continues to be formed at a continuously decreasing rate. However, the actual hypochlorous acid (chlorine) concentration in the bleach solution cannot be detected because of immediately further reaction with lignin or chlorite. Organic chlorine and chloride are formed in the former case, while chlorine dioxide is regenerated in the latter with simultaneous formation of chloride and chlorate. Since very little chlorate is formed when hypochlorous acid is captured by sulfamic acid at otherwise practical ClO_2 bleaching conditions, it is suggested that the chlorine dioxide regeneration reaction between chlorite and hypochlorous acid is mainly responsible for the chlorate formation. After the initial bleaching stage, excess chlorite also slowly decomposes in chloride and chlorine dioxide.

The total amount of organic chlorine, defined as the sum of AOX in the bleach liquor and organically bound chlorine in the pulp, is formed in the first ten minutes of chlorine dioxide bleaching. This finding, as well as the rapid initial formation of chloride, suggests that all organic chlorine is formed by extremely fast reactions during chlorine dioxide bleaching. The increase in AOX content of the solution during further bleaching can be explained by dissolution of the initially formed organic chlorine in the pulp. Approximately 86% of the total organic chlorine formation was shown to be associated with in-situ generated hypochlorous acid. Therefore, it is likely that most of the organic chlorine produced during chlorine dioxide bleaching of kraft pulp is formed by reaction between lignin and hypochlorous acid.

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CHAPTER 5

MECHANISM OF CHLORATE FORMATION DURING BLEACHING OF KRAFT PULP WITH CHLORINE DIOXIDE

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 reactions between chlorite and hypochlorous acid or chlorine. 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. Some of the variables discussed are: pH in the D prebleaching and D_1 stage, the chloride concentration, the delay time between the addition of chlorine and chlorine dioxide in a DC sequence, the order of addition of chlorine and chlorine dioxide, the unbleached kappa number, and pulp consistency. Since chlorate formation is undesirable from both an economical and environmental point of view, it is outlined in principle how chlorate formation can be minimized in practical operations.

INTRODUCTION

During pulp bleaching, part of chlorine dioxide is converted to 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 area 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.

A number of 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 function of process variables such as pH, chloride concentration, charging sequency and timing of chlorine and chlorine 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 differs 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 tank reactor (CSTR). 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 Chapter 3.

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 2½ hours at 45°C about one fifth of chlorine dioxide is converted to 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. More likely chlorate is the reaction product of different inorganic species 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

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

(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 or chlorine

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

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 that used for the unbleached pulp shown in Figure 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 1.

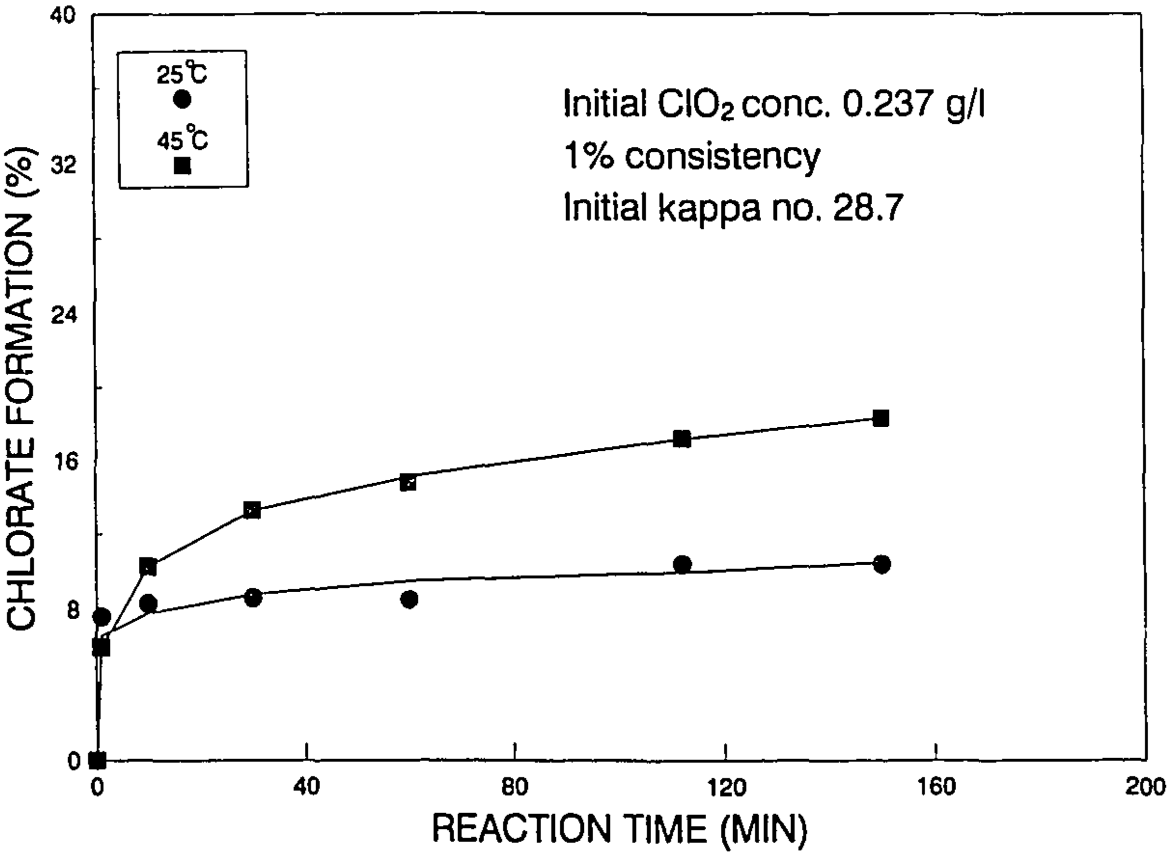

Figure 1. Comparison of chlorate formation during ClO_2 treatment of kraft pulp at 25 and 45°C

Time (Min)	Composition (% of atomic chlorine)		
	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 minutes: 3.6

Table 1. Chlorate formation during ClO_2 treatment of fully bleached pulp.

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 than that of the 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 chloride to chlorite molar ratio of 0.207. The initial pH of 2.57 was obtained by addition of sulfuric acid. The development chloride, hypochlorous acid, chlorite, chlorine dioxide and chlorate, as determined by IC analysis, is summarized in Table 2.

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 mass chlorine balance (last column in Table 2), these 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.

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

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

NI: IC peak too small to be integrated
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%.

Table 2. Chlorate formation by acid catalyzed decomposition of chlorite

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 2 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 chlorite acidic decomposition:

$$ClO_2^- \longrightarrow Cl^- + O_2 \qquad (6)$$

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 in situ generated HOCl. This can be achieved by the addition of sulfamic 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 sulfamic 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 experiment further supports that chlorate formation by ClO_2 disproportionation and acid decomposition of chlorite is negligible since these two reactions are not affected by the capture of hypochlorous acid. The final pH with and without sulfamic acid addition of the experiments in Figure 2 are 2.3 and 3.6 respectively.

Reaction Mechanism

It was found by Taube and Dodgen [16] that the stoichiometry of the reaction between chlorite and hypochlorous acid (or chlorine 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:

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

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

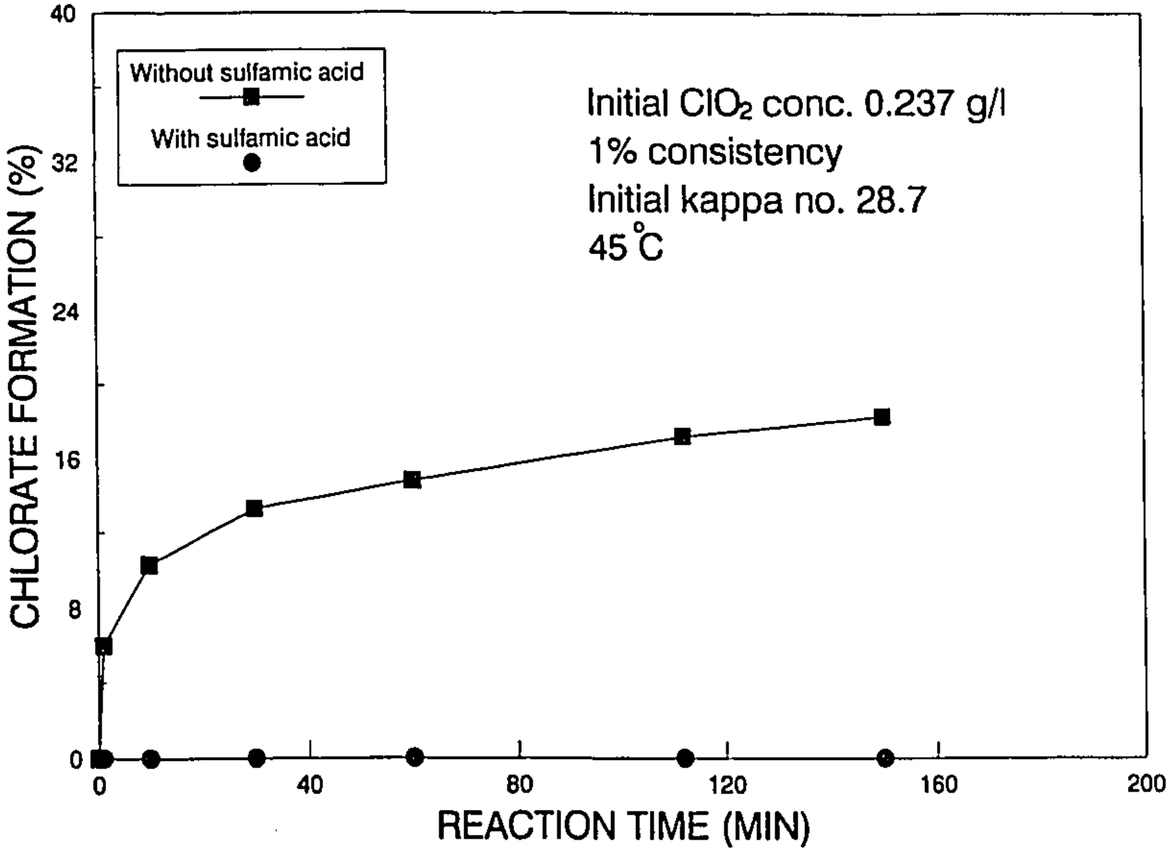

Figure 2. Development of chlorate formation during ClO_2 treatment of kraft pulp with or without the presence of sulfamic acid

$$[Cl{-}Cl{-}Cl <^{O}_{O}]^{-} \xrightarrow{k_3} [Cl{-}Cl <^{O}_{O}] + Cl^{-} \qquad (9)$$

$$[HO{-}Cl{-}Cl <^{O}_{O}]^{-} \xrightarrow{k_4} [Cl{-}Cl <^{O}_{O}] + OH^{-} \qquad (10)$$

$$2\ [Cl{-}Cl <^{O}_{O}] \xrightarrow{k_5} Cl_2 + 2\ ClO_2 \qquad (11)$$

$$[Cl{-}Cl <^{O}_{O}] + H_2O \xrightarrow{k_6} Cl^{-} + ClO_3^{-} + 2H^{+} \qquad (12)$$

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 $[Cl_2O_2]$ favors 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 $[Cl_2O_2]$ favoring the formation of chlorine dioxide (reaction 11) over chlorate (reaction 12). In other words, in the mechanism given by reactions (7) to (12), chlorine favors 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 3, 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:

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

With the equilibrium constant, K,

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

the chlorine/hypochlorous acid molar ratio can be written as

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

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

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

Table 3. Effect of pH on chlorate formation during ClO_2/Cl_2 prebleaching [19]

In earlier studies [3,6,20], it was reported that the amount of chlorate formed in the 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 a 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 to chlorate and chlorine dioxide. Therefore, a fair comparison of chlorate formation can only be made 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 present chlorate formation mechanism 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 in-situ formed hypochlorous acid 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 to 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 4, 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 favors the regeneration of ClO_2 rather than chlorate formation.

Initial chloride Concentration	Chlorate formation (as % of Cl_2 on pulp)		
	4% cons.	8% cons.	12% cons.
5g/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 hours, initial pH adjusted to 2 with H_2SO_4

Table 4. Effect of chloride addition on chlorate formation during ClO_2 bleaching [18].

Rapson and Anderson [21] found that the chlorate formation in D_1 and D_2 stages was only slightly decreased by an increased chloride ion concentration. The difference with 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 to 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 chlorite acidic decomposition reaction 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 5, show that the chlorate formation is reduced by a factor 2 when the delay time is extended from 10 to 120 seconds.

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

Experimental conditions: Same as Table 3

Table 5. Effect of delay time between addition of Cl_2 and ClO_2 on the chlorate formation in a DC sequence

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 chlorite acid catalyzed 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 4). This finding can be explained by the kinetics of the reaction mechanism represented by equations 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 favored 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.

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 favored. In practice this is done by recycling the acidic filtrate. An additional advantage of recycling of 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 minimized 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 minutes 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 favor 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 sulfamic 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 sulfamic acid addition should be about 60% of the molar ClO_2 charge. Another advantage of the sulfamic 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 [14]. However, only an economical and environmental analysis can establish whether the addition of sulfamic acid is practical.

CONCLUSIONS

Chlorate is mainly formed 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 sulfamic acid is added to the pulp suspension before ClO_2 addition.

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CHAPTER 6

THE CHARACTERISTICS OF PULP DEMETHYLATION DURING CHLORINE DIOXIDE BLEACHING

ABSTRACT

The methoxyl loss from softwood kraft pulp during chlorine dioxide treatment can be accounted for by methanol and the methoxyl content of dissolved organic material in the bleach filtrate. This was established by a methoxyl group mass balance made at different bleaching times. It was found the ClO_2 rather than the in-situ generated hypochlorous acid is mainly responsible for the methanol formation. It was shown that contrary to the bleaching behaviour with chlorine, demethylation by ClO_2 is restricted to free phenolic structures in lignin. Furthermore, the rates of formation of methanol and methoxyl group containing dissolved organic material are proportional to each other. The in-situ generated hypochlorous acid creates free phenolic groups in lignin which can be attacked by chlorine dioxide. The experimental evidence suggest that demethylation and delignification are closely related during ClO_2 treatment of softwood kraft pulp.

Keywords: demethylation, chlorine dioxide bleaching, delignification, phenolic group content, mechanism.

INTRODUCTION

The aromatic methoxyl group is an important functional group in the lignin structure. For example, it was stated [1] that the lignin content of wood and pulp can be quantified indirectly by determination of the methoxyl group content. The removal of methoxyl groups from lignin usually results in the formation of methanol. Ni et al [2] established that the amount of methanol released from kraft pulp after treatment with chlorine can be used to determine its lignin content. In a recently developed chlorination mechanism [3], it was shown that demethylation and delignification are closely related, and that all removed methoxyl groups can be accounted for by the amount of methanol produced. Since methanol can easily be measured by gas chromatographic analysis [2], it might be possible that the delignification process during chlorine dioxide bleaching of kraft pulp can also be characterized by the amount of methanol produced.

Only a few studies have been published which deal with demethylation of lignin or lignin model compounds by chlorine dioxide. Purves and co-workers [4,5] found that chlorine dioxide treatment of isolated black spruce lignin results in the formation of products having a lower methoxyl content than the raw material. It has been found [6] that the methoxyl group content of residual lignin after chlorine or chlorine dioxide bleaching is significantly lower than that of unbleached kraft lignin. Dence et al [7] showed that methanol was formed when lignin model compounds and wood meals were treated with chlorine dioxide. However, no information is available on the development of demethylation during ClO_2 treatment of kraft pulp, and whether demethylation and delignification are linked.

The objective of the present study is to quantitatively examine the development of the demethylation process and to establish its relationship with delignification during ClO_2 treatment of softwood kraft pulp.

RESULTS AND DISCUSSION

Methoxyl Mass Balance

A 28.7 kappa number unbleached kraft pulp was mixed at 25°C with chlorine dioxide at a consistency of 1% and an initial ClO_2 concentration of 0.237 g/l. These conditions represent an equivalent chlorine charge (or kappa) factor of 0.22. The filtrate was separated from the bleached pulp suspension and analyzed for methanol (see details in Experimental section). The methoxyl content of the chlorine dioxide treated pulp and the methanol concentration in the filtrate are listed in columns 2 and 3 of Table 1, respectively. The fourth column is the methanol concentration expressed as methoxyl group content based on pulp. The last column in the table is the percentage of the

Time (min)	OCH_3 in the pulp (%) *	Methanol conc. (ppm)	Methanol as OCH_3 (%)*	OCH_3 balance (%)
0	0.58	0	0	
1	0.45	6.8	0.066	89.0
10	0.38	13.9	0.135	88.8
30	0.34	16.3	0.157	85.7
60	0.32	16.9	0.164	83.4
112	0.31	17.6	0.171	82.9
150	0.28	18.9	0.183	79.8

Initial ClO_2: 0.237 g/l, Initial kappa no: 28.7, 1% consistency, 25°C

* % on oven dried pulp

Table 1. Methoxyl group mass balance during ClO_2 treatment.

methoxyl group content of the unbleached kraft pulp represented by the sum of columns 2 and 4. It shows that the methoxyl group mass balance during chlorine dioxide is always less than 100% and that the mass balance worsens as the reaction continues. Therefore, it seems likely that the dissolved lignin fragments still contain methoxyl groups.

The methoxyl group content of the dissolved lignin fragments was determined by the following method. The dissolved organic material in the chlorine dioxide filtrate was absorbed on two columns in series, each packed with granular activated carbon (GAC). The GAC with absorbed material was then analyzed for methoxyl group content according to TAPPI standard T209. Separate analysis of fresh GAC showed that it does not contain any methoxyl groups. It was also confirmed that methanol, a small and polar molecule, is not adsorbed by GAC. For further details of the determination of the methoxyl group content in spent chlorine dioxide bleach liquor, see the Experimental section at the end of this chapter.

A new methoxyl group mass balance including the methoxyl group content of the dissolved organic material in the filtrate is shown in Table 2. The fifth column in Table 2 shows that the dissolved organic material in the filtrate contained a significant amount of methoxyl groups and that this amount increases as the reaction progresses. As a result, the methoxyl mass balance shown in the last column of Table 2 improves considerably. This indicates that almost all the methoxyl groups removed from pulp during chlorine dioxide bleaching end up either as methanol or are still part of the dissolved lignin fragments in the filtrate.

Dence et al [7] found that methanol can be formed as a result of direct and/or indirect cleavage of methoxyl groups during ClO_2 treatment of lignin model compounds

Time (min)	OCH_3 in pulp (%)*	Methanol (ppm)	Methanol as OCH_3 (%)*	OCH_3 in filtrate (%)*	OCH_3 balance (%)
0	0.58	0	0	0	
1	0.45	7.1	0.069	0.042	96.7
10	0.38	13.6	0.132	0.051	97.1
30	0.34	16.5	0.160	0.057	96.0
60	0.32	16.7	0.162	0.073	95.7
112	0.31	17.4	0.169	0.078	96.0
150	0.28	18.5	0.179	0.088	94.3

Conditions the same as in Table 1.

* % on oven dried pulp

Table 2. Methoxyl group mass balance during ClO_2 treatment.

and wood meals. They used the term indirect cleavage to describe those situations where methanol is formed by hydrolysis in boiling water of intermediate reaction products such as muconic acid monomethyl ester or methoxy-*p*-benzoquinone. Direct cleavage was used to represent the reaction whereby methanol is liberated prior to rupture of the aromatic nucleus. Dence et al [7] showed that a good approximation of the methanol produced by direct cleavage can be obtained by distilling the reaction product mixtures at room temperature under reduced pressure, and measuring the amount of methanol in the distillate. The low temperature stability of muconic acid monomethyl ester and methoxy-*p*-benzoquinone intermediate towards hydrolysis was verified by applying this technique to a solution of ß-formyl muconic acid monomethyl ester and 5-chloro-2-methoxy-*p*-benzoquinone. They determined the sum of methanol obtained from direct and indirect cleavage by heat-distilling the reaction mixtures under neutral conditions at atmospheric pressure.

The concept of direct and indirect cleavage of methoxyl group as proposed by Dence et al [7] is most applicable to the present results. In Table 2, the fourth column (methanol as OCH_3) represents the amount of methoxyl groups removed by direct demethylation, while the fifth column (OCH_3 in filtrate) quantifies indirect demethylation. Thus the percentage of methoxyl groups removed by direct and indirect demethylation after two and one half hours of ClO_2 treatment are 30.9 and 15.2% respectively. This compares to 33% and 6% direct and indirect demethylation respectively after 2 hours treatment of a suspension of Norway spruce wood meal at an initial ClO_2/OCH_3 molar ratio of 3.0 as determined by Dence et al [7] with their technique. Dence et al [7] did not study the demethylation of kraft pulp.

It has been found [8,9] that about 60% of chlorine dioxide is converted into hypochlorous acid during the course of kraft pulp bleaching. The reason that hypochlorous acid is normally not detected during chlorine dioxide bleaching is because it is rapidly consumed in consecutive reactions. It is also known that extensive demethylation occurs during pure chlorine treatment of kraft pulp. Therefore, it might be that the in-situ generated hypochlorous acid is responsible for demethylation during chlorine dioxide bleaching as was suggested earlier by Dence et al [7].

In order to determine whether demethylation is caused by ClO_2 or in-situ generated hypochlorous acid, the experiment described in Table 2 was repeated with the addition of sulfamic acid to the pulp suspension prior to ClO_2 treatment. Sulfamic acid effectively removes hypochlorous acid [8] by the reaction:

$$H_2NSO_3^- + HClO \longrightarrow HClNSO_3^- + H_2O \qquad (1)$$

The sulfamic acid charge was in excess of that of ClO_2 by a 3 to 1 molar ratio. The development of the residual methoxyl content in the treated pulp, methanol in the filtrate and methoxyl group containing dissolved organic material in the filtrate are summarized in columns 2,3 and 5 of Table 3 respectively. As in Table 2, the last column in Table 3 shows that with these three quantities a closed methoxyl group mass balance is obtained. The significant amount of methanol and methoxyl group containing dissolved organic material in Table 3 shows that even with the removal of hypochlorous acid the direct and indirect demethylation reactions still proceed. Therefore, the conclusion is that ClO_2 directly participates in the demethylation reactions. More specifically, comparison of the methanol formation in Tables 2 and 3 reveals that ClO_2 is mainly responsible for the direct demethylation reaction.

Time (min)	OCH_3 in pulp (%)*	Methanol (ppm)	Methanol as OCH_3 (%)*	OCH_3 in filtrate (%)*	OCH_3 balance (%)
0	0.58	0	0	0	
1	0.452	8.1	0.079	0.046	99.5
10	0.405	13.5	0.130	0.070	104.3
30	0.367	14.1	0.136	0.078	100.2
60	0.333	15.4	0.149	0.084	97.6
150	0.322	16.2	0.157	0.091	98.3

Sulfamic acid 10.5 mM, 45°C, Initial ClO_2 conc. 0.237 g/l
1% consistency, initial kappa number 28.7

* % on o.d. dry pulp

Table 3. Methoxyl group mass balance during ClO_2 treatment in the presence of sulfamic acid.

The methoxy group removal by direct demethylation during ClO_2 treatment is plotted versus that removed by indirect demethylation (columns 4 and 5 in Table 3, respectively) in Figure 1. The data obtained in the presence of sulfamic acid can be correlated by a straight line which almost goes through the origin. This suggests that direct and indirect demethylation proceed in parallel reactions when chlorine dioxide is the only effective delignification reagent. From the slope of the straight line, it follows that the ratio of the rate of direct to indirect demethylation is 1.75.

Compared to the results with sulfamic acid, the data in Figure 1 obtained without sulfamic acid show that in the latter case indirect demethylation is generally smaller. This behaviour is in agreement with the finding (3) that the degree of indirect and direct demethylation is respectively insignificant and extensive when kraft pulp is treated with chlorine. Thus the data in Figure 1 suggests that the formation of hypochlorous acid during ClO_2 bleaching leads to increased direct demethylation at the expense of indirect demethylation.

Fully Methylated Pulp is Stable Towards ClO_2

The development of methanol production during ClO_2 treatment of kraft pulp in the presence of sulfamic acid is more clearly seen in Figure 2. The methanol production is initially very fast and most of the methanol is formed within the first 10 minutes. After 2.5 hours, about 30% of the methoxyl groups of the unbleached pulp are converted to methanol. This is small compared to about 80% conversion after standard treatment of the same type of pulp with chlorine [10]. The difference in the demethylation behaviour of chlorine and chlorine dioxide might be related to the fact that chlorine can react with both free phenolic and etherified lignin units, while chlorine dioxide is said

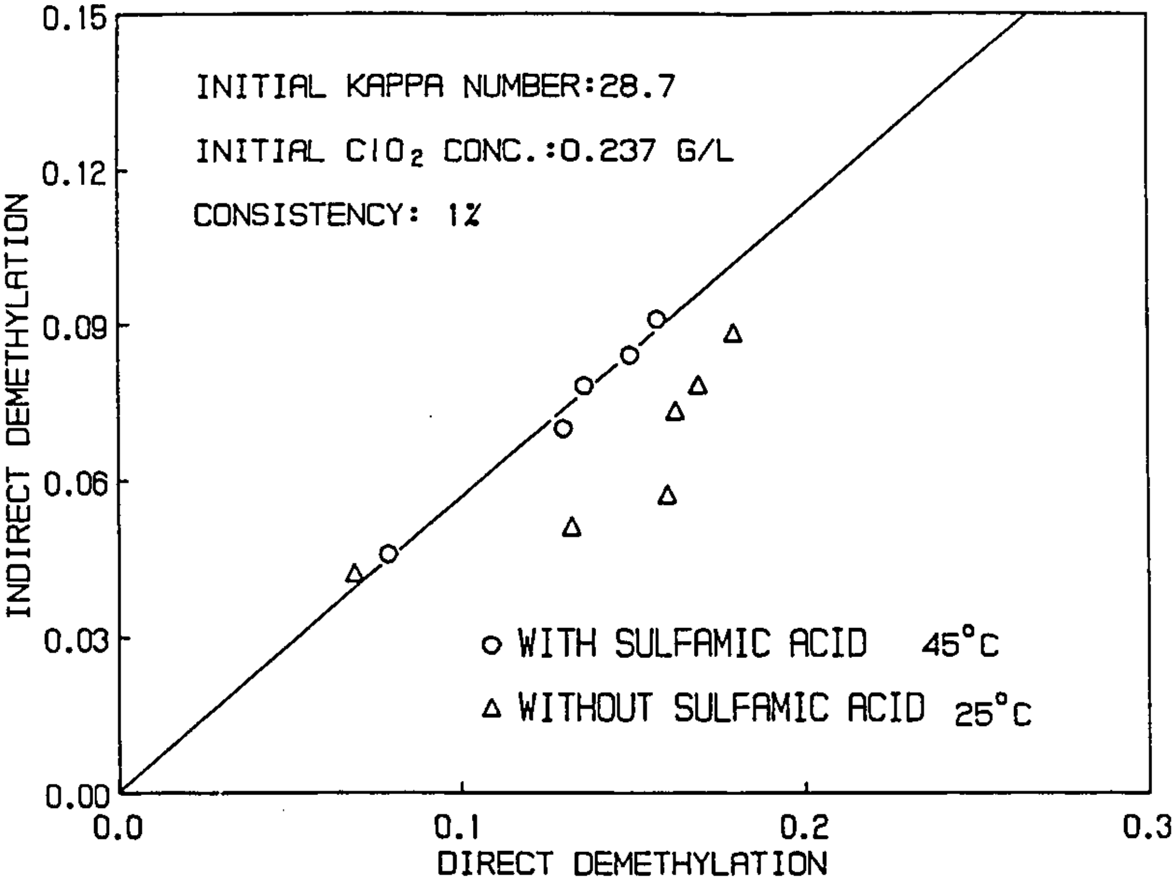

Figure 1. Relationship between direct and indirect demethylation during ClO_2 bleaching.

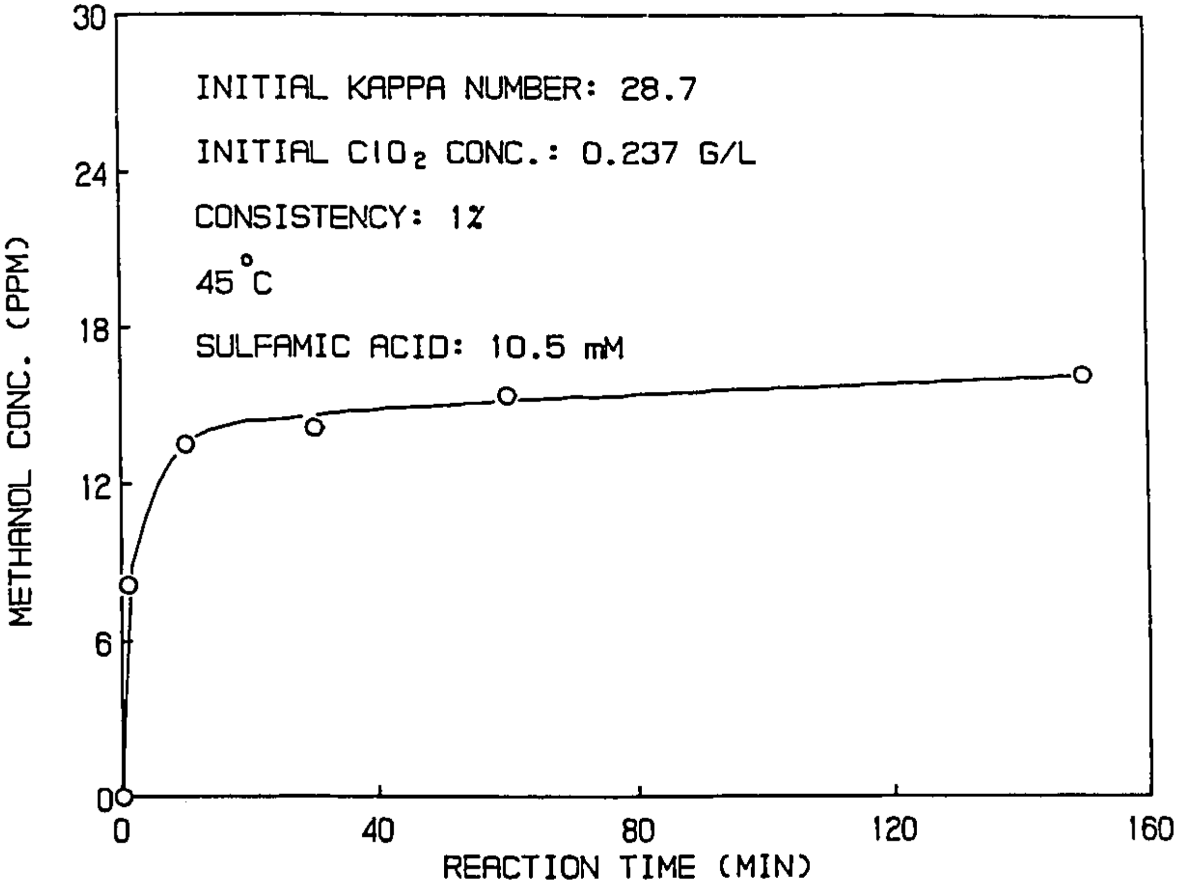

Figure 2. Development of methanol concentration during ClO_2 bleaching.

to be limited to free phenolic units only. As early as 1955 it was reported by Purves and co-workers [11] that etherified lignin model compounds are only slightly attacked by chlorine dioxide. An interesting paper by Germgard [12] showed that delignification by ClO_2 of methylated softwood kraft pulp was slower and much smaller than that of unmethylated pulp. However, since the methylated pulp was still significantly delignified, one cannot conclude that chlorine dioxide is only reactive towards lignin units with free phenolic hydroxyl groups.

In order to clarify this point, fully methylated pulp was prepared by repeatedly treating the unbleached kraft pulp with dimethyl sulfate. Subsequent treatment of the methylated pulp (kappa number 17.5) with a ClO_2 charge of 4.02% at 45°C for 45 minutes gave a methanol production equivalent to only 2.6% of the methoxyl content of the fully methylated pulp (0.03% on pulp). The kappa number after ClO_2 treatment was 15.5. Sulfamic acid was mixed with the methylated pulp suspension prior to addition of chlorine dioxide in order to eliminate possible demethylation by reaction intermediate hypochlorous acid. Therefore, it can be concluded that only lignin which possesses free phenolic groups can be demethylated by ClO_2.

Development of Free Phenolic Group Content of Lignin During ClO_2 Bleaching

Since it appears that only free phenolic lignin structures can be demethylated by ClO_2, it is of interest to study the development of the free phenolic group content of kraft pulp during ClO_2 treatment. The free phenolic hydroxyl content in pulp was determined by the periodate oxidation method. This method is based on the fact that a methoxyl group ortho to a free phenolic hydroxyl group is removed as methanol by the action of periodate, while aliphatic methoxyl groups are stable towards periodate (for detailed procedure see Experimental section at the end of the chapter). The method was tested on guaiacol and veratrol. Guaiacol gave a methanol formation of 93.2% of the theoretical value, while only 4.3% of the methoxyl groups in veratrol were converted to methanol. This confirms that the periodate oxidation method is fairly specific for the detection of methoxyl groups adjacent to free phenolic hydroxyl group.

The development of the phenolic hydroxyl content of kraft pulp during ClO_2 treatment in the presence of sulfamic acid is shown in Table 4. It shows that the percentage of methoxyl groups which are ortho to a phenolic hydroxyl group decreases immediately when chlorine dioxide is charged and that the percentage remains at about 5% after 10 minutes of reaction.

Time	Total OCH_3 in pulp	OCH_3 converted by $NaIO_4$	Phenolic OCH_3
(min)	(%)*	(%)*	(%)
0	0.58	0.205	35.3
1	0.452	0.0347	7.7
10	0.405	0.0216	5.3
30	0.367	0.0183	5.0
60	0.333	0.0171	5.1
150	0.322	0.0156	4.8

The same conditions as in Table 3
* % on oven dry pulp

Table 4. The development of the content of methoxyl groups ortho to a phenolic hydroxyl group during treatment of kraft pulp in the presence of sulfamic acid.

This suggests that the reaction between ClO_2 and free phenolic guaiacol lignin units is very fast. Considering that more than 56% of all the methoxyl groups of the unbleached kraft pulp are still present after 2.5 hours ClO_2 treatment, these results also confirm that ClO_2 is not reactive towards non phenolic lignin structures.

Table 4 also shows that in the unbleached kraft pulp about 35% of the methoxyl groups are ortho to a free phenolic hydroxyl group. It will be shown later that the molar ratio of OCH_3/lignin phenylpropane unit of the unbleached kraft pulp is 0.82. Therefore, the phenolic hydroxyl content of kraft lignin at about 48% pulp yield is about 0.29 per C_9 lignin monomer unit. This compares very favourably with a frequency of 0.27 phenolic hydroxyl groups per lignin monomer unit obtained recently by Gellerstedt and Lindfors [13] using the aminolysis method on a similar kraft pulp. This good agreement further supports the accuracy of the periodate oxidation method.

The same experiment was repeated but now without the presence of sulfamic acid. The results are shown in Table 5. Comparison of Table 5 with Table 4 shows that although the percentage of phenolic methoxyl groups also decreases very fast initially, it remains at a higher level of about 8% when hypochlorous acid is not captured. This

Time (min)	Total OCH_3 in pulp (%)*	OCH_3 converted by $NaIO_4$ (%)*	Phenolic OCH_3 (%)
0	0.58	0.205	35.3
1	0.45	0.0364	8.1
10	0.38	0.0296	7.8
30	0.34	0.0270	8.2
60	0.32	0.0255	8.0
112	0.31	0.0250	8.1
150	0.28	0.0239	8.5

The same conditions as in Table 1.

* % on oven dry pulp

Table 5. The development of the content of methoxyl groups ortho to a phenolic hydroxyl group during ClO_2 treatment of kraft pulp without sulfamic acid addition.

is in agreement with the concept whereby hypochlorous acid reacts with non phenolic lignin units and creates new free phenolic hydroxyl groups so that delignification by ClO_2 can continue. The increased delignification after 2.5 hours ClO_2 treatment is apparent from the decrease in total methoxyl group content of 0.322% to 0.28% respectively with or without hypochlorous acid capture. This relatively small decrease is to be expected when compared to the capture of about 60% of ClO_2 as hypochlorous acid [9], which is equivalent to a chlorine charge factor of 0.025, or 12% of a normal chlorine charge.

The creation of free phenolic hydroxyl groups by hypochlorous acid during ClO_2 bleaching could also explain the surprising result of Gianola and Meybeck [14] that chlorine dioxide reacts with etherified phenolics, while acid chlorite does not. In the former case, the generated hypochlorous acid creates the phenolic hydroxyl groups which ClO_2 can attack, while in the latter hypochlorous acid reacts preferentially with chlorite rather than the etherified phenolics. An extreme example of the useful effect of in-situ generated hypochlorous acid as demonstrated by Rapson et al [15] who found that all lignin could be removed from kraft pulp in a single bleaching stage when applying a large amount of chlorine dioxide for a very long time. ClO_2 was shown to be the only bleaching chemical which has this capacity. The reason that pure chlorine cannot delignify kraft pulp in one bleaching step even though non phenolic lignin structures are also attacked by chlorine is that extensive aromatic substitution of chlorine leads to the formation of stable "blocking groups" which prohibit further delignification [3].

The above results can help to explain why substitution of chlorine by chlorine dioxide can achieve more delignification than chlorine or chlorine dioxide alone and why the DC mode of addition is always favourable compared with the CD or C+D sequence at the same active chlorine charge. We have shown earlier [3] that delignification by chlorine during pulp chlorination can be described by two competing reactions: demethylation and aromatic substitution of the lignin monomer units. Chlorine aromatic substitution progressively retards delignification until fully chlorinated structures are formed and the so called "floor level" lignin content is reached. It was also established that "the floor level" lignin content is proportional to the initial lignin content. This suggests that the maximum degree of delignification can be increased if the lignin content of the pulp is lower when chlorine is charged.

In the DC mode, by charging ClO_2 first, the available free phenolic lignin is rapidly consumed and the final degree of delignification depends on the charge of ClO_2 and the reaction time. When chlorine is subsequently charged, the lignin content of the pulp is much lower. Since chlorine can attack both etherified and free phenolic lignin and the remaining lignin consumes less chlorine in substitution reactions, relatively more chlorine is available for delignification. Therefore, the applied chlorine is used more efficiently and the remaining lignin content will be lower. As the ClO_2 substitution ratio increases, the phenolic lignin will all be consumed, so that the excess ClO_2 can only react with newly formed free phenolic lignin generated by reaction intermediate hypochlorous acid. At very high ClO_2 substitution ratios, the chlorine supplied in a DC sequence is so small that its contribution to delignification becomes minimal. This explains why there exists an optimum ClO_2 substitution ratio for a DC sequence. In the CD mode, by charging chlorine first, the free phenolic content of lignin will be relatively low compared to that in the unbleached kraft pulp at the time when ClO_2 is charged. As a result the supplied ClO_2 is not as completely and efficiently used for delignification as when ClO_2 was added first to the unbleached kraft pulp.

Relationship Between Demethylation and Delignification

The relationship between demethylation and delignification during ClO_2 treatment in the presence of sulfamic acid was examined. Figure 3 shows the development of the methanol concentration in the filtrate and kappa number of the ClO_2 treated pulps. The observation can be made that the development of the methanol concentration is a mirror image of that of the kappa number, suggesting that direct demethylation is proportional to lignin removal. Since the direct and indirect demethylation rates are proportional to each other during ClO_2 treatment with sulfamic acid present, this suggests also that the methoxyl group loss is proportional to the lignin removal. In order to check this out, the pulp samples were analyzed for Klason and UV lignin content. These results, as well as the methoxyl content and kappa number of the bleached pulps are shown in Table. 6.

Time (min)	OCH_3 in pulp (%)*	Lignin content (%)*			Kappa	Lignin/Kappa (%)*	OCH_3/C_9 molar ratio **
		Klason	UV	Total			
0	0.58	3.82	0.42	4.24	28.7	0.148	0.82
1	0.452	2.24	0.89	3.13	17.1	0.183	0.86
10	0.405	1.89	0.81	2.70	15.1	0.179	0.89
30	0.367	1.63	0.82	2.45	13.9	0.176	0.89
60	0.333	1.57	0.84	2.41	13.3	0.181	0.82
150	0.322	1.43	0.85	2.28	12.8	0.178	0.84

The same conditions as in Table 3
* % on oven dry pulp
** Molecular weight of C_9 unit of 185 (16)

Table 6. Development of lignin and methoxyl content of ClO_2 treated pulp in the presence of sulfamic acid.

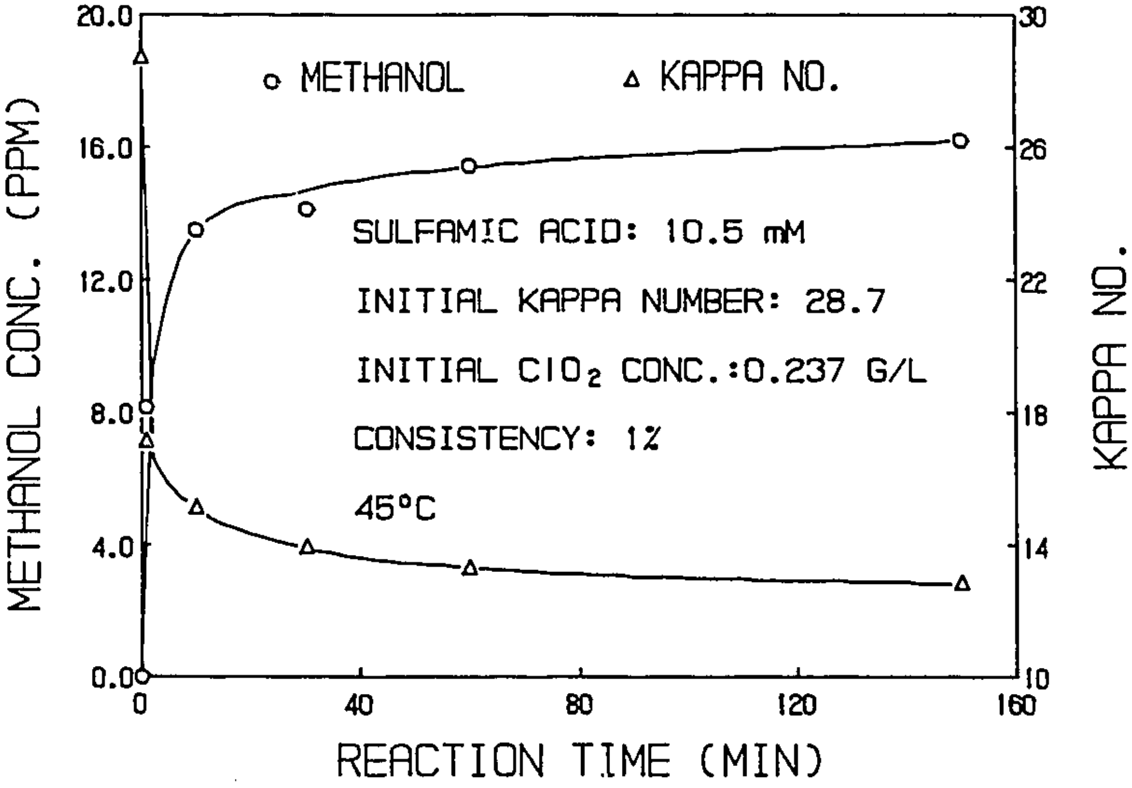

Figure 3. Demethylation and delignification during ClO_2 bleaching.

Column 7 in Table 6 shows that the ratio of lignin content to kappa number is different for chlorine dioxide treated pulp and unbleached kraft pulp, respectively 0.18 to 0.148. The present ratio of lignin content to kappa number for the unbleached pulp of 0.148 is very close to the generally accepted ratio of 0.15 for softwood kraft pulp. The increased ratio for ClO_2 treated pulp is not unexpected since the kappa number is a measure of the oxidation power of the pulp and chlorine dioxide is a strong oxidizing agent.

The methoxyl content of chlorine dioxide treated pulp (column 2) is plotted against the total lignin content (column 5) in Figure 4. A straight line fit through all the data points, including that of the unbleached kraft pulp, almost passes through the origin. Thus the methoxyl group removal is proportional to the lignin removal and the proportionality constant is equal to the OCH_3/C_9 molar ratio in the pulp. The latter is confirmed by the constant OCH_3/C_9 molar ratio of about 0.85 shown in the last column of Table 6. These results suggest that demethylation and delignification are closely related. Since it was shown earlier that the rates of direct and indirect demethylation are proportional to each other, it also means that both contribute to the overall delignification. In other words, when demethylation of the residual lignin takes place, it will be followed by delignification, while delignification will not always be followed by demethylation, since some of the dissolved material still contain methoxyl groups.

CONCLUDING REMARKS

A closed methoxyl group mass balance was obtained during the course of ClO_2 bleaching when the methoxyl content of unbleached kraft pulp was compared with the methanol and methoxyl group containing organic material in the filtrate. The formation of methanol is called direct demethylation, while formation of the methoxyl group containing dissolved organic material is called indirect demethylation. Chlorine dioxide

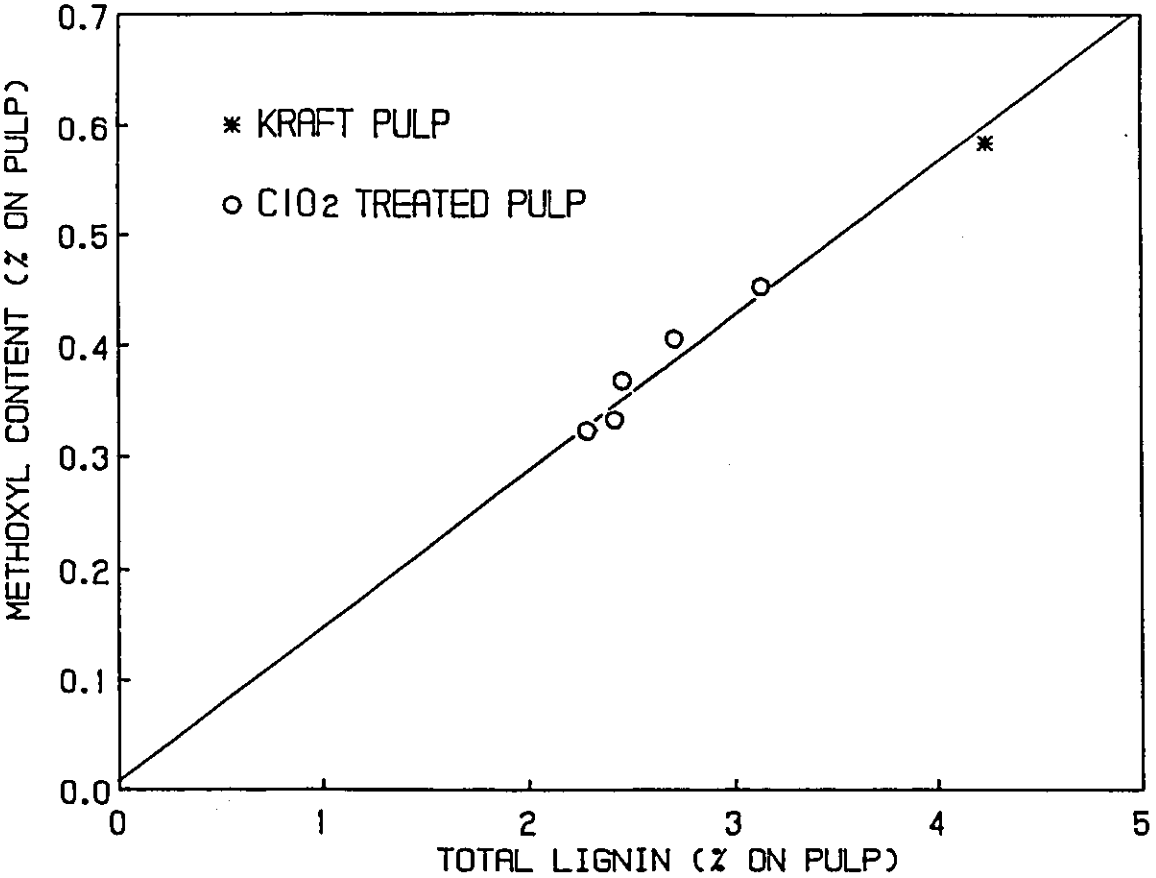

Figure 4. Relationship between methoxyl group and lignin content during ClO_2 bleaching.

rather than the in-situ generated hypochlorous acid is mainly responsible for the demethylation of kraft lignin. Contrary to chlorine which can demethylate both phenolic and non phenolic lignin, demethylation by ClO_2 is strictly limited to lignin units possessing phenolic hydroxyl groups. The number of free phenolic methoxyl groups per 100 lignin monomer units decreases during ClO_2 treatment with sulfamic acid present from about 29 for unbleached kraft lignin to about 7 units after 1 minute treatment and 4 units after 2.5 hours bleaching. The reaction intermediate hypochlorous acid creates phenolic groups and, as a result, further delignification [illegible] be achieved by applying more chlorine dioxide and by extending the reaction time. The methoxyl group removal rates by direct and indirect demethylation are proportional to each other, both resulting in delignification. The constant OCH_3 content of the residual lignin during ClO_2 treatment of softwood kraft pulp suggests that demethylation and delignification are closely related.

EXPERIMENTAL

A 28.7 kappa number black spruce pulp was used. The ClO_2 experiments were performed in a 3-neck round bottom flask. A chlorine dioxide solution was added to 4 grams of pulp, which was well dispersed in deionized water by mechanical stirring. A high ClO_2 concentration was used, so that the addition of the ClO_2 solution could be completed in about 5 seconds. The final pulp consistency was 1% and the kappa factor was 0.22.

The methoxyl content was determined according to Tappi standard T209. The methoxyl group content of the organic dissolved material was determined by passing 25 to 50 ml filtrate through two columns packed with approximately 40 mg granular activated carbon (GAC) each. The GAC with the absorbed material was then analyzed for its methoxyl content following Tappi standard T209. A separate analysis of fresh

GAC showed that it was free of methoxyl groups. Methanol is not absorbed by GAC, since the methanol concentration of a 63 ppm standard solution was unchanged when 2 ml was passed through the two columns in series.

The free phenolic hydroxyl content in unbleached and chlorine dioxide treated kraft pulp was determined according to the periodate oxidation method. Its principle is based on the fact that a methoxyl group ortho to a free phenolic hydroxyl group is removed as methanol by the action of periodate, while aliphatic methoxyl groups and etherified aromatic methoxyl groups are stable towards periodate. Adler and Hernestan [17] measured the liberated methanol by distillation, further purification and subsequent colorimetric analysis after reaction with chromotropic acid. Owing to the large number of steps involved in the analysis, losses of methanol are difficult to avoid. In a later study, Gierer et al [18] used gas chromatography to determine the released methanol. They also used glacial acetic acid in order to dissolve the lignin sample. The drawbacks of this method are that part of the methanol is esterified by acetic acid and that acetic acid is rather difficult to remove from the GC column used for methanol analysis. Carbohydrates, by far the main component in kraft pulp, are also oxidized by periodate. Therefore, a large excess of periodate must be used to assure complete liberation of methanol. The present experimental procedure is as follows: 0.46 g of sodium meta-periodate ($NaIO_4$) and 1 ml of 4N sulfuric acid were mixed, followed by addition of 2.8 ml of water. The sodium meta-periodate solution was cooled to 4°C before 0.2 g o.d. pulp was charged. The reaction mixture was maintained at 4°C in a refrigerator for 3 days. The pulp suspension was shaken occasionally during the period. Next, the filtrate was separated from the pulp, and the excess amount of periodate was eliminated by addition of sodium thiosulfate. The liquor sample was subsequently analyzed for methanol by GC.

The methanol concentration in the bleach filtrate was measured by GC (for details see ref. 2). The Kappa number and lignin content were determined according to CPPA standard G18 and G9 respectively. The UV lignin content was measured by the chemical analysis group of Paprican.

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CHAPTER 7

DELIGNIFICATION DURING CHLORINE DIOXIDE BLEACHING OF KRAFT PULP

ABSTRACT

The delignification of kraft pulp by ClO_2 is studied under conditions whereby one of the inorganic reaction intermediates, hypochlorous acid, is effectively captured. Under these conditions ClO_2 is the only delignification chemical. It is found that about 2 moles of hypochlorous are formed per mole of lignin monomer removed, and that about one mole of chlorite is initially formed per mole of lignin monomer ultimately removed. A modified ClO_2 delignification mechanism consisting of five consecutive reactions is proposed based on these results and other experimental evidence showing that: 1) only phenolic hydroxyl lignin structures are reactive towards chlorine dioxide at practical bleaching conditions, 2) ClO_2 reacts with phenoxy ion structures rather than with the undissociated phenolic groups in lignin, 3) demethylation and delignification are closely linked, and 4) the formation rates of methyl esters and methanol are proportional to each other.

INTRODUCTION

Progress towards the understanding of delignification during chlorine dioxide treatment of kraft pulp was mostly obtained through studies with lignin model compounds [1,2,3,4]. These studies focused primarily on product isolation and identification. The known products are muconic acid monomethyl ester and chlorinated 2-methoxy-*p*-quinone derivatives, accounting for only 30% of the substrate consumed. Part of the substrate was chlorine substituted [10], and believed to be formed by reaction with hypochlorous acid, a reaction intermediate generated during chlorine dioxide treatment. Most recently, our group found by capturing hypochlorous acid immediately following its formation, that the reaction of chlorine dioxide with lignin model compound vanillyl alcohol can be fully described by three parallel reactions: demethylation, formation of 2-methoxy-*p*-quinone and formation of lactone ester [20].

Experimental confirmation of the results obtained from lignin model compounds for actual ClO_2 treatment of kraft pulp is very difficult because of the complexity of the reaction system. Of the numerous publications on ClO_2 bleaching only a few have tried to establish the delignification mechanism based on measurements with actual pulp. In view of the increasing replacement of chlorine by chlorine dioxide in the first stage of an industrial kraft pulp bleaching sequence, it is of interest to understand the fundamental chemical transformations which result in delignification as a result of the chlorine dioxide treatment.

The present research approach is to follow the reaction of chlorine dioxide with pulp by quantitative determination of key reaction intermediates, products and lignin functional groups. A reaction mechanism is proposed based on the quantitative relationships between delignification and the formation of reaction intermediates and products on the knowledge generated in the previous chapters and on the lignin compound studies in literature.

RESULTS AND DISCUSSION

Unbleached kraft pulp (kappa no. of 28.7) at a consistency of 1% was subjected to chlorine dioxide at an initial concentration of 0.237 g/l or an equivalent chlorine charge factor of 0.22. The kappa number development at both 25°C and 45°C are displayed in Figure 1. It shows that the delignification is characterized by a very fast initial phase and a slow second phase, and that the delignification is more extensive at higher temperatures. The latter can be mostly attributed to the fact that chlorine dioxide and its reaction intermediate chlorite are fully consumed at 45°C, while a substantial amount of chlorite (~15% of the supplied ClO_2) remains after 150 minutes reaction at 25°C.

In Chapter 4, it was shown that 58% of the atomic chlorine supplied as ClO_2 is converted to hypochlorous acid after 150 minutes of reaction. Therefore, the delignification achieved in Figure 1 is the net effect of both chlorine dioxide and in-situ generated hypochlorous acid. In order to eliminate the contribution of hypochlorous acid towards delignification, the experiment at 45°C, shown in Figure 1, was repeated in the presence of 10.5 m mole/l sulfamic acid to capture all in-situ generated hypochlorous acid (5). Sulfamic acid was mixed with the pulp suspension prior to addition of ClO_2. The kappa number development with or without the presence of sulfamic acid are compared in Figure 2. It can be seen that the presence of sulfamic acid reduces the extent of delignification. The difference between the two curves can be thought to represent the contribution of hypochlorous acid towards delignification. The relatively

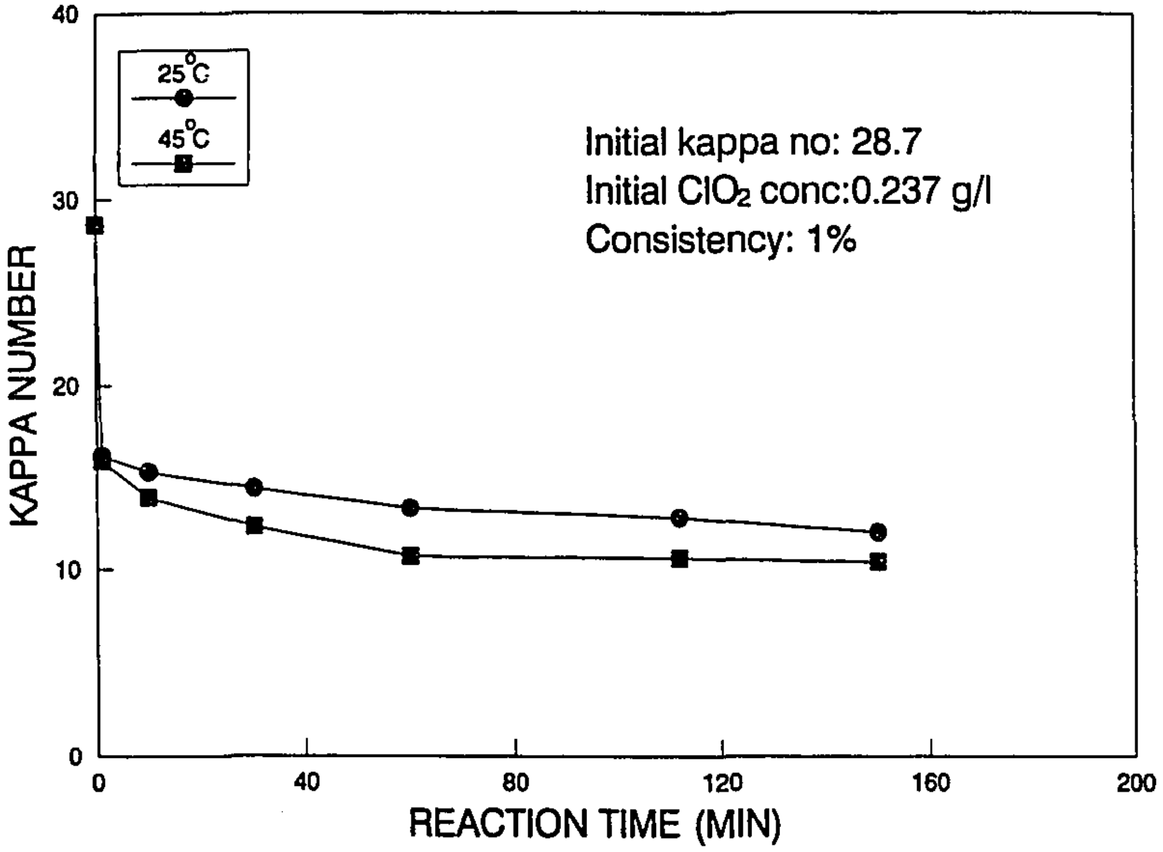


Figure 1. Comparison of kappa number development at 25°C and 45°C

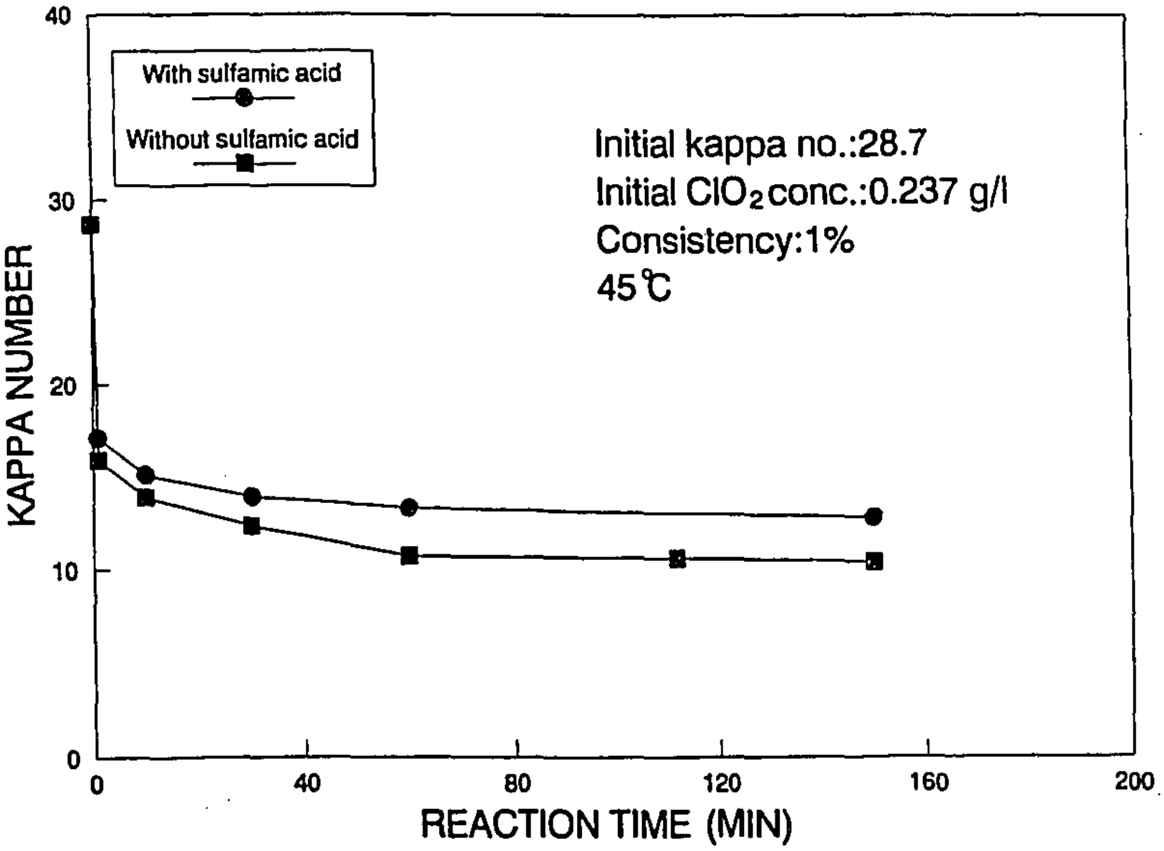


Figure 2. Comparison of kappa number development with and without the presence of sulfamic acid.

small magnitude of this contribution can be understood when it is realized that 58% of the chlorine dioxide charged as hypochlorous acid only represents 11% of a standard chlorine charge factor of 0.22.

It was suggested previously [5] that the reaction product of hypochlorous acid and sulfamic acid might still attack some highly reactive lignin. In order to evaluate the influence of this reaction product on delignification, an experiment was performed whereby the development of the HOCl-sulfamic acid reaction product (N-chlorosulfamic acid) during ClO_2 bleaching was simulated. This was done by adding at certain time intervals the appropriate amount of a mixture of chlorine and sulfamic acid to the pulp suspension. The results in Figure 3 show that the delignification caused by the reaction product of N-chlorosulfamic acid amounts to less than two kappa no. units after two and half hours. Included in Figure 3 is also one data point obtained after addition of only sulfamic acid to the pulp suspension. Comparison of this data point with the delignification achieved by the action of N-chlorosulfamic acid shows that the latter delignification is mostly the result of the acid treatment. Therefore, in the following discussion, the delignification due to chlorine dioxide is corrected for the decrease in lignin content due to the action of N-chlorosulfamic acid shown in Figure 3.

Reactive Lignin During Chlorine Dioxide Bleaching

It was found [13] that chlorine reacts both with phenolic and non-phenolic lignin structures. On the other hand, Logen et al [7] showed that non-phenolic lignin model compounds are only slightly attacked by chlorine dioxide. Germgard [8] showed that delignification is strongly reduced if softwood kraft pulp is partially methylated. However, the delignification achieved with the methylated pulp was still significant. Thus, in order to establish whether chlorine dioxide can only attack lignin structures with

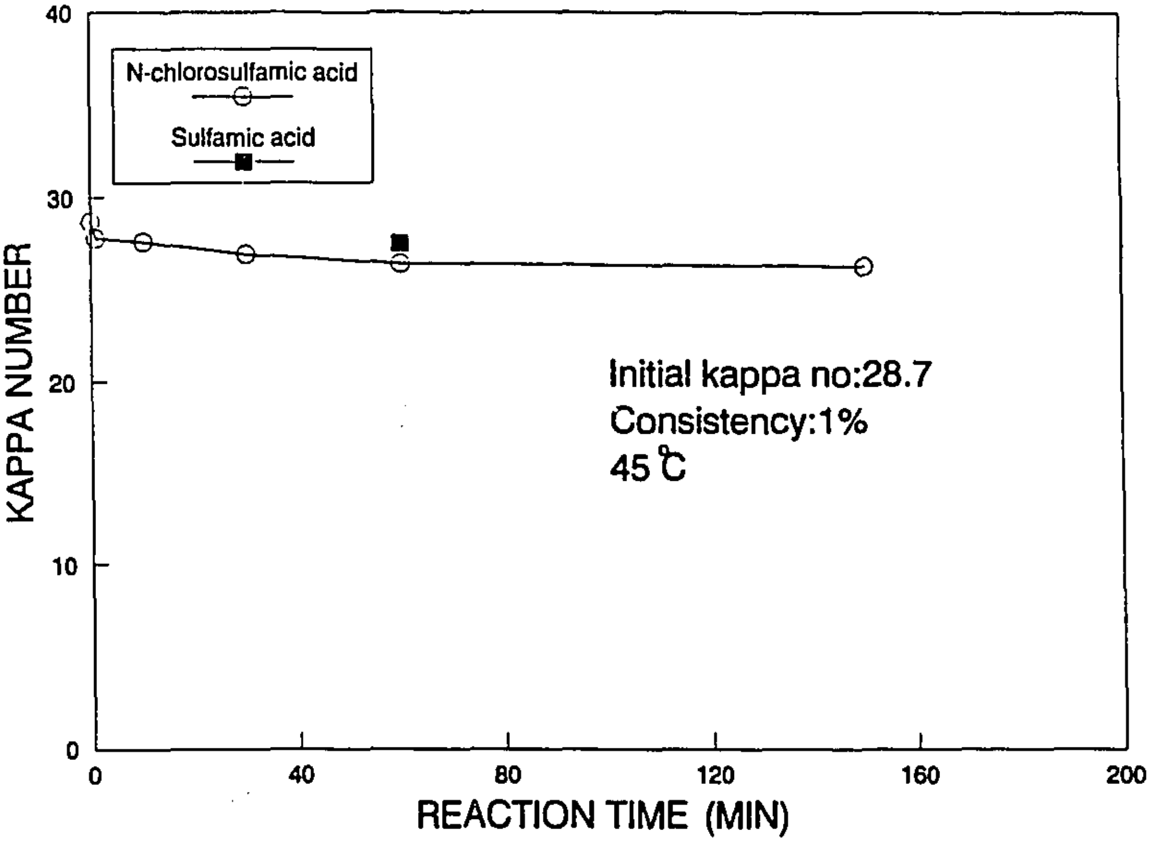


Figure 3. Delignification by N-chlorosulfamic acid or sulfamic acid.

phenolic hydroxyl groups, some experiments were performed with fully methylated pulp.

20 o.d. g of the kraft pulp was methylated at about 1.2% consistency by dropwise adding about 0.5 ml/min dimethyl sulfate under vigorous stirring. 30% (w/w) NaOH was added whenever the pH fell to approximately 8. The methylation which was performed at room temperature under a nitrogen atmosphere was found to proceed very slowly. After addition of 50 ml of dimethyl sulfate, the pulp slurry was thoroughly washed. This procedure was repeated several times, and the development of the methoxyl content of the pulp with increasing charge of dimethyl sulfate is shown in Figure 4. It can be seen that the methoxyl content of the pulp finally levels off and stabilizes after a total charge of about 300 ml of dimethyl sulfate. The final methoxyl content of 1.14%, after 350 ml of dimethyl sulfate, is almost double that of the unmethylated kraft pulp (0.58%). In Chapter 6, it was found that about 35% of the lignin monomer units in unbleached kraft pulp are phenolic in nature. Since the increase in methoxyl content is more than that corresponding to the methylation of the free phenolic groups, this result confirms that dimethyl sulfate reacts with both phenolic and aliphatic hydroxyl groups in lignin [9].

The fully methylated kraft pulp was then subjected to two chlorine dioxide charges of 2.01% and 4.02% respectively, the other conditions being: consistency of 1.5%, 45°C, 45 minutes and sulfamic acid concentration of 10.5 mM. The kappa number of the unbleached, methylated and the two ClO_2 treated methylated pulps are 28.7, 17.5, 15.4 and 15.5 respectively. The methanol concentration of 4.2 ppm measured by GC in both chlorine dioxide treated effluents corresponds to demethylation of only 2.6% of the methoxyl groups of the fully methylated pulp. No organic chlorine was detected in either effluents or pulps. Therefore, it can be concluded that the reaction

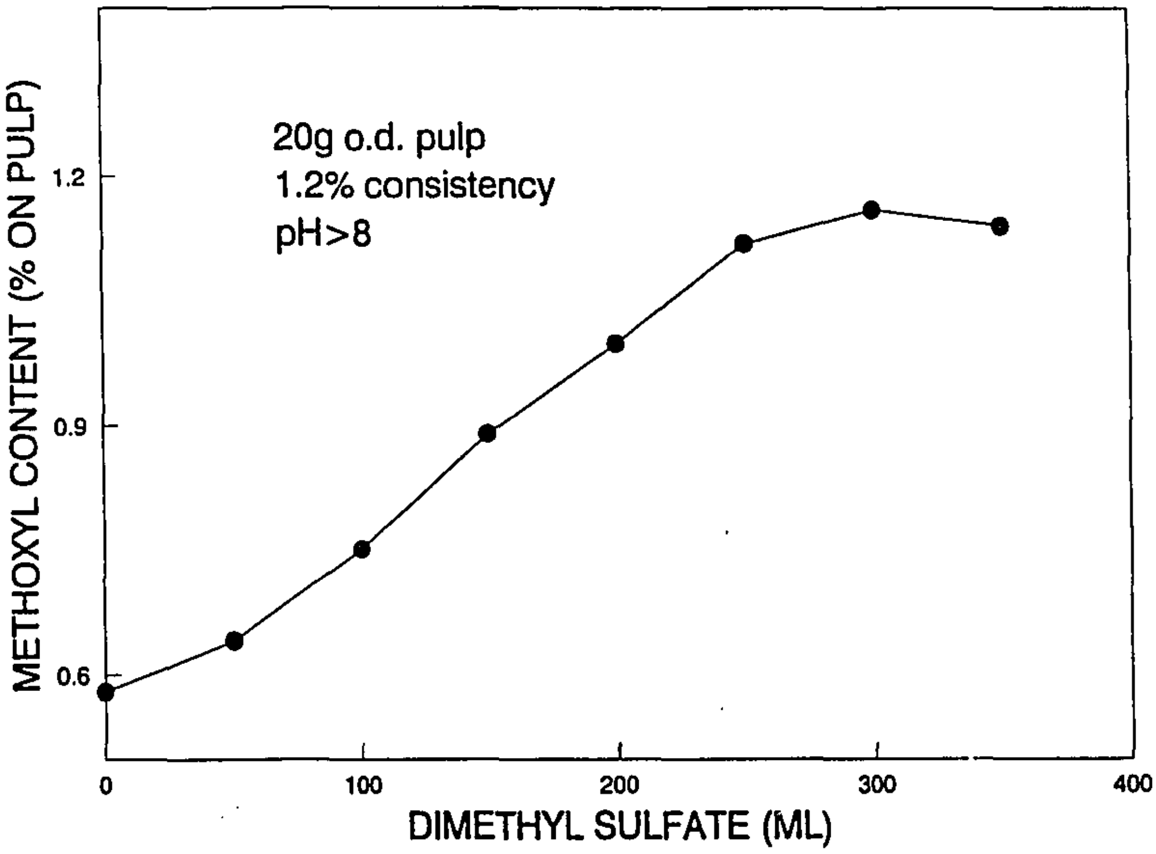


Figure 4. Development of the methoxyl content of kraft pulp during methylation with dimethyl sulfate.

between chlorine dioxide and non-phenolic lignin can be neglected under the conditions whereby the reaction intermediate, hypochlorous acid, is effectively removed.

Relationship Between Delignification and the Formation of Chlorite and Hypochlorous Acid.

It was found [5] that chlorite and hypochlorous acid are two reaction intermediates formed during chlorine dioxide treatment of pulp. In order to quantitatively describe the reaction pattern of delignification it is of interest to determine the relationship between the formation of these reaction intermediates and delignification.

The development of the chlorine containing species and the pulp UV + klason lignin content during ClO_2 bleaching in the presence of sulfamic acid are shown in Table 1.

Time (min)	Composition (% of atomic chlorine)						Chlorine Balance	Kappa No.	Lignin (%)
	Cl^-	HClO	ClO_2^-	ClO_2	ClO_3^-	Org-Cl			
0	0	0	0	100.0	0	0	100	28.7	4.24
1	31.9	28.1	24.7	ND	NI	0.9	87.8	17.1	3.13
10	26.3	41.5	22.0	ND	NI	1.0	92.9	15.1	2.70
30	27.0	51.1	17.5	ND	NI	1.4	98.9	14.9	2.45
60	28.3	57.3	11.8	ND	NI	1.6	100.6	13.3	2.41
150	30.3	58.4	6.5	ND	NI	2.2	98.9	12.8	2.28

NI: IC peak too small to be integrated
ND: not determined
1% consistency, 45°C, initial ClO_2 conc: 0.237 g/l, sulfamic acid: 10.5 m mole/l

Table 1. Development of liquor composition and pulp lignin content during ClO_2 treatment in the presence of sulfamic acid.

The fourth column shows that after an initial very fast formation, chlorite is gradually consumed. This pattern is in agreement with the knowledge obtained from lignin model compounds that chlorine dioxide is reduced to chlorite in the first reaction step [3,4]. Since the chlorite formation is so rapid, it will be assumed that all chlorite is formed immediately after contacting the pulp with ClO_2. Thus by extrapolating the chlorite content in Table 1 to zero time an instantaneous chlorite formation of 25% is obtained.

Following the mechanism proposed by Kolar et al [23] and Gierer [21], it will now be assumed that only those lignin monomer units which are initially attacked by ClO_2 under formation of chlorite can potentially be removed by ClO_2. If the lignin which can potentially be removed by ClO_2 is approximated by the difference between the unbleached lignin content and that remaining after 150 minutes of reaction (respectively 4.24 and 2.28%, Table 1), minus the lignin removed by the action of N-chlorosulfamic acid, a value of 1.68% lignin removed is calculated. Thus the molar ratio of lignin monomer units potentially removable by ClO_2 and initially formed chlorite becomes 1.03 if one assumes that the molecular weight of lignin monomer unit is 185 [6]. This suggests that for each mole of lignin monomer unit finally removed by the action of chlorine dioxide 1 mole of chlorite was formed initially.

The relationship between the formation of hypochlorous acid and delignification calculated as the difference between the unbleached lignin content and residual lignin content at different times is shown in Figure 5. The data points are reasonably represented by a straight line which almost goes through the origin, suggesting that there is unique stoichiometric relationship between delignification and hypochlorous acid formation. The same data is also listed in Table 2, except that the lignin removed (in column 3) is corrected for the small amount removed as a result of the action of N-chlorosulfamic acid.

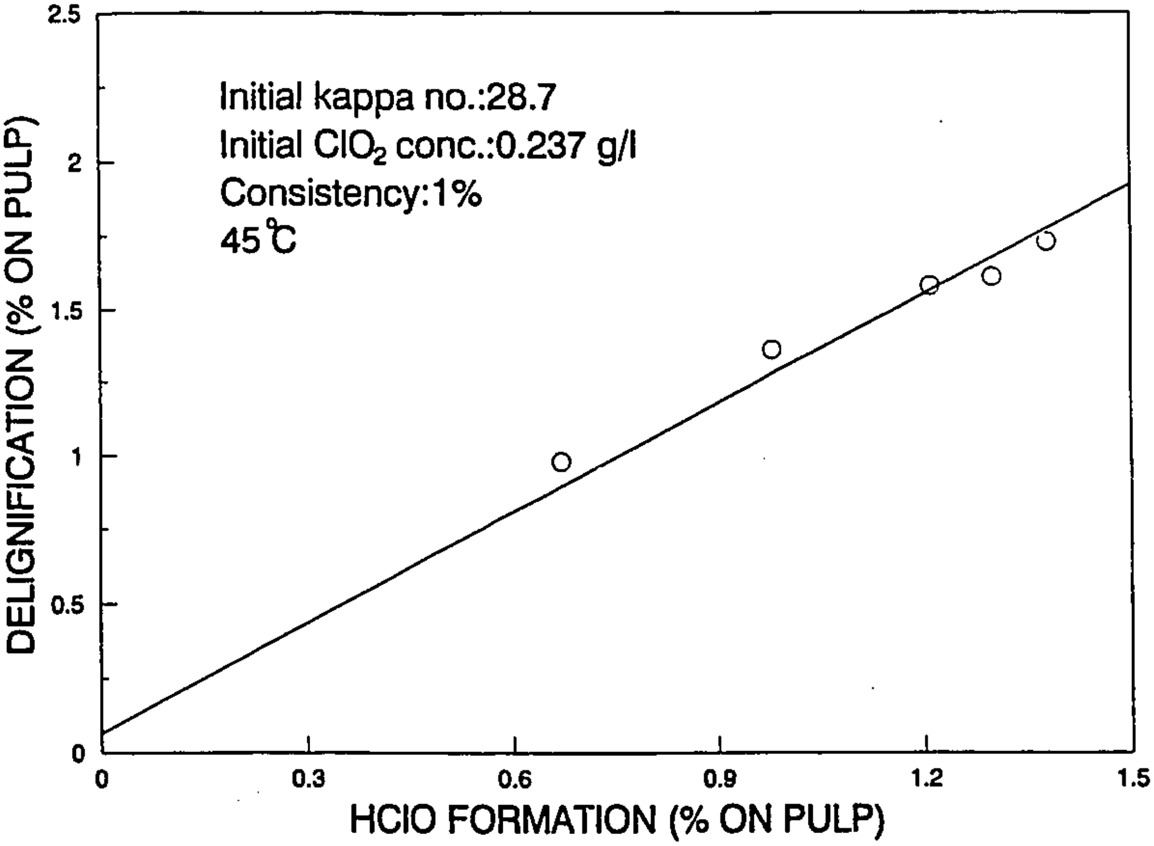


Figure 5. Relationship between hypochlorous acid formation and delignification during ClO_2 bleaching in the presence of sulfamic acid.

Time (min)	HClO (as ClO_2 % on pulp)	Lignin Removed * (% on pulp)	Lignin Removed * / HClO Formed molar ratio
0	0	0	-
1	0.67	0.98	0.53
10	0.98	1.36	0.50
30	1.21	1.58	0.48
60	1.36	1.61	0.43
150	1.38	1.73	0.46

Sulfamic acid 10.5 mM, 45°C, Initial ClO_2 conc. 0.237 g/l 1% consistency, Initial kappa number 28.7

* Corrected for lignin removed by the action of N-chlorosulfamic acid

Table 2. Relationship between hypochlorous acid formation and delignification during ClO_2 bleaching in the presence of sulfamic acid

The last column in Table 2 shows the molar ratio of lignin monomer (molecular weight 185) removed (due to ClO_2) to hypochlorous acid formed at the different times. Since all these values are close to about 0.5, these calculations suggest that approximately 2 moles of hypochlorous acid are formed per lignin monomer unit removed.

Effect of Lignin Content of Unbleached Pulp

In order to evaluate the influence of the lignin content of unbleached pulp on these two stoichiometric relationships, another kraft black spruce pulp of kappa number 39.9 was treated at 1% consistency and 45°C with ClO_2 charge of 2.93% corresponding to an active chlorine charge factor of 0.193. Sulfamic acid was added prior to the addition of chlorine dioxide at a concentration of 13.0 mmole/l.

Shown in Table 3 is the development of the chlorite content, the residual lignin content (determined as klason and UV lignin) and the HClO content expressed as % ClO_2 on pulp.

Time (min)	Chlorite (% on pulp)	Lignin Content (% on pulp)	Lignin removed* (% on pulp)	HClO (as ClO_2 % on pulp)	Lignin removed / HClO Formed Molar Ratio
0	0	6.06	0	0	-
1	0.744	4.44	1.43	0.98	0.53
10	0.607	4.08	1.74	1.31	0.49
30	0.401	3.78	2.01	1.52	0.48
60	0.270	3.72	2.06	1.61	0.47
150	0.141	3.63	2.14	1.65	0.47

Sulfamic acid, 13.0 mmole/1, 45°C, Initial CO_2 conc. 0.293 g/l
1% consistency, initial kappa no. 39.9
* Corrected for lignin removed by the action of N-chlorosulfamic acid

Table 3. Relationship between delignification and HClO formation during ClO_2 bleaching in the presence of sulfamic acid with 39.9 kappa pulp

With the assumption that the percentage of lignin removal as a result of the action of N-chlorosulfamic acid remains the same as in Figure 3 one can calculate a molar ratio of the lignin monomer units potentially removable by ClO_2 and initial formed chlorite of 1.04. This shows that the formation of about one mole of chlorite per mole of lignin monomer unit finally removed also holds in this case.

The molar ratio of lignin monomer units removed to hypochlorous acid formation at different reaction times was calculated in exactly the same manner as outlined in the previous sections and the results are listed in the last column of Table 3. It shows that again about 2 moles of hypochlorous acid are formed per mole of lignin monomer unit removed at any time during chlorine dioxide treatment. Therefore, it can be concluded that the two stoichiometric relationships between delignification and respectively the formation of hypochlorous acid and chlorite are unaffected by the changes in initial lignin content from 4.24 to 5.99% (41% difference) and chlorine dioxide concentration from 2.37 to 2.93 g/l (24% difference).

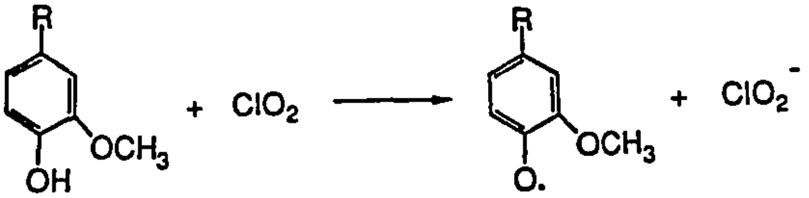
What is the First Reaction Step Between ClO_2 and Lignin?

Studies with lignin model compounds showed that an electron withdrawing group increases the reactivity of the substrate towards chlorine dioxide. For example, Strumila and Rapson [4] found that the reaction of vanillin, acetovanillone and guaiacol towards ClO_2 increases in the order:

vanillin > acetovanillone > guaiacol

The substituents at the para position of the phenolic group of these three compounds, respectively formyl, acetyl and hydrogen, are in decreasing order of electron withdrawing strength. This stabilizes the phenoxy anion formed after dissociation of the hydrogen ion from the phenolic group. In other words, when the acidity of the lignin model compounds increases, its reactivity towards chlorine dioxide increases. Nonni and Dence [10] also found that propioguaiacone reacts faster with ClO_2 than creosol does. The structural difference between these two compounds is that the former has an electron withdrawing group in the para position relative to the phenolic hydroxyl group, while creosol has a weak electron releasing group at the para position. Thus, the acidity of propioguaiacone is also higher than that of creosol. This indicates that reactions of chlorine dioxide with lignin model compounds are not simple oxidations, since generally an electron withdrawing substituent in the para or ortho position in phenol suppresses its potential for oxidation.

Lindgren [3], Gierer [21], and Strumila and Rapson [4] proposed the hydrogen abstraction by chlorine dioxide as the first reaction step of the oxidation of phenolic structures, resulting in the reduction of chlorine dioxide to chlorous acid ($HClO_2$) or chlorite and the formation of a reactive phenoxy free radical represented by :



However, this reaction is unlikely because electron withdrawing groups make the phenoxy radical less stable, and the predicted decrease in reactivity with increasing strength of the electron withdrawing groups is exactly opposite to the findings of Nonni and Dence [10] and Strumila and Rapson [4].

The question then remains what is the first reaction step between ClO_2 and phenolic structures? The dependence of the reactivity of chlorine dioxide on the acidity of lignin model compounds suggests that the first reaction step is the phenolic hydroxyl dissociation, and that then chlorine dioxide reacts with the phenoxy anion, rather than with the undissociated phenolic lignin units. Since the phenoxyl ion concentration increases with increasing acidity of the phenolic model compounds, its reactivity towards ClO_2 should also increase. This is confirmed by the results of Teder et al [11] who showed that the pulp delignification rate increases when the pH during ClO_2 treatment increases from 2 to 4. Further increase in the pH decreased the final degree of delignification because of the increased chlorine dioxide decomposition at higher pH so that less ClO_2 is available in the later stages of delignification.

Delignification Reaction Scheme During ClO_2 Treatment of Unbleached Pulp

Reaction mechanisms of the attack of phenolic structures by chlorine dioxide were proposed by Sarkanen et al [1], Dence et al [2], Lindgren [3], Strumila and Rapson [4] and Gierer [21]. All are similar and can be represented in Figure 6. In this mechanism chlorine dioxide abstracts a hydrogen atom from the phenolic hydroxyl group resulting in the formation of a chlorite ion and a phenoxy radical and its mesomeric cyclohexadienonyl radical resonance counterparts. The latter combine with chlorine dioxide forming unstable chlorite esters of ortho- and para-quinones which are subsequently hydrolyzed or undergo elimination of the para substituent to give quinoid or muconic acid-type structures, while chlorine dioxide is reduced to chlorite or hypochlorous acid.

There are a few weaknesses in this reaction mechanism. First of all, as explained above, direct abstraction of hydrogen from the phenolic structure by chlorine dioxide contradicts experimental evidence that electron withdrawing groups enhance the reactivity of the corresponding substrate. Secondly, it can not explain that about 50% and 55% of the atomic chlorine supplied as chlorine dioxide are converted to hypochlorous acid when respectively lignin model compounds [22] and oxygen-prebleached kraft pine pulp [23] were treated with chlorine dioxide. Thirdly, only the formation of 2-methoxyl-*p*-quinone results in cleavage of the lignin polymer chain and thus will ultimately contribute to

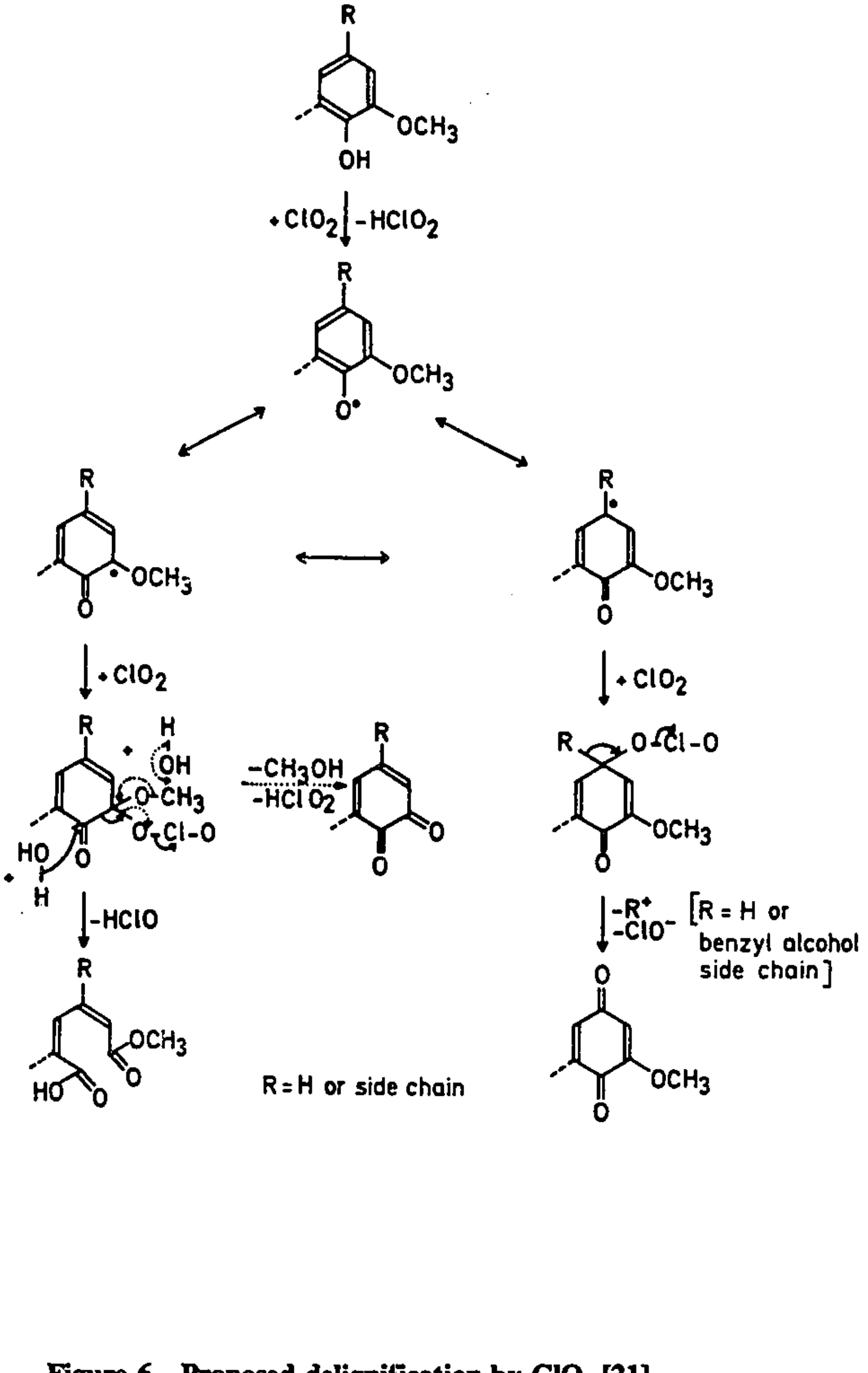


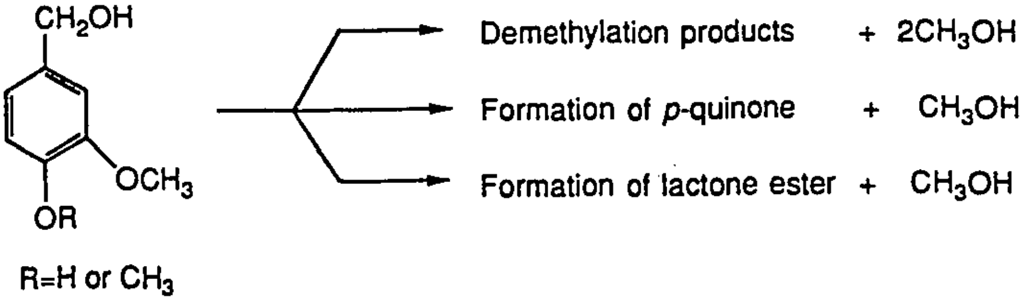
Figure 6. Proposed delignification by ClO_2 [21]

delignification. However, it is known that the formation of the p-quinone moiety is small [1,20]. Finally, the reaction products identified in experiments of lignin model compounds with chlorine dioxide on which the above mechanism is based only represent about 30% of the substrate consumed [1].

The experimental results related to delignification presented in the present and previous chapters can be summarized as follows:

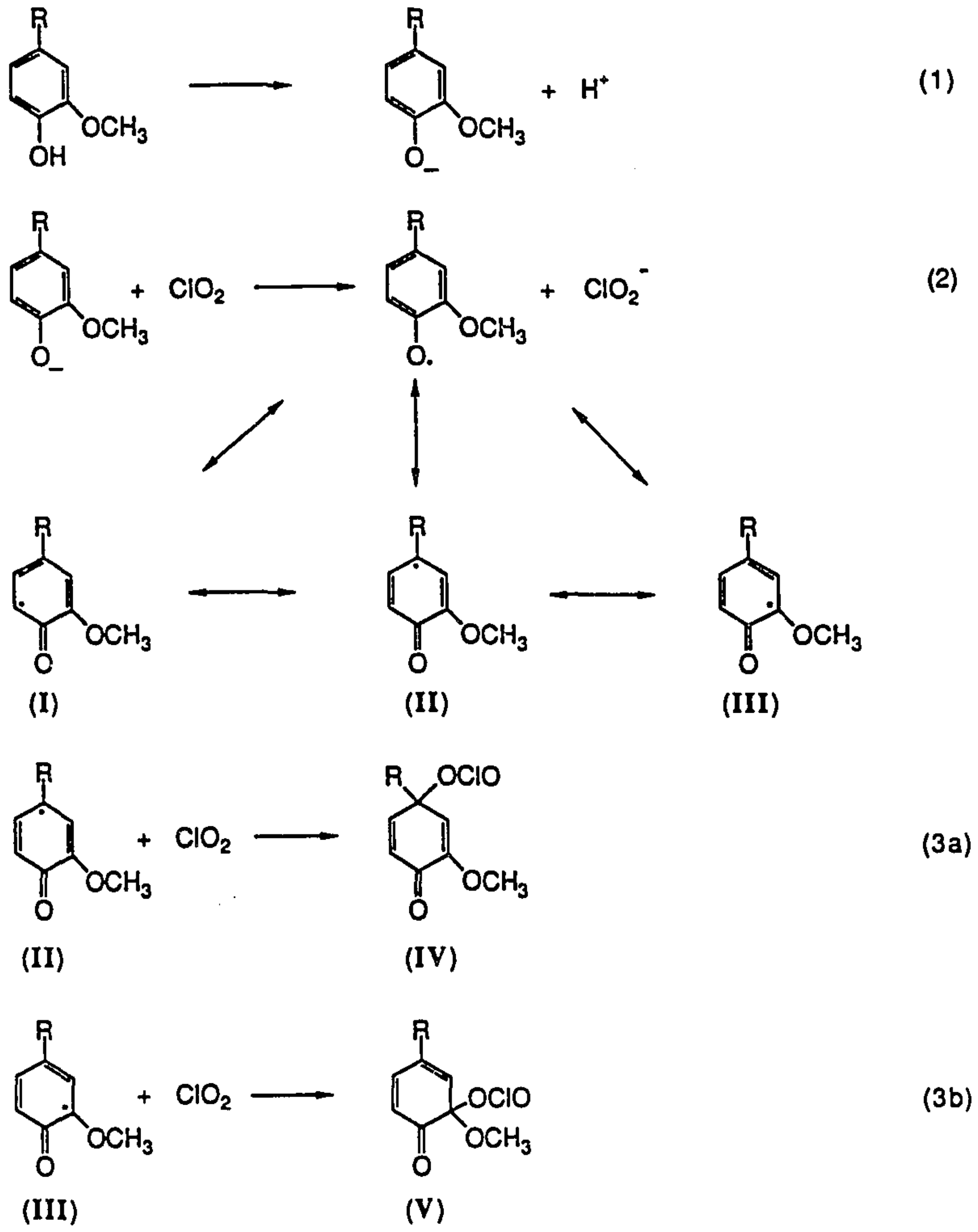
- Only phenolic hydroxyl lignin structures are reactive towards ClO_2 .
- Chlorine dioxide reacts with phenoxy ion structures rather than with the undissociated phenolic groups in lignin.
- About 1 mole of chlorite is formed initially per mole of lignin monomer unit ultimately removed during ClO_2 treatment of kraft pulp.
- Hypochlorous acid is formed as a reaction intermediate during ClO_2 treatment of unbleached pulp. For each mole of lignin monomer unit removed, about 2 moles of hypochlorous acid are formed.
- Demethylation and delignification are closely linked. The formation rates of potentially hydrolysable methyl esters (such as muconic acid monomethyl ester) and that of methanol, identified respectively as indirect and direct demethylations are proportional to each other (Chapter 6).

Recently, we [20] established that the consumption of lignin model compounds as a result of the sole action of chlorine dioxide (when HOCl is captured by sulfamic acid) can be fully represented by three parallel reaction pathways: demethylation, formation of 2-methoxy-*p*-quinone and the formation of muconic acid monomethyl ester, i.e.

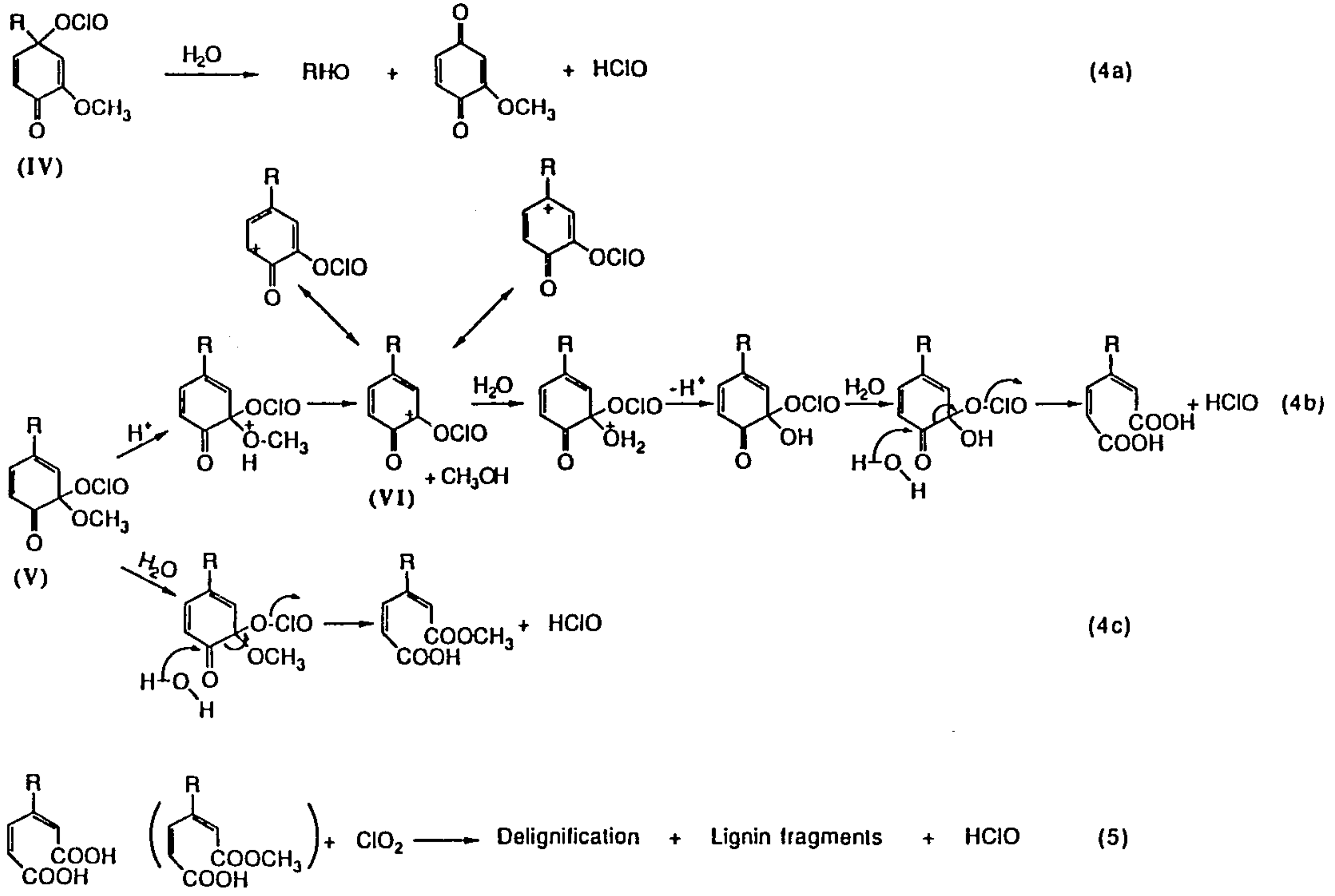


Based on the same concept, and with integration of the above stated evidence, the earlier proposed ClO_2 reaction mechanism [1,2,3,4,21] is modified to describe the reactions between chlorine dioxide and lignin in actual pulp. The modified reaction mechanism shown in Scheme 1 consists of the following five consecutive reactions:

1. A phenolic lignin unit dissociates to form a phenoxy anion (reaction 1).
2. Abstraction of an electron from the phenoxy anion by ClO_2 leads to the formation of chlorite and the phenoxy radical and its mesomeric resonance compounds (reaction 2).
3. Two of the three more stable resonance structures of the phenoxy radical are attacked by chlorine dioxide to form chlorite esters (reactions 3a and 3b).
4. Hydrolysis of the two chlorite esters. 2-methoxy-*p*-quinone is formed, accompanied by delignification and formation of 1 mole of hypochlorous acid when the para substituted chlorite ester is hydrolyzed (reaction 4a). There are two possible reaction paths for the other chlorite ester. In reaction 4b muconic acid is the reaction product, while in reaction 4c muconic acid monomethyl ester is formed. 1 mole of ClO_2 is reduced to hypochlorous acid in each case. The difference between these two paths is that in reaction 4b methanol is released by



Scheme I. Modified ClO_2 delignification mechanism



Scheme 1. Modified ClO$_2$ delignification mechanism (continued)

acid hydrolysis prior to rupture of the aromatic ring while in reaction 4c the rupture of the aromatic ring leads to the formation of the relatively stable muconic acid monomethyl ester. Thus, reaction 4b and 4c represent the lignin degradation steps representative of respectively direct and indirect demethylation.

5. The muconic acid type structures are further attacked by chlorine dioxide and cleaved from the lignin polymer under formation of hypochlorous acid.

The formation of phenoxy anions by dissociation of phenolic hydroxyl groups as the first step of delignification accounts for the observed reactivity order of the lignin model compounds as discussed earlier.

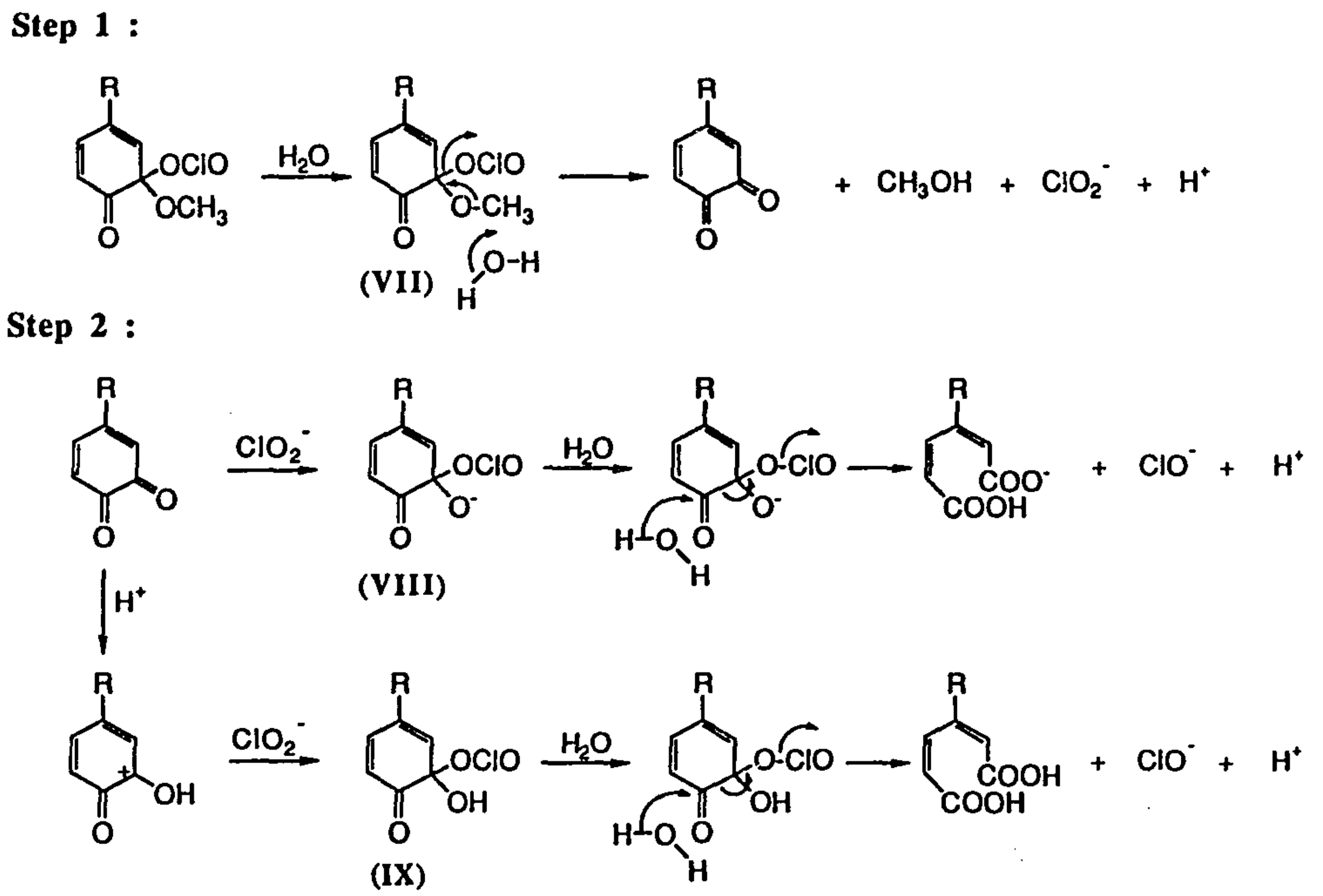
The second step of radical transfer between chlorine dioxide and the phenoxy anion is supported by the stoichiometry of 1 mole of "instantaneously" formed chlorite per mole of lignin monomer units finally removed, and by the experiments of Shen et al [12] who found that the reaction rate constant at room temperature (and pH between 11 and 12) between ClO_2 and phenol anion is extremely fast at 3.5×10^7 liter/mole. s.

The formed phenolic radical has three resonance structures I, II and III. However, structures II and III are more prevalent because of the stabilizing effect of respectively the electron releasing alkyl group and methoxyl group. Since an alkoxyl group is a stronger electron releasing substituent than an alkyl group, the attack of ClO_2 in reaction 3 preferentially occurs on the methoxyl substituted carbon atom. This is supported by the lignin model compounds studies of Sarkanen et al.[1], Lindgren [3] and our recent results [20] which show that the formation of *p*-quinone (as in reaction 4a) is always very small.

The hydrolysis of chlorite ester (V) can follow two reaction routes; attack of H^+ on the oxygen of the methoxyl group (reaction 4b) or attack of H-OH on the keto substituted carbon atom (reaction 4c). In reaction 4c, the mobile π electrons of the carbon-oxygen double bond are pulled towards the electronegative oxygen atom, so that the carbonyl carbon is electron deficient and therefore attacked by H_2O. This is supported by the formation of the reaction product muconic acid monomethyl ester in several lignin model compound studies [1,2,3,4,21]. In reaction 4b, the first step is the formation of the protonated ether. Methanol is subsequently released following a mechanism similar to that of transesterification [24] whereby carbonium ion (VI) is formed which is stabilized by two resonance structures. The carbonium ion then combines with water to form the protonated alcohol, which releases a hydrogen ion to form a hydroxyl group. In a subsequent reaction the hydroxyl-chlorite ester is attacked by H_2O similar to reaction 4c.

The indirect demethylation quantified by the methoxyl content of the dissolved organics in the filtrate is represented by reactions 4a and 4c. The ratio of indirect to total demethylation for ClO_2 treatment of kraft pulp was determined in Chapter 6 to be 0.3. This is in close agreement with the conversion of about 28% of the lignin model compound substrate to muconic acid monomethyl esters and methoxy-*p*-quinones reported in literature [2,3]. It also confirms that reaction 4b is dominant, accounting for about 70% of the total demethylation.

As an alternative for reaction 4b it can be speculated that *o*-quinone is formed as shown in Scheme II. However, we propose that the reaction does not stop here. The next step, shown in Scheme II, is either a nucleophilic attack of chlorite on the electron deficient carbonyl carbon of *o*-quinone, resulting in the formation of intermediate VIII, or the attack of H^+ on the electron rich oxygen of the carbonyl, rendering the carbonyl carbon even more electron deficient and reactive towards nucleophilic attack by chlorite



Scheme II. An alternative for reaction 4b of Scheme 1.

to form intermediate IX. Intermediates VIII and IX then react with water in the same way as reactions 4b and 4c in Scheme 1, resulting in the formation of muconic acid and hypochlorous acid. In direct support for the speculated Scheme 2 is that *o*-quinone has never been identified in any study of chlorine dioxide treatment of phenolic lignin model compound reported in literature.

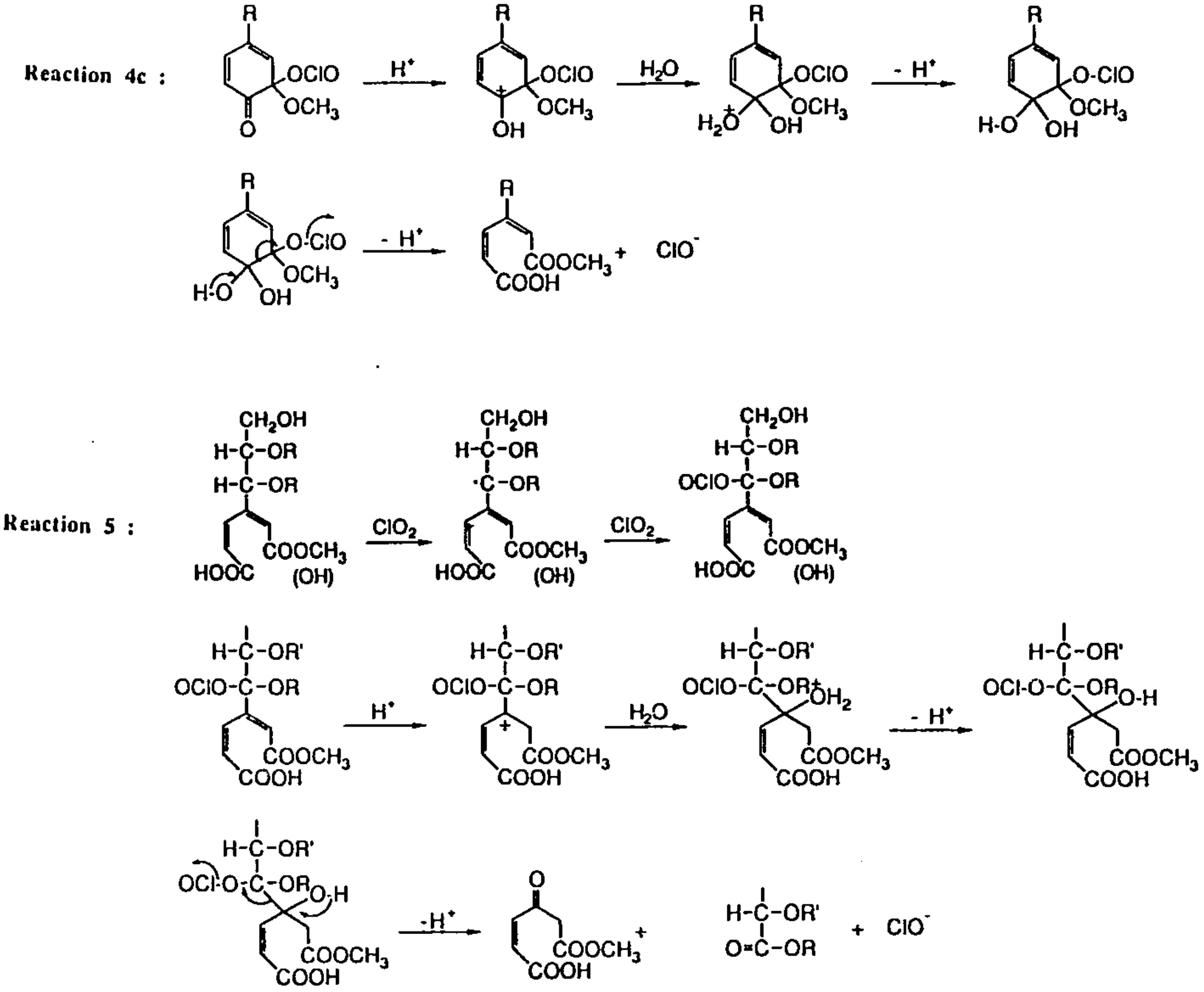
The four reactions described so far consume two moles of chlorine dioxide, each yielding respectively one mole of chlorite (reaction 2) and hypochlorous acid (parallel reactions 4a, 4b and 4c). The present experiments show that two moles of hypochlorous acid are formed per mole of lignin monomer unit removed. Furthermore, since the lignin chain is still intact after reactions 4b and 4c in Scheme 1 or Scheme 2 it is likely that further reactions with ClO_2 take place which lead to the formation of another mole of hypochlorous acid and cleavage of the muconic acid structure from the lignin chain as indicated by reaction 5 in Scheme 1.

Because the unspecified nature of reaction 5 in Scheme 1 is rather unsatisfactory, a tentative reaction path is proposed in Scheme 3: chlorine dioxide abstracts the allylic hydrogen with the formation of a new radical structure which then combines with another molecule of chlorine dioxide. Subsequent hydrolysis, similar to that in Reaction 4c of Scheme 1 results in cleavage of the lignin chain and the formation of hypochlorous acid.

CONCLUSIONS

A modified delignification mechanism by chlorine dioxide was proposed for softwood kraft pulp based on experimental evidence showing that 1) only phenolic hydroxyl lignin structures are practically reactive towards ClO_2 at practical bleaching conditions, 2) ClO_2 reacts with phenoxy ion structures rather than with the undissociated phenolic groups in lignin, 3) about 1 mole of chlorite is formed initially per mole of lignin monomer unit ultimately removed, 4) about 2 moles of hypochlorous acid are formed for each mole of lignin monomer unit removed and 5) demethylation and delignification are closely linked.

It is proposed that removal of phenolic lignin units by chlorine dioxide involves the following five consecutive reactions: 1) A phenolic lignin unit dissociates to form a phenoxy anion; 2) Abstraction of an electron from the phenoxy anion by chlorine dioxide leads to the formation of chlorite and the phenoxy radical and its three mesomeric resonance compounds; 3) The two more stable resonance structures of the phenoxy radical are attacked by chlorine dioxide to form chlorite esters; 4) Hydrolysis of the two chlorite esters. When the para substituted chlorite ester is hydrolyzed 2-methoxy-*p*-quinone is formed, accompanied by delignification and formation of 1 mole of hypochlorous acid. One mole of hypochlorous acid and muconic acid or muconic acid monomethyl ester are formed upon hydrolysis of the other chlorite ester; 5) Both the muconic acid and muconic acid monomethyl ester type of structures are further attacked by chlorine dioxide and cleaved from the lignin polymer under formation of another mole of hypochlorous acid.



Scheme III. Tentative reaction path for reaction 4c and reaction 5

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CHAPTER 8

REDUCTION OF AOX FORMATION DURING BLEACHING

ABSTRACT

It is accepted practice to add chlorine dioxide shortly before chlorine in a pulp chlorination stage. In the present study it is found that by introducing a washing step between the chlorine dioxide treatment and chlorine addition, a reduction in AOX formation by a factor of about three can be achieved, while maintaining the same degree of delignification as in a standard DC sequence. The organic chlorine formation during ClO_2 bleaching (with or without this so called intrastage washing step) can be further reduced by equimolar replacement of part of the chlorine dioxide by chlorite. The delignification is not affected by the substitution of chlorite for chlorine dioxide. In practice chlorite can be generated in situ from ClO_2 by addition of a small amount of hydrogen peroxide.

In order to facilitate the introduction of intrastage washing in a commercial bleach plant, it is investigated whether the chlorine dioxide treatment before the washing step can be shortened. An optimal time of about 10 minutes is found when the initial pH of the ClO_2 treatment is reduced to about 2. With these process modifications and ClO_2 and chlorine charges of respectively 1.20% and 1.53%, a kraft black spruce pulp with a kappa number of about 30 can be bleached to a kappa number of below 4 after caustic extraction, with an AOX production of less than 1.5 kg/ton for the untreated combined chlorination and extraction effluent.

INTRODUCTION

The chloro-organic compounds released from the pulp bleaching process are collectively identified as AOX (Adsorbable Organic Halides). A conventional chlorination and extraction stage will typically produce a combined effluent containing 6-8 kg of AOX per ton of bleached pulp prior to external treatment [1]. Demonstrated technologies to decrease the formation of chloro-organics when producing fully bleached pulp include 1) lowering the lignin content of pulp entering the bleach plant by extended delignification [2] and/or oxygen delignification [3]; 2) increasing replacement of chlorine by chlorine dioxide [4]; 3) reducing the chlorine charge factor combined with a peroxide reinforced oxidative extraction stage (Eo)[5]; 4) treatment of the bleach plant effluent in an aerated lagoon [6].

In Chapter 4 it was shown that most of the chloro-organics are formed from the reaction between dissolved lignin and hypochlorous acid, the intermediate produced when chlorine dioxide reacts with lignin. Hypochlorous acid is also consumed by chlorite in competing reactions leading to the regeneration of chlorine dioxide or the formation of chlorate (Chapter 5). This suggests that the formation of chloro-organics can be minimized during the chlorination stage by 1) promoting the reaction between hypochlorous acid and chlorite and 2) decreasing the (dissolved) lignin concentration. In the present chapter these two possibilities to reduce the AOX formation during conventional bleaching are further explored.

EXPERIMENTAL

The same 28.7 kraft black spruce pulp was bleached with chlorine dioxide in a similar manner as outlined in Chapter 3.

After chlorine dioxide treatment, the pulp was thoroughly washed by first applying a large amount of tap water, then the pulp slurry was transferred to a British handsheet making machine in which it contacted with water and subsequently drained for three times. Four litres of distilled water were used twice for a final wash of the pulp. The pulp sample was then saved in the form of a handsheet for further analysis.

The alkali extraction experiments were performed in a polyethylene bag. Pulp with the required amount of caustic soda solution and water were very well mixed before being placed in a constant temperature bath at 70°C. After one hour, the extracted pulp was thoroughly washed and air dried handsheets were prepared for future analysis.

The AOX content of the filtrate at different reaction times was measured with a Dohrmann DX20 analyzer. The organically bound chlorine content in chlorine dioxide treated pulp was determined using the method described in Chapter 3. The kappa number and viscosity were determined according to the CPPA standard method.

RESULTS AND DISCUSSION

Reduction of Organo-Chlorine Formation by Addition of Sodium Chlorite

The potential of chlorite as a scavenger of hypochlorous acid was first investigated. In one experiment sodium chlorite was mixed with the pulp suspension at a charge of 12% (as ClO_2^- on o.d. pulp), prior to addition of 6.31% (on o.d. pulp) of chlorine. The latter is equivalent to a chlorine charge factor of 0.22. The chlorite to chlorine molar charge ratio was chosen as 2.0, as required by the stoichiometry of the chlorine dioxide regeneration reaction.

$$2\ ClO_2^- + Cl_2 \longrightarrow 2\ Cl^- + 2\ ClO_2 \qquad (1)$$

For comparison, two other pulp bleaching experiments were performed; one with only chlorine at a charge of 6.31% on pulp and another with only chlorine dioxide at a charge of 12.0% on pulp.

The results in Table 1 show that the organic chlorine formation and final C kappa number of test 1 and test 3 are similar, while the organo-chlorine formation in test 2 is almost one order of magnitude larger. This indicates that reaction between hypochlorous acid (chlorine) and chlorite in test 1 is faster than the reaction between hypochlorous acid (chlorine) and lignin. In other words, chlorite could be regarded as a scavenger of hypochlorous acid (chlorine), which is responsible for most of the formation of chloro-organics (test 2). Therefore, it is expected that an increased concentration of chlorite during chlorine dioxide bleaching will favor the reaction between hypochlorous acid and chlorite over that of hypochlorous acid with lignin, so that the formation of organically bound chlorine will be reduced.

Test No.	1	2	3
AOX in filtrate (kg/ton)	0.62	5.40	0.53
Organic chlorine in C pulp (kg/ton)	0.57	3.90	0.47
Total organic chlorine (kg/ton)	1.19	9.30	1.00
C kappa no.	4.8	6.8	5.5

Test 1: chlorite charge 12.0% on pulp followed by a Cl_2 charge of 6.31% on pulp; initial and final pH of 2.78 and 2.28 respectively

Test 2: Cl_2 charge 6.31% on pulp

Test 3: ClO_2 charge 12.0% on pulp

Other conditions: 1% consistency, 45°C, 1.5 hrs., initial kappa no. 28.7

Table 1. The relative reaction rate of chlorite with chlorine or lignin

To prove this hypothesis, a number of experiments were performed whereby increasing amounts of sodium chlorite were first mixed with the unbleached pulp followed by a chlorine dioxide charge. The total amount of chlorine dioxide and chlorite added was the same in all experiments at 2.4% on pulp, an active chlorine corresponding to an active charge factor of 0.22. The formation of organically bound chlorine and the C kappa number for 0, 5, 10, 20 and 30 percent of the chlorine dioxide charged as chlorite are summarized in Table 2. No initial pH adjustment was made. The final pH was about 3.5 in all cases.

Replacement of ClO_2 by ClO_2^- (%)	Organic Chlorine (kg/ton o.d. pulp)			C kappa no.
	In effluent (as AOX)	In C pulp	Total	
0	0.48	0.43	0.91	10.8
5	0.47	0.38	0.85	9.9
10	0.45	0.35	0.80	10.3
20	0.41	0.36	0.77	10.5
30	0.37	0.37	0.74	10.6

Initial kappa no. 28.7, total active chlorine charge 6.31% on pulp, 45°C, 1 hr., 2% consistency, final pH of 3.5

Table 2. The effect of partial replacement of ClO_2 by chlorite on the organic chlorine formation at an active chlorine charge factor of 0.22

The results in Table 2 show that the AOX production and the organic chlorine content of the chlorinated pulp decrease with increasing chlorite substitution while the C kappa no. is unaffected. The percentage decrease in the total amount of organic chlorine is somewhat less than the percentage substitution of chlorine dioxide by chlorite.

With recycling of bleach effluents, the final pH in industrial practice is lower than 3.5, the value of the experiments shown in Table 2. Therefore, these five experiments were repeated with some HCl addition so that a final pH of 2.5 after 1 hour reaction was obtained. These results are summarized in Table 3.

The results in Table 3 again show that substitution of chlorine dioxide by chlorite leads to a reduction in AOX production. In this case the percentage decrease in AOX production is approximately equal to 0.8 times the percentage of chlorine dioxide substitution by chlorite. Again the C kappa number is unaffected by the chlorite substitution.

Replacement of ClO_2 by ClO_2^- (%)	**Organic chlorine content (kg/ton o.d. pulp)**			**C kappa no.**
	In effluent (as AOX)	**In C pulp**	**Total**	
0	0.59	0.55	1.14	10.4
5	0.56	0.54	1.10	9.8
10	0.57	0.48	1.05	10.0
20	0.49	0.46	0.95	10.8
30	0.45	0.41	0.86	10.8

Final pH of 2.5; other conditions are the same as in Table 2.

Table 3. The effect of partial replacement of ClO_2 by chlorite on the organic chlorine formation at an active chlorine charge factor of 0.22 and pH 2.5

In order to simulate a more practical chlorine dioxide charge equivalent to 50% substitution in the first chlorination stage, further experiments were performed for a chlorine dioxide charge of 1.20% (i.e. an active chlorine charge factor of 0.11). The initial pH was adjusted to pH 3 by addition of hydrochloric acid. The other experimental conditions are the same as those displayed in Table 2. The results in Table 4 again show that substitution of chlorine dioxide by chlorite leads to a reduction in production of organic chlorine but does not affect the C kappa number. It might be possible that with improved mixing the organic chlorine formation will be further reduced.

Replacement of ClO_2 by ClO_2^- (%)	Organic chlorine (kg/ton o.d. pulp)			C kappa no.
	In effluent (as AOX)	In C pulp	Total	
0	0.34	0.46	0.80	15.6
5	0.26	0.42	0.68	15.3
10	0.30	0.40	0.70	15.2
20	0.21	0.45	0.66	15.7
30	0.24	0.39	0.63	15.7

Initial kappa no. 28.7, total active chlorine charge 3.15% on pulp, 45°C, 1 hr., 2% consistency

Table 4. The effect of partial replacement of ClO_2 by chlorite on the organic chlorine formation at an active chlorine charge of 0.11

Reduction of Organo-Chlorine Formation by Addition of H_2O_2

Since chlorite is expensive, it is of practical interest to investigate whether a cheaper chemical is available which can convert ClO_2 in chlorite. Some commonly used reducing agents such as methanol, formaldehyde, ascorbic acid, sodium sulfite and sodium bisulfite were tried. However, the first two are unreactive, while the last three lead to complete conversion of ClO_2 to chloride instead of chlorite. Subsequently, it was found that hydrogen peroxide was very effective for the conversion of ClO_2 to chlorite according to the reaction:

$$2\ ClO_2 + H_2O_2 \longrightarrow 2\ H^+ + O_2 + 2\ ClO_2^- \qquad (2)$$

Hydrogen peroxide might appear to be an unlikely candidate for the reduction of chlorine dioxide because H_2O_2 is normally used as an oxidizing agent. However, the oxidation-reduction potentials of the half reactions of chlorine dioxide and hydrogen peroxide [8]

$$ClO_2\ (g) + e^- = ClO_2^- \qquad (3)$$

$$O_2 + 2\ H^+ + 2\ e^- = H_2O_2 \qquad (4)$$

are respectively +0.95 V and +0.69 V, so that in principle ClO_2 can be reduced by H_2O_2. The reaction between H_2O_2 and ClO_2 was tested by charging amounts of hydrogen peroxide to a ClO_2 solution. The composition of the solutions immediately after addition of H_2O_2 was determined by IC analysis and the results are shown in Table 5.

ClO_2 (m Mol)	H_2O_2 (m Mol)	ClO_2^- (m Mol)	Cl^- (m Mol)	ClO_3^- (m Mol)	ClO_2^-/H_2O_2 molar ratio
0.7052	0	0	0.0546	ND	
0.6689	0.0171	0.0360	0.0546	ND	2.10
0.6303	0.0342	0.0700	0.0553	ND	2.05
0.5433	0.0684	0.1442	0.0540	ND	2.10
0.4735	0.1026	0.2197	0.0559	ND	2.14
0.3403	0.1710	0.3365	0.0544	ND	1.97

45°C
ND: not detectable

Table 5. Chlorite formation from ClO_2 by addition of H_2O_2

From the last column, showing the molar ratio of chlorite formed to hydrogen peroxide added, as well as from the absence of newly formed chloride or chlorate, it can be concluded that within experimental error ClO_2 is quantitative converted into chlorite by H_2O_2 according to reaction equation (2).

In the previous section it was shown that partial replacement of chlorine dioxide by chlorite resulted in a decrease of the AOX formation during pulp bleaching with chlorine dioxide. Since hydrogen peroxide reacts with chlorine dioxide to form chlorite it is likely that the reduction in AOX formation can also be achieved by addition of H_2O_2

to ClO_2 before it is charged to the pulp. In order to confirm this, a series of experiments were done by adding different amounts of hydrogen peroxide to a ClO_2 solution before mixing it with the 28.7 kappa number kraft black spruce pulp. The active chlorine charge factor based on the amount of ClO_2 before its reaction with H_2O_2 is 0.11. The results are shown in Table 6.

H_2O_2 charge		**Calculated conversion of ClO_2 into ClO_2^- (%)**	**AOX (kg/ton)**	**Organic chlorine (kg/ton)**	**Total (kg/ton)**	**C kappa no.**
% on pulp	**H_2O_2/ClO_2 molar ratio**					
0	0	0	0.37	0.45	0.82	15.6
0.0145	0.024	4.8	0.32	0.42	0.74	15.7
0.029	0.048	9.6	0.31	0.42	0.73	15.5
0.058	0.096	19.2	0.26	0.41	0.67	15.8
0.087	0.144	28.8	0.26	0.39	0.65	15.7
0.145	0.240	48.0	0.24	0.37	0.61	15.9

Initial pH was adjusted to 3 by HCl, 1% consistency, 45°C, 30 mins.

Table 6. The effect of addition of H_2O_2 on the formation of organic chlorine and kappa number

The H_2O_2 charge is expressed both as percentage on pulp and molar fraction of the chlorine dioxide charge. The third column in Table 6, the calculated percent conversion of ClO_2 into ClO_2^- by H_2O_2, is obtained by multiplication of the molar charge ratio of H_2O_2 and ClO_2 by 200. As can be seen, the formation of organic chlorine and the C kappa no shown in Table 6 is essentially the same as listed in Table 4. This confirms that H_2O_2 can be used to reduce the organic chlorine formation during chlorine dioxide bleaching by partial conversion of chlorine dioxide to chlorite before its addition to pulp.

Another important application of the quantitative conversion of ClO_2 to ClO_2^- by

H_2O_2 is the elimination of chlorine from (industrial) ClO_2 solutions. When H_2O_2 is added to a chlorine containing chlorine dioxide solution, the generated chlorite will immediately react further with chlorine (or hypochlorous acid) to form chlorine dioxide, chloride and chlorate according to the overall reactions (Chapter 5).

$$2\ ClO_2^- + Cl_2 \longrightarrow 2\ Cl^- + 2\ ClO_2 \qquad (5)$$

and

$$HClO + ClO_2^- \longrightarrow H^+ + Cl^- + ClO_3^- \qquad (6)$$

The formation ratio of chlorine dioxide and chlorate depends on the pH and initial chlorine dioxide concentration, as discussed in detail in Chapter 5. Therefore, the overall reaction equations describing the elimination of chlorine (or hypochlorous acid) from a chlorine dioxide solution by addition of H_2O_2 are:

$$Cl_2 + H_2O_2 \longrightarrow 2H^+ + 2\ Cl^- + O_2 \qquad (7)$$

and

$$2\ HClO + 2\ ClO_2 + H_2O_2 \longrightarrow 4H^+ + 2\ Cl^- + O_2 + 2\ ClO_3^- \qquad (8)$$

From the equations predicting the relative contribution of chlorine and chlorine dioxide to AOX of a combined CE effluent [12], it follows that the AOX production of chlorine is 5 times larger than that of chlorine dioxide at the same active chlorine charge. Thus for an industrial ClO_2 solution containing Cl_2 at a concentration equivalent 10% substitution of ClO_2, elimination of all the Cl_2 by H_2O_2 addition would theoretically lead to a reduction of about 30% in the AOX of the combined CE effluent as compared to the case without H_2O_2 addition. Addition of H_2O_2 in excess of that needed to eliminate chlorine (or hypochlorous acid) leaves unconverted chlorite which will further contribute to the reduction of chloro-organics as described earlier.

Finally, it should be noted that the chemical cost of the addition of H_2O_2 to reduce the production of organic chlorine is relatively small, since the required charges of hydrogen peroxide are very small as can be seen from Table 6.

Intrastage Washing

In the previous section, it was shown that a charge of 1.20% ClO_2 to a 28.7 kappa number kraft pulp (equivalent to an active chlorine charge of 0.11) leads to a C kappa number of about 15.6. This means that almost 50% of the lignin has been removed from the unbleached pulp with an AOX content in the effluent of only 0.34 kg/ton pulp (see Table 4). When the pulp suspension is subsequently contacted with chlorine, as is typically done in an industrial DC chlorination stage, it is likely that the dissolved lignin will be competing with the residual lignin in the pulp for reaction with the charged chlorine. This will not only result in a less efficient use of chlorine for delignification, but also result in additional AOX. Thus, by introducing a washing stage between the consecutive additions of ClO_2 and Cl_2, it is expected that the delignification efficiency of chlorine will be increased while the total organic chlorine formation will be decreased.

This was tested by treating the standard pulp with a ClO_2 charge of 1.20% on pulp, (active chlorine charge factor of 0.11) at 45°C and 2% consistency for 45 minutes. After the 45 minutes reaction time both ClO_2 and the generated ClO_2^- are completely consumed. The kappa number and organic chlorine content of the chlorinated pulp are 15.8 and 0.50 kg/ton pulp respectively, while the AOX in the filtrate is 0.32% kg/ton pulp. The pulp was then thoroughly washed and further treated with different charges of pure chlorine water. The chlorination conditions are: 45°C, 1% consistency and 45 minutes contact time. The kappa number of the chlorine treated pulp was determined after washing, as well as the AOX content of the wash filtrate. Subsequently, the pulp was extracted with caustic soda. The extraction conditions used are: NaOH charge of 0.55 times the sum of active chlorine charges as chlorine dioxide and chlorine in the two separate stages, temperature of 70°C, 10% consistency and 1 hour reaction time. The kappa number after extraction, the viscosity of the extracted pulp and the AOX content of the extraction filtrate were also measured. The analysis results for the two different chlorine charges are identified in Table 7 as Tests 1 and 2.

Test	Cl_2 charge factor	Kappa number		Effluent AOX (kg/ton pulp)		NaOH charge	Viscosity D/C/E	Total AOX D+C+E	Total chlorine charge factor
		C	E	C	E	%	(mPa)	(kg/ton)	D+C
1	0.053	7.2	3.5	0.92	0.28	2.55	26.1	1.52	0.163
2	0.037	9.0	4.2	0.55	0.21	2.29	26.5	1.08	0.147
3	0.053	11.6	6.0	1.53*	0.48	2.57	—	2.01	0.163
4	0.110	6.7	3.4	4.03*	0.51	3.47	—	4.54	0.220

* AOX of the combined D/C stage

Table 7. The effect of intrawashing stage on organic chlorine formation

For comparison, two experiments which are performed following a conventional D/C E bleaching sequence are also included in Table 7 as Tests 3 and 4. Thus in Test 3 and Test 4 pure chlorine water is added 1 minute after addition of chlorine dioxide to the unbleached pulp without an intrastage washing step. The ClO_2 and Cl_2 charges in Test 3 are 1.2% and 1.52% (on o.d. pulp) respectively. In Test 4, the ClO_2 and Cl_2 charges are 1.20% and 3.16% respectively. Comparison of Test 3 and Test 1 shows that intrastage washing leads to a reduction of the combined AOX production of the D/C E stages from 2.01 to 1.52 kg/ton, respectively, while the CE kappa numbers are 6.0 and 3.5 respectively. Since the CE kappa number of Test 3 is rather high, a fairer evaluation of the effectiveness of intrastage washing is obtained when comparing Test 1 and Test 4, which have almost the same CE kappa number (3.4 and 3.5 respectively). In Test 4 the combined effect of the higher total active chlorine charge and the absence of intrastage washing leads to a combined AOX production of the D/C and E stages of 4.54 kg/ton o.d. pulp, or three times larger than that obtained in Test 1.

Next a series of bleaching experiments with intrastage washing were performed whereby the objective was to obtain a well delignified semi-bleached pulp (kappa < 4) at a total organic chlorine production (i.e. D, C and E effluents) of less than 1.5 kg/ton pulp. The variables were the charges of chlorine dioxide and chlorine. 5% of the chlorine dioxide in the D stage of the DC sequence with intrastage washing was substituted by chlorite. The results for two chlorine dioxide charges are given in Table 8.

Test	**Charge (% on pulp)**			**Org. Chlorine (kg/ton)**		**D Kappa no.**
	Chlorite	**ClO_2**	**Total**	**AOX**	**D pulp**	
A	0.06	1.14	1.20	0.22	0.35	14.6
B	0.084	1.596	1.68	0.35	0.42	12.0

45°C, 45 minutes, 2% consistency, initial and final pH are 3.0 and 2.5 respectively

Table 8. The organic chlorine formation and kappa number in the D stage

The active chlorine charges for Tests A and B are respectively 0.11 and 0.154. Some HCl was added to the mixture of chlorine dioxide and chlorite, giving a pH of 2.5 after 45 minutes reaction.

The chlorine dioxide treated and washed pulp samples A and B were then subjected to a mixture of chlorine and chlorine dioxide (ClO_2 substitution level of 15%).

Subsequently the pulps were extracted with caustic using the same standard conditions as for the experiments shown in Table 7. The results are shown in Table 9, with Tests A1 and A2, and B1 and B2 performed on the chlorine dioxide treated samples listed respectively as A and B in Table 8.

Test	Cl_2 charge (%)	Kappa number		Effluent AOX (kg/ton pulp)		NaOH charge (%)	Viscosity D/C/E (mPa)	Total AOX D+C+E (kg/ton)	Total chlorine charge factor D+C
		C	E	C	E				
A1	1.53	6.6	3.5	0.95	0.27	2.57	28.1	1.44	0.163
A2	1.05	8.1	3.7	0.44	0.17	2.31	27.5	0.83	0.147
B1	1.00	6.4	3.4	0.51	0.21	2.98	26.8	1.07	0.189
B2	0.70	7.6	3.8	0.38	0.13	2.82	26.4	0.86	0.178

Table 9. Effect of intrastage washing on organic chlorine formation

The results in Table 9 show that the total AOX production of less than 1.5 kg/o.d. ton pulp can be obtained with intrastage washing and different charge combinations of chlorine dioxide and chlorine in a C-W-C(D)-E bleaching sequence, while at the same time producing a well-delignified pulp after caustic extraction.

Effect of Instrastage Washing on Caustic Extraction

Because the total chlorine charge factor can be reduced significantly below the conventional value of 0.22 with intrastage washing (see Table 9), it is of interest to investigate whether a similar charge reduction can be realized for caustic in the extraction stage. The chlorinated and intrastage washed pulp was prepared as follows: first a ClO_2 charge of 1.20% (10% of which is converted to chlorite by addition of H_2O_2) for 30 minutes at 45°C, and the initial pH adjusted to 3.0; then intrastage washing followed by chlorination at a total active chlorine charge of 1.53% (ClO_2 substitution level of 20%), for 30 minutes at 45°C. In the subsequent extraction stage, the sodium hydroxide charge was varied from 0.586% to 2.57%. The other extraction conditions are: 70°C, 1 hour, 10% consistency. The kappa number after extraction, the AOX content in the extraction (E) filtrate and the final pH in the extraction stage are shown in Table 10.

NaOH (%)	Extracted Kappa no.	AOX	Final pH
0.586	4.9	0.39	10.1
0.84	4.3	0.40	11.1
1.285	3.9	0.42	11.8
1.80	3.7	0.42	12.0
2.57	3.6	0.25	12.3

Table 10. The effect of NaOH charge on E kappa number for chlorinated and intrastage washed pulp

It can be seen that the final pH is larger than 11 when the alkali charge is larger than or equal to 0.84%. It is of interest that the final pH is larger than 11 when the alkali charge is equal to 0.55 times the chlorination stage charge of 1.53%, as is recommended [14] for conventional chlorination. A final pH after 1 hour extraction above 11 is generally considered sufficient for efficient alkali extraction. It should also be noted that at an alkali charge of 2.57% (0.55 times the active chlorine charge of the "D" and "C" stages) the excess alkali results in significant dechlorination of the organic chlorine containing dissolved material in the E stage effluent. More importantly however, the present results show that with intrastage washing, a NaOH charge of 1.285% is sufficient to reach a kappa number after extraction of less than 4. This caustic charge should be compared to a charge of 3.47% which is recommended for extraction of the present 28.7 kappa pulp after a conventional chlorine bleaching stage (28.7 x 0.22 x 0.55 = 3.47%). For comparison, two conventional D/C E bleaching experiments were performed also with a caustic charge of 1.285%. In these tests, respectively, 1.53% and 3.16% (on pulp) of chlorine was added 1 minute after mixing the unbleached pulp with pure chlorine dioxide at a charge of 1.20% (on pulp). Then, after washing, both pulps were extracted with caustic soda at a charge of 1.285% but otherwise standard extraction conditions. The total active chlorine charge factors of these two tests are 0.163 and 0.22 respectively.

Test	Intrastage washing	Chlorine charge (%)	Total active chlorine charge factor	Kappa no. after E	Final pH in E
1	No	1.53	0.163	7.3	10.9
2	No	3.16	0.22	4.2	10.8
3	Yes	1.53	0.163	3.9	11.8

Chlorine dioxide charge: 1.20%; NaOH charge: 1.285%

Table 11. Comparison of intrastage washed and conventionally processed pulp

Comparison of the kappa number and final pH after caustic extraction of these two tests with the corresponding intrastage washing experiment in Table 11 shows that a caustic charge of 1.285% is insufficient for conventional bleaching. Therefore, by introducing a washing stage between the chlorine dioxide treatment and chlorine addition, a significant saving in caustic can be realized besides reducing the amount of AOX produced in the bleaching process.

Practical Implementation of Intrastage Washing

In the previous section it was shown that intrastage washing is beneficial both from the point of view of AOX reduction and chemical savings. However, the duration of the D stage in the intrastage washing experiments of 45 minutes requires the addition of another retention tower. In order to facilitate the industrial introduction of intrastage washing it is of interest to investigate whether the reaction time of the chlorine dioxide treatment before intrastage washing can be shortened.

At a chlorine dioxide charge of 1.20% on pulp, it was found that chlorine dioxide is completely consumed within 2 minutes (Chapter 4). This is in agreement with Histed et al (10) who found that ClO_2 is consumed within 2 minutes for an active chlorine charge factor of 0.19 and a ClO_2 substitution ratio of 50% at 30°C for a similar unbleached kraft pulp. However, a significant amount of residual chlorite still remains. Since chlorite is also an effective bleach chemical an intrastage washing operation at this point will result in a loss of potential delignification. Thus in order to shorten the D stage before intrastage washing, the conversion rate of chlorite to chlorine dioxide must be increased.

It is known that the rate of formation of chlorine dioxide from chlorite can be enhanced by increasing the acidity [11]. Shown in Figure 1 are the chlorite and chlorine dioxide concentrations during ClO_2 treatment of the standard kraft pulp without initial pH adjustment and with initial pH adjusted to 2.0 by addition of hydrochloric acid. It can be seen that chlorite is essentially consumed at about 30 and 10 minutes respectively

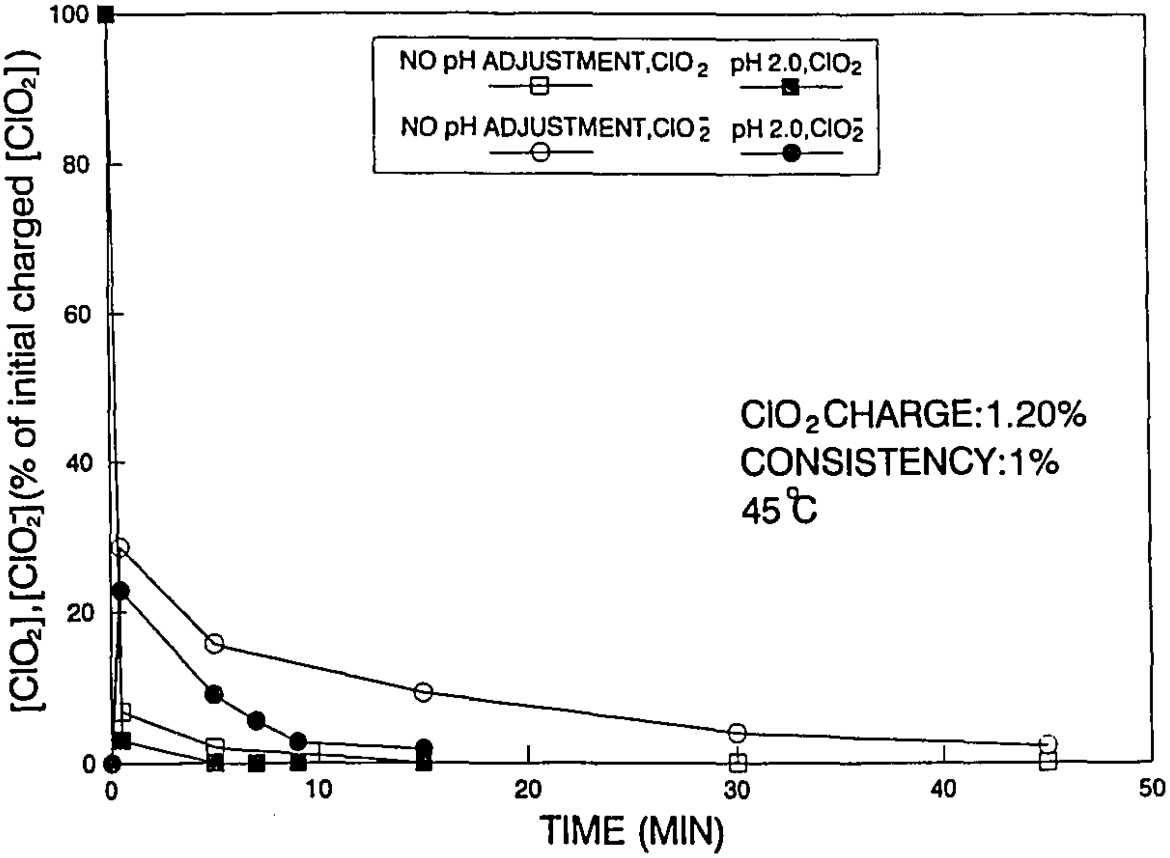

Figure 1. The development of residual ClO_2^- and ClO_2 in ClO_2 bleaching of kraft pulp at initial ClO_2 charge of 1.20% with and without pH adjustment.

without or with initial pH adjustment. This shows that the D-stage before intrastage washing can be shortened to about 10 minutes by initial acidification.

The development of the D kappa number and AOX formation during the D stage at an initial pH of 2 are shown in Figures 2 and 3 respectively. Also included are the corresponding values for the same pulp without pH adjustment after 45 minutes reaction. These results show that after 10 minutes at a pH of 2.0 the D kappa number and AOX formation have approached their respective plateau values, which are also close to the corresponding values obtained after 45 minutes without initial pH adjustment. Therefore, the benefits shown in the previous sections can also be obtained by performing the D stage in a retention leg (rather than a new tower) which provides a reaction time of about 10 minutes before the intrastage washing step. In practice, of course, one should use medium consistency operation for the D stage rather than the 1% consistency used in the present experiments.

ClO_2 Charge in the D Stage Before Intrastage Washing

In Chapter 7, it was found that chlorine dioxide essentially only attacks lignin with phenolic hydroxyl groups. Since a limited fraction of the lignin monomer units are free phenolic in nature, it is of interest to investigate the influence of the chlorine dioxide charge on the degree of delignification during ClO_2 bleaching before intrastage washing. The experiments are performed at 45°C and 1% consistency for 45 minutes on the standard unbleached kraft pulp. Sulfamic acid, a scavenger of hypochlorous acid, is mixed with the pulp suspension prior to addition of the ClO_2 solution because it is known that phenolic hydroxyl groups are formd when chlorine dioxide reaction intermediate hypochlorous acid reacts with non-phenolic lignin units. The development of the D kappa number versus ClO_2 charge in Figure 4 shows a breakpoint in the stoichiometric

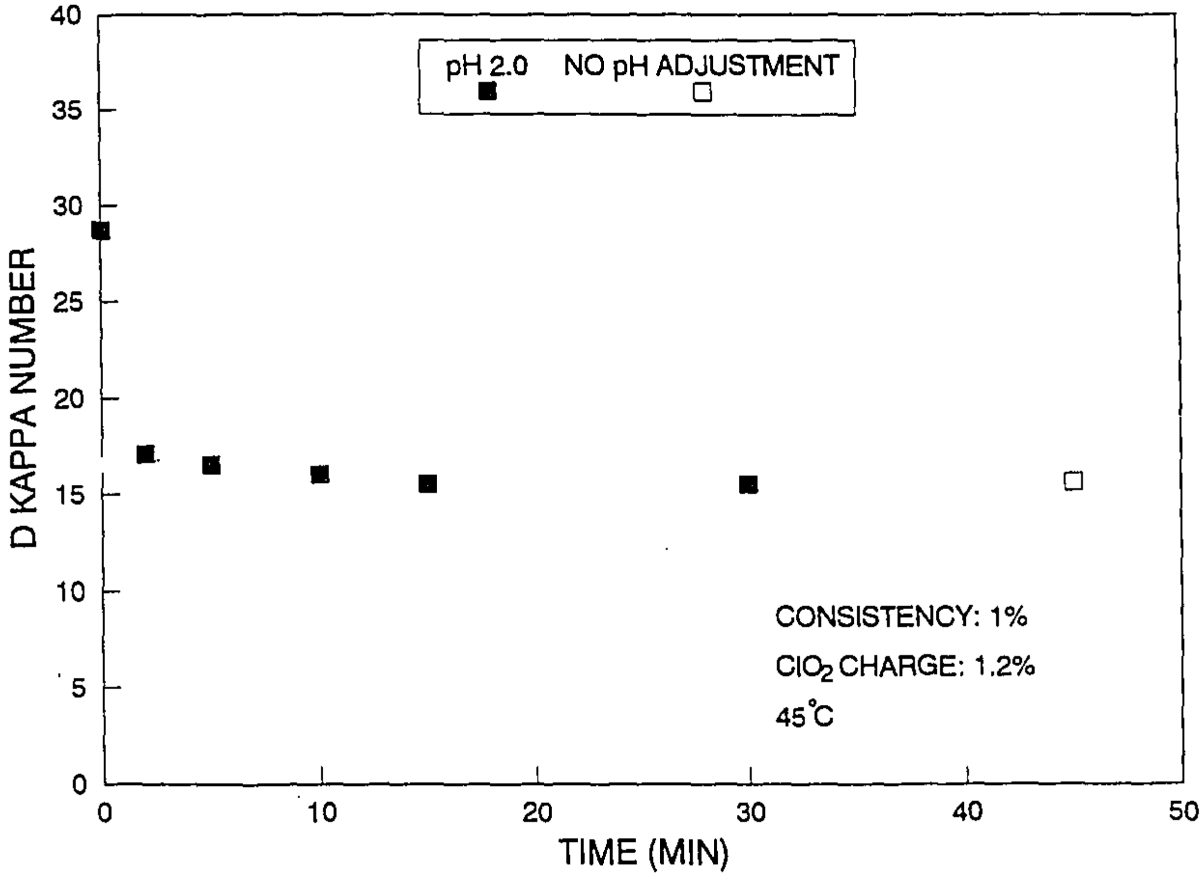

Figure 2. The development of the D kappa number in a D stage at an initial pH of 2.

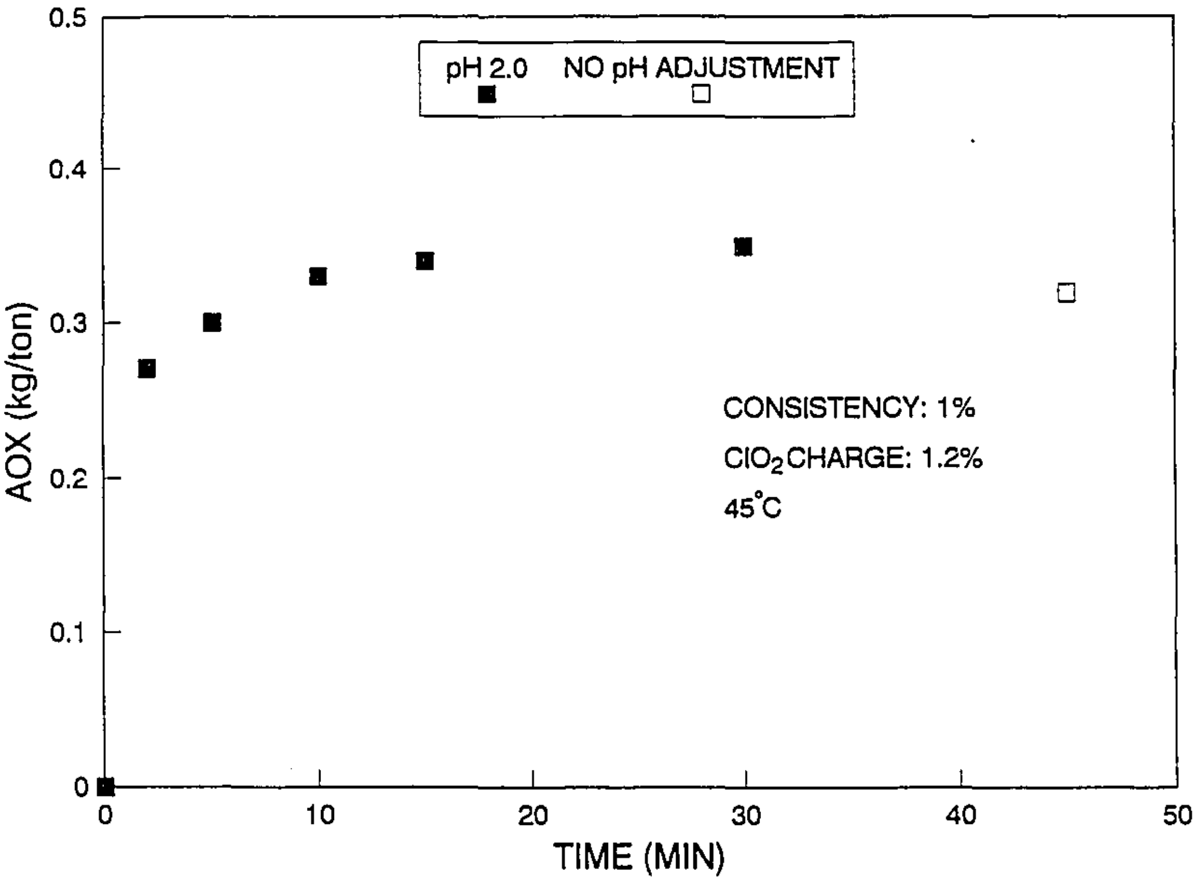

Figure 3. The development of AOX formation in a D stage at an initial pH of 2.

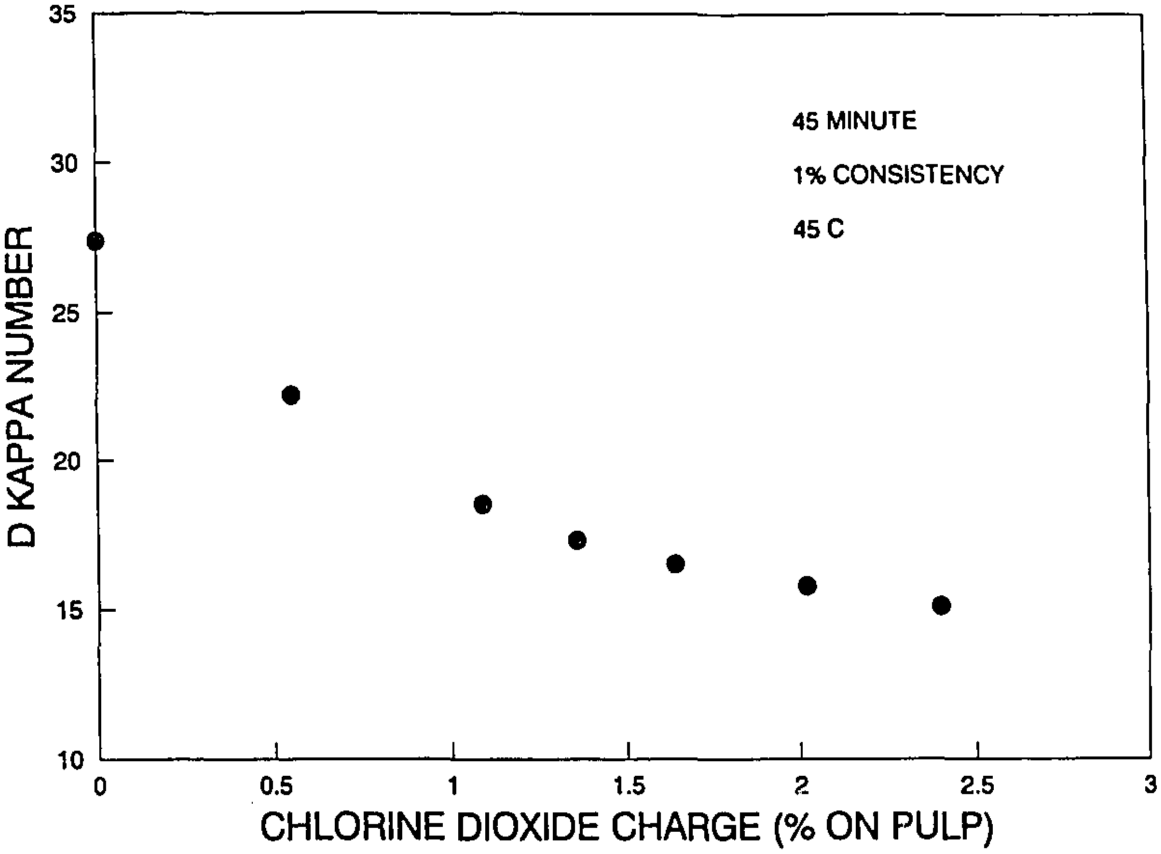

Figure 4. The effect of ClO_2 charge on D kappa number in D stage.

ratio of ClO_2 consumed per lignin removed at a ClO_2 charge of about 1.1 to 1.2% on pulp. For this particular pulp the transition point corresponds to a charge factor of about 0.11. Therefore, these results suggest that the intrastage washing is best performed after complete consumption of a pure chlorine dioxide charge equivalent to an active chlorine charge factor of 0.11. This is tested by comparing two particular instrastage washing sequences. In the first experiment (Test 1), 1.2% ClO_2 is charged in the D stage, followed by an intrastage washing step and then a C stage at a chlorine charge of 0.76% on pulp. In Test 2, almost the same total amount of ClO_2 is charged but now divided over two stages (D_1 and D_2). The two D stages are separated from each other by a C stage, also with a chlorine charge of 0.76% on pulp, and two intrastage washing stages. The other operating conditions are exactly the same in Test 1 and Test 2.

Test	D_1 stage			C stage			D_2 stage		
	ClO_2 charge (%)	AOX (kg/t)	kappa no.	Cl_2 charge (%)	kappa no.	AOX (kg/t)	ClO_2 charge (%)	AOX (kg/t)	kappa no.
1	1.20	0.31	15.9	0.76	10.3	0.53	—	—	—
2	0.76	0.20	19.8	0.76	13.9	0.50	0.39	0.20	10.3

D_1 conditions: 45°C, 1% consistency, 30 minutes,5% chlorite present
C conditions: 45°C, 1% consistency, ClO_2 substitution 20%, 30 min., active chlorine charge: 0.76%
D_2 conditions: 45°C, 1% consistency, 30 min., 5% chlorite present

Table 12. The effect of split ClO_2 charges on delignification and AOX formation

The results in Table 12 show that there is no improvement in terms of delignification or AOX formation when the ClO_2 charge is divided into two stages.

CONCLUSIONS

The formation of organic chlorine during the chlorination stage can be minimized by promoting the reaction between hypochlorous acid and chlorite during the treatment of pulp with chlorine dioxide, and by decreasing the concentration of dissolved lignin during the chlorine treatment of pulp. The former can be achieved by converting part of the chlorine dioxide to chlorite, while the latter is accomplished by introducing a washing stage between the sequential additions of chlorine dioxide and chlorine.

It was found that hydrogen peroxide can effectively convert chlorine dioxide to chlorite. For a typical unbleached kraft softwood pulp (kappa no. of about 30), H_2O_2 charge as low as 0.1% (on pulp) can reduce the AOX formation by about 25% while maintaining the same delignification as without H_2O_2 addition. The results also suggest that the addition of a small amount of hydrogen peroxide is very effective for elimination of chlorine from an industrial chlorine dioxide solution in order to reduce AOX formation.

The introduction of a washing step between the chlorine dioxide treatment and chlorine addition in a conventional D50C50 bleaching sequence leads to a reduction in AOX formation by a factor of nearly 3 while maintaining the same degree of delignification as conventional treatment. Other advantages of the introduction of this so called intrastage washing step are a reduction in the chlorine charge by a factor of about two and significant savings in the caustic requirement of the extraction stage. A pulp washer and a retention leg providing 10 minutes reaction time for the first chlorine dioxide treatment are needed for practical implementation of the intrastage washing technique in a conventional D/C E sequence.

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CHAPTER 9

CONCLUSIONS

GENERAL SUMMARY

This thesis is a fundamental study of chlorine dioxide bleaching of kraft pulp.

The transformation of chlorine dioxide to other chlorine species, such as chloride, hypochlorous acid, chlorite, chlorate, as well as organically bound chlorine in the pulp and bleach liquor was studied during ClO_2 prebleaching of kraft pulp. It was found that a major part of chlorine dioxide is rapidly converted to chlorite and hypochlorous acid when contacted with unbleached pulp. After the initial fast reaction, hypochlorous acid continues to be formed at a continuously decreasing rate. However, the actual hypochlorous acid concentration in the bleach liquor cannot be detected because of its immediate further reaction with lignin or chlorite. Organic chlorine and chloride are formed in the former case, while chlorine dioxide is regenerated in the latter with simultaneous formation of chloride and chlorate. After its initial rapid formation, chlorite is slowly decomposed in chloride and chlorine dioxide.

The total amount of organic chloride, defined as the sum of AOX in the bleach liquor and organically bound chlorine in the pulp, is formed in the first ten minutes of chlorine dioxide bleaching. This finding, as well as the rapid initial formation of chloride, suggests that all the organic chlorine is formed by an extremely fast reaction between chlorine dioxide and pulp. The increase in AOX content of the liquor during further bleaching can be explained by dissolution of the initially formed organic chlorine in the pulp. Approximately 85% of the total organic chlorine formation was shown to be associated with in-situ generated hypochlorous acid. Therefore, it is likely that all organic chlorine produced during chlorine dioxide bleaching of kraft pulp is formed by reaction between lignin and hypochlorous acid.

Chlorate formation during chlorine dioxide bleaching is mainly due to the reaction of two intermediates generated during chlorine dioxide bleaching, chlorite and hypochlorous acid. A theory which explains why more chlorate is formed with hypochlorous acid rather than with chlorine as reactant is presented which can explain the influence of process variables such as pH, chloride concentration, delay time between 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.

Chlorate formation is undesirable from both an economical and environmental point of view. It is proposed that the chlorate formation can be minimized by acidification of the bleach liquor, 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 sulfamic acid is added to the pulp suspension before ClO_2 addition.

A closed methoxyl group mass balance was obtained during the course of ClO_2 bleaching when the methoxyl content of unbleached kraft pulp was compared with methanol and methoxyl group containing organic material in the filtrate. The formation of methanol is called direct demethylation, while formation of the methoxyl group containing dissolved organic material is called indirect demethylation. Chlorine dioxide rather than the in-situ generated hypochlorous acid is mainly responsible for the demethylation of kraft lignin. Contrary to chlorine, which can demethylate both phenolic and non phenolic lignin, demethylation by ClO_2 under practical conditions is limited to lignin units possessing phenolic hydroxyl groups. The number of free phenolic methoxyl groups per 100 lignin monomer units decreases during ClO_2 treatment with sulfamic acid present from about 29 for unbleached kraft lignin to about 7 units after 1 minute treatment and 4 units after 2.5 hours of reaction. Without the presence of sulfamic acid, the reaction intermediate hypochlorous acid creates phenolic groups and, as a result, continued delignification can be achieved by applying more chlorine dioxide and by extending the reaction time. The methoxyl group removal rates by direct and indirect demethylation are proportional to each other, both resulting in delignification. The constant OCH_3 content of the residual lignin during ClO_2 treatment of softwood kraft pulp suggests that demethylation and delignification are closely related.

A modified delignification mechanism by chlorine dioxide was proposed for softwood kraft pulp based on experimental evidence showing that 1) only phenolic hydroxyl lignin structures are reactive towards ClO_2 at the practical bleaching conditions, 2) ClO_2 reacts with phenoxy ion structures rather than with the undissociated phenolic groups in lignin, 3) about 1 mole of chlorite is formed initially per mole of lignin monomer unit ultimately removed, 4) about 2 moles of hypochlorous acid are formed for each mole of lignin monomer unit removed and 5) demethylation and delignification are closely linked.

It is proposed that a phenolic lignin unit first dissociates to form a phenoxy anion, which is then attacked by the radical ClO_2 to form chlorite and the phenoxy radical. Two of the three more stable resonance structures of the phenoxy radical are subsequently attacked by chlorine dioxide to form chlorite esters, which are then hydrolyzed to form α-methoxy-*p*-quinone and muconic acid or muconic acid monomethyl ester type of structures. One mole of hypochlorous acid is formed during each hydrolysis. Both the muconic acid and muconic acid monomethyl ester type of structures are further attacked by ClO_2 and cleaved from the lignin polymer under formation of another mole of hypochlorous acid.

Finally, two techniques are evaluated to decrease the AOX formation in a bleach plant based on respectively the removal of hypochlorous acid by its reaction with chlorite, and on decreasing the dissolved lignin concentration. The former can be achieved either by mixing chlorite with pulp prior to the addition of chlorine dioxide or by converting part of chlorine dioxide to chlorite with hydrogen peroxide. The latter is accomplished by introducing a washing stage between the D and C stages.

Replacement of 30% of chlorine dioxide with chlorite can reduce AOX formation by about 25%. It was found that hydrogen peroxide quantitatively converts chlorine dioxide to chlorite. For a typical unbleached kraft softwood pulp (kappa no ~ 30), a peroxide addition of as low as 0.1% can reduce AOX formation by about 25% while the same degree of delignification during chlorine dioxide bleaching is maintained. It is also suggested that addition of a small amount of hydrogen peroxide is very effective for the quantitative removal of any chlorine present in chlorine dioxide solution in order to reduce the AOX formation.

By introducing a washing stage between the sequential additions of chlorine dioxide and chlorine in a conventional D50C50 bleaching sequence, the AOX formation can be reduced by a factor of nearly 3 while the same delignification degree is maintained. Thus, for a kraft softwood pulp with initial kappa no. of 28.7, a sequence involving ClO_2 treatment at a charge of 1.20% an initial pH of 2 and a reaction time of about 10 minutes at 45°C, followed by a so called intra stage washing step, then a chlorination stage with an active chlorine charge of 1.53% (ClO_2 substitution of about 15%) at 45°C for 45 minutes, and finally a caustic extraction at 70°C for an hour at a consistency of 10%, produces a well delignified pulp of kappa number of 3.5, with an AOX production of less than 1.5 kg/ton for the untreated combined ClO_2 treatment, chlorination and extraction effluent. The total active chlorine charge factor of the combined D and C stages is 0.163.

Finally, it is shown that the caustic requirement can significantly be reduced compared to conventional D/C E sequence when the intrastage washing technique is used.

CONTRIBUTIONS TO KNOWLEDGE

1. A complete chlorine mass balance was established throughout the chlorine dioxide treatment of softwood kraft pulp. Chlorine dioxide is transformed into chloride, hypochlorous acid, chlorite, chlorate as well as organically bound chlorine in the pulp and bleach liquor.
2. All organic chlorine, defined as the sum of AOX in the spent ClO_2 liquor and the organically bound chlorine in the ClO_2 treated pulp is formed within the first 10 minutes of reaction. Subsequently, the increase in AOX in solution is matched by an equivalent decrease of organically bound chlorine in the pulp. The organic chlorine during ClO_2 bleaching is mainly, if not all, formed from the reaction between lignin and hypochlorous acid.
3. Chlorate formation during chlorine dioxide bleaching is mainly due to the reaction of two intermediates generated during ClO_2 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.
4. 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 sulfamic acid.

5. There are direct and indirect demethylation reaction occurring during pulp ClO_2 bleaching. The methoxyl group removal by direct and indirect demethylation are proportional to each other. Demethylation and delignification are closely linked during ClO_2 bleaching. Chlorine dioxide rather than in-situ generated hypochlorous acid is mainly responsible for the demethylation.

6. A mechanistic basis has been provided for the long known facts that the delignification achieved by chlorine with substantial chlorine dioxide substitution is larger than that obtained by chlorine or chlorine dioxide alone, and that the delignification for the DC mode of addition always compares favourably the CD or C+D sequence at the same active chlorine charge.

7. It is shown that under practical operation conditions, the reaction between chlorine dioxide and non-phenolic lignin can be neglected compared to the reaction between chlorine dioxide and phenolic lignin.

8. For chlorine dioxide bleaching of softwood kraft pulp it has been found that about one mole of chlorite is formed initially per mole of lignin monomer unit ultimately removed, and that about two moles of hypochlorous acid are formed for each mole of lignin monomer unit removed during the bleaching process.

9. Based on the evidence in literature and the contributions 5, 7 and 8 a modified chlorine dioxide delignification mechanism for softwood kraft pulp is proposed.

10. The formation of organic chlorine during pulp ClO_2 bleaching can be decreased by promoting the reaction between hypochlorous acid and chlorite. This can be achieved either by mixing chlorite with pulp prior to the addition of chlorine

dioxide or by converting part of the chlorine dioxide to chlorite by addition of hydrogen peroxide.

11. The formation of organic chlorine during chlorination can be decreased by removing the lignin dissolved during chlorine dioxide treatment before the subsequent addition of chlorine. In practice this can be accomplished by introducing a washing stage between the D and C stages.

12. A novel bleach sequence is developed whereby ClO_2 and chlorine are added to a 30 kappa number kraft pulp at charges of respectively 1.20% and 1.53%, resulting in a kappa number of less than 4 after caustic extraction and with an AOX production of less than 1.5 kg/ton for the untreated combined chlorination and extraction effluent.

RECOMMENDATIONS AND SUGGESTIONS FOR FUTURE WORK

1. To study the stoichiometric relationships between hypochlorous acid and chlorite formation and the degradation of dimeric lignin model compounds when the latter are treated with chlorine dioxide in the presence of sulfamic acid.

2. To study the degradation of dimeric (or trimeric) lignin model compounds during chlorine dioxide treatment in the presence of sulfamic acid.

3. To develop a kinetic model which describes the disappearance of chlorine dioxide, the formation of chlorate and the lignin consumption with time during chlorine dioxide bleaching based on the inorganic and delignification reaction presented in this thesis.

4. To study the fundamentals of chlorine dioxide treatment of other pulps such as hardwood kraft pulp and ALCELL ® pulp.

5. To study the effect of intrastage washing on TCDD and TCDF formation.

6. To test the intrastage washing and H_2O_2 addition to ClO_2 technique on the AOX and dioxin formation in a commercial bleach plant.
7. To investigate whether the addition of just a sufficient amount of sulfamic acid can totally eliminate the formation or organic chlorine during the chlorine dioxide brightening bleaching stages. Then explore the viability of the sulfamic acid addition in a commercial bleach plant.