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REACTIONS OF CHLORINE (III) AND THEIR KINETICS IN THE CHLORINE DIOXIDE BLEACHING OF KRAFT PULPS

Doctoral Dissertation

Tuula Lehtimaa

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Abstract	
<p>The reactions of Cl(III) were investigated utilizing iodometric titration in combination with DMSO and EDTA to prevent undesired side reactions. Among a large group of suggested Cl(III) decomposition reactions, two reactions were found to be adequate to describe the Cl(III) decomposition in the absence of metals and HOCl. The rate parameters (k – rate coefficient, E_a – activation energy) were determined for these reactions.</p> <p>The reaction between Cl(III) and HOCl is known to start with the formation of a Cl₂O₂ intermediate. The Cl₂O₂ intermediate was found to be formed through both, hypochlorous acid and chlorine. The kinetic parameters were obtained for the reaction between chlorous acid and hypochlorous acid. The reaction rate between chlorine and chlorite was found to be restricted by the kinetics of the HOCl/Cl₂ equilibrium. The extremely fast Cl₂O₂ consuming reactions were identified among a group of suggested reactions and their relative rates were determined.</p> <p>Kinetic parameters were identified for several aldehydes with Cl(III). Aldehyde groups were shown to be present in kraft pulps and a considerable amount of aldehydes was found to be formed during chlorine dioxide bleaching. These aldehydes seemed to originate both from carbohydrates and lignin and the amount was dependent on the ClO₂ dosage used. According to the results obtained, it was concluded that the reaction between Cl(III) and aldehydes may contribute substantially to the overall Cl(III) consumption during chlorine dioxide bleaching.</p> <p>Chlorine dioxide prebleaching (D₀-stage) experiments were conducted to gain more knowledge of the rate of the different reactions and on the time-dependent behavior of various components. Kappa number reduction, hexenuronic acid depletion, chlorination and chlorine dioxide consumption were all found to be fast reactions, with almost everything occurring during the first minute of bleaching. Cl(III) was an exception. The amount of Cl(III) first increased rapidly and then decreased slowly.</p>	
Keywords	Chlorite, chlorous acid, chlorine dioxide, hypochlorous acid, bleaching
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<p>Cl(III):n reaktioita tutkittiin jodometrisen titrauksen avulla käyttäen DMSO:ta ja EDTA:ta estämään häiritsevien sivureaktioiden tapahtuminen. Useiden Cl(III):n itsehajoamiselle ehdotettujen reaktioiden joukosta löydettiin kaksi reaktiota, jotka riittivät kuvaamaan Cl(III):n itsehajoamista metallien ja HOCl:n poissa ollessa. Nopeusparametrit (k – nopeusvakio, E_a – aktivoitumisenergia) määritettiin näille reaktioille.</p> <p>Cl(III):n ja HOCl:n välisen reaktion tiedetään alkavan Cl₂O₂ välituotteen muodostumisella. Cl₂O₂ välituotteen havaittiin muodostuvan sekä alikloorihapokkeen että kloorin kautta. Nopeusparametrit määritettiin kloorihapokkeen ja alikloorihapokkeen väliselle reaktiolle. HOCl-Cl₂ tasapainon todettiin rajoittavan kloorin ja kloriitin välisen reaktion nopeutta. Kirjallisuudessa ehdotettujen erittäin nopeiden Cl₂O₂:ta kuluttavien reaktioiden joukosta identifioitiin oleelliset reaktiot ja niiden suhteelliset nopeudet määritettiin.</p> <p>Useiden aldehydien reaktioille Cl(III):n kanssa määritettiin nopeusparametrit. Sulfaattisellujen todettiin sisältävän aldehydyryhmiä ja niitä havaittiin syntyvän huomattavia määriä lisää klooridioksidivalkaisussa. Nämä aldehydit olivat ilmeisesti peräisin sekä hiilihydraateista että ligniinistä ja niiden määrä riippui käytetystä ClO₂ annoksesta. Saatujen tulosten perusteella pääteltiin, että Cl(III):n ja aldehydien välinen reaktio voi olla huomattavissa määrin vastuussa Cl(III):n kulutuksesta klooridioksidivalkaisussa.</p> <p>Klooridioksidilla suoritettiin esivalkaisukokeita (D₀-vaihe), jotta saataisiin lisää tietoa eri reaktioiden nopeuksista sekä eri komponenttien käyttäytymisestä ajan funktiona. Kappaluvun lasku, heksenuronihapon kulutus, kloorautuminen sekä klooridioksidin kulutus olivat kaikki nopeita reaktioita. Niissä tapahtui suurin muutos valkaisu ensimmäisen minuutin aikana. Cl(III) oli poikkeus. Sen määrä ensin kasvoi nopeasti, minkä jälkeen se kului hitaasti.</p>			
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PREFACE

This study was carried out in the Department of Forest Products Technology at the Helsinki University of Technology during 2004-2010. The financial support from several institutes and companies – the Finnish Funding Agency for Technology and Innovation (TEKES), Andritz, Arkema, CTS-ÅF, Kemira, Metsä Botnia, Pöyry, Stora Enso, VTT and Forestcluster Ltd – is gratefully appreciated.

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My loving thanks go to my husband Pasi for his love and belief in me during these years. Warm thanks also to the other members of my family for their endless support.

Vantaa, May 10th, 2010

Tuula Lehtimaa

LIST OF PUBLICATIONS

This thesis is based on the results presented in six publications that are referred to by Roman numerals in the text.

- Paper I** Lehtimaa, T., Tarvo, V., Mortha, G., Kuitunen, S., Vuorinen, T., Reactions and Kinetics of Cl(III) Decomposition *Ind. Eng. Chem. Res.* **2008**, *47* (15), 5284–5290
- Paper II** Tarvo, V., Lehtimaa, T., Kuitunen, S., Alopaeus, V., Vuorinen, T., Aittamaa, J., The Kinetics and Stoichiometry of the Reaction between Hypochlorous Acid and Chlorous acid in Mildly Acidic Solutions. *Ind. Eng. Chem. Res.* **2009**, *48* (13), 6280–6286
- Paper III** Lehtimaa, T., Kuitunen, S., Tarvo, V., Vuorinen, T., Kinetics of aldehyde oxidation by chlorous acid. *Ind. Eng. Chem. Res.* **2010**, *49* (6), 2688-2693
- Paper IV** Lehtimaa, T., Kuitunen, S., Tarvo, V., Vuorinen, T., Reactions of aldehydes with Cl(III) in Chlorine Dioxide Bleaching. Accepted for publication in *Holzforsch.* **2010**
- Paper V** Lehtimaa, T., Tarvo, V., Kuitunen, S., Jääskeläinen, A.-S., Vuorinen, T., The effect of process variables in chlorine dioxide prebleaching of birch kraft pulp. Part 1. Inorganic chlorine compounds, kappa number, lignin and hexenuronic acid content. *J. Wood Chem. Technol.* **2010**, *30* (1), 1-18
- Paper VI** Lehtimaa, T., Tarvo, V., Kuitunen, S., Jääskeläinen, A.-S., Vuorinen, T., The effect of process variables in chlorine dioxide prebleaching of birch kraft pulp. Part 2. AOX and OX formation. *J. Wood Chem. Technol.* **2010**, *30* (1), 19-30

Author's contribution to the appended joint publications:

- I** Tuula Lehtimaa was mainly responsible for the experimental design, performed the majority of the experimental work, partly analyzed the results, and wrote main part of the manuscript.
- II** Tuula Lehtimaa was partly responsible for the experimental design, performed part of the experimental work, and wrote parts of the manuscript.
- III** Tuula Lehtimaa was responsible for the experimental design, performed part of the experimental work, analyzed the results, and wrote the manuscript.
- IV** Tuula Lehtimaa planned the experiments, conducted parts of the experiments, analyzed the results, and wrote the manuscript.
- V-VI** Tuula Lehtimaa planned the experiments with the co-authors, performed parts of the experimental work, analyzed the results, and wrote the manuscripts.

LIST OF ABBREVIATIONS

Act. Cl/Adt	Active chlorine / tonne of air dry pulp
AOX	Adsorbable organic halogens
A-Stage	Acid hydrolysis stage
DMSO	Dimethylsulfoxide
ECF-bleaching	Elemental chlorine free bleaching
EDTA	Ethylenediaminetetraacetic acid
HexA	Hexenuronic acid
OX	Organically bound halogens

TABLE OF CONTENTS

PREFACE.....	i
LIST OF PUBLICATIONS.....	ii
LIST OF ABBREVIATIONS	iii
1 INTRODUCTION.....	1
1.1 Chemistry of chlorine dioxide bleaching.....	2
1.2 Modeling of chlorine dioxide bleaching.....	3
2 OBJECTIVES AND OUTLINE OF THE STUDY	5
3 EXPERIMENTAL	6
3.1 Inorganic reactions of Cl(III).....	6
3.2 Organic reactions of Cl(III)	6
3.3 Pulp treatments with Cl(III).....	7
3.4 Chlorine dioxide bleaching.....	8
3.5 Calculation of kinetic parameters	9
4 RESULTS AND DISCUSSION	10
4.1 Self-decomposition of Cl(III)	10
4.1.1 Effect of metals.....	11
4.1.2 Cl(III) decomposition in the absence of metals.....	12
4.1.3 Kinetics of Cl(III) decomposition in absence of metals	15
4.2 Reaction of Cl(III) with HOCl.....	16
4.2.1 Testing of reported reaction models	17
4.2.2 Reaction stoichiometry and kinetic parameters	18
4.3 Reaction of Cl(III) with aldehydes	22
4.3.1 Monomeric aldehydes.....	22
4.3.2 Aldehyde groups in pulp.....	26
4.3.3 Practical significance in chlorine dioxide bleaching	28
4.4 Chlorine dioxide bleaching.....	29
4.4.1 Kappa number and hexenuronic acid content.....	29
4.4.2 Chlorination of organic structures	32
4.4.3 Inorganic chlorine compounds.....	37
5 CONCLUDING REMARKS	42
6 REFERENCES.....	43

1 INTRODUCTION

Chlorine dioxide is the most utilized chemical in pulp bleaching. The first mills started to use chlorine dioxide as early as 1945 and it replaced chlorine as the most common bleaching chemical in the production of chemical pulp at the end of the 1980s [Sixta et al. 2006]. Nowadays at least 75 % of all bleached chemical pulp produced in the world is bleached with chlorine dioxide [Hamzeh et al. 2007]. In addition to pulp bleaching, chlorine dioxide is also used in many other applications such as water treatment, textile bleaching, bleaching of some food products (flour, fats, sugar) and as a disinfectant agent [Masschelein 1979, Katz and Narkis 2001].

Chlorine dioxide has a much smaller environmental impact than chlorine since ClO_2 forms considerably less chlorinated organic compounds than Cl_2 does. It has been stated that the formation of chlorinated organics was reduced by 80 % when chlorine was replaced by chlorine dioxide [Germgård and Larsson 1983, Lachenal et al. 1998, Sixta et al. 2006]. In addition, the use of chlorine dioxide has totally eliminated the formation of the most harmful polychlorinated organic compounds [Bright et al. 2000, Sixta et al. 2006]. Even though the environmental aspects of chlorine dioxide bleaching have lately been an issue in the media, ECF bleaching is still considered the best available technology (BAT) in pulp production [European IPPC Bureau, BREF (12.2001)]. Thus chlorine dioxide is recommended to be used in all new and old kraft pulp bleaching plants.

Although the chemistry of chlorine dioxide bleaching has been a research subject for over three decades, the chemistry that takes place in chlorine dioxide bleaching is not yet fully understood. In particular the kinetics of the individual reactions has not been studied to any large extent. This information is required in order to be able to understand which reactions have significance in chlorine dioxide bleaching and which are too slow to be important. In addition, the information on the reactions of different inorganic chlorine compounds formed in chlorine dioxide bleaching is, in part, inconsistent and indefinite.

1.1 Chemistry of chlorine dioxide bleaching

Chlorine dioxide bleaching involves a complex mixture of organic and inorganic compounds. These compounds react with each other in numerous ways making the chemistry of chlorine dioxide bleaching difficult to investigate and understand.

Chlorine dioxide bleaching starts with a fast reaction between chlorine dioxide (ClO_2) and phenolic lignin structures [Lindgren 1971, Hoigné and Bader 1994]. This reaction produces chlorite (ClO_2^-) and hypochlorous acid (HOCl) in a molar ratio 1:1 [Kolar et al. 1983]. These compounds can react together very rapidly forming an intermediate Cl_2O_2 , which reacts further forming chlorate and chlorine dioxide [Taube and Dodgen 1949, Kieffer and Gordon 1968a, Schmitz and Rooze 1981, Peintler et al. 1990, Nicoson and Margerum 2002, Horváth et al. 2003]. The chlorite formed can also self-decompose in acidic conditions and form hypochlorous acid and chlorate (ClO_3^-) [Hong and Rapson 1968, Kieffer and Gordon 1968a, Downs and Adams 1973, Horváth et al. 2003, Taube and Dodgen 1949]. Hypochlorous acid is in equilibrium with chlorine (Cl_2) [Kolar et al. 1983, Deborde and von Gunten 2008]. Both of these species (HOCl and Cl_2) are able to oxidize and chlorinate various organic structures [Gierer 1986], resulting in chlorinated organic compounds that can be harmful for the environment [de la Mare et al 1954, Brage et al 1991b, Joncourt et al. 2000]. Figure 1 presents a simplified scheme of the reactions taking place in chlorine dioxide bleaching.

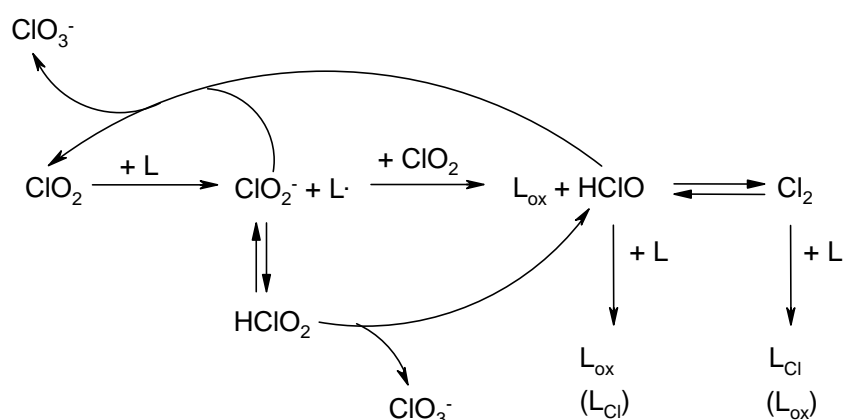


Figure 1. A simplified scheme of the reactions in chlorine dioxide bleaching. L = lignin, $L\cdot$ = lignin radical, L_{ox} = oxidized lignin and L_{Cl} = chlorinated lignin

In reality, carbohydrates, hexenuronic acid, extractives and non-process elements also contribute to the reactions of various chlorine compounds. In addition, the reactions are affected by the heterogeneous nature of lignin. Lignin is a complex netpolymer containing various functional groups that can react in different ways during ClO₂ bleaching. The different oxidation products of lignin are numerous as are their further reactions with different chlorine species during ClO₂ bleaching.

1.2 Modeling of chlorine dioxide bleaching

Several approaches have been utilized in previous chlorine dioxide bleaching models. Since this work was conducted as a part of a project where a phenomenon-based model for pulp bleaching was developed, modeling is discussed briefly in this chapter.

So far most models of chlorine dioxide bleaching have been based on correlations to predict the kappa number development [Germgård 1982b, Savoie and Tessier 1997, Chandranupap and Nguyen 2000, Barroca et al. 2001, Tessier and Savoie 1997]. An extended version by Mortha et al. [2001] is capable of predicting the development of pH and the concentration of different inorganic chlorine species in addition to the kappa number. The advantage of these models is their easy usability and that they give some information on how changes in process conditions affect the resulting kappa number. However, due to their simple nature, the models are usable only in very restricted conditions. The models are also rather case-sensitive, meaning that they are valid only for the pulp and mill that they were designed for.

A more advanced model has been reported by Gu and Edwards [2003]. It includes several chemical reactions of chlorine dioxide and chlorine with different organic pseudo-compounds either in the pulp or in the surrounding liquor. Yet the reactions are very limited in number and the effects of diffusion and two separate liquid phases are excluded. The model also involves some inorganic reactions but their stoichiometries and rates are fitted to give the desired outcome disregarding the reactions and kinetics that have been reported in literature. Thus, although possessing a better ability than the previous models to predict different parameters in bleaching, the model is still rather simplified.

In our approach the real chemistry and other essential phenomena taking place in chlorine dioxide bleaching are implemented in the model at molecular level. This approach means that the various reactions taking place in bleaching need to be included in the model in a much more comprehensive and accurate manner than in any of the previous bleaching models [Tarvo et al. 2008, Tarvo et al 2010]. When considering the complexity of chlorine dioxide bleaching it may be understood that, in order to obtain a good prediction, the model must include a large number of reactions that are chosen carefully to make sure that they really are the most relevant for chlorine dioxide bleaching conditions.

2 OBJECTIVES AND OUTLINE OF THE STUDY

This work consists of several attempts to resolve further the role of different inorganic chlorine compounds, especially of Cl(III), in chlorine dioxide bleaching. Because it is not a delignifying or bleaching agent as such, the reactions of Cl(III) have only been considered in rather general terms so far. However, Cl(III) reacts in chlorine dioxide bleaching with various organic and inorganic structures and compounds, resulting in the formation of various chlorine compounds, including the very reactive hypochlorous acid.

This work was realized as a part of a project, which aimed at developing a phenomenon-based molecular level computer model for pulp bleaching. The model describes quantitatively the reactions of various inorganic chlorine compounds and includes a very extensive library of the reactions between these inorganic chlorine compounds and pseudo-lignin and carbohydrate structures [Tarvo et al 2010]. During this project an extensive amount of literature was surveyed and the information found was implemented in the model. The research work reported here has been conducted to fill the gaps of knowledge in the literature or to solve topics that have been reported in conflicting ways. The main objective of this thesis was to clarify the reactions of Cl(III) and their relative importance in chlorine dioxide bleaching.

3 EXPERIMENTAL

3.1 Inorganic reactions of Cl(III)

The experiments on the self-decomposition of Cl(III) (Paper I) and its reaction with HOCl (Paper II) were carried out in a double wall, thermostated 200 ml glass reactor equipped with a Teflon lid. A magnetic stirrer was used for mixing. In Paper I the reaction medium included DMSO and EDTA to prevent hypochlorous acid and metal ions from causing undesired side reactions. Sampling from the reactor was conducted with a glass pipette at selected time intervals. In Paper II the samples withdrawn were treated immediately with DMSO to terminate the reaction (immediate trapping of residual HOCl) and to prevent hypochlorous acid from interfering with the titration. The amounts of residual chlorine compounds were determined by iodometric titration as described by Wartiovaara [1982]. The measurement uncertainty of the titration was estimated to be $\pm 8 \times 10^{-2}$ mM for chlorine dioxide and $\pm 2 \times 10^{-2}$ mM for both chlorite and chlorate.

3.2 Organic reactions of Cl(III)

The treatment of organic compounds with Cl(III) (Papers III and IV) was carried out with the same equipment as described above for the inorganic reactions of Cl(III). In these experiments also the reaction medium included DMSO and EDTA to prevent undesired side reactions with hypochlorous acid and metal ions. The organic compounds studied were formaldehyde, acetone, 4-ethylguaiacol, vanillin, veratraldehyde, benzaldehyde, D-glucose, glycolaldehyde, 5-formyl-2-furancarboxylic acid and 2,4,6-trimethylphenol (Figure 2). The residual Cl(III) concentration was determined by iodometric titration as described by Wartiovaara [1982]. The measurement uncertainty of the titration was estimated to be $\pm 2 \times 10^{-2}$ mM.

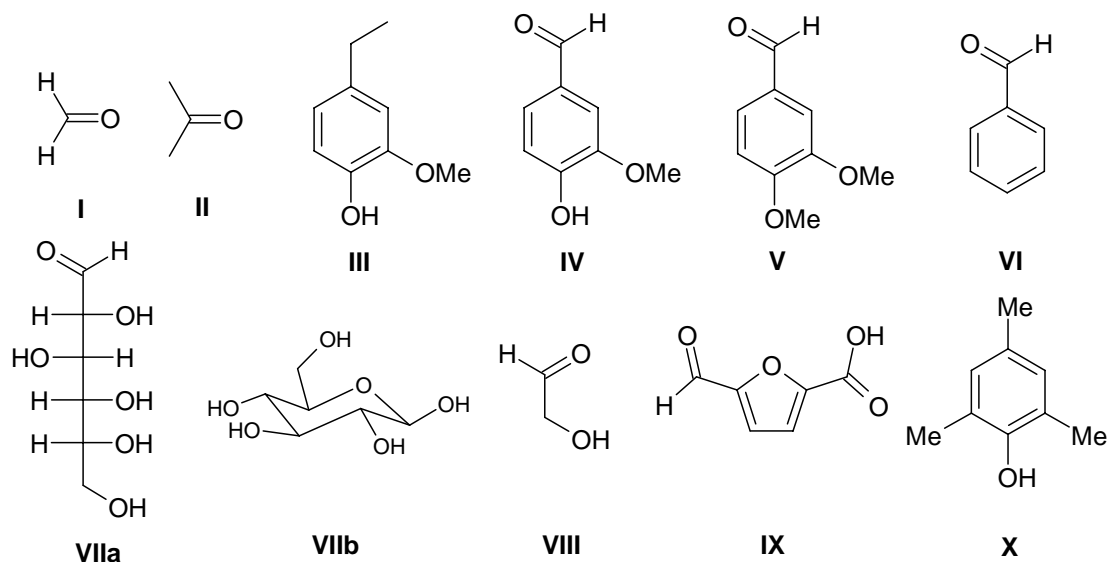


Figure 2. The structures of I. formaldehyde, II. acetone, III. ethylguaiacol, IV. vanillin, V. veratraldehyde, VI. benzaldehyde, VII. glucose in the aldehyde form (a) and cyclic form (b), VIII. glycolaldehyde, IX. 5-formyl-2-furancarboxylic acid and X. 2,4,6-trimethylphenol.

3.3 Pulp treatments with Cl(III)

The pulps used in the Cl(III) experiments (Paper IV) were obtained from Finnish pulp mills. Prior to the experiments some of the pulps were bleached with varying chlorine dioxide dosages using 20 g o.d. pulp in plastic bags at 11% pulp consistency at 50°C. After bleaching, the pulps were immersed in an ice water bath to stop all reactions. Then they were washed with de-ionized water and homogenized. The kappa numbers of the pulps were determined according to standard SCAN-C 1:00.

The reactivity of the pulps with Cl(III) was tested as described in chapter 3.2 for organic compounds. The pulp consistency of the reaction medium was 1 % and included 12 mM DMSO and 0.2 mM EDTA to prevent undesired side reactions.

3.4 Chlorine dioxide bleaching

The oxygen-delignified kraft pulp used (Papers V and VI) was obtained from a Finnish pulp mill producing fully bleached birch pulp. The pulp was subjected to chlorine dioxide bleaching using different chlorine dioxide dosages (15, 20, and 30 kg act. Cl/Adt) at 10 % pulp consistency in plastic bags. In addition, the effect of an acidic treatment (A-stage) prior to chlorine dioxide bleaching was tested with a dosage of 20 kg act. Cl/Adt. The A-stage was performed in a plastic bag at 90°C, pH 2.5 and 11% pulp consistency for three hours. The pulp was not washed before the following chlorine dioxide stage in order to simulate the carryover of reaction products from the A-stage to the D₀-stage. For each series 1-, 5-, 10-, 20-, and 30-minute reaction times were carried out in separate batches.

After bleaching, the pulp was immersed in an ice water bath to terminate all reactions. The pulp was then washed with de-ionized water and homogenized. The kappa number was determined according to standard SCAN-C 1:00. The aromatic lignin and hexenuronic acid (HexA) contents were determined using UV resonance Raman (UVR) spectroscopy as described by Jääskeläinen et al. [2005]. The measurement uncertainty of this method for these samples was calculated to be ± 1.7 meq/kg for HexA and ± 4 % for the removal of aromatic lignin. The phenolic lignin content of the pulp was measured according to Warsta et al. [2006]. The measurement uncertainty of this method was calculated to be 0.3 mmol/kg pulp for the analyzed sample.

The amount of organically bound chlorine in the filtrate (AOX) and pulp (OX) was measured with an AOX-analyzer (Thermo Electron, Dextar) as described in standards SFS-EN 1485 and SCAN-CM 52:94, respectively. The concentrations of chlorine dioxide, chlorite + chlorous acid (Cl(III)), and chlorate in the filtrate were determined by iodometric titration according to Wartiovaara [1982] (the measurement uncertainty was ± 0.08 mM for chlorine dioxide and ± 0.02 mM for chlorite and chlorate). The amount of chloride was measured by ion chromatography (Dionex ICS-1500) according to SFS-EN ISO 10304-4.

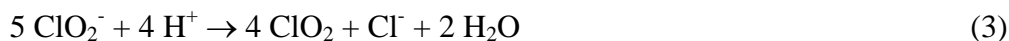
3.5 Calculation of kinetic parameters

The kinetic parameters (Papers I-III) were optimized using KinFit software [Jakobsson and Aittamaa 2009a]. The Levenberg-Marquardt method [Press et al. 1989] was applied with uniform weighting. In Papers I and III the rate coefficients (k) and their temperature dependencies (E_a – energy of activation) were fitted against the Cl(III) concentration data recorded in the experiments. In Paper II the observed time dependencies of the concentrations of chlorine dioxide and chlorate were utilized in addition to the Cl(III) concentration data. Confidence limits of 95 % were obtained from a statistical analysis using Student T -distribution. Computational repetitions of the laboratory experiments were carried out with Flowbat software [Jakobsson and Aittamaa 2009b].

4 RESULTS AND DISCUSSION

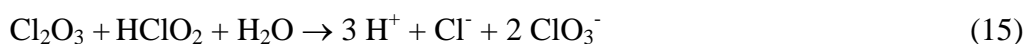
4.1 Self-decomposition of Cl(III)

In an aqueous solution chlorite is in equilibrium with its acidic form, chlorous acid (HClO_2) according to Reaction 1. Together they form the total amount of chlorine (III) [Gordon et al. 1972]. The K_a value of this equilibrium has been reported to be (at room temperature) 1.1×10^{-2} M [Gordon et al. 1972, Downs and Adams 1973]. Several papers have been published on the self-decomposition of Cl(III). It is evident that the numerous reactions are complex and involve many different inorganic chlorine compounds [Emmenegger and Gordon 1967, Gordon et al. 1972, Aieta and Roberts 1986, Peintler et al. 1990, Ni et al. 1993b]. The literature published so far gives conflicting information on the kinetics as well as on the reactions included in the decomposition of chlorite. Sometimes the decomposition of Cl(III) is referred to as net reactions such as those presented in Reactions 2-4 [Gordon et al. 1972, Downs and Adams 1973, Ni et al. 1992, Deshwal et al. 2004]. However, these net reactions, producing chlorine dioxide and chlorate, are composed of a series of elementary reactions [Taube and Dodgen 1949, Hong and Rapson 1968, Kieffer and Gordon 1968a, Kieffer and Gordon 1968b]. In addition to the initial Cl(III) decomposition, they include several follow-up reactions of the formed reactive species. The stoichiometries of the subsequent reactions are dependent on the reaction conditions and therefore Reactions 2-4 do not describe the decomposition properly other than for the conditions in which they were defined.



Only a limited number of studies have been carried out on the decomposition of Cl(III) in the absence of the reactive intermediates that are formed during the decomposition. [Hong and Rapson 1968, Kieffer and Gordon 1968a, Schmitz and Rooze 1981, Horváth et al 2003]. At least the following reaction routes (Reactions 5-15) have been postulated to be involved in the decomposition of Cl(III) without the participation of intermediate components [Taube and Dodgen 1949, Hong and Rapson 1968, Kieffer and Gordon 1968a,

Kieffer and Gordon 1968b, Downs and Adams 1973, Schmitz and Rooze 1981, Horváth et al. 2003].



In our experiments DMSO was used to trap the intermediately formed hypochlorous acid and chlorine. Thus their participation in the reactions was prevented which made the monitoring of the pure self-decomposition of Cl(III) possible. The results presented in this chapter can be found in Paper I.

4.1.1 Effect of metals

The disproportionation of Cl(III) has been reported to be fastest at pH 2-3 and extremely slow at pH 4 [Kieffer and Gordon 1968b]. This trend differs from our observations when chelation was used to trap the metal ions present in the reagents as impurities. However, when these metal ions were not trapped with EDTA, the maximum reaction rate was indeed seen at pH 2. Chlorine dioxide formation was also apparent in this case. At pH 1 and 3.5 the decomposition rate was practically unaffected by chelation. This indicates that the presence of metal ions has a significant effect only at around pH 2.

The catalyzing effect of Fe^{3+} ions on the self-decomposition of Cl(III) was discovered over three decades ago [Ondrus and Gordon 1972]. It has been reported that the rate of the Fe^{3+} ion catalyzed reaction increases with increasing pH in the pH range of 0.3-2.5 [Ondrus and

Gordon 1972, Fábíán and Gordon 1991b, Fábíán and van Eldik 1993, Fábíán 2001, Wang et al. 2004] and that the catalyzed reaction is about 500 times faster than uncatalyzed self-decomposition. The effect of Fe^{3+} ions is not seen at higher pH values due to their hydroxylation and the formation of polynuclear iron compounds [Fábíán and Gordon 1991a, Fábíán and Gordon 1991b].

4.1.2 Cl(III) decomposition in the absence of metals

When EDTA was used to prevent the possible catalysis of metal ions, chlorine dioxide was not formed in the decomposition of Cl(III) in the presence of DMSO. Without DMSO, chlorine dioxide formation was apparent. Since DMSO traps hypochlorous acid and elemental chlorine, blocking their further reactions [Imazuimi et al. 1995, Lachenal et al. 1998, Yoon and Wang 2002], chlorine dioxide formation must involve the intermediately formed HOCl. Since chlorine dioxide formation was not observed in the presence of excess DMSO, it can be concluded that chlorine dioxide is not a product of the pure decomposition of chlorous acid or chlorite. Thus hypochlorous acid, chlorate and chloride are the only possible stable chlorine containing products originating from Cl(III) self-decomposition. This leads to the conclusion that Reactions 2 and 3 are not valid as such. Also the formation of the Cl_2O_2 intermediate through Reactions 12+14 can be considered irrelevant since Cl_2O_2 is known to produce chlorine dioxide in its follow-up reactions [Peintler et al. 1990, Nicoson and Margerum 2002, Horváth et al. 2003].

The decomposition rate of Cl(III) decreased rapidly as the pH increased from 1 to 3 (Figure 3). Neutral Cl(III) solutions are known to be practically stable [Gordon et al. 1972]. As the pK_a value of HClO_2 (Reaction 1) is 2.0 [Gordon et al. 1972, Downs and Adams 1973], at pH 3 over 90 % of Cl(III) is present as chlorite. Reaction 6 would require the decomposition of Cl(III) to occur at all pH levels where both chlorous acid and chlorite are present in considerable quantities. However, the decomposition rate was practically negligible even at pH 3. Thus it was concluded that chlorous acid is responsible for the decomposition of Cl(III) while chlorite is stable and that Reaction 6 can be disregarded.

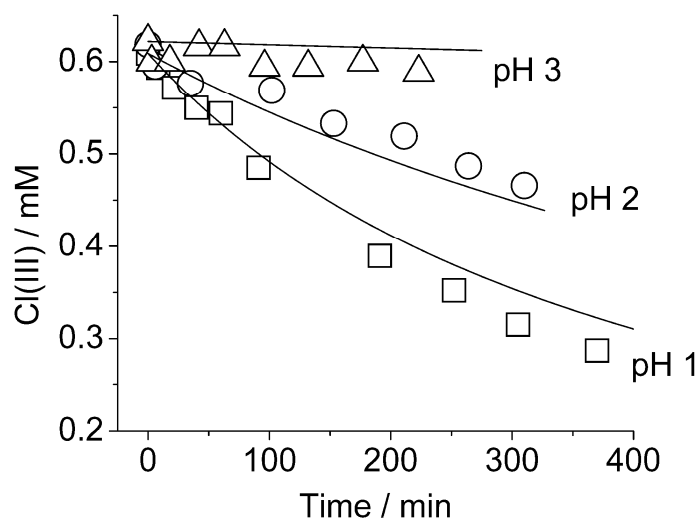


Figure 3. The decomposition of Cl(III) as a function of time at 60°C at pH 1 (□), pH 2 (○) and pH 3 (Δ) with $[Cl(III)]_0 = 0.6$ mM, $[DMSO]_0 = 12$ mM, $[NaCl]_0 = 5.16$ mM, and $[EDTA]_0 = 10$ mM. The lines show the prediction with the rate parameters obtained.

Chlorate formation was observed in all the experiments where Cl(III) decomposition occurred (Figure 4). Lowering the pH from 2 to 1 increased chlorate formation. However, the increase was not as substantial as the increase in Cl(III) decomposition. Reaction 5 has been suggested to depict the self-decomposition of Cl(III) in the absence of chloride ions [Hong and Rapson 1968, Kieffer and Gordon 1968a, Downs and Adams 1973, Taube and Dodgen 1949]. Our experimental results support this route; the chlorate formation corresponded to the stoichiometry of Reaction 5. Reaction 4 was considered inappropriate because it predicts more chlorate to be formed than what was observed. Reactions 12 and 13 are kinetically and by stoichiometry equivalent to Reaction 5. On the basis of the results obtained, the possible role of the Cl_2O_3 intermediate cannot be commented upon. Thus it is only stated that if these very fast intermediate reactions are left out of consideration, the decomposition of Cl(III) in the absence of chloride ions can be represented with Reaction 5.

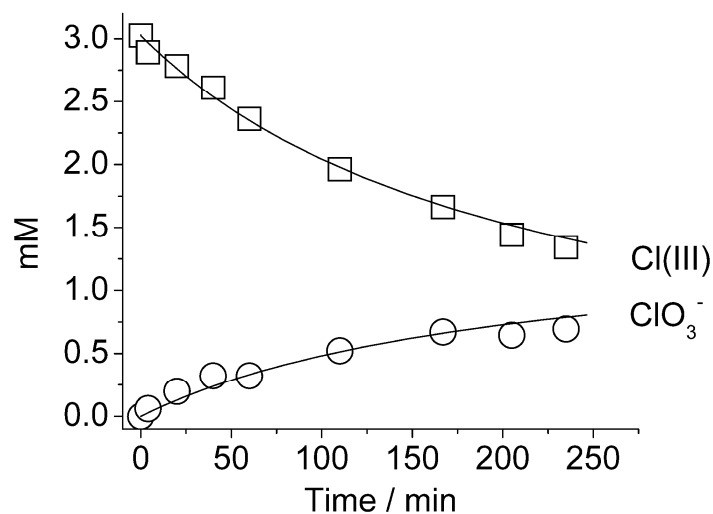


Figure 4. Conversion of Cl(III) (\square) to chlorate (ClO_3^-) (\circ) as a function of time with $[\text{Cl(III)}]_0 = 3.0 \text{ mM}$ in the presence of DMSO ($c_0 = 0.24 \text{ M}$) at pH 2 and $T = 60^\circ\text{C}$. ($[\text{NaCl}]_0 = 5.16 \text{ mM}$, $[\text{EDTA}]_0 = 10 \text{ mM}$). The lines show the prediction with the rate parameters obtained.

The effect of chloride ion concentration on the decomposition of Cl(III) was studied at pH 1 and 2. At pH 2, the chloride concentration (0.5-50 mM) had only a small effect whereas at pH 1 chloride clearly catalyzed the decomposition; the more chloride present, the faster the decomposition (Figure 5).

Reactions 7-11 have been suggested earlier to describe the chloride-catalyzed decomposition of Cl(III). Reactions 10 and 11 were disregarded as the observed effect of pH was more pronounced than would derive only from the Cl(III) equilibrium (Reaction 1). Reaction 7 as well as Reactions 8+9 present the hydronium and chloride ion catalyzed decomposition of HClO_2 . This stoichiometry of the catalysis is in accordance with the experimental results; chloride ion concentration affects the decomposition substantially only at low pH values where the hydronium ion concentration is high and therefore the rate of Reaction 7 becomes important. Whether Reaction 7 or Reaction 8 followed by Reaction 9 is the more appropriate representation for this decomposition cannot be judged on the basis of our measurements. Since both routes result in the same overall equation, it can be stated that Reaction 7 describes the chloride-catalyzed decomposition if the very short-lived intermediates are ignored.

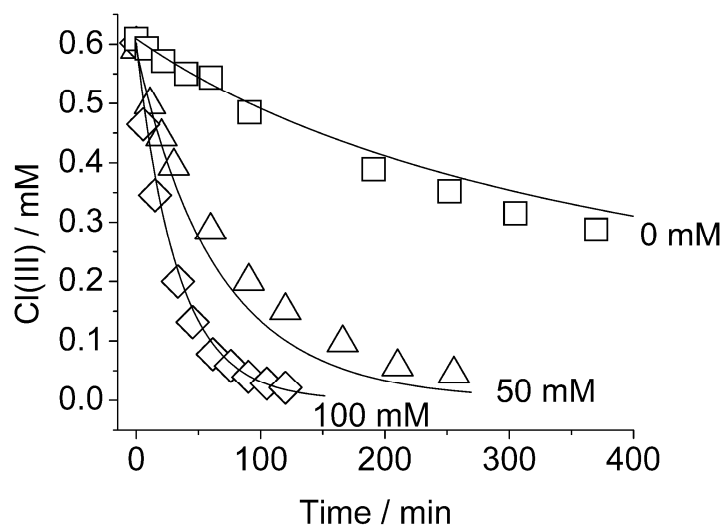


Figure 5. *Cl(III) decomposition as a function of time with different added chloride concentrations, 0 mM (\square), 50 mM (Δ), and 100 mM (\diamond), at pH 1 and 60°C with $[Cl(III)]_0 = 0.6$ mM, $[DMSO]_0 = 12$ mM and $[EDTA]_0 = 10$ mM. The lines show the prediction with the rate parameters obtained.*

4.1.3 Kinetics of Cl(III) decomposition in absence of metals

The rate parameters (k – rate coefficient, E_a – activation energy) were determined for Reactions 5, 7 and 12+15, which were found plausible based on reaction stoichiometry. The reactions were assumed to obey elementary kinetics (Eqs. 16 - 18). As Reaction 12 has been introduced only on a speculative level, Reactions 12 and 15 were combined to give an apparent third order reaction with respect to $HClO_2$ for r_{15} .

$$r_5 = -\frac{d[Cl(III)]}{dt} = k_5[HClO_2]^2 \quad (16)$$

$$r_7 = -\frac{d[Cl(III)]}{dt} = k_7[HClO_2][Cl^-][H^+] \quad (17)$$

$$r_{15} = -\frac{d[Cl(III)]}{dt} = k_{15}[Cl_2O_3][HClO_2] = k'_{15}[HClO_2]^3 \quad (18)$$

The rate coefficient for Reaction 15 could not be identified, i.e. statistical analysis gave large confidence limits for the parameters. Omitting Reaction 15 from the model and refitting the reaction parameters had no effect on the values obtained for Reactions 5 and 7. Thus, Reaction 15 was considered insignificant in our experimental conditions. The rate parameters obtained for Reactions 5 and 7 are shown in Table 1 along with their 95 % confidence limits. The modeled and experimentally observed Cl(III) concentrations are shown in Figures 3-5. As can be seen from the figures, these reactions and the reaction parameters obtained predicted the decomposition of Cl(III) well. Thus it can be concluded that among the large group of suggested reactions, Reactions 5 and 7 are adequate to describe Cl(III) decomposition in the absence of metals and HOCl.

Table 1. The rate constants and activation energies of Reactions 5 and 7. Parameter intervals represent 95 % confidence limits.

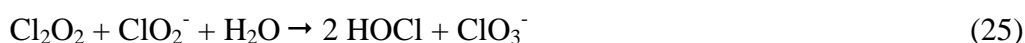
Reaction	k (25°C)	E _a (kJ/mol)
5 2 HClO ₂ → HOCl + H ⁺ + ClO ₃ ⁻	0.0021 ± 0.0002 M ⁻¹ s ⁻¹	84 ± 9
7 HClO ₂ + Cl ⁻ + H ⁺ → 2 HOCl	0.0027 ± 0.0001 M ⁻² s ⁻¹	70 ± 3

4.2 Reaction of Cl(III) with HOCl

The literature does not provide a clear consensus on the reactions between Cl(III) and HOCl. The reported rate constants in particular are far from consistent. Therefore experiments were conducted to resolve the valid reactions and their kinetics in chlorine dioxide bleaching conditions. The results presented in this chapter can be found in more detail in Paper II.

The formation of a dichlorine dioxide intermediate (Cl₂O₂) has been reported to occur through Reactions 19 [Taube and Dodgen 1949, Emmenegger and Gordon 1967, Hong and Rapson 1968, Kieffer and Gordon 1968a, Kieffer and Gordon 1968b, Schmitz and Rooze 1981, Peintler et al. 1990, Gordon and Tachiyashiki 1991, Fabian and Gordon 1992, Jia et al. 2000, Horvath et al. 2003] and 20 [Taube and Dodgen 1949, Emmenegger and Gordon 1967, Aieta and Roberts 1986, Peintler et al. 1990, Nicoson and Margerum 2002]. Cl₂O₂ is a short-lived intermediate that reacts further very rapidly [Peintler et al. 1990, Jia et al. 2000, Nicoson and Margerum 2002, Horvath et al. 2003]. The rate coefficients proposed by

various authors for the formation of Cl_2O_2 vary within 5 orders of magnitude [Peintler et al. 1990, Hong and Rapson 1968, Jia et al. 2000, Gordon and Tachiyashiki 1991] and the rate expressions involve either chlorous acid or chlorite ion as the reactive species [Jia et al. 2000]. The proposed Cl_2O_2 consuming reaction schemes differ even more and produce deviating overall stoichiometries. The essential mechanistic alternatives for the follow-up reactions of Cl_2O_2 are presented in Reactions 21-25 [Taube and Dodgen 1949, Hong and Rapson 1968, Nicoson and Margerum 2002, Schmitz and Rooze 1981, Peintler et al. 1990, Horvath et al. 2003, Jia et al. 2000, Fabian and Gordon 1992].



4.2.1 Testing of reported reaction models

First, the validity of the models reported earlier in literature [Hong and Rapson 1968, Peintler et al. 1990, Horvath et al. 2003, Jia et al. 2000] was tested in the pH region used in experiments. The experimental Cl(III) decomposition results were compared against the predictions (Figure 6). The predicted rates were either substantially too low or too high. It was also checked whether Cl(III) depletion could result from the reaction between chlorine and chlorite (Reaction 20) alone. The rate constant of this reaction was obtained from Aieta and Roberts [1986]. From Figure 6 it is evident that Reaction 20 is not fast enough to explain the observed Cl(III) decay, and Reaction 19 must contribute in the rate determining step.

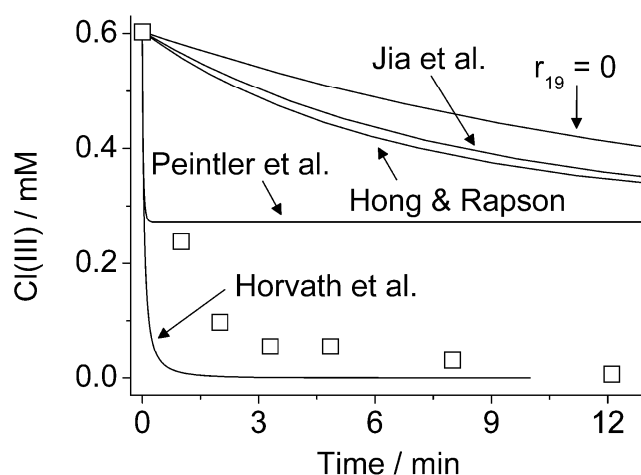


Figure 6. *Cl(III) depletion predictions (lines) using previously reported kinetic models [Hong & Rapson 1968, Peintler et al. 1990, Horvath et al. 2003, Jia et al. 2000] and a case where Reaction 19 is fully omitted ($r_{19} = 0$) as well as the experimentally observed Cl(III) decay (□) at 25 °C with initial pH 3.0 and $[Cl(III)]_0 = 0.6$ mM, $[HOCl]_0 = 0.17$ mM.*

4.2.2 Reaction stoichiometry and kinetic parameters

An example of the development of chlorine dioxide, chlorite and chlorate concentrations during the reaction between Cl(III) and HOCl is shown in Figure 7. Chlorine dioxide was the main product among the compounds monitored. The Cl(III) depletion and chlorate formation increased with temperature (Figure 7). The results indicate that an increasing temperature slightly favors chlorate production over chlorine dioxide.

The reaction proceeded faster at lower pH (Figure 8). Chlorine dioxide and chlorate were formed in constant proportions independent of pH indicating that pH had a negligible effect on the overall stoichiometry.

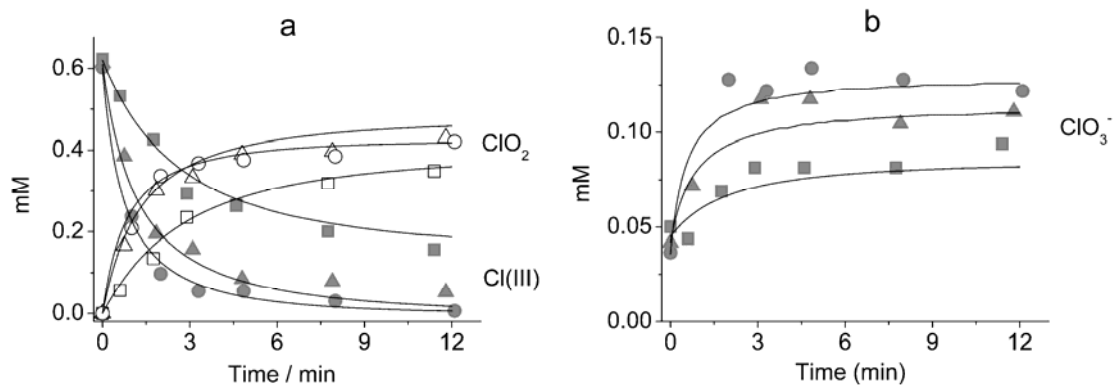


Figure 7. The effect of temperature on (a) Cl(III) depletion (filled symbols), chlorine dioxide formation (empty symbols) and (b) chlorate formation at 6°C (□), 16°C (Δ) and 25°C (○) at initial pH₀ 3.0, [Cl(III)]₀ = 0.6 mM, [HOCl]₀ ≈ 0.18 mM and [ClO₃⁻]₀ = 0.05 mM. The lines illustrate the predictions according to the kinetic parameters obtained in this study.

Chlorate may be formed according to Reactions 21, 22, and 25. The majority of the chlorate formation occurred at the beginning of the reaction, where the chlorite concentration is notable. Since the rate of Reaction 25 is first order with respect to Cl₂O₂ and chlorite whereas the other possible chlorate forming reaction, Reactions 21 and 22, do not involve chlorite, it was concluded that Reaction 25 is the primary chlorate forming reaction. Furthermore, Reaction 25 generates hypochlorous acid and leads to the high Cl(III) conversions associated with chlorate formation. If Reaction 22 between Cl₂O₂ and the hydroxide ion was important, the overall stoichiometry should change with pH. This was not observed in the pH range studied. This conclusion was verified with parameter regression. Rate coefficients k₂₁ and k₂₂ could not be properly identified while k₂₅ was well identified, indicating that the chlorate formation can be adequately predicted without the Reactions 21 and 22.

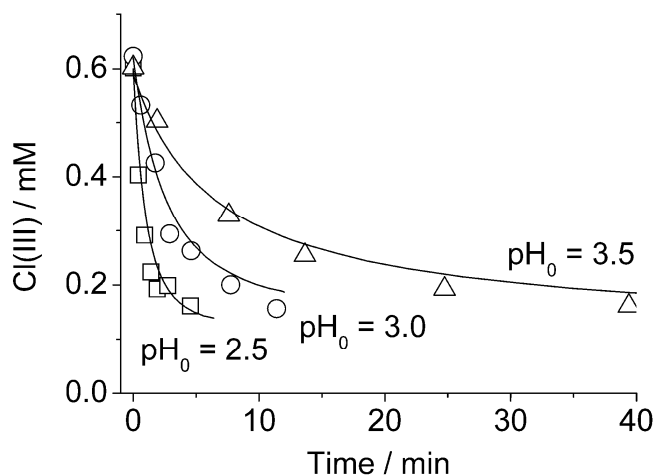


Figure 8. *Cl(III) depletion at initial pH 2.5 (\square), 3.0 (\circ) and 3.5 (Δ) at 6°C with $[Cl(III)]_0 = 0.6$ mM, $[HOCl]_0 = 0.16$ mM and $[ClO_3^-]_0 = 0.05$ mM. The lines illustrate the predictions according to the kinetic parameters obtained in this study.*

Chlorine dioxide could be formed through Reactions 23, 24, or both. As Reaction 23 is a second order process with regards to Cl_2O_2 it should be important whenever Cl_2O_2 is formed, i.e. $Cl(III)$ is consumed rapidly. Thus the relative chlorine dioxide production should increase with temperature and acidity if Reaction 23 was meaningful. However, the experimental results showed that pH had an insignificant stoichiometric effect and that high temperature instead of increasing actually suppressed chlorine dioxide production. Therefore the minor importance of Reaction 23 is evident from the experimental results. Parameter regression supported this conclusion as rate coefficient k_{23} could not be identified well. This suggests that it is not a meaningful reaction.

Successful reproduction of the experimental results required the inclusion of Reaction 26, the equilibrium between elemental chlorine, hypochlorous acid and chloride, in the regression procedure. It was observed that between the consecutive Reactions 26 and 20, the first one was rate limiting, meaning that the formation of chlorine from hypochlorous acid was slower than its reaction with chlorite. Thus all chlorine formed is almost instantaneously consumed in a reaction with chlorite.



The kinetic parameters for Reactions 19, 20, 24 and 25 are given in Table 2. The kinetic parameters for Reaction 20 were obtained from the literature while others were determined using parameter regression. Additionally, the equilibria between hypochlorous acid and chlorine (Reaction 26) and chlorous acid and chlorite (Reaction 1) as well as the self-protonolysis of water were included in the regression procedure. Model predictions were found to coincide well with the experimental results (Figures 7-8). The obtained k_{19} value is more than one order of magnitude smaller than the literature value for k_{20} (Table 2). In accordance with this, Cl(III) is reported to react faster with elemental chlorine than with hypochlorous acid [Emmenegger and Gordon 1967]. Among the product stoichiometry determining routes, rate coefficients were identified for Reactions 24 and 25. The Cl_2O_2 consuming reactions are known to be extremely fast [Peintler et al. 1990, Horvath et al. 2003], and consequently only the ratio of rates r_{24} and r_{25} could be determined. The rate parameters for Reaction 25 were well identified after fixing $k_{24} = 8.4 \cdot 10^{11} [\text{Cl}] \text{ M}^{-2}\text{s}^{-1}$ (according to Horvath et al. [2003]) and $E_{a,24} = 50 \text{ kJ/mol}$. Reaction 19 is considerably slower than the subsequent Cl_2O_2 consuming reactions. Hence, Reaction 19 is rate limiting in the overall reaction and the relative rates of the Cl_2O_2 consuming paths 24-25 dictate the stoichiometry observed.

Table 2. Rate parameters for the essential reactions participating in the HOCl- HClO_2 reaction. Parameter intervals represent 95 % confidence limits.

Reaction		k (12°C)	E_a (kJ/mol)
19	$\text{HOCl} + \text{HClO}_2 \rightarrow \text{Cl}_2\text{O}_2 + \text{H}_2\text{O}$	$406 \pm 93 \text{ M}^{-1}\text{s}^{-1}$	54 ± 13
20	$\text{Cl}_2 + \text{ClO}_2^- \rightarrow \text{Cl}_2\text{O}_2 + \text{Cl}^-$	^a $1.0 \cdot 10^4 \text{ M}^{-1}\text{s}^{-1}$	^a 39.9
24	$\text{Cl}_2\text{O}_2 + \text{ClO}_2^- \rightarrow 2 \text{ClO}_2 + \text{Cl}^-$	^b $8.4 \cdot 10^9 \cdot [\text{Cl}] \text{ M}^{-2}\text{s}^{-1}$	^b 50
25	$\text{Cl}_2\text{O}_2 + \text{ClO}_2^- + \text{H}_2\text{O} \rightarrow 2 \text{HOCl} + \text{ClO}_3^-$	$5.3 (\pm 0.7) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	78 ± 6

^a Obtained from Aieta and Roberts [1986]

^b a fixed value, k obtained from Horvath et al. [2003]

4.3 Reaction of Cl(III) with aldehydes

When the reactions discussed in chapters 4.1 and 4.2 and their rate parameters were implemented in our chlorine dioxide bleaching model, it was noticed that the Cl(III) consumption observed was inadequately predicted [Tarvo et al. 2010]. Therefore, attention was paid to the reaction between chlorous acid and pulp related aldehydes in order to resolve whether this reaction contributes substantially to Cl(III) consumption in chlorine dioxide bleaching. The results in this chapter can be found in more detail in Papers III and IV.

4.3.1 Monomeric aldehydes

Aldehydes have been shown to react with Cl(III) [Jeanes and Isbell 1941]. The reaction mechanism adopted from Isbell and Sniegowski [1964] is presented in Reaction 27. The literature does not give a clear picture on whether chlorous acid or chlorite ion is the reacting species with the aldehydes. Our kinetic experiments showed that chlorous acid is responsible for the oxidation of aldehydes as has been presented previously by Jeanes and Isbell [1941]. In addition, the observation on the selectivity of chlorous acid towards aldehydes [Jeanes and Isbell 1941] was confirmed. Alcohols and ketones were found to be unreactive while all the compounds containing an aldehyde group reacted with chlorous acid. The consumption of Cl(III) in the presence of formaldehyde, vanillin and glucose is presented in Figure 9. The reaction parameters for all the aldehydes used were determined based on Cl(III) consumption at several temperature levels. The decomposition reactions of chlorous acid (Reactions 5 and 7) were taken into account in the fitting, their kinetic parameters were obtained from Paper I. Reactions of Cl(III) and aldehydes with the HOCl formed (Reaction 27) were prevented by means of DMSO. The kinetic parameters obtained are given in Table 3 along with their 95% confidence limits. The calculated Cl(III) depletion at 25°C based on the kinetic constants for glucose, vanillin and formaldehyde is shown as lines in Figure 9. As can be seen from the 95% confidence limits in Table 3 and the Cl(III) decomposition predictions in Figure 9, the rate parameter fittings were successful. The reactions can be modeled accurately with the rate parameters obtained.

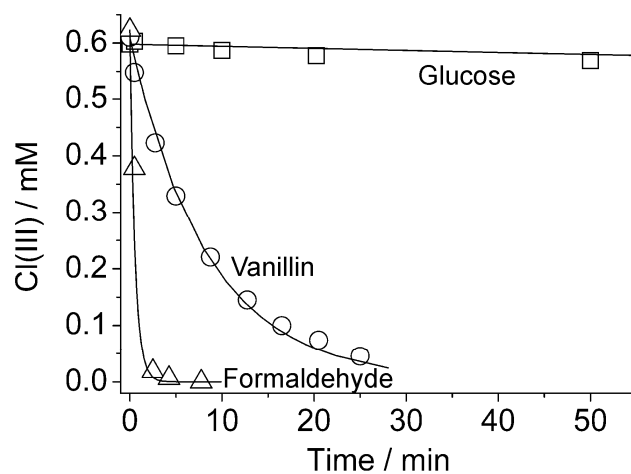
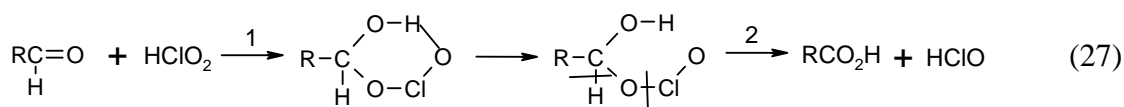


Figure 9. Oxidation of glucose (\square), vanillin (O) and formaldehyde (Δ) by Cl(III) at $\text{pH } 2.0$ at 25°C . Initial concentrations of the reagents were $[\text{aldehyde}]_0 = 6.0 \text{ mM}$ and $[\text{Cl(III)}]_0 = 0.6 \text{ mM}$. The lines illustrate the fit according to the rate parameters in Table 3.

Table 3. Rate constants (at 25°C) and activation energies as well as their 95 % confidence limits for the reaction of chlorous acid with aldehydes.

Reactant	k (25°C) ($\text{M}^{-1}\text{s}^{-1}$)	E_a (kJ/mol)
Formaldehyde	11.0 ± 0.8	54 ± 5
Unhydrated formaldehyde	1.2×10^4	-
Vanillin	0.59 ± 0.02	44 ± 4
Veratraldehyde	1.00 ± 0.03	42 ± 2
Benzaldehyde	5.6 ± 0.3	26 ± 3
Glucose	$3.39 (\pm 0.08) \times 10^{-3}$	63 ± 2
Free aldehydes of glucose ¹	104 ± 2	32 ± 1
Glycolaldehyde	39.0 ± 1.9	45 ± 3
Unhydrated glycolaldehyde	4.5×10^2	-
5-formyl-2-furancarboxylic acid	5.2 ± 0.2	37 ± 2

¹⁾ The effect of mutarotation was taken into account.

Angyal [1984] has reported that at 20°C only 0.002 % of glucose is in the aldehyde form (VIIa in Figure 2) while the rest is in cyclic form (VIIb). This mutarotation explains the clearly different reaction rate obtained for the oxidation of glucose compared with the other aldehydes (Table 3). The rate parameters for the oxidation of the free aldehyde groups in glucose by chlorous acid were calculated by implementing the kinetics of the mutarotation of glucose in the fitting. The rate constants for the mutarotation were obtained from Pigman and Isbell [1968] and the activation energies were estimated so that the temperature dependency of the amount of free aldehydes corresponded to the data reported by Hayward and Angyal [1977]. The kinetic parameters obtained (Table 3) can be considered to represent the oxidation of the free aldehyde groups (reducing ends) in cellulose.

The rate determining step in the oxidation of aldehydes by chlorous acid was investigated with deuteriated benzaldehyde (α -d₁). It is known that carbon-deuterium (C-D) bonds are broken down more slowly than the corresponding carbon-hydrogen (C-H) bonds [Sykes 1972]. The ratio k_{C-H}/k_{C-D} has been shown to be ~3-8 [Sykes 1972]. Thus if the detachment of the proton in the aldehyde group (step 2 in Reaction 27) was the rate determining step, the reaction rate should be 3-8 times slower with the α -d₁-benzaldehyde than with the undeuteriated one. The Cl(III) depletion with both the unlabeled and labeled benzaldehyde is presented in Figure 10. It can clearly be seen that the reaction proceeded at a similar rate at all temperatures irrespective of the presence of deuterium. For example, at 25°C the rate coefficients were 5.0 and 5.6 M⁻¹s⁻¹ for the deuteriated and the undeuteriated benzaldehyde, respectively. Thus it was concluded that the addition of chlorous acid to the aldehyde (step 1 in Reaction 27) is the rate determining-step in this reaction.

Some aldehydes like formaldehyde are easily hydrated [Bell 1966]. In an aqueous solution less than 0.05% of formaldehyde is in the aldehyde form, the rest is hydrated [Guthrie 1975]. In addition, glycolaldehyde is hydrated fairly easily, only 10% is in the aldehyde form in aqueous solution at room temperature [Sørensen 1972]. Hydration might be a restricting factor in the reaction between chlorous acid and aldehyde since chlorous acid is known to react only with the aldehyde [Jeanes and Isbell 1941]. Rate constants for the oxidation of the unhydrated formaldehyde and glycolaldehyde by chlorous acid were calculated while taking into account the kinetics of the hydration [Guthrie 1975, Bell and

Evans 1966, Sørensen 1972]. These values are given in Table 3. The hydration clearly affects the oxidation rate of aldehydes by chlorous acid. In the cases where the aldehyde in question is easily hydrated, the dehydration reaction may become the rate determining step depending on the concentration of HClO_2 .

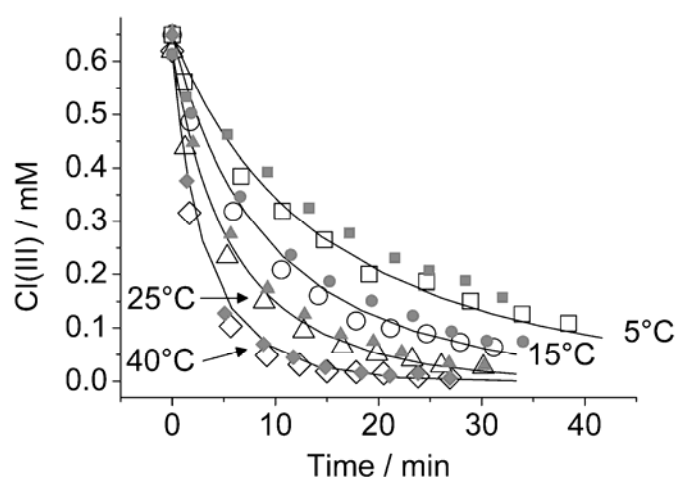


Figure 10. Oxidation of benzaldehyde (open symbols) and deuteriated benzaldehyde (filled symbols) by Cl(III) at pH 2.0 at 5 (\square) 15 (O), 25 (Δ) and 40°C (\diamond). Initial concentrations of the reagents were $[\text{benzaldehyde}]_0 = 1.2 \text{ mM}$ and $[\text{Cl(III)}]_0 = 0.6 \text{ mM}$. Lines illustrate the fit according to the rate parameters in Table 3.

Based on the results with aromatic aldehydes (vanillin, veratraldehyde and benzaldehyde), it was concluded that lignin structures possessing an aldehyde group react with chlorous acid in chlorine dioxide bleaching to form hypochlorous acid. Their reaction rates (0.59, 1.00, and $5.6 \text{ M}^{-1}\text{s}^{-1}$, respectively at 25°C) are high enough to compete with other Cl(III) consuming reactions in chlorine dioxide bleaching. The reaction rates of free aldehyde groups in carbohydrates (104 and $450 \text{ M}^{-1}\text{s}^{-1}$ at 25°C for glucose and glycolaldehyde) are also high enough to contribute to the Cl(III) consumption. In addition, it was discovered that a degradation product of hexenuronic acid, 5-formyl-2-furancarboxylic acid, can contribute to the consumption of Cl(III) in an A/D-prebleaching stage.

4.3.2 Aldehyde groups in pulp

When treated with Cl(III) in the presence of EDTA and DMSO, different pulps consumed varying amounts of Cl(III). This consumption was regarded as an indication of the amount of aldehyde structures present in the pulp. According to Paper III and Jeanes and Isbell [1941], Cl(III) is selectively reactive with aldehyde structures. Brown softwood kraft pulp, that had not been oxygen delignified, consumed the highest amount of Cl(III) while the least Cl(III) was consumed by the pulps that had the lowest kappa numbers. The consumption of Cl(III) by brown softwood kraft pulp (SW) and oxygen delignified softwood kraft pulp (O-SW) are presented in Figure 11.

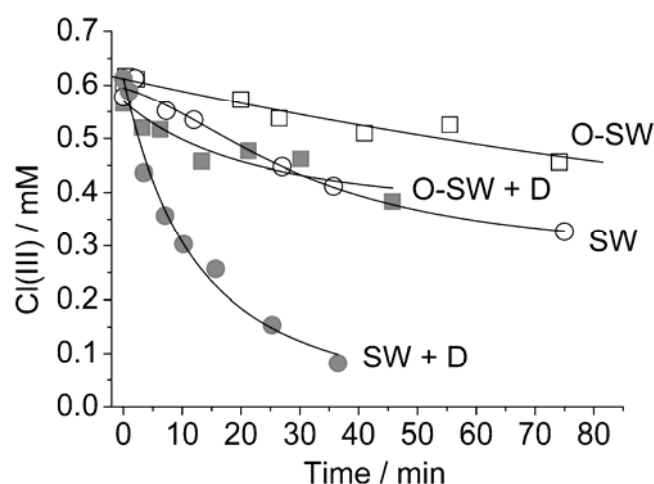


Figure 11. Cl(III) consumption by brown softwood kraft pulp (kappa 31) (O) and O₂-delignified softwood kraft pulp (kappa 12.8) (□) before (empty symbols) and after (filled symbols) 1 minute chlorine dioxide treatments at 50°C at 10 % pulp pulp consistency. The ClO₂ dosages were 42 kg act Cl/Adt and 13 kg act Cl/Adt for the SW and the O-SW pulps, respectively. The Cl(III) treatments were carried out at 1 % pulp consistency at pH 2 and 60°C in the presence of DMSO and EDTA.

Chlorine dioxide bleaching increased the consumption of Cl(III) considerably, as shown in Figure 11. The impact that chlorine dioxide bleaching had on Cl(III) consumption was almost linearly dependent on the chlorine dioxide charge (Figure 12) or the consumption of active bleaching chemical (not shown). The pulp composition seemed to have a small effect. If the pulp was O₂-delignified prior to the chlorine dioxide treatment, the Cl(III)

consumption was not as extensive. These results show that aldehyde groups are formed in the pulp during chlorine dioxide bleaching.

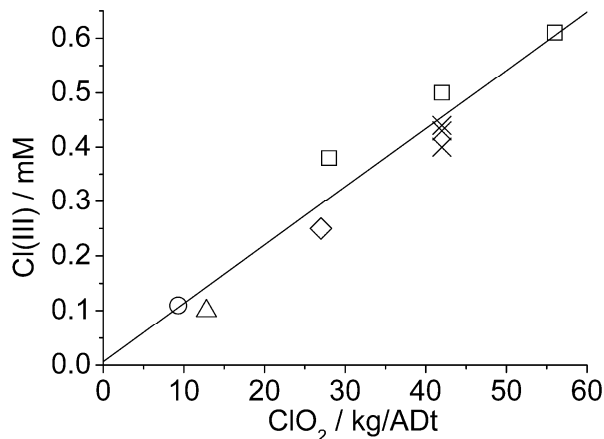


Figure 12. The amount of Cl(III) consumed by kraft pulps in 30 minutes after 1 min treatments with varying charges of ClO₂ at 50°C at 10 % pulp consistency for brown softwood (kappa 31) (□), D₀-EO bleached softwood (kappa 5.7) (○), O₂-delignified softwood (kappa 12.8) (△) and O₂-delignified hardwood kraft pulp (kappa 15) (◇). For SW, different bleaching times (5, 10 and 30 min) are also shown (×). The Cl(III) treatments were carried out at 1 % pulp consistency at pH 2 and 60°C in the presence of DMSO and EDTA .

At least part of the aldehydes formed in chlorine dioxide bleaching originates from carbohydrates. It is known that aldehyde groups can be formed through oxidation of primary alcohol groups at C-6 of glucose units of cellulose by the hypochlorous acid (or chlorine) formed in situ [Croon and Dillén 1968]. To find out whether lignin also contributes to the aldehyde formation observed, a phenolic compound, 2,4,6-trimethylphenol, was treated with chlorine dioxide in the presence of DMSO. As DMSO is known to capture HOCl effectively, as discussed previously, Cl(III) can only react with the aldehydes or undergo self-decomposition (Reactions 6-7). In the experiment an instantaneous consumption of chlorine dioxide was observed accompanied by a rapid formation of Cl(III) similar to what has been reported in chlorine dioxide bleaching [Kolar et al. 1983, Svenson et al 2005]. After the rapid formation of Cl(III), it was consumed at a rate that was much higher than the rate of self-decomposition of Cl(III). Since the fast

reaction of Cl(III) with HOCl was prevented by DMSO and as chlorous acid is known to be selectively reactive with aldehyde structures, this result indicates that some aldehyde structures are formed during the oxidation of 2,4,6-trimethylphenol by chlorine dioxide.

4.3.3 Practical significance in chlorine dioxide bleaching

In addition to Cl(III), the aldehyde structures present in pulp can react with hypochlorous acid (HOCl) [Jeanes and Isbell 1941]. This reaction is known to be fast ($6.0 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ at 25°C for formaldehyde) [Chinake et al. 1998], although HOCl also reacts very rapidly with many other structures [Anbar and Ginsburg 1954, Gierer 1986, Spickett et al. 2000]. It has been stated that due to its rapid reactions HOCl is not present in measurable quantities during chlorine dioxide bleaching [Ni et al. 1992]. This leads to the conclusion that the majority of the aldehydes are oxidized by chlorous acid since its concentration is several times higher than the concentration of HOCl.

Among the various Cl(III) reactions during chlorine dioxide bleaching, the reaction with hypochlorous acid (Reaction 19) is clearly the fastest one. Chlorous acid reacts with hypochlorous acid at a rate ($1.1 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ at 25°C , from Paper II) that is over 25 times higher than with any of the aldehydes used in the experiments reported in Paper III. However, since the concentration of HOCl is almost non-existent during ClO_2 bleaching as discussed above, not all chlorous acid can react with it and thus the reactions with aldehydes become possible. The reaction rates obtained for vanillin, veratraldehyde and benzaldehyde in Paper III (0.59 , 1.00 , and $5.6 \text{ M}^{-1}\text{s}^{-1}$, respectively) show that lignin structures possessing an aldehyde group may react with chlorous acid in chlorine dioxide bleaching. Also, the oxidation of free aldehyde groups in carbohydrates by chlorous acid will contribute to Cl(III) consumption. Thus the oxidation of aldehyde groups in cellulose by chlorous acid can have a real significance in maintaining the strength properties of pulp, as has been suggested before by Croon and Dillén [1968]. According to the results, it is concluded that the reaction between Cl(III) and aldehydes may contribute substantially to the overall Cl(III) consumption during chlorine dioxide bleaching.

4.4 Chlorine dioxide bleaching

So far only a few studies have been published on the progress of chlorine dioxide prebleaching (D₀-stage) as a function of time. Even in these studies, only a few variables have been monitored [Germgård 1982a, Kolar et al. 1983, Ni et al. 1992, Reeve et al. 1995, Svenson et al. 2005]. In order to gain more knowledge on the rate of different reactions and on the time-dependent behavior of various components, several prebleaching experiments were executed with hardwood pulp. In these experiments, the charge of chlorine dioxide was varied and the effect of a preceding A-stage was studied. The results presented in this chapter are taken from Papers V-VI.

4.4.1 Kappa number and hexenuronic acid content

At the beginning of a chlorine dioxide prebleaching stage, the kappa number is reduced very rapidly (Figure 13). This is due to the fast reaction between chlorine dioxide and phenolic lignin [Lindgren 1971, Hoigné and Bader 1994].

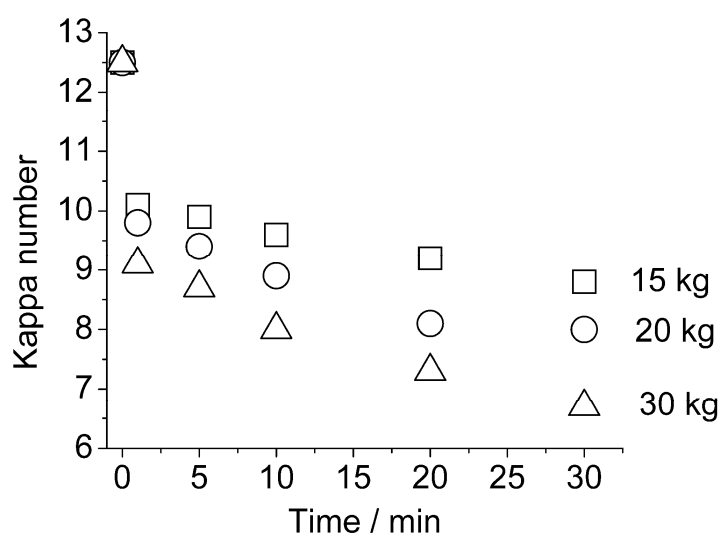


Figure 13. The development of kappa number with different dosages of active chlorine, 15 kg act. Cl/Adt (□), 20 kg act. Cl/Adt (○) and 30 kg act. Cl/Adt (△) as a function of time at 45°C.

Higher ClO_2 charges are known to result in lower kappa numbers. In our experiments this was seen especially in the slower part of the bleaching (Figure 13). Also the removal of aromatic lignin was enhanced as expected with higher dosages of chlorine dioxide (40 % with 15 kg, 49 % with 20 kg and 52 % with 30 kg of ClO_2). This is illustrated in Figure 14 where the UVRR spectra of the bleached pulps with different chlorine dioxide dosages are presented. With higher chlorine dioxide charges the heights of the aromatic lignin band (1605 cm^{-1}) and the HexA band (1655 cm^{-1}) were reduced.

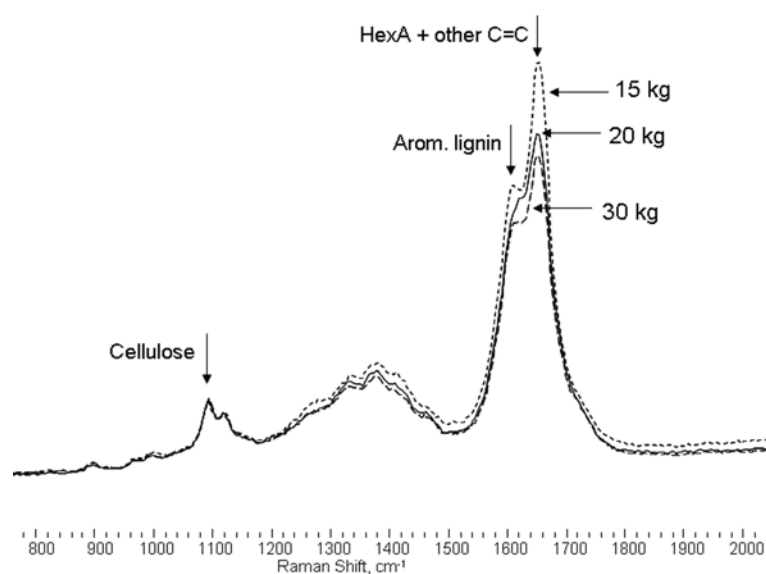


Figure 14. UVRR spectra of D_0 pulps (45°C , 30 minutes) with different dosages of active chlorine, 15 kg act. Cl/Adt , 20 kg act. Cl/Adt and 30 kg act. Cl/Adt . The height of the spectra were normalized to the cellulose band at 1094 cm^{-1} .

Hypochlorous acid is formed in the fast reaction between chlorine dioxide and phenols [Kolar et al. 1983]. It reacts rapidly with organic compounds such as hexenuronic acid [Vuorinen et al. 2007]. Higher chlorine dioxide charges resulted in increased hexenuronic acid removal (Figures 14-15). This is consistent with the amount of ClO_2 consumed. The more ClO_2 is consumed, the more HOCl is formed and is available to react with HexA. The effect was not so pronounced with the 30 kg dosage, which is most likely due to the fact that ClO_2 was not fully consumed with this, the largest, dosage and thus no excess HOCl was formed.

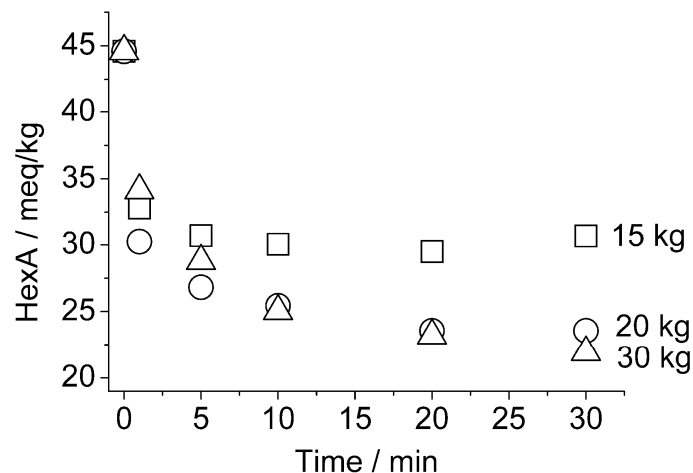


Figure 15. The removal of hexenuronic acid with different dosages of active chlorine, 15 kg act. Cl/Adt (\square), 20 kg act. Cl/Adt (\circ) and 30 kg act. Cl/Adt (Δ) as a function of time at 45°C.

When approximately 45 % (20 meq/kg) of the hexenuronic acid in the pulp was removed in an A-stage prior to the D₀-stage, the kappa number was reduced by four units (Table 4). According to Li and Gellerstedt [1997] 10 meq of hexenuronic acid in 1 kg of pulp corresponds to 0.84-0.86 kappa number units. In our case this would mean that the removal of HexA reduced the kappa number by only 1.7 units. The rest of the kappa number decrease (2.3 units) must be due to altered lignin structures and the dissolution of residual lignin. This was supported by the change observed in the aromatic lignin content (Table 4, Δ arom. lignin). This effect has been examined in more detail by Furtado et al. [2001] who noticed that an A-stage also removes lignin from the pulp.

The amount of ClO₂ consumed stayed unchanged after an A-stage verifying that ClO₂ itself reacts only very slowly with hexenuronic acid [Costa and Colodette 2007, Törngren and Ragnar 2002]. As ClO₂ reacts primarily with phenolic lignin structures, it seems that they are mostly unaffected by the A-stage. Even if these phenolic structures are dissolved during the A-stage as reported by Furtado et al [2001], they are still able to react with ClO₂, since no washing is performed between the A- and D₀- stages.

Table 4. The decrease of kappa number, hexenuronic acid content and percentage of aromatic lignin removed in a D₀-stage (20 kg act. Cl / Adt, 45°C) with and without a preceding A-stage.

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

4.4.2 Chlorination of organic structures

Chlorinated organic compounds (AOX and OX) are formed in chlorine dioxide bleaching when intermediately formed hypochlorous acid (HOCl) and chlorine (Cl₂) react with organic structures present in the filtrate (AOX) or in the fibers (OX) [Wajon et al. 1982, Gunnarsson and Ljunggren 1996b]. Hypochlorous acid and chlorine are in equilibrium according to Reaction 26 [Kolar et al. 1983, Deborde and von Gunten 2008]. Both HOCl and Cl₂ react rapidly with lignin and hexenuronic acid [Ni et al 1995a, Vuorinen et al. 2007]. Both of them also chlorinate various structures in pulp [de la Mare et al. 1954, Brage et al. 1991b, Gunnarsson and Ljunggren 1996b, Joncourt et al. 2000, Costa and Colodette 2007, Deborde and von Gunten 2008].

The chlorination of organic compounds was observed to be very fast at the beginning of the D₀-stage, but the rate decreased as the bleaching continued (Figures 16-17). This is in

agreement with previous studies [Ni et al. 1992, Ni and van Heiningen 1993a, Reeve et al. 1995]. Hypochlorous acid is produced in the reactions of chlorine dioxide [Kolar et al. 1983, Ni et al. 1992]. Since the consumption of chlorine dioxide is known to be very fast at the beginning of bleaching [Kolar et al. 1983], a relatively high amount of HOCl (and Cl₂) is present during this initial stage. This leads to the rapid chlorination observed [Kolar et al. 1983].

AOX formation, though rather rapid during the initial phase, was much more moderate than OX formation (Figure 16). 20-50% of AOX was formed during the first minute. This result is in agreement with earlier publications, where 30-50 % of AOX was formed at the beginning of the D₀-stage [Ni et al. 1992, Ni and van Heiningen 1993a, Reeve et al. 1995, Joncourt et al. 2000]. AOX is usually considered to be formed as organic compounds in the filtrate are chlorinated, but part of the AOX may be derived from the dissolution of OX [Ni and van Heiningen 1993a].

Previously it has been shown that higher chlorine dioxide dosages lead to increased AOX formation [Reeve et al. 1995, Gunnarsson and Ljunggren 1996a, Ljunggren et al. 1996]. At the beginning of the D₀-stage, AOX formation was quite independent of the chlorine dioxide charge (Figure 16). At longer delays, the amount of AOX formed was lower with the 15 kg dosage. No clear differences were observed between the 20 and 30 kg dosages. This could be due to overdosing because not all of the ClO₂ was consumed during bleaching with the 30 kg dosage.

Higher chlorine dioxide dosages produced more OX (Figure 16). The differences in OX levels were notable as early as the first minute and stayed fairly constant throughout the bleaching. This is in agreement with the results of Ragnar and Törngren [2002], who stated that OX is formed in relation to the chlorine dioxide charge. Others [Gunnarsson and Ljunggren 1996a, Ljunggren et al. 1996] have claimed that only a slight or no increase of OX was observed when the chlorine dioxide charge was increased.

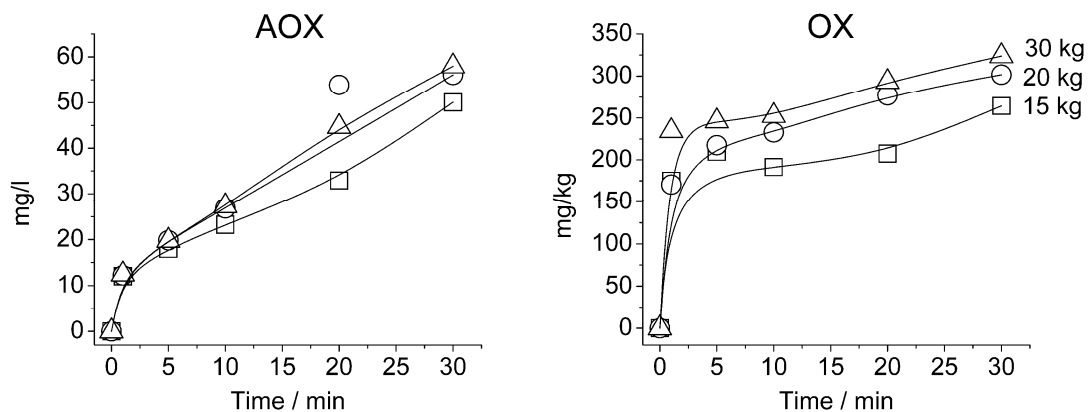


Figure 16. The formation of AOX and OX with different dosages of active chlorine, 15 kg act. Cl/Adt (\square) 20 kg act. Cl/Adt (o) and 30 kg act. Cl/Adt (Δ) as a function of time at 45°C.

After the D₀-stage, 14-21 mol-% of chlorine dioxide had ended up as AOX or OX (Table 5). This is consistent with the results of Björklund et al. [2004], who reported that after bleaching O₂-delignified birch 16-21 mol-% of the chlorine dioxide charged ended up either as AOX or OX. For Ni et al. [1992] this figure was only ~ 7% when bleaching softwood kraft pulp. Even though the total amount of organic chlorine (AOX+OX) was higher with the bigger dosages (3.2 kg/Adt with 15 kg/Adt dosage and 4.2 kg/Adt with 30 kg/Adt dosage) the fraction of Cl bound to organic compounds was lower with bigger chlorine dioxide dosages (Table 5). It seems that rather than chlorinating, the additional ClO₂ was mainly consumed in other reactions and ended up as chloride or chlorate, as will be discussed later.

The results obtained on the chlorination of pulp led to the conclusion that there is some other phenomenon besides chlorine dioxide dosage that restricts the extent of chlorination. Two possibilities were considered. One was that the amount of HOCl/Cl₂ that is formed mainly from the reaction between chlorine dioxide and phenols would remain fairly constant. As the extent of this reaction is almost solely dependent on the amount of phenols that are available for oxidation by chlorine dioxide (assuming that the chlorine dioxide dosage is sufficient for their oxidation), this explanation seems plausible.

Table 5. *The amount of organic chlorine (AOX and OX) as a percentage of consumed ClO₂.*

ClO₂ (kg/Adt)	1 min	5 min	10 min	20 min	30 min
15	10 %	13 %	12 %	15 %	21 %
20	8 %	11 %	13 %	18 %	18 %
30	9 %	9 %	10 %	11 %	14 %
20 ¹	9 %	11 %	10 %	11 %	14 %

¹The D₀-stage was preceded by an A-stage.

The other possibility originates from previous studies on the chlorination of natural organic matter with chlorine by Gallard and von Gunten [2002a, 2002b]. They observed a rapid initial phase after which the amount of chlorinated compounds increased more slowly. They attributed the fast initial phase to the reactions of HOCl with dihydroxybenzenes and the slower phase to the reactions between monohydroxybenzenes and HOCl. The same phenomenon could partly explain the trend observed in pulp bleaching: structures that are susceptible to chlorination would react fast with HOCl/Cl₂ in the initial phase and structures that are chlorinated more slowly would account for the slower phase. In that case, the extent of chlorination would be mostly dependent on the amount of reactive structures in the pulp. This is also supported by a previous study on the chlorination of oxygen-delignified softwood kraft pulp [Lehtimaa et al. 2009].

Different structures were considered as possible substrates for the rapid chlorination. The presence of polyphenolic compounds in the pulp, especially after O₂-delignification, is highly improbable and thus the structures that Gallard and von Gunten [2002a, 2002b] suggested as responsible for the rapid chlorination, can not be responsible for the rapid chlorination in pulp. The possible role of phenols was considered next but when comparing the reaction rates of phenolic structures with chlorine dioxide and hypochlorous acid, it became obvious that the reaction rates were much lower with HOCl. It seems probable that almost all of the available phenols present in the pulp would react with ClO₂ rather than with HOCl, and thus phenols are unlikely to be responsible for the chlorination observed. Larson and Rockwell [1979] have shown that HOCl chlorinates certain carboxylic acid structures. The reaction rates of carboxylic acids with HOCl seem to be much faster [Zhou et al. 2008] than with chlorine dioxide [Hoigné and Bader 1994]. However, carboxylic acids

are found so abundantly in chlorine dioxide bleaching (e.g. hexenuronic acid and muconic acids) [Gellerstedt and Lindfors 1987, Gierer 1990, Buchert et al. 1995, Ragauskas et al. 1998] that it seems unlikely that their availability would be the restricting factor for chlorination. Whether chlorination is more restricted by the pulp composition or the HOCl/Cl₂ formation or both cannot be resolved here.

The AOX originating from the D₀-stage consists partly of the chlorination products of HexA [Björklund et al. 2002, Freire et al. 2003a, Björklund et al. 2004, Freire et al. 2004]. When part of the HexA was removed from the pulp with hot acidic treatment (A-stage) before the D₀-stage, the final amount of AOX decreased drastically, by approximately 40 % (Figure 17). The proportion of AOX originating from HexA has been suggested as anything between 27 % up to as much as 80 % of the total amount of AOX [Freire et al. 2003a, Björklund et al. 2004, Freire et al. 2004]. Their inconsistent results may be at least partly explained by the unstable nature of HexA-originated AOX. It has been stated that this AOX can be degraded easily (Björklund et al. 2004, Lehtimaa et al. 2008). The initial rate of AOX formation was unaffected by the A-stage. This implies that the majority of AOX formation at the beginning would be due to chlorination of the dissolved lignin rather than HexA.

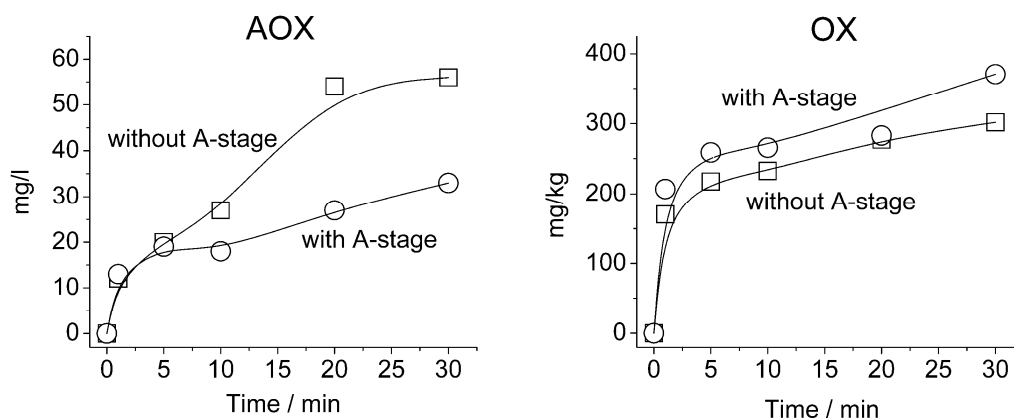


Figure 17. The formation of AOX and OX with (o) and without (□) acid treatment as a function of time at 45°C.

The amount of OX formed augmented slightly when the pulp was subjected to an acidic treatment prior to the D₀-stage. Similar behavior has been noted by Björklund et al. [2004]. It has been found that most OX appears to be attached to lignin, and that HexA is not a

source of OX [Ragnar and Törngren 2002, Björklund et al. 2004]. Thus the elevated amount of OX formation is due to the more extensive chlorination of lignin that arises from the higher amount of HOCl/Cl₂ present. This is caused by the constant ClO₂ consumption regardless of the A-stage. This should lead to unvarying chlorite and hypochlorous acid formation irrespective of the preceding A-stage. Since the pulp contains less HexA after an A-stage, there is more HOCl available to chlorinate lignin.

4.4.3 Inorganic chlorine compounds

The majority of the chlorine dioxide is consumed at the very beginning of the bleaching stage (Figure 18). This is due to the fast reaction between chlorine dioxide and phenolic lignin [Lindgren 1971, Hoigné and Bader 1994]. As a result of this reaction both chlorite and hypochlorous acid are formed [Kolar et al. 1983]. With 20 and 30 kg act. Cl/Adt the same amount of chlorine dioxide was consumed during the first minute (10.7 and 10.8 mM, respectively). This constant consumption implies that this was the amount of ClO₂ required to oxidize the available phenols and therefore the initial ClO₂ consumption was not higher with the 30 kg dosage.

The phenol content of the residual lignin was 0.79 mol/kg lignin in the pulp used. Using the total lignin content of the pulp (calculated from the kappa number and hexenuronic acid content), the phenol content of the pulp was calculated to be 10.3 mmol/kg pulp. According to a widely presented reaction scheme [Lindgren 1971, Kolar et al. 1983, Brage et al. 1991a] two ClO₂ equivalents should be consumed in the initial reaction with a phenolic structure. This would correspond to 2.3 mM consumption of ClO₂ in the fast initial reaction at the pulp consistency used. Yet the consumption observed at the beginning of bleaching was three times higher. This merely indicates that the primary reaction products are oxidized further by chlorine dioxide as has been discussed earlier [Chirat et al. 2000, Hamzeh et al. 2007]. It has also been suggested that there would be multiple parallel reactions occurring during the ClO₂ oxidation of phenols [Brogdon et al. 2004]. Other reactions, such as reactions with extractives [Björklund Jansson et al. 1995, Freire et al. 2003b] and reactions with new phenolic groups formed by the action of HOCl [Ni et al. 1995b, Joncourt et al. 2000], may also contribute to the initial ClO₂ consumption.

Similarly to the observations of Gunnarsson and Ljunggren [1996a], higher ClO_2 dosages increased the formation of chlorate and chloride, which are the final products in ClO_2 bleaching (Figure 18). However, the proportion of chlorine dioxide converted to ClO_3^- and Cl^- stayed constant even though the dosage was varied indicating that the stoichiometries of the different reactions producing chlorate and chloride stayed unchanged irrespective of the amount of ClO_2 .

According to the results of Svenson et al. [2005], half of all chlorate and chloride is formed during the first 5 minutes. This was also observed in our experiments. Ni et al. [1992] reported that in their experiments 10-18 % of ClO_2 was turned into chlorate and 63-75 % into chloride. In our experiments on average 12 % and 48 % of ClO_2 was turned into chlorate and chloride, respectively. The results are comparable, when taking into account the different experimental conditions used.

The amount of Cl(III) (chlorite + chlorous acid) increased at the beginning of bleaching and then decreased slowly (Figures 18-19), which is similar to what has been reported earlier [Kolar et al. 1983, Svenson et al. 2005]. Cl(III) is formed in the reaction between chlorine dioxide and phenolic lignin structures as discussed above. An equal amount of Cl(III) was formed with 20 and 30 kg act. Cl/Adt (Figure 18). This is consistent with the fact that the same amount of ClO_2 was consumed independent of whether the charge was 20 or 30 kg/Adt. With the 15 kg/Adt dosage less Cl(III) was formed, but the ratio was similar to the larger dosages: approximately one third of the consumed ClO_2 was turned into Cl(III). It is known that ClO_2 should be converted into chlorite (ClO_2^-) and hypochlorous acid (HOCl) in this initial reaction at a molar ratio of 1:1 [Kolar et al. 1983]. This means that roughly 5.3 mM of Cl(III) should be formed when 10.7 mM of ClO_2 is consumed. However, the amount was only 3.0 mM. It is assumed that this difference results from chlorous acid reacting rapidly with the HOCl formed. A clear indication of this is the fast chlorate and chloride formation (Figure 18) caused mainly by Reactions 24 and 25.

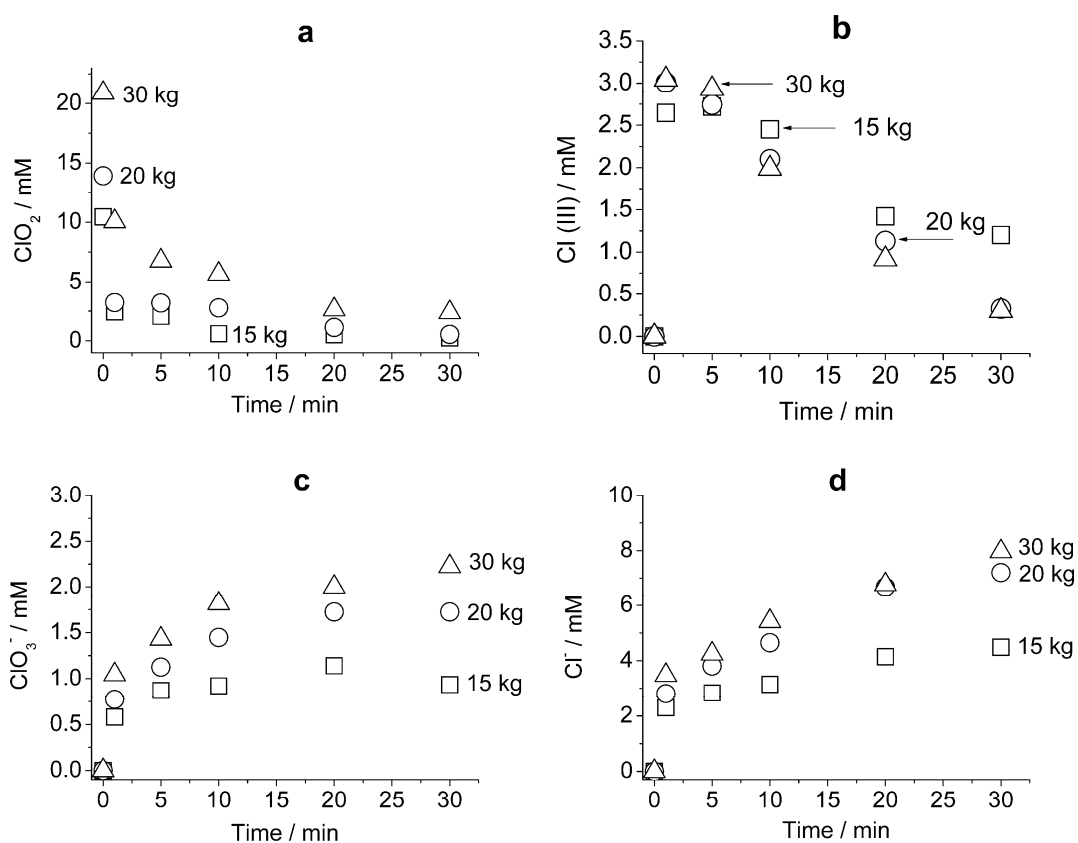


Figure 18. The effect of different dosages of active chlorine, 15 kg act. Cl/Adt (\square), 20 kg act. Cl/Adt (\circ) and 30 kg act. Cl/Adt (\triangle) to a) chlorine dioxide, b) Cl(III) (=chlorite + chlorous acid), c) chlorate and d) chloride as a function of time at 45°C.

The consumption of Cl(III) is due to several simultaneous reactions. The fastest reaction of Cl(III) seems to be its reaction with HOCl. This reaction and its kinetics were discussed in chapter 4.2 (Paper II). The reaction rate was found to be 1.1×10^3 at 25°C. Even though this reaction is fast, it is not able to consume all the Cl(III) formed, as HOCl is consumed in large amounts also in rapid reactions with organic structures. The reaction rate of HOCl has been determined to be $400 \text{ M}^{-1}\text{s}^{-1}$ with HexA and $40 \text{ M}^{-1}\text{s}^{-1}$ with lignin at 25°C [Vuorinen et al. 2007]. Even though the reaction rate with HexA is lower than with chlorous acid, HOCl reacts more extensively with HexA, since the amount of HexA present in pulp during prebleaching is higher than the amount of chlorous acid. Also, a reaction with lignin takes place because the amount of lignin can be much higher than the amount of HexA or

chlorous acid. Due to its fast reactions, the amount of HOCl is practically unmeasurable during a D₀-stage; it is consumed instantaneously after its formation [Ni et al. 1992].

Another indication of the fact that the reaction between HOCl and Cl(III) is not solely sufficient to describe the Cl(III) decay comes from the stoichiometries of Reactions 19 + 24 and 19 + 25. These stoichiometries show that one hypochlorous acid molecule should consume multiple Cl(III) molecules. However, the depletion of Cl(III) is very slow and thus other reactions of HOCl seem to be consuming the majority of the hypochlorous acid formed in-situ.

The self-decomposition reactions of chlorous acid were discussed in detail in chapter 4.1 (Paper I). They are rather slow reactions and do not contribute significantly to the consumption of Cl(III) even in a chlorine dioxide prebleaching stage. The metal catalysis of Cl(III) decomposition [Schmitz and Rooze 1984, Joncourt et al. 1998] should not contribute to the Cl(III) depletion in our results, since the pH during bleaching was always above 2.7 where the Fe³⁺ ions are incapable of reacting with ClO₂⁻ [Fábián and Gordon 1991a, Fábián and Gordon 1991b]. However, it has been stated that if the pH during ClO₂ bleaching is too low, the presence of iron will lead to increased cellulose degradation as well as increased AOX and chlorate formation [Joncourt et al. 1998].

The reaction between chlorous acid and aldehydes seems to contribute significantly to Cl(III) consumption as discussed in chapter 4.3. The HOCl formed through these reactions contributes to the overall degree of oxidation in chlorine dioxide bleaching, but the majority of the hypochlorous acid is produced in the reaction between phenolic lignin and chlorine dioxide [Kolar et al. 1983, Ni et al. 1992].

The inorganic chlorine compound that was mostly affected by the implementation of an A-stage was Cl(III) (Figure 19). After the A-stage, the amount of Cl(III) formed was halved in the following D₀-stage. This is logical, since after the A-stage the pulp contains less hexenuronic acid to react with HOCl. This “left-over” HOCl is free to react more extensively with chlorous acid (according to Reaction 19), lowering the amount of Cl(III) observed. Another contributing factor is that during the A-stage ~10% of HexA is converted into 5-formyl-2-furoic acid [Teleman et al. 1996, Vuorinen et al. 1997]. In Paper III this aldehyde structure was shown to be reactive with chlorous acid. Since the A-stage in our

case removed 20 meq/kg of HexA, the amount of 5-formyl-2-furoic acid formed should be approximately 2 meq/kg. Taking into consideration the pulp consistency in the bleaching experiments this amount can account for only 0.22 mM Cl(III) consumption. Since the reduction in Cl(III) was over 1.5 mM, it can be concluded that the 5-formyl-2-furoic acid contributed only very slightly to the increased Cl(III) consumption. The main reason leading to the lower Cl(III) concentration seems to be the higher amount of HOCl that is available to react with Cl(III). This led also to a slightly faster formation of chloride and chlorate as they are the final products in this reaction.

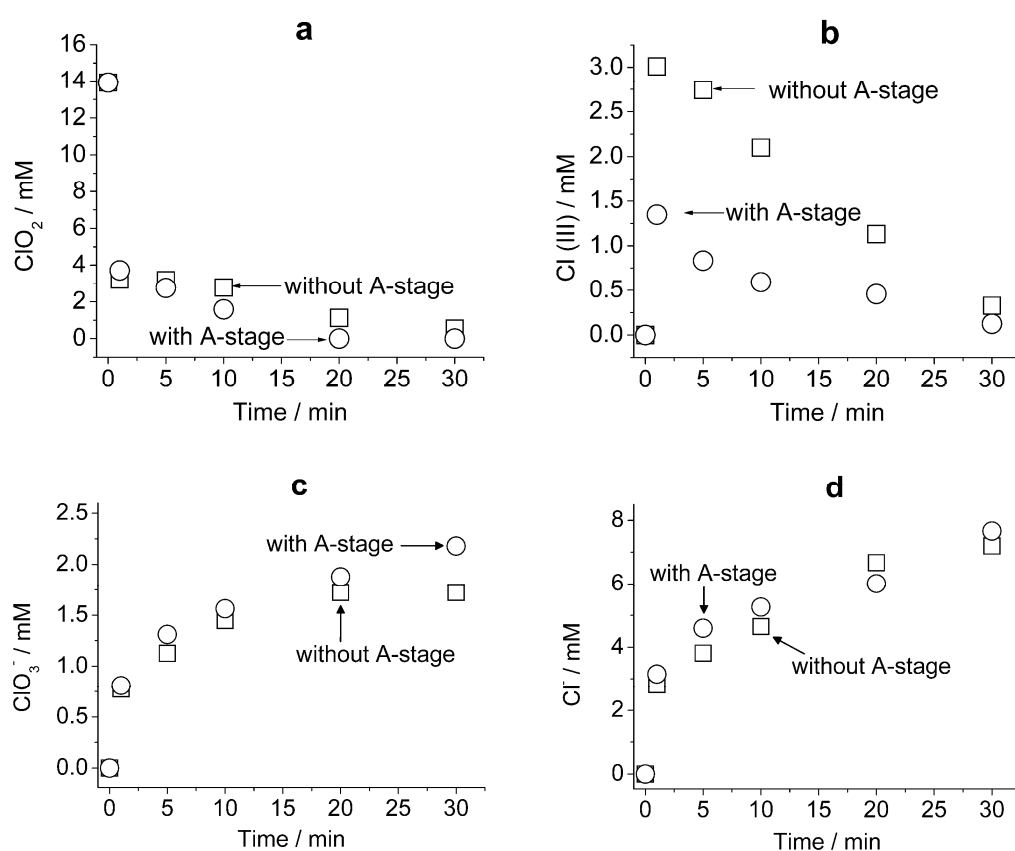


Figure 19. The development of a) chlorine dioxide, b) Cl(III) (=chlorite + chlorous acid), c) chlorate and d) chloride in a D₀-stage with (o) and without (□) a preceding A-stage as a function of time with 20 kg act. Cl/Adt at 45°C.

5 CONCLUDING REMARKS

The role of chlorine (III) in chlorine dioxide bleaching was clarified by investigating the kinetics of its reactions and their importance during chlorine dioxide bleaching. It was discovered that the self-decomposition of Cl(III) has practically no significance in bleaching conditions and that the fastest reaction consuming Cl(III) is the reaction between Cl(III) and HOCl/Cl₂. Aldehydes were shown to contribute substantially to Cl(III) depletion. Through the oxidation of aldehyde groups in cellulose, Cl(III) may have a positive effect on the viscosity of the pulp. In the future, the presence of these aldehydes should be verified with another method and their origin and amount should be clarified.

Even though Cl(III) is not a delignifying or bleaching agent as such, its reactions partly determine how much chlorine dioxide, hypochlorous acid, and chlorate are formed during a chlorine dioxide bleaching stage. These compounds dictate how much chlorination and delignification take place during a chlorine dioxide stage and are thus important in bleaching.

This work clarified the overall chemistry during chlorine dioxide bleaching and enabled its modeling more precisely. Through the knowledge of Cl(III) chemistry gained, the accuracy of the model has been improved. The simplified scheme of the reactions taking place in chlorine dioxide bleaching that was presented in Figure 1 can now be modified according to our results to give the revised scheme, although still simplified, presented in Figure 20.

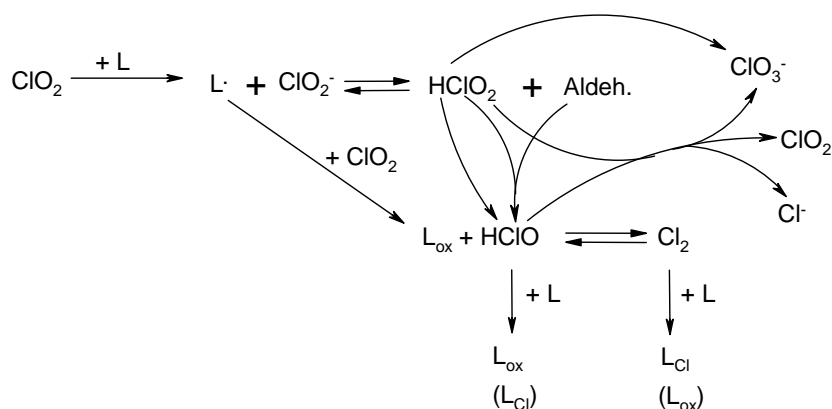


Figure 20. An updated simplified scheme of the reactions in chlorine dioxide bleaching.

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