

OZONE-BASED ECF BLEACHING OF SOFTWOOD KRAFT PULP

by

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SUMMARY

The objective of this work was to explore fundamental aspects of utilizing (DZ) and (ZD) bleaching stages in the prebleaching of oxygen delignified Scandinavian softwood kraft pulp, and compare paper properties of fully bleached pulps with a DEoD₁ED₂ bleached ECF reference pulp. According to the literature, the use of chlorine dioxide and ozone in combination in (DZ) and (ZD) bleaching stages seems advantageous from both environmental and economical points of view. A significant reduction in the formation of chloro-organic compounds and efficient delignification relative to chemical consumption is obtained.

The use of chlorine dioxide and ozone in combination in (DZ)Eo and (ZD)Eo prebleaching of oxygen delignified kraft pulp has been shown to be efficient in terms of delignification. When the (DZ)Eo prebleaching process was applied, a synergetic delignification effect was obtained giving better delignification than should be expected from the effect of chlorine dioxide and ozone separately.

The efficient delignification obtained in (DZ)Eo and (ZD)Eo prebleaching seems reasonable due to the ability of chlorine dioxide and ozone to degrade different types of lignin structures. Whereas chlorine dioxide mainly degrades phenolic lignin structures, ozone is capable of degrading both phenolic and non-phenolic lignin structures. Both chlorine dioxide and ozone are strong oxidants, but ozone seems to be more efficient in this respect since more carboxyl groups were implemented in the residual lignin at the same degree of delignification. The large number of carboxyl groups introduced in the lignin structure seems to govern the solubilization of the lignin in chlorine dioxide and ozone bleaching. The superior delignification efficiency of (DZ)Eo prebleaching versus (ZD)Eo prebleaching may be explained by that the (DZ) treatment initially allows chlorine dioxide to degrade the phenolic lignin structures, and leaves the non-phenolic and less reactive lignin structures for the ozone treatment.

The chlorine dioxide treatment in the (DZ) and (ZD) prebleaching stages differ from chlorine dioxide prebleaching by the lower chlorine dioxide charge applied. By studying effects of chlorine dioxide charge in prebleaching, it was shown that chlorine dioxide prebleaching gives efficient delignification relative to chemical consumption and a lower chlorate formation when a low chlorine dioxide charge is applied. An explanation may be that the reaction intermediate hypochlorous acid reacts with residual lignin and contributes to the delignification. At higher chlorine dioxide charges less reactive lignin structures are present and hypochlorous acid reacts to a larger extent inorganically and forms chlorate. In practice, a low chlorine dioxide charge is utilized in both (DZ) and (DC) stages, which both have been shown to be very efficient in terms of delignification. The superior delignification efficiency of (DZ)Eo prebleaching versus (ZD)Eo prebleaching may be explained by that hypochlorous acid reacts with lignin and contributes to the delignification in the (DZ) stage. In the (ZD) stage less reactive

residual lignin structures are present, and hypochlorous acid probably reacts to a larger extent inorganically and forms chlorate.

Physical paper properties of D_{Eo}Q(PO), (DZ)E_oD₁ED₂ and (DZ)E_oQ(PO) bleached pulps to 88% ISO brightness were compared to the same properties of a D_{Eo}D₁ED₂ bleached ECF reference pulp.

(DZ)E_o prebleaching applied in a (DZ)E_oD₁ED₂ bleaching sequence reduced the AOX formation and the COD effluent load by 25% and 9% respectively. The tear strength was maintained, but the (DZ)E_o prebleaching seems to have a slight negative effect on fibre strength as indicated by lower wet zero span strength of beaten (DZ)E_oD₁ED₂ and (DZ)E_oQ(PO) bleached pulps.

Pressurized peroxide final bleaching applied in a D_{Eo}Q(PO) bleaching sequence reduced the AOX formation by 30%, but the COD effluent load was increased by 29%. Pressurized peroxide final bleaching yielded pulps with higher fibre charge than chlorine dioxide final bleaching. Compared to the chlorine dioxide final bleached pulps, the increased number of charged groups in D_{Eo}Q(PO) and (DZ)E_oQ(PO) bleached pulps seemed to promote increased fibre swelling of both unbeaten and highly beaten pulps. The more swollen unbeaten Q(PO) final bleached pulps formed denser paper sheets with higher tensile strength and wet zero span strength. A highly charged and swollen pulp seems to be advantageous with respect to beatability when the pulp is beaten to a target tensile strength.

PREFACE

This thesis is submitted in partial fulfilment of the *doktor ingeniør* degree at the Norwegian University of Science and Technology. The work has been carried out at Norwegian Pulp and Paper Research Institute (PFI) from 1997 to 2000, with Professor Peder Kleppe as supervisor. The doctoral study was funded by Norske Skog ASA, Borregaard Industries Ltd., Södra Cell AB, Peterson Linerboard and the Research Council of Norway.

This thesis includes the following papers as journal articles referred to as **Papers I-III** in the text:

I. Toven, K., Gellerstedt, G., Kleppe, P. and Moe, S. "The use of chlorine dioxide and ozone in combination in prebleaching", Submitted for publication in *Journal of Pulp and Paper Science*.

II. Toven, K. and Kleppe, P. "Low-charge chlorine dioxide prebleaching", Submitted for publication in *Nordic Pulp and Paper Research Journal*.

III. Toven, K., "Swelling and physical properties of ECF light bleached softwood kraft pulps", Submitted for publication in *Tappi Journal*.

Some of the results have been presented in another context at international conferences.

Toven, K., "Ozone based ECF bleaching of oxygen delignified kraft pulp", *Int. Pulp Bleach. Conf.*, Helsinki, 2:377-382 (1998).

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LIST OF ABBREVIATIONS

A	:	Acid wash
AOX	:	Dissolved chloro-organic compounds
C	:	Chlorine bleaching
COD	:	Chemical Oxygen Demand. Water soluble organic substance
D	:	Chlorine dioxide bleaching
DMSO	:	Dimethyl sulfoxide
DTPA	:	Diethylene triamine pentaacetic acid
(DZ)	:	Sequential addition of first chlorine dioxide and then ozone without intermediate washing
E	:	Alkaline extraction
ECF	:	Elemental Chlorine Free. Pulp bleaching process in which chlorine dioxide is used alone or in combination with TCF chemicals. Chlorine gas, hypochlorous acid or hypochlorite ion are not utilized.
Eo	:	Oxygen reinforced alkaline extraction
Eop	:	Oxygen and hydrogen peroxide reinforced alkaline extraction
EDTA	:	Ethylenediamine tetraacetic acid
Kappa number, (K)	:	The kappa number is an estimate of the lignin content in pulp. It is defined as the number of millilitres of a 20 mM solution of potassium permanganate that is consumed by one gram of dry pulp under standardised conditions (SCAN-C 1:77)
O	:	Oxygen delignification
OCI	:	Chlorinated organic compounds in pulp
P	:	Hydrogen peroxide bleaching
(PO)	:	Oxygen pressurized hydrogen peroxide bleaching at elevated temperature
Q	:	Chelating agent
SCAN	:	Scandinavian pulp, paper and board standardized test
TCF	:	Total Chlorine Free. Pulp bleaching is carried out without the use of any chlorine-containing chemicals. Typical TCF chemicals are hydrogen peroxide, ozone, oxygen and peracetic acid
WRV	:	Water retention value. The water retention vale is an empirical measure of the capacity of fibres to hold water
Z	:	Ozone bleaching
(ZD)	:	Sequential addition of first ozone and then chlorine dioxide without intermediate washing

TABLE OF CONTENTS

ABSTRACT	3
PREFACE	5
ACKNOWLEDGEMENTS	7
LIST OF ABBREVIATIONS	9
TABLE OF CONTENTS	11
 CHAPTER 1	
INTRODUCTION	15
1.1 Background	15
1.2 Objectives of the study	17
1.3 Outline of the thesis	17
 CHAPTER 2	
MATERIALS AND METHODS	19
2.1 Pulps	19
2.2 Laboratory bleaching	19
2.2.1 DEo, (DZ)Eo, (ZD)Eo and ZEO prebleaching in MC mixer	19
2.2.2 Low consistency D, (DZ) and (ZD) prebleaching in glass reactor	20
2.2.3 Final bleaching	21
2.3 Isolation of residual lignins	21
2.4 Other analyses applied	23
2.4.1 Fibre charge	23
2.4.2 Hexenuronic acid	24
 CHAPTER 3	
SYNERGETIC DELIGNIFICATION IN THE (DZ) PROCESS (PAPER I)	25
3.1 The use of chlorine dioxide and ozone in combination	25
3.1.1 Literature review	25
3.1.2 Mill experience	26
3.2 The use of the (DZ) and (ZD) stages in prebleaching	26
3.3 Concluding remarks	30

CHAPTER 4**THE COMPLEMENTARY LIGNIN CHEMISTRY OF CHLORINE DIOXIDE****AND OZONE (PAPER I) 31**

- 4.1 Structural changes in lignin in alkaline cooking 31
- 4.2 Structural changes in residual lignin in chlorine dioxide
and ozone prebleaching 32
 - 4.2.1 Lignin isolation 32
 - 4.2.2 Phenolic hydroxyl groups 33
 - 4.2.3 Oxidation of lignin in prebleaching 34
 - 4.2.4 (DZ) versus (ZD) 36
- 4.3 Concluding remarks 37

CHAPTER 5**LOW-CHARGE CHLORINE DIOXIDE PREBLEACHING (PAPER II) 39**

- 5.1 The ideal situation for chlorine dioxide bleaching 39
- 5.2 Major reactions of chlorine dioxide in prebleaching 40
- 5.3 Inorganic reactions during chlorine bleaching 41
- 5.4 Effects of hypochlorous acid 44
- 5.5 Effects of chlorine dioxide charge in prebleaching 45
- 5.6 Applications of low chlorine dioxide charge 48
 - 5.6.1 (DZ) and (ZD) stages 48
 - 5.6.2 Sequential charging of chlorine dioxide 49
 - 5.6.3 Similarities between (DC)/(CD) and (DZ)/(ZD) stages 50
- 5.7 Concluding remarks 51

CHAPTER 6**PAPER PROPERTIES OF FINAL BLEACHED PULPS (PAPER III) 53**

- 6.1 Pulp and effluent characteristics 53
- 6.2 Paper properties of unbleached pulps 54
- 6.3 Effect of bleaching on charged groups in the pulp 55
- 6.4 Effect of charged groups on swelling 56
- 6.5 Physical paper properties of beaten pulps 57
- 6.6 Concluding remarks 59

CHAPTER 7**CONCLUDING REMARKS 61**

- 7.1 Synergetic delignification in the (DZ) process (Chapter 3) 61
- 7.2 The complementary lignin chemistry of chlorine dioxide and ozone
(Chapter 4) 61
- 7.3 Effect of chlorine dioxide charge in chlorine dioxide bleaching (Chapter 5) ... 61
- 7.4 Physical properties of final bleached pulps (Chapter 6) 62

LIST OF REFERENCES 63

COLLECTION OF PAPERS

PAPER I 69

PAPER II 79

PAPER III 89

C H A P T E R

1

INTRODUCTION

1.1 Background

In the 20th century, environmental concern has been a major driving force for the development of new pulping technology. As new technology has been developed, stricter environmental regulations for discharges have forced a fast implementation of new technology in mills. The development has changed the chemical pulping processes from discharging about 50% of the wood material to the recipient in the beginning of the 20th century to the modern mill with very low amounts of discharge. In the 1920s the regeneration system for sulphate cooking chemicals was developed in Canada. Instead of discharging the cooking liquor to the recipient, the dissolved organic material was concentrated and burned to release the inorganic ions for reuse and to provide fuel. The sulphate cooking process was termed the kraft process due to the strength of the fibres, and the energy efficient chemical recovery system and the strength of the fibres made the kraft pulping process the dominant pulping process. The use of the chemical recovery system became widespread all over the world in the 1940s. The kraft processes produced stronger but substantially darker pulps than sulphite and groundwood pulping processes and required bleaching. In the period 1900 to 1930 multistage hypochlorite bleaching with interstage washing (HEH bleaching sequence) and ways of utilizing chlorine gas (C) in bleaching was developed. Chlorine dioxide bleaching (D) was first practiced in the 1940s and led to the CEDED high-brightness bleaching process in the 1950s with minimum loss of pulp strength. In 1970, the first commercialized oxygen delignification system was started up in South Africa. The bleaching filtrate from the oxygen stage could be carried back for destruction in the recovery system, thus having a low environmental impact. The lignin content in the pulp sent to the bleach plant was reduced, which cut both the consumption of bleaching chemicals and the discharge from the bleach plant. Ever since the first oxygen delignification system was introduced, the industrial use of oxygen delignification has expanded rapidly. In the 1980s, improved pulping processes with extended delignification and medium consistency washing and mixing technology were developed. As oxygen delignification, the improved pulping processes with extended delignification reduced both the need for bleaching chemicals and the discharge from the bleach plant. At the end of the 1980s partial substitution of chlorine dioxide for chlorine became widely accepted, as a result of concern for the formation of toxic dioxins and other stable chlorinated organic substances in chlorine

bleaching. The use of chlorine was questioned and a very quick development away from the use of chlorine gas as bleaching agent was seen. In the early 1990s complete substitution of chlorine by chlorine dioxide into DEDED bleaching developed rapidly, which is known as elemental chlorine-free (ECF) bleaching. Thereafter increased demand on the European market for “environmentally superior” pulps that were bleached without chlorine containing chemicals as well as the desire for a closed bleach plant promoted the use of totally chlorine-free (TCF) chemicals in bleaching. Chlorides and chlorinated organic compounds, which form in chlorine and chlorine dioxide bleaching, was considered to make the closed bleach plant difficult due to their corrosive nature. However, irrespective of whether TCF chemicals are used or not, the development towards a closed bleach plant has some challenges to overcome before it can be realized.

At present, the quest of the industry is totally effluent-free (TEF) pulping, even though strictly speaking, this is not achievable. ECF pulps are being accepted as the standard market pulp, and several independent studies have shown that there is no provable environmental impact of the discharge of chloro-organic compounds (AOX) when the amount discharged is kept at a reasonably low level [2]. In addition, the use of TCF chemicals also has some negative effects from an environmental point of view. TCF chemicals require the use of chelating agents and often generate increased amounts of dissolved organic material, neither of which are desired components in the bleach plant effluent. In the TEF concept, the focus is no longer solely on bleaching, but on the whole production line. It is less important whether the bleaching is carried out with chlorine containing bleaching chemicals or not, as long as the effluents can be recycled and no harmful or problematic substances are released to the environment. This goal is believed to be achievable using both TCF and ECF bleaching sequences. However, even though major improvements in pulping technology have been made from an environmental point of view, bleaching filtrates are still today discharged to the recipient and therefore many of the remaining negative environmental effects of pulp production originate in the bleach plant. A further reduction in effluents and improved techniques for purification of effluents are both ways of reducing the problem.

The choice of bleaching technology is a result of many considerations. Important factors are investment costs, operating costs, the discharge of organic and chloro-organic material, health and safety, and product quality of the bleached pulp. In this study it was decided to explore a bleaching process which seems to be beneficial from both an environmental and cost-efficient view relative to traditional ECF bleaching. The environmental aspect was to reduce the discharge of organic and inorganic chloro-compounds by reducing the overall chlorine dioxide consumption. Some chlorine dioxide was to be replaced by TCF chemicals in ECF-light bleaching sequences, meaning bleaching sequences of low overall chlorine dioxide consumption. In addition, it was desirable to reduce the chemical costs and maintain the strength properties at the same level as traditional ECF bleached pulp.

Two recently developed bleaching concepts which according to the literature appear to be beneficial in terms of both environmental aspects and chemical costs, have been studied. Lachenal *et al.* [3] and Dillner and Tibbling [4] has been shown that some

chlorine dioxide can be replaced by ozone in prebleaching by utilizing (DZ) or (ZD) bleaching stages. Besides a significant reduction in the formation of chloro-organic compounds, the bleaching concepts also seem promising with respect to chemical costs. Paper properties of final bleached pulp have been reported to be similar to traditional ECF bleached pulp. In final bleaching, pressurized peroxide bleaching, Q(PO), is a promising bleaching concept which may replace chlorine dioxide final bleaching, D₁ED₂ [5]. Pressurized peroxide bleaching means oxygen pressurized hydrogen peroxide bleaching at high temperature, and has been shown to be beneficial in several aspects relative to traditional atmospheric hydrogen peroxide bleaching. The reaction time is reduced considerably, higher pulp viscosity is obtained, the amount of hydrogen peroxide needed to achieve a certain brightness is reduced and the maximum obtainable brightness level is raised [5].

1.2 Objectives of the study

The major objective of this work was to explore the effects of using ozone in (DZ) and (ZD) bleaching stages in ECF bleaching of oxygen delignified softwood kraft pulp. The use of (DZ) and (ZD) stages in prebleaching is considered to be one way of reducing the chlorine dioxide consumption in traditional ECF bleaching and to provide a more economical and environmental feasible way of bleaching oxygen delignified kraft pulp. Fundamental aspects of using a combination of chlorine dioxide and ozone in prebleaching were investigated, and paper and effluent properties of fully bleached pulps were compared to a DEoD₁ED₂ bleached reference pulp.

1.3 Outline of the thesis

This thesis comprises results from papers that have been published or submitted for publication in journals, referred to as **Papers I - III** in the text.

Chapter 1 describes the background for the study and the objectives of this work.

Chapter 2 presents the experimental procedures and methods applied.

Chapter 3 gives a literature review about the use of (DZ) and (ZD) bleaching stages in the bleaching of kraft pulps. The delignification efficiency of (DZ)Eo and (ZD)Eo prebleaching of oxygen delignified kraft pulp is investigated and compared to chlorine dioxide and ozone prebleaching separately (**Paper I**).

Chapter 4 establishes the differences between chlorine dioxide and ozone in their ability to degrade different types of lignin structures. Residual lignins are isolated from untreated and prebleached pulps and structural changes in residual lignin structure upon chlorine dioxide and ozone prebleaching is studied (**Paper I**).

Chapter 5 describes the effects of using low chlorine dioxide charge in chlorine dioxide prebleaching. Low chlorine dioxide charge is utilized in the (DZ) process and (ZD) process (**Paper II**).

Chapter 6 compares the paper properties of (DZ)EoD₁ED₂, (DZ)EoQ(PO) and DEoQ(PO) bleached pulps with a DEoD₁ED₂ bleached reference pulp (**Paper III**).

Chapter 7 presents the overall conclusions of this work.

CHAPTER

2

MATERIALS AND METHODS

2.1 Pulps

Two industrially produced oxygen delignified softwood kraft pulps were used in the experiments. Characteristics of the pulps are given in Table 2.1. Both pulps A and B in Table 2.1 were used for studying prebleaching effects of using chlorine dioxide and ozone in combination, whereas pulp B was used in all other experiments. All pulps were made of mixtures of Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*).

Table 2.1: Characteristics of the industrially produced¹⁾ oxygen delignified kraft pulps employed in the study.

Pulp	Kappa number	Brightness % ISO	Viscosity dm ³ /kg	Raw material
(A) ²⁾	13.2	42	965	42% <i>Picea abies</i> , 53% <i>Pinus sylvestris</i> and 5% saw mill chips (mixture of <i>Picea abies</i> and <i>Pinus sylvestris</i>)
(B) ³⁾	12.7	36	930	70% <i>Picea abies</i> , 30% <i>Pinus sylvestris</i> and 30% saw mill chips (mixture of <i>Picea abies</i> and <i>Pinus sylvestris</i>)

¹⁾Tofte mill, Norway ²⁾Kappa number after the cook 24-25, residual alkali 9-11 g/l

³⁾Kappa number after the cook 21-22, residual alkali 7-8 g/l.

2.2 Laboratory bleaching

2.2.1 DEo, (DZ)Eo, (ZD)Eo and ZEO prebleaching in MC mixer

Both pulps A and B in Table 2.1 were washed with distilled water, pH adjusted with sulphuric acid and washed with distilled water again. The pulps were then adjusted to pH 3 prior to Z and (ZD) stages and to pH 4 prior to D and (DZ) stages. The pulps were prebleached according to the sequences DEo, (DZ)Eo, (ZD)Eo and ZEO. The final pH in the D, (DZ) and (ZD) stages was about 2.4 and about 2.6 in the Z stage. The D, (DZ), (ZD) and Z stages were performed at 10% consistency and 50°C in a high shear medium

consistency (MC) mixer (CMS 2040). High shear intensity mixing was applied during the injection of chemicals and intervals of low intensity mixing were applied to secure uniform temperature in the pulp during the treatments. Ozone was injected from a gas container and the ozone concentration in the container (amount ozone per pressure drop) was determined by iodometric titration. The gas was injected by opening a valve manually trying to achieve a certain pressure drop corresponding to desired ozone charge in the container. However, since the injection went fast and the pressure in the gas container dropped quickly due to the adiabatic expansion of the gas, it was difficult to exactly reach the desired final pressure in the ozone container. Thus, the injected amount of ozone did not always become exactly the planned amount. Chlorine dioxide was injected accurately from liquid cylinders, and the chlorine dioxide concentration was determined by iodometric titration immediately before injection. The retention time of D and Z stages was 30 minutes, and the retention times of D and Z in the (DZ) and (ZD) stages were 30 and 10 minutes respectively. The alkali extraction stages, Eo, were done in autoclaves at 90°C, 0.5 MPa O₂ pressure, 1% NaOH charge, for 60 minutes.

Prebleached pulps were analysed for kappa number (SCAN C1:77), brightness (SCAN C11:95), viscosity (SCAN C15:88) and organic bound chlorine in pulp (OCI, SCAN W 9:89). Bleaching filtrates were analysed for COD_{Cr} (Dr. Lange), AOX (SCAN W 9:89), and inorganic chloro-compounds (chlorate and chloride) by ion chromatography.

2.2.2 Low consistency D, (DZ) and (ZD) prebleaching in glass reactor

In order to study the concentration profiles of inorganic chloro-compounds during chlorine dioxide bleaching some pulp was bleached at low consistency in a continuously stirred batch glass reactor. Chlorine dioxide charge was varied (0.5, 0.75 and 1.0%) by varying pulp consistency (2, 1.33 and 1%), and keeping the total liquid volume and the amount of chlorine dioxide injected constant. Throughout the treatment, pulp suspension samples were taken out and filtrated on a Büchner funnel. The filtrates were cooled in an ice bath and analysed directly for chlorine dioxide, chlorite, chloride and chlorate concentration by ion chromatography (Dionex 4000i). As chlorine dioxide and chlorite gave the same peak in the chromatogram, their concentrations were measured by analysing two samples in which the chlorine dioxide was removed by nitrogen in one of the samples. The (ZD) stage was performed by bubbling ozone (approx. 0.4% consumed) through the pulp suspension prior to the chlorine dioxide treatment.

Chlorine dioxide solution was prepared in the laboratory. Sodium chlorate (200 g) and crystallized sodium oxalic acid (200 g) were mixed with a cooled sulphuric acid solution (120 ml concentrated H₂SO₄ in 400 ml water) and warmed in a water bath to 60°C in a ventilated closet. Chlorine dioxide gas was formed and the gas was led through a bottle with water for washing, and collected in a water-filled brown bottle (2 l) placed in an ice bath. After about five hours the reaction was completed, and the chlorine dioxide solution was stored in a refrigerator. Preparation and handling of chlorine dioxide must be done with caution due to the risk of explosion. The composition of the prepared solution was determined by ion chromatography. The strength of the chlorine dioxide solution was about 28 g ClO₂/l and the relative ratio of inorganic chloro-compounds 98 mole% ClO₂, 2 mole% Cl⁻ and 0.1% ClO₃⁻. Technical sodium chlorite was applied in some experiments. The composition of the salt was also determined by ion

chromatography. The salt contained 0.80 g NaClO₂/g and 0.13 g NaCl/g, whereas no chlorate was present.

2.2.3 Final bleaching

Pulp (B) in Table 2.1 was prebleached according to the sequences DEo and (DZ)Eo as described in Section 2.2.1. Three portions were prepared of each prebleaching sequence and the portions mixed before final bleaching. Two final bleaching sequences were applied, Q(PO) and D₁ED₂. Chemicals were charged in order to achieve a final brightness of 88% ISO. Prior to the D₁ stage the pulp was acidified by sulphuric acid to pH 6, and the D₁, E and D₂ stages were performed in plastic bags in water bath at 70°C using retention times of two, one and three hours respectively. Chemical charges were 0.5% ClO₂ in the D₁ stage, 0.4% NaOH in the E stage and 0.2% ClO₂ in the D₂ stage. The chelation stage, Q, was done in a plastic bag in a water bath for one hour at pH 5.5, 70°C, and 0.3% EDTA was charged. Pressurized peroxide stage, (PO), was performed by charging 4.0% H₂O₂, 1.6% NaOH, 0.3% MgSO₄ and 0.2% DTPA and keeping the pulp in plastic bags within rotating autoclaves at 105°C, 0.5 MPa oxygen pressure for two hours. All treatments were done at 10% pulp consistency, and the pulps were washed with hot distilled water in between the bleaching stages. After the bleaching sequence the pulps were washed with distilled water and pH adjusted to pH 5-6 with SO₂-water.

Final bleached pulps were analysed for kappa number (SCAN C 1:77), brightness (SCAN C 11:95) and viscosity (SCAN C 15:88). Laboratory sheets were prepared of unbeaten and beaten pulps, and the sheets analysed for tear strength (SCAN P 11:96), tensile strength (SCAN P 16:76), water retention value (SCAN C-102XE) and Scott bond strength (Scott Internal Bond Tester).

2.3 Isolation of residual lignins

Residual lignins were isolated from both the oxygen delignified kraft pulp (B) in Table 2.1 and DEo and ZEO laboratory prebleached pulps, see Section 2.2.1. In addition, residual lignin was isolated from an industrially produced (Tofte mill) unbleached kraft pulp of kappa 24.3 and viscosity 990 dm³/kg. The unbleached kraft pulp was made of 30% *Picea abies*, 50% *Pinus sylvestris* and 20% saw mill chips (mixture of *Picea abies* and *Pinus sylvestris*). Before isolating lignin by acid hydrolysis [6] pulps were extracted with acetone to remove extractives. Acetone extracted pulps were refluxed for two hours with 0.1 M HCl in dioxane-water v/v 82:18 and the dioxane was evaporated on rotavapor. During evaporation, water was added subsequently in order to avoid strong acidity. The remaining solution was dialysed (MW cut off > 1000 g/mole) for three days to remove hydrochloric acid. Thereafter the solution was concentrated by evaporation on a rotavapor and freeze dried. The lignin residue was extracted with pentane in order to remove remaining extractives [6]. Amounts of lignin isolated and kappa numbers of the pulps before and after acid hydrolysis are given in Table 2.2. The yield of lignin isolated is estimated using the correlation $\% \text{ lignin} = 0.15 \cdot \text{Kappa number}$.

Isolated lignins were analysed for uncondensed β-aryl ether structures by thioacidolysis [7] and free phenolic hydroxyl groups by a modified UV-ionization difference method

Table 2.2: Isolation of residual lignins by acid hydrolysis.

Pulp	Kappa number	Kappa number after extraction	Lignin isolated, g/100 g pulp	Yield ¹⁾ , %
Unbleached	24.3	8.8	1.81	50
O	12.7	3.3	0.78	41
ODEo	3.7	0.9	0.26	47
OZEo	4.0	1.2	0.36	60

¹⁾Yield = 100 • (Lignin isolated)/(0.15 • Kappa number).

[8, 9]. The types of β -O-4 structures and phenolic phenyl propane structures analysed are illustrated in Figure 2.1.

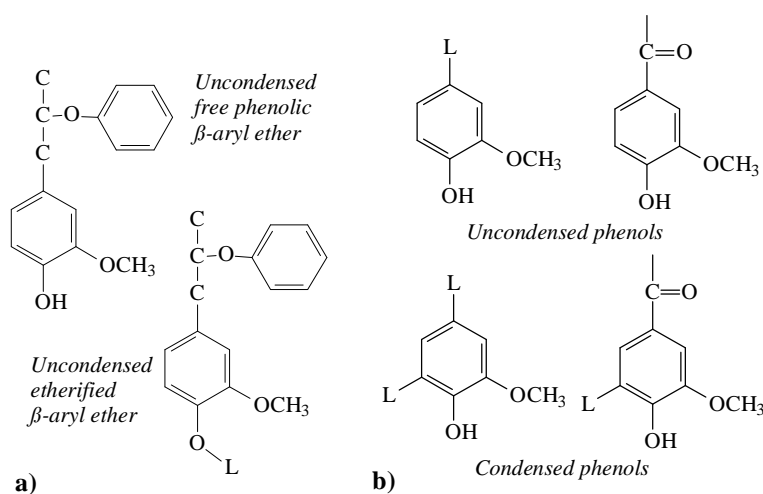


Figure 2.1 a) Type of β -O-4 structures analysed by thioacidolysis [7] b) Type of phenolic phenyl propane units analysed by UV spectroscopy [8, 9].

Carboxyl groups in residual lignins were quantified by conductometric titration [10]. Prior to the determination the carboxyl groups, the material must be in proton form. Due to the isolation method applied the residual lignin were already in proton form and no ion exchange was needed. Some residual lignin (30 mg) was dissolved in dioxane/water 4:1 and subsequently poured into 0.001 M NaCl solution. HCl (50 μ mole) was added and the solution titrated at a slow rate with 0.1 M NaOH. The titration curves are shown in Figure 2.2..Heuts [11] found that conductometric titration yielded higher values for carboxyl acid groups in residual lignin than ³¹P NMR determination, and suggested that acidic phenolic groups might contribute in the determination.

The elemental composition and methoxyl content of the residual lignins was analysed by Analytische Laboratorien in Gummersbach [12].

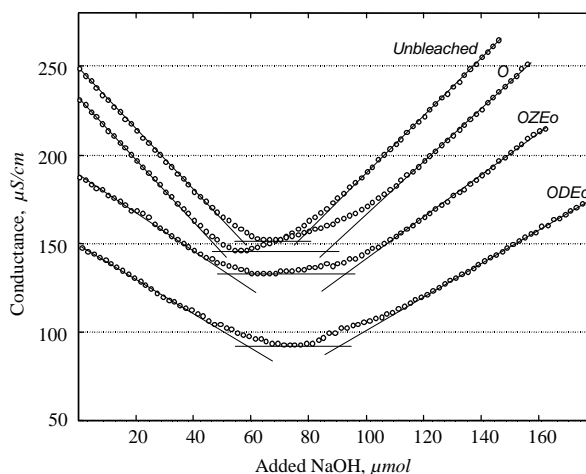


Figure 2.2 Carboxyl groups in residual lignins determined by conductometric titration [10].

Some of the data on functional groups in lignin are recalculated using an average molecular weight for C₉ based spruce lignin of 183 g/mole [13] in order to *estimate* the number of groups per 100 phenyl propane units.

2.4 Other analyses applied

2.4.1 Fibre charge

The fibre charge of prebleached and final bleached pulps was analysed by polyelectrolyte adsorption [14]. Before analysis the pulps were washed with water, treated with 0.01 M HCl for two hours and washed again with deionized water until pH 5. The carboxyl groups were then converted to their Na-form by treating the pulps with 1 mM NaHCO₃ solution at pH 9 for two hours. To remove excess electrolyte, the pulps were washed with deionized water until the conductivity of the washing filtrate was less than 5 μS/cm. A minimum of five different pulp samples was immersed in dilute NaCl solution, pH adjusted to pH 8 and different amounts of 3.6-ionene (polybrene) were added in excess. The pulp suspensions were stirred for 30 minutes and filtrated on a Büchner funnel. The filtrates were titrated with a 0.001M standard anionic polyelectrolyte solution, using Mütek charge detector to detect the end point of titration. The adsorbed amount of polymer is plotted versus the equilibrium concentration of polymer (in the filtrates), and the fibre charge estimated by extrapolating the data to zero equilibrium concentration of polybrene. The polybrene applied had a molecular weight of about $8 \cdot 10^3$ g/mole and a charge density of $5.12 \cdot 10^{-3}$ mole eq/g and was applied without further purification.

According to Wåberg *et al.* [15], the true radius of gyration of polybrene is between 26 Å (random coil) and 225 Å. It has been shown that non-ionic polymers with a diameter larger than 50 Å are excluded from the smallest pores in the fibres. Thus, polybrene may have accessibility to even the smallest pores in the fibres [15]. It was decided to utilize a ionic strength of 0.01 M NaCl and pH 8 during the adsorption of polybrene since Wåberg *et al.* [16] found that these conditions gave about the same values for fibre charge as those obtained by conductometric titration [10]. However, when analysing fibre charge on four different fully bleached chemical pulps by both polyelectrolyte titration and conductometric titration, higher fibre charge values were obtained by polyelectrolyte titration. The results are given in Table 2.3 and show that about 12-20 $\mu\text{mole/g}$ higher values was obtained by polyelectrolyte titration. The charge level of the pulps did not influence the difference much.

Table 2.3: Comparison of polyelectrolyte titration and conductometric titration for determination of the total number of charged groups in chemical pulps.

Pulp	Polyelectrolyte titration	Conductometric titration ¹⁾	Difference
	$\mu\text{mole/g}$	$\mu\text{mole/g}$	$\mu\text{mole/g}$
ECF bleached softwood kraft pulp	49	33	16
ECF bleached softwood sulphite pulp	41	29	12
TCF bleached softwood kraft pulp	90	74	16
TCF bleached hardwood kraft pulp	134	114	20

¹⁾Average values from five laboratories measured in a ring-test under the development of a standardized SCAN method for measuring fibre charge.

2.4.2 Hexenuronic acid

The amount of hexenuronic acid groups in the pulps was determined by UV spectroscopy [17]. The applied method correlates well with other methods although somewhat higher values are obtained [18].

C H A P T E R

3

SYNERGETIC DELIGNIFICATION IN THE (DZ) PROCESS (PAPER I)

The industrial use of ozone in bleaching is rather limited due to its lower selectivity towards lignin. Ozone may oxidize carbohydrates forming carbonyl and carboxylic structures within the polysaccharide chains [19]. Upon alkaline treatment these groups may cause chain breakage and loss in pulp viscosity. Because of this selectivity problem ozone is usually applied at the beginning of a bleaching sequence where the cellulose degradation is retarded by the high amount of lignin present or only small amounts of ozone are applied. The industrial use of ozone is increasing. Recently it was reported that 19 pulp mills utilize ozone in pulp bleaching throughout the world [20]. Ozone is a very powerful oxidizing agent capable of oxidizing all types of lignin structures. The reaction with pulp is completed within seconds which reduces the need for large bleaching towers in the bleach plant.

3.1 The use of chlorine dioxide and ozone in combination

3.1.1 Literature review

A very interesting prebleaching process is the use of ozone in combination with chlorine dioxide in (DZ) and (ZD) bleaching stages. The following advantages have been found:

- The AOX formation is reduced considerably compared to traditional ECF bleaching. Relative to chlorine dioxide prebleaching, some reduction in AOX formation is expected due to the reduced chlorine dioxide consumption. However, the actual AOX formation in the (DZ)Eop prebleaching became even lower than should be expected from the chlorine dioxide charge [3, 4]. An explanation might be that the latter ozone treatment degrades some of the dissolved chloro-organic compounds. Roy-Arcand *et al.* [21] showed that ozonation effectively degrades dissolved chlorinated phenols and gave some reduction in COD.
- The bleaching concept is cost efficient due to efficient delignification. The use of (DZ) and (ZD) bleaching stages give very efficient delignification relative to chemical consumption [3, 4]. When ozone was applied in a (DZ)EoD₁ED₂ sequence,

Chirat and Lachenal [22] found that the total chlorine dioxide consumption could be reduced by 1.0% for hardwood and 0.8% for softwood pulp compared to a traditional DEoD₁ED₂ bleaching sequence. 0.25% and 0.7% ozone were used for the hardwood and softwood pulp respectively, corresponding to chlorine dioxide-ozone replacement ratios of 4 kg ClO₂/kg O₃ for the hardwood pulp and 1.7 kg ClO₂/kg O₃ for the softwood pulp. From the number of oxidation equivalents of chlorine dioxide and ozone 1 kg O₃ should replace 1.7 kg. ClO₂, but when considering that chlorine dioxide uses its oxidation potential more efficiently than ozone an even lower replacement ratio should be expected.

- Paper properties and pulp strength seem to be maintained despite the use of ozone Dillner and Tibbling [4] reported that the pulp viscosity could be maintained in the (DZ) stage by keeping the ozone charge and temperature low. The paper properties of final bleached pulp did not appear to differ from that of a conventional ECF bleached pulp, and normal pulp strength could be maintained. Lachenal *et al.* [3] compared the selectivity of various combinations of D and Z and found that the selectivity was superior for the DZ process compared to the ZD process. The selectivity was measured as the decrease in kappa number versus the degree of polymerization of cellulose. In addition, the simplified one-stage (DZ) treatment, without washing in between the chlorine dioxide and the ozone treatment, was even more selective than the two-stage DZ treatment. Both findings were surprising since ozone usually is less harmful at high lignin contents and the presence of dissolved organic material often has a negative effect. It was speculated that the chlorine dioxide modifies the residual lignin making it more reactive towards ozone, and that dissolved organic material may act as a radical scavenger in the latter ozone treatment.

3.1.2 Mill experience

The (DZ) and (ZD) bleaching technology has already been implemented in some mills. Some literature mill data are given in Table 3.1. The experience from three mills was presented at the 2000 IPBC conference in Halifax [23, 24, 25]. As a result of conversion from an OODEopDP bleaching sequence to an OO(ZD)(OP)PDP bleaching sequence, the Wisaforest pulp mill has reported a reduction in the COD and AOX effluent loads of 27% and 71% respectively [23]. In addition, the bleaching chemical costs was reduced by 16%. The Espanola mill converted from an ODcEDnD to an OA(ZD)EDnD sequence and obtained a reduction in AOX, COD and the colour of the effluent [24]. Pulp strength and pulp viscosity were maintained, the extractive content in the pulp was reduced, and high replacement ratios of 2.5-3.5 kg ClO₂/kg O₃ improved the bleaching economy. The Luíz Antfônio pulp mill chose to install the (DZ) process since the process made the best use of already installed equipment and since the process provided the best effluent and pulp quality [25]. Later on, the mill converted to a (ZD) process mainly due to material incompatibility. The (DZ) stage was disadvantageous since residual chlorine dioxide caused corrosion in the ozone gas scrubber.

3.2 The use of the (DZ) and (ZD) stages in prebleaching

In this study, the effects of utilizing (DZ)Eo and (ZD)Eo prebleaching of oxygen delignified softwood kraft pulp were investigated. DEo and ZEo prebleaching were used

Table 3.1: Mills using (DZ) and (ZD) technology.

Mill	Location	Pulp 1)	κ ²⁾ a. O	Bleaching sequence	ClO ₂ , Act. Cl kg/adt	AOX kg/t	COD kg/t	Ref
StoraEnso	Billerud, Sweden	SW	13	OADEopDED ³⁾	-	0.83	-	[26]
				OA(ZD)EopDED	-	0.45	-	
Wisaforest Kymmene	Pietarsaari, Finland	HW	14	OODEopDP ³⁾	44	0.5	58	[23]
				OO(ZD)OpPDP	18	0.2	44	
Sappi	Ngodwana, South Africa	SW	10	O(ZD)O/EoD	-	-	-	[26]
Espanola 1, Domtar Inc	Canada	HW	-	ODcEDnD ³⁾	-	0.47	-	[24]
				OA(ZD)EDnD	-	0.18	-	
Luíz Antônio, VCP	Luíz Antônio, Brazil	HW	11	O(CD)EopD ³⁾	51	-	37 ⁴⁾	[25]
				OO(ZD)EopD	50	-	29 ⁴⁾	
Jacarei, VCP	Jacarei, Brazil	HW	8	OOpZDnD ³⁾	30	-	-	[25]
				OOZD(PO)	16	-	-	

¹⁾SW: softwood, HW: hard wood ²⁾Kappa number after 1st or 2nd oxygen stage

³⁾Bleaching sequence before conversion to (ZD) bleaching technology ⁴⁾COD in prebleaching.

as reference treatments. Chirat *et al.* [27] studied the effect of (DZ) and (ZD) treatments of both untreated and oxygen delignified softwood and hardwood kraft pulps and found that untreated and oxygen delignified pulps responded differently to the treatments. In terms of delignification, the (DZ) stage was the most efficient treatment for the untreated kraft pulp whereas the (ZD) stage was the most efficient treatment for the oxygen delignified pulp. Chirat *et al.* [27] suggested that the fact that the number of free phenolic groups in lignin is reduced in oxygen delignification could explain the different behaviour of the pulps.

In the present study the experimental design was chosen in order to verify whether there is a synergetic delignification effect when chlorine dioxide and ozone are used in combination. The chemical charges for the DEo and ZEO reference bleaching sequences were selected to be 0.95% ClO₂ and 0.67% O₃, whereas the chemical charge of chlorine dioxide and ozone in the (DZ)Eo and (ZD)Eo were selected pairs of A•0.95% ClO₂ and (1-A)•0.67% O₃, A=[0.2, 0.4, 0.5, 0.6, 0.8]. Kappa numbers are plotted versus the injected amount ozone in Figure 3.1, and additional data are given in Table 3.2. The selection of chemical charges in the DEo and ZEO reference sequences was done in order to achieve a kappa number of about 4.0 after alkaline extraction. However, as the results in Figure 3.1 show, the applied chlorine dioxide charge was overestimated in this respect.

Figure 3.1 shows that the (DZ)Eo prebleaching process is superior to the (ZD)Eo process in terms of delignification. A synergetic delignification effect is obtained in the (DZ)Eo process giving higher delignification than should be expected from the effect of chlorine

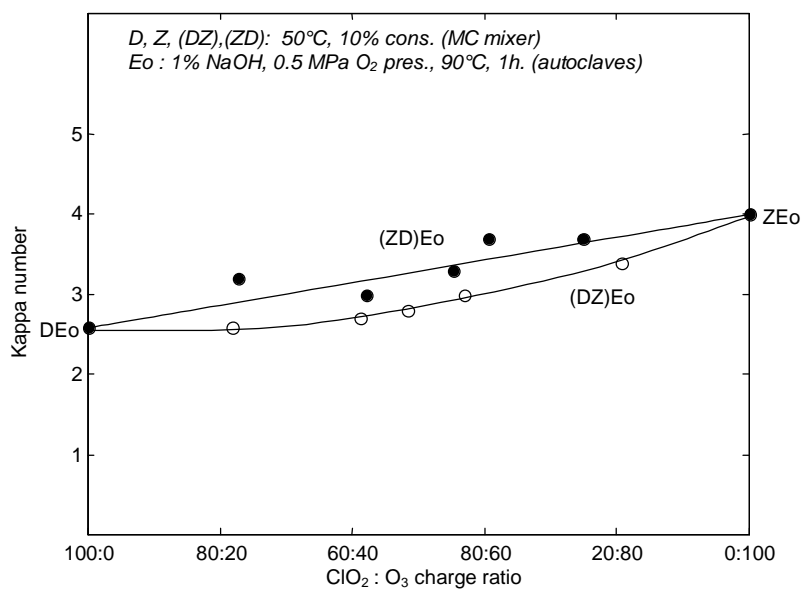


Figure 3.1 Effect of (DZ)Eo and (ZD)Eo prebleaching of oxygen delignified kraft pulp.

Table 3.2: Effect of (DZ)Eo and (ZD)Eo prebleaching of oxygen delignified kraft pulp¹⁾.

DEo, (DZ)Eo, ZEO					DEo, (ZD)Eo, ZEO				
ClO ₂	O ₃	Kappa number	Brigh-ness	Visco-sity	ClO ₂	O ₃	Kappa number	Brigh-ness	Visco-sity
%	%		%ISO	dm ³ /kg	%	%		%ISO	dm ³ /kg
100	0	2.6	66.2	943	100	0	2.6	66.2	943
80	22	2.6	67.9	844	80	23	3.2	65.9	889
60	41	2.7	68.7	784	60	42	3.0	67.1	876
50	48	2.8	68.6	787	50	55	3.3	65.5	867
40	57	3.0	67.0	777	40	61	3.7	64.7	847
20	81	3.4	64.8	788	20	75	3.7	64.5	764
0	100	4.0	62.0	780	0	100	4.0	62.0	780

¹⁾Starting pulp: Kappa number 13.2, viscosity 965 dm³/kg (Pulp A in Table 2.1)

²⁾ClO₂ and O₃ charge as percent of 0.95% ClO₂ and 0.67% O₃ respectively

dioxide and ozone separately. If no synergetic delignification effect occurred after using chlorine dioxide and ozone in combination, the kappa numbers of both (DZ)Eo and (ZD)Eo prebleached pulps should form a straight line between the kappa numbers of the DEo and ZEO reference pulps. Some deviations between the injected amount of ozone relative to the planned amounts, see Section 2.2.1, do not seem to be affected by the difference between (DZ)Eo and (ZD)Eo prebleaching.

In order to verify and further investigate the superiority of the (DZ)Eo prebleaching process another oxygen delignified kraft pulp was prebleached in the same way. The chlorine dioxide charge in the DEo prebleaching was reduced in order to achieve approximately the same degree of delignification for the two reference treatments. Three batches of each sequence were bleached and mixed before analysis. The pulp and effluent characteristics are given in Table 3.3.

Table 3.3: Pulp and effluent characteristics of DEo, (DZ)Eo, (ZD)Eo and ZEO prebleached of oxygen delignified kraft pulps¹⁾.

	DEo	(DZ)Eo	(ZD)Eo	ZEO
ClO ₂ consumed, %	0.65	0.32	0.33	-
O ₃ consumed, %	-	0.36	0.36	0.63
ClO ₃ ⁻ , mole% of ClO ₂ ²⁾	21	13	29	-
AOX, kg Cl/t ³⁾	0.38	0.15	0.21	-
COD, kg/t ³⁾	20.9	21.8	25.0	24.0
Brightness, %ISO	62.3	63.9	63.7	60.7
Kappa number	3.7	3.1	3.4	4.0
HUA, μmole/g	9.7	7.9	n.a.	6.7
Δκ _(HUA) ⁴⁾	0.8	0.7	n.a.	0.6
Viscosity, dm ³ /kg	790	690	720	690
OCl, kg Cl/t odp.	0.13	0.14	0.14	-

¹⁾ Starting pulp: Kappa number 12.7, viscosity 930 dm³/kg (Pulp B in Table 2.1).

²⁾ 1st stage ³⁾ Sum of 1st and 2nd stage ⁴⁾ Δκ=0.086·HUA, HUA = hexenuronic acid [μmol/g] [29].

In agreement with previous results, the data in Table 3.3 show that the (DZ)Eo process is the most efficient in terms of delignification. Both the results in Table 3.2 and Table 3.3 show that the improved delignification of the (DZ)Eo prebleaching is accompanied by a lowered viscosity. However, lower viscosities do not necessarily imply poorer selectivity since comparison should be made at the same degree of delignification.

Non-lignin structures like hexenuronic acid has been found to contribute to the kappa number determination [28]. The hexenuronic acid content in the prebleached pulps and its contribution to the kappa number are given in Table 3.3. Hexenuronic acid accounts for about 0.6-0.8 kappa units in prebleached pulps. At the same degree of delignification ozone seems to be more efficient in degrading hexenuronic acid groups than chlorine dioxide. However, a somewhat different ability to degrade hexenuronic acid does not seem to explain the lower kappa number of the (DZ)Eo prebleached pulp. The higher chlorine dioxide-ozone replacement ratios in (DZ) and (ZD) stages for hardwood pulps than softwood pulps may be related to that ozone is more efficient in degrading hexenuronic acid groups than chlorine dioxide.

As mentioned previously, Chirat *et al.* [27] found that the (ZD) stage was the most efficient treatment for the oxygen delignified kraft pulp whereas the (DZ) stage was the most efficient treatment for the unbleached pulp. It was suggested that the efficient delignification obtained in both the (DZ) and (ZD) stages was due to the ability of chlorine dioxide and ozone to degrade different lignin structures. The different behaviour of unbleached and oxygen delignified pulp was suggested to be related to the decrease in phenolic lignin structures in oxygen delignification. In contrast to the results of Chirat *et al.* [27], the results presented here imply that the (DZ)Eo process is the most efficient also for oxygen delignified pulps.

In order to investigate whether the efficient delignification obtained in both (DZ) and (ZD) stages and the superior delignification efficiency of (DZ)Eo prebleaching versus (ZD)Eo prebleaching could be related to lignin chemistry, residual lignins were isolated and analysed from untreated (oxygen delignified) pulp and chlorine dioxide and ozone prebleached pulps. The results from these investigations are presented in Chapter 4.

The results in Table 3.3 show that the chlorate formation in the (DZ) stage is lower than in the D and (ZD) stages. Surprisingly low chlorate formation relative to the chlorine dioxide charge in the (DZ) process was also commented by Dillner and Tibbling [4]. The chlorate formation represents a waste of oxidation power in chlorine dioxide bleaching. Similar to the superiority of the (DZ)Eo process versus the (ZD)Eo process established here, the (DC)E treatment has also been shown to be more efficient in terms of delignification than the (CD)E treatment [30, 31, 32]. As the chlorate formation also has been reported to be lower in the (DC) process than the (CD) process [31] it is tempting to speculate that the efficient delignification obtained in both the (DZ) and (DC) stages might be related to the initial chlorine dioxide treatment. The main difference between the initial chlorine dioxide treatment in the (DZ) and (DC) stages from the D stage is the lower chlorine dioxide charge applied. Thus, it is possible that low-charge chlorine dioxide bleaching yields more efficient delignification. This hypothesis is explored further in Chapter 5.

3.3 Concluding remarks

The use of chlorine dioxide and ozone in combination in (DZ)Eo and (ZD)Eo prebleaching of oxygen delignified kraft pulp has been shown to be efficient in terms of delignification. When the (DZ)Eo prebleaching process was applied, a synergetic delignification effect was obtained giving better delignification than should be expected from the effect of chlorine dioxide and ozone separately.

CHAPTER

4

THE COMPLEMENTARY LIGNIN CHEMISTRY OF CHLORINE DIOXIDE AND OZONE (PAPER I)

In Chapter 3 it was shown that the delignification efficiency of the (DZ)Eo prebleaching process was superior to the (ZD)Eo process. Chirat *et al.* [27] suggested that the positive effect of using chlorine dioxide and ozone in combination was due to their ability to degrade different lignin structures. Residual lignin structures were isolated and analysed from untreated oxygen delignified pulp and chlorine dioxide and ozone prebleached pulps in order to explore this hypothesis and to try to explain the superior delignification efficiency of the (DZ)Eo process versus the (ZD)Eo process.

4.1 Structural changes in lignin in alkaline cooking

The purpose of pulping and bleaching is to remove lignin and chromophoric groups in the pulp and leave the cellulose as unaffected by the treatment as possible. About 25-30% of softwood consist of lignin and it is located both within and in between the fibres in wood. Lignin is a three-dimensional, amorphous biopolymer consisting of phenylpropane units with an oxygen atom in the *p*-position (as OH or OC-) and with none, one or two methoxyl groups in the *o*-position to this oxygen atom. The phenylpropane units are linked to each other in many different ways. The type and approximate amounts of the most frequent inter unit linkages in spruce milled wood

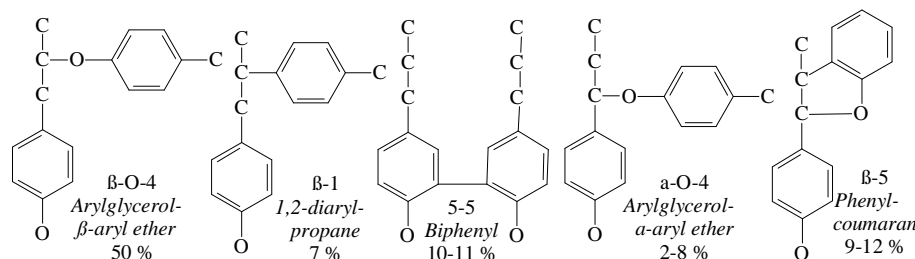


Figure 4.1 Most common inter-unit linkages in Norway spruce milled wood lignin [33].

lignin (*Picea abies*) are illustrated in Figure 4.1 [33]. β -O-4 linkages are the most frequent linkages, contributing to about 50% of the total number of inter unit linkages in the lignin structure [33]. The alkyl aryl ether structures are cleaved to an extensive degree in kraft cooking. The reaction is of great importance for the delignification both due to the large amount of β -aryl ether structures present, but also due to that the cleavage of the alkyl-aryl ether linkages is the only reaction known to cause fragmentation of the lignin macromolecule. About 80-85% of the phenolic β -aryl ether bonds in wood lignin are cleaved in kraft cooking [34, 35].

The cleaving of alkyl-aryl ether linkages leads to the formation phenolic end groups in lignin. Hence, the content of phenolic hydroxyl groups in the residual lignin increases. The phenolic group is able to ionize under alkaline conditions and is of great importance for the solubility of the kraft lignin. The content of phenolic hydroxyl groups in wood (*Picea abies* and *Pinus sylvestris*) has been determined to about 13 per 100 phenylpropane units [36, 37]. After alkaline cooking the content of phenolic hydroxyl groups in kraft pulp residual lignin has increased to about 30 phenolic hydroxyl groups per 100 phenylpropane units [9, 35, 37], depending on the degree of delignification. Yang and Lai [38] also showed that the free phenolic group content in kraft residual lignin (*Picea abies*) increases with delignification, and found that low sulphidity cooking yielded higher content of free phenolic groups in residual lignin. At 25% sulphidity about 38 per 100 phenylpropane units were present in kappa 25 kraft residual lignin, whereas about 33 per 100 phenylpropane unite were present in kraft residual lignin at the same degree of delignification when 40% sulphidity was utilized. The dissolved lignin in black liquor contains as much as about 75 phenolic hydroxyl groups per 100 phenylpropane units, which underscores the importance of the cleavage of aryl ether linkages for delignification and the phenolic hydroxyl groups for lignin solubility [39]. Except for a small number of carboxylic acid groups, the phenolic group is the only type of functional group present conferring water solubility to the kraft lignin.

4.2 Structural changes in residual lignin in chlorine dioxide and ozone prebleaching

4.2.1 Lignin isolation

The residual lignin in the pulp is incorporated in the fibre wall and must be extracted from the wood before it can be analysed. The isolation of lignin from a chemical pulp is a difficult task. The residual lignin content is low and some of the lignin is probably linked to carbohydrates [33]. It has been suggested that the alkaline stable lignin-carbohydrate (LC) ether bonds form during kraft cooking [40] and that the residual lignin is linked to the polysaccharides in such a way that neither mild acid hydrolysis nor alkali treatment can completely release it [41]. No method is available for extracting lignin without introducing structural changes like breaking or creating linkages or introducing or removing functional groups. For instance, in the isolation of milled wood lignin, the substantial grinding required leads to the formation of new phenolic structures [42]. Lignin isolation by acid hydrolysis probably leads to cleavage of aryl ether linkages and condensation reactions between adjacent lignin structures may occur [43]. Isolation by enzymatic hydrolysis leads to lignin samples being contaminated by

proteins which obstructs analysis. When isolated, the complexity of the lignin structure limits the structural analysis of lignin to analysing characteristic structural elements and functional groups such as hydroxyl, carbonyl and vinylic groups in the lignin.

In this investigation, residual lignins are isolated from pulps by acid hydrolysis [6]. Acid hydrolysis yields lignins in which no carbohydrates are present. Gellerstedt and Heuts [43] pointed out that aryl ether linkages that are sensitive to acid hydrolysis are probably cleaved during the isolation, and some new phenolic end groups are liberated in the lignin. Condensation reactions between adjacent lignin structures could also occur, but such reactions, if they occur at all, seem to be of minor importance [6]. Thus, except for an increase in the amount of phenolic groups, the lignin structure seems to be rather unaffected by the isolation procedure [43].

The data in Table 2.2 (page 22) estimate that only 40-60% of the theoretical amount of lignin in the pulps was isolated. Such low yields of lignin are common when residual lignins are isolated by acid hydrolysis. However, it can be speculated whether the isolated lignin is representative for all the residual lignin in the pulp. The total lignin content was estimated using the correlation $\% \text{ lignin} = 0.15 \cdot \text{kappa number}$. This is only an approximate correlation since non-lignin structures like hexenuronic acid have been found to contribute to the kappa number [28].

4.2.2 Phenolic hydroxyl groups

As mentioned in Section 4.1 the cleavage of alkyl-aryl ether linkages in kraft cooking generates phenolic end groups in the kraft pulp residual lignin. The content of β -O-4 structures in the residual lignins was analysed by thioacidolysis [7] and the results are given in Table 4.1. In Norway spruce (*Picea abies*) milled wood lignin (MWL) the content of β -O-4 structures has been determined to 1006 $\mu\text{mole/g}$ lignin [7]. Hence, the results in Table 4.1 indicate that about 86% of the original β -O-4 linkages in wood have been cleaved in the investigated unbleached kraft pulp. The oxygen delignified pulp and the unbleached kraft pulp are not comparable with respect to β -O-4 content in residual lignins since the pulps origin from different cooks. Upon chlorine dioxide and ozone prebleaching of the oxygen delignified pulp the relative amount of β -O-4 structures in residual lignin decreases. It seems reasonable that the β -O-4 structures are preferably attacked in prebleaching since a recent study found that high amounts of β -O-4 structures in kraft pulp residual lignin was advantageous with respect to bleachability [44].

Table 4.1: Effect of chlorine dioxide and ozone prebleaching on the amount of β -aryl ether structures in residual lignin. The amount of β -O-4 structures was analysed by thioacidolysis [7].

	Unbleached ¹⁾		O		ODEo		OZEo	
	$\mu\text{mole/}$ g lignin	$\#/100$ $\text{C}_9 \text{ units}$	$\mu\text{mole/}$ g lignin	$\#/100$ $\text{C}_9 \text{ units}$	$\mu\text{mole/}$ g lignin	$\#/100$ $\text{C}_9 \text{ units}$	$\mu\text{mole/}$ g lignin	$\#/100$ $\text{C}_9 \text{ units}$
β -O-4 structures	141	2.6	186	3.4	136	2.5	121	2.2

¹⁾ The untreated kraft pulp does not origin from the same cook as the other pulps.

In addition to promote water solubility of the lignin, the free phenolic group is the most important functional groups in terms of reactivity. In most chemical reactions on lignin, the phenolic phenylpropane units are preferably attacked. The effect of prebleaching of oxygen delignified kraft pulp on the content of phenolic lignin structures in residual lignin is illustrated in Figure 4.2.

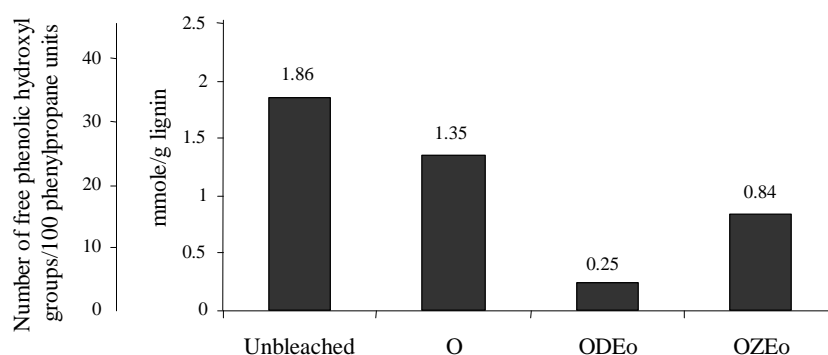


Figure 4.2 Effect of chlorine dioxide and ozone prebleaching on the content of free phenolic groups in residual lignin.

The results in Figure 4.2 clearly illustrate that chlorine dioxide preferably attacks phenolic lignin structures. The content of free phenolic hydroxyl groups in the ODEo residual lignin has decreased over 80% compared to the free phenolic hydroxyl group content in the oxygen delignified kraft pulp residual lignin. The ozone treatment also yielded a significant decrease in the content of phenolic lignin structures. Thus, even though ozone is capable of degrading non-phenolic lignin structures it seems to prefer to attack phenolic lignin structures when they are present. About 80-85% of the phenolic lignin structures in the residual lignins were of the uncondensed type, see Figure 2.1.

4.2.3 Oxidation of lignin in prebleaching

The predominant mode of lignin removal in bleaching goes through the oxidation of lignin. Acidic and carbonyl groups are formed which increase alkali solubility of the lignin polymer and induce cleavage of carbon-carbon and carbon-oxygen bonds. Muconic acids are formed when aromatic rings are degraded and aliphatic acids are formed when carbonyl groups in the side chains are oxidized. Gellerstedt *et al.* [45] found that the carboxyl group content increased from 1.0 mmole/g in unbleached kraft pulp residual lignin to 1.7 and 4.9 mmole/g in residual lignins of oxygen delignified pulp and ODEo prebleached pulp respectively. The effect of the carboxyl groups on lignin solubilization was illustrated by the fact that the dissolved lignin from a bleaching stages always contained a higher amount of carboxyl groups than residual lignin in the pulp. Native lignins contain few, if any, carboxyl groups [33]. The need for a comprehensive oxidation of the lignin to obtain lignin dissolution and a high degree of delignification in

a bleaching stage is further supported by the fact that the depolymerization of the lignin in bleaching treatments can be rather low. In contrast to chlorine, chlorine dioxide yields a low degree of depolymerization of the kraft lignin [46]. Upon ozone treatment almost no depolymerization of the lignin takes place [46, 47]. The effect of chlorine dioxide and ozone in prebleaching on the number of carboxyl groups in residual lignin is illustrated in Figure 4.3.

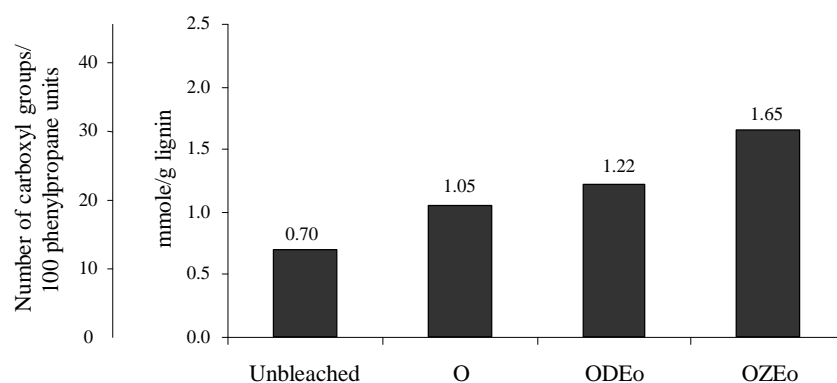


Figure 4.3 Effect of chlorine dioxide and ozone prebleaching on the content of carboxyl groups in residual lignin.

Figure 4.3 shows that the number of carboxyl groups in residual lignin has increased considerably upon prebleaching. In the OZEo prebleached pulp, about 30 per 100 phenylpropane units in residual lignin contained carboxyl groups. At the same degree of delignification, the ozone treatment yielded more carboxyl groups in the residual lignin structure than chlorine dioxide treatment. The increase in carboxyl group content in residual lignin upon chlorine dioxide was less than results reported by Gellerstedt *et al.* [45]. A difference which may be of importance in this respect, is that the probably most oxidized low molecular lignin material is removed by dialysis in the lignin isolation procedure applied, see Chapter 2.3. In the study of Gellerstedt *et al.* [45] hydrochloric acid was removed by repeated centrifugation of the lignin in water.

The change in elemental composition of the residual lignins in Table 4.2 also reveals the extensive oxidation which has occurred in oxygen delignification and prebleaching. The calculated number of double bond equivalents, DBE, represents the degree of unsaturation and mainly reflects the presence of aromatic rings and inter-unit linkages connecting the phenylpropane monomer units [39]. By comparison, the elemental composition of milled wood spruce lignin (*Picea abies*) has been determined to be $C_9H_{8.05}O_{2.84}(OCH_3)_{0.95}$, DBE=5.5 [48].

The results in Table 4.2 also show that a substantial demethoxylation has occurred, especially in the chlorine dioxide prebleached pulp. The demethoxylation is caused by

Table 4.2: Effect of prebleaching on elemental composition of residual lignin.

	Elemental composition	DBE ¹⁾	M _w ²⁾
Unbleached	C ₉ H _{8.64} O _{2.99} S _{0.07} (OCH ₃) _{0.73}	5.3	190
O	C ₉ H _{8.40} O _{3.11} S _{0.07} (OCH ₃) _{0.70}	5.5	190
ODEo	C ₉ H _{11.1} O _{5.00} S _{0.05} (OCH ₃) _{0.40} ³⁾	4.3	213
OZEo	C ₉ H _{10.0} O _{4.33} S _{0.07} (OCH ₃) _{0.51}	4.7	205

¹⁾ When the elemental composition (incl. OCH₃) is given in the form C_aH_bO_cS_d, then the number of double bond equivalents, DBE, is given by: $DBE = \frac{1}{2}[(2a+2)-b]$

²⁾ Molecular weight of the residual lignin based on a C₉ unit ³⁾ ¹³C-NMR analysis showed traces of carbohydrate impurities in the sample. Residual lignin was later on re-isolated from the ODEo treated pulp before analysing for free phenolic groups and carboxyl groups.

the oxidation of aromatic rings, see Figure 5.1, which probably reflects the low degree of unsaturation of the ODEo residual lignin.

As mentioned in Section 2.3, the number of functional groups per 100 phenylpropane units have been estimated by using a molecular weight of 183 g/mole. Freudenberg and Neish [13] compared literature data on elemental composition of lignin and calculated an average C₉ based molecular weight for spruce lignin of 183 g/mole. In the same way, the apparent molecular weight is calculated from the elemental composition data for the residual lignins isolated in Table 4.2. The C₉ based molecular weight of the residual lignin seems to increase by the oxidation of the lignin in pulping and bleaching. Hence, the number of functional groups per 100 phenylpropane units in Table 4.1, Figure 4.2 and Figure 4.3 are probably somewhat overestimated.

Sun and Argyropoulos [49] found similar changes in residual lignin structure as presented here when treating unbleached softwood (*Picea mariana*) kraft residual lignin directly with various bleaching chemicals. Chlorine dioxide treatment caused a higher reduction in free phenolic group content than ozone, whereas ozone treatment generated more carboxyl groups in the residual lignin structure. A substantial demethoxylation occurred upon chlorine dioxide treatment, whereas the ozone treatment caused no change in the methoxyl content.

4.2.4 (DZ) versus (ZD)

The superior delignification efficiency of the (DZ)Eo process versus the (ZD)Eo process may be explained by the different ability of chlorine dioxide to degrade non-phenolic lignin structures. Whereas chlorine dioxide mainly degrades phenolic lignin structures, ozone attacks both phenolic and non-phenolic lignin structures. However, ozone also seems also to prefer to attack phenolic lignin structures when they are present. Thus, the (DZ) treatment seems to be the most efficient, allowing chlorine dioxide initially to degrade the phenolic lignins and leave the non-phenolic and less reactive lignin structures for the ozone treatment.

4.3 Concluding remarks

The efficient delignification obtained when chlorine dioxide and ozone are used in combination seems reasonable due to their ability to degrade different types of lignin structures. Whereas chlorine dioxide mainly degrades phenolic lignin structures, ozone is capable of degrading both phenolic and non-phenolic lignin structures. Both chlorine dioxide and ozone are strong oxidants, but ozone seems to be more efficient in this respect since more carboxyl groups were implemented in the residual lignin at the same degree of delignification. The large number of carboxyl groups introduced in the lignin structure seems to govern the solubilization of the lignin in chlorine dioxide and ozone bleaching.

The superior delignification efficiency of (DZ)Eo prebleaching versus (ZD)Eo prebleaching may be explained by that the (DZ) treatment initially allows chlorine dioxide to degrade the phenolic lignin structures, and leaves the non-phenolic and less reactive lignin structures for the ozone treatment.

C H A P T E R

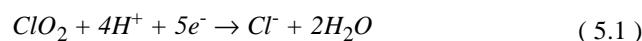
5

**LOW-CHARGE CHLORINE DIOXIDE
PREBLEACHING (PAPER II)**

In Chapter 3 it was shown that the delignification efficiency of the (DZ)Eo prebleaching process was superior to the (ZD)Eo process. It was also found that the (DZ) stage generated less chlorate than the (ZD) and D stages. Similar results have been shown when comparing (DC)E prebleaching and (CD)E prebleaching. The (DC)E process was more efficient in terms of delignification than the (CD)E process [30, 31, 32], and less chlorate was formed in the (DC) stage than the (CD) stage [31]. Thus, it could be speculated that the efficient delignification obtained in both the (DZ) and (DC) stages might be related to the initial chlorine dioxide treatment. The main difference between the initial chlorine dioxide treatment in the (DZ) and (DC) stages from D prebleaching is the lower chlorine dioxide charge applied. In most studies of inorganic reactions in chlorine dioxide bleaching rather high chlorine dioxide charges have been applied, corresponding to the amounts of chlorine dioxide applied in practice. It is possible that low-charge chlorine dioxide bleaching yields more efficient use of the bleaching chemical. This hypothesis was to be explored.

5.1 The ideal situation for chlorine dioxide bleaching

When used to delignify pulp under acidic conditions, chlorine dioxide is reduced in a complex reaction pattern, including lignin degrading reactions and inorganic reactions. Within a few minutes chlorine dioxide is consumed forming chlorous acid (HClO_2), hypochlorous acid (HOCl), chlorate (ClO_3^-), and chloride (Cl^-). Chloride and chlorate are stable ions while chlorous acid and hypochlorous acid are usually involved in further reactions. The ideal situation for maximum oxidation of lignin would be if all chlorine dioxide was reduced to chloride ion, Cl^- , with corresponding maximum oxidation of lignin.



However, in chlorine dioxide bleaching some of the chlorine dioxide is oxidized into chlorate. Chlorate is a stable ion representing a loss of oxidation power in chlorine dioxide bleaching. An old idea is to try to modify process conditions in order to reduce

the chlorate formation and thereby achieving a more efficient use of the bleaching chemical. Germgård *et al.* [50] investigated the chlorate formation in chlorine dioxide prebleaching and final bleaching, and concluded that the chlorate formation is not a measure of the efficiency in chlorine dioxide bleaching. However, later studies have shown that the chlorate formation is a result of complex inorganic reactions which are affected by the conditions applied [51, 52, 53].

5.2 Major reactions of chlorine dioxide in prebleaching

Chlorine dioxide reacts rapidly with phenolic lignin structures in the pulp. A proposed reaction pattern for the reactions between chlorine dioxide and phenolic lignin structures is summarized in Figure 5.1 [54].

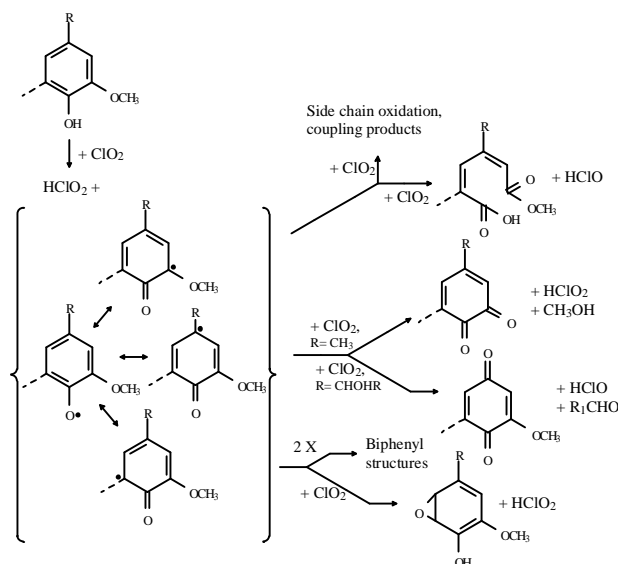


Figure 5.1 Chlorine dioxide reactions with phenolic rings in lignin [54].

In theory, chlorine dioxide can also attack non-phenolic lignin structures in a similar way, but at a greatly reduced rate. Initially, phenoxy radicals and chlorite (or chlorous acid, see Equation (5.2)) are formed by one electron oxidation. Coupling of the various phenoxy radicals with additional chlorine dioxide leads to the formation of chlorous acid esters. On decomposition, the chlorous acid esters are converted to benzoquinone or corresponding catechols and muconic acid monomethyl esters or their lactonized forms. Chlorite and hypochlorous acid are released in one- or two-electron oxidation reactions. Wajon *et al.* [55] studied the reaction of chlorine dioxide with a phenol model compound. The results corresponded to a reaction mechanism in which the rate-determining step is the initial removal of one electron from the substrate by chlorine dioxide forming a phenoxy radical and chlorite. Subsequently, chlorine dioxide adds to the phenoxy radical, most frequently in the *para* position, forming *p*-benzoquinone with

the concomitant release of hypochlorous acid. The mechanism is in agreement with that about 0.5 mole chlorite was formed per mole chlorine dioxide reduced.

Besides oxidating phenolic lignin structures a significant amount of chlorine dioxide is consumed in reaction with hexenuronic acid groups in the pulp. The content of hexenuronic acid groups and phenolic lignin structures in the investigated pulps are given in Table 5.1. The content of free phenolic groups in lignin is estimated by isolating residual lignins by acid hydrolysis [6] and measuring the amount of phenolic phenol propane groups in the residual lignins by UV spectroscopy [17].

Table 5.1: Content of phenolic lignin structures and hexenuronic acid groups in unbleached, oxygen delignified, and ODEo prebleached kraft pulp.

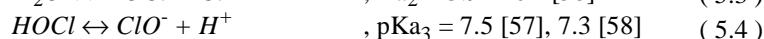
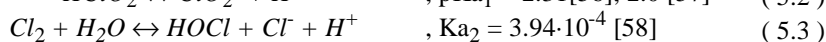
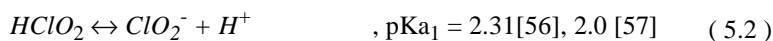
Pulp	Kappa number	Free phenolic groups		Hexenuronic acid
		<i>mmole/g res. lign.</i>	<i>μmole/g pulp¹⁾</i>	<i>μmole/g pulp</i>
Unbleached	24.3	1.86	68	16.9
O	12.7	1.35	26	17.7
ODEo ²⁾	3.7	0.25	1.4	9.7

¹⁾ Assumed a lignin content of % lignin = $0.15 \cdot \text{Kappa number}$ and a molecular weight of spruce lignin of 183 g/mole [13] ²⁾ 0.65% ClO₂ charge.

The results in Table 5.1 show that about 95% of the phenolic lignin structures and 45% of the hexenuronic acid groups in the oxygen delignified kraft pulp are degraded in DEo prebleaching. The relative amount of phenolic lignin structures in residual lignin has decreased over 80%. According to the mechanism between chlorine dioxide and phenolic lignin structures in Figure 5.1, two equivalents of chlorine dioxide should be consumed for each phenolic phenylpropane unit. As the hexenuronic acid group also has been found to consume two equivalents of chlorine dioxide [59], 0.59% chlorine dioxide should theoretically be consumed if chlorine dioxide degraded all phenolic phenylpropane units and hexenuronic acid groups in the present oxygen delignified pulp.

5.3 Inorganic reactions during chlorine bleaching

Typical concentration profiles for inorganic chloro-compounds during chlorine dioxide bleaching are illustrated in Figure 5.2. Initially, chlorite forms rapidly and is mainly consumed during the treatment. Chlorous acid is in acid equilibrium with chlorite (ClO₂⁻) (5.2), and hypochlorous acid is in equilibrium with chlorine (Cl₂) in acidic solution (5.3) and hypochlorite (ClO⁻) in neutral solution (5.4)..



Thus, in a typical pH range of 2.5-4 for chlorine dioxide bleaching, chlorite is the main species present, whereas the presence of chlorine versus hypochlorous acid is dependent

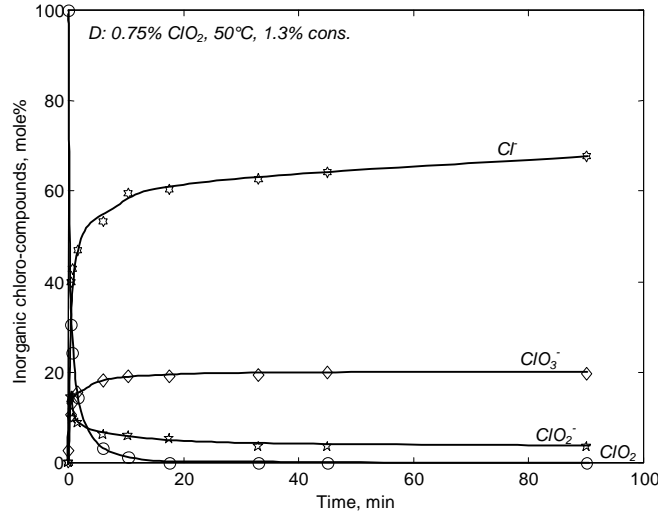
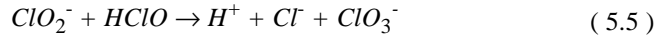


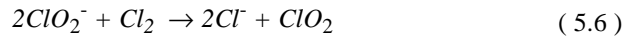
Figure 5.2 Typical concentration profiles for chlorine dioxide, chlorite, chlorate and chloride in chlorine dioxide prebleaching. Hypochlorous acid was not analysed.

on both pH and chloride concentration.

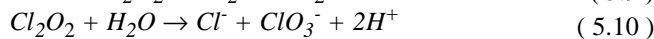
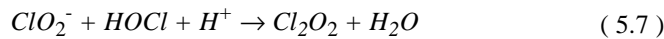
Chlorite and hypochlorous acid may react inorganically and form chlorate. Ni *et al.* [52] studied the reaction and observed that only a small amount of chlorate was formed when hypochlorous acid was captured by a radical scavenger (sulfamic acid). Consequently, essentially all chlorate seems to be formed in reactions in which hypochlorous acid is involved. The reaction between chlorite and hypochlorous acid was found to correspond for essentially all chlorate formation in chlorine dioxide bleaching [52]:



At more acidic conditions the equilibrium (5.3) shifts towards chlorine, and chlorine reacts with chlorite and regenerates chlorine dioxide:

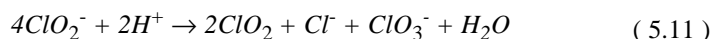


Both reactions (5.5) and (5.6) are very rapid under acidic conditions [60]. A reaction mechanism for the two reactions was proposed by Taube and Dodgen [61] and later expanded by Emmenegger and Gordon [60]. A common reaction intermediate, Cl_2O_2 , is formed in both reactions:

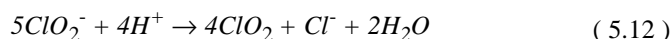


The reaction mechanism explains several experimental findings. Chlorine dioxide regeneration has been found to be favoured by acidification [60] and chloride addition [50, 62], whereas chlorate formation is favoured at low pulp consistency [60]. Both acidification and chloride addition shift the HOCl/Cl₂-equilibrium (5.3) towards chlorine. Chlorine dioxide regeneration is favoured since the reaction rate of reaction (5.8) is much faster than reaction (5.7) and the second-order reaction (5.9) is favoured by a high intermediate concentration. At low pulp consistency the first-order chlorate formation (5.10) is favoured over the second-order chlorine dioxide regeneration.

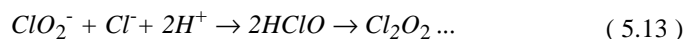
As illustrated in Figure (5.2) chlorite forms initially in chlorine dioxide bleaching and is mostly consumed throughout the treatment. Chlorite is consumed in the rapid reaction with hypochlorous acid (5.5), but may also decompose under acidic conditions and regenerate chlorine dioxide. Kieffer and Gordon [63] studied the acid catalysed disproportionation of chlorite and found that the stoichiometry in the pH range 0.3-3 can be approximated by:



Chloride was found to catalyse the disproportionation, changing the stoichiometry to:



whereas more chlorine dioxide respective chloride and no chlorate was formed. Smithz and Rooze [64] suggested another mechanism in which hypochlorous acid is generated and reacts further according to Equations (5.7), (5.9) and (5.10).



A later study indicated that neither the reaction (5.11) nor the reaction (5.13) occur to any noticeable extent since no detectable amount of chlorate or hypochlorous acid was formed in an acidic chlorite solution during 150 minutes at pH 2.6 and 45°C [52]. Initially, chlorine dioxide and chloride were formed at a high ClO₂/Cl⁻-ratio which decreased throughout the treatment. Thus, the reaction pattern appears to be more complex than suggested by Equations (5.11) and (5.12).

Irrespective of mechanism, acid catalysed disproportionation of chlorite is a slow reaction. The maximum reaction rate occurs at pH~2.0, about the pKa of chlorous acid [65, 66]. Kieffer and Gordon [66] stated that only when pH is less than 3 will more than one percent sodium chlorite decompose within a retention time of ten minutes.

The decomposition of chlorite under chlorine dioxide prebleaching conditions with and without pulp present is studied in Table 5.2. The results in Table 5.2 show that only small amounts of chlorite is decomposed during 30 minutes at pH 3.5, while about 23% chlorite is decomposed during 30 minutes at pH 2.5. Considering that other chlorite consuming reactions take place and the rather short retention time applied, acid catalysed disproportionation of chlorite is probably of minor importance in prebleaching.

Table 5.2: Acid catalysed disproportionation of chlorite¹⁾.

NaClO ₂ ¹⁾ , mole/l	pH ²⁾	Pulp ³⁾	Time, min	Residual ClO ₂ ⁻ , %	Formed Cl ⁻ , %
0.01		-	30	100	2
0.01	3.5	-	60	89	5
0.008 ⁴⁾		+	30	60	18
0.01		-	30	77	13
0.01	2.5	-	60	66	22
0.008		+	30	45	24

¹⁾ Some chloride (0.19 mole Cl⁻/mole ClO₂⁻) was present in the NaClO₂ salt applied. ²⁾ Citric acid buffer was added ³⁾ Oxygen delignified kraft pulp at 8% pulp consistency in plastic bags ⁴⁾ Equals 0.6% ClO₂ charge.

Chlorite may act as a bleaching agent itself under acidic conditions. Rapson [67] found that chlorite reacts with unbleached kraft pulp releasing chloride at pH values below 4. At higher pH values the reactivity decreased rapidly, and at pH values greater than 5, chlorite was stable in pulp suspensions. However, to what extent chlorite reacted with pulp itself or was decomposed by acid catalysed decomposition is unclear. The results in Table 5.2 show that chlorite is consumed at a higher rate when pulp is present. Thus, either the pulp catalyses the acid-catalysed decomposition of chlorite or some chlorite reacts with the pulp itself. No chlorate was formed in any of the experiments.

5.4 Effects of hypochlorous acid

Hypochlorous acid has been generally considered to be destructive to cellulose and therefore avoided in pulp bleaching [68]. Radical scavengers like sulfamic acid and phenolic compounds have been added to prevent cellulose degradation during acidic hypochlorite bleaching. According to the literature the hypochlorous acid formed seems to determine both the AOX formation [69] and the chlorate formation [52] in chlorine dioxide bleaching. By capturing hypochlorous acid by sulfamic acid, Ni *et al.* [52] found that hypochlorous acid attributed to at least 86% of the chloro-organic compounds formed in chlorine dioxide treatment of unbleached kraft pulp. Others studies have also verified that hypochlorous acid is the main component forming organically bound chlorine (AOX and OCl) in chlorine dioxide bleaching. Wajon *et al.* [55] studied the reaction between chlorine dioxide and a phenol model compound, and found that chlorophenols were only formed when phenols were present in excess. Hypochlorous acid also seems to be essential for the delignification in chlorine dioxide bleaching. Joncourt *et al.* [53] found that the delignification in chlorine dioxide treatment of unbleached kraft pulp was reduced by about one third when hypochlorous acid was captured by DMSO.

Studies by both Kolar *et al.* [51] and Ni *et al.* [52] showed that hypochlorous acid is formed in excess relative to chlorite in chlorine dioxide bleaching. Kolar *et al.* [51] captured about 50 mole% hypochlorous acid of charged chlorine dioxide (kappa factor 0.16) by DMSO during chlorine dioxide prebleaching of oxygen delignified kraft pulp. About 20-30 mole% chlorite formed initially and was consumed throughout the

treatment. Kolar *et al.* [51] suggested that the excess formation of hypochlorous acid versus chlorite may be explained by chlorine dioxide being reduced to both chlorite and monochlorine monoxide, and the latter reduced by lignin to hypochlorous acid. Quite similar, Ni *et al.* [52] captured 58 mole% hypochlorous acid (kappa factor 0.22) by sulfamic acid and measured an initial formation of 25 mole% chlorite during chlorine dioxide delignification of unbleached kappa kraft pulp. Joncourt *et al.* [53] estimated an even higher hypochlorous acid formation of 75 mole% in chlorine dioxide delignification of unbleached kraft pulp. The estimate was made by assuming that hypochlorous acid accounts for all AOX formation and extrapolate plot of AOX formation versus added amount of radical scavenger (DMSO). In the study by Joncourt *et al.* [53] the chlorate formation only was reduced from 19.4% to 16.5% when a rather high amount of radical scavenger was added. According to Ni *et al.* [52] there should not be any chlorate formation if all hypochlorous acid is captured by a radical scavenger, since the reaction between hypochlorous acid and chlorite (5.5) was found to account for essentially all chlorate formation in chlorine dioxide bleaching.

5.5 Effects of chlorine dioxide charge in prebleaching

The charge in a prebleaching stage is usually determined by the desired final brightness and number of bleaching stages available. Here, it was desired to achieve a final brightness of 88% ISO in a DEoD₁ED₂ bleaching sequence of an oxygen delignified kraft pulp. Hence, a chlorine dioxide charge of 0.65% ClO₂ (kappa factor 0.13) was required in the prebleaching stage and 0.70% ClO₂ in the D₁ED₂ final bleaching stages. The delignification effect versus chemical consumption in DEo and ZEO prebleaching is illustrated in Figure 5.3. Both D and Z stages were performed in a MC mixer to ensure proper mixing, and all chlorine dioxide and ozone charged was consumed throughout the treatments.

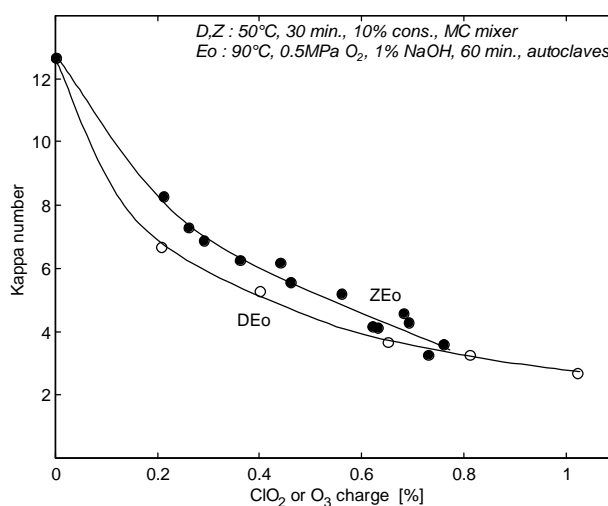


Figure 5.3 DEo and ZEO prebleaching of oxygen delignified kraft pulp.

According to Figure 5.3, chlorine dioxide appears to be a more efficient delignifying agent than ozone when small chemical charges are applied.

The chlorate formation was measured in filtrates from the chlorine dioxide bleaching stages, and the relative amount of chlorate formed is plotted versus chlorine dioxide charge in Figure 5.4.

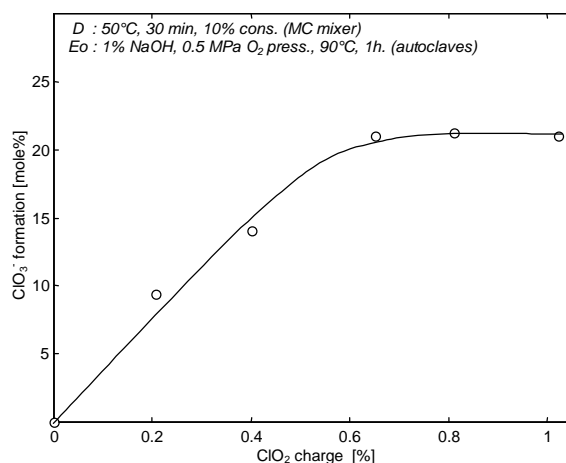


Figure 5.4 Chlorate formation in chlorine dioxide prebleaching of oxygen delignified kraft pulp.

Figure 5.4 shows that the chlorate formation rises with increasing chlorine dioxide charge up to about 0.65% chlorine dioxide. At higher chlorine dioxide charges the chlorate formation seems to stabilize at about 21 mole% ClO_3^- . As previously mentioned the chlorate formation represents a waste of oxidation power in chlorine dioxide bleaching. Thus, the efficient delignification and lower chlorate formation obtained when low chlorine dioxide charges are applied in chlorine dioxide prebleaching may be related to more efficient use of the bleaching chemical. The small decrease in kappa number upon chlorine dioxide charges above 0.6% in Figure 5.4 is probably related to the few accessible reactive structures remaining in the pulp. In Section 5.2 it was estimated that 0.59% chlorine dioxide would theoretically be required to degrade all phenolic lignin structures and hexenuronic acid groups in the pulp.

The chlorate and chloride formation during low consistency chlorine dioxide prebleaching is shown in Figure 5.5. In agreement with previous results, the chlorate formation rises with increasing chlorine dioxide charge. When 0.5% and 0.75% chlorine dioxide are applied, all chlorate seems to form within a few minutes. At 1.0% chlorine dioxide charge a considerable amount of the chlorate that is generated is formed more slowly throughout the treatment. The initial fast chlorate formation is accompanied by a rapid decrease in chlorite concentration, indicating that the chlorate is formed by the reaction between hypochlorous acid and chlorite, see Equation (5.5). According to the

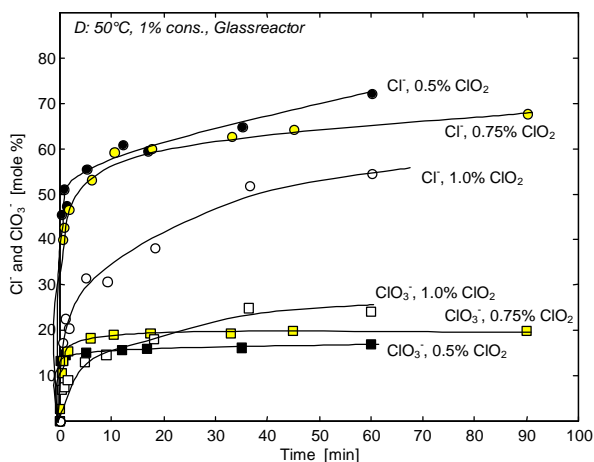


Figure 5.5 Chloride and chlorate formation during low consistency chlorine dioxide prebleaching.

literature [51, 52, 53] hypochlorous acid is formed in excess to chlorite. Provided the stoichiometry of Equation (5.5) applies, hypochlorous acid should remain even if all the generated chlorite reacted with hypochlorous acid. Hypochlorous acid reacts also with lignin. The increased chlorate formation at high chlorine dioxide charge may be explained by the fact that lower amount of reactive lignin structures present when hypochlorous acid is generated. The chlorine dioxide has oxidized the most reactive lignin structures before hypochlorous acid is formed, and hypochlorous acid probably reacts to a larger extent inorganically and forms chlorate. At 1.0% chlorine dioxide charge a major portion of the formed chlorate was generated rather slowly throughout the treatment. Considering that both the reaction between hypochlorous acid and chlorite is fast and that the hypochlorous acid is formed in excess to chlorite, it is possible that chlorate is formed from hypochlorous by another slow reaction when a low amount of residual lignin is present.

The importance of the residual lignin content for the chlorate formation is also supported by the results of Germgård *et al.* [50]. In prebleaching of oxygen delignified kraft pulp 5-20% of the consumed chlorine dioxide was converted to chlorate, whereas 25-50% chlorate was formed in chlorine dioxide final bleaching. In final bleaching the chlorate formation increased linearly with consumed chlorine dioxide, corresponding to a constant percentage of charged chlorine dioxide. According to the theory presented, these results should imply that the residual lignin content in prebleached pulps is so low that the hypochlorous acid formed in final bleaching generates chlorate independently of the chlorine dioxide charge applied.

5.6 Applications of low chlorine dioxide charge

The previous results have indicated that chlorine dioxide prebleaching is efficient in terms of delignification when a low chlorine dioxide charge is applied. Low chlorine dioxide charge is utilized in practice in the (DC) [30] and (DZ) stages [3, 4], which both have been found to be very efficient in terms of delignification. Another utilization of low chlorine dioxide charge could be the use of sequential charging of low amounts of chlorine dioxide instead of the traditional batch charging.

5.6.1 (DZ) and (ZD) stages

An application of using low chlorine dioxide charge is in the (DZ) and (ZD) bleaching stages. Here, chlorine dioxide and ozone are injected subsequently to one another allowing the first injected chemical to be consumed before the other one is injected. In Chapter 3 it was shown that the delignification efficiency of the (DZ)Eo prebleaching was superior to the (ZD)Eo prebleaching. It was also found that the chlorate formation was lower in the (DZ) than the (ZD) and D stages. A balance of inorganic and organic chloro-compounds formed in DEo, (DZ)Eo and (ZD)Eo prebleaching is compared in Table 5.3. Other pulp and effluents characteristics are given in Table 3.3 (page 29).

Table 5.3: Balance of inorganic and organic chloro-compounds formed in the DEo, (DZ)Eo and (ZD)Eo prebleaching of oxygen delignified kraft pulp.

	ClO ₂ ¹⁾ charge	Cl ⁻	ClO ₃ ⁻	AOX, 1 st stg. 2 nd stg.		OCI ²⁾	SUM ³⁾
	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	%
DEo	3.61 (100)	2.22 (61)	0.76 (21)	0.32 (9)	0.06 (2)	0.13 (4)	(96)
(DZ)Eo	1.78 (100)	1.20 (68)	0.23 (13)	0.13 (7)	0.02 (1)	0.14 (8)	(97)
(ZD)Eo	1.83 (100)	1.13 (62)	0.53 (29)	0.17 (9)	0.03 (2)	0.14 (8)	(110)

¹⁾ Enclosed values are relative amounts in percent ²⁾ Organic bound chlorine in the pulp ³⁾ As percent of charged ClO₂.

The results in Table 5.3. show that the (DZ)Eo prebleaching process yielded less formation of both chlorate and chloro-organic compounds. The lower chlorate formation in the (DZ) stage versus the D stage is in agreement with the previous results in Figure 5.4. and related to the lower chlorine dioxide charge applied. The higher chlorate formation in the (ZD) stage versus the (DZ) may be related to less reactive lignin structures being present during the chlorine dioxide treatment in the (ZD) stage. Both ozone and chlorine dioxide have oxidized lignin in the (DZ) stage before the hypochlorous acid is generated, and hypochlorous acid probably reacts to a larger extent inorganically and forms chlorate.

The chlorate and chloride formation during low consistency D and (ZD) treatments is shown in Figure 5.6. Since the chlorate and chloride concentrations remain unchanged upon ozonation when all chlorine dioxide and chlorite are consumed, the formation of inorganic chloro-compounds in D and (DZ) stages are equal at the same chlorine dioxide charge. In agreement with the previous results, Figure 5.6 shows that the (DZ) process

yields less chlorate formation than the (ZD) treatment. Like the chlorate formation at high chlorine dioxide charge (1.0%) in Figure 5.5, a significant portion of the chlorate formed in the (ZD) treatment is generated rather slowly throughout the treatment.

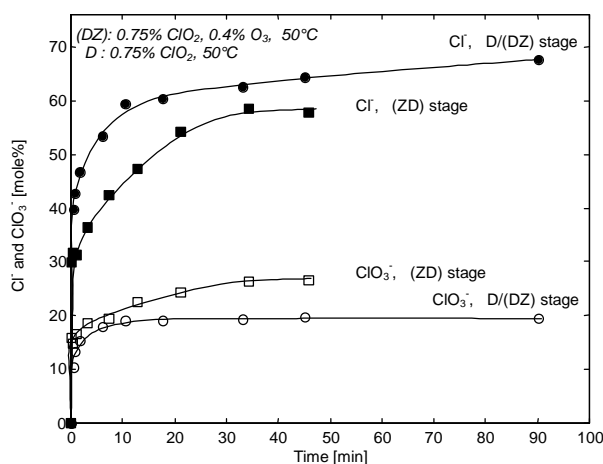


Figure 5.6 Chloride and chlorate formation during low consistency D/(DZ) and (ZD) treatment of oxygen delignified kraft pulp.

5.6.2 Sequential charging of chlorine dioxide

The effect of sequential charging was tested by chlorine dioxide prebleaching experiments performed in plastic bags at 8% pulp consistency in buffered solutions at pH 2.5 and 3.5. The retention time in between the charges was varied in order to investigate the possible effects of residual chlorite. The results for the experiments performed at pH 3.5 are given in Table 5.4. Neither the chlorine dioxide bleaching experiments at pH 3.5 nor pH 2.5 showed any typical difference in chlorate formation or brightness development between sequential and batch charging. The measured concentrations of chlorate and chloride were low compared to earlier experiments. Some experiments were repeated without buffer addition but the buffer did not seem to influence the results to any noticeable extent.

In Section 5.6.3 it was suggested that the lower chlorate formation and increased delignification of the (DZ) treatment versus the (ZD) treatment could be explained by that the chlorine dioxide treatment was more efficient in the (DZ) stage than the (ZD) stage. The results indicated that hypochlorous acid to a larger extent reacts with lignin and contributes to delignification in the (DZ) stage, whereas it reacts inorganically and forms chlorate in the (ZD) stage when less reactive residual lignin structures are present. In relation to these results it seems reasonable that splitting the chlorine dioxide charge in a (D₁...D_i)Eo process is not beneficial compared to a DEo process. Like the chlorine dioxide treatment in the (DZ) stage, the first chlorine dioxide treatments in the (D₁...D_i) stage probably work efficiently, but as the number of reactive lignin structures in the pulp decreases the latter probably do not. Recently, Lachenal and Chirat [70] also

Table 5.4: Effect of sequential charging in buffered¹⁾ chlorine dioxide prebleaching of oxygen delignified kraft pulp²⁾.

ClO ₂ , %	ClO ₃ ⁻ , % of ClO ₂					Cl ⁻ , % of ClO ₂					Brightness, %ISO				
	0.2	0.4	0.6	0.8	1.0	0.2	0.4	0.6	0.8	1.0	0.2	0.4	0.6	0.8	1.0
Batch	4.5	7.2	9.9	11.7	11.3	47	53	49	45	45	44.9	46.8	48.3	50.7	52.3
Seq. 30 s. ³⁾	4.2	8.5	10.8	11.3	11.0	49	58	54	49	44	-	44.7	47	49.9	52.3
Seq. 5 min.	-	8.0	8.1	10.0	10.1	-	58	48	57	44	-	45.1	48.5	53.1	52.3
Seq. 30 min	-	9.0	9	-	-	-	83	50	-	-	-	45.8	51.1	-	-
Seq. 30 min ⁴⁾	-	11	13	-	-	-	62	57	-	-	-	45.1	49.8	-	-

¹⁾ Citric acid buffer at pH 3.5 ²⁾ Kappa number 12.7, 36% ISO brightness. D-stage: 50°C, 8% consistency, water bath ³⁾ Sequential charging was done by charging x times of 0.2% ClO₂. Intervals between the charges were 30 seconds, 5 minutes and 30 minutes ⁴⁾ No buffer applied. Start pH was 4.0 and final pH 2.4.

investigated effects of splitting the chlorine dioxide charge in prebleaching. In agreement with the previous results, splitting the chlorine dioxide charge in a DDDE process did not lead to any improvement compared to a DE process. Lachenal and Chirat [70] suggested that chlorine dioxide reacts with oxidized lignin which has not yet gone into solution, since no improvement was obtained when the pulp was washed between the chlorine dioxide treatments. Sequential charging of low amounts of chlorine dioxide is only beneficial when the pulp is pH adjusted or treated with alkaline between the charges [53, 70].

5.6.3 Similarities between (DC)/(CD) and (DZ)/(ZD) stages

Quite similar to the superiority of (DZ)Eo prebleaching versus (ZD)Eo prebleaching, the delignification efficiency of (DC)E prebleaching has been shown to be superior to (CD)E prebleaching [30, 31, 32]. The chlorate formation has also been reported to be lower for the (DC) stage than the (CD) stage [31]. Ni *et al.* [71] explained the difference by chlorite decomposing and regenerating chlorine dioxide according to Equation (5.12) in the (DC) stage, whereas chlorate formation takes place by Equation (5.5) in the (CD) treatment since hypochlorous acid from the C-treatment is present when chlorite is generated in the latter D-treatment. However, the explanation does not seem likely when considering that the acid catalysed decomposition of chlorite is a very slow reaction, and that sufficient amounts of hypochlorous acid should be present for reacting with chlorite in both (CD) and (DC) stages since hypochlorous acid is formed in excess to chlorite in chlorine dioxide bleaching [51, 52, 53]. Thus, extra hypochlorous acid from the initial C-treatment should not influence on the chlorate formation in the latter D treatment since, according to the stoichiometry in Equation (5.5), only one equivalent of hypochlorous acid is consumed in the reaction with chlorite. Another explanation could

be that the difference in chlorate formation of the (DC) and (CD) stages is related to different amount of reactive lignin structures present during the chlorine dioxide treatment. In the (CD) treatment less unoxidized residual lignin is present since chlorine has oxidized lignin prior to the chlorine dioxide treatment. Thus, in the absence of reactive lignin structures the hypochlorous acid generated in the latter chlorine dioxide treatment probably reacts to a larger extent inorganically and forms chlorate. In the (DC) treatment more residual lignin is present when hypochlorous acid is generated, and it may react with residual lignin and contribute to delignification.

Both chlorine and ozone are stronger oxidants than chlorine dioxide, capable of oxidizing non-phenolic lignin structures. In this respect the (DC) and (DZ) stages also seem to be most reasonable. Chlorine dioxide is initially allowed to attack phenolic lignin structures, whereas the non-phenolic and less reactive lignin structures are left for the stronger oxidant.

5.7 Concluding remarks

Chlorine dioxide prebleaching has been shown to give efficient delignification relative to chemical consumption when a low chlorine dioxide charge is applied. The effect may be explained by that the reaction intermediate hypochlorous acid reacts with residual lignin and contributes to delignification. At higher chlorine dioxide charges less reactive lignin structures are present and hypochlorous acid probably reacts to a larger extent inorganically and forms chlorate.

In practice, a low chlorine dioxide charge is used in the (DZ) and (DC) stages, which both have been shown to be very efficient in terms of delignification. Sequential charging of small amounts of chlorine dioxide was not beneficial compared to traditional batch charging.

CHAPTER

6

**PAPER PROPERTIES OF FINAL
BLEACHED PULPS (PAPER III)**

The use of (DZ) and (ZD) stages in prebleaching is believed to be way of reducing the chlorine dioxide consumption in traditional ECF bleaching and make possible a more economical and environmental feasible way of bleaching oxygen delignified kraft pulp. Therefore, effects of using (DZ) and (ZD) bleaching stages in the prebleaching of oxygen delignified softwood kraft pulp has been explored in this study. In Chapter 3 it was shown that the (DZ)Eo prebleaching could be a good alternative to DEo prebleaching by providing efficient delignification relative to chemical consumption and a significant reduction in formation of chloro-organic compounds. In order to establish whether the pulp quality is maintained when (DZ)Eo prebleaching is utilized, paper properties after full bleaching must be compared with the ECF reference pulp. In addition to D₁ED₂ reference final bleaching, it was chosen to apply pressurized peroxide final bleaching, Q(PO). Pressurized peroxide bleaching has been shown to be beneficial in several aspects compared to traditional atmospheric hydrogen peroxide bleaching. The reaction time is reduced considerably, the amount of hydrogen peroxide needed to achieve a certain brightness is reduced, maximum obtainable brightness level is raised and higher pulp viscosity is obtained [5]. Hence, the bleaching sequences applied were (DZ)EoD₁ED₂, (DZ)EoQ(PO), DEoQ(PO) and the DEoD₁ED₂ reference sequence.

6.1 Pulp and effluent characteristics

Oxygen delignified kraft pulp was prebleached according to the sequences (DZ)Eo and DEo as described in Section 2.2.1. Three batches of each sequence were bleached and mixed before analysis and final bleaching. Pulp and effluent characteristics of (DZ)Eo prebleached pulps are given in Table 6.1. Compared to the reference sequence, (DZ)Eo prebleaching yielded a reduction in AOX and COD formation of 47% and 7% respectively. In addition, the (DZ)Eo prebleaching sequence was not optimized with respect to ozone-chlorine dioxide replacement ratio. Since the kappa number of the (DZ)Eo prebleached pulp was lower than the DEo prebleached pulp, it should be possible to reduce the chlorine dioxide charge in the (DZ) stage and still achieve the same final bleaching as the reference pulp. In this case an even lower AOX formation should be obtained.

Table 6.1: Characteristics of prebleached pulps.

	ClO ₂ charge, kg aCl/t	Kappa number	Viscosity, dm ³ /kg	COD, kg/t	AOX, kg/t	OCI, kg/t
DEo	3.61	3.7	840	20.0	0.32	0.08
(DZ)Eo	1.84 (-49%)	3.1	730	18.7 (-7%)	0.17 (-47%)	0.07

Even though a rather low ozone charge of 0.36% has been applied here, the results in Table 6.1 show that the viscosity of the (DZ)Eo prebleached pulp is significant lower than the reference pulp. The viscosity drop is probably due to that ozone may oxidize polysaccharide chains and form carbonyl and carboxylic structures within the polysaccharide chains. Such groups may cause chain cleavage and loss in pulp viscosity upon alkali treatment. However, even though the pulp viscosity of (DZ)Eo prebleached pulps is significant lower than the DEo prebleached pulp, the pulp characteristics of final bleached pulps in Table 6.2 show that the difference in pulp viscosity has decreased considerably after final bleaching.

The pulp and effluent characteristics of final bleached pulps are given in Table 6.2. Chemical charges in final bleaching were chosen in order to achieve a final brightness target of 88% ISO. Compared to the ECF reference, the total AOX formation was reduced by 25% in the (DZ)EoD₁ED₂ sequence, 30% in the DEoQ(PO) sequence and 64% in the (DZ)EoQ(PO) sequence. The D₁ED₂ final bleaching accounted for 38% and 58% of the total AOX formation in the DEoD₁ED₂ and (DZ)EoD₁ED₂ sequence respectively.

The (DZ)Eo prebleaching seemed to yield a small reduction in COD effluent load, whereas a substantial increase in dissolution of organic material took place when Q(PO) final bleaching was applied. The dissolution of organic material represents both an increased effluent load and a yield loss.

Table 6.2: Characteristics of effluents and final bleached pulps.

	ClO ₂ charge, kg aCl/t	AOX, kg/t	COD, kg/t	Bright- ness, % ISO	Viscosity, dm ³ /kg	OCI, kg/t
DEoD ₁ ED ₂	7.5	0.53	28.9	88.4	753	0.08
(DZ)EoD ₁ ED ₂	5.7 (-24%)	0.40 (-25%)	26.4 (-9%)	87.5	745	0.08
DEoQ(PO)	3.6 (-52%)	0.37 (-30%)	37.3 (+29%)	87.5	773	0.09
(DZ)Eo(PO)	1.8 (-76%)	0.19 (-64%)	37.2 (+29%)	87.7	730	0.03

6.2 Paper properties of unbeaten pulps

Paper properties of unbeaten pulps are given in Table 6.3. Generally, differences in paper properties were small. The tear index and fibre-fibre strength (Scott Bond) were about equal for all pulps. However, the Q(PO) the final bleached pulps seemed to be

Table 6.3: Paper properties of unbeaten ECF bleached kraft pulps.

	DEoD ₁ ED ₂	(DZ)EoD ₁ ED ₂	DEoQ(PO)	(DZ)EoQ(PO)
Tear index, mNm^2/g	20.5	20.7	20.7	20.7
Tensile index, Nm/g	25.9	25.2	26.8	27.8
Density, kg/m^3	606	609	619	623
Wet zero span, Nm/g	93.2	91.7	97.6	92.6
Scott Bond, J/m^2	100	109	109	109
WRV, g/g	1.14	1.17	1.22	1.21
Viscosity, dm^3/kg	753	745	773	730

somewhat more swollen than the D₁ED₂ final bleached pulps, and denser paper sheets with higher tensile strength and wet zero span strength were formed.

Similar results were obtained by Laine and Stenius [72] when studying effects of fibre charge on paper properties of industrially bleached kraft pulps. Increased fibre charge was found to promote increased fibre swelling. Increased fibre swelling further promotes fibre flexibility [73] and yields more fibre-fibre contacts. As the fibres remain in contact and form bonds at their intersections upon drying [74] improved fibre flexibility yields denser paper sheets with higher relative bonded area. As the differences in paper properties of unbeaten pulps in Table 6.3 can be explained by differences in swelling it was decided to further investigate the swelling properties of the pulps.

6.3 Effect of bleaching on charged groups in the pulp

A major number of carboxyl groups in wood materials is the 4-O-methyl glucuronic acid side groups of xylan. Sjöström [33] reported that the content of 4-O-methyl glucuronic acid in *Picea abies* and *Pinus sylvestris* were 70 and 80 $\mu\text{mole/g}$ respectively. During kraft cooking a significant number of the methyl glucuronic acid groups is converted to hexenuronic acid groups. Hence, hexenuronic acid is a major contributor to the fibre charge in kraft pulps, and the variation in fibre charge of ECF and TCF bleached pulps can be largely explained in terms of selective reactions of hexenuronic groups with various bleaching chemicals [75, 76].

The development of total amount of charged groups in the pulps, hexenuronic acid groups and acid groups attached to lignin in the bleaching sequences applied is shown in Figure 6.1. The amount of carboxyl groups attached to lignin was estimated by analysing carboxyl group content in isolated residual lignins by conductometric titration and assuming that total lignin content in the pulps can be estimated by $\% \text{ lignin} = 0.15 \cdot \text{Kappa number}$. Only four of the pulps were analysed for carboxyl groups in residual lignin. According to Figure 6.1, the hexenuronic acid groups and charged groups attached to the lignin structure account for about 15% and 20% of the total number of charged groups in the unbleached kraft pulp respectively. However, as mentioned in Section 2.4.1, the total number of charged groups determined by polyelectrolyte titration seemed to be somewhat overestimated. Compared to conductometric titration polyelectrolyte titration yielded about 15-20 $\mu\text{mole/g}$ higher

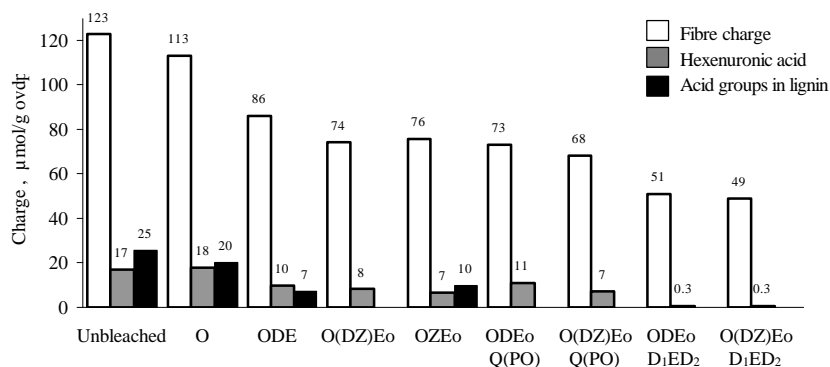


Figure 6.1 The change in total number of charged groups, hexenuronic acid groups and carboxyl groups attached to lignin in bleaching.

values for the fibre charge for four chemical pulps at different charge levels. Even though the total number of charged groups probably is somewhat overestimated, the hexenuronic acid groups and acid groups attached to lignin account for only about 40% of the total number of charged groups in the pulps. Some of the remaining carboxyl groups may be 4-O-methyl glucuronic acid groups which are not converted to hexenuronic acid groups in the cook.

In agreement with the literature [75, 76], Figure 6.1 shows that chlorine dioxide and ozone reduces the number of charged groups in the pulp, whereas the amount of charged groups in the pulps remained about constant upon hydrogen peroxide and oxygen treatment. At the same degree of delignification, ozone prebleaching yielded somewhat more efficient degradation of hexenuronic acid groups than chlorine dioxide did. After chlorine dioxide final bleaching only traces of hexenuronic acid remained in the pulp, whereas a significant amount of hexenuronic acid groups remained in pressurized peroxide final bleached pulps. As the variations in the total number of charged groups in the pulps resemble the variations in the hexenuronic acid group content, the total number of charged groups was also significantly higher for the pressurized peroxide final bleached pulps than the chlorine dioxide final bleached pulps.

6.4 Effect of charged groups on swelling

Generally swelling of cellulosic fibres is governed by the swelling of polysaccharides and the osmotic pressure created within the fibres due to the dissociation of small ions from charged groups. The swelling is restricted by the ability of the fibre wall to resist the swelling pressure. Upon drying, swelling is reduced due to increased interfibrillar bonding, termed hornification. Charged groups promote the swelling of rewetted fibres by increasing the osmotic pressure and by reducing the degree of hornification upon drying [75, 77]. According to Salmén and Berthold [78] ionic changes mainly affect the surface water of the fibres. Swelling properties of the various ECF bleached pulps are given in Table 6.4.

Table 6.4: Effect of fibre charge on fibre swelling.

	DEoD ₁ ED ₂	(DZ)EoD ₁ ED ₂	DEoQ(PO)	(DZ)EoQ(PO)
Fibre charge, $\mu\text{mole/g}$	51	49	73	68
WRV, g/g ¹⁾	1.14	1.17	1.22	1.21
WRV-WRV _{NaCl} , g/g ²⁾	0.01	0.02	0.04	0.06
Sodium content, ppm ³⁾	153	140	137	198

¹⁾Rewetted sheets ²⁾WRV in water - WRV in 0.1 M NaCl ³⁾100 ppm Na = 4.4 $\mu\text{mole Na/g}$

The results in Table 6.4 indicate that Q(PO) final bleached pulps are somewhat more swollen than the D₁ED₂ final bleached pulps. According to the 12th proposal for a standardized SCAN method for determination of the water retention value (WRV, SCAN-C 102 XE), the average coefficient of variation between replicates when five replicates are applied is 1.03%, corresponding to a standard deviation of 0.01 g/g at a WRV level of 1.2 g/g. Hence, even though the differences in WRV in Table 6.4 seem small, the measured differences is believed to be significant. The positive effect of charged groups on swelling is illustrated by the difference in water retention value of fibres in water respective salt solution, WRV-WRV_{0.1M NaCl}. According to the Donnan Theory [79] salt addition will reduce the difference in total ion concentration between the cell wall and external medium, and reduce the osmotic swelling pressure created by the charged groups. Hence, the results in Table 6.4 indicate that the improved swelling of the Q(PO) final bleached pulps can be related to the higher number of charged groups present in these pulps.

Lindström and Carlsson [77] have shown that the ionic form affects the fibre swelling. The degree of hornification in drying decreased when the pulps were dried with the acidic groups in their ionized form (e.g. in the presence of Na⁺) instead of in their protonized form. In the bleaching sequences applied, the final bleaching stages were both acidic and alkaline, but the pulps were washed with distilled water and pH adjusted to pH 5-6 with SO₂-water after final bleaching. Thus, both chlorine dioxide final bleached pulps and pressurized peroxide final bleached pulps were dried in their protonized form. Laine and Stenius [72] studied the swelling properties of bleached softwood pulps dried in ionized Na-form and found that the water retention value of rewetted sheets increased by about 0.005 units per charge unit. The results in Table 6.4 indicate that carboxyl groups in the pulps promote swelling even when present in their protonized form.

6.5 Physical paper properties of beaten pulps

Physical paper properties of beaten pulps are compared in Table 6.5. The results show that the tear index at tensile index 70 Nm/g of the (DZ)EoD₁ED₂ bleached and the DEoQ(PO) bleached pulps were about equal to that of the reference pulp. However, the wet zero span strength was about 8% lower for the pulps in which (DZ)Eo prebleaching had been applied. Thus, the (DZ) stage seems to have a slightly negative effect on the fibre strength.

Table 6.5: Effect of beating on paper properties.

	DEoD ₁ ED ₂	(DZ)EoD ₁ ED ₂	DEoQ(PO)	(DZ)EoQ(PO)
Wet zero span, Nm/g ¹⁾	112	103	112	103
Tear index, mNm ² /g ¹⁾	13.4	14.1	13.7	12.3
Density, kg/m ³ ¹⁾	775	762	770	782
PFI rev. ¹⁾	3400	3000	2600	3000
Gürley, µm/Pas ¹⁾	16	13	9	6
Light scatt., m ² /kg ¹⁾	20.7	20.8	20.8	20.8
WRV-WRV _{NaCl} , g/g ²⁾	0.06	0.03	0.09	0.09
Shopper Riegler, ml ²⁾	26.5	26.5	29.0	29.0
Scott Bond, J/m ² ³⁾	330	300	310	280

¹⁾ At tensile strength 70 Nm/g ²⁾ At 4000 PFI rev. ³⁾ At sheet density 750 kg/m³

The effect of charged groups on swelling, expressed by WRV-WRV_{NaCl}, seemed to increase at a high degree of beating. Accordingly, Salmén and Berthold [78] observed that the increase in swelling when changing ionic form from proton form to sodium form was substantially higher for highly beaten pulps. The effect may be explained by that the fibrillated material created in beating having less restricting forces to the osmotic pressure created by the charged groups compared to the unbeaten fibre wall.

The results in Table 6.4 indicated that the unbeaten Q(PO) final bleached pulps were somewhat more swollen due to the higher amount of charged groups present. Upon a high the degree of beating the results in Table 6.5 indicated that the difference in swelling between the Q(PO) and the D₁ED₂ final bleached pulps was further increased. Since increased swelling yields increased fibre flexibility and sheets of higher degree of bonding, highly charged and swollen pulps should be advantageous with respect to beatability when beating to a target tensile strength. Table 6.5 show that beatability, meaning the number of PFI mill revolutions required to reach tensile index 70 Nm/g, was better for the DEoQ(PO) pulp than the DEoD₁ED₂ pulp, but equal for the (DZ)EoQ(PO) and (DZ)EoD₁ED₂ pulps. However, the differences in beatability may be influenced by fibre curl introduced by the fibres by the mixing at medium consistency in the first bleaching stage [80]. Somewhat curled fibres probably explains that all pulps required a rather high amount of energy to reach tensile index of 70 Nm/g. To minimize this effect, pulps were only mixed by high intensity during injection of bleaching chemicals. Since the rewetted zero span tensile strength describes both the strength properties of single fibres and the degree of fibre deformation [81], the lower wet zero span values of the (DZ)Eo prebleached could be related to more curled fibres. However, considering both the low degree of mixing applied and that lower wet zero span values also were obtained after beating, this is not believed to be the case. PFI mill beating is known to straighten curled fibres [82].

6.6 Concluding remarks

Physical paper properties of (DZ)EoD₁ED₂, DEoQ(PO) and (DZ)EoQ(PO) bleached oxygen delignified softwood kraft pulps were compared to the same properties of a DEoD₁ED₂ bleached ECF reference pulp.

(DZ)Eo prebleaching applied in a (DZ)EoD₁ED₂ bleaching sequence reduced the AOX formation and the COD effluent load by 25% and 9% respectively. The tear strength was maintained, but the (DZ)Eo prebleaching seems to have a slight negative effect on fibre strength as indicated by lower wet zero span strength of beaten (DZ)EoD₁ED₂ and (DZ)EoQ(PO) bleached pulps.

Pressurized peroxide final bleaching in a DEoQ(PO) bleaching sequence reduced the AOX formation by 30%, but the COD effluent load was increased by 29%. Q(PO) final bleaching yielded pulps with higher fibre charge than chlorine dioxide final bleaching. Compared to the D₁ED₂ final bleached pulps, the increased number of charged groups in DEoQ(PO) and (DZ)EoQ(PO) bleached pulps seemed to promote increased fibre swelling of both unbeaten and highly beaten pulps. The more swollen unbeaten Pressurized peroxide final bleached pulps formed denser paper sheets with higher tensile strength and wet zero span strength. A highly charged and swollen pulp seems to be advantageous with respect to beatability when the pulp is beaten to a target tensile strength.

The use of both (DZ)Eo prebleaching and pressurized peroxide final bleaching in a DEoQ(PO) bleaching sequence reduced the AOX formation by 64%, but the tear strength and the wet zero span strength of beaten pulp were also lowered.

C H A P T E R

7

CONCLUDING REMARKS**7.1 Synergetic delignification in the (DZ) process
(Chapter 3)**

The use of chlorine dioxide and ozone in combination in (DZ)Eo and (ZD)Eo prebleaching of oxygen delignified kraft pulp has been shown to be efficient in terms of delignification. When the (DZ)Eo prebleaching process was applied, a synergetic delignification effect was obtained giving better delignification than should be expected from the effect of chlorine dioxide and ozone separately.

7.2 The complementary lignin chemistry of chlorine dioxide and ozone (Chapter 4)

The efficient delignification obtained when chlorine dioxide and ozone are used in combination seems reasonable due to their ability to degrade different types of lignin structures. Whereas chlorine dioxide mainly degrades phenolic lignin structures, ozone is capable of degrading both phenolic and non-phenolic lignin structures. Both chlorine dioxide and ozone are strong oxidants, but ozone seems to be more efficient in this respect since more carboxyl groups were implemented in the residual lignin at the same degree of delignification. The large number of carboxyl groups introduced in the lignin structure seems to govern the solubilization of the lignin in chlorine dioxide and ozone bleaching.

The superior delignification efficiency of (DZ)Eo prebleaching versus (ZD)Eo prebleaching may be explained by that the (DZ) treatment initially allows chlorine dioxide to degrade the phenolic lignin structures, and leaves the non-phenolic and less reactive lignin structures for the ozone treatment.

7.3 Effect of chlorine dioxide charge in chlorine dioxide bleaching (Chapter 5)

Chlorine dioxide prebleaching has been shown to give efficient delignification relative to chemical consumption when a low chlorine dioxide charge is applied. The effect may

be explained by that the reaction intermediate hypochlorous acid reacts with residual lignin and contributes to delignification. At higher chlorine dioxide charges less reactive lignin structures are present and hypochlorous acid probably reacts to a larger extent inorganically and forms chlorate.

In practice, a low chlorine dioxide charge is used in the (DZ) and (DC) stages, which both have been shown to be very efficient in terms of delignification. Sequential charging of small amounts of chlorine dioxide was not beneficial compared to traditional batch charging.

7.4 Physical properties of final bleached pulps (Chapter 6)

Physical paper properties of (DZ)EoD₁ED₂, DEoQ(PO) and (DZ)EoQ(PO) bleached oxygen delignified softwood kraft pulps were compared to the same properties of a DEoD₁ED₂ bleached ECF reference pulp.

(DZ)Eo prebleaching applied in a (DZ)EoD₁ED₂ bleaching sequence reduced the AOX formation and the COD effluent load by 25% and 9% respectively. The tear strength was maintained, but the (DZ)Eo prebleaching seems to have a slight negative effect on fibre strength as indicated by lower wet zero span strength of beaten (DZ)EoD₁ED₂ and (DZ)EoQ(PO) bleached pulps.

Pressurized peroxide final bleaching applied in a DEoQ(PO) bleaching sequence reduced the AOX formation by 30%, but the COD effluent load was increased by 29%. Q(PO) final bleaching yielded pulps with higher fibre charge than chlorine dioxide final bleaching. Compared to the D₁ED₂ final bleached pulps, the increased number of charged groups in DEoQ(PO) and (DZ)EoQ(PO) bleached pulps seemed to promote increased fibre swelling of both unbeaten and highly beaten pulps. The more swollen unbeaten Q(PO) final bleached pulps formed denser paper sheets with higher tensile strength and wet zero span strength. A highly charged and swollen pulp seems to be advantageous with respect to beatability when the pulp is beaten to a target tensile strength.

The use of both (DZ)Eo prebleaching and pressurized peroxide final bleaching in a DEoQ(PO) bleaching sequence reduced the AOX formation by 64%, but both the tear strength and the wet zero span strength of beaten pulp were also reduced.

LIST OF REFERENCES

1. Dence, C.W. and Reeve, W. "Pulp bleaching - principles and practice", Tappi press, Atlanta, Georgia (1996)
2. Gullichsen J., "Bleaching, the Scandinavian situation", *Int. Pulp Bleach. Conf.*, Helsinki, Keynote lecture (1998)
3. Lachenal, D., Taverdet, M.T. and Muguet, M., "Improvement in the ozone bleaching of kraft pulps", *Int. Pulp Bleach. Conf.*, Stockholm, 2:33-43 (1991)
4. Dillner, B. and Tibbling, P., "Use of ozone at medium consistency for fully bleached pulp", *Int. Pulp Bleach. Conf.*, Stockholm, 2:59-74 (1991)
5. Dillner, B. and Tibbling, P., "TCF bleaching can be carried out in different bleaching systems", *XXV EUCEPA Conf.*, Vienna, 1:65-83 (1993)
6. Gellerstedt, G., Pranda J. and Lindfors, E-L., "Structural and molecular properties of residual birch kraft lignins", *J. Wood Chem. Technol.*, 14(4):467-482 (1994)
7. Rolando, C., Monties B. and Lapierre, C., "Thioacidolysis" in *Methods in Lignin Chemistry* (Lin S.Y. & Dence C.W., Editors), Springer-Verlag, Berlin, 334-349 (1992)
8. Zakis, G.F., "Functional analysis of lignins and their derivatives", Transl. by Porozny R. and Joyce T. W., TAPPI Press, Atlanta, Ga, 43-49 (1994)
9. Tamminen, T., Hortling, B., Poppius-Levlin, K. and Sundquist, J., "Connections between bleachability and residual lignin structure", *7th Int. Symp. on Wood and Pulp. Chem.*, Beijing, 3:228-232 (1993)
10. Katz, S., Beatson, R.P. and Scallan A.M., "The determination of strong and weak acid groups in sulfite pulps", *Svensk Papperstidn.*, 87(6):R48-R53 (1984)
11. Heuts, L., "The lignin chemistry of OQP-bleaching - an analytical study", Ph.D. thesis, Department of Pulp and Paper Chemistry and Technology, KTH, Stockholm, 1999
12. Analytische Laboratorien, Gummersbach, Germany
13. Freudenberg, K. and Neish, A.C., "Constitution and biosynthesis of lignin", Springer Verlag, New York, (1968)
14. Hynynen, R., Laine, J. and Stenius, P., "Determination of the charge of cellulosic fibres by polyelectrolyte adsorption", *NORDPAP DP1/46*, SCAN Forsk report 702 (1998)
15. Wåberg, L., Winter, L. and Lindström, T., "Determination of ion-exchanged capacity of carboxymethylated cellulose fibres using colloid and conductometric titrations" in *Papermaking raw materials*, *Trans. of the 8th Fund. Res. Symp.*, 917-922 (1985)
16. Wåberg, L., Ödberg, L. and Glad-Nordmark, G., "Charge determination of porous substrates by polyelectrolyte adsorption", *Nord. Pulp Pap. Res. J.*, 4(2):71-76 (1989)
17. Gellerstedt, G. and Li, J., "An HPLC method for the quantitative determination of hexeneuronic acid groups in chemical pulps", *Carbohydr. Res.*, 294:41-51 (1996)

18. Tenkanen, M., Gellerstedt, G., Vuorinen, T., Teleman, A., Perttula, M., Li, J. and Büchert, J., "Determination of hexenuronic acid in softwood kraft pulps by three different methods", *J. Pulp Pap. Sci.*, 25(9): 306-311 (1999)
19. Dence, C.W., Reeve, D.W., "The technology of chemical pulp bleaching" in "Pulp Bleaching - Principles and Practice", Tappi press, Atlanta, IV.5, 325 (1996)
20. Rice, R. G., "Ozone in United States of America-State of the Art", *13th Ozone World Congress*, Kyoto, 2:1099-1101 (1997)
21. Roy-Arcand, L., Archibald, F.S. and Briere, F., "Combined biological and chemical treatment of a kraft bleach plant effluent", *5th Int. Symp. on Wood and Pulp. Chem.*, Raleigh, Nc,1:727-734 (1989)
22. Chirat, C. and Lachenal D., "Other ways to use ozone in a bleaching sequence", *Tappi J.*, 80(9):209-214 (1997)
23. Siltala, M., Winberg, K. and Keskinen, N. "Low cost and high quality softwood pulp production by combining high cooking kappa, extended oxygen delignification and Z/D bleaching", *Int. Pulp Bleach. Conf.*, Halifax, 1:217-224 (2000)
24. Munro, F. and Griffiths, J. "Operating experience with an ozone-based ECF bleaching sequence", *Int. Pulp Bleach. Conf.*, Halifax, 1:225-230 (2000)
25. Rodrigues, M., Peixoto, M. A. L. and Zolio, A. "Improvements in the bleach plants", *Int. Pulp Bleach. Conf.*, Halifax, 1:231-238 (2000)
26. Homer, G., Epiney, M., Muguet, M. and Johnson, S., "DZ state-of-the-art ECF bleaching: part I", *Pulp Pap. Can.*, 98(8):42-49 (1997)
27. Chirat, C., Lachenal, D., Angelier, R. and Viardin, M.T., "(DZ) and (ZD) bleaching: Fundamentals and application", *Int. Pulp Bleach. Conf.*, Washington, 1:197-202 (1996)
28. Li, J., "Toward an accurate determination of lignin in chemical pulps. The meaning of kappa number as a tool for analysis of oxidizable groups", Ph.D. thesis, Department of Pulp and Paper Chemistry and Technology, KTH, Stockholm, 1999.
29. Li, J. and Gellerstedt, G., "The contribution to kappa number from hexenuronic acid groups in xylan", *Carbohydr. Res.*, 302(3-4):213-218 (1997)
30. Jack, W.Q. and Feller, L. D., "Lower-cost pulp bleaching with chlorine dioxide as the first treatment", *Pulp Pap. Mag. Can.*, 68(9):T461-T471 (1967)
31. Reeve, D.W. and Rapson, W. H., "Developments in chlorine dioxide bleaching", *Tappi Pulp. Conf.*, Atlanta, Ga, 403-409 (1980)
32. Germgård, U. and Karlsson, R.-M., "Bleaching of birch kraft pulp with different fractions of chlorine dioxide in the prebleaching", *Nord. Pulp and Paper Res. J.*, 3(4):166-170 (1988)
33. Sjöström, E., "Wood Chemistry: fundamentals and applications", 2nd ed., Academic Press, Orlando (1993)
34. Gellerstedt, G., Lindfors, E-L., Lapierre, C. and Monties, B., "Structural changes in lignin during kraft cooking. Part 2. Characterization by acidolysis", *Svensk Papperstidn.*, 87(9):R61-R67 (1984)
35. Johansson E., Suckling, I.D. and Ede, R.M., "The effect of O and OO delignification on the structure of residual lignin from pinus radiata pulp", *9th Int. Symp. on Wood and Pulp. Chem.*, Montreal, Quebec, 1: J1-1-J1-4 (1997)
36. Lai, Y-Z., Guo, X. and Situ, W., "Estimation of phenolic hydroxyl groups in wood by periodate oxidation method", *J. Wood Chem. Technol.*, 10(3):365-377 (1990)

37. Gellerstedt, G. and Lindfors, E-L., "Structural changes in lignin during kraft cooking. Part 4. Phenolic hydroxyl groups in wood and kraft pulps", *Svensk Papperstidn.*, 87(15):R115-R118 (1984)
38. Yang, R. and Lai, Y-Z., "The influence of kraft cooking conditions on the nature of residual lignin", *9th Int. Symp. on Wood and Pulp. Chem.*, Montreal, Quebec, 2:53-1-53-4 (1997)
39. Robert, D.R., Bardet, M., Gellerstedt, G. and Lindfors, E-L., "Structural changes in lignin during kraft cooking. Part 3. On the structure of dissolved lignins", *J. Wood Chem. Technol.*, 4(3):239-263 (1984)
40. Iversen, T. and Wannström S., "Lignin-carbohydrate bonds in a residual lignin isolated from pine kraft pulp", *Holzforschung*, 40(1):19-22 (1986)
41. Gellerstedt, G. and Al-Dajani, W.W., "On the bleachability of kraft pulps", *9th Int. Symp. on Wood and Pulp. Chem.*, Montreal, Quebec, 1:A1-1-A1-4 (1997)
42. Chang, H-M., Cowling, E.B., Brown, W., Adler, E. and Miksche, G.E., "Comparative studies on cellulytic enzyme lignin and milled wood lignin of sweetgum and spruce", *Holzforschung*, 29(5):153-159 (1975)
43. Gellerstedt, G. and Heuts, L., "Changes in the lignin structure during a totally chlorine free bleaching sequence", *J. Pulp Pap. Sci.*, 23(7):J335-J339 (1997)
44. Gellerstedt, G. and Wafa Al-Dajani, W., "On the structure of residual lignins in alkaline pulps.", *10th Int. Symp. on Wood and Pulp. Chem.*, Yokohama, 1:346-349 (1999)
45. Gellerstedt, G., Lindfors, E-L., Petterson, M., Sjöholm, E. and Robert, D., "Chemical aspects on chlorine dioxide as a bleaching agent for chemical pulps", *6th Int. Symp. on Wood and Pulp. Chem.*, Melbourne, Victoria, 1:331-336 (1991)
46. Lachenal, D., Fernandes, J.C. and Froment P. J., "Behaviour of residual lignin in kraft pulp during bleaching", *J. Pulp Pap. Sci.*, 21(5):J173-J177 (1995)
47. Månsson, P. and Öster, R., "Ozonation of kraft lignin", *Nord. Pulp Pap. Res. J.*, 3(2):75-81 (1988)
48. Chang, H-M., Cowling, E.B., Brown, W., Adler, E. and Miksche, G.E., "Comparative studies on cellulolytic enzyme lignin and milled wood lignin of sweetgum and spruce", *Holzforschung*, 29(5):153-159 (1975)
49. Sun, Y. and Argyropoulos, D.S., "A comparison of the reactivity and the efficiency of ozone, chlorine dioxide, dimethyldioxirane and hydrogen peroxide with residual kraft lignin", *Holzforschung*, 50(2):175-182 (1996)
50. Germgård, U., Teder, A. and Tormund, D. "Chlorate formation during chlorine dioxide bleaching of softwood kraft pulp", *Pap. Puu*, 61(3):127-133 (1981)
51. Kolar, J.J., Lindgren, B.O. and Pettersson, B. "Chemical reactions in chlorine dioxide stages of pulp bleaching", *Wood Sci. Technol.*, 17:117-128 (1983)
52. Ni, Y., Kubes, G. J. and van Heiningen, A.R.P., "Rate processes of chlorine species distribution during chlorine dioxide prebleaching of kraft pulp", *Nord. Pulp Pap. Res. J.*, 7(4):200-204 (1992)
53. Joncourt, M. J., Froment, P., Lachenal, D. and Chirat, C., "Reduction of the formation of AOX during chlorine dioxide bleaching", *Tappi Pulp. Conf.*, Chicago, Il., 1:149-152 (1995)
54. Dence, C.W. and Reeve, W. "Pulp bleaching - principles and practice", Tappi Press, Atlanta, Georgia, III 3, 134 (1996)

55. Wajon, J.E., Rosenblatt, D.H. and Burrows, E.P., "Oxidation of phenol and hydroquinone by chlorine dioxide", *Environ. Sci. Technol.*, 16(7):396-402 (1982)
56. Kieffer, R.G. and Gordon, G., "Disproportion of chlorous acid. II Kinetics", *Inorg. Chem.*, 7(2):239-244 (1968)
57. Joncourt, M.J., Mortha, G. and Lachenal, D., "Investigations on the effect of additives during ClO₂ bleaching", *9th Int. Symp. on Wood and Pulp. Chem.*, Montreal, Quebec, 1:J6-1-J6-5 (1997)
58. Dence, C.W. and Annergren, G. E., "Chlorination" in *The bleaching of pulp* (Singh, R. P., Ed.), Tappi Press, Atlanta, Ga., 30 (1979)
59. Vourinen, T., Buchert, A., Teleman, A., Tenkanen, M. and Fagerström, P., "Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps", *Int. Pulp Bleach. Conf.*, Washington, D.C., 1:43-51 (1996)
60. Emmenegger, F. and Gordon, G., "The rapid reaction between sodium chlorite and chlorine", *Inorg. Chem.*, 6(3):633-635 (1967).
61. Taube, H. and Dodgen, H. "Applications of radioactive chlorine to the study of the mechanisms of reactions involving changes in the oxidation state of chlorine", *Am. Chem. Soc. J.*, 71:330 (1949)
62. Reeve, D.W. and Weishar, K.M., "Chlorine dioxide delignification - process variables", *Tappi J.*, 74(6):164-167 (1991)
63. Kieffer, R.G. and Gordon, G., "Disproportion of chlorous acid. I. Stoichiometry", *Inorg. Chem.*, 7(2):235-239 (1968)
64. Schmitz, G. and Rooze, H. "Mécanisme des réactions du chlorite et du dioxyde de chlore. 1. Stoechiométrie des réactions du chlorite et cinétique en présence d'orthotolidine", *Can. J. Chem.*, 58(8):1177-1187 (1981)
65. Hong, C. C. and Rapson, W. H., "Kinetics of disproportionation of chlorous acid", *Can. J. Chem.*, 46:2053-2060 (1968)
66. Gordon, G., Keiffer, R. G. and Rosenblatt, D. H., "The chemistry of chlorine dioxide", *Progr. Inorg. Chem.*, 115:200-286 (1972)
67. Rapson, W., "The role of pH in bleaching pulp", *Tappi*, 39(5):284-295 (1956)
68. Larson, L.E. in *Handbook of pulp and paper technology*, 2nd ed. Reinhold, New York, 272 (1970)
69. Ni, Y., Kubes, G. J. and van Heiningen, A.R.P., "Mechanism of formation of chloroorganics during chlorine dioxide prebleaching of kraft pulp", *Nord. Pulp Pap. Res. J.*, 8(4):350-351 (1993)
70. Lachenal, D. and Chirat, C., "Improvement of ClO₂ delignification in ECF bleaching", *Int. Pulp Bleach. Conf.*, Halifax, 1:159-162 (2000)
71. Ni, Y., Kubes, G.J. and van Heiningen, A.R.P., "Mechanism of chlorate formation during bleaching of kraft pulp with chlorine dioxide", *J. Pulp Paper Sci.*, 19(1):J1-J6 (1993)
72. Laine, J. and Stenius, P., "Effect of charge on the fibre and paper properties of bleached industrial kraft pulps", *Pap. Puu*, 79(4):257-266 (1997)
73. Scallan, A. M. and Grignon, J., "Swelling and elasticity of the cell walls of pulp fibres", *J. Pulp Paper Sci.*, 18(5):J188-J193 (1992)
74. Page, D.H., Tydeman, P.A. and Hunt, M., "The behaviour of fibre-to-fibre bonds in sheet under dynamic conditions" in *Formation and structure of paper*, *Trans. of the 2nd Oxford Symp.*, 1:249-263 (1961)

-
75. Laine, J., "Effect of ECF and TCF bleaching on the charge properties of kraft pulp", *Pap. Puu*, 79(8):551-559 (1997)
 76. Büchert, J., Teleman, A., Harjunpää, V., Tenkanen, M., Viikari, L. and Vuorinen, T., "Effect of cooking and bleaching on the structure of xylan in conventional pine kraft pulp", *Tappi J.*, 78(11):125-130 (1995)
 77. Lindström, T. and Carlsson, G., "The effect of carboxyl groups and their ionic form during drying on the hornification of cellulose fibres", *Svensk Papperstidn.* 85(15):R146-R151 (1982)
 78. Salmén, L. and Berthold, J., "The swelling ability of pulp fibres" in Fundamentals of papermaking materials, *Trans. of the 11th Fund. Res. Symp.* 2:683-701 (1997)
 79. Bolam, T.R., "The Donnan Equilibria", Bell, London (1932)
 80. Haukjem, S. and Toven, K., "Pressurized peroxide bleaching in MC mixer", PFI report 12/96 (1996)
 81. Mohlin, U-B. and Alfredsson, C., "Fibre deformation and its implication in pulp characterization", *Nord. Pulp Pap. Res. J.*, 5(4):172-179 (1990)
 82. Page, D.H., Seth, R.S., Jordan, B.D. and Barbe, M.C., "Curl, crimps, kinks and microcompressions in pulp fibres - Their origin, measurement and significance" in Papermaking raw materials, *Trans. of the 8th Fund. Res. Symp.*, 1:183-227 (1985)

PAPER I

Toven, K., Gellerstedt, G., Kleppe, P. and Moe, S.

“The use of chlorine dioxide and ozone in combination in prebleaching”

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Use of Chlorine Dioxide and Ozone in Combination in Prebleaching

K. TOVEN, G. GELLERSTEDT, P. KLEPPE and S. MOE

(DZ)Eo prebleaching of oxygen-delignified softwood kraft pulp gave a synergistic delignification effect compared to the effect of chlorine dioxide and ozone separately, and the (DZ)Eo process was somewhat better than (ZD)Eo prebleaching in terms of delignification. The solubilization of the lignin in chlorine dioxide and ozone bleaching seems to be governed by the large number of carboxyl groups introduced into the lignin structure. The efficient delignification obtained in (DZ)Eo prebleaching may be explained by the ability of chlorine dioxide and ozone to degrade different types of lignin structures. Whereas chlorine dioxide mainly degrades phenolic lignin structures, ozone is capable of degrading both phenolic and non-phenolic lignin structures. The (DZ) treatment initially allows chlorine dioxide to degrade the phenolic lignin structures, and leaves the non-phenolic and less reactive lignin structures for the ozone treatment.

Le pré-blanchiment (DZ)Eo de pâtes kraft de résineux délignifiées à l'oxygène a permis d'obtenir un effet de délignification synergique, comparativement à l'effet du bioxyde de chlore et de l'ozone utilisés séparément, et le procédé (DZ)Eo s'est révélé meilleur que le pré-blanchiment (ZD)Eo pour la délignification. La solubilisation de la lignine lors du blanchiment au bioxyde de chlore et à l'ozone semble être régie par le grand nombre de groupes carboxyles introduits dans la structure de la lignine. La délignification efficace obtenue grâce au pré-blanchiment (DZ)Eo peut s'expliquer par la capacité du bioxyde de chlore et de l'ozone à dégrader différents types de structures de lignine. Alors que le bioxyde de chlore dégrade surtout les structures phénoliques de la lignine, l'ozone peut en dégrader autant les structures phénoliques que non phénoliques. Le traitement (DZ) permet d'abord au bioxyde de chlore de dégrader les structures phénoliques et laisse les structures non phénoliques et moins réactives pour être traitées à l'ozone.

INTRODUCTION

Chlorine dioxide is an excellent bleaching agent because of its selectivity towards lignin. Totally chlorine free (TCF) chemicals, like hydrogen peroxide and ozone, cause somewhat more degradation of the cellulose in the pulp during delignification. Therefore, it is difficult to avoid chlorine dioxide if one wishes to produce a chemical pulp with high strength properties. However, environmental aspects and market demands have forced increased use of TCF chemicals in pulp bleaching.

Ozone is a very efficient oxidant, capable of oxidizing all types of lignin structures. However, ozone may also oxidize polysaccharide chains, forming carbonyl and carboxylic structures. Upon alkaline treatment these groups may cause chain breakage and loss in pulp viscosity. Therefore, ozone is usually used in the beginning of a bleaching sequence, where the cellulose degradation is retarded by the high amount of lignin present, or only small charges of ozone are applied.

An interesting, rather new bleaching concept is the use of chlorine dioxide and ozone in combination in the same bleaching stage [1,2]. Effective delignification is obtained, adsorbable organic halide (AOX) formation is reduced and pulp viscosity is mostly maintained because of the rather low ozone charge applied. Lachenal et al. [1] found that the selectivity expressed by the decrease in kappa number versus the degree of polymerization was superior for the DZ treatment in which chlorine dioxide was used before ozone, compared to the ZD treatment. In addition, the simplified one-stage (DZ) treatment, without washing in between the chlorine dioxide and the ozone

treatment, was even more selective than the two-stage DZ treatment. Both findings were surprising since ozone usually is less harmful at high lignin contents and since the presence of dissolved organic material often has a negative effect. It was speculated that the chlorine dioxide modifies the residual lignin and makes it more reactive towards ozone, and that dissolved organic matter may act as a radical scavenger during the latter ozone treatment.

Chirat and Lachenal [3] found that the total chlorine dioxide consumption could be reduced by 1.0% for hardwood and 0.8% for softwood pulp when using a (DZ)EoD₁ED₂ sequence to 88% ISO brightness instead of a traditional DEoD₁ED₂ sequence. Amounts of 0.25 and 0.7% ozone were used for the hardwood and softwood pulp, respectively, corresponding to an ozone-chlorine dioxide replacement ratio of 0.25 kg O₃/kg ClO₂ for the hardwood pulp and 0.58 kg O₃/kg ClO₂ for the softwood pulp. Oxygen-delignified softwood kraft pulp was found to respond differently to the (DZ) and (ZD) treatments than the unbleached pulp [4]. In this case, the (ZD) treatment was found to be the most efficient

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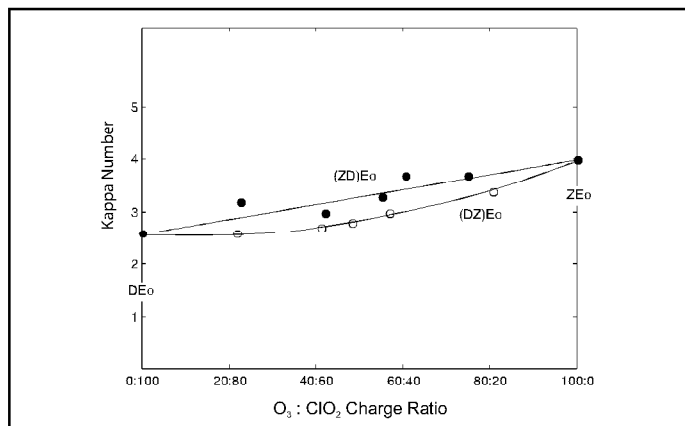


Fig. 1. Delignification in DEo, (DZ)Eo, (ZD)Eo and ZEO prebleaching of oxygen-delignified kraft pulp. D, Z, (DZ), (ZD): 50°C, 10% cons. (MC mixer); Eo: 1% NaOH, 0.5 MPa O₂ press., 90°C, 1 h (autoclaves)

treatment in terms of delignification. Chirat et al. [4] suggested that the fact that the number of free phenolic groups in lignin is reduced in oxygen delignification could explain the different behaviour of the oxygen-treated pulp. In contrast to ozone, chlorine dioxide reacts almost exclusively with phenolic lignin structures.

The (DZ) and (ZD) bleaching technologies already have been implemented in some mills and experience from three mills was presented at the 2000 International Pulp Bleaching Conference [5–7]. Two of the mills reported reduction in both COD and AOX effluent load as well as in bleaching chemical costs [5,6]. The Lufz Antônio pulp mill, Lufz Antônio, Brazil, initially installed the (DZ) process since the process provided the best effluent and pulp quality, but later the mill converted to a (ZD) process, mainly due to corrosion problems [7].

The object of this work was to explore effects of using chlorine dioxide and ozone in combination in the prebleaching of oxygen-delignified kraft pulp from a fundamental point of view. The delignification efficiency of using chlorine dioxide and ozone in combination was investigated, and the prebleaching effects of chlorine dioxide and ozone were related to residual lignin structure.

EXPERIMENTAL

Two industrially produced softwood (mixture of *Picea abies* and *Pinus sylvestris*) oxygen-delignified kraft pulps (kappa numbers 13.2 and 12.7) were used in the experiments. The pulps were washed and acidified with sulphuric acid and prebleached according to the sequences DEo, (DZ)Eo, (ZD)Eo and ZEO. The pulps were pH adjusted with sulphuric acid to pH = 3 prior to Z and (ZD) stages and to pH 4 prior to the D and (DZ) stages. Final pH after the D, (DZ) and (ZD) stages was ~2.4 while it was ~2.6 after the Z treatment. The D, (DZ), (ZD) and Z stages were all performed at 50°C and 10% pulp consistency in a high-shear medium-consistency mixer (CMS 2040).

Ozone was injected from a gas container and the ozone concentration in the container measured by iodometric titration. The gas was injected by opening a valve manually, trying to

achieve a certain pressure drop in the container. However, since the injection was fast and the pressure in the gas container dropped quickly due to the adiabatic expansion of the gas, it was difficult to reach exactly the desired final pressure in the ozone container. Thus, the injected amount of ozone was measured accurately by the pressure drop, but the amount of ozone injected was not always the exact amount planned. Chlorine dioxide was injected quite accurately from liquid cylinders, and the chlorine dioxide concentration was determined by iodometric titration immediately before injection.

The retention time of the D and Z stages was 30 min, while the retention time of D and Z in the (DZ) and (ZD) stages was 30 and 10 min, respectively. Rather long retention times were chosen to ensure that all of the initial injected chemical in the (DZ) or the (ZD) stage is consumed before the other chemical is injected. Pulps were subjected to high-intensity mixing during injection of chemicals, whereas intervals of low-intensity mixing were applied to secure uniform temperature in the pulp throughout the treatment.

The alkali extraction stages, Eo, were done in autoclaves at 90°C, 0.5 MPa O₂ pressure, 1% NaOH charge, for 60 min. The pulps were analyzed for kappa number (SCAN-C 1:77) [8], brightness (SCAN-C 11:95) [9], viscosity (SCAN-C 15:88) [10] and hexenuronic acid content [11]. Bleaching filtrates were analyzed for AOX (SCAN-W 9:89) [12], chlorate ions by ion chromatography and chemical oxygen demand (COD) by a photometric method using a Dr. Lange apparatus [13]. Organically bound chlorine in pulp, OCl, was analyzed by burning and titrating a known amount of pulp in

a Euroglass apparatus according to the SCAN method for AOX determination [12].

Residual lignins were isolated from acetone-extracted pulps by acid hydrolysis [14]. The pulps were refluxed for 2 h with 0.1 mol/L HCl in dioxane–water v/v 82:18. Thereafter, the dioxane was evaporated with subsequent addition of water to avoid strong acidity. The solution was dialyzed for three days to remove hydrochloric acid and low molecular weight material, evaporated on a rotavapour and freeze dried. Finally, the lignin was extracted with pentane to remove remaining extractives [14]. Residual lignins were analyzed for β-aryl ether content by thioacidolysis [15], free phenolic hydroxyl groups by ultraviolet spectroscopy [16,17], carboxyl groups by conductometric titration [18], elemental composition and methoxyl content.

Heuts [19] suggested that acidic phenolic groups may contribute in the determination of carboxylic groups in residual lignins since conductometric titration yielded higher values for carboxyl group content than ³¹P nuclear magnetic resonance (NMR) determination. Some obtained data and some of the literature data on functional groups in lignin are recalculated using a molecular weight for a spruce lignin "monomer" of 183 g/mol [20] to estimate the number of functional groups per 100 phenylpropane units.

RESULTS AND DISCUSSION Synergistic Delignification in the (DZ) Process

The effects of using chlorine dioxide and ozone in combination in the prebleaching of oxygen-delignified softwood kraft pulp were investigated. Pulp and effluent properties of (DZ)Eo and (ZD)Eo prebleached pulps were compared to the DEo and ZEO reference pulps. The chemical charges for the DEo and ZEO reference sequences were selected to be 0.95% ClO₂ and 0.67% O₃, respectively. To compare the delignification effect with respect to chemical consumption the chemical charges of chlorine dioxide and ozone in the (DZ)Eo and (ZD)Eo were selected pairs of A · 0.95% ClO₂ and (1–A) · 0.67% O₃ where A = [0.2, 0.4, 0.5, 0.6, 0.8]. Kappa numbers are plotted versus the

**TABLE I
DEo, (DZ)Eo, (ZD)Eo AND ZEO PREBLEACHING OF
OXYGEN-DELIGNIFIED KRAFT PULP**

Charge		DEo, (DZ)Eo, ZEO			Charge		DEo, (ZD)Eo, ZEO		
ClO ₂ %	O ₃ %	K	Br. % ISO	Visc. dm ³ /kg	ClO ₂ %	O ₃ %	K	Br. % ISO	Visc. dm ³ /kg
100	0	2.6	66.2	943	100	0	2.6	66.2	943
80	22	2.6	67.9	844	80	23	3.2	65.9	889
60	41	2.7	68.7	784	60	42	3.0	67.1	876
50	48	2.8	68.6	787	50	55	3.3	65.5	867
40	57	3.0	67.0	777	40	61	3.7	64.7	847
20	81	3.4	64.8	788	20	75	3.7	64.5	764
0	100	4.0	62.0	780	0	100	4.0	62.0	780

–Starting pulp: kappa number 13.2, brightness 42% ISO, viscosity 965 dm³/kg.

–ClO₂ and O₃ charge as percent of 0.95% ClO₂ and 0.67% O₃, respectively. The charged amount of ClO₂ equals the consumed amount of ClO₂.

–κ – kappa number; Br. – brightness; Visc. – viscosity

injected amount of ozone in Fig. 1, and additional data are given in Table I.

Figure 1 shows that (DZ)Eo prebleaching gives somewhat better delignification than (ZD)Eo prebleaching. In fact, the (DZ)Eo treatment seems to give a synergistic delignification effect, giving a higher delignification than should be expected from the effect of chlorine dioxide and ozone separately. If there were no synergistic delignification effect of using chlorine dioxide and ozone in combination, the kappa numbers of the (DZ)Eo and (ZD)Eo prebleached pulps should have formed straight lines between the kappa numbers of the DEo and ZEO reference pulps. Some deviations between the injected amount of ozone relative to the planned amounts do not seem to have affected the difference between (DZ)Eo and (ZD)Eo.

To study structural changes in the residual lignin structure after chlorine dioxide and ozone prebleaching, another oxygen-delignified kraft pulp was bleached in the same way. The chlorine dioxide charge in the DEo reference prebleaching was reduced to achieve the same degree of delignification as that after ZEO prebleaching. To get a representative pulp and enough pulp for residual lignin isolation, three batches of each prebleaching sequence were bleached and mixed before analysis. The pulp and effluent characteristics are given in Table II. In agreement with previous results, the data in Table II show that (DZ)Eo prebleaching is the most efficient treatment in terms of delignification. The results in Tables I and II both show that the improved delignification of the (DZ)Eo prebleached pulps is accompanied by a lowered viscosity. However, lower viscosities of (DZ)Eo prebleached pulps do not necessarily imply poorer selectivity since comparison should be made at the same degree of delignification. After final bleaching, the difference in pulp viscosity decreased [21].

Non-lignin structures like hexenuronic acid have been found to contribute to the kappa number determination [22]. The hexenuronic acid content in the prebleached pulps and its contribution to the kappa number are given in Table II. Hexenuronic acid accounts for ~0.6–0.8 kappa units in prebleached pulps. At the same degree of delignification, ozone seems to be more efficient in degrading hexenuronic acid groups than does chlorine dioxide. However, a somewhat different ability to degrade hexenuronic acid does not seem to explain the lower kappa number of the (DZ)Eo prebleached softwood pulp. Hardwood pulps contain more hexenuronic acid groups than softwood pulps. As mentioned, Chirat and Lachenal [3] found that the chlorine dioxide–ozone replacement ratio of (DZ) and (ZD) stages is higher for hardwood pulps than softwood pulps, which may be because ozone appears to be more efficient in degrading hexenuronic acid groups than does chlorine dioxide.

Table II shows that chlorate formation is lower in the (DZ)Eo prebleaching. Chlorate formation represents a waste of oxidation power in chlorine dioxide bleaching. Previ-

TABLE II
CHARACTERISTICS OF PULP AND EFFLUENTS FROM
PREBLEACHING OF OXYGEN-DELIGNIFIED KRAFT PULP

Pulp ¹	DEo	(DZ)Eo	(ZD)Eo	ZEO
ClO ₂ charge, as % ClO ₂	0.65	0.32	0.33	–
O ₃ charge, %	–	0.36	0.36	0.63
ClO ₃ ⁻ mol% of ClO ₂ ²	21	13	29	–
AOX, kg Cl/t. o.d. t ³	0.38	0.15	0.21	–
COD, kg/t ³	20.9	21.8	25.0	24.0
Kappa number (k)	3.7	3.1	3.4	4.0
HUA, μmol/g	9.7	7.9	n.a.	6.7
Δκ(HUA) ⁴	0.8	0.7	n.a.	0.6
Brightness, %ISO	62.3	63.9	63.7	60.7
Viscosity, dm ³ /kg	790	690	720	690
OCl, kg Cl/t. o.d. t	0.13	0.14	0.14	–

1. Starting pulp: Kappa number 12.7, brightness 36% ISO, viscosity 930 dm³/kg.

2. 1st stage.

3. Sum of 1st and 2nd stages.

4. Δκ = 0.086 • HUA, HUA = hexenuronic acid (μmol/g) [24].

ously, it has been shown that the relative amount of chlorate formed in chlorine dioxide prebleaching increases with chlorine dioxide charge [23]. As chlorine dioxide prebleaching also appeared very efficient in terms of delignification when small chemical charges are applied, it was suggested that the reaction intermediate hypochlorous acid reacts differently depending on chlorine dioxide charge. At low chlorine dioxide charge, hypochlorous acid may react with residual lignin and contribute to delignification, whereas at higher chlorine dioxide charges less reactive residual lignin structures are present and hypochlorous acid reacts to a larger extent inorganically, and forms chlorate [23]. Analogously, the increased chlorate formation in the (ZD) stage can be related to the fact that hypochlorous acid to a larger extent reacts inorganically, since both ozone and chlorine dioxide have oxidized most of the reactive lignin structures prior to the generation of hypochlorous acid. Initially, the (DZ) stage is a chlorine dioxide treatment using low chlorine dioxide charge. Thus, the efficient delignification obtained in (DZ)Eo treatment might be due to efficient delignification in the initial chlorine dioxide treatment [23].

As mentioned previously, Chirat et al. [4] found that the (ZD) stage was the most efficient treatment for the oxygen-delignified kraft pulp, whereas the (DZ) stage was the most efficient treatment for the unbleached pulp. It was suggested that the efficient delignification obtained in both the (DZ) and (ZD) stages was due to the ability of chlorine dioxide and ozone to degrade different lignin structures. The different behaviour of unbleached and oxygen-delignified pulp was suggested to be related to the decrease in phenolic lignin structures in oxygen delignification.

In contrast to the results of Chirat et al. [4], the results presented here imply that the (DZ)Eo process is the most efficient for oxygen-delignified pulps also. It is difficult to speculate why the two studies come to different conclusions, but the way the (DZ) and (ZD) bleaching stages are performed in the laboratory is probably critical. The fact that different

pulp consistencies were applied in the two studies may have influenced the results. Except for a few pilot scale experiments, Chirat et al. [4] performed (DZ) and (ZD) stages at low pulp consistency, whereas the experiments performed in this study were done at medium consistency.

To investigate whether the efficient delignification obtained in both (DZ) and (ZD) stages and the superior delignification efficiency of (DZ)Eo prebleaching versus (ZD)Eo prebleaching could be related to lignin chemistry, residual lignins were isolated and analyzed from untreated (oxygen-delignified) pulp and chlorine dioxide and ozone prebleached pulps.

Lignin Isolation

Lignin isolation from a chemical pulp is a difficult task. The residual lignin content is low and some of the lignin is probably linked to carbohydrates [25]. It has been suggested that alkali-stable lignin–carbohydrate ether bonds form during kraft cooking [26], and the residual lignin is linked to the polysaccharides in such a way that neither mild acid hydrolysis nor alkali treatment can completely release it [27].

In this investigation, residual lignins are isolated from pulps by acid hydrolysis [14]. Acid hydrolysis yields pure lignins with no residual carbohydrates present. Gellerstedt and Heuts [28] pointed out that aryl ether linkages that are sensitive to acid hydrolysis are probably cleaved during the isolation and that condensation reactions between adjacent lignin

TABLE III
ISOLATION OF RESIDUAL LIGNINS
BY ACID HYDROLYSIS

Pulp	Kappa number	Lignin isolated, g/100 g pulp	Yield, % ¹
O	12.7	0.78	41
ODEo	3.7	0.26	47
OZEo	4.0	0.36	60

1. Based on % lignin = 0.15 • κ.

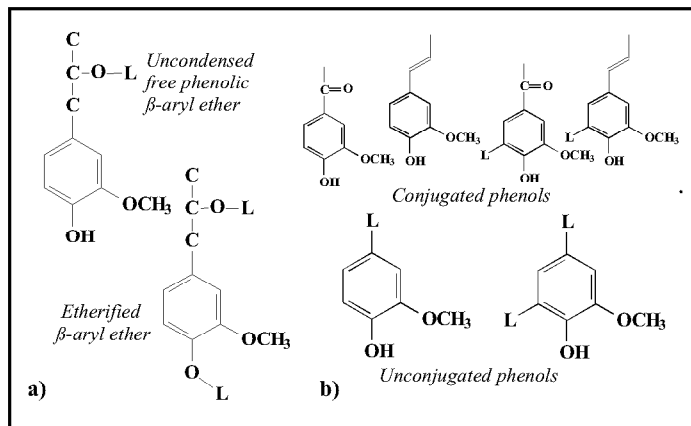


Fig. 2. a) Uncondensed β -aryl ethers and some etherified β -aryl ethers are analyzed by thioacidolysis [15,29]. b) Type of phenolic phenylpropane units analyzed by UV spectroscopy [16,17].

structures could occur. However, except for an increase in the amount of phenolic groups, the lignin structure seems to be rather unaffected by the isolation procedure [28]. As the results in Table III reveal, the yield of residual lignin isolated by acid hydrolysis is quite low. Thus, it can be speculated whether the isolated lignin is representative of all the residual lignin in the pulp. The total lignin content is estimated using the correlation

$$\% \text{ lignin} = 0.15 \cdot \kappa$$

where κ is kappa number, which is a rather approximate correlation since non-lignin structures like hexenuronic acid have been found to contribute to the kappa number [22].

Phenolic Hydroxyl Groups

During alkaline cooking, the cleavage of alkyl-aryl ether structures (β -O-4) is the main reaction causing fragmentation of the lignin macromolecule. In spruce milled wood lignin (*Picea abies*), β -O-4 linkages have been found to contribute to about 50% of the total number of interunit linkages in the lignin structure [25]. Thus, the reaction behaviour of the β -aryl ether structures is of great importance for the delignification in alkaline cooking. Thioacidolysis can be applied to analyze uncondensed β -aryl ethers in wood material [15]. Here, uncondensed β -aryl ethers are defined as phenylpropane units which are not involved in carbon-carbon or diphenylether bonds [29]. In addition to uncondensed β -aryl ethers, thioacidolysis also includes β -aryl ethers linked by an ether linkage at C4 to the α or β position of an adjacent unit in the measurement [29] (see Fig. 2). About 85 and 80% of the uncondensed β -aryl ether bonds in wood lignin have been found to be cleaved during kraft pulping of *Pinus sylvestris* [30] and *Pinus radiata* [31], respectively.

The cleaving of alkyl-aryl ether linkages during alkaline cooking leads to formation of new phenolic end groups, increasing the content of phenolic hydroxyl groups in the residual lignin. In wood lignin, the content of phenolic hydroxyl groups has been determined to be ~13 per 100 phenylpropane units for both *Picea*

per 100 phenylpropane units [17,31,33]. The dissolved lignin in black liquor contains as many as 75 phenolic hydroxyl groups per 100 phenylpropane units, which underscores the effect of the phenolic hydroxyl groups on lignin solubility and the importance of aryl ether cleavage for delignification [34]. From a reactivity point of view, the most important functionality in kraft lignin is the free phenolic group. In most chemical reactions on lignin, phenolic phenylpropane units are preferentially attacked. In addition, the phenolic group is able to ionize under alkaline conditions improving the aqueous solubility of the lignin [34]. The phenolic group is the only type of functional group, except for a small number of carboxylic acid groups, conferring water solubility on unbleached kraft lignin.

Table IV shows the effect of chlorine dioxide and ozone prebleaching on the content of β -aryl ether structures and phenolic lignins in oxygen-delignified kraft pulp. The results clearly illustrate that chlorine dioxide preferentially attacks phenolic lignin structures. Upon chlorine dioxide prebleaching of the oxygen-delignified pulp, the relative content of free phenolic hydroxyl groups in residual lignin has decreased over 80%. The ozone treatment also yielded a substantial decrease in the content of phenolic lignin structures. Thus, even though ozone is capable of degrading all types of lignin structures, it also seems to prefer to attack phenolic lignin structures when they are present. About 80% of the phenolic lignin structures in the analyzed residual lignins were of the unconjugated types (Fig. 2).

Oxidation of Lignin in Prebleaching

The predominant mode of lignin removal in bleaching is the oxidation of lignin. Acidic and carbonyl groups are formed which increase the water solubility of the lignin polymer and induce cleavage of carbon-carbon and carbon-oxygen bonds. Muconic acids form when aromatic rings are degraded and aliphatic acids form when carbonyl groups in the side chains are oxidized. Gellerstedt et al. [35] found that the carboxylic acid content in softwood kraft lignin increased from 1.0 to 1.7 and

**TABLE IV
EFFECT OF CHLORINE DIOXIDE AND OZONE PREBLEACHING ON THE CONTENT OF FREE PHENOLIC PHENYLPROPANE UNITS AND β -ARYL ETHER STRUCTURES**

	Phenolic phenylpropane units		β -O-4 structures	
	mmol/g lignin	No./100 C9 units	μ mol/g lignin	No./100 C9 units
O	1.35	25	186	3.4
ODEo	0.25	4.6	136	2.5
OZEo	0.84	15	121	2.2

abies and *Pinus sylvestris* [32,33]. After kraft pulping, the content of phenolic hydroxyl groups in residual lignins has increased to ~30 phenolic hydroxyl groups

4.9 mmol/g after oxygen delignification and ODEo prebleaching, respectively. The dissolved lignin from the bleaching stages always contained a higher amount of carboxyl groups than did residual lignin in the pulp. Native lignins contain few, if any, carboxyl groups [25]. The need for a comprehensive oxidation of the lignin to obtain lignin dissolution and a high degree of delignification in a bleaching stage is further supported by the fact that depolymerization of lignin in bleaching treatments can be rather low. In contrast to chlorine, chlorine dioxide yields a low degree of depolymerization of the kraft lignin [36], whereas almost no depolymerization occurs in ozone treatment [36,37].

The oxidizing effect of chlorine dioxide prebleaching and ozone prebleaching is illustrated by the increase in carboxyl group content in residual lignin in Table V. Although the differences were smaller than the results of Gellerstedt et al. [35], the results in Table V also show that the number of carboxyl groups in residual lignin increases upon prebleaching. At the same degree of delignification, the ozone treatment yields more carboxyl groups in the residual lignin than does chlorine dioxide. The change in elemental composition of the residual lignins also reveals the extensive oxidation which has occurred in prebleaching. The calculated double bond equivalents (DBE) values represent the degree of unsaturation and mainly reflect the presence of aromatic rings and interunit linkages connecting the phenylpropane monomer units [34]. In comparison, the elemental composition of milled wood spruce lignin (*Picea abies*) has been determined to be $C_9H_{8.05}O_{2.84}(OCH_3)_{0.95}$, DBE = 5.5 [38] and unbleached kraft pulp (*Picea abies* and *Pinus sylvestris*) $C_9H_{8.64}O_{2.99}S_{0.07}(OCH_3)_{0.73}$, DBE = 5.3.

The results in Table V also show that a substantial demethoxylation has occurred, especially in the chlorine dioxide prebleached pulp. The demethoxylation is caused by the oxidation of aromatic rings which probably reflects the low degree of unsaturation of the ODEo residual lignin.

Sun and Argyropoulos [39] found changes in residual lignin structure similar to those presented here when treating unbleached softwood (*Picea mariana*) kraft residual lignin directly with various bleaching chemicals. Chlorine dioxide treatment caused a higher reduction in free phenolic group content than did ozone, whereas ozone treatment generated more carboxyl groups in the residual lignin structure. A substantial demethoxylation oc-

TABLE V
OXIDATION OF LIGNIN IN PREBLEACHING

	Carboxyl groups		Elemental composition	DBE ¹
	mmol/g lignin	No./100 C9 units		
O	1.0	19	C ₉ H _{8.40} O _{3.11} S _{0.07} (OCH ₃) _{0.70}	5.5
ODEo	1.2	22	CH _{11.1} O _{5.00} S _{0.05} (OCH ₃) _{0.40} ²	4.3
OZEo	1.7	30	C ₉ H _{10.0} O _{4.33} S _{0.07} (OCH ₃) _{0.51}	4.7

1. Given the elemental composition (incl. OCH₃) in the form C_aH_bO_cS_d, then DBE = ½[(2a + 2) - b].
2. ¹³C NMR showed traces of carbohydrate impurities in the sample. Residual lignin was later re-isolated from the ODEo-treated pulp before analyzing for free phenolic groups and carboxyl groups.

curred upon chlorine dioxide treatment, whereas the ozone treatment caused no change in the methoxyl content.

(DZ) Versus (ZD)

Better delignification efficiency of the (DZ)Eo process versus the (ZD)Eo process may be explained by the differing ability of chlorine dioxide to degrade non-phenolic lignin structures. Whereas chlorine dioxide mainly degrades phenolic lignin structures, ozone attacks both phenolic and non-phenolic lignin structures. However, ozone also seems to prefer to attack phenolic lignin structures when they are present. Thus, the (DZ) treatment seems to be more efficient, allowing chlorine dioxide initially to degrade the phenolic lignins and leave the non-phenolic and less reactive lignin structures for the ozone treatment.

CONCLUSIONS

The use of chlorine dioxide and ozone in (DZ) and (ZD) bleaching stages yields efficient delignification in prebleaching of oxygen-delignified kraft pulp. The (DZ)Eo process was somewhat better than the (ZD)Eo process, and a synergistic delignification effect was observed by achieving better delignification than should be expected from the use of chlorine dioxide and ozone separately.

The efficient delignification obtained in (DZ)Eo and (ZD)Eo prebleaching seems reasonable because of the ability of chlorine dioxide and ozone to degrade different types of lignin structures. Whereas chlorine dioxide mainly degrades phenolic lignin structures, ozone is capable of degrading both phenolic and non-phenolic lignin structures. Both chlorine dioxide and ozone are strong oxidants, but ozone seems to be more efficient in this respect since more carboxyl groups were measured in the residual lignin at the same degree of delignification. The large number of carboxyl groups introduced into the lignin structure seems to govern the solubilization of the lignin in chlorine dioxide and ozone bleaching.

The superior delignification efficiency of (DZ)Eo prebleaching versus (ZD)Eo prebleaching may be explained by hypothesizing that the (DZ) treatment initially allows

chlorine dioxide to degrade the phenolic lignin structures, leaving the non-phenolic and less reactive lignin structures for the ozone treatment.

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REFERENCES

- LACHENAL, D., TAVERDET, M.T. and MUGUET, M., "Improvement in the Ozone Bleaching of Kraft Pulps", Proc. Intl. Pulp Bleaching Conf., Stockholm, Sweden, 2:33-43 (1991).
- DILLNER, B. and TIBBLING, P., "Use of Ozone at Medium Consistency for Fully Bleached Pulp", Proc. Intl. Pulp Bleaching Conf., Stockholm, Sweden, 2:59-74 (1991).
- CHIRAT, C. and LACHENAL, D., "Other Ways to Use Ozone in a Bleaching Sequence", *Tappi J.* 80(9):209-214 (1997).
- CHIRAT, C., LACHENAL, D., ANGELIER, R. and VIARDIN, M.T., "(DZ) and (ZD) Bleaching: Fundamentals and Application", *J. Pulp Paper Sci.* 23(6):J289-J292 (1997).
- SILTALA, M., WINBERG, K. and KESKINEN, N., "Low Cost and High Quality Softwood Pulp Production by Combining High Cooking Kappa, Extended Oxygen Delignification and Z/D Bleaching", Preprints Intl. Pulp Bleaching Conf., PAPTAC, 1:217-224 (2000).
- MUNRO, F. and GRIFFITHS, J., "Operating Experience with an Ozone-Based ECF Bleaching Sequence", Preprints Intl. Pulp Bleaching Conf., PAPTAC, 1:225-230 (2000).
- RODRIGUES, M., PEIXOTO, M.A.L. and ZOLIO, A., "Improvements in the Bleach Plants", Preprints Intl. Pulp Bleaching Conf., PAPTAC, 1:231-238 (2000).
- "Kappa Number", SCAN-C 1:00, Scandinavian Pulp, Paper and Board Testing Comm. (2000).
- "ISO Brightness", SCAN-C 11:95, Scandinavian Pulp, Paper and Board Testing Comm. (1995).
- "Viscosity in Cupriethylenediamine Solution", SCAN-C 15:88, Scandinavian Pulp, Paper and Board Testing Comm. (1988).

- GELLERSTEDT, G. and LI, J., "An HPLC Method for the Quantitative Determination of Hexenuronic Acid Groups in Chemical Pulps", *Carbohydr. Res.* 294:41-51 (1996).
- "Organically Bound Chlorine by the AOX Method", SCAN-W 9:89, Scandinavian Pulp, Paper and Board Testing Comm. (1989).
- HAPPALA, K. and STARCK, B., "Chemical Oxygen Demand (COD_{Cr}) - Results Obtained by the Closed Tube Method and the Standard Procedure are in Agreement", *Vatten* 42(4):311-315 (1986).
- GELLERSTEDT, G., PRANDA, J. and LINDFORS, E.-L., "Structural and Molecular Properties of Residual Birch Kraft Lignins", *J. Wood Chem. Technol.* 14(4):467-482 (1994).
- ROLANDO, C., MONTIES, B. and LAPIERRE, C., "Thioacidolysis" in *Methods in Lignin Chemistry* S.Y. Lin and C.W. Dence, Eds., Springer-Verlag, Berlin, Germany, 334-349 (1992).
- ZAKIS, G.F., "Functional Analysis of Lignins and their Derivatives", Transl. by R. Porozny and T.W. Joyce, TAPPI PRESS, 43-49 (1994).
- GÄRTNER, A., GELLERSTEDT, G. and TAMMINEN, T., "Determination of Phenolic Hydroxyl Groups in Residual Lignin Using a Modified UV-Method", *Nordic Pulp Paper Res. J.* 14(2):163-170 (1999).
- KATZ, S., BEATSON, R.P. and SCALLAN, A.M., "The Determination of Strong and Weak Acid Groups in Sulfite Pulps", *Svensk Papperstidn.* 87(6):R48-R53 (1984).
- HEUTS, L., "The Lignin Chemistry of OQP-bleaching - An Analytical Study", Doctoral Thesis, Dept. Pulp Paper Chem. Technol., KTH, Stockholm, Sweden (1999).
- FREUDENBERG, K. and NEISH, A.C., "Constitution and Biosynthesis of Lignin" in *Molecular Biology, Biochemistry and Biophysics*, Springer Verlag, New York, NY, USA (1968).
- TOVEN, K., "Swelling and Physical Properties of ECF/ECF Light Bleached Softwood Kraft Pulps", Preprints Intl. Pulp Bleaching Conf., PAPTAC, 2:189-192 (2000).
- LI, J., "Toward an Accurate Determination of Lignin in Chemical Pulps. The Meaning of Kappa Number as a Tool for Analysis of Oxidizable Groups", Doctoral Thesis, Dept. Pulp Paper Chem. Technol., KTH, Stockholm, Sweden (1999).
- TOVEN, K., "Ozone Based ECF Bleaching of Oxygen Delignified Kraft pulp", Doctoral Thesis, Dept. Chem. Engin., Norwegian Univ. Sci. Technol., Trondheim, Norway (2000).
- LI, J. and GELLERSTEDT, G., "The Contribution to Kappa Number from Hexenuronic Acid Groups in Xylan", *Carbohydr. Res.* 302(3-4):213-218 (1997).
- SJÖSTRÖM, E., *Wood Chemistry: Fundamentals and Applications*, 2nd ed., Academic Press, Orlando, FL, USA (1993).
- IVERSEN, T. and WANNSTRÖM, S., "Lignin-Carbohydrate Bonds in a Residual Lignin Isolated from Pine Kraft Pulp", *Holzforchung* 40(1):19-22 (1986).
- GELLERSTEDT, G. and AL-DAJANI, W.W., "On the Bleachability of Kraft Pulps", Preprints 9th Intl. Symp. Wood Pulping Chem., PAPTAC, 1:A1-1- A1-4 (1997).
- GELLERSTEDT, G. and HEUTS, L., "Changes in the Lignin Structure During a Totally Chlorine Free Bleaching Sequence", *J. Pulp Paper Sci.* 23(7):J335-J339 (1997).
- LAPIERRE, C., POLLET, B., TOLLIER, M.-T., CHABBERT, B., MONTIES, B. and ROLANDO, C., "Molecular Profiling of Lignins by Thioacidolysis: Advantages and Limitations

- Through Ten Years of Practice", Proc. 7th Intl. Symp. Wood Pulping Chem., Beijing, China, 2:818-828 (1993).
30. GELLERSTEDT, G., LINDFORS, E-L., LAPIERRE, C. and MONTIES, B., "Structural Changes in Lignin During Kraft Cooking. Part 2. Characterization by Acidolysis", *Svensk Papperstidn.* 87(9):R61-R67 (1984).
31. JOHANSSON E., SUCKLING, I.D. and EDE, R.M., "The Effect of O and OO Delignification on the Structure of Residual Lignin from *Pinus radiata* Pulp", Preprints 9th Intl. Symp. Wood Pulping Chem., PAPTAC, 1:J1-1-J1-4 (1997).
32. LAI, Y-Z., GUO, X. and SITU, W., "Estimation of Phenolic Hydroxyl Groups in Wood by Periodate Oxidation Method", *J. Wood Chem. Technol.* 10(3):365-377 (1990).
33. GELLERSTEDT, G. and LINDFORS, E-L., "Structural Changes in Lignin During Kraft Cooking. Part 4. Phenolic Hydroxyl Groups in Wood and Kraft Pulps", *Svensk Papperstidn.* 87(15):R115-R118 (1984).
34. ROBERT, D.R., BARDET, M., GELLERSTEDT, G. and LINDFORS, E-L., "Structural Changes in Lignin During Kraft Cooking. Part 3. On the Structure of Dissolved Lignins", *J. Wood Chem. Technol.* 4(3):239-263 (1984).
35. GELLERSTEDT, G., LINDFORS, E-L., PETERSON, M., SJÖHOLM, E. and ROBERT, D., "Chemical Aspects of Chlorine Dioxide as a Bleaching Agent for Chemical Pulps", Proc. 6th Intl. Symp. Wood Pulping Chem., Parkville, Victoria, Australia, 1:331-336 (1991).
36. LACHENAL D., FERNANDES, J.C. and FROMENT, P.J., "Behaviour of Residual Lignin in Kraft Pulp during Bleaching", *J. Pulp Paper Sci.* 21(5):J173-J177 (1995).
37. MÅNSSON, P. and ÖSTER, R., "Ozonation of Kraft Lignin", *Nordic Pulp Paper Res. J.* 3(2): 75- 81 (1988).
38. CHANG, H-M., COWLING, E.B., BROWN, W., ADLER, E. and MIKSCH, G.E., "Comparative Studies on Cellulolytic Enzyme Lignin and Milled Wood Lignin of Sweetgum and Spruce", *Holzforschung* 29(5):153-159 (1975).
39. SUN, Y. and ARGYROPOULOS, D.S., "A Comparison of the Reactivity and the Efficiency of Ozone, Chlorine Dioxide, Dimethyldioxirane and Hydrogen Peroxide with Residual Kraft Lignin", *Holzforschung* 50(2):175-182 (1996).
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- REFERENCE:** TOVEN, K., GELLERSTEDT, G., KLEPPE, P. and MOE, S., Use of Chlorine Dioxide and Ozone in Combination in Prebleaching, *Journal of Pulp and Paper Science*, 28(9):305-310 September 2002. Paper offered as a contribution to the Journal of Pulp and Paper Science. Not to be reproduced without permission from the Pulp and Paper Technical Association of Canada. Manuscript received November 7, 2000; revised manuscript approved for publication by the Review Panel April 18, 2002.
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PAPER II

Toven, K. and Kleppe, P.
“Low-charge chlorine dioxide prebleaching”

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Low-charge chlorine dioxide prebleaching

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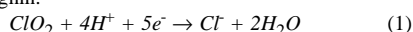
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SUMMARY

Effects of using low chlorine dioxide charge in prebleaching have been investigated. Chlorine dioxide prebleaching has been shown to give efficient delignification relative to chemical consumption when low chlorine dioxide charge is applied. An explanation may be that the reaction intermediate hypochlorous acid reacts with residual lignin and contributes to the delignification when a low chlorine dioxide charge is applied. At higher chlorine dioxide charges less reactive lignin structures are present and hypochlorous acid reacts to a larger extent inorganically and forms chlorate. In practice, a low chlorine dioxide charge is utilized in the (DZ) and (DC) stages, which both have been shown to be very efficient in terms of delignification. Sequential charging of small amounts of chlorine dioxide was not beneficial compared to traditional batch charging.

INTRODUCTION

When used to delignify pulp under acidic conditions, chlorine dioxide is reduced in a complex reaction pattern including lignin degrading reactions and inorganic reactions. Within a few minutes chlorine dioxide is consumed forming chlorous acid (HClO_2), hypochlorous acid (HOCl), chlorate (ClO_3^-), and chloride (Cl^-). Chloride and chlorate are stable ions while chlorous acid and hypochlorous acid are usually involved in further reactions. The ideal situation for maximum oxidation of lignin would be if all chlorine dioxide was reduced to chloride ion, Cl^- , with corresponding maximum oxidation of lignin.



However, during chlorine dioxide bleaching some of the chlorine dioxide is oxidized to chlorate. Chlorate is a stable ion representing a waste of oxidation power in chlorine dioxide bleaching. An old idea is to try to modify process conditions to reduce the chlorate formation and achieve a more efficient delignification. Germgård *et al.* [1] investigated the chlorate formation in chlorine dioxide prebleaching and final bleaching, and concluded that the chlorate formation is not a measure of the efficiency in chlorine dioxide bleaching. Later studies have shown that the chlorate formation is a result of complex inorganic reactions which are affected by the conditions applied [2,3,4]. In most studies on inorganic chemistry in chlorine dioxide bleaching rather high chlorine dioxide charges have been applied, corresponding to the amounts of chlorine dioxide applied in practice. In this study, effects of using low chlorine dioxide

charge in the prebleaching of oxygen delignified kraft pulp have been investigated. Low chlorine dioxide charge is utilized in both the (DC) [5] and (DZ) stages [6, 7], which both have been found very efficient in terms of delignification. In the following, the inorganic chemistry in chlorine dioxide bleaching is briefly summarized. Thereafter effects of chlorine dioxide charge on delignification efficiency and formation of inorganic chloro-compounds in chlorine dioxide prebleaching is studied. Finally, effects of utilizing low chlorine dioxide charge in (DZ) and (ZD) bleaching stages and sequential charging of low amounts of chlorine dioxide is investigated.

EXPERIMENTAL

An industrial oxygen delignified softwood (mixture of *Picea abies* and *Pinus sylvestris*) kraft pulp of kappa 12.7, brightness 36% ISO and viscosity 930 dm^3/kg was applied in the experiments. The pulp was prebleached according to the sequences DEo, (DZ)Eo, (ZD)Eo and ZEo. The D, Z, (DZ) and (ZD) stages were done at 50°C for 30 minutes in a MC mixer (CMS 2040). Pulp was acidified with sulphuric acid to pH 3 prior to Z and (ZD) stages and to pH 4 prior to D and (DZ) stages. Upon chlorine dioxide treatment the pH dropped immediately to about 2.6 and final pH were about 2.4 in both the D, (DZ) and (ZD) stages. The oxygen reinforced alkali extraction stages, Eo, were done in autoclaves at 90°C, 0.5 MPa O_2 pressure, 1% NaOH, for 60 minutes.

In order to study concentration profiles of inorganic chloro-compounds during chlorine dioxide bleaching some pulp was bleached at low consistency in a continuously stirred batch glass reactor. Chlorine dioxide charge was varied (0.5, 0.75 and 1.0% ClO_2) by varying the pulp consistency (2, 1.33 and 1%), and keeping the total liquid volume and the amount of chlorine dioxide injected constant. Throughout the treatment pulp suspension samples were taken out and filtrated on Büchner funnel. The filtrates were cooled on ice bath and analysed directly on chlorine dioxide, chlorite, chloride and chlorate concentration by ion chromatography (Dionex 4000i). As chlorine dioxide and chlorite yielded the same peak in the chromatogram, their concentrations were measured by analysing two samples in which chlorine dioxide was removed by nitrogen in one of the samples. The (ZD) stage was performed by bubbling ozone (ca. 0.4% consumed) through the pulp suspension prior to the chlorine dioxide treatment.

RESULTS AND DISCUSSION

Reaction with phenolic lignin structures

Chlorine reacts rapidly with phenolic lignin structures in the pulp. A proposed reaction pattern for the reactions between chlorine dioxide and phenolic lignin structures is summarized in Figure 1 [8]. Theoretically, chlorine dioxide can also attack non-phenolic lignin structures in

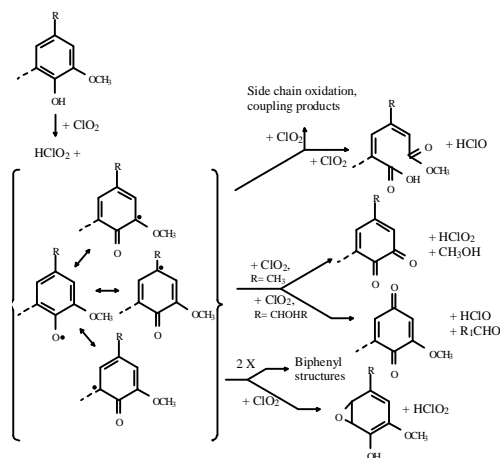
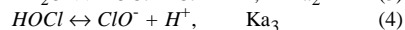
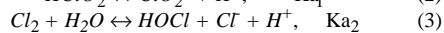
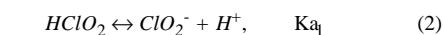


Figure 1. Chlorine dioxide reactions with phenolic rings in lignin [8].

a similar way, but at a greatly reduced rate. Initially, phenoxy radicals and chlorite (or chlorous acid, see Equation (2)) form by one electron oxidation. Coupling of phenoxy radical with additional chlorine dioxide leads to the formation of chlorous acid esters. On decomposition, the latter structures are converted to benzoquinone or corresponding catechols and muconic acid monomethyl esters or their lactone forms. Chlorite and hypochlorous acid are released in one- or two-electron oxidation reactions. Wajon *et al.* [9] studied the reaction of chlorine dioxide with a phenol model compound. The results corresponded to a reaction mechanism in which the rate-determining step is the initial removal of one electron from the substrate by chlorine dioxide forming a phenoxy radical and chlorite. Subsequently, chlorine dioxide adds to the phenoxy radical, most frequently in the *para* position, forming *p*-benzoquinone with the concomitant release of hypochlorous acid. The mechanism is in agreement with that about 0.5 mole chlorite was formed per mole chlorine dioxide reduced [9].

Acid-base equilibria

Being acids the presence and reactivity of chlorous acid and hypochlorous acid are dependent on pH. Chlorous acid is in acid equilibrium with chlorite (ClO_2^-) (2), and hypochlorous acid is in equilibrium with chlorine (Cl_2) in acidic solution (3) and hypochlorite (ClO^-) in neutral solution (4).

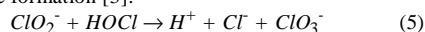


Reported equilibrium constants are $pK_{a1}=2.31$ [10], 2.0 [11], $K_{a2} = 3.94 \cdot 10^{-4}$ [12], and $pK_{a3} = 7.5$ [11], 7.3 [12]. Thus, in a typical pH range of 2.5-4 for chlorine dioxide bleaching, chlorite is the main species present.

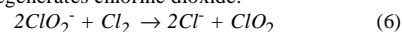
The presence of chlorine versus hypochlorous acid is dependent on both pH and chloride concentration.

Chlorate formation and chlorine dioxide regeneration

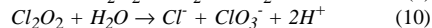
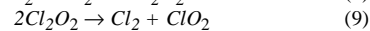
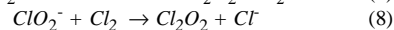
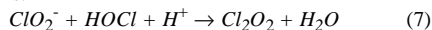
Ni *et al.* [3] captured hypochlorous acid by sulfamic acid in chlorine dioxide treatment of unbleached kraft pulp and found that only a small amount of chlorate was formed. Consequently, essentially all chlorate seems to be formed in reactions in which hypochlorous acid is involved. The reaction between chlorite and hypochlorous acid was found to account for essentially all chlorate formation [3]:



At more acidic conditions the Cl_2 -HOCl-equilibrium (3) is shifted towards chlorine, and chlorite reacts with chlorine and regenerates chlorine dioxide:



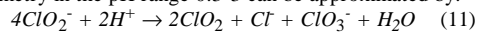
Both reactions (5) and (6) are very rapid under acidic conditions [13]. A reaction mechanism for the two reactions was proposed by Taube and Dodgen [14] and later expanded by Emmenegger and Gordon [13]. A common reaction intermediate, Cl_2O_2 , is formed in both reactions:



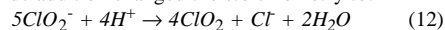
The reaction mechanism explains several experimental findings. Chlorine dioxide regeneration has been found to be favoured by acidification [13] and chloride addition [1,15], whereas chlorate formation is favoured at low pulp consistency [13]. Both acidification and chloride addition shift the HOCl/ Cl_2 -equilibrium (3) towards chlorine. Chlorine dioxide regeneration is favoured since the reaction rate for reaction (8) is much higher than for reaction (7) and the second-order reaction (9) is favoured by a high intermediate (Cl_2O_2) concentration. At low pulp consistency the first-order chlorate formation (10) is favoured over the second-order chlorine dioxide regeneration.

Acid catalysed disproportionation of chlorite

Chlorite is generated initially during chlorine dioxide bleaching and consumed throughout the treatment. As mentioned, chlorite is consumed in the rapid reaction with hypochlorous acid (7), but under acidic conditions it may also decompose and regenerate chlorine dioxide. Kieffer and Gordon [16] investigated the acid catalysed disproportionation of chlorite and found that the stoichiometry in the pH range 0.3-3 can be approximated by:



Chloride addition changed the stoichiometry to:



whereas more chlorine dioxide respective chloride and no chlorate was formed. Smits and Rooze [17] suggested another mechanism in which hypochlorous acid is generated and reacts further according to the Equations (7), (9) and (10).

Table 1. Acid catalysed disproportionation of chlorite in buffered solutions¹⁾.

$NaClO_2$ mole/l	pH	Pulp ²⁾	Time min.	Residual ClO_2^- %	Formed Cl^- ³⁾ %
0.01	-	-	30	100	2
0.01	3.5	-	60	89	5
0.008 ⁴⁾	-	+	30	60	18
0.01	-	-	30	77	13
0.01	2.5	-	60	66	22
0.008	-	+	30	45	24

¹⁾Citric acid buffer solutions ²⁾Oxygen delignified kraft pulp, 8% pulp consistency ³⁾Chloride present in the $NaClO_2$ salt applied (0.19 mole Cl^- /mole ClO_2^-) is subtracted ⁴⁾Equals 0.6% ClO_2 charge



A later study showed that reaction (11) and (13) do not occur to any noticeable extent since no detectable amount of chlorate or hypochlorous acid was formed in an acidic chlorite solution during 150 minutes at pH 2.6 and 45°C [3]. Initially chlorine dioxide and chloride were formed at a high ClO_2/Cl^- -ratio which decreased throughout the treatment. Thus, the reaction pattern appears to be more complex than suggested by Equations (11) and (12).

Irrespective of the mechanism, acid catalysed disproportionation of chlorite is a slow reaction. The maximum reaction rate occurs at pH values about the pKa of chlorous acid [18,19]. Kieffer and Gordon [10] stated that only when pH is less than 3 will more than one percent sodium chlorite decompose within a retention time of ten minutes. The decomposition of chlorite under chlorine dioxide prebleaching conditions with and without pulp present is studied in Table 1. The results in Table 1 show that about almost no chlorite is decomposed during 30 minutes at pH 3.5, while about 23% is decomposed during the same time at pH 2.5.

A subject of little attention in the literature is that chlorite may act as a bleaching agent itself under acidic conditions. Rapson [20] found that chlorite reacts with unbleached kraft pulp releasing chloride at pH values below 4. The reactivity decreased rapidly at higher pH values, and at pH values greater than 5, chlorite was stable in pulp suspensions. However, to what extent chlorite reacted with pulp itself or was decomposed by acid catalysed decomposition is unclear. The results in Table 1 show that chlorite is consumed at a higher rate when pulp is present. Thus, either the pulp catalyses the decomposition of chlorite or some chlorite reacts with the pulp itself. No chlorate was formed in any of the experiments.

AOX formation

Among others, Ni *et al.* [21] has verified that hypochlo-

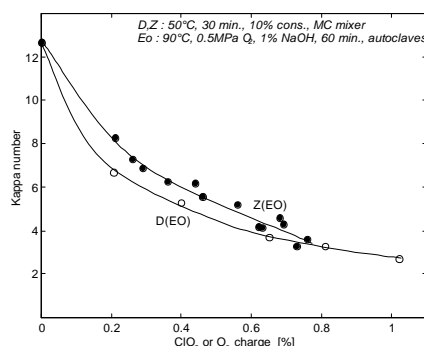


Figure 2. DEo and ZEO prebleaching of oxygen delignified kraft pulp.

rous acid is the main component forming organically bound chlorine (AOX and OCl) in chlorine dioxide delignification. By capturing hypochlorous acid by a radical scavenger, hypochlorous acid was found to attribute to at least 86% of the chloro-organic compounds formed. Wajon *et al.* [9] studied the reaction between chlorine dioxide and a phenol model compound, and found that chloro-phenols were only formed when phenol was present in excess.

Effects of chlorine dioxide charge in prebleaching

The charge in a prebleaching stage is usually determined by the desired final brightness and number of bleaching stages available. Here, it was desired to achieve a final brightness of 88% ISO in a DEoD₁ED₂ bleaching sequence of an oxygen delignified kraft pulp. Hence, a chlorine dioxide charge of 0.65% ClO_2 (kappa factor 0.13) was required in the prebleaching stage and 0.70% ClO_2 in the D₁ED₂ final bleaching stages. The delignification effect versus chemical consumption in the prebleaching is illustrated in Figure 2. By comparing the delignification efficiency of chlorine dioxide prebleaching to ozone prebleaching, chlorine dioxide appears to be a more efficient delignifying agent when small chemical charges are applied. Both the D and the Z stage were performed in a MC mixer to ensure proper mixing, and all the chlorine dioxide and ozone charged was consumed during the treatments.

The chlorate formation was measured in filtrates from the chlorine dioxide bleaching stages, and the relative amount of chlorate formed is plotted versus chlorine dioxide charge in Figure 3. The amount of chlorate formed rises with increasing chlorine dioxide charge up to about 0.65% chlorine dioxide, and seems to stabilize at a chlorate formation of about 21 mole% ClO_3^- upon further increase in chlorine dioxide charge. As previously mentioned the chlorate formation represents a waste of oxidation power during chlorine dioxide bleaching. Thus, it is tempting to assume that the apparently efficient delignification at low chlorine dioxide

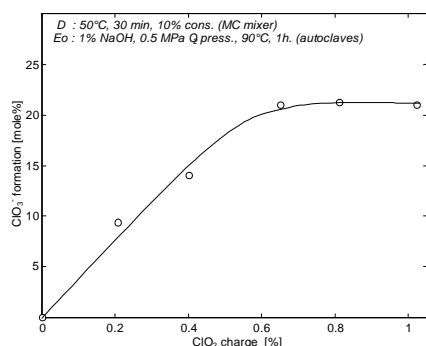


Figure 3. Chlorate formation in chlorine dioxide prebleaching of oxygen delignified kraft pulp.

charge may be related to the relatively lower chlorate formation when low chlorine dioxide charges is applied.

Besides oxidating phenolic lignin structures a significant amount of chlorine dioxide is consumed in reaction with hexenuronic acid groups in the pulp. The content of hexenuronic acid groups and phenolic lignin structures for the current pulps are given in Table 2. The content of free phenolic groups in lignin was estimated by isolating residual lignins by acid hydrolysis [22] and measuring the amount of phenolic phenolpropane groups in the residual lignins by UV spectroscopy [23]. The results in Table 2 show that about 95% of the phenolic lignin structures and 45% of the hexenuronic acid groups in the oxygen delignified kraft pulp are degraded in DEo prebleaching. The relative amount of phenolic lignin structures in residual lignin has decreased over 80%. According to the proposed mechanism between chlorine dioxide and phenolic lignin structures in Figure 1, two equivalents of chlorine dioxide should be consumed for each phenolic phenyl propane unit reacted. As the hexenuronic groups also has been found to consume two equivalents of chlorine dioxide [24], 0.59% chlorine dioxide should theoretically be consumed if all phenolic phenyl propane units and hexenuronic groups was degraded by chlorine dioxide in the present oxygen delignified pulp. The small decrease in kappa number upon chlorine dioxide charges above 0.6% in Figure 2 is probably related to limited accessibility of the remaining reactive structures in the pulp.

The effect of hypochlorous acid

According to the literature only the hypochlorous acid formed seems to determine both the AOX formation and the chlorate formation in chlorine dioxide bleaching. Hypochlorous acid also seems to be essential for the delignification in chlorine dioxide bleaching. Joncourt *et al.* [4] found that the delignification in chlorine dioxide treatment of unbleached kraft pulp was reduced by about one third when a radical scavenger (DMSO) was added. Hypochlorous acid is very reactive and has been

Table 2. Content of phenolic lignin structures and hexenuronic acid groups (HUA) in unbleached, oxygen delignified and ODEo prebleached kraft pulp.

Pulp	Kappa number	Free phenolic groups		HUA
		mmole/g. res. lign.	μmole/g. pulp ¹⁾	μmole/g. pulp
Unbleached	24.3	1.86	68	16.9
O	12.7	1.35	26	17.7
ODEo ²⁾	3.7	0.25	1.4	9.7

¹⁾ Assumed a lignin content of % lignin = $0.15 \cdot \text{Kappa number}$ and a C₉-based molecular weight for spruce lignin of 183 g/mole [26]. ²⁾ 0.65% ClO₂ charged.

generally considered to be destructive to cellulose and therefore avoided in pulp bleaching [25]. Radical scavengers like sulfamic acid and phenolic compounds have been added to prevent cellulose degradation during acidic hypochlorite bleaching. Studies by both Kolar *et al.* [2] and Ni *et al.* [3] showed that hypochlorous acid is formed in excess relative to chlorite in chlorine dioxide bleaching. Kolar *et al.* [2] captured about 50 mole% hypochlorous acid of charged chlorine dioxide (kappa factor 0.16) by DMSO during chlorine dioxide prebleaching of oxygen delignified kraft pulp. About 20-30 mole% chlorite was formed initially and consumed throughout the treatment. Kolar *et al.* [2] suggested that the excess formation of hypochlorous acid versus chlorite may be explained by chlorine dioxide being reduced to both chlorite and monochlorine monoxide, and the latter reduced by lignin to hypochlorous acid. Ni *et al.* [3] captured 58 mole% hypochlorous acid (kappa factor 0.22) and measured an initial chlorite formation of 25 mole% during chlorine dioxide delignification of unbleached kappa kraft pulp. Joncourt *et al.* [4] estimated an even higher formation of 75 mole% hypochlorous acid in chlorine dioxide delignification of unbleached kraft pulp. The estimate was made by assuming that hypochlorous acid accounts for all AOX formation and extrapolate the plot of the AOX formation versus added amount of radical scavenger (DMSO). In the study by Joncourt *et al.* [4] the chlorate formation only was reduced from 19.4% to 16.5% when a rather high amount of radical scavenger was added. According to Ni *et al.* [3] there should not be any chlorate formation if all hypochlorous acid is captured by a radical scavenger, since equation (5) was found to account for essentially all chlorate formation during chlorine dioxide bleaching.

The chlorate and chloride formation during low consistency chlorine dioxide prebleaching is shown in Figure 4. In agreement with the results in Figure 3, the chlorate formation rises with increasing chlorine dioxide charge. When 0.5% and 0.75% chlorine dioxide are applied, all chlorate seems to form within a few minutes. At 1.0% ClO₂ charge a considerable amount of the chlorate that is generated is formed more slowly throughout the treat-

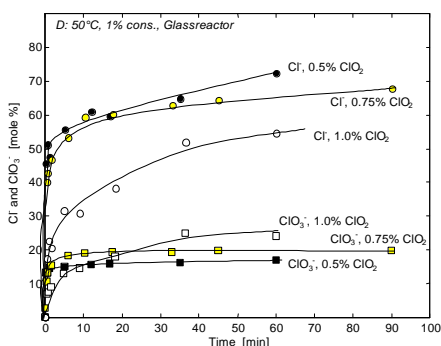


Figure 4. Chloride and chlorate formation during low consistency chlorine dioxide prebleaching.

ment.

The initial fast chlorate formation is accompanied by a rapid decrease in chlorite concentration, indicating that the chlorate is formed by the reaction between hypochlorous acid and chlorite, see Equation (5). According to the literature [2, 3, 4] hypochlorous acid is formed in excess to chlorite. Provided the stoichiometry of Equation (5) applies hypochlorous acid should remain even if all the generated chlorite reacted with hypochlorous acid. Hypochlorous acid reacts also with lignin. The increased chlorate formation at high chlorine dioxide charge may be explained by that less residual lignin is present when hypochlorous acid is generated. The chlorine dioxide has oxidized the most of the reactive lignin structures before hypochlorous acid is formed, and hypochlorous acid probably reacts to a larger extent inorganically and forms chlorate. At 1.0% chlorine dioxide charge, a major portion of the formed chlorate was generated rather slowly throughout the treatment. Considering that both the reaction between hypochlorous acid and chlorite is fast and that the hypochlorous acid is formed in excess to chlorite, it is possible that chlorate is formed from hypochlorous by another slow reaction when low amount of residual lignin is present.

The importance of residual lignin content for the chlorate formation is also supported by the results of Germgård *et al.* [1]. In prebleaching of oxygen delignified kraft pulp 5-20% of the consumed chlorine dioxide was converted to chlorate, whereas 25-50% chlorate was formed in chlorine dioxide final bleaching. In final bleaching the chlorate formation increased linearly with consumed chlorine dioxide, corresponding to a constant percentage of charged chlorine dioxide. According to the theory presented, these results should imply that the residual lignin content in prebleached pulps are so low that the hypochlorous acid formed in final bleaching generates chlorate independently of the chlorine diox-

Table 3. Balance of inorganic and organic chloro-compounds formed in the DEo, (DZ)Eo and (ZD)Eo prebleaching of oxygen delignified kraft pulp

	DEo		(DZ)Eo		(ZD)Eo	
	kg/t	%	kg/t	%	kg/t	%
<i>Kappa</i>	3.7		3.1		3.4	
ClO ₂ charge	3.61 ¹⁾	100	1.78	100	1.83	100
Cl ⁻	2.22	61	1.20	68	1.13	62
ClO ₃ ⁻	0.76	21	0.23	13	0.53	29
AOX, 1 st stg.	0.32	9	0.13	7	0.17	9
2 nd stg.	0.06	2	0.02	1	0.03	2
OCl	0.13	4	0.14	8	0.14	8
SUM	3.48	96	1.73	97	2.01	110

ide charge applied.

(DZ) and (ZD) stages

An application of low chlorine dioxide charge is in the (DZ) and (ZD) bleaching stages. Here, chlorine dioxide and ozone is injected subsequent to one another allowing the first injected chemical to be consumed before the other is injected. It has been shown that (DZ)Eo prebleaching of oxygen delignified kraft pulp is more efficient in terms of delignification than (ZD)Eo prebleaching [27]. A synergetic delignification effect was observed in the (DZ) treatment giving a higher delignification than would be expected from the effect of chlorine dioxide and ozone separately. A balance of inorganic and organic chloro-compounds formed in DEo, (DZ)Eo and (ZD)Eo prebleaching is compared in Table 3. The most efficient delignification and the lowest chlorate formation were obtained in the (DZ)Eo prebleaching sequence. Less chlorate formation in the (DZ) stage compared to the D stage is in agreement with the results in Figure 3 and related to the lower chlorine dioxide charge applied. The higher chlorate formation in the (ZD) stage versus the (DZ) may be related to less reactive lignin structures being present during the chlorine dioxide treatment in the (ZD) stage. Both ozone and chlorine dioxide have oxidized lignin in the (DZ) stage before the hypochlorous acid is generated, and hypochlorous acid probably reacts to a larger extent inorganically and forms chlorate.

The chlorate and chloride formation during low consistency D and (ZD) treatments are shown in Figure 5. Since the chlorate and chloride concentrations remain unchanged upon ozonation when all chlorine dioxide and chlorite are consumed, the formation of inorganic chloro-compounds in the D and (DZ) stage are equal at the same chlorine dioxide charge. In agreement with the previous results, Figure 5 shows that the (DZ) process yields less chlorate formation than the (ZD) treatment. Like the chlorate formation at high chlorine dioxide charge (1.0%) in Figure 4, a significant portion of the chlorate formed in the (ZD) treatment is generated rather slowly throughout the treatment

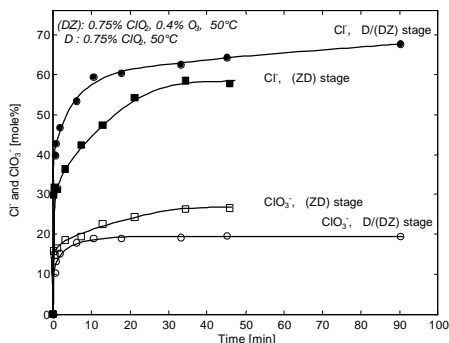


Figure 5. Chloride and chlorate formation during low consistency D/(DZ) and (ZD) treatment of oxygen delignified kraft pulp.

Sequential charging

The effect of sequential charging was tested by chlorine dioxide prebleaching experiments performed in plastic bags at 8% pulp consistency in buffered solutions at pH 2.5 and 3.5. The retention time in between the charges was varied in order to investigate the possible effects of residual chlorite. The results for the experiments performed at pH 3.5 are given in Table 4. Neither the chlorine dioxide bleaching experiments at pH 3.5 nor pH 2.5 showed any typical difference in chlorate formation or brightness development between sequential and batch charging. The measured concentrations of chlorate and chloride were systematically lower compared to earlier experiments. Some experiments were repeated without buffer addition but the buffer did not seem to influence the results to any noticeable extent.

Previously it was suggested that the lower chlorate formation and increased delignification of the (DZ) treatment versus the (ZD) treatment could be explained by that the chlorine dioxide treatment was more efficient in the (DZ) stage than the (ZD) stage. The results indicated that hypochlorous acid to a larger extent reacts with lignin and contributes to delignification in the (DZ) stage, whereas it reacts inorganically and forms chlorate

rate in the (ZD) stage when less reactive residual lignin structures are present. In relation to these results it seems reasonable that splitting the chlorine dioxide charge in a (D₁..D_i)Eo process is not beneficial compared to a DEo process. Like the chlorine dioxide treatment in the (DZ) stage, the first chlorine dioxide treatments in the (D₁..D_i) stage probably work efficiently, but as the number of reactive lignin structures in the pulp decreases the latter chlorine dioxide treatments probably do not. Recently, Lachenal and Chirat [28] also investigated effects of splitting the chlorine dioxide charge in prebleaching. In agreement with the previous results, splitting the chlorine dioxide charge in a DDDE process did not lead to any improvement compared to a DE process. Lachenal and Chirat [28] suggested that chlorine dioxide reacts with oxidized lignin which has not yet gone into solution, since no improvement was obtained when the pulp was washed between the chlorine dioxide treatments. Sequential charging of low amounts of chlorine dioxide is only beneficial when the pulp is pH adjusted or treated with alkaline between the charges [4, 28].

Similarities between (DC)/(CD) and (DZ)/(ZD) stages

Quite similar to the superiority of (DZ)Eo prebleaching versus (ZD)Eo prebleaching, the delignification efficiency of (DC)E prebleaching has been shown to be superior to (CD)E prebleaching [5, 29, 30]. The chlorate formation has also been reported to be lower for the (DC) stage than the (CD) stage [29]. Ni *et al.* [31] explained the difference in chlorate formation by chlorite decomposing and regenerating chlorine dioxide as in Equation (12) in the (DC) stage, whereas chlorate formation takes place by Equation (5) in the (CD) treatment since hypochlorous acid from the C-treatment is present when chlorite is generated in the latter D-treatment. However, the explanation does not seem likely when considering that the acid catalysed decomposition of chlorite is a very slow reaction, and that sufficient amounts of hypochlorous acid should be present for reacting with chlorite in both (CD) and (DC) stages since hypochlorous acid is formed in excess to chlorite in chlorine dioxide bleaching [2, 3, 4]. Thus, extra hypochlorous acid from the initial C-treatment should

Table 4. Effect of sequential charging in buffered¹⁾ (pH 3.5) chlorine dioxide prebleaching of oxygen delignified kraft pulp²⁾.

ClO ₂ charge, %	ClO ₃ ⁻ , % of charged ClO ₂					Cl ⁻ , % of charged ClO ₂					Brightness, %ISO				
	0.2	0.4	0.6	0.8	1.0	0.2	0.4	0.6	0.8	1.0	0.2	0.4	0.6	0.8	1.0
Batch	4.5	7.2	9.9	11.7	11.3	47	53	49	45	45	44.9	46.8	48.3	50.7	52.3
Seq., 30 s. ³⁾	4.2	8.5	10.8	11.3	11.0	49	58	54	49	44	-	44.7	47	49.9	52.3
Seq., 5 min.	-	8.0	8.1	10.0	10.1	-	58	48	57	44	-	45.1	48.5	53.1	52.3
Seq., 30 min.	-	9.0	9	-	-	-	83	50	-	-	-	45.8	51.1	-	-
Seq., 30 min. ⁴⁾	-	11	13	-	-	-	62	57	-	-	-	45.1	49.8	-	-

¹⁾Citric acid buffer ²⁾Starting pulp: Kappa number 12.7, 36% ISO brightness. D-stage: 50°C, 8% consistency, water bath ³⁾Sequential charging was done by charging x times of 0.2% ClO₂. Intervals between the charges were 30 seconds, 5 minutes and 30 minutes. ⁴⁾No buffer applied. Start pH was 4.0 and final pH 2.4.

not influence on the chlorate formation in the latter D treatment since, according to the stoichiometry of Equation (5), only one equivalent of hypochlorous acid is consumed in the reaction with chlorite. Another explanation could be that the difference in chlorate formation of the (DC) and (CD) stages is related to different amount of reactive lignin structures present during the chlorine dioxide treatment. In the (CD) treatment less unoxidized residual lignin is present since chlorine has oxidized lignin prior to the chlorine dioxide treatment. Thus, in the absence of reactive lignin structures the hypochlorous acid generated in the latter chlorine dioxide treatment probably reacts to a larger extent inorganically and forms chlorate. In the (DC) treatment more residual lignin is present when hypochlorous acid is generated, and it may react with residual lignin and contribute to delignification.

The superior delignification efficiency of (DZ)Eo prebleaching versus (ZD)Eo prebleaching can also be explained by the ability of chlorine dioxide and ozone to degrade different types of lignin structures [32]. Chlorine dioxide mainly degrades phenolic types of lignin structure whereas ozone is capable of degrading both phenolic and non-phenolic lignin structures. In the (DZ) stage, chlorine dioxide is allowed to attack phenolic lignin structures initially and the non-phenolic and less reactive lignin structures are left for the ozone treatment [32]. Since chlorine, like ozone, is a stronger oxidant than chlorine dioxide, the same argumentation should apply for the superiority of the (DC) treatment versus the (CD) treatment.

CONCLUSIONS

Chlorine dioxide prebleaching has been shown to give efficient delignification relative to chemical consumption when a low amount of chlorine dioxide is applied. The effect may be explained by that the reaction intermediate hypochlorous acid reacts with residual lignin and contributes to delignification when low chlorine dioxide charge is applied. At higher chlorine dioxide charges less reactive lignin structures are present and hypochlorous acid reacts to a larger extent inorganically and forms chlorate.

In practice, a low chlorine dioxide charge is used in the (DZ) and (DC) bleaching stages, which both have been shown to be very efficient in terms of delignification. Sequential charging of small amounts of chlorine dioxide was not beneficial compared to traditional batch charging.

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LITERATURE

1. Germgård, U., Teder, A. and Tormund, D. "Chlorate formation during chlorine dioxide bleaching of softwood kraft pulp", *Pap. Puu*, 61(3):127-133 (1981)
2. Kolar, J.J., Lindgren, B.O. and Pettersson, B. "Chemical reactions in chlorine dioxide stages of pulp bleaching", *Wood Sci. Technol.* 17:117-128 (1983)
3. Ni, Y., Kubes, G. J. and van Heiningen, A.R.P., "Rate processes of chlorine species distribution during chlorine dioxide prebleaching of kraft pulp", *Nord. Pulp and Paper Res. J.* 7(4):200-204 (1992)
4. Joncourt, M. J., Froment, P., Lachenal, D. and Chirat, C., "Reduction of the formation of AOX during chlorine dioxide bleaching", *Tappi Pulping Conf.*, Chicago, 1:149-152 (1995)
5. Jack, W. Q. and Feller, L. D., "Lower-cost pulp bleaching with chlorine dioxide as the first treatment", *Pulp Pap. Mag. Can.* 68(9):T461-T471 (1967)
6. Dillner, B. and Tibbling, P., "Use of ozone at medium consistency for fully bleached pulp", *Int. Pulp Bleaching Conf.*, Stockholm, 2:59-74 (1991)
7. Lachenal, D., Taverdet, M.T. and Muguet, M., "Improvement in the ozone bleaching of kraft pulps", *Int. Pulp Bleaching Conf.*, Stockholm, 2:33-43 (1991)
8. Dence, C.W. and Reeve, W., "Pulp Bleaching - Principles and Practice", TAPPI press, Atlanta, Georgia, chap. III 3, 134 (1996)
9. Wajon, J. E., Rosenblatt, D. H. and Burrows, E.P., "Oxidation of phenol and hydroquinone by chlorine dioxide", *Env. Sci. Technol.* 16(7):396-402 (1982)
10. Kieffer, R. G. and Gordon, G., "Disproportion of chlorous acid. II Kinetics", *Inorg. Chem.* 7(2):239-244 (1968)
11. Joncourt, M.J., Mortha, G. and Lachenal, D., "Investigations on the effect of additives during ClO₂ bleaching", *9th Int. Symp. on Wood and Pulp- ing Chem.*, 1:J6-1-J6-5 (1997)
12. Dence, C. W. and Annergren, G. E., "Chlorination" in "The bleaching of pulp" (Ed. Singh, R. P.), Tappi Press, 30 (1979)
13. Emmenegger, F. and Gordon, G., "The rapid reaction between sodium chlorite and chlorine", *Inorg. Chem.* 6(3):633-635 (1967)
14. Taube, H. and Godgen, H., "Applications of radioactive chlorine to the study of the mechanisms of reactions involving changes in the oxidation state of chlorine", *Am. Chem. Soc. J.* 71:330 (1949)
15. Reeve, D. W. and Weishar, K. M., "Chlorine dioxide delignification - process variables", *Tappi J.* 74(6):164-167 (1991)

16. Kieffer, R. G. and Gordon, G., "Disproportion of chlorous acid. I. Stoichiometry", *Inorg. Chem.* 7(2):235-239 (1968)
17. Schmitz, G. and Rooze, H. "Mécanisme des réactions du chlorite et du dioxyde de chlore. 1. Stoechiométrie des réactions du chlorite et cinétique en présence d'ortho-tolidine", *Can. J. Chem.* 58(8):1177-1187 (1981)
18. Hong, C. C. and Rapson, W. H., "Kinetics of disproportionation of chlorous acid", *Can J. Chem.* 46:2053-2060 (1968)
19. Gordon, G., Keiffer, R. G. and Rosenblatt, D. H., "The chemistry of chlorine dioxide", *Progress in inorg. chem.* 115:200-286 (1972)
20. Rapson, W., "The role of pH in bleaching pulp", *Tappi J.* 39(5):284-295 (1956)
21. Ni, Y., Kubes, G. J. and van Heiningen, A.R.P., "Mechanism of formation of chloro-organics during chlorine dioxide prebleaching of kraft pulp", *Nordic Pulp Paper Res. J.* 8(4):350-351 (1993)
22. Gellerstedt, G., Pranda J. and Lindfors, E-L., "Structural and molecular properties of residual birch kraft lignins", *J. Wood Chem. Technol.* 14(4):467-482 (1994)
23. Gellerstedt, G. and Li, J., "An HPLC method for the quantitative determination of hexenuronic acid groups in chemical pulps", *Carbohydr. Res.* 294:41-51 (1996)
24. Vourinen, T., Buchert, A., Teleman, A., Tenkanen, M., Fagerström, P., "Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps", *Int. Pulp Bleaching Conf.*, Atlanta, 1:43-51 (1996)
25. Larson, L.E. in Handbook of pulp and paper technology, 2nd edn. Reinhold, New York, 272 (1970)
26. Freudenberg, K. and Neish, A.C., "Constitution and biosynthesis of lignin", Springer Verlag, New York (1968)
27. Toven, K., "Ozone based ECF bleaching of oxygen delignified kraft pulp", *Int. Pulp Bleaching Conf.*, Helsinki, 2:377-382 (1998)
28. Lachenal, D. and Chirat, C., "Improvement of ClO₂ delignification in ECF bleaching", *Int. Pulp Bleaching Conf.*, Halifax, 1:159-162 (2000)
29. Reeve, D. W. and Rapson, W. H., "Developments in chlorine dioxide bleaching", *Tappi Pulping Conf.*, Atlanta, 403-409 (1980)
30. Germgård, U. and Karlsson, R.-M., "Bleaching of birch kraft pulp with different fractions of chlorine dioxide in the prebleaching", *Nord. Pulp and Paper Res. J.* 3(4):166-170 (1988)
31. Ni, Y., Kubes, G.J. and van Heiningen, A.R.P., "Mechanism of chlorate formation during bleaching of kraft pulp with chlorine dioxide", *J. Pulp Paper Sci.* 19(1):J1-J6 (1993).
32. Toven, K., Gellerstedt, G., Kleppe, P. and Moe, S., "The use of chlorine dioxide and ozone in

combination in prebleaching", Submitted for *Journal of Pulp and Paper Science*

PAPER III

Toven, K.

“Swelling and physical properties of ECF light bleached softwood kraft pulps”

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Physical and swelling properties of ozone based ECF bleached softwood kraft pulps

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SUMMARY

Physical properties of DEoQ(PO), (DZ)EoD₁ED₂ and (DZ)EoQ(PO) bleached oxygen delignified softwood kraft pulps were compared to the same properties of a DEoD₁ED₂ bleached ECF reference pulp. Both (DZ)Eo prebleaching and pressurized peroxide final bleaching reduced the AOX formation considerably, however the Q(PO) final bleaching also increased the COD effluent load. The tear strength was maintained, but the (DZ)Eo prebleaching seems to have a slight negative effect on fibre strength as indicated by lower wet zero span strength of beaten (DZ)EoD₁ED₂ and (DZ)EoQ(PO) bleached pulps. Pressurized peroxide final bleaching yielded pulps with higher fibre charge than chlorine dioxide final bleaching. Compared to the D₁ED₂ final bleached pulps, the increased number of charged groups in DEoQ(PO) and (DZ)EoQ(PO) bleached pulps seemed to promote increased fibre swelling of both unbeaten and highly beaten pulps. The more swollen unbeaten Q(PO) final bleached pulps formed denser paper sheets with higher tensile strength and wet zero span strength. A highly charged and swollen pulp seems to be advantageous with respect to beatability when the pulp is beaten to a target tensile strength.

INTRODUCTION

The interest for totally chlorine free (TCF) bleaching chemicals as a replacement for chlorine dioxide has accelerated in the 1990s due to both market demand and a desire for further reduce in discharge of chlorinated compounds. An important reason for the limited use of TCF chemicals is their low selectivity towards lignin, which cause reduced pulp viscosity and fibre strength [1]. The paper properties is the subject of this paper, and the TCF chemicals ozone and hydrogen peroxide have been applied in two rather recently developed bleaching concepts which according to the literature appear to be beneficial from both an environmental and cost-efficient view relative to traditional ECF bleaching. The bleaching sequences are termed ECF light due to the reduced consumption of chlorine dioxide.

Studies have shown that ozone with advantage can be used in combination with chlorine dioxide in (DZ) and (ZD) prebleaching stages [2,3]. The formation of chloro-organic compounds is reduced, and the viscosity of the pulp is maintained when the ozone charge is kept low [2]. In addition, the concept is efficient in terms of both delignification and chemical savings. Ozone can be charged both prior to and after the chlorine dioxide addi-

tion in (ZD) and (DZ) stages respectively [4]. However, relative to chemical charges the (DZ) treatment has been shown to give the most efficient delignification of oxygen delignified kraft pulp [5]. The (DZ) treatment gave a synergetic delignification effect giving better delignification than expected from the effect of chlorine dioxide and ozone separately. From a practical point of view, the (DZ) and (ZD) bleaching stages are interesting since the ozone treatment quite easily can be implemented in an existing bleach plant without investing in new expensive and space demanding bleaching towers. Pressurized peroxide bleaching has been shown to be a possible alternative to chlorine dioxide final bleaching. Pressurized peroxide bleaching, (PO), means oxygen pressurized hydrogen peroxide treatment at high temperature, and has been shown to be beneficial in several aspects compared to traditional atmospherical hydrogen peroxide bleaching [6]. The reaction time is reduced considerably, the amount of hydrogen peroxide needed to achieve a certain brightness is reduced, maximum obtainable brightness level is raised and higher pulp viscosity is obtained [6]. The objective of this study is to compare physical paper properties of various ECF light bleached oxygen delignified softwood kraft pulps to a traditional DEoD₁ED₂ ECF reference pulp. The ECF light bleaching sequences applied were (DZ)EoD₁ED₂, (DZ)EoQ(PO) and DEoQ(PO).

EXPERIMENTAL

An industrial oxygen delignified softwood (70:30 mixture of *Picea abies* and *Pinus sylvestris*) kraft pulp of kappa 12.7, brightness 36% ISO and viscosity 930 dm³/kg was applied in the experiments. After laboratory washing, the pulp was pH adjusted by H₂SO₄ to pH 4, and bleached according to the sequences DEoD₁ED₂, DEoQ(PO), (DZ)EoD₁ED₂ and (DZ)EoQ(PO). The initial D or (DZ) stage was performed at 50°C for 40 minutes in a high shear medium consistency (MC) mixer. During injection of chemicals the pulps were fluidized by high intensity mixing, and the chemical charges were 0.65% ClO₂ and 0.33% ClO₂ + 0.36% O₃ in the D and (DZ) stages respectively. In the (DZ) stage, ozone was injected after 30 minutes, when all chlorine dioxide and chlorite should be consumed. The oxygen reinforced alkali extraction stage, Eo, was performed in autoclaves for one hour at 90°C, applying 1% NaOH charge and 0.5 MPa oxygen pressure. The batches of DEo and (DZ)Eo prebleached pulps were divided in two portions for D₁ED₂ and Q(PO) final bleaching.

Pulps were acidified by H₂SO₄ to pH 6 prior to the D₁ stage. D₁, E and D₂ stages were performed in a water bath at 70°C employing retention times of two, one and three hours respectively. Chemical charges were 0.5% ClO₂ in the D₁ stage, 0.4% NaOH in the E stage and 0.2% ClO₂ in the D₂ stage. Chelation, Q, was done in plastic bags in a water bath for one hour at pH 5.5 and 70°C, charging 0.3% EDTA. Pressurized peroxide stage,

(PO), was performed by charging 0.3% MgSO₄, 0.2% DTPA, 1.6% NaOH and 4.0% H₂O₂ and keeping the pulp in plastic bags within rotating autoclaves at 105°C, 0.5 MPa oxygen pressure for two hours. All treatments were done at 10% pulp consistency, and the pulps were washed with hot distilled water in between bleaching stages and after the bleaching sequence.

Pulps were analysed for kappa number (SCAN C 1:77), brightness (SCAN C 11:95), viscosity (SCAN C 15:88), tear strength (SCAN P 11:96), tensile strength (SCAN P 16:76), water retention value (SCAN C-102XE), Scott bond strength, AOX and OCl in pulp: SCAN W 9:89. The fibre charge was analysed by polyelectrolyte adsorption [8] on pulps converted to Na-form [9]. 3.6-ionene (polybrene) with a molecular weight of about 8·10³ g/mole and charge density of 5.12·10⁻³ mole eq/g. was applied without further purification. Hexenuronic acid content was determined by UV spectroscopy [10]. The applied method correlates well with other methods, but somewhat higher values are obtained [11]. Carboxylic acid content in lignin was estimated by analysing carboxylic acid content in residual lignins by conductometric titration [12] and assuming that total lignin content in the pulps was given by % lignin = 0.15·Kappa number. Residual lignins were isolated from the pulps by acidolysis [13].

RESULTS AND DISCUSSION

Bleaching sequences

The pulp and effluent characteristics of final bleached pulps are given in Table 1. Chemical charges in final bleaching were chosen in order to achieve a final brightness target of 88% ISO. Compared to the ECF reference, the total AOX formation was reduced by 25% in the (DZ)EoD₁ED₂ sequence, 30% in the DEoQ(PO) sequence and 64% in the (DZ)EoQ(PO) sequence. The D₁ED₂ final bleaching accounted for 38% and 58% of the total AOX formation in the DEoD₁ED₂ and (DZ)EoD₁ED₂ sequence respectively. The (DZ)Eo prebleaching seemed to yield a small reduction in COD effluent load, whereas a substantial increase in dissolution of organic material took place when Q(PO) final bleaching was applied. The dissolution of organic material represents both an increased effluent load and a yield loss. Even though a rather low ozone charge of 0.36% has been applied here, the results in Table 1 show a significant lower viscosity for the (DZ)Eo prebleached pulp compared to the reference pulp. As mentioned, ozone may oxidize polysaccharide chains and form carbonyl and carboxylic structures within the polysaccharide chains. These groups may cause chain cleavage and loss in pulp viscosity upon alkali treatment. However, even though the pulp viscosity of

Table 1. Characteristics of pulps and effluents

	ECF reference	Ozone added	Peroxide added	Ozone + peroxide added
<i>Prebleaching:</i>	DEo	(DZ)Eo	DEo	(DZ)Eo
ClO ₂ , kg Cl/t	3.61	1.84	3.61	1.84
AOX, kg/t	0.32	0.17	0.32	0.17
OCl, kg/t	0.08	0.07	0.08	0.07
Kappa number	3.7	3.1	3.7	3.1
Viscosity, dm ³ /kg	840	730	840	730
<i>Final bleaching:</i>	D₁ED₂	D₁ED₂	Q(PO)	Q(PO)
ClO ₂ , kg Cl/t	3.89	3.89	-	-
AOX, kg/t	0.21	0.23	0.05	0.02
COD, kg/t	8.9	7.7	17.3	18.5
OCl, kg/t	0.08	0.08	0.09	0.03
Viscosity, dm ³ /kg	750	750	770	730
Brightn., %ISO	88.4	87.5	87.5	87.7
Sum ClO ₂ , kg Cl/t	7.5	5.7	3.6	1.8
Sum AOX, kg/t	0.53	0.40	0.37	0.19
Sum COD, kg/t	28.9	26.4	37.3	37.2

(DZ)Eo prebleached pulps is significant lower than the DEo prebleached pulp, the results in Table 1 also show that the difference in pulp viscosity decreases considerably after final bleaching.

Physical properties of unbeaten pulps

The paper properties of unbeaten pulps are given in Table 2. Generally, differences in paper properties were small, and the tear index and fibre-fibre strength (Scott Bond) were about equal for all pulps. However, the Q(PO) the final bleached pulps seemed to be somewhat more swollen than the D₁ED₂ final bleached pulps, and somewhat denser paper sheets with higher tensile strength and wet zero span strength were formed.

Similar results were obtained by Laine and Stenius [14] when studying effects of fibre charge on paper properties of industrially bleached kraft pulps. Increased fibre charge was found to promote increased fibre swelling and flexibility of the fibres. Increased fibre flexibility further promoted fibre conformability and yielded more fibre-fibre contacts. As the fibres remain in contact and form bonds at their intersections upon drying [15] improved fibre flexibility yields denser sheets with higher relative bonded area. The fibre-fibre strength (Scott bond) did not vary much for the pulps investigated. As the differences in paper properties of unbeaten pulps in Table 2 can be explained by differences in

Table 2. Paper properties of unbeaten ECF bleached kraft pulps.

	DEoD ₁ ED ₂	(DZ)EoD ₁ ED ₂	DEoQ(PO)	(DZ)EoQ(PO)
Tear index, mNm ² /g	20.5 ± 0.7	20.7 ± 0.8	20.7 ± 0.8	20.7 ± 0.7
Tensile index, Nm/g	25.9 ± 0.9	25.2 ± 1.1	26.8 ± 1.1	27.8 ± 1.2
Density, kg/m ³	606 ± 9	609 ± 8	619 ± 9	623 ± 10
Wet zero span, Nm/g	93 ± 5	92 ± 4	98 ± 5	93 ± 4
Scott Bond, J/m ²	100 ± 12	109 ± 10	109 ± 12	109 ± 10
WRV, g/g	1.14	1.17	1.22	1.21
Viscosity, dm ³ /kg	750	790	770	730

Errors are estimated by the standard deviation of replicates

Table 3. Development of charged groups in kraft pulp in bleaching

Pulp	Fibre charge $\mu\text{mole/g}$	Hexenuronic acid $\mu\text{mole/g}$	Carboxylic groups in lignin $\mu\text{mole/g}$
Unbleached	123	16.9	25
O	113	17.8	20
ODEo	86	9.7	7
O(DZ)Eo	74	7.9	-
OZEo	76	6.7	10
ODEoD ₁ ED ₂	51	0.3	-
O(DZ)EoD ₁ ED ₂	49	0.3	-
ODEoQ(PO)	73	10.3	-
O(DZ)EoQ(PO)	68	7.0	-

swelling it was decided to further investigate the swelling properties of the pulps.

Effect of bleaching on fibre charge

During kraft cooking a significant number of the initial 4-O-methyl glucuronic acid side groups of xylan is converted to hexenuronic acid groups. Sjöström [16] reported that the content of methyl glucuronic acid groups in *Picea abies* and *Pinus Sylvestris* were 70 and 80 $\mu\text{mole/g}$ respectively. Hexenuronic acid is a major contributor to the fibre charge in unbleached kraft pulp, and the variation in fibre charge of ECF and TCF bleached pulps can be largely explained in terms of selective reactions of hexenuronic groups with various bleaching chemicals [7, 17].

The development of total amount of charged groups in the pulps, hexenuronic acid groups and acid groups attached to lignin in the bleaching sequences applied in this study are shown in Table 3. The results indicate that the hexenuronic acid groups and charged groups attached to the lignin structure account for about 15% and 20% of the total number of charged groups in the unbleached kraft pulp respectively. However, the total number of charged groups determined by polyelectrolyte titration is probably somewhat overestimated. When comparing the polyelectrolyte titration method with conductometric titration [12], polyelectrolyte titration gave about 15-20 $\mu\text{mole/g}$ higher values for the fibre charge for four different chemical pulps of different charge levels. Even though the total number of charged groups probably is somewhat overestimated, the hexenuronic acid groups and acid groups attached to lignin account for only about 40% of the total number of charged groups in the pulps. Some of the remaining carboxyl groups may be 4-O-methyl glucuronic acid groups which were not converted to hexenuronic acid groups in the cook.

In agreement with the literature [7, 17], the results in Table 3 show that chlorine dioxide and ozone reduces the number of charged groups in the pulp, whereas the amount of charged groups in the pulps remain about

Table 4. Effect of fibre charge on fibre swelling

	DEo D ₁ ED ₂	(DZ)Eo D ₁ ED ₂	DEo Q(PO)	(DZ)Eo Q(PO)
Fibre charge, $\mu\text{mole/g}$	51	49	73	68
WRV, g/g ¹⁾	1.14± 0.01	1.17± 0.01	1.22± 0.01	1.21± 0.01
WRV-WRV _{NaCl} , g/g ²⁾	0.01	0.02	0.04	0.06
Na content, ppm ³⁾	153	140	137	198

¹⁾Rewetted sheets ²⁾WRV in water - WRV in 0.1 M NaCl
³⁾100 ppm Na = 4.4 $\mu\text{mole Na/g}$

constant upon hydrogen peroxide and oxygen treatment. At the same degree of delignification, ozone prebleaching yielded somewhat more efficient degradation of hexenuronic acid groups than chlorine dioxide did. After chlorine dioxide final bleaching only traces of hexenuronic acid remained in the pulp, whereas a significant amount of hexenuronic acid groups remained in pressurized peroxide final bleached pulps. As the variations in the total number of charged groups in the pulps resemble the variations in the hexenuronic acid group content, the total number of charged groups was also significantly higher for the pressurized peroxide final bleached pulps than the chlorine dioxide final bleached pulps.

Effect of charged groups on swelling

Generally swelling of cellulosic fibres is governed by the swelling of polysaccharides, and the osmotic pressure created within the fibres due to the dissociation of small ions from charged groups. The swelling is restricted by the ability of the fibre wall to resist the swelling pressure. Upon drying, swelling is reduced due to increased interfibrillar bonding termed hornification. Charged groups promote the swelling of rewetted fibres both by increasing the osmotic pressure and by reducing the degree of hornification upon drying [18, 14]. According to Salmén and Berthold [19] ionic changes mainly affect the surface water of the fibres.

Swelling properties of the various ECF bleached pulps are given in Table 4. Q(PO) final bleached pulps are slightly more swollen than the D₁ED₂ final bleached pulps. Although the differences in WRV in Table 4 seem small they are believed to be significant. The errors in WRV are estimated by the standard deviation between replicates, and the obtained errors correspond well to the average standard deviation between replicates reported in the method (SCAN C 62:00). The positive effect of charged groups on swelling is illustrated by the difference in water retention value of fibres in water respective salt solution, WRV-WRV_{0.1M NaCl}. According to the Donnan Theory [20] salt addition will reduce the difference in total ion concentration between the cell wall and external medium, and reduce the osmotic swelling pressure created by the charged groups. The results in Table 4 indicate that the improved swelling of the Q(PO) final bleached pulps can be related to the higher number of charged groups present in these pulps.

Table 5. Effect of beating on paper properties

	DEoD ₁ ED ₂	(DZ)EoD ₁ ED ₂	DEoQ(PO)	(DZ)EoQ(PO)
Wet zero span, Nm/g ¹⁾	112 ± 6	103 ± 5	112 ± 5	103 ± 6
Tear index, mNm ² /g ¹⁾	13.4 ± 0.8	14.1 ± 0.9	13.7 ± 0.8	12.3 ± 0.9
Density, kg/m ³ ¹⁾	775 ± 8	762 ± 9	770 ± 9	782 ± 9
PFI mill rev. ¹⁾	3400 ± 200	3000 ± 200	2600 ± 200	3000 ± 200
Scott Bond, J/m ² ²⁾	330 ± 30	300 ± 40	310 ± 30	280 ± 30
Gürley, µm/Pas ¹⁾	16	13	9	6
Light scatt., m ² /kg ¹⁾	20.7	20.8	20.8	20.8
WRV-WRV _{NaCl} , g/g ³⁾	0.06	0.03	0.09	0.09
Shopper Riegler, ml ³⁾	26.5	26.5	29.0	29.0

¹⁾At tensile strength 70 Nm/g ²⁾At sheet density 750 kg/m³ ³⁾At 4000 PFI rev. Errors are estimated from linear regression curves of the paper property versus beating degree.

Lindström and Carlsson [18] have shown that the ionic form affects the fibre swelling. The degree of hornification in drying decreased when the pulps were dried with the acidic groups in their ionized form (e.g. in the presence of Na⁺) instead of in their protonized form. In the bleaching sequences applied, the final bleaching stages were both acidic and alkaline, but the pulps were washed with distilled water and pH adjusted to pH 5-6 with SO₂-water after final bleaching. Thus, both chlorine dioxide final bleached pulps and pressurized peroxide final bleached pulps were dried in their protonized form. Laine and Stenius [14] studied the swelling properties of bleached softwood pulps dried in ionized Na-form and found that the water retention value of rewetted sheets increased by about 0.005 units per charge unit. The results in Table 4 indicate that carboxyl groups in the pulps promote swelling even when presented in their protonized form.

Physical properties of beaten pulps

Table 5 compares the physical properties of beaten pulps. The tear index at tensile index 70 kNm/kg of the (DZ)EoD₁ED₂ bleached and the DEoQ(PO) bleached pulps was about equal to that of the ECF reference. However, the wet zero span strength of beaten pulps was about 8% lower for the pulps in which the (DZ) treatment had been applied. Thus, the (DZ) stage seems to have a slightly negative effect on the fibre strength.

The effect of charged groups on swelling, expressed by WRV-WRV_{NaCl}, seemed to increase at a high degree of beating. Accordingly, Salmén and Berthold [19] observed that the increase in swelling when changing ionic form from proton form to sodium form was substantially higher for highly beaten pulps. The effect may be explained by that the fibrillated material created in beating having less restricting forces to the osmotic pressure created by the charged groups compared to the unbeaten fibre wall.

As mentioned previously, increased swelling promotes increased fibre flexibility and sheet of higher tensile strength. Since charged groups promote increase in swelling in both unbeaten and highly beaten pulps, pulps

containing a large number of charged groups should be advantageous with respect to beatability when beating to a target tensile strength. A drawback might be a too great increase in drainage resistance. As shown in Table 5 the more swelled Q(PO) bleached fibres also were the ones with the highest Shopper Riegler values.

The results in Table 2 indicated that the unbeaten Q(PO) final bleached pulps were somewhat more swollen due to the higher amount of charged groups present. Upon a high the degree of beating the results in Table 5 indicated that the difference in swelling between the Q(PO) and the D₁ED₂ final bleached pulps was further increased. Since increased swelling yields increased fibre flexibility and sheets of higher degree of bonding, highly charged and swollen pulps should be advantageous with respect to beatability when beating to a target tensile strength. Table 5 shows that beatability, meaning the number of PFI mill revolutions required to reach tensile index 70 Nm/g, was better for the DEoQ(PO) pulp than the DEoD₁ED₂ pulp, but equal for the (DZ)EoQ(PO) and (DZ)EoD₁ED₂ pulps.

The differences in beatability may be influenced by fibre curl introduced by the fibres by the mixing at medium consistency in the first bleaching stage [21]. Somewhat curled fibres probably explains that all pulps required a rather high amount of energy to reach tensile index of 70 Nm/g. To minimize this effect, pulps were only mixed by high intensity during injection of bleaching chemicals. Since the rewetted zero span tensile strength describes both the strength properties of single fibres and the degree of fibre deformation [22], the lower wet zero span values of the (DZ)Eo prebleached could be related to more curled fibres. However, considering both the low degree of mixing applied and that lower wet zero span values also were obtained after beating, this is not believed to be the case. PFI mill beating is known to straighten curled fibres [23].

CONCLUSIONS

Physical paper properties of DEoQ(PO), (DZ)EoD₁ED₂ and (DZ)EoQ(PO) bleached pulps to 88% ISO brightness were compared to the same properties of a DEoD₁ED₂ bleached ECF reference pulp.

(DZ)Eo prebleaching applied in a (DZ)EoD₁ED₂ bleaching sequence reduced the AOX formation by 25% and the COD effluent load by 9%. The tear strength was maintained, but the (DZ)Eo prebleaching seems to have a slight negative effect on fibre strength as indicated by

lower wet zero span strength of beaten (DZ)EoD₁ED₂ and (DZ)EoQ(PO) bleached pulps.

Pressurized peroxide final bleaching in a DEoQ(PO) bleaching sequence reduced the AOX formation by 30%, but the COD effluent load was increased by 29%. Q(PO) final bleaching yielded pulps with higher fibre charge than chlorine dioxide final bleaching. Compared to the D₁ED₂ final bleached pulps, the increased number of charged groups in DEoQ(PO) and (DZ)EoQ(PO) bleached pulps seemed to promote increased fibre swelling of both unbeaten and highly beaten pulps. The more swollen unbeaten Q(PO) final bleached pulps formed denser paper sheets with higher tensile strength and wet zero span strength. A highly charged and swollen pulp seems to be advantageous with respect to beatability when the pulp is beaten to a target tensile strength.

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REFERENCES

1. GURNAGUL, N., PAGE, D.H., PAICE, M.G., "The effect of cellulose degradation on the strength of wood pulp fibres", *Nord. Pulp and Paper Res. J.* 7(3):152-154 (1992)
2. DILLNER, B., TIBBLING, P., "Use of ozone at medium consistency for fully bleached pulp", *Int. Pulp Bleach. Conf.*, Stockholm, 2:59-74 (1991)
3. LACHENAL, D., TAVERDET, M.T., MUGUET, M., "Improvement in the ozone bleaching of kraft pulps", *Int. Pulp Bleach. Conf.*, Stockholm, 2:33-43 (1991)
4. CHIRAT, C., LACHENAL, D., ANGELIER, R., VIARDIN, M.-T., "(DZ) and (ZD) bleaching: Fundamentals and application", *J. Pulp Pap. Sci.* 23(6):J289-J292 1997
5. TOVEN, K., "Ozone based ECF bleaching of oxygen delignified kraft pulp", Doctoral Thesis 98:00, Department of chemical engineering, Norwegian University of science and technology, Trondheim (2000).
6. DILLNER, B., TIBBLING, P., "TCF bleaching can be carried out in different bleaching systems", *XXV EUCEPA Conf.*, Vienna, 1:65-83 (1993).
7. LAINE, J., "Effect of ECF and TCF bleaching on the charge properties of kraft pulp", *Pap. Puu* 79(8):551-559 (1997)
8. HYNYNEN, R., LAINE, J., STENIUS, P., "Determination of the charge of cellulosic fibres by polyelectrolyte adsorption", *NORDPAP DP1/46*, SCAN Forsk report 702 (1998).
9. WÄBERG, L., ÖDBERG, L., GLAD-NORMARK, G., "Charge determination of porous substrates by polyelectrolyte adsorption", *Nord. Pulp and Pap. Res. J.* 4(2):71-76 (1989)
10. GELLERSTEDT, G., LI, J., "An HPLC method for the quantitative determination of hexenuronic acid groups in chemical pulps", *Carbohydr. Res.* 294:41-51 (1996)
11. TENKANEN, M., GELLERSTEDT, G., VUORINEN, T., TELEMAN, A. PERTTULA, M., LI, J., BÜCHERT, J., "Determination of hexenuronic acid in softwood kraft pulps by three different methods", *J. Pulp Pap. Sci.* 25(9): 306-311 (1999)
12. KATZ, S., BEATSON, R.P., SCALLAN, A.M., "The determination of strong and weak acidic groups in sulfite pulps", *Svensk Papperstidn.* 87(6):R48-R53 (1984)
13. GELLERSTEDT, G., PRANDA, J., LINDFORS, E.-L., "Structural and molecular properties of birch kraft residual lignin", *J. Wood Chem. Technol.* 14(4):467-482 (1994)
14. LAINE, J., STENIUS, P., "Effect of charge on the fibre and paper properties of bleached industrial kraft pulps", *Pap. Puu* 79(4):257-266 (1997)
15. PAGE, D.H., TYDEMAN, P.A., HUNT, M., "The behaviour of fibre-to-fibre bonds in sheet under dynamic conditions". In "Formation and structure of paper", *Trans. of the 2nd Oxford Symp.*, 1:249-263 (1961)
16. SJÖSTRÖM, E., "Wood Chemistry: fundamentals and applications", 2nd ed., Academic Press, Orlando (1993)
17. BÜCHERT, J., TELEMAN, A., HARJUNPÄÄ, V., TENKANEN, M., VIIKARI, L., VUORINEN, T., "Effect of cooking and bleaching on the structure of xylan in conventional pine kraft pulp", *Tappi J.* 78(11):125-130 (1995)
18. LINDSTRÖM, T., CARLSSON, G., "The effect of carboxyl groups and their ionic form during drying on the hornification of cellulose fibres", *Svensk Papperstidn.* 85(15):R146-R151 (1982)
19. SALMEN, L., BERTHOLD, J., "The swelling ability of pulp fibres" In "Fundamentals of papermaking materials", *Trans. of the 11th Fundamental Research Symposium*, 2:683-701 (1997)
20. BOLAM, T.R., "The Donnan Equilibria", Bell, London (1932).
21. HAUKJEM, S., TOVEN, K., "Pressurized peroxide bleaching in MC mixer", PFI report 12/96 (1996)
22. MOHLIN, U-B., ALFREDSSON, C., "Fibre deformation and its implication in pulp characterization", *Nord. Pulp and Pap. Res. J.* 5(4):172-179 (1990)
23. PAGE, D.H., SETH, R.S., JORDAN, B.D., BARBE, M.C., "Curl, crimps, kinks and micro compressions in pulp fibres - Their origin, measurement and significance" in Papermaking raw materials, *Trans. of the 8th Fund. Res. Symp.*, 1:183-227 (1985)