

# On the Process Development of an ECF Light Bleaching Sequence for the Production of High Quality Softwood Kraft Pulp and Low AOX Formation

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# Abstract

The aim of this work is to contribute to the process development of the ECF light bleaching sequence Q(OP)D(PO) by providing a better understanding of the bleaching of softwood kraft pulp. There are few published studies on this type of sequence, and more knowledge is needed on how to reduce environmental impact, improve cost-effectiveness and ensure a high pulp quality.

Firstly, this research showed that using a pH buffer to stabilize the pH at a near-neutral level during bleaching with chlorine dioxide can lower the formation of adsorbable organically bound halogens (AOX) without altering the bleaching efficiency. A near-neutral pH decreases the formation of strongly chlorinating species so that the AOX content in the bleaching effluents is reduced by up to 30%. The increased pH in the near-neutral pH D stage compared with the reference lowered the chlorine dioxide consumption, resulting in a higher kappa number and viscosity. A lower degradation of hexenuronic acid correlated well with a lower AOX content in the effluents, affirming earlier theories that hexenuronic acid has an important impact on AOX formation.

Secondly, this research aimed at studying bleachability in (OO)Q(OP)D(PO). The bleachability was defined as delignifying and brightness gain bleachability, which is suited to ECF light bleaching sequences. The delignifying and brightness gain bleachability were used to evaluate the stages in (OO)Q(OP)D(PO) in regard to the unbleached kappa number. When comparing different stages, it is possible to distinguish the bleaching efficiency in each stage. For this ECF light sequence, the bleachability depends on the purpose of the stage. It was found that in the stages that are mainly delignifying (OO and D), a higher unbleached kappa number is beneficial for the delignifying bleachability, although the brightness gain is not improved. However, in the stages that are mainly brightness increasing (OP and PO), the brightness gain bleachability is improved by a lower unbleached kappa number.

Thirdly, the bleaching of the pulp samples in this study with the ECF light sequence was most effective with a kappa number around 32 after cooking. Although an even higher kappa number resulted in a higher yield after cooking, it seemed that this bleaching sequence cannot preserve the yield gain. Kappa number 32 also gave the best results in regard to brightness ceiling and viscosity. On the other hand, kappa number 27 was the most favourable with regard to yellowing and chemical charge.



# Sammanfattning

Syftet med denna forskning är att bidra till utvecklingen av blekning med ECF light-sekvensen Q(OP)D(PO), genom en ökad förståelse för blekning av barrsulfatmassa. I nuläget finns det få publicerade artiklar om ECF light blekning, och massaindustrin behöver mer kunskap om hur man minskar dess miljöpåverkan, förbättrar kostnadseffektiviteten och säkerställer en hög massakvalitet.

I den första delen av forskningen kunde vi påvisa en metod för att minska bildandet av adsorberbara organiskt bundna halogener (AOX). Detta genom att stabilisera pH-värdet strax under neutralt med hjälp av en pH-buffert vid blekning med klordioxid. Halterna av AOX reducerades med upp till 30% utan försämrad blekningseffektivitet. Reduktionen beror troligtvis på att förändringen av pH-värdet bidrar till att undvika de optimala förhållanden som behövs för att bilda de starkt klorinerande ämnen som står för bildandet av AOX. Höjningen av pH jämfört med referensen ledde också till en minskad förbrukning av klordioxid under blekningen, vilket ökade massans kappatal och viskositet. Resultaten visade också att nedbrytningen av hexenuronsyra försämrades, vilket korrelerade väl med lägre halter av AOX. Detta bekräftar tidigare slutsatser om att hexenuronsyra ger ett stort bidrag till AOX-bildningen.

I den andra delen av forskningen, var syftet att definiera blekbarhet på ett sätt som passar ECF light-blekningssekvenser. Resultatet blev delignifierande och ljushetshöjande blekbarhet, vilka användes för att utvärdera stegen i sekvensen (OO)Q(OP)D(PO) med avseende på oblekt kappatal. När stegen i sekvensen utvärderas separat med dessa två blekbarhetskoncept, kan man bedöma blekningseffekten i varje steg. För denna blekningssekvens visade det sig att blekbarheten för ett specifikt steg beror på dess syfte. I de steg som främst är menade att verka delignifierande (OO och D) är det bättre med ett högre oblekt kappatal för den delignifierande blekbarheten. Den ljushetshöjande blekbarheten påverkades inte. I de steg som främst ska verka ljushetshöjande (OP och PO) är det bättre med ett lägre oblekt kappatal.

Resultaten visade också att blekningen av dessa massaprover med denna blekningssekvens var som mest effektiv med ett oblekt kappatal runt 32. Ett högre kappatal än så gav visserligen ett högre utbyte efter koket, men blekningssekvensen lyckades inte bevara utbytesvinsten. Kappatal 32 gav också bäst resultat med avseende på ljushetstak och viskositet. Däremot var ett kappatal runt 27 bättre för eftergulning och kemikalieförbrukning.



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With gratitude,  
Sara





# Table of contents

<b>Abstract</b> .....	<b>i</b>
<b>Sammanfattning</b> .....	<b>iii</b>
<b>Acknowledgement</b> .....	<b>v</b>
<b>List of papers</b> .....	<b>ix</b>
<b>Conferences and related material</b> .....	<b>x</b>
<b>Abbreviations</b> .....	<b>xi</b>
<b>1 Introduction</b> .....	<b>1</b>
1.1 Chemical constituents of wood .....	1
1.2 Wood pulping .....	3
1.3 Bleaching of chemical pulp.....	5
1.4 Characterization of bleached pulp samples .....	9
1.4.1 Lignin content .....	9
1.4.2 Brightness and yellowing .....	9
1.4.3 Hexenuronic acid.....	10
1.4.4 Limiting viscosity .....	10
1.5 Environmental impact of chemical pulp bleaching.....	11
1.5.1 Adsorbable organically bound halogens (AOX) .....	11
1.5.2 Bleachability .....	14
1.6 Aims of the present research .....	16
<b>2 Experimental</b> .....	<b>17</b>
2.1 Materials.....	17
2.2 Methods.....	17
2.3 Analysis.....	19
2.3.1 HexA analysis .....	19
2.3.2 Accelerated ageing of pulp samples .....	19
2.3.3 DRUVIS.....	19
2.3.4 Charged groups .....	20
2.3.5 Chlorine dioxide consumption .....	20
2.3.6 AOX content.....	20

<b>3 Results and discussion</b> .....	<b>21</b>
3.1 Near-neutral pH D stage.....	21
3.1.1 Effect on brightness and kappa number.....	21
3.1.2 Effect on AOX formation.....	24
3.1.3 AOX formation in relation to HexA content.....	27
3.1.4 Near-neutral pH D stage – Summary.....	30
3.1.5 Near-neutral pH D stage – Future research.....	30
3.2 Bleachability in an ECF light bleaching sequence.....	31
3.2.1 Bleachability definition.....	31
3.2.2 Effect of unbleached kappa number on bleaching.....	31
3.2.3 Effect of unbleached kappa number on bleachability.....	37
3.2.4 Yield gain with a higher kappa number?.....	43
3.2.5 Unbleached kappa number for (OO)Q(OP)D(PO) – Summary.....	44
3.2.6 Bleachability – Future research.....	45
<b>4 Conclusions</b> .....	<b>46</b>
<b>5 References</b> .....	<b>47</b>

# List of papers

This thesis is based on the following papers, referred to by their Roman numerals in the text:

Paper I        “Reduction of Adsorbable Organically bound Halogens (AOX) formation at near-neutral pH chlorine dioxide bleaching of softwood kraft pulp.” Starrsjö, S., Sevastyanova, O., Sandström, P., Fiskari, J., Boman, M., Lindström, M. E. *Holzforschung*, 74(6) 597-604, (2020).

Paper II        “Assessment of Q(OP)D(PO) bleachability of softwood kraft pulp.” Starrsjö, S., Boman, M., Sevastyanova, O., Lindström, M. E., Fiskari, J. Submitted to *Nord. Pulp Pap. Res. J.* 2021-03-29.

The author’s contribution to the papers:

Paper I        Principal author: carried out literature review, pre-study, all experimental work, interpretation of results together with co-authors and most of the manuscript preparation.

Paper II        Principal author: carried out literature review, all experimental work, interpretation of results together with co-authors and most of the manuscript preparation.

# Conferences and related material

## Poster presentation

“Reduction of AOX formation in chlorine dioxide bleaching of softwood kraft pulp.” Starrsjö, S. *Proc. Of Treeseearch Progress*, Kolmården, Sweden, 7-8 May (2019).

## Oral presentation and conference paper

“Reduction of AOX formation in chlorine dioxide bleaching of softwood kraft pulp.” Starrsjö, S., Sevastyanova, O., Sandström, P., Fiskari, J., Lindström, M. E. *Proc. of the 20<sup>th</sup> International Symposium on Wood, Fibre and Pulping Chemistry*, Tokyo, Japan, 9-11 Sept. (2019).

## Oral presentation

“Optimization of modern bleaching sequences: chemistry of bleaching.”  
Forskningsagendans dag, 13 Jan. (2021).

# Abbreviations

AOX	Adsorbable organically bound halogens
COD	Chemical oxygen demand
C stage	Bleaching with elemental chlorine
DP	Degree of polymerization
DRUVIS	Diffuse reflectance UV-Vis spectrophotometry
D stage	Bleaching with chlorine dioxide
ECF	Elemental chlorine free
ECF light	Elemental chlorine free bleaching with low charges of chlorine dioxide
E stage	Alkaline extraction
HexA	Hexenuronic acid
H stage	Bleaching with sodium hypochlorite
odt	Oven dry ton
OP stage	Bleaching with mainly oxygen and some hydrogen peroxide
O stage	Bleaching with oxygen, often called oxygen delignification
OXE	Oxidation equivalents
PO stage	Bleaching with mainly hydrogen peroxide and some oxygen
P stage	Bleaching with hydrogen peroxide
Q stage	Metal ion chelating treatment in a bleaching sequence
TCF	Totally chlorine free
Z stage	Bleaching with ozone



# 1 Introduction

## 1.1 Chemical constituents of wood

Wood is a natural material that is produced by seed-bearing plants belonging to the phylum *Spermatophytae*. Wood fibres consist of the organic polymers cellulose, hemicellulose and lignin, which together make up a complex but highly ordered material. Wood classifies into softwood (long fibres) and hardwood (short fibres). Softwoods are conifers and hardwoods are angiosperms, *i.e.* deciduous trees. In Scandinavian forestry, the most common softwood species are spruce and pine, and the most common hardwood is birch.

Cellulose is the main component in wood fibre – approximately 40-45% of the dry substance – and is the most abundant polymer on earth (Sjöström 1993). The cellulose chain is a very long and unbranched carbohydrate made up of repeating  $\beta$ -D-glucopyranoside monomer units. The glucose units are linked together by  $\beta$ -glycosidic bonds, with an average degree of polymerization (DP) up to 15 000. Cellulose chains connect to each other through hydrogen and Van der Waals bonds to form crystalline fibrils, which stabilize and stiffen the chemical structure, making cellulose the strength-bearing component of wood, Figure 1.

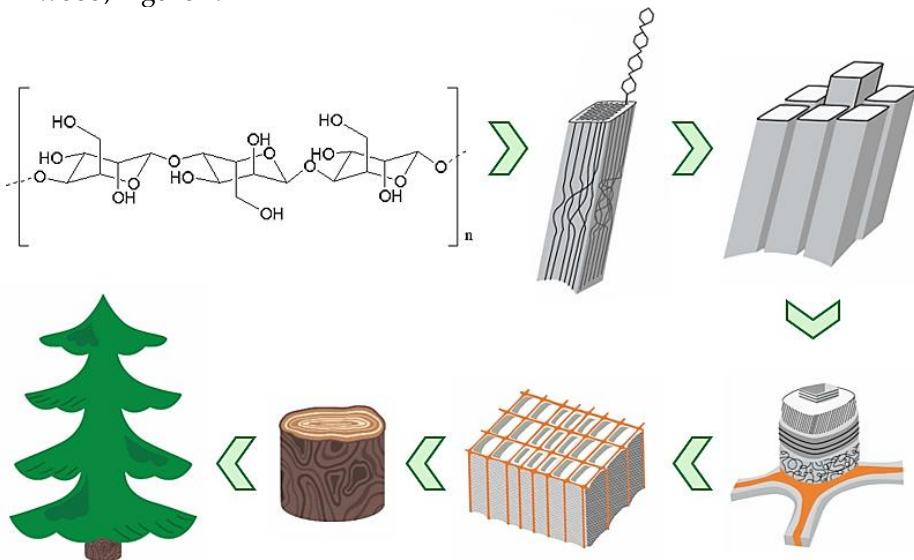


Figure 1. Wood, wood fibres and cellulose on multiple levels  
Adapted from a design by Jenny Wallmark.

Hemicelluloses are generally branched heteropolysaccharides built up by the monomer units, such as glucose, mannose, xylose, arabinose and galactose. Certain uronic acids, such as 4-*O*-methylglucuronic acid, and acetyl groups are also present as side groups on hemicellulose. The hemicelluloses form a matrix around the cellulose fibrils, contributing to the mechanical properties of wood. The DP is often around 100-200 for wood hemicelluloses. The dominating hemicelluloses are glucomannans and xylans. The hemicellulose content is about 17% for softwoods and 25% for hardwoods.

The lignin content is about 28% for softwoods and 20% for hardwoods (Heitner *et al.* 2010). It is believed that lignin is an amorphous and highly cross-linked polymer that holds the cellulose fibrils and hemicellulose together, giving stiffness to the cell walls. The lignin polymer is mainly built of three monomer types, *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, Figure 2. The main monomer for softwood is coniferyl alcohol. In hardwoods, both coniferyl alcohol and sinapyl alcohol are consistently occurring. The monomers and polysaccharides link together into a complex network in the wood via different types of covalent bonds (Lawoko *et al.* 2006), of which the most abundant is the  $\beta$ -O-4 ether bond, Figure 2. Much research is being conducted with the goal to find applications for lignin once it has been removed from wood (Sipponen *et al.* 2019).

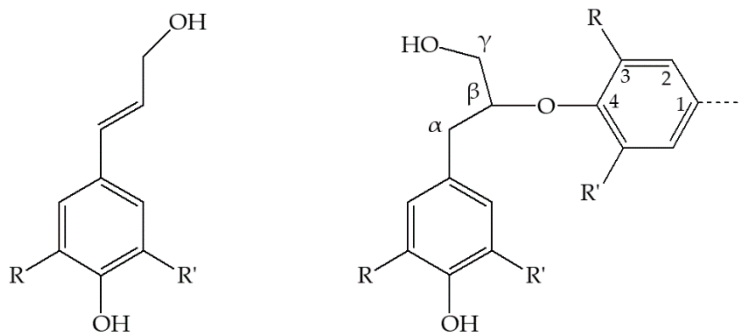


Figure 2. Left: Lignin monomers: *p*-coumaryl alcohol R=R'=H. Coniferyl alcohol R=H, R'=OCH<sub>3</sub>. Sinapyl alcohol R=R'=OCH<sub>3</sub>. Right:  $\beta$ -O-4 ether bond.



Besides the large polymers mentioned above, wood contains low molecular mass organic compounds called extractives (1-5% of dry substance) and inorganic material (ash content around 1%). The content and composition vary depending on the tree species. Some extractives play a role in the metabolism of the cells, others protect the tree from, *e.g.*, fungi and insects. Many of them cause issues for pulp manufacturers, contributing to toxicity, foaming, odour and deposits. However, when separated from the pulp, some of the extractives can be used for specialty chemicals or biofuels, or provide energy through combustion. The inorganic compounds are often also problematic. For example, transition metal ions such as iron and manganese disturb oxygen-based bleaching processes when they catalyse the decomposition of hydrogen peroxide into hydroxyl radicals.

## 1.2 Wood pulping

The purpose of a pulping process is to liberate fibres from the wood matrix. Manufacturers can then convert the pulp into many different products, such as printing paper, tissue and packaging board. Pulp production is adapted to provide pulp that meet the large variety of product demands. There are two ways to liberate the fibres, mechanical or chemical pulping, or a combination of the two. Mechanical pulping requires a large amount of energy but has a very high yield. Chemical pulping has a lower yield, with only about half of the wood turned into pulp. However, the dissolved organic material is combusted to generate energy, making the process self-sufficient in steam and electricity. The most important chemical pulping processes are kraft and sulfite pulping.

This research focuses on the production of kraft pulp. Kraft pulping is the dominant chemical pulping technology, representing over 97% of the world production of chemical pulp, Figure 3. The process was invented in 1879 by Carl Dahl from Germany, and the first kraft pulp mill went into operation in 1890 in Sweden (Biermann 1996). In the kraft digester, wood chips and cooking liquor (an aqueous solution of NaOH and Na<sub>2</sub>S) are heated to a temperature of 160-180°C, whereby most of the lignin, Figure 4, some of the hemicellulose and a little cellulose are dissolved, liberating the fibres and making them more flexible. The chemical fibres conform easily to each other when forming the product, providing better mechanical properties. However, the pulp obtained is highly coloured, which is why a bleaching process often follows the kraft cook.

During kraft pulping, carbohydrates are subjected to some chemical degradation. As a result, the cellulose yield and fibre strength are reduced. Alkaline degradation affects hemicelluloses even more than cellulose, due to their low degree of polymerization (Matthews 1974). The peeling reaction and alkaline hydrolysis are two suggested carbohydrate degradation mechanisms that can take place during a cook (Sjöström 1993).

Hexenuronic acid (HexA) forms in the cook through the degradation of the xylan side group 4-*O*-methylglucuronic acid, Figure 5. The elimination of methanol is increased by a high pH and temperature, leaving only about 12% of the carboxyl groups in xylan as the original glucuronic acid (Potthast *et al.* 2006). HexA groups contribute to the kappa number, cause yellowing of paper and consume bleaching chemicals.

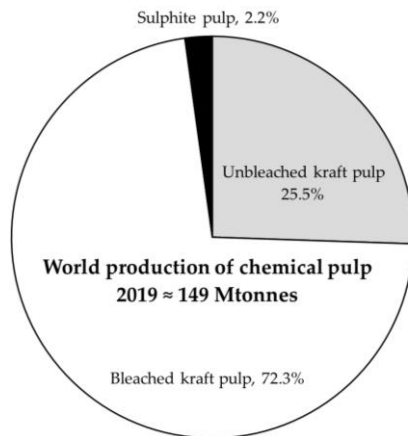


Figure 3. Chemical pulp production for 2019 (Food and Agriculture Organization 2021)

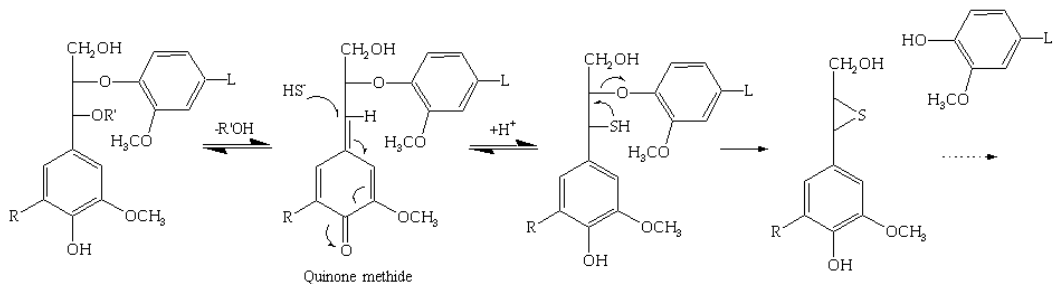


Figure 4. Reaction scheme for the cleavage of phenolic  $\beta$ -O-4 structures in lignin under kraft pulping conditions. Competing reactions may start from the quinone methide.

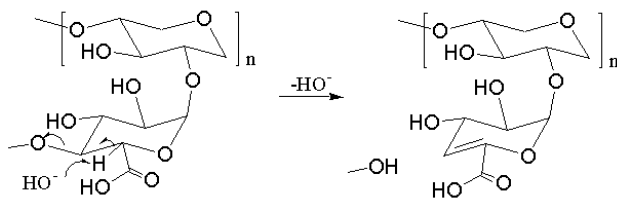


Figure 5. Reaction scheme for the formation of HexA residues from xylan under alkaline conditions in the cook

### 1.3 Bleaching of chemical pulp

Bleaching of chemical pulp is the process by which residual lignin, chromophores and residual extractives are removed from unbleached pulp to produce a bright and clean pulp for products such as printing paper, tissue and packaging board. In 2019, over 72% of the world production of chemical pulp was bleached kraft pulp, Figure 3, which corresponds to about 108 million tonnes. The bleaching process is often costly in terms of chemicals and energy and consumes bleaching agents, the production and use of which may negatively affect the environment. In addition, bleaching chemicals may deteriorate the mechanical properties of pulp. So, why bleach pulp at all? There are apparent reasons, such as the need for white and spotless printing paper for good contrast and readability. In addition, the bleaching process removes extractives, dots, specks and shives that have taste and odour and can cause allergic reactions, which is not suitable in, *e.g.*, food packaging board and hygiene products. Another goal of the bleaching process is to obtain pulp with high brightness stability. Consumer demand also regulates the production of bleached pulp. An ongoing trend is the shift of consumers towards unbleached or semi-bleached pulp in applications for which bleached pulp is not needed (Arla Foods 2019).

The kraft cooking is stopped before the delignification is complete, since the reactions at the end of the cook become less selective towards delignification but more favouring of carbohydrate degradation, which causes yield and strength loss. Instead, the more selective bleaching reactions finalize the delignification. The goal of chemical pulp bleaching is to remove residual lignin, chromophores, HexA groups and the compounds that leave taste and odour mentioned above. Preferably, this is done with minimal cost, environmental impact and damage to the fibres while providing a high yield. To achieve this while maintaining high selectivity, the pulp is bleached in a sequence, alternating between bleaching stages, Figure 6. The different bleaching chemicals react with the complex lignin polymer in different ways, thus maintaining high selectivity.

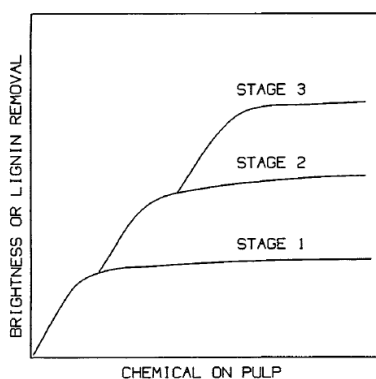


Figure 6. Hypothetical brightness increase vs chemical dosage for three bleaching stages  
Adapted from Biermann (1996)

The need for efficient bleaching processes emerged in the beginning of the twentieth century with the introduction of kraft pulping, which could produce stronger but darker pulp. At that time, hypochlorite,  $\text{ClO}^-$  (H stage), was often used in one or two stages, *e.g.* HEH (Dence and Reeve 1996). Elemental chlorine,  $\text{Cl}_2$  (C stage), was used to bleach cellulose for the first time in 1784 by Scheele and became commonly used as wood pulp bleaching agent in the 1930s. After a C stage, an alkaline extraction (E stage) would follow in the sequence, ending with an H stage. However, to improve the brightness of the kraft pulp, the conditions in the H stage had to be so severe that they damaged the pulp. Chlorine dioxide (D stage) was then implemented as a bleaching agent in the 1950s. A common sequence then was CEDED. The growing awareness of the environmental impact of the C and H stages drove the industry towards bleaching D stages and, around 1970, oxygen

delignification, O<sub>2</sub> (O stage). As environmental concerns over chlorine-based bleaching chemicals grew, hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> (P stage), and ozone, O<sub>3</sub> (Z stage), gained greater popularity as bleaching agents during the 1990s (Dence and Reeve 1996).

A summary of common bleaching chemicals is presented in Table 1.

Table 1. Summary of bleaching stages and the chemicals used  
Oxidation equivalents (OXE) from Grundelius, 1993

Bleaching stage	Chemical		OXE/kg
C	Elemental chlorine	Cl <sub>2</sub>	28.20
D	Chlorine dioxide	ClO <sub>2</sub>	74.12
E	Alkaline extraction	NaOH	
H	Hypochlorite	NaClO	26.86
O	Oxygen	O <sub>2</sub>	125.00
P	Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	58.79
Paa	Peracetic acid	CH <sub>3</sub> CO <sub>2</sub> OH	26.30
Q	Metal chelator	<i>e.g.</i> EDTA	
Z	Ozone	O <sub>3</sub>	125.00

Besides old-fashioned bleaching with chlorine and sodium hypochlorite, bleaching sequences can be divided into two categories, elemental chlorine free (ECF) and totally chlorine free (TCF). In ECF sequences, the process is based on D stages followed by alkaline extraction, often reinforced with O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. ClO<sub>2</sub> reacts as an electrophilic oxidant with high selectivity towards lignin, Figure 7. ClO<sub>2</sub> can degrade phenolic and nonphenolic lignin structures, aromatic rings and HexA (Heitner *et al.* 2010). The purpose of alkaline extraction is to dissolve and remove the oxidized and degraded lignin from fibres. In TCF sequences, pulp is bleached with chemicals that do not contain any chlorine, often oxygen-based chemicals such as H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub>, or peracetic acid. In a P stage, hydroperoxide anion, HO<sub>2</sub><sup>-</sup>, reacts as a nucleophile with phenolic lignin and chromophores (Heitner *et al.* 2010). The previously mentioned issues with transition metal ions that catalyse the degradation of H<sub>2</sub>O<sub>2</sub> into hydroxyl radicals, which can oxidize and depolymerize cellulose, are to some extent solved with a Q stage. In the Q stage, a metal chelator is added to bind the metal ions into complexes that can be washed away from the pulp.

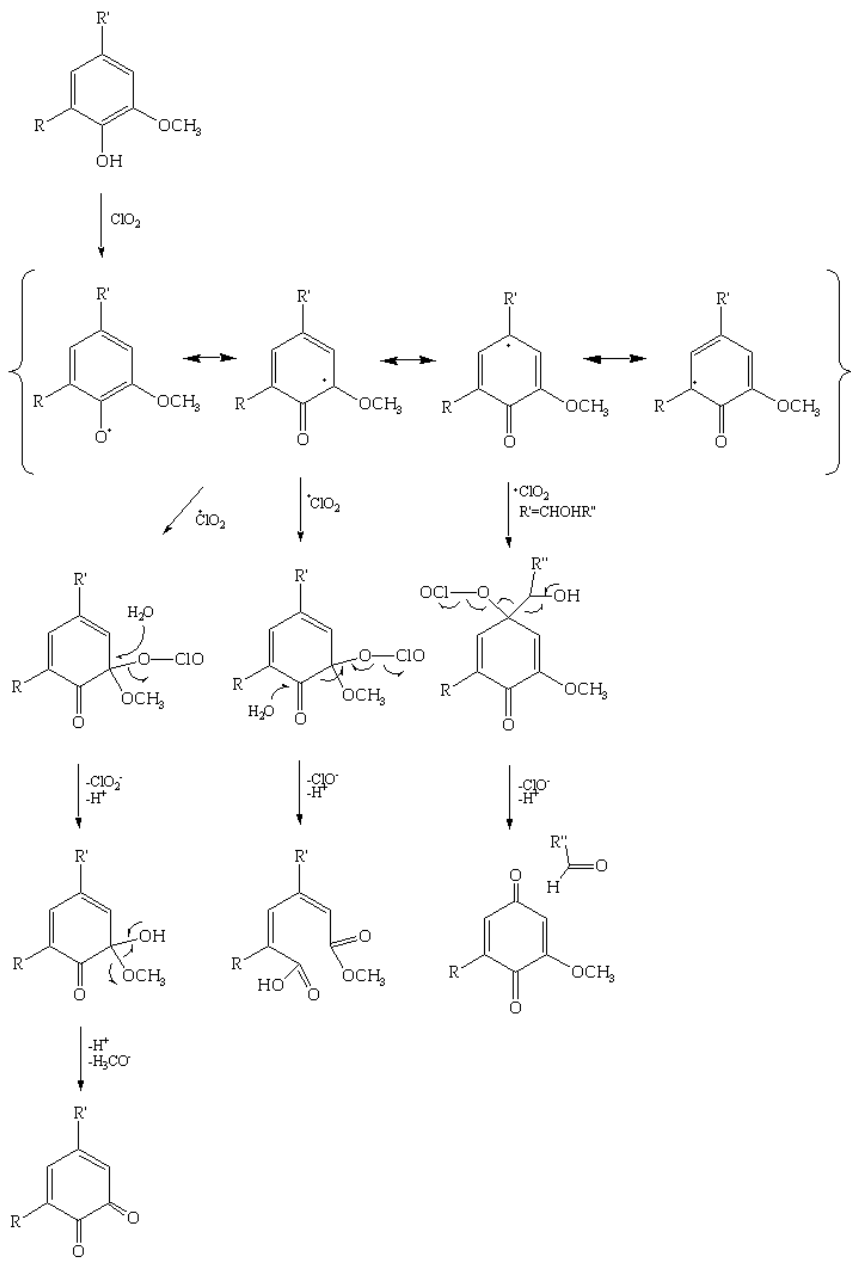


Figure 7. Chlorine dioxide reactions with phenolic rings in lignin

Recently, a new type of bleaching sequence has been developed and implemented in a number of pulp mills. ECF light bleaching sequences combine the efficiency and high selectivity of chlorine dioxide bleaching with more environmentally friendly oxygen-based bleaching chemicals such as ozone and hydrogen peroxide. However, better understanding of optimal bleach plant operating parameters is needed to minimize environmental impact and cost while assuring high pulp quality. In addition, modern kraft pulp mills produce pulp in such large quantities that even though the impact per tonne of pulp produced is low, the total environmental impact can be high without optimization. This research will focus on the process development of the ECF light bleaching sequence Q(OP)D(PO) of softwood kraft pulp.

## 1.4 Characterization of bleached pulp samples

The analysis of chemical pulps constitutes a challenge for analytical chemists, due to the complexity of the material. Bleached chemical pulp contains so little residual lignin that it is difficult to analyse the lignin structures. Here follows a summary of the pulp characterization methods used in this research.

### 1.4.1 Lignin content

The most common method to determine the residual lignin content in pulp is the kappa number determination. Both industry and research laboratories use it frequently as a simple and fast quality control to evaluate the performance of the kraft cook and bleaching progression. The measurement is based on the principle that lignin will consume an applied oxidant at a much faster rate than carbohydrates, whereby oxidant consumption can be correlated to lignin content (Lin and Dence 1992). In the ISO standard, pulp samples are treated with a solution of potassium permanganate. After ten minutes, the reaction is stopped by potassium iodide, which is then titrated with sodium thiosulfate. The remaining amount of iodide determines the amount of permanganate consumed, and thus the amount of lignin in the sample (ISO 302:2015). However, the kappa number is only a rough estimate of lignin content as other structures in the pulp can be oxidized and contribute to the measurement (Sevastyanova 2005), *e.g.* HexA groups (Li and Gellerstedt 1998), carbonyls and other 'non-lignin' structures (Li *et al.* 2002).

### 1.4.2 Brightness and yellowing

Bleached pulp is traded based on brightness. When only small amounts of residual lignin content remain in the pulp, the kappa number is no longer a

good estimation of the bleaching progress, in which case the brightness measurement prevails. The ISO method measures a pulp sample's ability to reflect diffuse light, where the result is a percentage of absolute reflectance (100%) (ISO 2470-1:2016). The human eye is sensitive to the colour yellow, which is why the method measures how yellow a pulp sample is (Rydholm 1965). Since a yellow object absorbs blue light rather than reflecting it, the reflectance of a blue light with a wavelength of 457 nm is determined.

Yellowing of a paper product means loss in brightness due to ageing factors. Since brightness is an important quality parameter of pulp, a tendency for brightness reversion is a serious problem. The causes of yellowing are either chemical or physical. Chemical factors include HexA groups (Vuorinen *et al.* 1999, Granström *et al.* 2001), carbonyls (Ahn *et al.* 2019), residual lignin (Rydholm 1965) and transition metal ions (Czepiel 1960). Physical factors such as high humidity, low pH, high temperature (Granström *et al.* 2001) and UV light (Chirat and de la Chapelle 1999) accelerate yellowing.

#### **1.4.3 Hexenuronic acid**

HexA groups are unwanted in the final bleached pulp as they contribute to the kappa number, reduce brightness stability and consume bleaching chemicals as they degrade. Therefore, it is of interest to determine the amount of HexA groups in a pulp, for which several methods are available (Tenkanen *et al.* 1999, Ragnar 2001, Potthast *et al.* 2006). Since HexA groups are unstable in acidic conditions, an acidic treatment can selectively degrade them; quantification of the hydrolysis product is then conducted either directly or after chemical conversion into UV active compounds. A kappa number measurement before and after hydrolysis can give an indication of the amount of HexA in a pulp sample, whereby the content in the pulp is calculated using the molar oxidation equivalent of 8.6 (Li and Gellerstedt 1998).

#### **1.4.4 Limiting viscosity**

The limiting viscosity of a pulp in cupri-ethylenediamine is a rough estimate of the DP of the cellulose and therefore gives an indication of how much the fibres have been degraded in the pulping or bleaching process (Rydholm 1965). A direct relationship between fibre strength and viscosity has not been found, but it has been shown that fibre strength rapidly falls below a critical DP (Gurnagul *et al.* 1992, Oglesby *et al.* 2016). The limiting viscosity is effectively used by pulp mills as an internal estimate of 'how well the process



is going'. However, the results should not be used to compare pulp from different mills or types of wood (Lapierre *et al.* 2006). In a laboratory study, the viscosity results are useful for comparing the effect on pulp quality and fibre strength, for example by varying the parameters of bleaching stages for a certain starting pulp.

In the measurement, the sample solution (pulp dissolved in cupri-ethylenediamine solvent) goes through a capillary tube viscometer at 25°C, and the viscosity is calculated with the efflux time (ISO 5351:2010). The longer the time it takes for the sample to exit the viscometer, the larger the cellulose DP.

## 1.5 Environmental impact of chemical pulp bleaching

The bleaching process may negatively affect the environment since it requires strong bleaching chemicals and a large amount of heat and electrical energy. Significant improvements have been made to reduce environmental impact (Stratton *et al.* 2004), but modern pulp mills produce pulp on such a large scale that the total emissions become an issue. Environmental concerns are therefore a priority when it comes to bleaching chemical pulp.

To reduce the environmental impact of a bleach plant, there are a few aspects to consider. For example, it is important to reduce the discharge of toxic or organic compounds (such as adsorbable organically bound halogens, AOX, and chemical oxygen demand, COD) and consumption of water, energy and chemicals. Low chemical consumption can be achieved by, for example, studying what gives good bleachability for the process in question. Below follows more information on how AOX and bleachability can be used as monitors for the environmental impact of a bleach plant.

### 1.5.1 Adsorbable organically bound halogens (AOX)

AOX is an analytical convention that is useful in describing bleaching effluent quality. In bleaching with ClO<sub>2</sub>, chlorine atoms bind with organic matter to form chlorinated organic compounds, such as chloroguaiacols and chlorophenols (Isoaho *et al.* 2012, Fiskari *et al.* 2016). These compounds do not easily decompose in nature and some are toxic, mutagenic and carcinogenic (Ali and Sreekrishnan 2001). Much of the AOX formed can be degraded by external treatment of the bleach plant effluents (Savant *et al.* 2006). However, even a small amount of AOX in the effluent discharge is undesirable since it does not naturally belong in the surrounding environment (Ali and Sreekrishnan 2001). It is important to note that the AOX measurement is a sum

parameter. The ISO standard measures the total content of organically bound chlorine, bromine and iodine that can be adsorbed on activated carbon under specified conditions (ISO 9652:2004). Thus, the measured AOX does not provide any information regarding the toxicity of the compounds or degree of substitution (which affects the toxicity and stability). Effluents from ECF light bleach plants are expected to contain low amounts of AOX due to low charges of  $\text{ClO}_2$ , with mainly monochlorinated phenolic compounds.

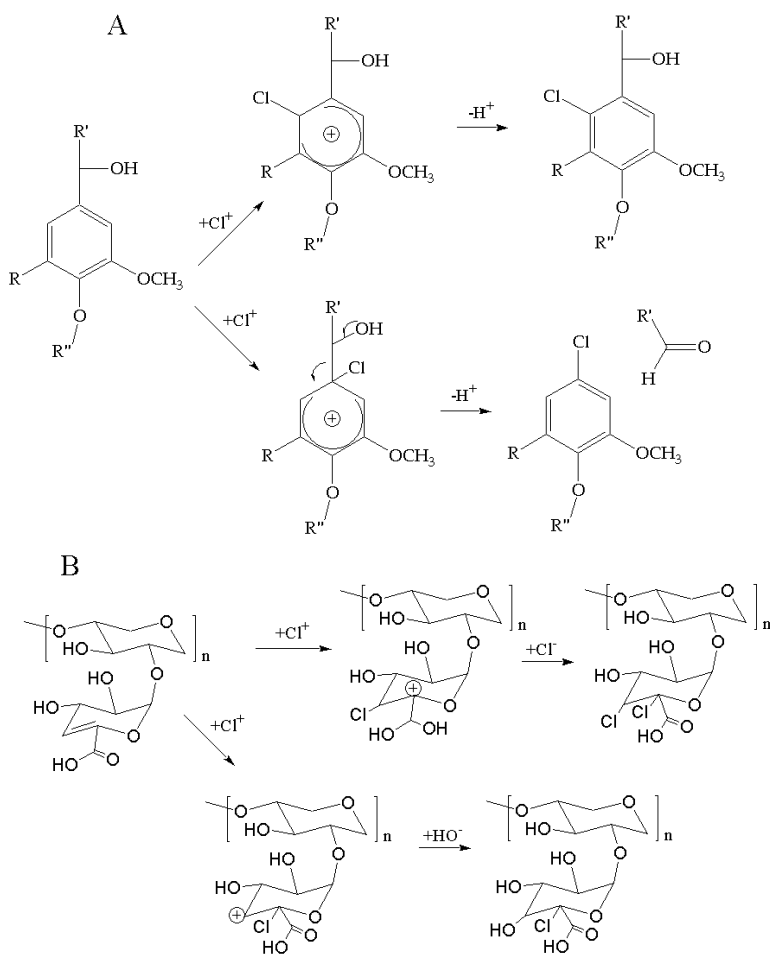
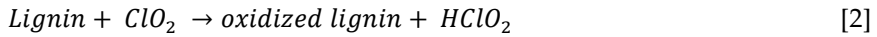
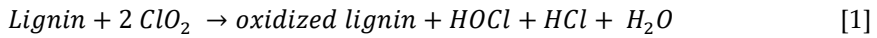


Figure 8. Reaction schemes for AOX formation during bleaching with chlorine dioxide from A) non-phenolic lignin structures and B) HexA

AOX is formed as a by-product when ClO<sub>2</sub> reacts with the residual lignin and HexA in pulp, Figure 8. From ClO<sub>2</sub>, hypochlorous acid (HOCl) and chlorite ion (ClO<sub>2</sub><sup>-</sup>) form according to reactions [1] and [2]. Cl<sub>2</sub> forms in equilibrium with HOCl according to reaction [3]. Due to the acid formation, a rapid decrease in the pH occurs. A low pH in the D stage (final pH below 3) results in significant formation of HOCl and Cl<sub>2</sub>. HOCl, ClO<sub>2</sub><sup>-</sup> and Cl<sub>2</sub> are all capable of acting as chlorinating agents and producing AOX (Dence and Reeve 1996). Ni *et al.* (1991) showed that during the D stage, most of the AOX forms in the first ten minutes. About 90% of the AOX is due to the reaction between lignin and HOCl (Ni *et al.* 1991).



There are some methods to reduce AOX formation and discharge (Ragnar and Törngren 2002, Fiskari *et al.* 2016), of which reducing the amount of chlorine-containing bleaching chemicals is the most effective. Decreasing the carry-over decreases chlorine dioxide consumption and AOX formation (Lehtimaa *et al.* 2010). In addition, reducing the lignin content in the incoming pulp can reduce AOX formation (Bergnor *et al.* 1988, Björklund *et al.* 2004). An effective way to reduce AOX discharge is through alkaline extraction following chlorination (Cook 1991, Ljunggren *et al.* 1996). An alternative is to increase the pH in the D stage (Hart and Connell 2008). This will influence which reactions occur and disfavours those that form AOX.

One method to reduce ClO<sub>2</sub> consumption – and thereby AOX formation – is to use a pH buffer to control the pH during the D stage. Early work by Rapson (1956) showed that a maximum brightness increase could be achieved by using a pH buffer close to neutral pH. In the work by Jiang and Berry (2011), carbon dioxide (CO<sub>2</sub>) was added to a pulp sample before the final D stage to generate a sodium bicarbonate buffer *in situ*. A buffer has the best capacity to stabilize the pH around the pK<sub>a</sub>, which is why the D stages were done around pH 6.4. The stabilization of pH at a near-neutral level favoured brightening reactions, thereby reducing the need for ClO<sub>2</sub> while improving pulp quality in terms of brightness stability and viscosity. In addition, the amounts of organic chlorine in the filtrate and pulp decreased dramatically. Mill trials

resulted in the implementation of the new technology in multiple mills in North America without major capital expenditures (Audet *et al.* 2014, Radiotis *et al.* 2018). Ribeiro *et al.* (2014) obtained similar results: with the addition of 3 kg CO<sub>2</sub>/odt, they saved 3 kg ClO<sub>2</sub>/odt whilst conserving brightness and pulp quality and increasing brightness stability. With a reduced ClO<sub>2</sub> dosage, the formation of AOX is expected to be lowered, although neither of the previously mentioned works confirmed this.

### 1.5.2 Bleachability

One approach to improving the bleaching process by lowering chemical consumption is evaluating bleachability, *i.e.* how well pulp responds to bleaching chemicals. What gives good bleachability varies depending on the bleaching sequence, and the treatment history of the unbleached pulp is an important contributor (Gustavsson *et al.* 1999, Ragnar 2004). The effect of pulping conditions on bleachability has been a subject of much research. Cooking at higher effective and residual alkali and temperature gives better bleachability but does not favour yield and selectivity (Carnö *et al.* 1975, Sjöström 1998, Colodette *et al.* 2002, Axelsson *et al.* 2002, Gellerstedt and Wafa Al-Dajani 2003, Axelsson and Lindström 2004, Axelsson *et al.* 2004). Ionic strength and the origin of the raw materials are also contributing factors (Sjöström 1999, Martino *et al.* 2013). Structures in the pulp can affect bleachability, including residual lignin characteristics and lignin-carbohydrate complexes. A high  $\beta$ -aryl ether content in the residual lignin after the cook contributes to better bleachability from alkaline peroxide bleaching (Gustavsson *et al.* 1999, Gellerstedt and Wafa Al-Dajani 2000). The amount of delignification in the cook and oxygen delignification also affects bleachability, with a higher unbleached lignin content being more beneficial (Axelsson *et al.* 2004, Pascoal Neto *et al.* 2002, Bourbonnais *et al.* 2004, Segura *et al.* 2016). The optimal brown stock kappa number for pulping and bleaching costs depends on the sequence and the brightness target (Hart and Connell 2006).

Bleachability is used with various definitions in the literature. The concept of oxidation equivalents (OXE) was defined by Grundelius (1993) as the combined oxidizing power of all bleaching chemicals in a sequence. It is often converted to OXE per kappa number units to reach a certain brightness. However, the OXE concept has been criticized for not accounting for the differences in reaction patterns between the numerous bleaching chemicals (Ragnar 2004).

To summarize the discussions about bleachability in the literature, many studies show that bleachability depends on the preceding treatment of the pulp. This is due to the difference in composition and structure of the lignin and carbohydrates present in the unbleached pulp. However, what exactly gives good bleachability depends on the specific pulping conditions and bleaching process. Modern ECF light sequences have improved significantly in recent years. Nonetheless, more information about the requirements for good bleachability is needed. I found no published work covering bleachability of the ECF light bleaching sequence for softwood kraft pulp. This research aims at filling this research gap.

## 1.6 Aims of the present research

The aim of this work is to contribute to the process development of the ECF light bleaching sequence Q(OP)D(PO). There are few published studies on ECF light sequences, and more knowledge is needed on how to reduce environmental impact and improve cost-effectiveness while ensuring high pulp quality for this particular sequence.

In 2018, the pulp mill SCA Östrand completed a new fibre line, producing 840 000 tonnes of bleached softwood kraft pulp during 2020 (SCA 2020). The fibre line includes a new bleach plant, allowing for both ECF light and TCF bleaching. Prior to the above-mentioned ECF light bleaching sequence, the pulp is treated with double oxygen delignification stages (OO). Due to the mill's large production capacity, it is very important to optimize the process. Östrand released 5% of the total AOX emissions in Sweden during 2020 (Naturvårdsverket 2020), despite the use of ECF light bleaching sequence with low charges of ClO<sub>2</sub>.

In paper I, I examined the effect of near-neutral pH on AOX formation in an intermediate D stage – a single D stage in the middle of the ECF light bleaching sequence. CO<sub>2</sub> was used to generate a bicarbonate buffer *in situ*, stabilizing the pH at a near-neutral level during the D stage. The hypothesis of this research is that a near-neutral pH will decrease the formation of strongly chlorinating species, reducing AOX formation.

In paper II, I studied the bleachability in (OO)Q(OP)D(PO). The pulp bleachability was evaluated for three softwood kraft pulp samples with brown stock kappa numbers 27, 32 and 35. They were bleached and analysed with regard to yield, pulp viscosity, carbohydrate content and brightness ceiling. The bleachability was defined as delignifying and brightness gain bleachability; see section 3.2.1.

## 2 Experimental

### 2.1 Materials

The starting materials were softwood kraft pulp samples collected from different locations in the fibre line at SCA Östrand pulp mill, Table 2. In paper I, the pulp was collected after bleaching with (OO)Q(OP). In paper II, the pulp samples were brown stock pulp with varying kappa numbers. Upon collection, the pulp samples were washed with deionized water, dewatered to 30% consistency, homogenized and stored in polyethylene bags at 5°C.

Table 2. Starting pulp samples collected at SCA Östrand pulp mill

Sample	Date, time	Kappa number	ISO brightness, %	Viscosity, ml/g
(OO)Q(OP)	2018-04-04	7.0	64.8	870
K27	2020-03-17, 10:30	26.6	29.5	1091
K32	2020-03-24, 10:55	31.9	26.8	1123
K35	2020-02-18, 17:30	34.9	27.8	1085

### 2.2 Methods

The laboratory bleaching stages in the sequence (O1O2)Q(OP)D(PO) were carried out according to Table 3.

- The pressurized stages (O1, O2, OP and PO) were conducted in Teflon-lined autoclaves in a preheated rotating polyethylene glycol bath. The oxygen delignification was configured to remove 60% of the unbleached kappa number to resemble a pulp mill case. The sodium hydroxide (NaOH) charge was varied to achieve the desired kappa number and final pH.
- The Q stage was done in polyethylene bags in a preheated water bath. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and NaOH was added to reach the target final pH.
- The H<sub>2</sub>O<sub>2</sub> charge in the OP stage was varied to achieve the same incoming kappa number in the D stage for all three samples. A series of OP stages was used to find the accurate H<sub>2</sub>O<sub>2</sub> charges.
- The D stages were conducted in polyethylene bags in a preheated water bath. NaOH was added to reach the target final pH. The ClO<sub>2</sub> charge 7.6-8 kg/odt was used for the final brightness 88% ISO. The ClO<sub>2</sub> charge 3.8 kg/odt was used for the final brightness 85% ISO. The D stages in paper I were carried out in triplicate. However, for further pulp analysis (HexA, charged groups, viscosity, yellowing), a single pulp sample of each kind

was chosen based on the AOX content in the effluent to be as similar to the mean value as possible.

- In the near-neutral D stages, CO<sub>2</sub> addition was done with two charges. 10 kg CO<sub>2</sub>/odt was chosen as it is the highest feasible charge for industrial-scale application. 30 kg CO<sub>2</sub>/odt was chosen as an extreme value to ensure an effect at laboratory scale. Dry ice was quickly measured on a scale and then added to the polyethylene bag containing pulp, water and NaOH. The applied charges of CO<sub>2</sub> for 70 g pulp were 0.7 g and 2.1 g of dry ice respectively. The bag was sealed and the CO<sub>2</sub> mixed with the pulp. The ClO<sub>2</sub> was added to the bag with a syringe; the hole was then sealed off and the suspension thoroughly mixed and placed in a water bath.
- In the final bleaching stage, PO, five different charges of H<sub>2</sub>O<sub>2</sub> were applied to reach a final brightness in the interval 87-92% ISO and to find the brightness ceiling for all pulp samples. Interpolation was used to calculate the pulp values at 88% ISO.
- The pulp yield was measured gravimetrically for the laboratory oxygen delignification and bleaching stages. The oxygen delignification yield was measured with seven replications. The bleaching yield was measured with two replications. The cook yield was estimated based on laboratory cooking data from a previous study, by which the kappa number was plotted against total gravimetric yield.

Table 3. Laboratory parameters for oxygen delignification and bleaching. odt=oven dry ton. In O1, the sodium hydroxide charge was 26 kg/odt for K27, 31 for K32 and 30 for K35. The same denotation goes for the hydrogen peroxide charge in the OP stage. In PO, five hydrogen peroxide charges between 2 and 15 kg/odt were applied. In paper I, the D stage temperature was 70°C and in paper II it was 80°C.

		O1	O2	Q	OP	D	PO
O <sub>2</sub>	MPa	1	0.5		0.5		0.5
NaOH	kg/odt	26/31/30					
MgSO <sub>4</sub>	kg/odt	2			1		0.5
ClO <sub>2</sub>	kg/odt					3.8, 7.6, 8	
H <sub>2</sub> O <sub>2</sub>	kg/odt				3/6/8		2, 3.5, 5, 10, 15
EDTA	kg/odt			1.5			
Time	min	20	60	70	120	60	140
Temperature	°C	85	100	85	95	70/80	100
Consistency	%	12	12	10	12	12	12
Final pH			11-11.5	4.5	10.5-11	3-6	10-11



## 2.3 Analysis

The pulp samples were analysed as per the following ISO standards:

- ISO 3688 (1999) – Pulps – Preparation of laboratory sheets for the measurement of diffuse blue reflectance factor (ISO brightness).
- ISO 2470 (2016) – Paper, board and pulps – Measurement of diffuse blue reflectance factor – Part 1: Indoor daylight conditions (ISO brightness).
- ISO 302 (2004) – Pulps – Determination of Kappa number.
- ISO 5351 (2010) – Pulps – Determination of limiting viscosity number in cupri-ethylenediamine (CED) solution.
- SCAN-CM 71:09 – Pulps – Carbohydrate composition. The hemicellulose fractions were calculated from the monosaccharides according to Matthews (1974). The lignin content was calculated from the kappa number, with the factor 0.153 (Dence and Reeve 1996).

### 2.3.1 HexA analysis

The HexA content in the pulp samples was determined according to Vuorinen *et al.* 1999 (the HUT method), with modifications according to the work by Chakar *et al.* (2000). 7 g of dry pulp was suspended in 300 ml of 8 mmol/l sodium formate buffer at pH 3.5. The pulp suspension was boiled with reflux for 3 hours, after which the pulp was filtered and washed with Milli-Q water. The kappa number of the sample was measured before and after acid hydrolysis. The contribution of HexA to the kappa number was used to calculate the content of HexA in the pulp; 10  $\mu\text{mol}$  of HexA corresponds to 0.86 kappa number units (Li and Gellerstedt 1998).

### 2.3.2 Accelerated ageing of pulp samples

Accelerated aging was done according to Sevastyanova (2005). During the aging procedure, handsheets with a grammage of 200 g/m<sup>2</sup> and a moisture content of 7% were exposed to thermal yellowing. The handsheets were sealed in polyethylene bags and placed in a waterbath at 70°C for up to 11 days. The ISO brightness was measured before and after the aging, whereby the brightness loss was calculated as the difference.

### 2.3.3 DRUVIS

Diffuse reflectance UV-Vis spectrophotometry (DRUVIS) was done according to Ragnar (2001) with a Varian Cary 1 equipped with a diffuse reflectance

accessory. The diffuse reflectance of a stack of handsheets with a grammage of 60 g/m<sup>2</sup> was measured in triplicate for each sample. k/s was calculated according to the Kubelka-Munk theory.

#### **2.3.4 Charged groups**

The total amount of charged groups in the pulp was measured by conductometric titration according to Katz *et al.* (1984) with modifications. 1 g dry pulp was washed for 5 minutes in 100 ml MilliQ water. After dewatering, the pulp was re-diluted with 100 ml MilliQ water and the pH adjusted to 2. After 15 minutes, the pulp was dewatered and washed with 3x100 ml MilliQ water. The titration was done with 0.01 M NaOH.

#### **2.3.5 Chlorine dioxide consumption**

The D stage bleaching effluents were analysed for ClO<sub>2</sub> consumption by iodometric titration according to T 611 (2007).

#### **2.3.6 AOX content**

The D stage bleaching effluents were analysed for AOX with ISO 9562 (2005) by Eurofins Environment Testing Sweden AB. Upon collection of the filtrates, the ClO<sub>2</sub> concentration was measured as described above. The remaining amounts of ClO<sub>2</sub> were neutralized by a minimum amount of sodium sulfate. The filtrates were stored in a fridge for up to 1 day before being moved to the analysis laboratory by refrigerated transport.

# 3 Results and discussion

## 3.1 Near-neutral pH D stage

### 3.1.1 Effect on brightness and kappa number

Near-neutral pH bleaching was achieved with the addition of CO<sub>2</sub> in the form of dry ice, stabilizing the pH before ClO<sub>2</sub> addition. As the near-neutral final pH will favour brightening reactions over delignifying reactions, it is expected that the near-neutral pH D stages will result in pulp samples with a higher brightness and kappa number. The D stage bleaching results are presented in Table 4.

In this study, D stages at near-neutral pH do not provide a brightness gain when compared with the reference bleaching, as is shown in Figure 9. However, even though the ClO<sub>2</sub> consumption is up to 17% lower for the near-neutral bleaching, the same brightness as the reference is obtained. Jiang and Berry (2011) and Ribeiro *et al.* (2014) found that the brightness increased while ClO<sub>2</sub> consumption decreased with a higher final pH. This was likely due to a higher formation of chlorite ion, ClO<sub>2</sub><sup>-</sup>, which becomes unreactive at near-neutral pH.

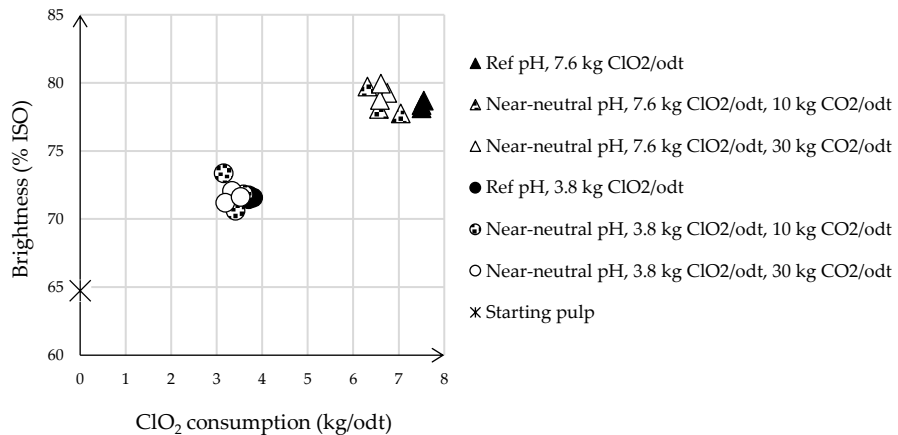


Figure 9. Effect of near-neutral pH in D stage on the ISO brightness and ClO<sub>2</sub> consumption

Table 4. D stage bleaching results in triplicate repetitions and average values. odt=oven dry ton pulp.

Sample	Final pH	ClO <sub>2</sub> cons. (%)	ISO brightness (%)	Kappa number	AOX (kg/odt)
1 Ref pH, 7.6 kg ClO <sub>2</sub> /odt	4.2	98.7	78.4	1.96	0.213
2 Ref pH, 7.6 kg ClO <sub>2</sub> /odt	4.0	98.7	78.1	1.97	0.161
3 Ref pH, 7.6 kg ClO <sub>2</sub> /odt	3.9	99.3	78.7	1.91	0.132
Average	4.0	98.9	78.4	1.9	0.17
Standard deviation	0.09	0.3	0.23	0.03	0.03
1 Near-neutral pH, 7.6 kg ClO <sub>2</sub> /odt, 10 kg CO <sub>2</sub> /odt	6.1	83.1	79.7	2.52	0.088
2 Near-neutral pH, 7.6 kg ClO <sub>2</sub> /odt, 10 kg CO <sub>2</sub> /odt	6.2	86.4	78.1	2.75	0.125
3 Near-neutral pH, 7.6 kg ClO <sub>2</sub> /odt, 10 kg CO <sub>2</sub> /odt	5.3	92.7	77.8	2.67	0.154
Average	5.8	87.4	78.5	2.6	0.12
Standard deviation	0.40	4.0	0.86	0.10	0.03
1 Near-neutral pH, 7.6 kg ClO <sub>2</sub> /odt, 30 kg CO <sub>2</sub> /odt	5.7	88.8	79.3	2.37	0.169
2 Near-neutral pH, 7.6 kg ClO <sub>2</sub> /odt, 30 kg CO <sub>2</sub> /odt	5.9	86.6	78.8	2.54	0.125
3 Near-neutral pH, 7.6 kg ClO <sub>2</sub> /odt, 30 kg CO <sub>2</sub> /odt	6.0	87.0	79.9	2.36	0.176
Average	5.9	87.5	79.3	2.4	0.16
Standard deviation	0.14	0.9	0.49	0.08	0.02
1 Ref pH, 3.8 kg ClO <sub>2</sub> /odt	3.4	97.4	71.8	3.24	0.154
2 Ref pH, 3.8 kg ClO <sub>2</sub> /odt	3.3	97.4	71.5	3.27	0.139
3 Ref pH, 3.8 kg ClO <sub>2</sub> /odt	3.2	100.0	71.6	3.28	0.139
Average	3.3	98.3	71.6	3.3	0.14
Standard deviation	0.07	1.2	0.12	0.02	0.007
1 Near-neutral pH, 3.8 kg ClO <sub>2</sub> /odt, 10 kg CO <sub>2</sub> /odt	5.4	94.5	71.8	3.46	0.147
2 Near-neutral pH, 3.8 kg ClO <sub>2</sub> /odt, 10 kg CO <sub>2</sub> /odt	5.7	89.8	70.6	3.85	0.132
3 Near-neutral pH, 3.8 kg ClO <sub>2</sub> /odt, 10 kg CO <sub>2</sub> /odt	6.0	83.1	73.4	3.57	0.125
Average	5.7	89.1	71.9	3.6	0.13
Standard deviation	0.24	4.7	1.13	0.16	0.009
1 Near-neutral pH, 3.8 kg ClO <sub>2</sub> /odt, 30 kg CO <sub>2</sub> /odt	5.7	87.9	72.1	3.72	0.081
2 Near-neutral pH, 3.8 kg ClO <sub>2</sub> /odt, 30 kg CO <sub>2</sub> /odt	5.8	84.0	71.2	3.93	0.103
3 Near-neutral pH, 3.8 kg ClO <sub>2</sub> /odt, 30 kg CO <sub>2</sub> /odt	5.5	92.8	71.6	3.72	0.103
Average	5.6	88.2	71.6	3.8	0.10
Standard deviation	0.14	3.6	0.36	0.10	0.01

As expected, the altered near-neutral pH results in a higher kappa number than the reference, Figure 10. The kappa number is higher after near-neutral pH bleaching compared with the reference, correlated with  $\text{ClO}_2$  consumption. Delignifying reactions are favoured at lower pH, as chlorine species that are more reactive toward lignin are formed in this region. In contrast, delignifying reactions are less favoured at a near-neutral pH than for the reference case. This is in accordance with earlier work on the pH dependence of delignification (Hart and Connell 2008).

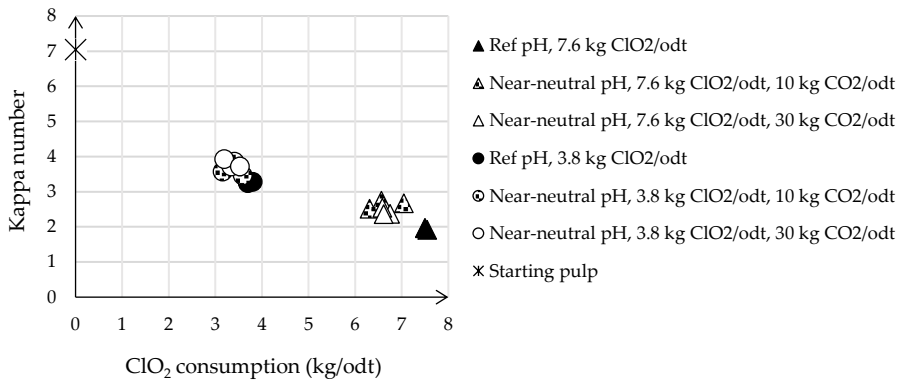


Figure 10. Effect of near-neutral pH in D stage on the kappa number and  $\text{ClO}_2$  consumption

In the near-neutral pH D stages, different reactions took place compared with the reference case, changing the kappa number and brightness 'route' from the same starting pulp, Figure 11. The increase in pH changes the chemical mix in the bleaching liquor, influencing which chlorine species are formed and thereby which reactions are favoured. Our results show that the addition of  $\text{CO}_2$  lowered  $\text{ClO}_2$  consumption and as a result reduced delignification, but that the near-neutral pH favoured brightness increase, which reached the same level as the reference.

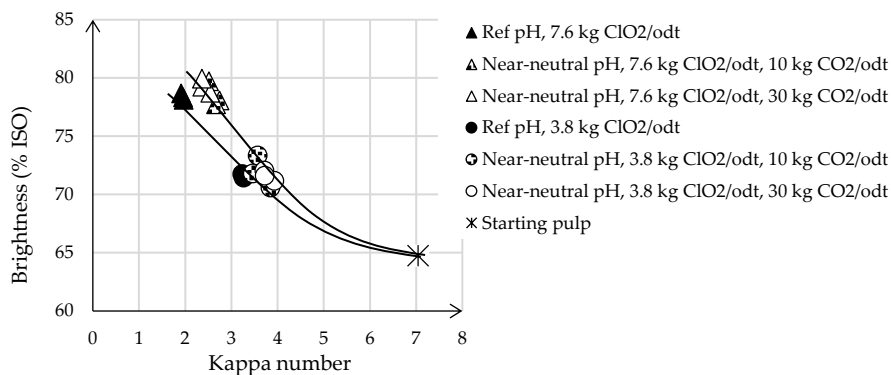


Figure 11. Brightness and kappa number route from starting pulp to after D stage

### 3.1.2 Effect on AOX formation

A near-neutral pH will decrease the formation of strongly chlorinating species in the D stage, such as  $\text{Cl}_2$  and  $\text{HOCl}$ . The hypothesis of this research is that the reduction of the chlorinating species will reduce AOX formation, lowering the environmental impact of the bleach plant.

The results show that the AOX formation is dependent on the final pH of the D stage, Figure 12, which is in accordance with earlier research (Joncourt 2000). The measured AOX contents in this study are all moderate due to low  $\text{ClO}_2$  charges, and therefore the differences between samples are small.

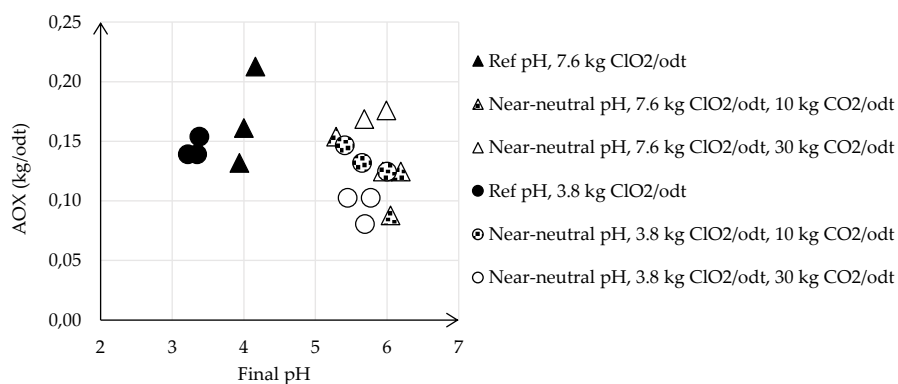


Figure 12. Dependence of AOX in D stage effluents on final pH

The results indicate that the addition of CO<sub>2</sub> can reduce AOX formation by up to 30%, Table 4. The near-neutral pH reduces the AOX content for both ClO<sub>2</sub> charges, although the effect is more consistent for the lower ClO<sub>2</sub> charge. It was expected that 30 kg CO<sub>2</sub>/odt would lower AOX formation by more than 10 kg CO<sub>2</sub>/odt, as a higher buffer concentration would increase the buffering effect. This was the case for the pulps bleached with a lower ClO<sub>2</sub> charge. However, the AOX results for the pulps bleached with a higher ClO<sub>2</sub> charge were not consistent with this trend. The reason for this is not understood. However, the standard deviations of the AOX for the triplicate bleedings in this study are 10-25% of the average, and the coefficient of variation of the repeatability given in the ISO standard for AOX measurement is 5-6%. This means that the statistical variation of the AOX results is quite large.

As mentioned above, the near-neutral pH lowered the ClO<sub>2</sub> consumption required to reach a certain brightness. A lowered ClO<sub>2</sub> consumption could by itself lower AOX formation (regardless of the near-neutral pH), as this means that fewer chlorinating species have been consumed and formed chlorinated organic substances. However, the results in Figure 13 suggest that it is not lowered consumption that reduces AOX formation in this case, as AOX values in a large interval are found within a small consumption interval. There is no trend indicating that the AOX formation corresponds to lowered consumption.

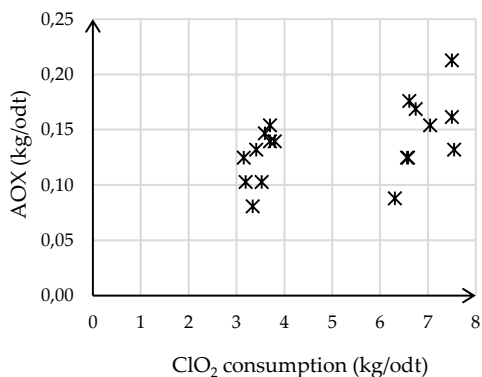


Figure 13. Effect of varying ClO<sub>2</sub> consumption on AOX formation

The intrinsic viscosity is higher after near-neutral bleaching compared with the reference bleaching, Figure 14. This result indicates that a near-neutral pH D stage can reduce carbohydrate degradation and in turn increase the fibre strength properties. This effect is probably due to the initial pH of the D stages. Traditionally, the final pH of a D stage is controlled by NaOH addition. The initial pH has to be in the alkaline range to end the stage with a final pH around 3. A high concentration of hydroxyl ions in the beginning of the D stage promotes the formation of hypochlorite ion,  $\text{ClO}^-$ , from  $\text{HClO}$ .  $\text{ClO}^-$  is a strong but non-selective bleaching agent that may degrade carbohydrates. When adding the buffer before  $\text{ClO}_2$  addition, the initial pH will be lowered, reducing the formation of  $\text{ClO}^-$ , thereby reducing the degradation of cellulose and in turn viscosity loss.

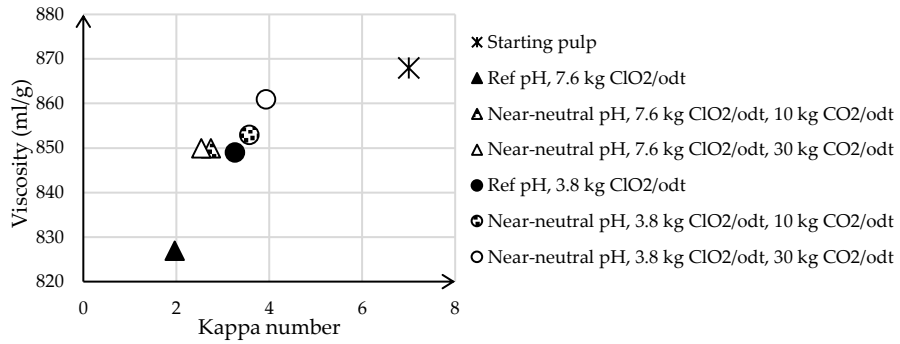


Figure 14. Pulp viscosity for some pulps after D stage. The standard deviation for viscosity is 13.



### 3.1.3 AOX formation in relation to HexA content

More HexA remained in the pulp samples after a near-neutral pH D stage than in the reference pulp samples, Figure 15. The reason is likely that the higher pH reduces the formation of  $\text{Cl}_2$ . Earlier research has shown that HexA is mainly degraded by  $\text{Cl}_2$ , whereby chlorinated dicarboxylic acids are formed, *i.e.* compounds that contribute to the AOX (Björklund *et al.* 2002).

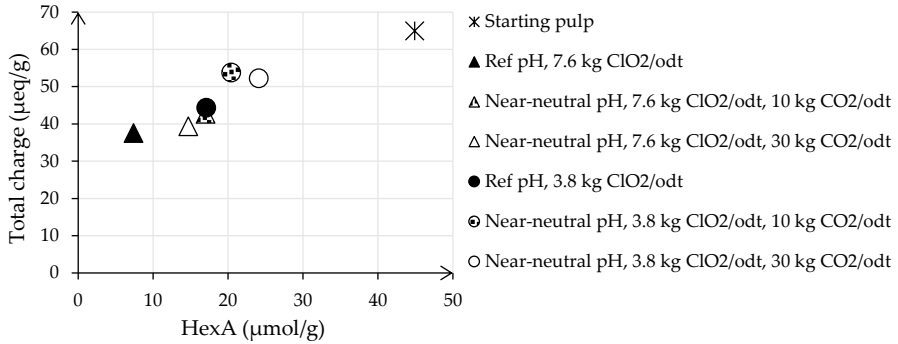


Figure 15. Correlation between HexA and total charge in the pulp after the D stage. Standard deviations for HexA contents are between 0.1 and 0.9. Standard deviations for total charges are between 0.03 and 0.84.

The degradation of HexA correlates well with the amounts of AOX formed in the D stages, Figure 16. HexA is therefore a likely contributor to the higher AOX formation in the reference samples, in accordance with results from Björklund *et al.* (2002) and Törngren and Ragnar (2002). Some studies have shown that the AOX formed from HexA is less stable than that from lignin (Björklund *et al.* 2004).

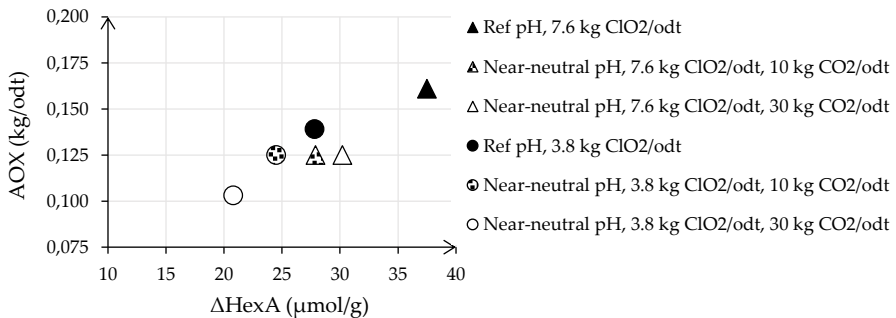


Figure 16. Correlation between the change of hexenuronic acid content in the pulps in the D stage and the AOX content in the D stage effluents.

The total amount of charged groups, mainly carboxylic acids, in the pulp after the D stage is also affected by the addition of CO<sub>2</sub>, with more charge remaining in those pulps that have been bleached with a near-neutral pH D stage. There is a correlation between the total charge and the remaining HexA in the pulps, Figure 15, indicating that it is mainly the removal of the carboxylic acid on HexA that causes the decrease of charge density.

HexA is known to cause yellowing of pulp samples (Granström *et al.* 2001). The higher HexA content in the pulp samples bleached with a near-neutral pH D stage is therefore expected to cause more yellowing than the reference pulp samples. On the other hand, the lower pH in the reference case will cause a higher occurrence of HOCl in the bleaching liquor. HOCl introduces aldehyde and keto groups in cellulose (Lewin and Epstein 1962), which are known to cause yellowing (Ahn *et al.* 2019). To quantify the yellowing issues of the samples, they were subjected to accelerated ageing for 11 days. Figure 17 shows that more thermal yellowing occurs in pulp samples bleached with a near-neutral pH D stage. The brightness loss correlates well with the HexA content in the samples.

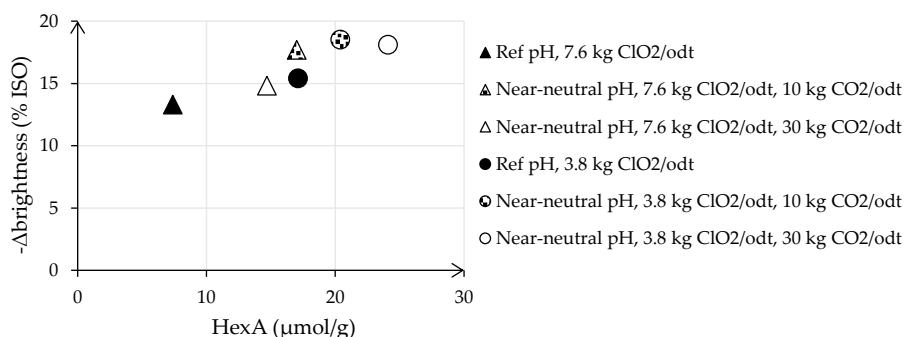


Figure 17. Correlation between the brightness loss during 11 days of thermal treatment and the content of hexenuronic acid in the pulps after D stage. Standard deviations for HexA contents are between 0.1 and 0.9

HexA groups also contribute to the kappa number. The most likely explanation for the elevated kappa numbers after near-neutral pH D stages is found in the kappa number fractionation, reported in Figure 18. It seems that even though the kappa numbers of the pulp samples bleached with a near-neutral pH D stage are higher, the residual lignin content (corrected kappa number) is not higher than for the reference case. The increased residues of HexA increase the kappa number.

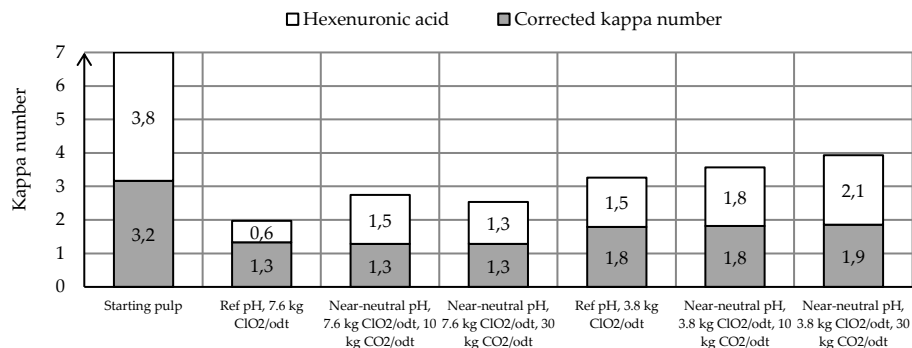


Figure 18. Contribution of HexA to the kappa number. Here, the remains of the kappa number after subtraction of HexA is labelled 'Corrected kappa number' where mainly lignin but also other structures such as carbonyls contribute.

The increased amount of HexA groups and the yellowing they cause after near-neutral pH D stage is an issue for pulp manufacturers that has to be considered. However, the raw material in this case is softwood, which in general does not contain high amounts of xylan, and in turn HexA groups, compared with hardwood. Since the HexA content is low for softwood pulp, the yellowing issues are usually not the focus of buyers. However, I would like to propose some ideas on how to reduce the HexA content in pulp bleached with a near-neutral pH D stage. An enzymatic pre-treatment with xylanase, in this case in the Q stage, is one way to reduce the xylan and HexA content in pulp prior to the D stage. Xylanase has proved to be a suitable method to remove xylan, while increasing bleachability and lowering ClO<sub>2</sub> consumption (Valls *et al.* 2010, Nie *et al.* 2015). Using acid hydrolysis can also remove the HexA groups prior to the D stage (Vuorinen *et al.* 1999).

The difference in HexA content arises in the D stage in the sequence Q(OP)D(PO). This means that the HexA groups can either be reduced before or after the D stage. If some of the HexA groups were removed before the D stage, it might mean that the effect of the near-neutral pH on AOX formation is lost or too small to be measurable. However, even though there is a correlation between HexA content reduction and AOX formation, Figure 16, other structures such as lignin could also have an impact on the reduced AOX formation of the near-neutral pH D stage.

### **3.1.4 Near-neutral pH D stage – Summary**

The results indicate that the addition of CO<sub>2</sub> can reduce AOX content in the D stage effluents by up to 30%. The brightness gain of the near-neutral pH obtained in earlier studies was not achieved here. However, the same brightness as for the reference was obtained with lower ClO<sub>2</sub> consumption. The kappa number was higher after near-neutral pH bleaching compared with the reference, correlating with the ClO<sub>2</sub> consumption. The pulp viscosity was slightly higher after a near-neutral pH D stage.

Less HexA was removed with a near-neutral pH D stage. The degradation of HexA correlated well with the AOX content in the effluents, affirming earlier theories that HexA has a major impact on AOX formation. The higher quantities of residual HexA and lignin resulted in more thermal yellowing of the pulp samples bleached with a near-neutral pH D stage.

### **3.1.5 Near-neutral pH D stage – Future research**

The above results can be applied to an intermediate D stage in an ECF bleaching sequence in a softwood kraft pulp mill. More research is needed to establish the effects of a near-neutral pH D stage on AOX formation when the D stage is at the beginning or end of an ECF sequence. Additionally, the effect of greater ClO<sub>2</sub> charges should be further investigated. The impact of the starting pH was not investigated in this study, it would be interesting to address this in future studies to better understand how the pH profile affects bleaching efficiency during a D stage. It is also important to examine which chlorinated organic compounds can be found in the D stage effluents when near-neutral bleaching is applied to evaluate their impact on the mill surroundings. After some additional laboratory studies, it would be interesting to test the near-neutral pH D stage at industrial scale to investigate if AOX is also reduced when filtrate closure, varying kappa numbers and process parameters are taken into account.

## 3.2 Bleachability in an ECF light bleaching sequence

### 3.2.1 Bleachability definition

In this study, bleachability is defined as delignifying bleachability and brightness gain bleachability. The delignifying bleachability is defined as kappa number units reduced per kilo of bleaching chemical for each stage, [1]. The brightness gain bleachability is defined as units of brightness increase per kilo of bleaching chemical for each stage, [2]. They are both devised such that a higher value means better bleachability. The pulp bleachability in the ECF light bleaching sequence Q(OP)D(PO) and preceding oxygen delignification (Ox. del.) is studied in the following chapters using these two definitions:

Delignifying bleachability:

$$\frac{-(\text{kappa number of pulp after stage } X - \text{kappa number of pulp before stage } X)}{\text{Charge bleaching chemical in stage } X \text{ [kg/odt]}} \quad [1]$$

Brightness gain bleachability:

$$\frac{\text{ISO brightness of pulp after stage } X \text{ [% ISO]} - \text{ISO brightness of pulp before stage } X \text{ [% ISO]}}{\text{Charge bleaching chemical in stage } X \text{ [kg/odt]}} \quad [2]$$

### 3.2.2 Effect of unbleached kappa number on bleaching

Three softwood kraft pulp samples with brown stock kappa numbers 27, 32 and 35 were bleached and analysed with regard to yield, pulp viscosity, carbohydrate content and brightness ceiling. In combination with the bleachability results, the aim was to determine the best suited kappa number of the three samples for this particular bleaching sequence. The study is illustrated in Figure 19.

The bleaching results are summarized in Table 5. The difference in the unbleached kappa number between the three pulp samples was gradually reduced throughout the bleaching sequence to imitate pulp mill practice. During the oxygen delignification, kappa number reductions between 60.2% and 61.1% were obtained. Instead of aiming at the same kappa number after oxygen delignification for the three pulp samples, the desired degree of delignification was set at 60%, which resulted in varying kappa numbers. This figure was chosen to maintain high selectivity during delignification. The oxygen delignification of K35 would otherwise have to be carried out under very harsh conditions to reach the same kappa number as K27. This would

probably have caused unnecessary viscosity loss (Annergren *et al.* 1998, Poukka *et al.* 1999). In the OP stage, the hydrogen peroxide charge was varied to ensure a similar incoming kappa number for the D stage. This was achieved with kappa numbers between 6.9 and 7.9 after the OP stage.

Unbleached softwood kraft pulp	Ox. del. 60% kappa reduction	OP	D	PO	
K27	K27 Ox. del.	K27 OP	K27 D	K27 PO 2 K27 PO 3.5 K27 PO 5 K27 PO 10 K27 PO 15	Interpolation K27 PO 88
K32	K32 Ox. del.	K32 OP	K32 D	K32 PO 2 K32 PO 3.5 K32 PO 5 K32 PO 10 K32 PO 15	Interpolation K32 PO 88
K35	K35 Ox. del.	K35 OP	K35 D	K35 PO 2 K35 PO 3.5 K35 PO 5 K35 PO 10 K35 PO 15	Interpolation K35 PO 88

Figure 19. Schematic illustration of pulp samples and laboratory procedure. The digit after PO is the H<sub>2</sub>O<sub>2</sub> charge. PO 88 are values interpolated to 88% ISO.

Table 5. Bleaching results – kappa number, brightness and intrinsic viscosity. The digit after PO is the hydrogen peroxide charge. PO 88 represents the interpolated values calculated for 88% ISO.

Pulp	Unbleached	Ox. del.	OP	D	PO 2	PO 3.5	PO 5	PO 10	PO 15	PO 88
Kappa number										
K27	26.6	10.6	6.9	1.7	0.64	0.58	0.58	0.51	0.48	0.62
K32	31.9	12.4	7.1	1.7	0.66	0.61	0.57	0.53	0.49	0.65
K35	34.9	13.6	7.9	2.0	0.84	0.79	0.73	0.67	0.65	0.80
Brightness (% ISO)										
K27	29.5	41.7	59.9	73.4	87.3	88.7	89.6	90.8	92.0	88.0
K32	26.8	40.2	65.6	75.6	87.6	89.4	90.6	91.5	92.3	88.0
K35	27.8	40.0	67.5	75.3	86.9	88.4	89.3	91.3	91.9	88.0
Viscosity (ml/g)										
K27	1091	910	877	863	854	841	819	748	784	848
K32	1123	918	887	875	853	845	831	775	791	851
K35	1085	914	872	858	831	798	777	716	635	806

The pulp brightness was consistently increased throughout the fibre line. In the OP stage however, the brightness increased unevenly across the three pulp samples, Figure 20. Since a higher dosage of H<sub>2</sub>O<sub>2</sub> was needed to reach a kappa number of around 7 for K35, the highest brightness increase was observed in this pulp. However, the viscosities were similar for all the pulp samples after the OP stage, Figure 21. Here an advantage emerges with ending the cook at a higher kappa number: a brighter pulp can be obtained after OP when compared at the same kappa number and viscosity. This is in accordance with earlier studies that achieved similar results. Rööst *et al.* (2000) observed higher brightness after oxygen delignification when comparing the same kappa number and viscosity.

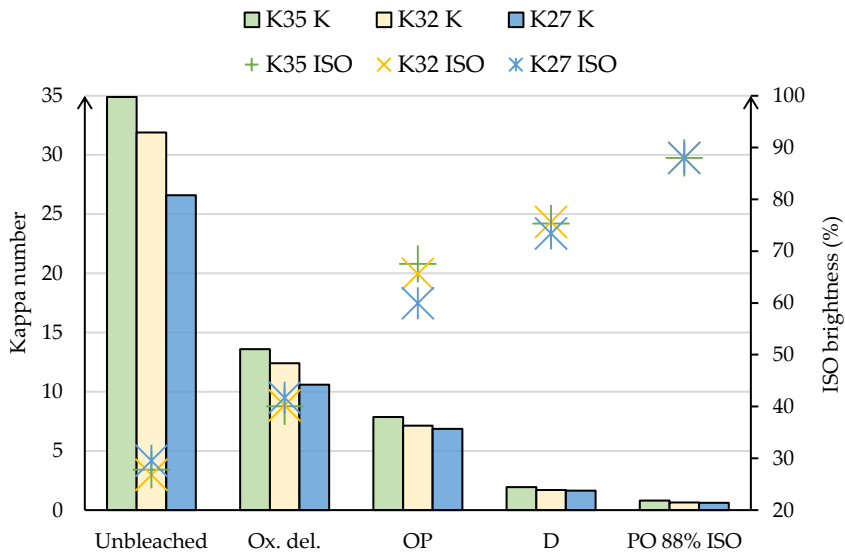


Figure 20. Kappa number (K) and brightness (ISO) development through the fibre line to PO 88% ISO

The intrinsic viscosities were reduced as the brightness and number of bleaching stages increased, Figure 21. The viscosity was similar for the three unbleached pulp samples, which followed the same reduction pattern through oxygen delignification and the OP stage. After the D stage, there was evidence that K32 had a higher viscosity than the other two pulp samples.

After bleaching to full brightness, it was clear that the pulp with the lowest intrinsic viscosity was K35. Contrary to expectations (Hart and Connell 2006), it seems that this pulp is more liable to viscosity loss during the PO stage. The unexpected viscosity loss could be explained by a difference in the metal ion profile in the pulp samples. Manganese, copper and iron ions are detrimental to the OP/PO stages, reacting with superoxide anions and forming hydroxyl radicals (Dence and Reeve 1996). However, it seems that metal ions are not the reason for the viscosity loss observed for K35 in the PO stage since the transition metal ion contents in the pulp samples were similar after the D stage, Table 6. Furthermore, the addition of magnesium sulfate is a mitigating factor of this effect.

Another possible explanation for the viscosity loss of K35 is that this bleaching sequence is not potent enough to reduce the higher unbleached kappa number at 35 without overcharging the bleaching chemicals and damaging the fibres. With regard to intrinsic viscosity, the preferred unbleached kappa number of the three pulp samples is 32, which could represent an optimum value. A similar optimum value was found by Poukka *et al.* (1999) for D(EOP)DD-bleached softwood kraft pulp but at a higher kappa number.

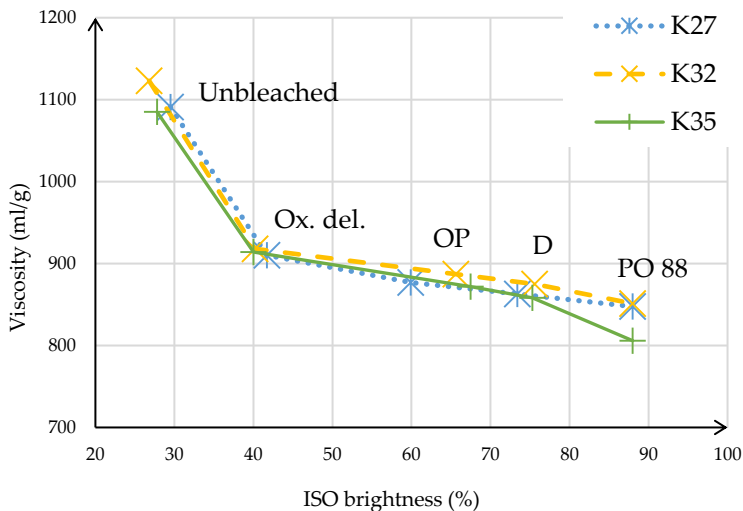


Figure 21. Intrinsic viscosity and brightness through the fibre line to 88% ISO



Table 6. Metal ion content in pulp samples (mg/kg)

Pulp	After Q stage			After D stage		
	Fe	Mn	Cu	Fe	Mn	Cu
K27	3.9	0.7	<0.1	3.6	0.06	<0.1
K32	3.1	0.5	<0.1	3.8	0.05	<0.1
K35	5.0	0.7	<0.1	3.7	0.06	<0.1

After bleaching with varying hydrogen peroxide charges in the last stage, PO, the brightness ceiling for each pulp was obtained, Figure 22. It seems the brightness ceiling is highest for K32, although the difference between the three pulp samples is very small. Since K32 and K35 have a higher brightness after the D stage compared with K27 (due to previously mentioned higher hydrogen peroxide charge in the OP stage), they will preserve a higher brightness after the PO stage at a given charge and also a higher brightness ceiling.

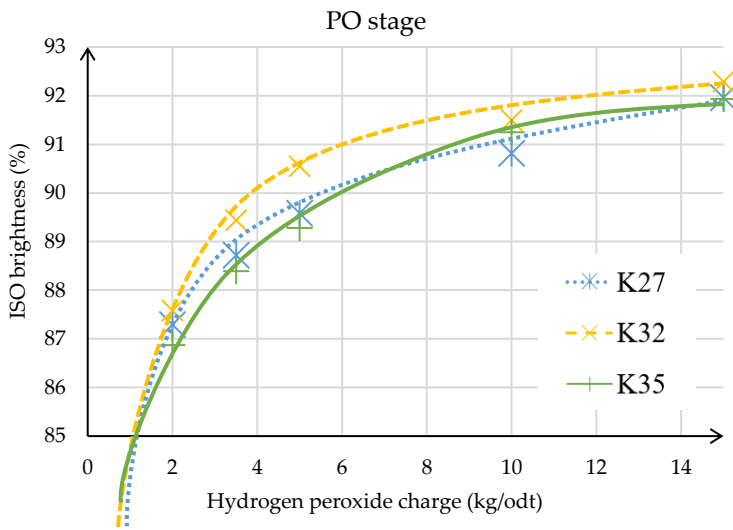


Figure 22. Brightness development in the PO stage

The brightness stability is presented in Figure 23. In accordance with the literature, it was found that pulp samples with a lower unbleached kappa number had a higher brightness stability (Rööst *et al.* 2000). The difference in brightness stability between the samples was large after the OP stage; this reduced after the D stage and was small after the PO stage.

The difference in brightness stability is most likely due to differences in lignin and HexA content. H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> cannot degrade HexA, which means that the differences in HexA as a result of the cook are still present in the pulp samples and affect the brightness stability after the OP stage (Table 7). The HexA content in K35 and K32 are similar after oxygen delignification and the OP stage. However, there is more lignin left in K35, increasing brightness loss for that sample.

After the D stage, the difference in brightness stability between the samples is reduced. The explanation for this is that ClO<sub>2</sub> can degrade lignin and HexA, *i.e.* remove some of the structures that cause brightness loss. However, the HexA content in the samples after the D stage varied between 4.2 and 6.5, with more HexA left in K35 than K32. This could be due to small variations in the final pH in the D stage. Due to limits in the kappa number measurement, the HexA content of the samples after the PO stage was not measured. However, the small variations in brightness stability after the PO stage is most likely due to lingering variations in residual lignin and HexA content.

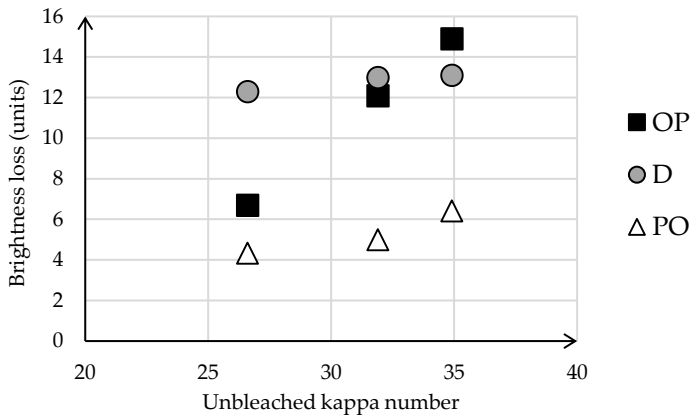


Figure 23. Brightness loss after treatment for seven days, for OP, D and PO pulp samples. PO samples were chosen at ca 88% ISO (K27 PO 3.5, K32 PO 2, K35 PO 3.5).

Table 7. Hexenuronic acid content in pulp samples (µml/g)

Pulp	Ox. del.	OP	D
K27	29.1	30.6	4.2
K32	38.1	37.3	4.5
K35	37.7	37.8	6.5

### **3.2.3 Effect of unbleached kappa number on bleachability**

The bleachability results for the three pulp samples with varying unbleached kappa numbers are presented in Tables 8-9 and Figures 24-25. The pulp samples were collected at similar residual and effective alkali levels during cooking to ensure this parameter would not influence bleachability. The temperature and final pH in the laboratory bleaching stages were kept at the same levels for all pulp samples (see Table 3 for more bleaching parameters) so as not to have an impact on bleaching efficiency. However, pulp mills are very complex and there is no guarantee that the unbleached kappa number is the only parameter with an effect on bleachability that varied during the sampling.

The results in Table 8 show that the chemical charge and sum of OXE increase as the kappa number increases. This was expected, as a higher dosage of  $H_2O_2$  is needed to reduce the higher kappa numbers. Overall OXE bleachability is improved by a higher unbleached kappa number, as seen in many previous studies. However, in the OXE calculations, the residual chemicals were not taken into account, due to a lack of equipment to measure residual  $O_2$ . Instead, the total charges of bleaching chemicals were used. Since an excess of  $O_2$  is used in the laboratory method, the  $O_2$  charges are extreme. Hence, the sum of OXE is large. In addition, the OXE bleachability does not take into account the fact that the bleaching chemicals react in different ways with the pulp.

Instead, bleachability will hereafter be evaluated as delignifying bleachability and brightness gain bleachability. With these definitions, it is possible to compare the effect of different stages and adjust the bleach plant parameters according to the delignifying or brightness gain target for the product. The results in Table 9 show that in the bleaching stages that are highly delignifying (oxygen delignification and D stage), a higher unbleached kappa number is beneficial to delignifying bleachability. In the bleaching stages where the objective is mainly brightness increase (OP and PO), a lower unbleached kappa number is preferable for brightness gain bleachability.

Table 8. Chemical charges in oxygen delignification and bleaching to 88% ISO. For the OXE calculation, 74.12 OXE/kg ClO<sub>2</sub>, 58.79 OXE/kg H<sub>2</sub>O<sub>2</sub> and 125.0 OXE/kg O<sub>2</sub> were used (Grundelius 1993).

Stage	Chemical		K27	K32	K35
Ox. del.	O <sub>2</sub>	kg/odt	155	155	155
	NaOH	kg/odt	26	31	30
OP	O <sub>2</sub>	kg/odt	77.5	77.5	77.5
	H <sub>2</sub> O <sub>2</sub>	kg/odt	3	6	8
D	ClO <sub>2</sub>	kg/odt	8	8	8
PO	O <sub>2</sub>	kg/odt	77.5	77.5	77.5
	H <sub>2</sub> O <sub>2</sub>	kg/odt	2.3	2.7	3.1
∑OXE	OXE/odt		39654.5	39854.4	39995.5
OXE/Δkappa number	OXE/odt.ΔK		1525.2	1277.4	1172.9

Table 9. Bleachability results, including summary of bleachability results.

A higher unbleached kappa number is positive (+), negative (-) or neutral (/) for the bleachability.

Pulp	Ox. del.	OP	D	PO 2	PO 3.5	PO 5	PO 10	PO 15
Delignifying bleachability (-Δkappa number/kg bleaching chemical)								
	NaOH	H <sub>2</sub> O <sub>2</sub>	ClO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>
K27	0.62	1.23	0.65	0.53	0.32	0.22	0.12	0.08
K32	0.63	0.88	0.68	0.52	0.31	0.23	0.12	0.08
K35	0.71	0.71	0.74	0.58	0.35	0.25	0.13	0.09
Brightness gain bleachability (ΔISO brightness/kg bleaching chemical)								
	NaOH	H <sub>2</sub> O <sub>2</sub>	ClO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>
K27	0.47	6.07	1.69	6.95	4.37	3.24	1.74	1.24
K32	0.43	4.23	1.25	6.00	3.94	3.00	1.59	1.11
K35	0.41	3.44	0.98	5.80	3.74	2.80	1.60	1.11

The DRUVIS reflectance spectra, Figures 26-27, are helpful for visualizing the overall performance of the bleaching sequence. When presented as the difference between spectra, Table 10, where the spectrum of the preceding pulp is subtracted from the spectrum after a given stage, the bleaching work of a given stage can be quantified.

### 3.2.3.1 Oxygen delignification

During oxygen delignification, delignifying bleachability is slightly improved with a higher unbleached kappa number, Figure 24. The NaOH charge was the lowest for K27, as was expected due to its lowest kappa number reduction. However, the NaOH charge was slightly higher for K32 than K35, even

though the kappa number reduction was lower for K32 than K35. This resulted in better delignifying bleachability for K35 than K32. This is also visible in the DRUVIS difference data in Table 10, where the removal of lignin is greater for K35 than K32.

The unbleached kappa number does not affect the brightness gain bleachability during oxygen delignification, Figure 25. This is expected since the main objective of the oxygen delignification stage is not brightness increase. Oxygen oxidizes deprotonated phenolic structures in the lignin, depolymerizing and increasing hydrophilicity via the formation of superoxide anion,  $O_2 \bullet$ . Brightness improvement is moderate but occurs when superoxide anion is turned into  $H_2O_2$ .

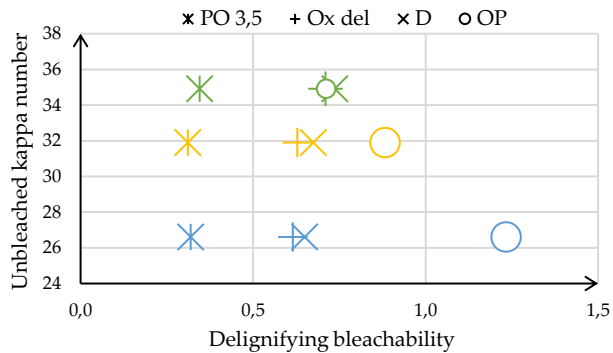


Figure 24. Effect of unbleached kappa number on delignifying bleachability. A higher bleachability value means better bleachability.

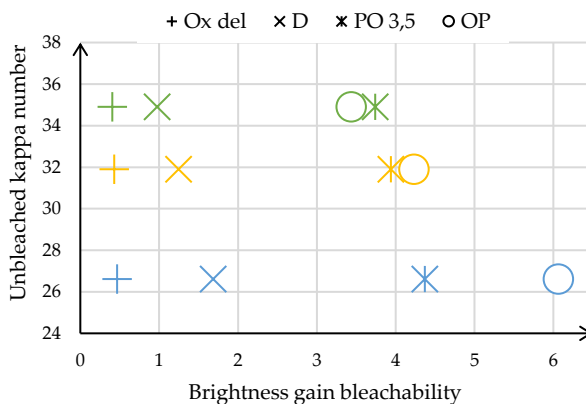


Figure 25. Effect of unbleached kappa number on brightness gain bleachability. A higher bleachability value means better bleachability.

### 3.2.3.2 OP stage

In the OP stage, delignifying and brightness gain bleachability is better with a lower unbleached kappa number. The hydroperoxide anion,  $\text{HOO}^-$ , attacks and eliminates coloured structures in the lignin and depolymerizes phenolic lignin structures. In combination with  $\text{O}_2$ , the objectives of this stage are both delignification and brightness increase. In Table 10, it can be seen that the lower  $\text{H}_2\text{O}_2$  charge for K27 resulted in a lower bleaching effect (lower negative values for both HexA and lignin) in the OP stage than for the other two pulp samples. However, it seems that a lower charge is beneficial for bleachability in this stage.

One possible reason for the differences in bleachability between the pulp samples in the OP stage is the variation in the metal ion content after the Q stage (Table 6). However, the differences are small and this is most likely not the complete explanation. The differences in HexA content in the pulp samples after oxygen delignification, Table 7, could also affect bleachability. A high HexA content will retain more metal ions in the pulp, decreasing the selectivity of the OP stage. Whether the decreased bleachability at higher unbleached kappa numbers depends on HexA and lignin structures or harmful metal ions in the pulp is unknown. However, it seems that the higher  $\text{H}_2\text{O}_2$  charge used in the OP stage to compensate kappa number 35 was an overcharge.

### 3.2.3.3 D stage

In the D stage, the delignifying bleachability is slightly improved with a higher kappa number, and brightness gain bleachability is better with a lower kappa number.  $\text{ClO}_2$  reacts fast with phenolic lignin structures and slowly with non-phenolic lignin structures, and it can degrade HexA (Bergnor-Gidnert *et al.* 1998) and increase brightness via chlorination of double bonds.  $\text{ClO}_2$  works as a radical scavenger, so the selectivity of the D stage remains very high. Even though this D stage is an intermediate D stage, it is more delignifying than one might expect, with kappa number reductions of about 20% for all pulp samples. This is due to the low final pH of the D stage, which in this study was kept at pH 3. An intermediate D stage such as this can be used to manage changes in the bleaching process, such as varying incoming kappa numbers or lack of brightness. It is not a designated delignifying stage such as a  $\text{D}_0$  stage but can be used in favour of delignification when needed.

### 3.2.3.4 PO stage

In the PO stage, brightness gain bleachability (compared at H<sub>2</sub>O<sub>2</sub> charge of 3.5 kg/odt) is better with a lower unbleached kappa number. The delignifying bleachability in PO is the same for all pulp samples and is the lowest for all bleaching stages, which is expected since the objective of the final bleaching stage is brightness increase and to reduce brightness reversion of the product. According to the DRUVVIS difference data in Table 10, the PO stage of K27 is the most effective and the PO stage of K35 the least effective of the three pulps.

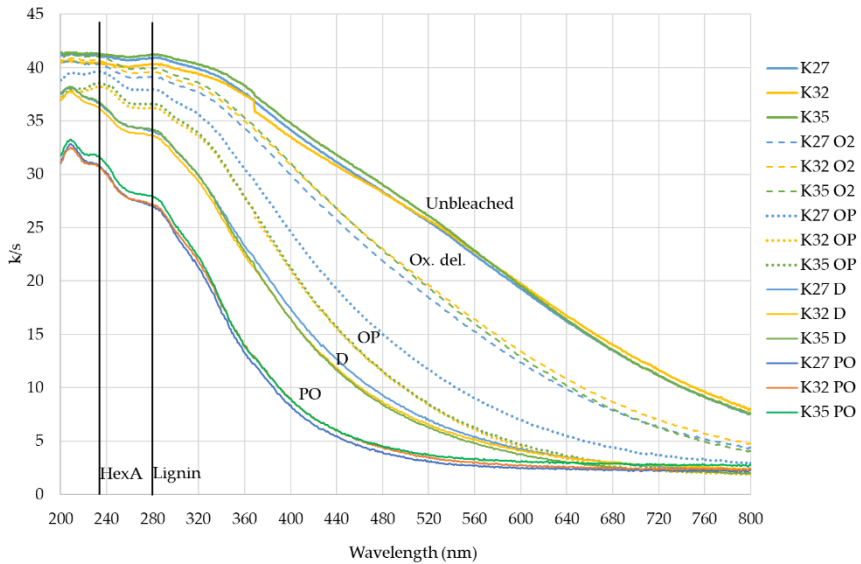


Figure 26. DRUVVIS reflectance spectra, development of bleaching

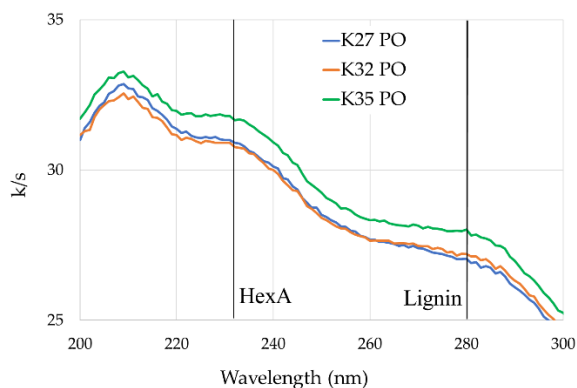


Figure 27. DRUVIS reflectance spectra. PO samples at ca 88% ISO (K27 PO 3.5, K32 PO 2, K35 PO 3.5).

Table 10. Difference between spectra before and after a given stage, for wavelengths 232 and 280 nm, which corresponds to HexA and lignin. *E.g.* the spectrum of an unbleached pulp is subtracted from the spectrum of the following oxygen delignified pulp to give the difference spectra, *i.e.* the bleaching work, of the oxygen delignification for that pulp. The values are then read from the difference spectra at 232 and 280 nm.

$\Delta(k/s)$	HexA (232 nm)				Lignin (280 nm)			
	Ox.del.	OP	D	PO	Ox.del.	OP	D	PO
K27	-0.8	-0.7	-2.9	-5.9	-1.8	-1.2	-3.9	-7
K32	0	-2.5	-2.0	-5.5	-0.8	-3.4	-2.5	-6.3
K35	-0.3	-2.5	-1.6	-5.2	-1.3	-3.4	-2.4	-6.3



### 3.2.4 Yield gain with a higher kappa number?

Bleached pulp yield plays an important role in the total bleached pulp cost. For bleachable pulp grades, the idea is to avoid the residual delignification phase of the cooking, where the selectivity for lignin removal is lost (MacLeod 2007). The gravimetric yield is given in Table 11. In accordance with earlier work, a higher unbleached kappa number resulted in a higher yield (Bergnor *et al.* 1988, Annergren *et al.* 1998, Poukka *et al.* 1999), as less lignin and hemicelluloses were removed from the wood. In the oxygen delignification, a higher unbleached kappa number resulted in a lower yield, as a constant delignification degree at 60% means more lignin is removed. The bleaching yield follows the same pattern, with lower yields for the samples with higher unbleached kappa numbers.

The question regarding yield is: Will the higher yield obtained in the cook with the higher unbleached kappa number be maintained throughout this particular bleaching sequence? For the sequence (OO)Q(OP)D(PO), the yield gain from cooking for kappa number 35 does not seem to be preserved after the bleaching. However, the results indicate that K32 obtains a higher total yield after the bleaching than K27, *i.e.* it seems there is an optimum total pulp yield around kappa number 32 for this bleaching sequence.

Table 11. Gravimetric yield for cook, oxygen delignification and bleaching to 88% ISO (%)

Sample	Cook	Ox. del. ±0.02	Bleaching ±0.07	Total
K27	44.9	96.6	96.6	41.9
K32	46.5	95.9	96.6	43.1
K35	47.5	95.6	94.1	42.7

The gravimetric yield is supported by the chemical composition, given in Table 12. As expected for unbleached pulp samples, a lower kappa number correlates with less hemicellulose in relation to cellulose, as the cook is driven longer and degrades more lignin and hemicellulose, in accordance with Esteves *et al.* (2021). However, after bleaching, the pulp with the most hemicellulose in relation to cellulose is K32, not K35. It seems this bleaching sequence cannot maintain the higher hemicellulose content that was achieved after the cook, as the higher lignin content of K35 required a high bleaching chemical charge to reach a sufficiently high brightness.

Table 12. Chemical composition, per cent of pulp and ratio of hemicellulose to cellulose for unbleached and bleached pulp at ca 88% ISO

Sample	Cellulose	Glucos- mannan	Xylan	Galacto- glucomannan	Lignin	Hemi/cell
K27	79.0	7.7	8.9	0.3	4.1	0.215
K32	78.0	7.6	9.1	0.4	4.9	0.220
K35	77.4	7.8	9.0	0.4	5.3	0.223
K27 PO 3.5	82.6	8.1	9.0	0.2	0.1	0.209
K32 PO 2	82.3	8.1	9.3	0.2	0.1	0.214
K35 PO 3.5	82.7	7.8	9.2	0.2	0.1	0.208

### 3.2.5 Unbleached kappa number for (OO)Q(OP)D(PO) – Summary

In this study the bleaching efficiency between three brown stock softwood kraft pulp samples with kappa numbers of 27, 32 and 35 were compared. According to the results, the ECF light bleaching sequence (OO)Q(OP)D(PO) is most effective with a kappa number around 32. Although a higher kappa number than 32 resulted in a higher yield after cooking, it seems that this bleaching sequence cannot preserve the yield gain. Out of the three pulp samples, kappa number 32 also gave the best results with respect to brightness ceiling and viscosity. This kappa number region has also been found to be beneficial for other bleaching sequences with similar brightness targets (Annergren *et al.* 1998, Poukka *et al.* 1999, Hart and Connell 2006). On the other hand, in this study, kappa number 27 was most favourable with regard to yellowing and chemical charge.

Increasing the unbleached kappa number has traditionally proven to be beneficial for yield and fibre strength (MacLeod 2007). However, eventually the kappa number limit will be reached, at which point increasing the kappa number is no longer beneficial; bleaching cannot preserve the yield gains. It is likely that for ECF light sequences this limit is reached earlier (in terms of kappa number) than for traditional ECF sequences. Lower charges of delignifying bleaching agents (*i.e.* ClO<sub>2</sub>) means that less residual lignin can be removed. Even though oxygen and hydrogen peroxide can also degrade and dissolve lignin to some extent, delignification is not as selective when the sequence contains fewer bleaching agents (Annergren *et al.* 1998). It could be that the 'lighter' (*i.e.* the lower the ClO<sub>2</sub> charges) the ECF, the lower the optimal unbleached kappa number.

### **3.2.6 Bleachability – Future research**

The results of the bleachability study can be applied to the ECF light bleaching sequence (OO)Q(OP)D(PO) in a softwood kraft pulp mill. Here, we have established how the unbleached kappa number influences bleachability for this particular sequence. It would be interesting to investigate if the same results were obtained for other ECF light sequences.

Other parameters than the unbleached kappa number can be varied and investigated in terms of their effect on bleachability. For example, the kappa number after the oxygen delignification or OP stage would be interesting to investigate with regard to bleachability. As mentioned above, it might be that the 'lighter' the ECF sequence, the lower the optimal unbleached kappa number. Therefore, it might be interesting to try varying ClO<sub>2</sub> charges. How other raw materials, for example hardwoods, affect ECF light bleachability can also be studied.

As analytical methods improve, it will be easier to study the chemical structures of lignin. It would be interesting to look deeper into the chemical structures and try to find correlations between the structures and bleachability. What type of lignin bonds or lignin-carbohydrate complexes influence the bleaching efficiency and, in particular, the separate bleaching stages?

## 4 Conclusions

The aim of this work is to contribute to the process development of the ECF light bleaching sequence Q(OP)D(PO) by providing a better understanding of bleaching of softwood kraft pulp. The main conclusions from this work are listed below.

- Using a pH buffer to stabilize pH at near-neutral during a D stage can lower AOX formation without altering bleaching efficiency. A near-neutral pH decreases the formation of strongly chlorinating species so that the AOX content in the bleaching effluent is reduced by up to 30%.
- A D stage with a near-neutral pH can be achieved with the addition of CO<sub>2</sub>, which generates a bicarbonate buffer *in situ*, stabilizing the pH at near neutral during bleaching.
- The increased pH in the near-neutral pH D stage reduces ClO<sub>2</sub> consumption, resulting in a higher kappa number and viscosity. The degradation of HexA correlates well with the AOX content in the effluents, affirming earlier theories that HexA has an important impact on AOX formation.
- Delignifying and brightness gain bleachability can be used to separately evaluate the bleachability of the stages in a bleaching sequence so that it is possible to distinguish the bleaching efficiency in each stage.
- For this particular ECF light sequence, the bleachability depends on the purpose of the stage. In the stages that are highly delignifying (OO and D), a higher unbleached kappa number is beneficial to the delignifying bleachability, although brightness gain is not improved. However, in the stages that are highly brightness increasing (OP and PO), brightness gain bleachability is improved by a lower unbleached kappa number.
- The bleaching of three softwood kraft pulp samples with the ECF light sequence is most effective for a brown stock kappa number around 32. Although a higher kappa number than 32 resulted in higher yield after cooking, it seems that this bleaching sequence cannot preserve the yield gain. Kappa number 32 also gave the best results in regard to brightness ceiling and viscosity. On the other hand, kappa number 27 was the most favourable with regard to yellowing and chemical charge.

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