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**VIPP** VALUES CREATED IN  
FIBRE-BASED PROCESSES  
AND PRODUCTS

Caroline Wilke

# The Impact of Dissolved Matter on Fiberline Processes



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Faculty of Health, Science and Technology

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Chemical Engineering

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DOCTORAL THESIS | Karlstad University Studies | 2018:29

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## **Abstract**

The impact of dissolved matter on the performance of four fiberline process stages was investigated: oxygen delignification, hot acid treatment, chlorine dioxide bleaching, and hydrogen peroxide reinforced alkaline extraction. In particular the impact on delignification due to dissolved lignin was studied.

The impact of unoxidized and oxidized dissolved matter on lignin and carbohydrate degradation was investigated in a laboratory oxygen delignification stage. It was concluded that the delignification was decreased by the presence of unoxidized dissolved matter but increased in the case of oxidized dissolved matter. Both types of dissolved matter comparably increased the carbohydrate degradation. Thus, the presence of unoxidized dissolved matter impaired the selectivity. In the case of oxidized dissolved matter, the selectivity was affected in the same way as when using a higher sodium hydroxide charge.

The presence of dissolved matter reduced the efficiency of a laboratory hot acid stage, and subsequently further affected the chemical demand in a following chlorine dioxide stage. In a laboratory chlorine dioxide stage, the presence of dissolved matter reduced the delignification. The additional chemical demand required to compensate for this reduction was proportional to the content of dissolved matter. Moreover, the total chemical demand was found proportional to the total kappa number of the pulp, that is the sum of the fiber and filtrate kappa numbers. Finally, the presence of dissolved matter in a laboratory hydrogen peroxide reinforced alkaline extraction stage reduced both the delignification and the brightness.

Furthermore, mill studies showed that the content of dissolved lignin varied significantly, and often more than the fiber-bound lignin, in a bleaching stage. For chlorine dioxide stages, it was proposed that the chemical consumption could be reduced by controlling the chemical charge based on the sum of the fiber-bound lignin and the dissolved lignin.

## Sammanfattning

Utlöst material i massasuspensionen påverkar effektiviteten av processtegen i ett massabruk. De fyra processteg som undersöktes närmare i detta projekt var syrgasdelignifiering, klordioxidblekning, varmt syrasteg och alkaliskt extraktionssteg förstärkt med väteperoxid. Huvudsyftet var att undersöka hur delignifieringen påverkades av utlöst material, framförallt utlöst lignin, i olika laboratoriestudier.

I ett syrgassteg undersöktes effekten av ooxiderat och oxiderat utlöst material på lignin- och cellulosedbrytningen. Delignifieringen minskade av ooxiderat utlöst material medan den ökade av oxiderat utlöst material. Cellulosedbrytningen ökade dock av båda typerna av utlöst material. Selektiviteten påverkades således negativt av ooxiderat utlöst material medan den påverkades på samma sätt som ökad natriumhydroxidsats av oxiderat utlöst material.

Utlöst material reducerade effektiviteten av ett varmt syrasteg och påverkade således även kemikaliebehovet i ett efterföljande klordioxidsteg. Utlöst material i ett klordioxidsteg minskade delignifieringen. Det högre kemikaliebehovet som krävdes för att kompensera för denna reduktion var proportionellt mot halten utlöst material. Dessutom var det totala kemikaliebehovet proportionellt mot det totala kappatalet, alltså summan av fiber- och filtratkappatalen. Slutligen minskade både delignifieringen och ljusheten av utlöst material i ett alkaliskt extraktionssteg förstärkt med väteperoxid.

Vidare visade fabriksstudier i ett bleksteg att halten utlöst lignin varierade mycket och ofta mer än det bundna ligninet i fibrerna. Om kemikaliesatsen i ett klordioxidsteg baseras på summan av det bundna ligninet i fibrerna och det utlösta ligninet, mätt som totalt kappatal, skulle kemikaliebehovet kunna minskas.

## List of Publications

This thesis is based upon the following six papers, referred to by the Roman numerals I-VI. The papers are summarized in section 8 and included as appendices. Apart from the results presented in Papers I-VI, additional data are also presented in section 4.

- I **A new sensor and a novel control concept for optimized fiber line operation**  
Niclas Andersson, Caroline Wilke, Tom Biazzo, Rick van Fleet and Ulf Germgård  
*Tappi Journal 13(10): p. 39-45 (2014)*
  
- II **Impact of dissolved lignin in oxygen delignification and chlorine dioxide stages**  
Caroline Wilke, Niclas Andersson, Rick van Fleet, Akhlesh Mathur and Ulf Germgård  
*Tappi Journal 15(3): p. 167-174 (2016)*
  
- III **Impact of dissolved matter in the oxygen delignification stage**  
Caroline Wilke, Niclas Andersson and Ulf Germgård  
*Tappi Journal 16(5): p. 275-284 (2017)*
  
- IV **Oxygen delignification – Laboratory evaluation of the impact of dissolved organic matter, sodium carbonate and sodium thiosulfate**  
Caroline Wilke, Niclas Andersson and Ulf Germgård  
*Submitted for publication*
  
- V **Impact of dissolved organic matter in D<sub>0</sub>- and AD<sub>0</sub>-stages in bleaching of birch kraft pulp**  
Caroline Wilke, Niclas Andersson and Ulf Germgård  
*Submitted for publication*

## VI **Impact of dissolved organic matter in hydrogen peroxide reinforced alkaline extraction stages**

Caroline Wilke, Niclas Andersson and Ulf Germgård

*Submitted for publication*

### **Related publications**

- **Dissolved lignin in the fiber line pulp slurry – A parameter of great importance**  
Caroline Wilke  
*3<sup>rd</sup> Avancell Conference, Gothenburg, Sweden: p. 47-50 (2013)*
- **Dissolved lignin in the pulp slurry can significantly increase the consumption of ClO<sub>2</sub> in a D<sub>0</sub>-stage**  
Caroline Wilke, Niclas Andersson and Ulf Germgård  
*International Pulp Bleaching Conference, Grenoble, France: p. 222-227 (2014)*
- **Dissolved lignin in the pulp slurry consumes ClO<sub>2</sub> in proportion to its kappa number in a D<sub>0</sub>-stage**  
Caroline Wilke  
*FPIRC International Summer Conference, Grenoble, France: p. 59-61 (2015)*
- **Measurement of dissolved lignin, and its impact in fiberline unit operations**  
Niclas Andersson, Caroline Wilke, Akhlesh Mathur, Dan Smith and Ulf Germgård  
*International Pulp Bleaching Conference, Porto Seguro, Brazil: p. 88-94 (2017)*

## **The Author's Contribution**

- I Performed the experimental work and interpreted the results. The article was written in collaboration with the co-authors.
- II Performed the experimental work and interpreted the results. The majority of the writing was undertaken by the principal author, in collaboration with the co-authors.
- III Performed the experimental work and interpreted the results. The majority of the writing was undertaken by the principal author, in collaboration with the co-authors.
- IV Performed the experimental work and interpreted the results. The majority of the writing was undertaken by the principal author, in collaboration with the co-authors.
- V Performed the experimental work and interpreted the results. The majority of the writing was undertaken by the principal author, in collaboration with the co-authors.
- VI Performed the experimental work and interpreted the results. The majority of the writing was undertaken by the principal author, in collaboration with the co-authors.

## Abbreviations

AOX	Adsorbable Organic Halogen
A-stage	Hot acid stage
ClO <sub>2</sub>	Chlorine dioxide
CO <sub>3</sub> <sup>2-</sup>	Carbonate ion
COD	Chemical Oxygen Demand
D <sub>0</sub> -stage	First chlorine dioxide stage
ECF	Elemental Chlorine Free
(EP)-stage	Hydrogen peroxide reinforced alkaline extraction stage
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
HexA	Hexenuronic acid
HS <sup>-</sup>	Hydrogen sulfide ion
HW	Hardwood
NaOH	Sodium hydroxide
O <sub>2</sub>	Oxygen
O <sub>2</sub> -stage	Oxygen delignification stage
OH <sup>-</sup>	Hydroxide ion
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	Thiosulfate ion
SW	Softwood
TCF	Totally Chlorine Free

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# 1 Background

The pulp, paper and board industries annually produce about 180 million tons of pulp and 410 million tons of paper and board, both from virgin and recycled fibers [1, 2]. The investment capital of a new pulp and paper mill is 2-3 billion USD, and with an annual production of 1-2 million tons, it is important for the mills to be very cost effective [3]. It is well-known that the processes used in the pulp industry are demanding with respect to the consumption of chemicals, water and energy. Pulp mills employ different control strategies to decrease the consumption of raw materials while still maintaining a high quality of their products. Relatively small savings of chemicals, water and energy, per ton of pulp, will make a significant difference on an annual basis, thus heightening the need for reliable and accurate measurements.

To operate a pulp mill in an efficient manner, it is imperative to identify the key process parameters, and base process control solutions on those variables. Residual lignin is one of the most important parameters in chemical pulping since lignin acts as a glue that binds the cellulose and the hemicellulose together. Thus, the lignin needs to be degraded and dissolved to liberate the cellulose and hemicellulose fibers [4-7]. Most mills base their process control on measurements of only the content of the fiber-bound lignin. The degraded and dissolved lignin residues and other dissolved substances in the pulp slurry are merely seen as a disturbance and are not measured directly. Studies have however shown that dissolved matter, especially dissolved lignin, also consumes bleaching chemicals [8-16].

A satisfactory way to continuously measure the dissolved lignin content is thus needed for mills to charge the correct amount of bleaching chemicals to obtain a desired final brightness. By not measuring the dissolved lignin content, pulp mills underestimate the total bleaching chemical demand. Even though studies have shown that the most important dissolved component to measure is dissolved lignin, there has hitherto been no sensors available on the market that directly measures that parameter [17-21].

## 1.1 Wood composition

Wood is a heterogeneous material mainly composed of cellulose, hemicellulose, lignin and extractives. The relative composition of the organic components, shown in Table 1, varies between species, and is dependent on for example the place of growth and the age of the tree. Inorganic components, such as carbonates, phosphates and various cations like calcium, sodium and iron, are also present in wood in small amounts [6, 22-25].

*Table 1: Chemical composition of wood, measured as percentage [6, 22-25].*

Component	Softwood	Hardwood
Cellulose	37-47	39-49
Hemicellulose	20-32	17-35
Lignin	25-33	16-26
Extractives	1-5	2-8

Cellulose is the main component in the cell wall and serves as a skeleton, i.e. it provides support to the cell structure. It is a linear and unbranched polymer of glucose units, where every second unit is rotated 180 degrees, thus forming cellobiose units. The degree of polymerization (DP) is up to 15 000 [26-28]. Cellulose is surrounded by hemicellulose and lignin in a matrix in the cell wall.

Hemicellulose, an amorphous polymer with a degree of polymerization up to 250, is oriented along the cellulose. The chemical composition of hemicellulose in softwood and hardwood trees is different, and the predominant hemicelluloses are glucomannan in softwood and xylan in hardwood [27, 29, 30].

Extractives are organic compounds of low molecular weight, e.g. various aliphatic compounds such as fats, waxes and sterols, and their most important function is to protect the wood from fungal and bacterial attack [31-33].

Lignin, one of the most abundant biopolymers, is hydrophobic and prevents the wood cell from swelling in water, thus making the cell waterproof. It also serves as a barrier and protects the wood against microbial degradation. Lignin binds cellulose and hemicellulose together by encompassing the space between them, thus providing stiffness to the cell wall. Most of the lignin is found between glucmannan and xylan, and covalent bonds between lignin and both types of hemicellulose are common. So-called lignin-carbohydrate complexes (LCC) may also occur between lignin and cellulose [34-37].

Lignin has a very complex structure that is neither linear nor branched, but rather three-dimensional. The large polymer consists of different building blocks called monolignols that contain phenolic groups. The monolignols are mainly connected with ether bonds (C-O-C) and carbon-carbon bonds (C-C), where the  $\beta$ -O-4 ether linkage is the most frequently occurring bond [34-37].

The three most common monolignols are coniferyl alcohol, *p*-coumaryl alcohol and sinapyl alcohol, and their structures are shown in Figure 1. Softwood lignin is almost exclusively comprised of coniferyl alcohol with only small amounts of *p*-coumaryl alcohol and either none or traces of sinapyl alcohol. Hardwood lignin contains both coniferyl and sinapyl alcohols in large quantities and the distribution varies from equal parts up to three times more sinapyl alcohol. Small amounts of *p*-coumaryl alcohol can also be found in hardwood. Hardwood generally contains less lignin than softwood [24, 34, 35].

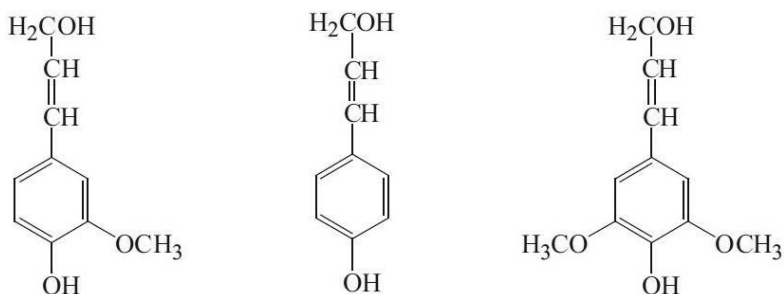


Figure 1: The three most common monolignols with phenolic groups. From left to right: coniferyl alcohol, *p*-coumaryl alcohol and sinapyl alcohol [34].

## 1.2 The kraft pulp mill fiberline

In 1879, Carl F. Dahl, a German chemist, invented the sulfate pulping process, also known as the kraft pulping process, with sodium hydroxide and sodium sulfide as cooking chemicals. The sulfide increased the delignification rate while the reaction rate of cellulose and hemicellulose degradation was not significantly affected compared to other pulping processes, and strong pulp was therefore produced [38-40]. The kraft pulp was however much darker than the pulp from the sulfite process, the most common pulping process at the time. It was not until the mid-1940s, when chlorine dioxide bleaching was implemented, that a satisfactory bleaching process became available, which enabled the kraft pulping process to produce fully bleached pulp [39-41].

The main purposes of chemical pulping is to liberate fibers from the matrix containing lignin and hemicellulose, and making the fibers softer and more flexible [4, 7, 39]. Since lignin glues all the components together, liberation of the fibers in chemical pulping is achieved by removal of lignin through additions of cooking chemicals. The active components that degrade lignin in the kraft cooking liquor are hydroxide ( $\text{OH}^-$ ) and hydrogen sulfide ( $\text{HS}^-$ ) ions. The cooking chemicals react with the wood chips in the digester at elevated temperature (140-170°C) for 3-4 hours, thus hydrolyzing and dissolving the major portion of the lignin [4, 5, 40, 42, 43].

During chemical pulping, most of the lignin is degraded and dissolved when mainly inter-linkages between phenolic groups are cleaved. Although non-phenolic lignin structures are less reactive than phenolic lignin structures, non-phenolic groups can also be cleaved [4, 5, 35, 44, 45]. More than 90% of the lignin is usually removed in the cooking stage but removing all the lignin in that stage would totally degrade the carbohydrates. Since the lignin remaining in the fibers is the main cause of color and could also cause brightness reversion upon storage, it is important to remove the last fraction. Oxygen delignification and bleaching are more selective than the cooking stage and are thus used for this final removal. During these process stages, lignin is oxidized, dissolved and eliminated from the fibers, resulting in fewer chromophores and thus a brighter pulp [43, 46-50].

The kraft pulp mill fiberline normally consists of cooking, oxygen delignification and several bleaching stages along with numerous washing stages and screening. For environmental and economic reasons, a chemical recovery system is also necessary [51-53].

### **1.2.1 Washing**

Washing is an essential step in the pulp mill fiberline and washing stages are commonly found after each process stage. Washing is often divided into two types: brown stock washing between the cooking and oxygen delignification stages, and bleach plant washing. The main purpose of both types of washing is to remove dissolved matter from the pulp slurry [54-56].

In brown stock washing, the removed dissolved matter is sent to the recovery system. The dissolved organic matter, mainly dissolved lignin and carbohydrates, is dried and finally burned in the recovery boiler, thus turned into energy. The dissolved inorganic matter, i.e. spent cooking chemicals, is regenerated in the chemical recovery system and later reused in the cooking stage [51-55, 57].

In bleach plant washing, the removal of dissolved matter is important since, if not removed, the dissolved matter will react with the bleaching chemicals in the next stage and thus cause both higher chemical consumption and/or lower brightness of the pulp. As opposed to brown stock washing, the dissolved matter in the bleach plant is not recovered but instead sent to the external effluent treatment plant for final degradation [58-60].

To gain the best washing result, a large amount of wash water should be used. However, due to environmental, economic and energy restrictions, only a relatively small volume is used. The amount of wash water used in the brown stock washing is often described by the dilution factor, which is defined as the difference between the amount of wash water added to the last washer (per ton of pulp) and the amount of liquor that is discharged with the washed pulp (per ton of pulp). A high dilution factor correlates with better washing after the oxygen

delignification stage, but since more wash water is used, the evaporation load will increase [58, 59, 61, 62].

To reduce the fresh water demand, countercurrent washing systems are implemented in all modern fiberlines. Thus, wash water is recirculated in the system, where the most contaminated water is used for the least washed pulp, and vice versa. Recycling of wash water is both economically and environmentally beneficial: the use of fresh water is drastically reduced and the need for evaporation is acceptable [54, 58, 63-65]. There are three distinct types of countercurrent washing systems: direct, jump-stage and split-flow.

In direct countercurrent washing, clean water is used in the last washer only, and the whole filtrate from that washer is then used as wash water in the previous washer. Direct countercurrent washing is always used in the brown stock washing but also in the bleach plant. In the bleach plant, an acidic stage is often followed by an alkaline stage for better bleaching result. Thus, in direct countercurrent washing in the bleach plant, the acidic and alkaline filtrates are mixed. This mixture of filtrates can cause problems such as precipitates in the washers [58, 60, 63].

In jump-stage countercurrent washing, the acidic and alkaline filtrates are therefore separated. The acidic filtrates are only used as wash water in the washers after acidic stages, and the alkaline filtrates are only used after alkaline stages, i.e. the filtrates 'jump' a preceding washer. Relatively clean water is used in the last alkaline and acidic washers [58, 60, 63]. A schematic illustration of a jump-stage countercurrent washing system is shown in Figure 2.

In the split-flow countercurrent washing, both alkaline and acidic filtrates are used in the same washer, although not totally mixed. Filtrate similar to the previous bleaching stage is used in the first showers of the washer, and filtrate similar to the next stage is then added in the following showers [58, 60, 63]. Thus, for the  $E_1$ -washer in Figure 2, alkaline  $E_2$ -filtrate would be used first since the pulp exited the alkaline  $E_1$ -stage, and the acidic  $D_1$ -filtrate would then be added since the pulp will enter the acidic  $D_1$ -stage.

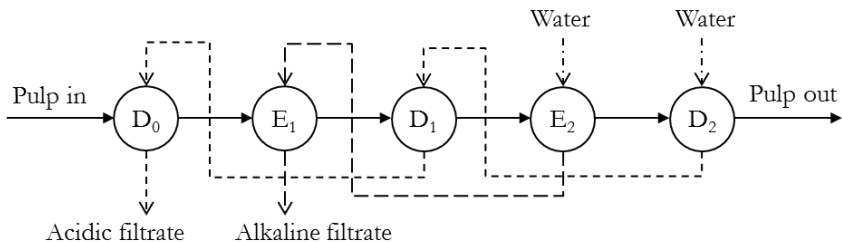


Figure 2: Jump-stage countercurrent washing system, where the acidic (*D*) and alkaline (*E*) filtrates are separated. The circles represent the washers after the corresponding bleaching stages. (Redrawn from [63])

### 1.2.2 Oxygen delignification

The first commercial installation of a single stage high consistency (25-30%) oxygen delignification stage ( $O_2$ -stage) was in South Africa in 1970. The use of oxygen had previously been known but it was not until the introduction of magnesium salts that the pulp strength could be preserved. The single stage high consistency  $O_2$ -stage achieved about 30% delignification for softwood pulp, but the more modern single stage medium consistency (10-12%)  $O_2$ -stage increased the delignification for softwood pulp to 40-50%. Finally, the two-stage system was introduced in full scale in the mid-1990s and it enabled the delignification for softwood pulp to increase to 50-65% [48, 66-70].

The  $O_2$ -stage is more selective compared to a prolonged cook with respect to carbohydrate degradation versus lignin degradation. This means that with the implementation of an  $O_2$ -stage after the cooking stage, the pulp can be delignified more while still preserving the strength. Since the pulp is usually more delignified after an  $O_2$ -stage compared to after the cooking stage, the chemical consumption in the following bleach plant is also reduced with the implementation of an  $O_2$ -stage. Since oxygen is less expensive than other bleaching chemicals, the bleaching cost is usually also decreased [48, 66, 67, 69, 71-74].

The use of oxygen delignification provides an opportunity for recycling of  $O_2$ -stage filtrates to the brown stock washing, thus decreasing the effluent load to the receiving water. Oxygen delignification is thus seen

as an environmentally friendly bleaching stage and the pulp industry is trying to maximize the use of oxygen delignification [48, 67-70, 73, 74].

The most important factors in oxygen delignification are alkali charge, reaction temperature, pressure and retention time where the alkali charge is commonly 15-35 kg NaOH/ton of pulp, the temperature is 85-105°C, the inlet pressure is 7-8 bars, the outlet pressure is 4-5 bars, and the retention time is 50-60 minutes. In a two-stage system, the first stage usually has lower reaction temperature and retention time, but higher pressure and alkali charge compared to the second stage. In an O<sub>2</sub>-stage, increasing alkali charge, temperature or pressure results in higher delignification but also higher carbohydrate degradation, i.e. lower viscosity and yield [48, 66-70, 73, 74].

The alkali charge should be high enough to result in final pH 10.5-11 for good delignification since that is the pK<sub>a</sub> value of the phenolic structures in lignin. At pH below 9.5, the phenolic groups in lignin are not ionized, and the delignification will thus be reduced [48, 70, 73-75]. The solubility of oxygen in water is low, so good mixing of the oxygen gas into the pulp slurry is important. The solubility increases with increasing pressure, but even at relatively high pressures, the solubility of oxygen is low [48, 70, 73, 74, 76].

### **1.2.3 Bleaching**

Bleaching of pulp has become increasingly important in the last decades due to the higher demand for white paper products with good printing qualities. The bleaching process does not only increase the brightness of the pulp, but it improves the printing qualities of the finished paper product as well. Bleaching can also remove bark, dirt, shives and extractives, thus creating a cleaner paper. Furthermore, the amount of substances that could cause odor or taste can also be reduced during bleaching, which is especially important for packages or paper products that come in contact with food [46-49, 77].

After oxygen delignification, approximately 5% of the original lignin content in the wood remains in the fibers. Most of that remaining lignin

is removed in the beginning of the bleaching sequence. At the end of the bleach plant, the residual lignin content is extremely low and the purpose of bleaching is to increase the brightness [46-50]. Examples of factors influencing the bleaching performance are time, pulp consistency, temperature, pH, residual lignin content, dissolved matter, metal ions and pretreatment [41, 73].

Chlorine was often used as a bleaching chemical in the past, but due to environmental reasons, many mills replaced it stepwise with chlorine dioxide, hydrogen peroxide and oxygen, starting in the 1970s [41, 46, 48, 78-81]. A bleaching sequence that does not contain chlorine is referred to as Elemental Chlorine Free (ECF) bleaching. Bleaching without any chlorine containing chemicals was tried in mill scale for the first time in 1990 and it was denoted Totally Chlorine Free (TCF) bleaching. The aim was to avoid the formation of any chlorine containing organics (measured as AOX), and chemicals such as hydrogen peroxide and ozone are common in the TCF bleaching sequence. However, TCF bleaching of kraft pulp is not very common today since it is in most cases very expensive, and modern ECF bleaching is from an environmental point of view at least as good as TCF bleaching [41, 46, 48].

Some common bleaching chemicals with their chemical formulas, abbreviations and pH ranges are listed in Table 2. Acidic and alkaline stages are often mixed in a bleaching sequence for better results and two common ECF bleaching sequences are D(EO)DD and D(EO)D(PO) [46, 48, 82].

*Table 2: Common bleaching chemicals with their chemical formulas, abbreviations and pH ranges.*

Bleaching chemical	Formula	Abbreviation	pH range
Oxygen	O <sub>2</sub>	O	Alkaline
Chlorine dioxide	ClO <sub>2</sub>	D	Acidic
Sodium hydroxide	NaOH	E	Alkaline
Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	P	Alkaline
Ozone	O <sub>3</sub>	Z	Acidic

### 1.2.3.1 Chlorine dioxide

Chlorine dioxide bleaching was introduced on a commercial scale in 1946. The role of chlorine dioxide in the bleach plant is twofold: mainly delignification at the beginning of the sequence and mainly brightening at the end [41, 48, 83, 84]. Chlorine dioxide reacts with phenolic groups in the lignin molecule, thus generating phenoxy radicals. The phenoxy radicals further react with chlorine dioxide, resulting in either ring openings of the lignin molecule to muconic acids or side chain cleavage to quinones [71, 83, 85, 86].

When a chlorine dioxide stage is implemented early in the bleaching sequence, e.g. after an oxygen delignification stage, it is often referred to as a D<sub>0</sub>-stage. Although the D<sub>0</sub>-stage is mainly a delignifying stage, it will also increase the brightness of the pulp. The final pH is 2-4, the temperature is 40-70°C and the retention time is 40-70 minutes. The ClO<sub>2</sub> charge is dependent on the lignin content in the ingoing pulp, e.g. the oxygen delignified pulp. The initial reaction of chlorine dioxide is very fast and most of the chlorine dioxide is consumed within the first few seconds [48, 67, 79, 83-85, 87].

The later chlorine dioxide bleaching stages are mainly brightening stages and are often referred to as D<sub>1</sub>- and D<sub>2</sub>-stages. Temperature, retention time and final pH are normally higher in a D<sub>2</sub>-stage compared to a D<sub>1</sub>-stage, and furthermore, these factors are higher in both stages compared to a D<sub>0</sub>-stage. The ClO<sub>2</sub> charge is divided between the D<sub>1</sub>- and D<sub>2</sub>-stages at a charge ratio of 2:1 to 3:1 between D<sub>1</sub> and D<sub>2</sub> to ensure maximum brightening [48, 83, 85, 87, 88].

### 1.2.3.2 Hydrogen peroxide

Hydrogen peroxide as a bleaching agent in the final bleaching stages was introduced in chemical pulp mills in the late 1970s for brightening improvement. With the introduction of TCF bleaching in the 1990s, the demand for hydrogen peroxide grew quickly [8, 89, 90]. Hydrogen peroxide is very sensitive towards metal ions, especially manganese,

iron and copper, so chelating agents are often added in a preceding chelation stage, denoted Q-stage [8, 48, 89, 91-93].

On chemical pulps, hydrogen peroxide is often used together with oxygen, denoted (PO)- or (EOP)-stages, to enhance the bleaching effect. Hydrogen peroxide, alone or together with oxygen, is used for delignification in the early stages of bleaching and used in the final stages for brightness enhancement [8, 48, 89, 90, 92-96].

Hydrogen peroxide can also be used to reinforce the alkaline extraction stage, denoted (EP)-stage. Even with small amounts of hydrogen peroxide, the brightness of the pulp is significantly increased. According to studies, 2.5 kg H<sub>2</sub>O<sub>2</sub>/ton of pulp can result in an increased brightness by up to 10% ISO. Another benefit of reinforcement with hydrogen peroxide is that the higher brightness also results in a lower chemical demand, e.g. chlorine dioxide, in the final bleaching stages [8, 48, 89, 90, 92-96].

#### **1.2.4 Hexenuronic acid**

Hexenuronic acid (HexA) is formed when the 4-O-methylglucuronic acid substituent on xylan reacts with the cooking chemicals in an alkaline cook. HexA is stable in alkaline environments so a significant part of the HexA remains in the fibers after an alkaline cooking stage [5, 27, 97]. HexA is more pronounced in hardwood pulp than in softwood pulp due to the higher content of xylan in hardwood, and will subsequently affect the properties of hardwood pulp more than softwood pulp [27, 29].

Due to its stability in alkaline environments, HexA does not chemically react in an oxygen delignification stage. However, in acidic bleaching stages, such as chlorine dioxide and ozone, HexA will react and thus increase the bleaching chemical consumption [97-102]. HexA also reduces the brightness stability and thus causes brightness reversion of a fully bleached pulp upon storage, especially in conditions of high relative humidity and/or temperature. One reason for the brightness reversion is that HexA binds heavy metals [98, 100, 101, 103].

#### 1.2.4.1 Removal of HexA by hot acid treatment

In order to reduce the HexA content in an unbleached pulp, a hot acid stage (A-stage) can be included before the first acidic stage, e.g. a D<sub>0</sub>-stage, in the bleaching sequence [98-102]. During the A-stage reactions, at low pH (2-3), high temperature (90-100°C) and long retention time (2-3 hours), HexA is hydrolyzed and degraded. During acid hydrolysis, HexA is degraded to 2-furancarboxylic acid and 5-formyl-2-furancarboxylic acid, where about 90% of the degraded HexA consists of the former [98, 104-106]. Washing after the A-stage is optional, and the sequences are commonly referred to as AD with washing and (AD) without washing between the two stages.

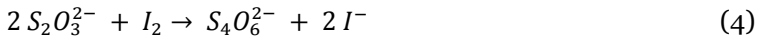
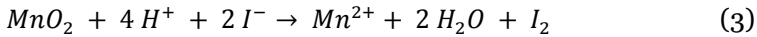
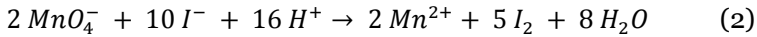
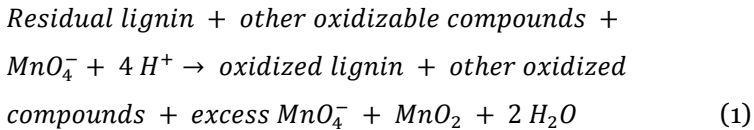
The high investment cost of an additional bleaching stage in the sequence, particularly with intermediate washing, has given mills an incentive to try to combine the A- and D<sub>0</sub>-stages into one stage, denoted hot D-stage or D\*-stage. This modified chlorine dioxide stage is a cost-effective alternative to particularly an AD-sequence but also to an (AD)-sequence. The D\*-stage, due to its high temperature and long retention time, reduces the HexA content in the fibers [100, 102, 107, 108].

Furthermore, the D\*-stage both generates less chlorinated organic substances and degrades more of them than a D<sub>0</sub>-stage, and the amount of chlorinated organic substances (AOX) in the bleach plant can thus be reduced by 40-50%. This reduction is also partly due to the HexA degradation since HexA contributes to AOX [100, 108-110]. The HexA degradation in an A-stage or in a D\*-stage can reduce the chlorine dioxide demand by 10-30% in the bleach plant [107, 111-113].

HexA is known to increase the chlorine dioxide demand, but studies have shown that it is not chlorine dioxide itself that reacts with HexA but rather intermediates of elemental chlorine (Cl<sub>2</sub>) and hypochlorous acid (HOCl) that are formed in situ [99, 109, 114-116]. The amount of the intermediates depends on reaction pH, and the HexA degradation efficiency is thus also pH dependent [114, 116, 117].

### 1.2.5 Determination of lignin content in the fibers

The residual lignin content in the fibers after cooking, oxygen delignification and early bleaching stages is often analyzed as the kappa number. The kappa number is defined as the consumption of 0.02 mol/L potassium permanganate (KMnO<sub>4</sub>) by one gram of pulp during ten minutes reaction at 25°C. The results are corrected to an assumed 50% permanganate consumption using an empirical correction factor, and the resulting value is presumed to be an indirect measurement of the lignin content in the fibers. Note however that the relationship between kappa number and lignin content depends on the wood species and the delignification procedure, i.e. there is no general and unambiguous relationship between the two [118-120]. The main reactions in the kappa number determination are shown in Equations 1-4 [120]:



As seen in Equation 1, not only lignin will consume permanganate but also other oxidizable compounds, especially HexA, thus contributing to a 'false kappa number' [98, 103, 121-123]. Li et al. [124] found that most of the oxidizable compounds are formed in the cooking and oxygen delignification stages. They further found that for an unbleached softwood pulp, one-quarter of the kappa number after the cooking stage originates from HexA and other oxidizable compounds. For an unbleached hardwood pulp, more than one-third of the kappa number originates from other compounds than lignin, predominantly HexA (Figure 3).

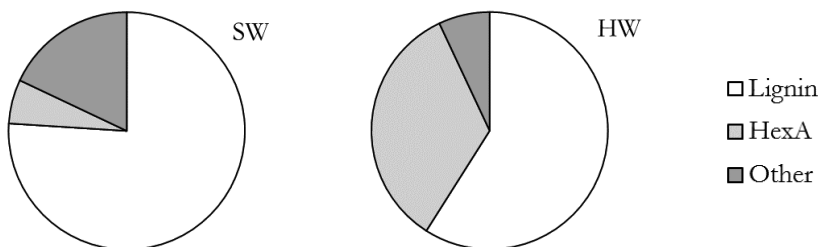


Figure 3: The contribution to kappa number from lignin, HexA and other oxidizable compounds for an unbleached spruce kraft pulp (left) and an unbleached birch kraft pulp (right). The figure is based on results presented in [124].

It is apparent that the high content of HexA in hardwood pulps affects the kappa number significantly. Li and Gellerstedt [122] found that 11.6-11.9  $\mu\text{mol}$  HexA is equivalent to 1 kappa number unit. In another study by the same authors, it was concluded that 3-6 kappa number units of a pulp sample are often due to HexA for an unbleached hardwood pulp and 1-3 kappa number units for an unbleached softwood pulp [125]. Thus, the kappa number should be divided into lignin, HexA and other oxidizable compounds according to Equation 5. Measuring the kappa number as an indication of the lignin content in the fibers can be misleading, especially for hardwood pulps, and it can thus result in an estimation of the lignin content that is too high.

$$K = L + H + \varepsilon \quad (5)$$

where  $K = \text{Kappa number}$

$L = \text{Kappa number due to lignin}$

$H = \text{Kappa number due to HexA}$

$\varepsilon = \text{Kappa number due to other oxidizable compounds}$

### 1.3 Dissolved matter

The dissolved matter in the fiberline consists of both organic and inorganic substances. The organic substances are dissolved residues from lignin, carbohydrates and extractives while the inorganic substances consist of spent chemicals from the different process stages. The dissolved matter in each stage can both originate from the previous stage, i.e. accompanying the pulp due to imperfect washing, or be generated in the current stage through e.g. degradation, oxidation and chlorination. With closed washing systems, dissolved matter will also originate from the recycled wash water. The chemical composition of the filtrates from the cooking stage, the oxygen delignification stage and the bleach plant will thus differ depending on for example wood material, bleaching sequence, wash water and conditions used in the different stages [20, 21, 69, 70, 126].

Most of the delignification of the fibers occurs in the cooking stage, but a significant amount of the lignin will still be bound to the fibers after the cook, and dissolved lignin is thus generated in the whole fiberline. Dissolved matter from the cooking stage, the oxygen delignification stage and the bleach plant will influence the delignification of the fibers due to e.g. increased chemical demand [21, 127, 128]. For instance, inadequate brown stock washing will lead to a higher content of dissolved matter entering the bleach plant. Thus, when the fibers are bleached to a certain degree of delignification or to a specific brightness, the chemical demand in the bleach plant will be increased. If the dissolved matter is not compensated for by a higher chemical charge, the consumption of chemicals by the dissolved matter will lead to a reduced delignification or brightness.

In the bleach plant, most of the dissolved matter is produced in the first stages, e.g. in the D<sub>0</sub>- and E<sub>1</sub>-stages in an ECF mill. Studies have shown that dissolved kraft lignin, i.e. from the cooking stage, affects the delignification in D<sub>0</sub>- and E<sub>1</sub>-stages more negatively than dissolved O<sub>2</sub>-lignin. Furthermore, dissolved O<sub>2</sub>-lignin has a larger negative impact on delignification than dissolved D<sub>0</sub>-lignin. Hence not only the magnitude of the dissolved lignin content but also the type will influence the various process stages [17-19].

### **1.3.1 Quantification and measurement of dissolved matter**

Traditionally, the remaining dissolved matter in the outgoing pulp after a washing stage is referred to as 'carryover' for that specific component. The amount of inorganic cooking chemicals remaining in the pulp slurry after the brown stock wash, or after the oxygen delignification stage if that is available, is called 'wash loss' and refers to the amount of cooking chemicals that were lost per ton of pulp from the chemical recovery system. However, the terms 'carryover' and 'wash loss' are often interchangeable, and one can for instance speak of organic versus inorganic carryover. Furthermore, wash loss can refer to the washable substances that remain in the pulp slurry after a washing stage and that also cause a 'loss' of chemicals, i.e. both organic and inorganic dissolved substances that consume bleaching chemicals [20, 21, 56, 58, 59, 129].

Wash loss, referring to inorganic dissolved matter, was in the past measured as salt cake loss, i.e. the remaining amount of sodium sulfate in the pulp slurry after brown stock washing. The measurement of sodium as an indication of wash loss was however seriously questioned with the introduction of oxygen delignification, where sodium is one of the active chemicals and is added as either oxidized white liquor or pure sodium hydroxide [21, 56, 59, 130, 131]. Conductivity, i.e. the ionic concentration of substances in a solution, is also used as it correlates with the content of inorganic dissolved matter, mainly sodium. Thus, conductivity sensors can be used in the brown stock washing to measure the inorganic wash loss continuously. However, the sensors can only be installed in filtrate streams, thus not measuring wash loss directly in the pulp slurry [59, 131, 132].

The main disadvantage of using methods based on conductivity and salt cake loss is that the organic substances are disregarded. In the analyses, it is assumed that organic and inorganic substances are washed out of the pulp at the same rate. However, the organic substances are significantly bigger than the inorganic substances, and thus have lower mobility and transfer rate. Thus, the dissolved organic carryover can be higher than the inorganic wash loss when estimated as e.g. salt cake loss [21, 130, 133]. According to Cullinan [133], dissolved lignin carryover can theoretically be 2-5 times the size of

sodium losses at the same dilution factor. A corresponding comparison of several pulp mills made by Stromberg [130] showed that the dissolved organic matter content could differ by as much as a factor of four at the same salt cake loss, i.e. the ratio between organic and inorganic dissolved matter content was found to be between 1:1 and 4:1.

Nowadays, the content of dissolved organic matter is often characterized as chemical oxygen demand (COD). COD is a collective measurement of all organic substances that can be oxidized by potassium dichromate ( $K_2Cr_2O_7$ ) [134, 135]. Studies have however shown that only a few of the oxidizable substances, quantified by the COD analysis, have a negative impact on the chemical consumption in the bleach plant. Moreover, there may also be non-oxidizable substances that consume bleaching chemicals [17-21, 136]. Further disadvantages of COD characterization are that the analysis is labor-intensive and thus costly, and environmentally problematic due to the potassium dichromate used in the analysis [20, 21, 131]. Total organic carbon (TOC) has gained interest lately since it is more environmentally friendly than COD and it measures the carbon content of all organic substances, i.e. both oxidizable and non-oxidizable compounds [137-139].

Another possible analysis of carryover is to measure total dissolved solids, i.e. both organic and inorganic substances. It can be used for measurement in the brown stock washing and correlates well with COD [131, 140]. Total dissolved solids also correlate with refractive index, and refractometers can thus be used in the brown stock washing to continuously measure the dissolved matter content. Lignin has a high refractive index, and variations in dissolved lignin content will thus affect the refractive index of the pulp slurry. However, some inorganic salts can also have a significant impact on the refractive index, and most of these salts have no bearing on the performance of the process stages in the fiberline [131, 132, 141-143].

Thus, only some of the dissolved substances entering a process stage will have an impact on e.g. delignification or chemical consumption in that particular stage. Sillanpää [21] therefore suggested that the definition of carryover and/or wash loss prior to a particular process stage should only incorporate those dissolved substances that “cause addi-

tional chemical consumption or a decrease in the process response” in the subsequent stage, i.e. not all of the dissolved substances that can be quantified by various analyses, but only the ones that actually have a significant impact.

#### *1.3.1.1 Determination of dissolved lignin content*

Dissolved lignin is both the most frequently occurring and the most important dissolved component with respect to chemical consumption in the bleach plant. Dissolved lignin also has an impact on key parameters such as kappa number and brightness if not compensated for by a higher chemical charge [17-19, 138]. Even though it is well known that the content of dissolved lignin in pulp slurries often is high and can have a significant impact on process performance, it is typically not measured on a continuous basis in pulp mills. Several studies have concluded that online measurement of the dissolved lignin content would be useful for process control and optimization [17-21].

The dissolved lignin content can however be measured offline in the laboratory. Lignin strongly absorbs ultraviolet (UV) light due to its aromatic nature and it can thus be measured by ultraviolet spectroscopy. The light absorption can then be correlated with the dissolved lignin content by the Beer-Lambert law. Lignin has a sharp peak at wavelength 205 nm and a maximum at wavelength 280 nm [144-147].

‘Liquid kappa number’, i.e. the difference between the kappa numbers of unwashed and washed pulp samples, can be used to determine the dissolved lignin content in a filtrate, but a disadvantage is that two measurements need to be conducted [129]. ‘Filtrate kappa number’, described in detail in section 3.1.1, is a similar method that directly measures the kappa number of the filtrate, i.e. only one measurement is required. The kappa number analysis will however not only include dissolved lignin but also other oxidizable compounds, such as certain carbohydrate residues.

### ***1.3.2 Dissolved matter in the oxygen delignification stage***

Dissolved matter entering the O<sub>2</sub>-stage will be a combination of two types: unoxidized and oxidized dissolved matter. The unoxidized dissolved matter originates from the cooking stage and is carried over to the O<sub>2</sub>-stage if not removed in the brown stock washing. The oxidized dissolved matter originates in the O<sub>2</sub>-stage and is recycled from the post-O<sub>2</sub> washing into the O<sub>2</sub>-stage as wash water and/or dilution medium prior to the O<sub>2</sub>-stage. There is a continuous recirculation of filtrates in the fiberline, and the oxidized dissolved matter will thus be oxidized several times [69, 70, 73, 74, 148, 149].

The amount of dissolved matter as well as the distribution between unoxidized and oxidized dissolved matter entering the O<sub>2</sub>-stage will be determined by the degree of delignification in the cooking and O<sub>2</sub>-stages, and by the degree of pre- and post-O<sub>2</sub> washing. According to Miller et al. [148], the filtrate part of the pulp slurry entering the O<sub>2</sub>-stage consists of 70-92% oxidized dissolved matter, depending on dilution factor and number of washing stages prior to the O<sub>2</sub>-stage. Thus, the O<sub>2</sub>-stage is operated in a relatively closed system.

The delignification in the O<sub>2</sub>-stage is strongly influenced by the presence of dissolved matter in the pulp slurry. It is mainly dissolved lignin and inorganic sulfur compounds, such as hydrogen sulfide and thiosulfate, that react with oxygen and hydroxide, thus affecting the oxygen delignification reactions. According to previous studies, unoxidized dissolved matter reduces the degree of delignification more than oxidized dissolved matter [19, 70, 73-75, 127, 142, 148-154]. Some studies have even indicated that oxidized dissolved matter could be beneficial to the delignification [66, 75, 151]. Other studies have suggested that, due to the residual alkali in the unoxidized dissolved matter, the delignification could be increased by small amounts of unoxidized dissolved matter [148, 150, 152, 154].

### **1.3.3 Dissolved matter in the bleach plant**

Bleach plant closure, with recycling of bleaching filtrates, is an essential part in pulp mills since it reduces the pollution of the receiving water. The striving for effluent minimization stems mainly from environmental concerns and stricter regulations with respect to water and energy usage. However, the use of recycled water instead of fresh water causes reactions between dissolved matter and bleaching chemicals, thus e.g. increasing the chemical consumption. The accumulation of dissolved matter can also lead to build up of substances that can cause scaling problems. Despite the negative impact of bleach plant closure, most mills have at least partial closure [60, 63, 127, 128, 155-158].

The chlorine dioxide that is charged in the D<sub>0</sub>-stage is mainly consumed in reactions with fiber-bound lignin and dissolved organic matter in the filtrate [9, 10, 13-17, 157]. Studies have shown that dissolved organic matter consumes 10-25% of the chlorine dioxide charged in the D<sub>0</sub>-stage, thus significantly increasing the chemical demand [127, 159, 160]. Studies have also shown that the presence of dissolved organic matter in a D<sub>0</sub>-stage decreases the degree of delignification, the brightness and the intrinsic viscosity if not compensated for by a higher chlorine dioxide charge [12, 13, 159, 160].

HexA in a D<sub>0</sub>-stage consumes chlorine dioxide, so implementing an A-stage prior to a D<sub>0</sub>-stage thus reduces the chemical demand in a D<sub>0</sub>-stage when a certain degree of delignification is desired. However, the degraded and dissolved HexA residues after an A-stage can also consume chlorine dioxide in a subsequent D<sub>0</sub>-stage if not removed in intermediate washing. When employing a D\*-stage, both lignin and HexA are degraded and dissolved, and chlorine dioxide is thus consumed simultaneously in lignin and HexA reactions [97-100, 102, 104, 108, 113, 116, 161].

Hydrogen peroxide is consumed by dissolved matter in P-, (EP)-, (PO)- or (EOP)-stages, thus increasing the consumption of bleaching chemicals. If the dissolved matter is not compensated for by higher chemical charges, the degree of delignification and/or the brightness will be reduced [8, 11, 12, 18, 127].

## 2 Objectives

The main objective of this project was to develop better knowledge about the impact of dissolved matter on the performance of some of the key process stages in a chemical pulping fiberline.

- Investigate the impact of dissolved matter in an oxygen delignification stage on delignification and selectivity and determine the differences between unoxidized and oxidized dissolved matter.
- Investigate the impact of dissolved organic matter in a hot acid stage and further determine if the possible impact on the efficiency of a hot acid stage will affect the chemical demand in a subsequent chlorine dioxide stage.
- Investigate the impact of dissolved organic matter in a chlorine dioxide stage on delignification and determine the chlorine dioxide demand of the dissolved organic matter relative to that of the fiber-bound lignin.
- Investigate the impact of dissolved organic matter in a hydrogen peroxide reinforced alkaline extraction stage on delignification and brightness.
- Investigate the correlations between different methods used to measure the dissolved lignin content and determine typical variability of the dissolved lignin content in different mill positions.

### 3 Experimental

#### 3.1 Analyses used

The standards used for the analyses in the experiments are listed in Table 3. The sodium content was measured with atomic flame spectroscopy and light absorption was determined with a spectrophotometer with 10 mm cuvettes. Conductivity, refractive index and pH were measured at room temperature with devices for those specific purposes respectively. COD was measured using the closed tube method with Hach-Lange cuvettes.

*Table 3: Standards used for the analyses of the collected fiber and filtrate samples.*

Analysis	Standard
Kappa number	ISO 302
Viscosity	ISO 5351
Brightness	ISO 3688, ISO 2470
COD	ISO 15705
Hydroxide ions	SCAN N-33:94
Hydrogen sulfide ions	SCAN N-31:94
Carbonate ions	SCAN-N 32:98
Thiosulfate ions	SCAN-N 36:98

##### 3.1.1 Filtrate kappa number

Analysis of the kappa number of the filtrates was used to determine the concentration of dissolved organic matter, predominantly lignin. The filtrate kappa number was determined in the same way as the fiber kappa number but used a certain volume of filtrate as the basis. The filtrate kappa number was thus measured per milliliter of filtrate instead of per gram of fiber, which is the case in the standard procedure for fibers. The filtrate kappa number and the fiber kappa number are used to calculate the total kappa number. An illustration of the different types of kappa numbers is shown in Figure 4.

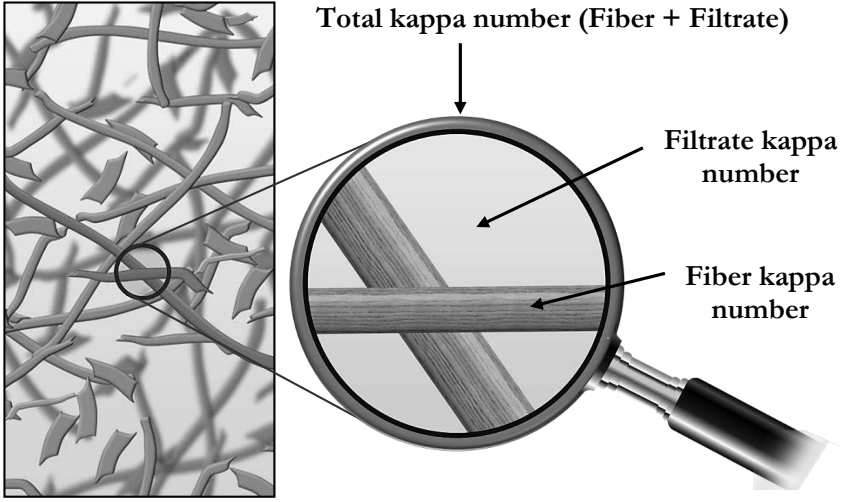


Figure 4: An illustration of fiber, filtrate and total kappa numbers.

To compare the filtrate and fiber kappa numbers, the filtrate kappa number needs to be converted to fiber basis. By considering the pulp consistency and by assuming a filtrate density of 1 g/mL, a filtrate kappa number per gram fiber can be calculated according to Equation 6. For example, at 10% pulp consistency, the filtrate volume is 9 m<sup>3</sup>/ton of pulp, and the filtrate kappa number per gram fiber is thus nine times the filtrate kappa number per milliliter of filtrate. The total kappa number is defined as the sum of the fiber kappa number and the filtrate kappa number (on fiber basis) according to Equation 7.

$$K_f = K_v * \frac{100 - cs}{cs} \quad (6)$$

$$K_T = K_F + K_f \quad (7)$$

where  $K_f$  = Filtrate kappa number (per gram fiber)

$K_v$  = Filtrate kappa number (per milliliter filtrate)

$cs$  = Pulp consistency (%)

$K_T$  = Total kappa number, i.e. of fiber and filtrate

$K_F$  = Fiber kappa number

## 3.2 Laboratory conditions

In the laboratory studies, the impact of dissolved matter was investigated in the oxygen delignification stage ( $O_2$ ), the hot acid stage (A), the first chlorine dioxide stage ( $DO$ ), and the hydrogen peroxide reinforced alkaline extraction stage ([EP]).

At the end of the retention time of each experiment, the samples were cooled to about  $10^\circ\text{C}$  to stop the reactions, and the filtrates were separated from the fibers. The fibers were then washed with deionized water, dewatered to 33-35% pulp consistency and stored in a fridge for further analysis.

### 3.2.1 Oxygen delignification stage

One pulp sample prior to the  $O_2$ -stage and two filtrate samples were collected in a Scandinavian softwood kraft pulp mill. The filtrate samples were collected so that one sample contained mainly unoxidized filtrate, i.e. prior to the  $O_2$ -stage, and one sample contained exclusively oxidized filtrate, i.e. after the  $O_2$ -stage. The pulp sample was well-washed and dewatered to 33-35% pulp consistency.

The  $O_2$ -experiments were conducted with 50 grams oven dry pulp diluted to 10% pulp consistency in 2.5 L stainless steel autoclaves immersed in a polyethylene glycol bath, and the laboratory procedure is depicted in Figure 5. The pulp samples were diluted to 10% pulp consistency with either deionized water and/or with filtrate. The filtrates were diluted with deionized water to simulate various levels of dissolved matter, measured as COD.

To investigate the impact of carbonate and thiosulfate ions,  $O_2$ -experiments were also conducted with specific additions of sodium carbonate or sodium thiosulfate respectively. In those experiments, 25 grams oven dry pulp was diluted to 10% pulp consistency with either deionized water and/or with filtrate corresponding to 100 kg COD/ton of pulp.

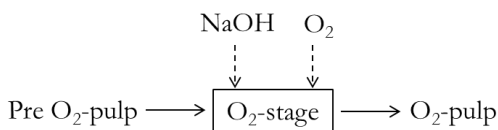


Figure 5: Laboratory procedure for the  $O_2$ -stage experiments. The pulp was diluted to 10% pulp consistency with deionized water, unoxidized filtrate or oxidized filtrate at various COD levels, thus resulting in two pulps at each COD level. In some of the experiments, carbonate or thiosulfate ions were also added in the  $O_2$ -stage.

The laboratory conditions for the experiments are listed in Table 4. Mills normally charge 1.0-1.4 kg  $O_2$  per kappa number reduction and per ton of pulp, equivalent to approximately 15-30 kg  $O_2$ /ton of pulp depending on initial kappa number and degree of delignification [69, 70, 73, 162]. The autoclaves in the experiments were pressurized with oxygen to 5 bars, which was equivalent to approximately 260 kg  $O_2$ /ton of pulp, i.e. in significant excess. The oxygen consumption by dissolved matter would thus not result in oxygen depletion in the experiments.

Table 4: Conditions used in the  $O_2$ -stage experiments.

Consistency, %	10
Temperature, °C	90
Pressure, bar	5
Time, h	2
COD, kg/ton pulp	0-100
NaOH, % on pulp	2-4
MgSO <sub>4</sub> , % on pulp	0.2
CO <sub>3</sub> <sup>2-</sup> , g/L	0-4
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , g/L	0-0.4

### 3.2.2 Hot acid stage

One  $O_2$ -pulp sample with the corresponding filtrate was collected prior to the  $D_0$ -stage in a Scandinavian hardwood kraft pulp mill. The pulp sample was dewatered to 33-35% pulp consistency, and half of the pulp sample was then well-washed and further dewatered to 33-35% pulp consistency.

The hot acid experiments were conducted with 50 grams oven dry pulp diluted to 10% pulp consistency in sealed polyethylene bags immersed in a heated water bath, and the laboratory procedure is depicted in Figure 6. The samples used in the experiments consisted of one well-washed pulp sample, hereafter referred to as ‘Reference pulp’, and one pulp sample containing dissolved organic matter, hereafter referred to as ‘Pulp with filtrate’. After cooling, only half of each A-pulp was well-washed and the other half remained unwashed. Thus, two washed A-pulps and two unwashed A-pulps were produced.

The four different A-pulps were finally bleached with chlorine dioxide. The D<sub>O</sub>-experiments were conducted with 25 grams oven dry pulp diluted to 10% pulp consistency in sealed polyethylene bags immersed in a heated water bath. The experiments with the unwashed A-pulps simulated an A-stage without a wash prior to the D<sub>O</sub>-stage, i.e. (AD)-stage, whereas the well-washed A-pulps simulated an A-stage with a wash prior to the D<sub>O</sub>-stage, i.e. AD-stage.

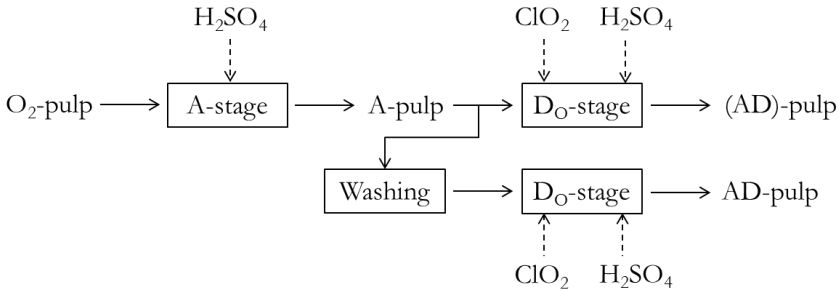


Figure 6: Laboratory procedure for the A-stage experiments. The O<sub>2</sub>-pulp was diluted to 10% pulp consistency with either deionized water or filtrate, thus resulting in two A-pulps and subsequently in two (AD)-pulps and two AD-pulps.

For the well-washed O<sub>2</sub>-pulp, i.e. the Reference pulp, a conventional D<sub>O</sub>-stage and a hot D<sub>O</sub>-stage (D\*-stage) were also conducted for comparison. The bleaching conditions for the combined A- and D-stage experiments are shown in Table 5. The kappa factor was calculated as percentage active chlorine charge per kappa number of the fibers entering the respective D-stages. The initial pH was adjusted with additions of sulfuric acid to 2.5 and 2.0 for the A- and D-stage experiments respectively.

Table 5: Conditions used in the combined A- and D-stage experiments. The kappa factor was calculated as percentage active chlorine charge per kappa number of the fibers entering the respective D-stages. Note that for the combined AD-stage experiments, the conditions in the respective A- and D<sub>0</sub>-stages are separated by ‘/’.

	A	AD	(AD)	D <sub>0</sub>	D*
Consistency, %	10	10	10	10	10
Temperature, °C	90	90 / 60	90 / 60	60	90
Time, h	3	3 / 1	3 / 1	1	3
Kappa factor	--	0.2	0.2	0.2	0.2

### 3.2.3 Chlorine dioxide stage

One O<sub>2</sub>-pulp and two filtrate samples were collected prior to the D<sub>0</sub>-stage in a Scandinavian softwood kraft pulp mill. Additionally, one O<sub>2</sub>-pulp and two filtrate samples were collected prior to the D<sub>0</sub>-stage in a Scandinavian hardwood kraft pulp mill. The pulp samples were dewatered to 33-35% pulp consistency, and half of the pulp from each sample was then well-washed and further dewatered to 33-35% pulp consistency.

The D<sub>0</sub>-experiments were conducted with 25 grams oven dry pulp diluted to 10% pulp consistency in sealed polyethylene bags immersed in a heated water bath, and the laboratory procedure is depicted in Figure 7. The samples used in the experiments consisted of one well-washed pulp sample, hereafter referred to as ‘Reference pulp’, and two pulp samples containing dissolved organic matter from either Filtrate 1 or Filtrate 2, hereafter referred to as ‘Pulp with Filtrate 1’ and ‘Pulp with Filtrate 2’ respectively, for both the softwood and hardwood experiments.

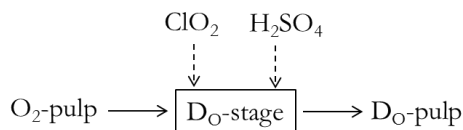


Figure 7: Laboratory procedure for the D<sub>0</sub>-stage experiments. The pulp was diluted to 10% pulp consistency with deionized water, Filtrate 1 or Filtrate 2, thus resulting in three different D<sub>0</sub>-pulpings at each chlorine dioxide charge.

The laboratory conditions for the experiments are listed in Table 6. The kappa factor, i.e. percentage active chlorine charge per kappa number of the well-washed O<sub>2</sub>-pulp, was based on the kappa number of the fibers. The initial pH was adjusted to 2.0 with additions of sulfuric acid.

Table 6: Conditions used in the D<sub>O</sub>-stage experiments. The kappa factor was calculated as percentage active chlorine charge per kappa number of the fibers.

Consistency, %	10
Temperature, °C	60
Time, h	1
Kappa factor	0.1-0.3

D<sub>O</sub>-filtrates were generated in the laboratory and the procedure is depicted in Figure 8, where the original filtrate is denoted ‘F’ and the generated D<sub>O</sub>-filtrate is denoted ‘f’. The generated D<sub>O</sub>-filtrates were recycled and mixed with well-washed O<sub>2</sub>-pulp samples. The pulp samples containing recycled filtrates were then bleached according to Table 6 at kappa factor 0.2, which was based on the kappa number of the fibers. One D<sub>O</sub>-experiment was also conducted where the generated filtrate from the well-washed Reference pulp was used as recycled filtrate, denoted ‘f<sub>0</sub>’.

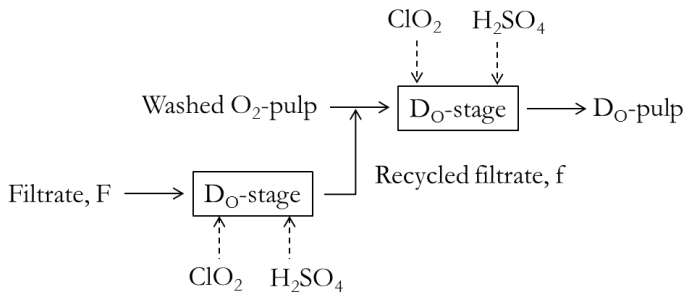


Figure 8: Laboratory procedure for the D<sub>O</sub>-stage experiments with recycled filtrates. The washed O<sub>2</sub>-pulp was diluted to 10% pulp consistency with recycled filtrate from the Reference pulp (f<sub>0</sub>), recycled Filtrate 1 (f<sub>1</sub>) or recycled Filtrate 2 (f<sub>2</sub>), thus resulting in three different D<sub>O</sub>-pulp.

### 3.2.4 Hydrogen peroxide reinforced alkaline extraction stage

One  $D_0$ -pulp sample prior to the (EP)-stage, two filtrate samples prior to the (EP)-stage, and one filtrate sample after the (EP)-stage were collected from a Scandinavian softwood kraft pulp mill. The collected pulp sample was dewatered to 33-35% pulp consistency. Half of the pulp was then well-washed and further dewatered to 33-35% pulp consistency.

The (EP)-experiments were conducted with 25 grams oven dry pulp diluted to 10% pulp consistency in sealed polyethylene bags immersed in a heated water bath and the laboratory procedure is depicted in Figure 9. The samples used in the experiments consisted of one well-washed pulp sample, hereafter referred to as ‘Reference pulp’, and three pulp samples containing dissolved organic matter from Filtrates 1, 2 or 3, hereafter referred to as ‘Pulp with Filtrate 1’, ‘Pulp with Filtrate 2’ and ‘Pulp with Filtrate 3’ respectively. The laboratory conditions used are listed in Table 7.

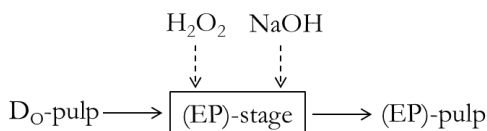


Figure 9: Laboratory procedure for the (EP)-stage experiments. The  $D_0$ -pulp was diluted to 10% pulp consistency with deionized water, Filtrate 1, Filtrate 2 or Filtrate 3, thus resulting in four different (EP)-pulp samples at each  $H_2O_2$  and NaOH charge.

Table 7: Conditions used in the (EP)-stage experiments.

Consistency, %	10
Temperature, °C	70
Time, h	1
$H_2O_2$ , % on pulp	0.3-1.5
NaOH, % on pulp	1.5-3.0

## 4 Results and Discussion

### 4.1 Impact of dissolved matter in an oxygen delignification stage

The pulp samples used in the oxygen delignification study were collected in the press prior to the O<sub>2</sub>-stage and the filtrates were collected from the pressure diffusers before and after the O<sub>2</sub>-stage, according to Figure 10. The unoxidized filtrate was presumed to contain primarily unoxidized dissolved matter with a small quantity of oxidized dissolved matter due to the countercurrent washing system. The oxidized filtrate was presumed to contain exclusively oxidized dissolved matter since it had passed the O<sub>2</sub>-stage at least once due to the continuous recycling of filtrates in the countercurrent washing system.

The sampling positions of the filtrates were chosen so that it would be possible to investigate the impact of each of the different types of dissolved matter. In a mill, the pulp slurry entering the oxygen delignification stage contains both unoxidized and oxidized dissolved matter due to the recycling of O<sub>2</sub>-stage filtrates. The following results are also presented in Papers III and IV.

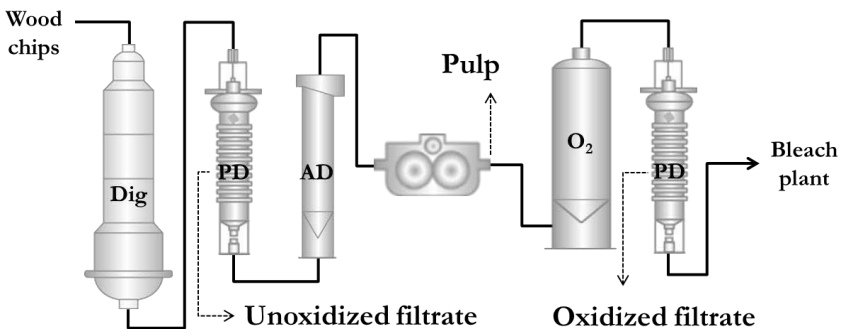


Figure 10: Sampling positions in the softwood pulp mill. PD and AD indicate a pressure diffuser and an atmospheric diffuser respectively.

Kappa number and viscosity of the pulp samples used in the experiments are presented in Table 8. The samples were collected at two different occasions and are referred to as Pulp I and II respectively.

Table 8: Summary of the properties of the well-washed pulp samples used in the oxygen delignification study.

	Pulp I	Pulp II
Kappa number	26.8	25.7
Viscosity, dm <sup>3</sup> /kg	1247	917

#### 4.1.1 Unoxidized dissolved matter versus oxidized dissolved matter

The efficiency of the O<sub>2</sub>-stage at constant NaOH charge, constant degree of delignification and constant final pH was investigated in the first part of the laboratory study with Pulp I. A well-washed pulp sample, with deionized water as dilution medium, was oxygen delignified at 2%, 3% and 4% NaOH charge, and the results after the O<sub>2</sub>-stage are shown in Table 9.

Table 9: Results after the O<sub>2</sub>-stage experiments with the well-washed reference pulp (Pulp I) at different NaOH charges.

NaOH charge, %	Kappa number	Viscosity, dm <sup>3</sup> /kg	Final pH
2	17.1	1020	11.8
3	15.1	1007	12.1
4	13.4	999	12.3

Experiments with added unoxidized or oxidized dissolved matter were also conducted at 2%, 3% and 4% NaOH charges. The quantity of unoxidized and oxidized dissolved matter was varied to simulate different carryover levels, measured as COD. The results from those experiments were interpolated to simulate two different cases: constant degree of delignification and constant final pH. The final kappa number and final pH were chosen so that they were industrially relevant. Furthermore, no or very little extrapolation was required to obtain those results. The chosen NaOH charge, kappa number and final pH for the three cases, i.e. constant NaOH charge, constant degree of delignification and constant final pH, are shown in Table 10.

Table 10: NaOH charge, final kappa number and final pH for the three cases, i.e. constant NaOH charge, constant degree of delignification and constant final pH.

Constant NaOH charge, % on pulp	2.0
Constant degree of delignification, final kappa number	15.0
Constant final pH	11.0

NaOH charge in the O<sub>2</sub>-stage versus COD content before the O<sub>2</sub>-stage for the three cases, i.e. constant NaOH charge (a), constant degree of delignification (b) and constant final pH (c), are shown in Figure 11 for the experiments containing unoxidized and oxidized dissolved matter. As can be seen for case with the unoxidized dissolved matter, the NaOH charge was increased with increasing COD to obtain a certain degree of delignification (b) and maintain a constant final pH (c). For the case with oxidized dissolved matter, the NaOH charge was moderately increased with increasing COD at constant final pH (c), and actually reduced with increasing COD at constant degree of delignification (b). Thus, both the type and the content of dissolved matter affected the required NaOH charge to obtain a specific delignification or final pH.

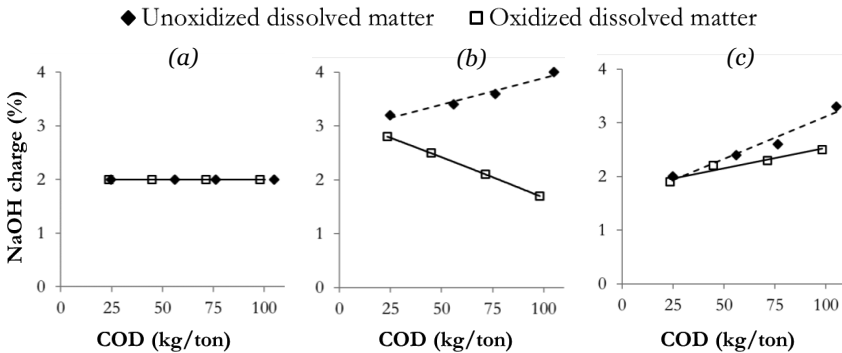


Figure 11: NaOH charge vs. initial COD content with unoxidized and oxidized dissolved matter at constant NaOH charge (a), constant degree of delignification (b) and constant final pH (c).

Resulting kappa number, viscosity and final pH corresponding to the NaOH charges in Figure 11, with unoxidized and oxidized dissolved matter, are shown in the following sections. Note that the results from the experiments at 2%, 3% and 4% NaOH charges were interpolated, and sometimes also extrapolated, to obtain the following results.

#### 4.1.1.1 Kappa number

Kappa number of the fibers after the O<sub>2</sub>-stage versus COD content before the O<sub>2</sub>-stage for the three cases, i.e. constant NaOH charge (a), constant degree of delignification (b) and constant final pH (c), are shown in Figure 12 for the experiments containing unoxidized and oxidized dissolved matter.

As can be seen for the unoxidized dissolved matter, the delignification was decreased with increasing COD at constant NaOH charge (a) but was apparently increased with increasing COD at constant final pH (c). The apparent positive impact was due to the increased NaOH charges (cf. Figure 11c).

For the oxidized dissolved matter, the delignification was increased with increasing COD both at constant NaOH charge (a) and constant final pH (c). One can also see that the delignification was higher for the oxidized dissolved matter than the unoxidized dissolved matter, compared at a given COD, at constant NaOH charge and constant final pH.

Note that constant degree of delignification (b) for both unoxidized and oxidized dissolved matter was achieved by varying the NaOH charges (cf. Figure 11b).

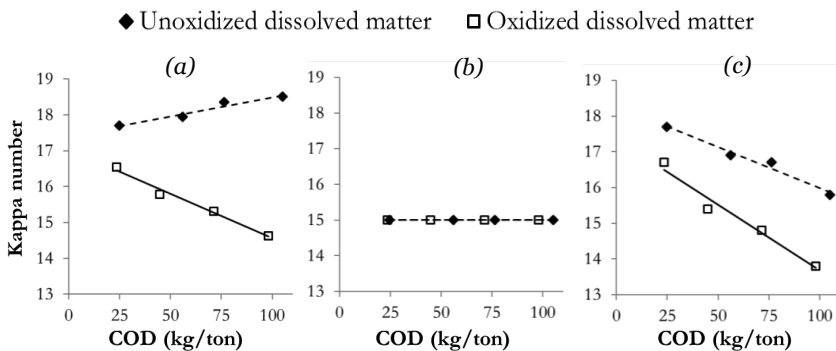


Figure 12: Kappa number vs. initial COD content with unoxidized and oxidized dissolved matter at constant NaOH charge (a), constant degree of delignification (b) and constant final pH (c).

#### 4.1.1.2 Viscosity

Viscosity of the fibers after the O<sub>2</sub>-stage versus COD content before the O<sub>2</sub>-stage for the three cases, i.e. constant NaOH charge (a), constant degree of delignification (b) and constant final pH (c), are shown in Figure 13 for the experiments containing unoxidized and oxidized dissolved matter.

As can be seen, the viscosity decreased with increasing COD for all three cases and for both types of dissolved matter. The correlation between viscosity and COD for the three cases was in agreement with the NaOH charges shown in Figure 11 since a high alkali charge is known to degrade carbohydrates.

At constant degree of delignification (b), the viscosity for the unoxidized dissolved matter was lower than in the other two cases. The viscosity for the oxidized dissolved matter was only moderately reduced. Thus, especially in the case of unoxidized dissolved matter, the carbohydrate degradation was higher than the lignin degradation.

At constant NaOH charge (a), the viscosity for the unoxidized dissolved matter was only moderately lower than for the oxidized dissolved matter. At constant final pH (c), the viscosity was reduced slightly more for the unoxidized dissolved matter compared to the case at constant NaOH charge.

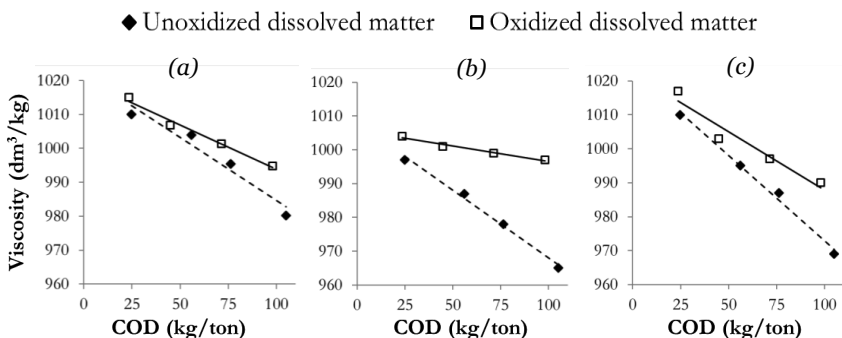


Figure 13: Viscosity vs. initial COD content with unoxidized and oxidized dissolved matter at constant NaOH charge (a), constant degree of delignification (b) and constant final pH (c).

### 4.1.1.3 Selectivity

Viscosity of the fibers after the O<sub>2</sub>-stage versus kappa number of the fibers after the O<sub>2</sub>-stage, i.e. selectivity, for the three cases, i.e. constant NaOH charge (a), constant degree of delignification (b) and constant final pH (c), are shown in Figure 14 for the experiments containing unoxidized and oxidized dissolved matter.

At constant NaOH charge (a), the selectivity for the unoxidized dissolved matter was different depending on COD level, i.e. a higher kappa number still resulted in a lower viscosity, thus suggesting that the carbohydrate degradation was increased with increasing COD while the lignin degradation was decreased. For the oxidized dissolved matter, the selectivity was only moderately affected with increasing COD at constant NaOH charge. Thus, the oxidized dissolved matter had a similar impact on selectivity as when using a higher alkali charge.

At constant degree of delignification (b), the viscosity was decreased with increasing COD, particularly for the unoxidized dissolved matter. Thus, increasing the NaOH charge to compensate for the negative impact on delignification by the unoxidized dissolved matter further impaired the selectivity. At constant final pH (c), the selectivity was lower for the unoxidized dissolved matter compared to the oxidized dissolved matter, partly due to the higher NaOH charges (cf. Figure 11c).

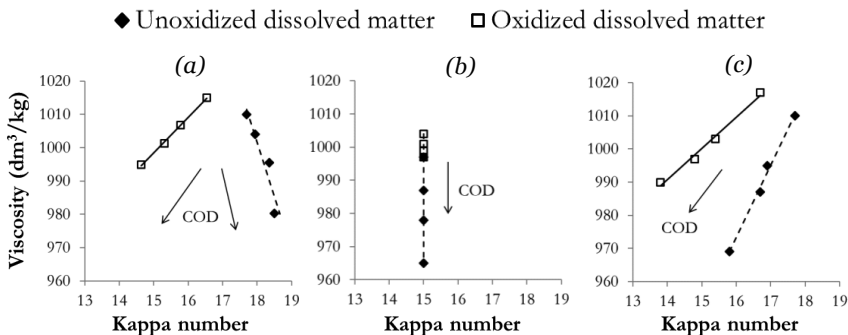


Figure 14: Viscosity vs. kappa number with unoxidized and oxidized dissolved matter at constant NaOH charge (a), constant degree of delignification (b) and constant final pH (c).

#### 4.1.1.4 Final pH

Final pH versus COD content before the O<sub>2</sub>-stage for the three cases, i.e. constant NaOH charge (a), constant degree of delignification (b), and constant final pH (c) are shown in Figure 15 for the experiments containing unoxidized and oxidized dissolved matter.

As can be seen, the final pH was decreased with increasing COD for both types of dissolved matter, thus indicating that the dissolved matter consumed sodium hydroxide. Note that constant final pH (c) was achieved by varying the NaOH charges (cf. Figure 11c).

At constant NaOH charge (a), the final pH was practically the same for the unoxidized and oxidized dissolved matter, compared at a given COD, thus suggesting that the two types of dissolved matter comparably consumed sodium hydroxide. The results however indicated that at high COD levels, the final pH was lower for the unoxidized dissolved matter than the oxidized dissolved matter.

At constant degree of delignification (b), the final pH for the unoxidized dissolved matter was only moderately reduced while for the oxidized dissolved matter, the final pH was drastically reduced. Note however that the NaOH charges in the case of oxidized dissolved matter were decreased with increasing COD (cf. Figure 11b).

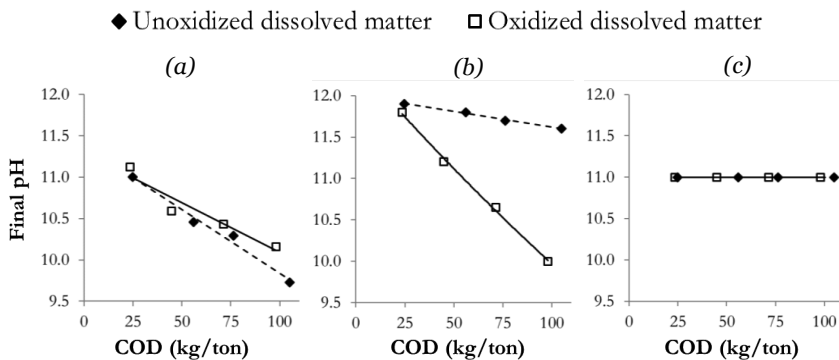


Figure 15: Final pH vs. initial COD content with unoxidized and oxidized dissolved matter at constant NaOH charge (a), constant degree of delignification (b) and constant final pH (c).

#### 4.1.1.5 Discussion

The results strongly indicated that employing a control system based on degree of delignification or final pH would yield very different results, in terms of kappa number and viscosity, depending on both the content and the type of dissolved matter. Different content and types of dissolved matter would also require different NaOH charges. The results would differ even more if the NaOH charge in an O<sub>2</sub>-stage remained constant over a period of time, despite changes in the content of dissolved matter due to e.g. variability in the cooking stage or the brown stock washing performance. The performance of an O<sub>2</sub>-stage would thus not only depend on the control system but also on the distribution between unoxidized and oxidized dissolved matter entering the O<sub>2</sub>-stage.

According to previous studies, the reactivity of the unoxidized dissolved matter is higher than that of the oxidized dissolved matter [17, 74, 148, 151]. The high reactivity would imply that more alkali is consumed by the unoxidized dissolved matter, thus resulting in less sodium hydroxide available to react with the fibers. The negative impact on delignification with increasing content of unoxidized dissolved matter at constant NaOH charge could be explained by the high alkali demand. Thus, to obtain a certain degree of delignification, an additional sodium hydroxide charge was required for the pulp containing unoxidized dissolved matter. According to Figure 11b, 100 kg COD/ton of pulp required 40 kg NaOH/ton of pulp to obtain kappa number 15 versus 30 kg NaOH/ton of pulp for the case with no dissolved matter. Thus, the additional alkali demand was equivalent to 0.1 kg NaOH per kg COD. The additional alkali demand will however depend on the degree of delignification, which in this case was 44%. At a lower degree of delignification, the additional alkali demand per kg COD would be lower, and vice versa.

For the pulp containing oxidized dissolved matter, a lower alkali charge was required to obtain a certain degree of delignification. According to Figure 11b at 100 kg COD/ton of pulp, only 17 kg NaOH/ton of pulp was required to obtain kappa number 15. The alkali demand was thus reduced by 0.13 kg NaOH per kg COD compared to the case with no

dissolved matter. The results thus suggested that oxidized dissolved matter had the same impact on delignification as sodium hydroxide. Studies have indicated that oxidized dissolved matter is unreactive towards sodium hydroxide, and thus not competing with the fiber-bound lignin [48, 66]. The lack of reactivity can explain why the alkali demand was not increased but cannot explain why it was even decreased.

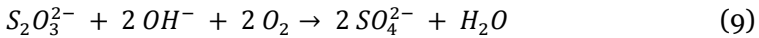
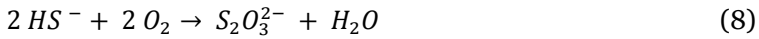
Free radicals such as hydroxyl radicals are formed in the O<sub>2</sub>-stage, and it has been reported that the formation of hydroxyl radicals is increased by dissolved matter, especially sulfur compounds such as sulfide and thiosulfate. The hydroxyl radicals do not only degrade lignin but also carbohydrates, through mainly random chain cleavage of the cellulose chain, thus impairing the selectivity [20, 68-70, 73, 154]. Studies have also shown that the presence of dissolved matter and residual alkali along with exothermic oxidation reactions of sulfur compounds increase the temperature in the O<sub>2</sub>-reactor, thus accelerating the degradation of carbohydrates [142, 152, 163]. The presence of dissolved sulfur compounds may partly explain why the viscosity was reduced even when the delignification was low for the pulp with unoxidized dissolved matter at constant NaOH charge (cf. Figure 14a). At constant degree of delignification, both sulfur compounds and higher alkali charges were probably responsible for the reduced viscosity for the pulp with unoxidized dissolved matter (cf. Figure 14b).

Dissolved matter in the O<sub>2</sub>-stage increases the generation of organic acids and carbon dioxide. More organic acids are generated with unoxidized dissolved matter than with oxidized dissolved matter, thus resulting in a higher alkali consumption due to neutralization reactions [70, 73-75, 142, 148, 153, 154]. More carbon dioxide is however generated with oxidized dissolved matter than with unoxidized dissolved matter, thus also resulting in a higher alkali consumption due to neutralization reactions [151, 153]. The final pH was decreased with increasing COD for both types of dissolved matter. At constant NaOH and at a given COD, the final pH was similar for unoxidized and oxidized dissolved matter, especially at lower COD (cf. Figure 15a). This suggested that the higher organic acid generation with the unoxidized dissolved matter and the higher carbon dioxide evolution with the oxidized dissolved

matter comparably consumed alkali, thus affecting the final pH of the filtrates similarly. However, the final pH for the unoxidized dissolved matter was reduced further at higher COD compared to the oxidized dissolved matter, suggesting that the correlation between unoxidized dissolved matter content and alkali demand was not linear.

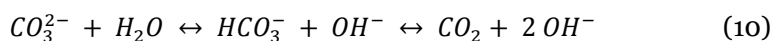
#### 4.1.2 Dissolved inorganic matter

Oxygen and hydroxide ions are consumed by dissolved inorganic matter, specifically thiosulfate ions ( $S_2O_3^{2-}$ ) and hydrogen sulfide ions ( $HS^-$ ), according to Equations 8 and 9. These reactions can occur e.g. during the completion of oxidation of white liquor, where thiosulfate is oxidized to sulfate [70, 164, 165]. Unoxidized filtrate will contain both thiosulfate and hydrogen sulfide ions, while the amount of the two ions in the oxidized filtrate will be significantly lower since it has already passed the  $O_2$ -stage at least once. Thus, unoxidized dissolved matter has a higher oxidant demand than oxidized dissolved matter partly due to the sulfur compounds [70, 74, 75, 142, 148, 153, 154].



According to Equations 8 and 9, one mole of hydrogen sulfide will consume one mole of oxygen and subsequently, via the formation of thio-sulfate, another mole of oxygen and one mole of hydroxide during the formation of sulfate. Thus, compensating for the reduced delignification with unoxidized dissolved matter by increasing the NaOH charge will still result in a higher oxygen consumption [152, 154]. Approximately 1 kg  $O_2$ /ton of pulp is required per kappa number reduction in the  $O_2$ -stage. 50% of the oxygen is consumed by lignin and carbohydrates, 10% by metals, 30% by thiosulfate and up to 10% by dissolved organic matter, where the oxidized dissolved matter consumes less than the unoxidized dissolved matter [70, 162]. In the current study, the oxygen was however overcharged and the consumption by the dissolved matter should thus not have resulted in oxygen depletion.

Dissolved inorganic matter in the form of residual alkali is positive for the delignification. The positive impact may not only be due to hydroxide ions, but also carbonate ions ( $\text{CO}_3^{2-}$ ). Carbonate is in equilibrium with bicarbonate and carbon dioxide according to Equation 10. As can be seen, carbonate ions could act as an alkaline buffer and potentially produce hydroxide ions. Even though the carbonate ion is a weaker base than the hydroxide ion, the equilibrium could still be shifted to the right when the carbonate content is very high. According to previous studies, carbonate ions improve the delignification in the  $\text{O}_2$ -stage, and could in fact replace hydroxide ions as the alkali source, albeit at slightly higher chemical charges compared to sodium hydroxide [149, 153, 166].



The  $\text{O}_2$ -stage itself is a source of carbonate ions. The carbon dioxide that is generated in the  $\text{O}_2$ -stage is neutralized to carbonate by reacting with hydroxide ions in the alkaline environment in the  $\text{O}_2$ -stage. Unstable organic acids are also formed during oxidation and could further react with hydroxide ions and generate carbonate in alkaline hydrolysis [149, 151, 153]. Thus, once the carbonate ions have been generated in the  $\text{O}_2$ -stage, they will be a source of alkali in the  $\text{O}_2$ -stage. The recycled filtrate containing oxidized dissolved matter will have a higher carbonate content than the unoxidized dissolved matter since the oxidized filtrate has already passed the  $\text{O}_2$ -stage at least once.

Carbonate ions could also react with hydroxyl radicals ( $\text{HO}^\bullet$ ), thus forming carbonate radicals ( $\text{CO}_3^{\bullet-}$ ), according to Equation 11. The formed carbonate radicals could oxidize lignin, thus increasing the delignification. The carbonate ion can act as a scavenger while reacting with the hydroxyl radical, thus reducing the carbohydrate degradation [167, 168]. Despite the different degree of delignification for the experiments with unoxidized and oxidized dissolved matter at constant NaOH charge, the viscosity was actually even moderately higher for the pulp containing oxidized dissolved matter at a given COD (cf. Figure 14a), thus indicating that the presence of carbonate ions in the oxidized filtrate increased the delignification while preserving the viscosity.



Thus, the differences observed between unoxidized and oxidized dissolved matter, in terms of lignin and carbohydrate degradation, could partly be explained by the additional alkali demand by e.g. sulfur compounds in the unoxidized dissolved matter, and the additional alkali contribution by carbonate ions in the oxidized dissolved matter.

#### 4.1.2.1 Filtrate composition

In order to further understand why the difference in delignification response occurred with unoxidized and oxidized dissolved matter, the composition of the filtrate samples was analyzed, and the results per COD are shown in Table 11.

It was observed that the content of thiosulfate and hydrogen sulfide ions was higher in the unoxidized filtrate. Both ions can directly and indirectly increase the hydroxide consumption during oxidation according to Equations 8 and 9.

It was further observed that the carbonate content was significantly higher in the oxidized filtrate and that the hydroxide content was significantly higher in the unoxidized filtrate. Residual hydroxide ions contribute alkali, and carbonate ions can act as a pH buffer and thus also be a source of alkali according to Equation 10.

Lastly, it was observed that the sodium content was higher in the oxidized filtrate, probably due to the NaOH charge in the previous O<sub>2</sub>-stage. The conductivity for the unoxidized and oxidized filtrates was 0.42 mS/m and 0.89 mS/m respectively, per g COD/L. The higher conductivity for the oxidized filtrate was probably due to the higher content of carbonate and sodium ions.

Table 11: Summary of the properties of the unoxidized and oxidized filtrate samples per g COD/L. Component:COD ratio is given in mg/L:g/L.

Component	Unoxidized filtrate	Oxidized filtrate
Carbonate	50.3	159.9
Hydroxide	10.8	1.5
Thiosulfate	15.9	6.9
Hydrogen sulfide	13.1	0.9
Sodium	159.5	265.1

Additional experiments were conducted with Pulp II (see Table 8) containing unoxidized or oxidized dissolved matter. The aim was to investigate the impact on the degree of delignification by the presence of thiosulfate and carbonate ions. Either sodium thiosulfate or sodium carbonate was added prior to laboratory O<sub>2</sub>-stage to pulp samples containing no dissolved matter, unoxidized dissolved matter or oxidized dissolved matter. The amount of unoxidized or oxidized dissolved matter present in the experiments corresponded to 100 kg COD/ton of pulp.

#### 4.1.2.2 Impact of thiosulfate

The obtained kappa number of the fibers after the O<sub>2</sub>-stage versus the initial thiosulfate ion content is shown in Figure 16a. It can be seen that the kappa number was higher when the thiosulfate content exceeded 0.2 g/L for the pulp containing no dissolved matter and the pulp containing unoxidized dissolved matter. However, the addition of thiosulfate appeared to have very little impact on the pulp containing oxidized dissolved matter.

The final pH, shown in Figure 16b, was not significantly influenced by the addition of thiosulfate in any of the three cases, thus suggesting that the hydroxide consumption by the thiosulfate ions only had a minor impact on final pH. Note however, that the final pH was different for the three cases, which is in agreement with previous results at 100 kg COD/ton of pulp (cf. Figure 15a).

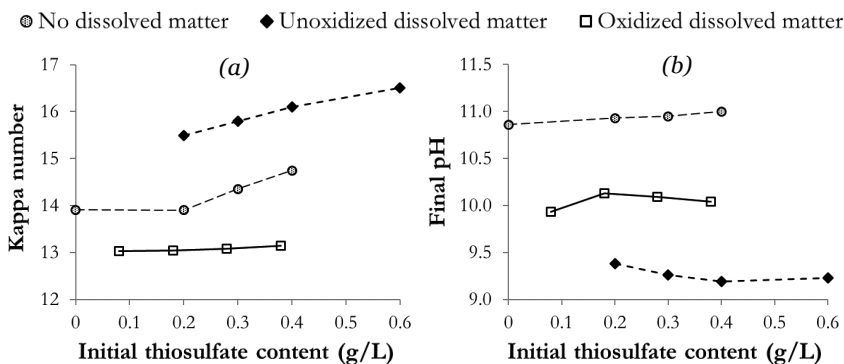


Figure 16: Kappa number (a) and final pH (b) vs. total initial thiosulfate content for the three cases, i.e. no dissolved matter, unoxidized dissolved matter and oxidized dissolved matter. The COD content for the experiments with unoxidized and oxidized dissolved matter was 100 kg/ton of pulp prior to the addition of sodium thiosulfate.

The relatively small impact on final pH by the thiosulfate ions is further supported by calculating the additional hydroxide demand of an addition of 0.2 g  $S_2O_3^{2-}/L$ , i.e. 1.8 mmol  $S_2O_3^{2-}/L$ . According to Equation 9, two moles of hydroxide ions are required to oxidize thiosulfate to sulfate, i.e. corresponding to 3.6 mmol/L in this case. In these experiments, 50 mmol NaOH/L was charged, and the hydroxide demand of 0.2 g  $S_2O_3^{2-}/L$  was thus only 7% of the charged hydroxide.

Similarly, the additional hydroxide demand of the residual thiosulfate ions and, indirectly, hydrogen sulfide ions, present in the filtrates could also be calculated. According to Table 12, the total consumption of hydroxide ions was significantly larger for the unoxidized filtrate compared to the oxidized filtrate. However, after considering the residual hydroxide ion content in the two filtrates (cf. Table 11), the total additional need of hydroxide ions due to the presence of residual thiosulfate and hydrogen sulfide ions was similar for both filtrates: 0.6 mmol/L and 0.7 mmol/L for the unoxidized and oxidized filtrates respectively.

Furthermore, the additional need of hydroxide corresponded to less than 1.5% of the charged sodium hydroxide. Thus, the additional hydroxide demand due to thiosulfate and, indirectly, hydrogen sulfide was very low compared to the charged hydroxide and could subse-

quently not be the explanation of either the low final pH or the low delignification obtained at constant NaOH charge when unoxidized dissolved matter was present.

*Table 12: The impact of the presence of hydrogen sulfide and thiosulfate ions on the hydroxide consumption in the O<sub>2</sub>-stage. 50 mmol OH<sup>-</sup>/L was charged in the experiments. The concentration of the compounds is given in mmol/L.*

Compound	Addition of 0.2 g S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> /L	Unoxidized filtrate	Oxidized filtrate
Initial HS <sup>-</sup>		5.0	0.3
Produced S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>		2.5	0.15
Initial S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>		1.8	0.7
Total S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	1.8	4.3	0.85
Consumption of OH <sup>-</sup>		8.6	1.7
Initial OH <sup>-</sup>		8.0	1.0
Total need of OH <sup>-</sup>	3.6	0.6	0.7

#### 4.1.2.3 Impact of carbonate

The obtained kappa number of the fibers after the O<sub>2</sub>-stage versus the initial carbonate ion content is shown in Figure 17a, and it can be seen that the kappa number was decreased when carbonate ions were added. The kappa number reduction was similar for all three cases: approximately 1.5 kappa units at 4 g CO<sub>3</sub><sup>2-</sup>/L. The kappa numbers with unoxidized dissolved matter were however higher compared to the other two cases since the unoxidized filtrate itself had a negative impact on the delignification (cf. Figure 12a).

According to Figure 17b, the final pH with unoxidized and oxidized dissolved matter was higher with increasing carbonate content. The second pK<sub>a</sub> value at 25°C for carbonate is at pH 10.3 [169]. Thus, it can be assumed that the alkaline buffering effect was high when the pH was below the pK<sub>a</sub> value [149, 153]. For the case with no dissolved matter, however, the final pH was reduced with increasing carbonate content but always remained above the pK<sub>a</sub> value. Thus, the improved delignification with increasing carbonate content for the sample with no

dissolved matter appeared not to be due to the pH buffering effect. The results are in agreement with a study by Allison et al. [149], who found that the delignification was moderately improved even when the final pH was higher than the  $pK_a$ .

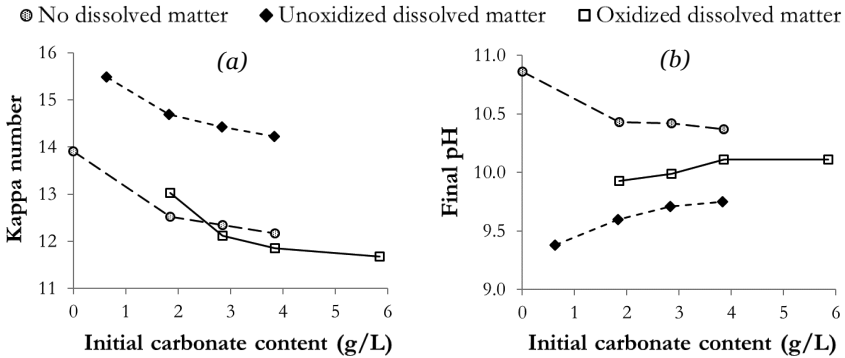


Figure 17: Kappa number (a) and final pH (b) vs. total initial carbonate content for the three cases, i.e. no dissolved matter, unoxidized dissolved matter and oxidized dissolved matter. The COD content for the experiments with unoxidized and oxidized dissolved matter was 100 kg/ton of pulp prior to the addition of sodium carbonate.

The presence of carbonate ions may thus explain the positive impact on delignification with oxidized dissolved matter. However, the different degrees of delignification obtained when the NaOH charge was adjusted to constant final pH (cf. Figure 12c) suggested that the carbonate ions are positive for the delignification even without the alkaline buffering effect that resulted in higher final pH.

It is possible that the carbonate ions could also affect the pH gradients, thus reducing the differences in pH during the various reactions in the  $O_2$ -stage. The decrease in reaction pH due to e.g. the generation of acids or the possible increase in pH due to other reactions in the  $O_2$ -stage could be evened out by the carbonate ions due to their alkaline buffering effect, thus improving the performance of the  $O_2$ -stage.

During the oxygen delignification reactions, small amounts of hydrogen peroxide are formed. Metals, e.g. iron and manganese, can decompose the generated hydrogen peroxide, thus reduce the positive impact

on delignification by the hydrogen peroxide [73, 94, 170]. It has previously been suggested that oxidized dissolved matter may act as a chelating agent, thus maximizing the positive impact on delignification by the generated hydrogen peroxide [48, 66]. It is now proposed that it is the carbonate ions in particular that have this impact.

## 4.2 Impact of dissolved organic matter in a hot acid stage

The pulp sample used in the hot acid study was collected from the screw in the filter prior to the D<sub>0</sub>-stage together with the corresponding filtrate according to Figure 18. The aim was to determine if dissolved organic matter, predominantly lignin residues, entering an A-stage affected the degree of HexA removal. The laboratory procedure and the conditions used were according to Figure 6 and Table 5. The following results are also presented in Paper V.

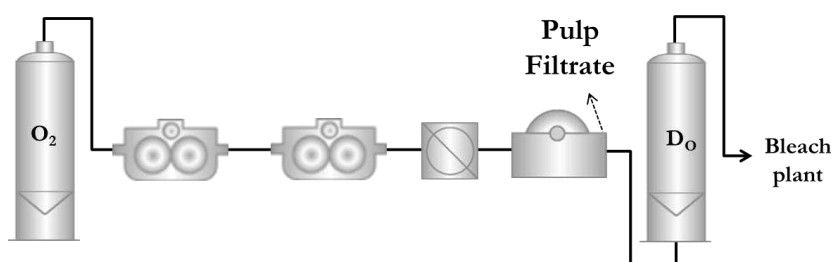


Figure 18: Sampling positions in the hardwood pulp mill, where the raw material was birch.

The kappa numbers before and after the A-stage for the Reference pulp and the Pulp with filtrate are shown in Table 13. Note that HexA and lignin were collectively quantified as kappa number, both for fibers and filtrates. As can be seen, the fiber kappa number after the A-stage for the Reference pulp was lower compared to the Pulp with filtrate. Thus, the presence of dissolved matter, predominantly lignin residues, influenced the removal and/or degradation of fiber-bound HexA.

Dissolved lignin was likely removed and/or degraded in the A-stage, and this could account for the differences in fiber kappa number reduction between the Reference pulp and the Pulp with filtrate. The removal of dissolved lignin was further supported by the filtrate kappa numbers, where the final filtrate kappa numbers were similar for the two cases even though Pulp with filtrate had a higher initial filtrate kappa number. The filtrate kappa numbers thus indicated that dissolved lignin originally present in the Pulp with filtrate was removed and/or degraded in the A-stage and subsequently reduced the HexA removal.

Table 13: Fiber and filtrate kappa numbers for the Reference pulp and the Pulp with filtrate, before and after the A-stage. The filtrate kappa numbers were calculated per gram fiber at 10% pulp consistency.

	Reference pulp	Pulp with filtrate
Initial fiber kappa number	12.5	12.5
Final fiber kappa number	8.6	10.0
Initial filtrate kappa number	0	1.1
Final filtrate kappa number	1.6	1.7

The conclusion that dissolved lignin is removed and/or degraded is further supported by studies that have shown that not only HexA but also easily accessible lignin is degraded in an A-stage [99, 111, 171]. In a study by Ikeda et al. [171], both lignin and HexA degradation were responsible for the kappa number reduction of a beech pulp, and in a study by Furtado et al. [111], about half of the kappa number reduction of a eucalyptus pulp was due to lignin removal. Ventorim et al. [99] further found that the reaction rate of lignin is higher than that of HexA in an A-stage. Other studies have however shown that the lignin degradation is very limited in an A-stage [107, 172].

#### 4.2.1 Combined A- and D<sub>0</sub>-stages

The two generated A-pulps were further treated with chlorine dioxide, with and without intermediate washing, thus simulating AD- and (AD)-stages respectively. The intention was to determine if dissolved organic matter, i.e. mainly lignin and HexA residues, after an A-stage influenced the delignification and the chlorine dioxide demand in a following D<sub>0</sub>-stage. D<sub>0</sub>- and D\*-stages were also conducted on the Reference pulp for comparison. The kappa factors in the various D-stage combinations were based on the kappa numbers of the fibers entering the D-stages.

The resulting kappa numbers after the A- and D-stage experiments are shown in Figure 19, including the results of the A-stage already presented in Table 13. Filtrate kappa numbers after the last stage, calculated per gram fiber at 10% pulp consistency, are also shown together

with the ClO<sub>2</sub> charges in the D-stages. The following observations can be made from Figure 19:

- For the (AD)-stage, i.e. without intermediate washing, the kappa numbers for the Reference pulp and the Pulp with filtrate were essentially the same despite different ClO<sub>2</sub> charges. Similar results were obtained for the AD-stages, i.e. with intermediate washing.
- When comparing intermediate washing, it is apparent that the washing only had a relatively small impact on the kappa number after the D<sub>0</sub>-stage, for both the Reference pulp and the Pulp with filtrate; only 0.3 kappa number units.
- The use of a D\*-stage instead of a D<sub>0</sub>-stage decreased the kappa number to 4.6 versus 6.2 at the same ClO<sub>2</sub> charge.

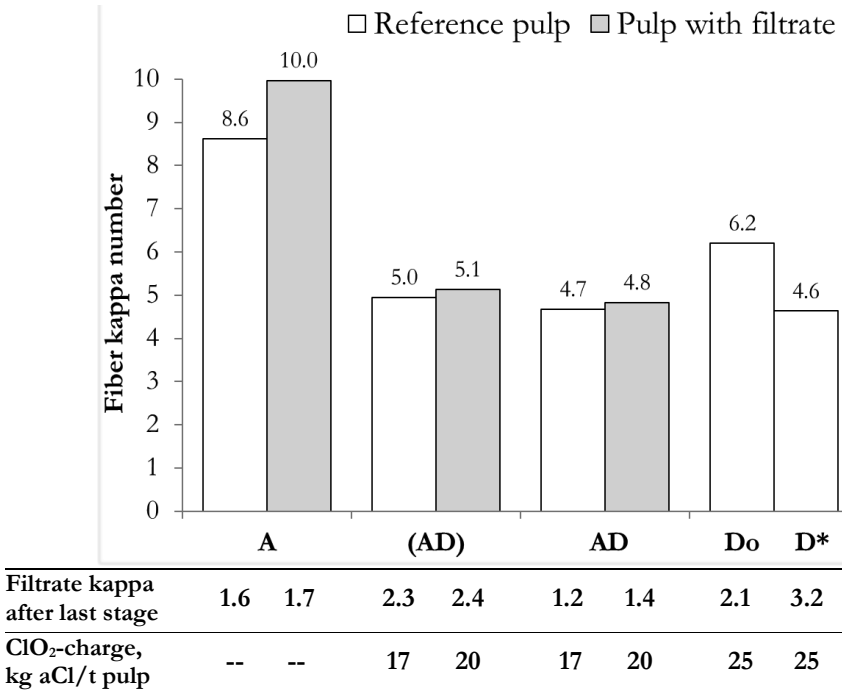


Figure 19: Fiber kappa numbers of the Reference pulp and the Pulp with filtrate after the various A- and D-stage experiments. Filtrate kappa numbers after the last stage, calculated per gram fiber at 10% pulp consistency, are also shown together with the ClO<sub>2</sub> charges in the D-stages.

Since the  $\text{ClO}_2$  charge was based on the kappa number of the fibers after the A-stage, the chemical charge for the Pulp with filtrate was 15% higher than that of the Reference pulp in the (AD)- and AD-stages. Had the  $\text{ClO}_2$  charge for the Reference pulp been equally high, the kappa number after the  $\text{D}_0$ -stage would have been lower in the (AD)- and AD-sequences compared to the Pulp with filtrate.

Previous reports have shown that A-filtrates consume chlorine dioxide rapidly, thus affecting the lignin removal in the fibers [46, 161]. Without intermediate washing prior to the  $\text{D}_0$ -stage, i.e. (AD)-stage, the hydrolysis products are still present and thus available to consume chlorine dioxide [100, 108, 113, 161]. However, other studies have shown that intermediate washing is not necessary because chlorine dioxide reacts much faster with lignin than dissolved HexA residues, i.e. most of the chlorine dioxide is consumed by lignin [105, 117]. The results presented here suggested that intermediate washing was not essential for the delignification in a  $\text{D}_0$ -stage and are thus in agreement with the latter references.

The use of a  $\text{D}^*$ -stage would decrease the chlorine dioxide demand if the pulp was bleached to the same kappa number as in a  $\text{D}_0$ -stage. Studies have shown that up to 30% reduction of chlorine dioxide is possible with a  $\text{D}^*$ -stage instead of a  $\text{D}_0$ -stage [100, 101, 112, 113]. Note however that a  $\text{D}^*$ -stage will remove more HexA than a  $\text{D}_0$ -stage, thus reducing the kappa number due to both lignin and HexA degradation.

In a  $\text{D}^*$ -stage, the degradation and the dissolution of both lignin and HexA consume chlorine dioxide [100, 116, 161]. A study by Ragnar [113], however, concluded that since there are no dissolved HexA residues present at the start of the  $\text{D}^*$ -stage, the chlorine dioxide will only react with lignin and be depleted before the dissolved HexA residues have been generated. Ventorim et al. [99], on the other hand, found that the reaction rate of HexA is actually higher with chlorine dioxide than with sulfuric acid, thus making the  $\text{D}^*$ -stage with simultaneous acid treatment less efficient compared to separate A- and  $\text{D}_0$ -stages. The results presented in Figure 19 also indicated that a  $\text{D}^*$ -stage was less efficient since the  $\text{ClO}_2$  charge needed to obtain the same final kappa number as in the AD-stage was almost 50% higher.

### **4.2.2 Light absorption spectra**

Both dissolved lignin and dissolved HexA residues can be quantified by measuring the light absorption of filtrate samples at specific wavelengths. During the A-stage treatment, HexA is degraded to 2-furancarboxylic and 5-formyl-2-furancarboxylic acids with absorption maxima at 245 nm and 285 nm respectively [98, 104]. The light absorption of the resulting filtrates from the experiments shown in Figure 19 was analyzed in a spectrophotometer after dilution 1:20, and the light absorption was recalculated to values corresponding to undiluted filtrates. The aim of the analysis was to investigate the degradation and dissolution of lignin and HexA in A- and D-stages.

The shape of the filtrate spectra was similar for the experiments with the Reference pulp and the Pulp with filtrate. Only the spectra of the resulting filtrates from the experiments with the Reference pulp are therefore shown in Figure 20. The spectrum of the original filtrate is also shown, and as expected, the O<sub>2</sub>-filtrate did not contain HexA residues.

According to Figure 20, the filtrate after the A-stage had a peak at 245-250 nm, thus indicating that HexA was dissolved from the fibers and further degraded to a significant amount 2-furancarboxylic acid. Although not shown here, the light absorption was 2.5 units lower for the Pulp with filtrate, indicating that less HexA was degraded and dissolved in that pulp compared to the Reference pulp, thus in agreement with the higher fiber kappa number of the Pulp with filtrate compared to the Reference pulp shown in Figure 19.

The peak at 245-250 nm was not present after the AD-stage since the intermediate washing removed the 2-furancarboxylic acid generated in the A-stage. The filtrate after the (AD)-stage however had a peak at 245-250 nm, thus indicating that the 2-furancarboxylic acid generated in the A-stage was not further degraded by the chlorine dioxide in the subsequent D<sub>0</sub>-stage. The small difference in kappa number between the (AD)- and AD-stages (cf. Figure 19) can thus be explained since the delignification in the D<sub>0</sub>-stage of the (AD)-sequence should not have been significantly affected by the presence of 2-furancarboxylic acid.

Previous studies have shown that chlorine dioxide is consumed in reactions with HexA [97-101]. The peak at 245-250 nm was not present after the D<sub>0</sub>-stage, indicating that 2-furancarboxylic acid was not generated in the reactions between HexA and chlorine dioxide. The peak was however present after the D\*-stage, but the light absorption was significantly lower compared to the A- and (AD)-stages. This suggested that less 2-furancarboxylic acid was generated in a D\*-stage compared to an A-stage.

The shape of the spectra after the AD- and D<sub>0</sub>-stages was practically identical, thus further indicating that chlorine dioxide in a D<sub>0</sub>-stage did not degrade and dissolve HexA into 2-furancarboxylic acid. According to Vuorinen et al. [105], HexA residues after a D-stage consist of unchlorinated and chlorinated dicarboxylic acids such as tetraric, pentaric, 2-chloro-2-deoxypentaric and 3-deoxy-3,3-dichloro-2-oxohexaric acids.

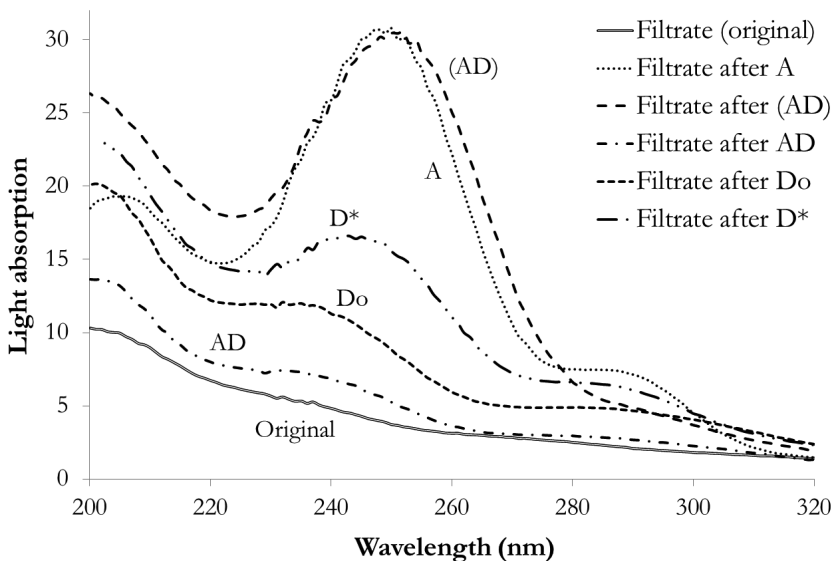


Figure 20: Light absorption of the filtrates vs. wavelength. The measured light absorption was recalculated to reflect undiluted filtrates.

### 4.3 Impact of dissolved organic matter in a chlorine dioxide stage

The pulp sample used in the chlorine dioxide study with softwood was collected after the press prior to the  $D_0$ -stage together with the corresponding filtrate, denoted Filtrate 2, according to Figure 21. The samples were collected after dilution of the pulp to medium consistency, i.e. the samples contained both  $O_2$ -filtrate and recycled  $D_0$ -filtrate, where approximately 7/9 was recycled  $D_0$ -filtrate. At this position, the content of dissolved organic matter was relatively low, so to achieve a higher content, a filtrate sample was also collected prior to the press, denoted Filtrate 1. This filtrate not only contained more dissolved organic matter but also exclusively  $O_2$ -filtrate since the wash water used in the press was not a recycled  $D_0$ -filtrate. The following results for softwood are unpublished, but similar results are presented in Paper II.

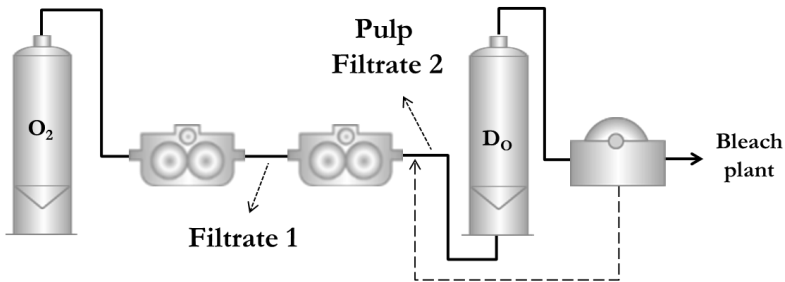


Figure 21: Sampling positions in the softwood pulp mill. The recycling of  $D_0$ -filtrate as dilution medium is also shown with a dashed arrow.

The pulp sample used in the chlorine dioxide study with hardwood was collected from the screw in the filter prior to the  $D_0$ -stage together with the corresponding filtrate, denoted Filtrate 2, according to Figure 22. Since the content of dissolved organic matter was relatively low at this position, a filtrate with a higher content was collected as well. The filtrate from the vat in the filter was too similar to Filtrate 2, so Filtrate 1 was collected earlier in the process, prior to a press. Both filtrates contained exclusively  $O_2$ -filtrate. The following results for hardwood are also presented in Paper V.

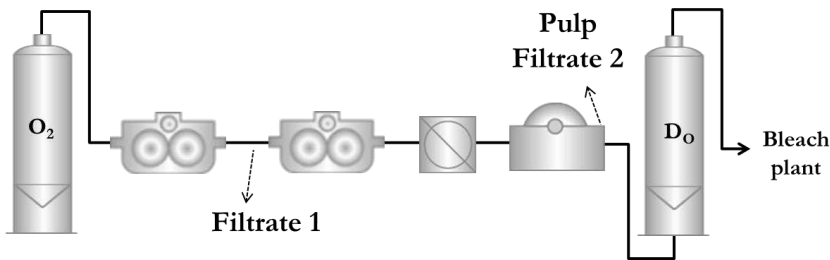


Figure 22: Sampling positions in the hardwood pulp mill, where the raw material was birch.

Two combinations of fibers and filtrates were investigated for the softwood pulp and the hardwood pulp, respectively. The fiber and filtrate kappa numbers for these four combinations, i.e. Pulp with Filtrates 1 and 2 at 10% pulp consistency for both softwood and hardwood, are shown in Table 14, and these were the starting points in all experiments.

Table 14: Fiber and filtrate kappa numbers before the  $D_0$ -experiments at 10% pulp consistency for the Pulp with Filtrates 1 and 2 for both softwood and hardwood.

	Softwood		Hardwood	
	Pulp with F1	Pulp with F2	Pulp with F1	Pulp with F2
Fibers	14.1	14.1	12.5	12.5
Filtrate	6.6	1.6	5.2	0.9

#### 4.3.1 Fiber kappa number versus total kappa number

The charge of chlorine dioxide in a  $D_0$ -stage is normally based mainly on the fiber kappa number of the well-washed pulp prior to the  $D_0$ -stage. However, dissolved organic matter, predominantly lignin residues, also consumes chlorine dioxide, and it was suggested that the additional chlorine dioxide was in proportion to the kappa number of the filtrate. To determine if this was the case, chlorine dioxide laboratory experiments were conducted on both softwood and hardwood pulps using different levels of dissolved organic matter (measured as filtrate kappa number) and different  $ClO_2$  charges (measured as per-

centage active chlorine charge per fiber kappa number, i.e. kappa factor).

Softwood and hardwood pulp samples containing dissolved organic matter from Filtrates 1 and 2, i.e. Pulp with Filtrates 1 and 2, were bleached at different kappa factors and compared to bleaching experiments with well-washed softwood and hardwood pulp samples respectively, i.e. Reference pulp. The results for the softwood pulp are shown in Figure 23a and the results for the hardwood pulp are shown in Figure 23b. The dotted line at kappa factor 0.2 and the resulting fiber kappa number for the Reference pulp was used as a comparison to the samples containing dissolved organic matter.

As can be seen, the fiber delignification was influenced by the dissolved organic matter, and the kappa factor required to obtain the same kappa number was higher when dissolved organic matter was present. For softwood, kappa factors 0.3 and 0.23 were required for the Pulp with Filtrates 1 and 2 respectively, i.e. 50% and 15% more chlorine dioxide respectively, compared to the Reference pulp. Similar results were obtained for the hardwood experiments. Thus, the additional chlorine dioxide required to obtain the same fiber kappa number was proportional to the filtrate kappa number contribution from the filtrates prior to the D<sub>0</sub>-stage (cf. Table 14).

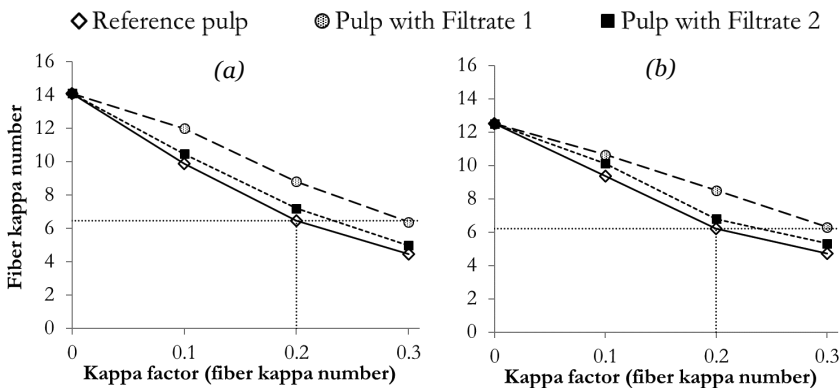


Figure 23: Fiber kappa number vs. kappa factor for softwood (a) and hardwood (b) pulps. The kappa factor was calculated as percentage active chlorine charge per fiber kappa number.

In Figure 24, the kappa factors were based on the total kappa number, i.e. the sum of the fiber and filtrate kappa numbers, and the kappa numbers from the experiments with and without dissolved organic matter followed one correlation, both for softwood (a) and hardwood (b). The additional chemical demand required to compensate for the reduced delignification was proportional to the content of dissolved matter. The total chlorine dioxide demand was thus proportional to the total kappa number of the pulp, i.e. the sum of the fiber and filtrate kappa numbers. This conclusion is in agreement with Blomberg et al. [160], who suggested that the additional  $\text{ClO}_2$  charge could be estimated by the kappa number of the filtrate, measured as liquid kappa number, i.e. the difference between the unwashed and washed kappa numbers.

Even though the analysis of filtrate kappa number not only measures the dissolved lignin content but also the content of other oxidizable compounds, it is clear that the potassium permanganate consumption in the kappa number determination correlated with the chlorine dioxide consumption by the dissolved organic matter in a  $\text{D}_0$ -stage. By measuring the fiber-bound lignin content as well as the dissolved lignin content into a  $\text{D}_0$ -stage as kappa number, pulp mills can apply chemicals based on the actual total bleach load, thus likely resulting in lower chemical cost and better pulp uniformity.

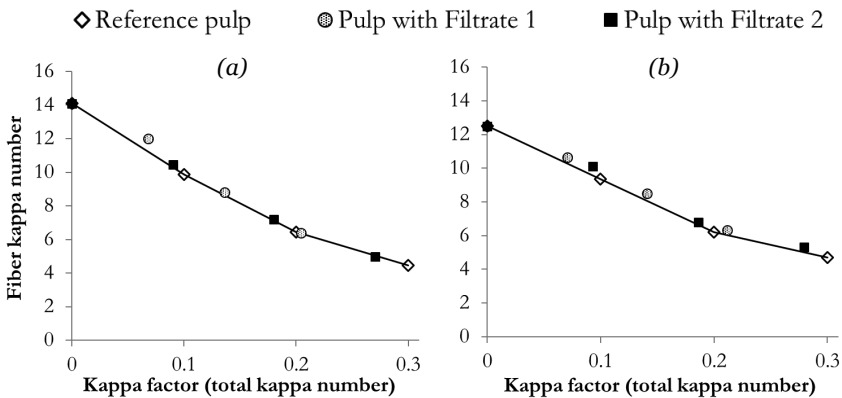


Figure 24: Fiber kappa number vs. kappa factor for softwood (a) and hardwood (b) pulps. The kappa factor was calculated as percentage active chlorine charge per total kappa number, i.e. the sum of the fiber and filtrate kappa numbers.

### 4.3.2 Recycling of filtrates

Since mills employ a countercurrent washing system, where filtrates are recycled and reused in previous stages as either wash water and/or dilution media, the impact on delignification and chlorine dioxide demand was also investigated with  $D_0$ -filtrates that were generated in laboratory experiments and reused together with well-washed pulp samples in new laboratory experiments.

As described earlier, the softwood Filtrate 2 mainly consisted of recycled  $D_0$ -filtrate, due to dilution prior to the  $D_0$ -stage. The results with Filtrate 2 showed that the chlorine dioxide consumption should be based on the total kappa number, thus indicating that recycled  $D_0$ -filtrate continued to consume chlorine dioxide when bleached a second time. Further experiments were however conducted according to Figure 8, with completely recycled filtrates.

In Table 15, the kappa numbers for the Reference softwood and hardwood pulps and the kappa numbers for the pulp samples containing recycled filtrates from the reference experiments, denoted ' $f_0$ ' (cf. Figure 8), are shown. As can be seen, the presence of recycled filtrate in the  $D_0$ -stage influenced the degree of delignification in the  $D_0$ -stage, and the kappa number of the Pulp with recycled filtrates was approximately 1 kappa number higher than that of the Reference pulp.

*Table 15: Fiber kappa numbers after the  $D_0$ -stage for softwood and hardwood pulps, with and without recycled filtrate  $f_0$ . The recycled filtrate  $f_0$  consisted of the generated  $D_0$ -filtrate from the experiment with the Reference pulp at kappa factor 0.2.*

	Softwood	Hardwood
Reference pulp	6.4	6.2
Pulp with $f_0$	7.4	7.1

Similar results of the impact of recycled filtrates were obtained when Filtrates 1 and 2, from both softwood and hardwood, were recycled, i.e.  $f_1$  and  $f_2$  according to Figure 8. The results from the hardwood experi-

ments, with the Reference pulp and the Pulps with recycled filtrates  $f_0$ - $f_2$ , are shown in Figure 25.

According to Figure 25a, where the kappa factor was based only on the fiber kappa number of the well-washed pulp, the fiber kappa numbers were higher for the experiments containing recycled filtrates compared to the kappa number of the Reference pulp.

When the fiber kappa number was plotted versus the kappa factor based on the total kappa number, i.e. the sum of the fiber and filtrate kappa numbers, the Pulp with recycled filtrates followed the correlation of the Reference pulp (Figure 25b), i.e. the filtrate kappa number of the recycled filtrates were in proportion to the additional chlorine dioxide demand.

Thus, recycled  $D_0$ -filtrates also consumed chlorine dioxide and negatively affected the delignification. The results are in agreement with a study by Fiskari et al. [12]. The results thus further supported that the  $ClO_2$  charge should be based on the total kappa number rather than on only the fiber kappa number.

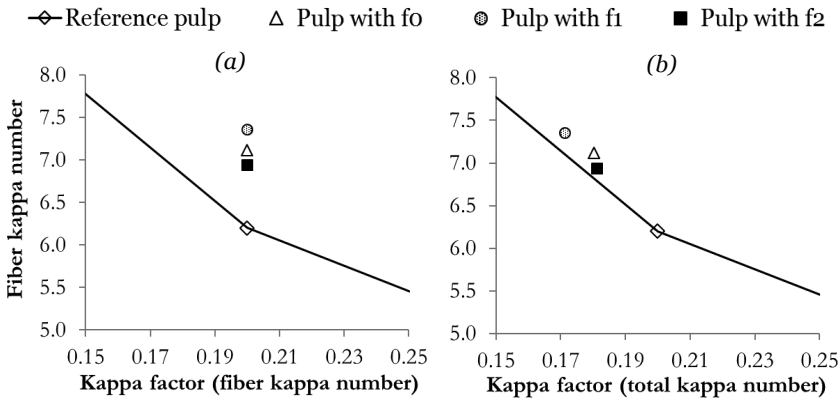


Figure 25: Fiber kappa number after the  $D_0$ -stage with recycled  $D_0$ -filtrates vs. kappa factor based on fiber kappa number (a) and total kappa number (b). The results of the Reference pulp and the Pulp with  $f_0$  are the same as in Table 15. The black line is based on the results of the Reference pulp shown in Figure 23b.

### 4.3.3 Reactivity of filtrates

The chlorine dioxide demand of filtrates entering the D<sub>0</sub>-stage seemed to be independent of the origin of the filtrates, i.e. O<sub>2</sub>-filtrates and recycled D<sub>0</sub>-filtrates consumed the same amount of chlorine dioxide, compared per filtrate kappa number. To further investigate the reactivity of the two types of filtrates, theoretical calculations of the filtrates in a D<sub>0</sub>-stage were constructed. The following results are unpublished but based on the results presented in Paper V.

The Reference pulp prior to the D<sub>0</sub>-stage did not contain O<sub>2</sub>-filtrate, so the generated filtrate present in the pulp after the laboratory D<sub>0</sub>-stage only consisted of dissolved organic matter generated in the D<sub>0</sub>-stage. The kappa number of this generated filtrate per fiber kappa number reduction in the D<sub>0</sub>-stage was calculated according to Equation 12, thus providing a constant at each kappa factor.

Assuming that the same constant of the D<sub>0</sub>-filtrate generation is valid also for the experiments where O<sub>2</sub>-filtrate was originally present into the D<sub>0</sub>-stage, a theoretical D<sub>0</sub>-filtrate generation could also be calculated for Filtrates 1 and 2. The constant from Equation 12 was thus multiplied by the kappa number reduction of the fibers at each kappa factor, thus resulting in a generated D<sub>0</sub>-filtrate for that particular experiment (Equation 13). This calculated filtrate kappa number was then subtracted from the measured kappa number of the filtrate, thus resulting in the contribution to kappa number from the remaining O<sub>2</sub>-filtrate (Equation 14).

$$c = \frac{K_{filtrate\ reference}}{\Delta K_{Fiber\ reference}} \quad (12)$$

$$K_g = c * \Delta K_{Fiber} \quad (13)$$

$$K_r = K_m - K_g \quad (14)$$

where  $c$  = Constant for the generation of filtrate kappa number  
in the  $D_0$ -stage at a specific kappa factor

$K_{filtrate\ reference}$  = Kappa number of the generated filtrate  
for the Reference pulp

$\Delta K_{Fiber\ reference}$  = Kappa number reduction of the fibers  
for the Reference pulp

$\Delta K_{Fiber}$  = Kappa number reduction of the fibers for the  
Pulp with filtrate

$K_g$  = Kappa number of the generated filtrate

$K_r$  = Kappa number of the remaining original filtrate

$K_m$  = Measured kappa number of the filtrate

The filtrate kappa numbers obtained according to Equations 12-14 for Filtrates 1 and 2 from the hardwood experiments versus kappa factors based on the fiber kappa number are shown in Figure 26.

For Filtrate 1 (Figure 26a), the measured filtrate kappa number was significantly lower at kappa factor 0.1 compared to the filtrate kappa number entering the  $D_0$ -stage, i.e. at kappa factor 0. The results thus suggested that a significant portion of the chlorine dioxide was consumed in reactions with the dissolved organic matter in the filtrate which originated from the  $O_2$ -stage.

At higher kappa factors, more dissolved organic matter was generated due to higher fiber delignification, and the measured filtrate kappa number started to increase. It can be seen that according to the calculations, approximately one-third of the original filtrate remained at kappa factor 0.3. The generated  $D_0$ -filtrate steadily increased with increasing kappa factor due to the higher fiber delignification.

For Filtrate 2 (Figure 26b), the curve of the measured filtrate kappa number was different, since it was relatively flat at kappa factor 0.1 compared to the starting value. However, the correlation for the remaining  $O_2$ -filtrate was similar to that of Filtrate 1, and approximately one-third of the original filtrate remained at kappa factor 0.3.

The generated D<sub>0</sub>-filtrate also followed a similar path as that of Filtrate 1, i.e. a steady increase in filtrate kappa number with increasing kappa factor due to the higher fiber delignification.

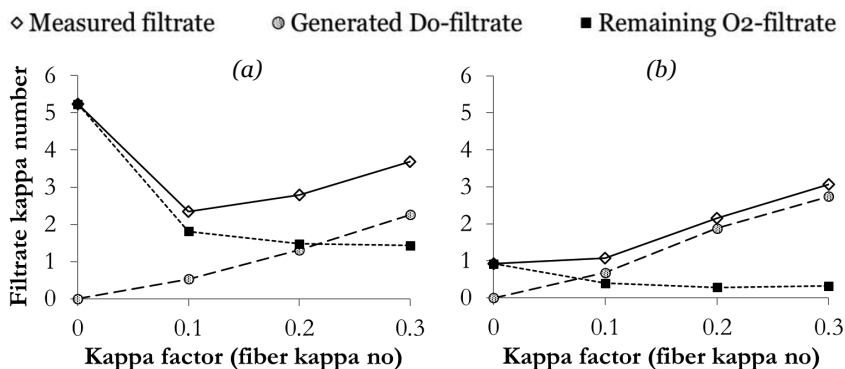


Figure 26: Illustration of the different types of filtrates present before and after a D<sub>0</sub>-stage for hardwood Filtrate 1 (a) and Filtrate 2 (b). The generated D<sub>0</sub>-filtrate and the remaining O<sub>2</sub>-filtrate were calculated according to Equations 12-14.

Similar results were obtained for the softwood pulps, where approximately one-third of the original O<sub>2</sub>-filtrate remained at kappa factor 0.3. Thus, one can conclude that the reactivity of the O<sub>2</sub>-filtrate was higher than that of the generated D<sub>0</sub>-filtrate since the kappa number of the O<sub>2</sub>-filtrate decreased whereas that of the D<sub>0</sub>-filtrate steadily increased. The results are in agreement with a study by Viirimaa et al. [17], who also found that the reactivity of dissolved O<sub>2</sub>-lignin was higher than that of dissolved D<sub>0</sub>-lignin.

The chlorine dioxide that was consumed by the filtrate was thus probably mainly consumed in reactions with dissolved organic matter from the O<sub>2</sub>-stage rather than in reactions with dissolved organic matter generated in the D<sub>0</sub>-stage. Furthermore, it was not possible to remove all of the O<sub>2</sub>-filtrate at the kappa factors used in the experiments. It is thus possible that recycled filtrates, even though they have passed through the D<sub>0</sub>-stage, still contain unreacted O<sub>2</sub>-filtrate that could continue to consume chlorine dioxide. However, when only D<sub>0</sub>-filtrate is present, it will also consume chlorine dioxide (cf. Table 15).

#### 4.4 Impact of dissolved organic matter in a hydrogen peroxide reinforced alkaline extraction stage

The pulp sample used in the hydrogen peroxide reinforced alkaline extraction study was collected from the screw in the filter prior to the (EP)-stage together with the corresponding filtrate, denoted Filtrate 2, according to Figure 27. Filtrate 2 consisted of a combination of D- and (EP)-filtrates due to recycling of wash water in the filter. Filtrate 1, containing mainly D-filtrate and with a higher content of dissolved organic matter, was collected from the vat in the filter. To investigate the impact of recycling with exclusively (EP)-filtrate, Filtrate 3 was collected from the screw in the filter after the (EP)-stage. Filtrates 1 and 2 were acidic filtrates while Filtrate 3 was alkaline. The following results are also presented in Paper VI.

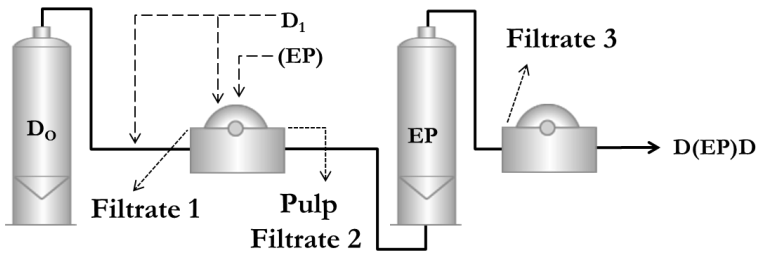


Figure 27: Sampling positions in the softwood pulp mill. The recycling of D<sub>1</sub>- and (EP)-filtrates as wash water and the recycling of D<sub>1</sub>-filtrate as dilution medium are also shown with dashed arrows.

Three combinations of fibers and filtrates were investigated. The well-washed pulp was used in the experiments with Filtrate 3 to ensure that the pulp slurry only contained recycled filtrate from the (EP)-stage. The kappa numbers of the fibers and the filtrates for the three combinations, i.e. Pulp with Filtrates 1-3 at 10% pulp consistency, are shown in Table 16, and these were the starting points in all experiments.

Table 16: Fiber and filtrate kappa numbers before the (EP)-experiments at 10% pulp consistency for the Pulp with Filtrates 1-3.

	Pulp with F1	Pulp with F2	Pulp with F3
Fibers	5.4	5.4	5.4
Filtrate	2.7	2.3	3.6

Table 17 shows fiber kappa number, brightness and final pH after the (EP)-stage, and initial pH after additions of 0.5% H<sub>2</sub>O<sub>2</sub> and 1.5% NaOH for the four different experiments, i.e. the Reference pulp and the Pulp with Filtrates 1-3. It is clearly shown that dissolved organic matter influenced the delignification of the Pulp with Filtrates 1 and 2 compared to the Reference pulp. The fiber kappa numbers obtained with Filtrates 1 and 2 were 21% and 13% higher respectively compared to the fiber kappa number of the Reference pulp. The brightness was 8% ISO lower with Filtrate 1 and 5% ISO lower with Filtrate 2 compared to the Reference pulp. The results are in agreement with previous studies that concluded that dissolved matter negatively influences both delignification and brightness [11, 12, 18].

Even though the original content of dissolved organic matter, measured as filtrate kappa number, was higher in Filtrate 3 compared to Filtrates 1 and 2, Filtrate 3 did not have an impact on delignification or brightness compared to the Reference pulp. Filtrate 3 contained exclusively (EP)-filtrate, thus indicating that a filtrate already exposed to hydrogen peroxide and sodium hydroxide will not continue to consume those chemicals when recycled in an (EP)-stage.

As further seen in Table 17, the final pH was considerably reduced when Filtrates 1 or 2 were present in the pulp slurry, probably explaining the poor fiber delignification and the lower brightness. During the (EP)-stage, hydrogen peroxide and sodium hydroxide react and generate perhydroxyl anions (HO<sub>2</sub><sup>-</sup>). The perhydroxyl anion is responsible for both the delignifying and brightening effects in an (EP)-stage and requires a high pH to be formed [8, 71, 90, 93, 170, 173]. A final pH of 10.5-11 is common in mills, and only Filtrate 1 obtained a lower pH, and subsequently had a more negative impact on both delignification and brightness [48, 90, 96, 174].

Filtrates 1 and 2 were originally acidic as they originated from the D<sub>0</sub>-stage, but as can be seen, the initial pH of the pulp samples, after additions of sodium hydroxide and hydrogen peroxide, was always alkaline. The alkali consumption by the acids in Filtrates 1 and 2 should not significantly affect the final pH since the NaOH charge was 1.5%, thus providing a significant amount of alkali available to react with the lignin in the fibers. The lower degree of delignification of the Pulp with Filtrates 1 and 2 was thus probably due to the reactions of sodium hydroxide and/or hydrogen peroxide with dissolved organic matter instead of fiber-bound lignin.

*Table 17: Results of the (EP)-experiments at 0.5% H<sub>2</sub>O<sub>2</sub> charge and 1.5% NaOH charge. The initial fiber kappa number was 5.4 and the initial brightness was 51.9% ISO. pH was measured at room temperature, and the initial pH was measured after additions of H<sub>2</sub>O<sub>2</sub> and NaOH.*

	Reference pulp	Pulp with Filtrate 1	Pulp with Filtrate 2	Pulp with Filtrate 3
Kappa number	3.4	4.1	3.9	3.4
Brightness, %	68.0	60.0	63.1	67.9
Initial pH	12.0	11.8	12.0	12.2
Final pH	11.8	9.6	10.8	11.9

#### **4.4.1 Different chemical charges**

Experiments with different hydrogen peroxide and sodium hydroxide charges were also conducted with the Reference pulp and the Pulp with Filtrates 1 and 2. The results at different H<sub>2</sub>O<sub>2</sub> charges are shown in Figure 28. According to Figure 28a, dissolved organic matter negatively influenced the kappa number reduction even at higher H<sub>2</sub>O<sub>2</sub> charges. An increased H<sub>2</sub>O<sub>2</sub> charge, up to 1% H<sub>2</sub>O<sub>2</sub> charge, increased the delignification, while increasing the charge to 1.5% resulted in only a minor further decrease in kappa number. The results thus indicated that the negative impact of the presence of dissolved organic matter could only partly be compensated for by increasing the H<sub>2</sub>O<sub>2</sub> charge alone.

There was a clear negative correlation between final brightness and final kappa number, as shown in Figure 28b, and the relationship was identical for the three cases. Increasing the H<sub>2</sub>O<sub>2</sub> charge improved the brightness, but the negative impact of dissolved organic matter from Filtrate 1 would have required higher H<sub>2</sub>O<sub>2</sub> charges than the range studied to obtain the same brightness as that of the Reference pulp.

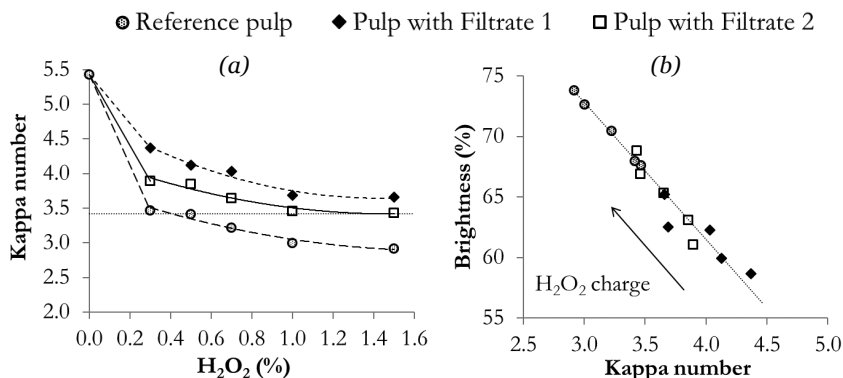


Figure 28: Kappa number vs. H<sub>2</sub>O<sub>2</sub> charge (a) and brightness vs. kappa number (b) at varying H<sub>2</sub>O<sub>2</sub> charges. The NaOH charge was 1.5% in all experiments. The dashed horizontal line at kappa number 3.4 in (a) represents the kappa number of the Reference pulp at 0.5% H<sub>2</sub>O<sub>2</sub> charge.

Results at different NaOH charges are shown in Figure 29. According to Figure 29a, carryover of dissolved organic matter could be compensated for in terms of delignification by increasing the alkali charge significantly. The obtained fiber kappa numbers of the Pulp with Filtrates 1 and 2, where 3% NaOH was charged, was the same as the kappa number of the Reference pulp at 1.5% NaOH charge. Furthermore, the final pH for Filtrates 1 and 2 at 3% NaOH charge was the same as the final pH of the filtrate from the Reference pulp at 1.5% NaOH charge.

In the range studied, a higher NaOH charge was not able to compensate for the reduced brightness due to the dissolved organic matter present in the filtrates (Figure 29b). The improved brightness was significantly smaller compared to the improved delignification with increased NaOH charge, and the Pulp with Filtrates 1 and 2 never obtained the same brightness as the Reference pulp. High alkali charges can cause

brightness reversion, which is likely the explanation for the smaller impact of increased alkali charge on brightness compared to delignification [8, 48, 93, 175].

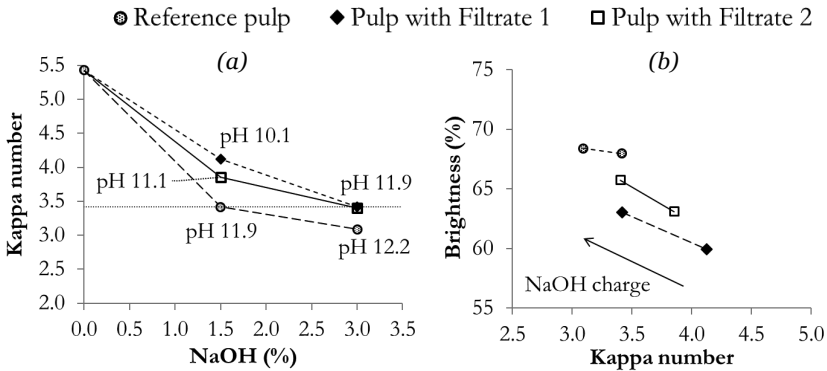


Figure 29: Kappa number vs. NaOH charge (a) and brightness vs. kappa number (b) at varying NaOH charges. Final pH of the experiments is shown in (a). The  $H_2O_2$  charge was 0.5% in all experiments. The dashed horizontal line at kappa number 3.4 in (a) represents that of the Reference pulp at 1.5% NaOH charge.

The results of this study indicated that good washing prior to an (EP)-stage is very important as the dissolved organic matter in  $D_0$ -filtrates significantly reduced the delignification and the brightness after the (EP)-stage. Hydrogen peroxide is also sensitive towards metals, which may accompany the dissolved matter [48, 67, 71]. Furthermore, residual chlorine dioxide entering an (EP)-stage can consume hydrogen peroxide and thus increase the chemical demand further [8]. It is also important to optimize the alkalinity in the (EP)-stage to obtain a balance between formation of perhydroxyl anions, decomposition of hydrogen peroxide and alkali darkening [8, 48, 90, 170, 173].

## 4.5 Dissolved lignin: correlations and variations

A new sensor that can continuously determine the dissolved lignin content in a fiberline has recently been developed. This inline sensor is based on multiple measurements of light absorption and it can be installed directly in a pulp stream. To investigate the variations in dissolved lignin content, the sensor was installed in a Scandinavian softwood kraft pulp mill. Manual samples were also collected and analyzed in the laboratory as light absorption, COD and filtrate kappa number, and the results were compared and correlated. The sensor was installed in three positions: one prior to the O<sub>2</sub>-stage and two prior to the D<sub>0</sub>-stage according to Figure 30. The pulp consistency at Installation 1 and 3 was 8-10% since the sensors were installed after the dilution from approximately 33% pulp consistency. The pulp consistency at Installation 2 was 4-5%. Some of the following results are also presented in Paper I while some are unpublished.

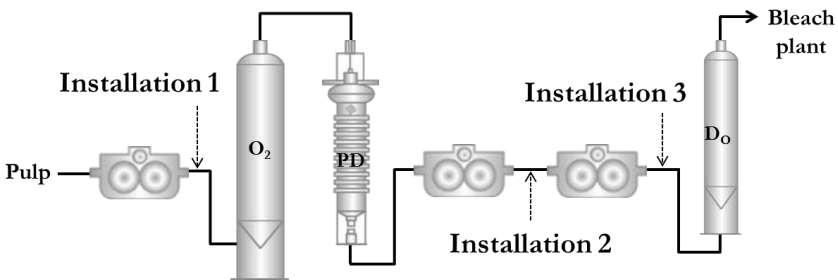


Figure 30: Installation points of the sensor in a Scandinavian softwood kraft pulp mill. The pulp consistency at Installation 1 and 3 was 8-10% and the pulp consistency at Installation 2 was 4-5%.

The lignin content is often correlated with the light absorption at wavelength 280 nm, but most filtrates are very dark and subsequently have a very high light absorption at this wavelength. To investigate if light absorption could be measured at higher wavelengths while still maintaining a high correlation with the dissolved lignin content, light absorption of several mill filtrate samples was measured at wavelengths 280, 365 and 465 nm. Filtrate samples collected at Installation 2 are shown in Figure 31. According to Figure 31a, the correlation between wavelengths 280 nm and 365 nm was excellent, with  $R^2=0.98$ .

The correlation between wavelengths 280 nm and 465 nm was also very good, with  $R^2=0.95$ . These results are further supported by Andersson et al. [176], who found that the wavelength selection used could be up to 500 nm while still maintaining a high correlation coefficient,  $R^2 \geq 0.95$ , to the dissolved lignin content.

Mills often estimate the washing efficiency by measuring COD before and after a washer, but this can only be done offline and the information can only be attained long after the pulp slurry has passed the sampling position. However, the dissolved lignin content can instead be estimated by measuring the kappa number of the filtrate, thus enabling a convenient comparison to the kappa number of the fibers. The relationships of COD and filtrate kappa number to light absorption at wavelength 280 nm can be seen in Figure 31b. The correlations obtained were very good and any of the three measurements could thus be used to estimate the dissolved lignin content.

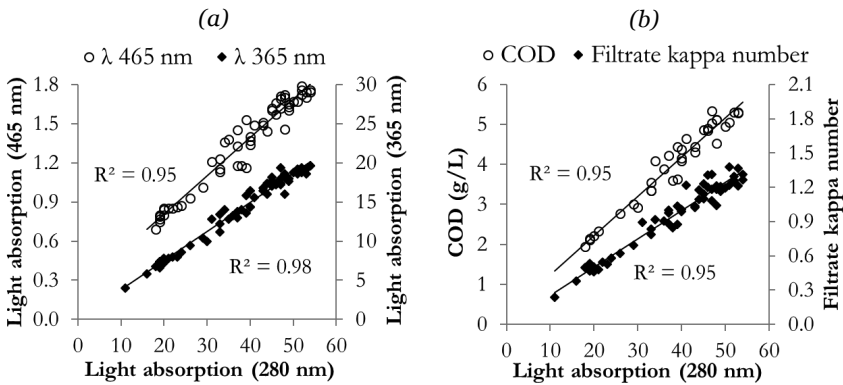
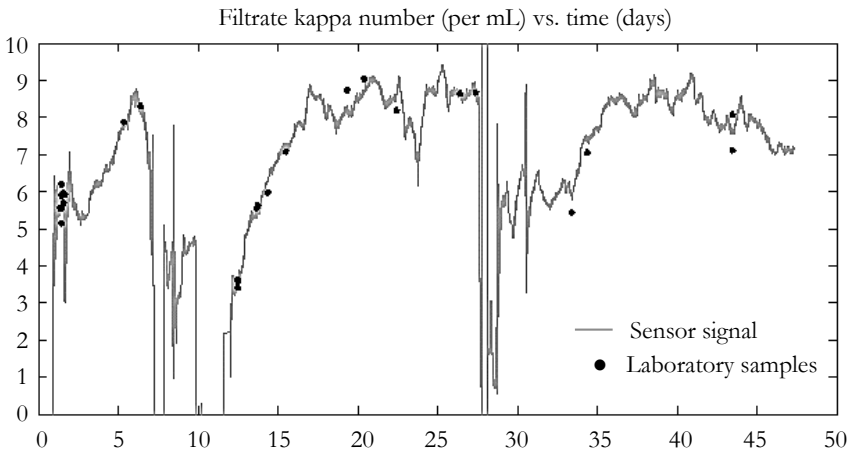


Figure 31: Light absorption at wavelengths 465 nm and 365 nm vs. light absorption at wavelength 280 nm (a), and COD and filtrate kappa number vs. light absorption at wavelength 280 nm (b). The filtrate samples were collected at Installation 2 in Figure 30. (Unpublished data, but similar results are presented in Paper I)

In a second study, the sensor was installed prior to the  $O_2$ -stage (Installation 1 in Figure 30) for several months and the sensor signal was continuously measured. The sensor signal during a period of 47 days along with laboratory reference data, measured as filtrate kappa

number, are shown in Figure 32. The fit between the sensor signal and the filtrate kappa numbers measured in the laboratory was very good. The filtrate kappa number per milliliter varied between 3 and 9. During the trial period, and at an average pulp consistency of 10%, the filtrate kappa number per gram of fiber was thus 27-81 with an average of 54, i.e.  $54 \pm 27$ . The average fiber kappa number at this position during the trial period was  $28 \pm 3$  units. Thus, the variations in filtrate kappa number were significantly higher than those of the fiber kappa number.



*Figure 32: A 47 days trend of the signal from the sensor, scaled to filtrate kappa number (per milliliter filtrate), compared to laboratory measurements. The sensor was installed at Installation 1 in Figure 30. ([177])*

The sensor was also installed prior to the D<sub>0</sub>-stage (Installation 2 in Figure 30) for several months. The sensor signal along with laboratory reference data during a period of 70 days are shown in Figure 33. Thus, the correlation between the sensor signal and the filtrate kappa number was excellent. It can also be seen that the filtrate kappa number varied significantly during the trial. The filtrate kappa number per milliliter varied between 0.3 and 1.7. During the trial period, and at an average pulp consistency of 4.5%, the filtrate kappa number per gram of fiber was thus 6-36 with an average of 21, i.e.  $21 \pm 15$ . The average fiber kappa number in this position was during the trial period  $13 \pm 2$  units. Thus, the variations in filtrate kappa number were significantly higher than those of the fiber kappa number in this position as well.

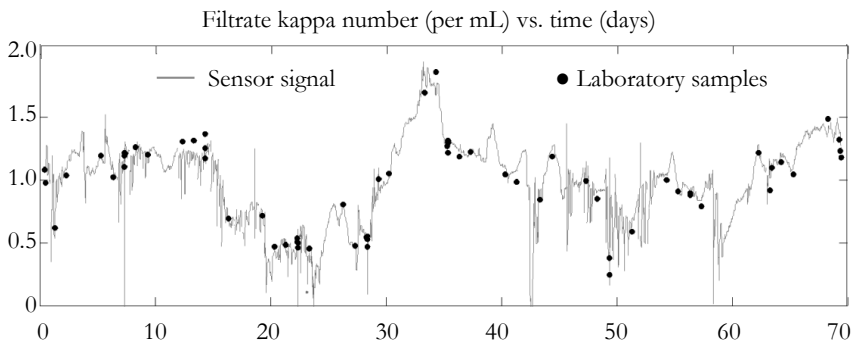


Figure 33: A 70 days trend of the signal from the sensor, scaled to filtrate kappa number (per milliliter filtrate), compared to laboratory measurements. The sensor was installed at Installation 2 in Figure 30. (Paper I)

Note that Installation point 2 in Figure 33 was prior to the last washer before the  $D_0$ -stage, and the filtrate entering the  $D_0$ -stage would thus have a lower dissolved lignin content. The sensor was therefore also installed after the last washer (Installation 3 in Figure 30). The average pulp consistency during the trial period was 9% at this position and the filtrate kappa number per gram of fiber was 0.6-2.6 with an average of 1.6, i.e.  $1.6 \pm 1.0$ . The average fiber kappa number during the trial period was  $13 \pm 2$  units. The filtrate kappa number was thus 10% of the total kappa number, i.e. the sum of the fiber and filtrate kappa numbers ( $13 + 1.6$ ), but the variations in the filtrate kappa number was 33% of the total variations of the fibers and the filtrate ( $2 + 1$ ).

By measuring not only the fiber-bound lignin but also the dissolved lignin content with the new sensor, the large variations could be accounted for. Over- or undercharging of chlorine dioxide could be avoided, which would otherwise lead to higher overall bleaching chemical cost. The  $ClO_2$  charge could thus be optimized by basing the chemical charge on the sum of the fiber-bound lignin and the dissolved lignin, measured as total kappa number. When using the total kappa number for feedforward control in a  $D_0$ -stage, mills can more accurately reach their target kappa number.

## 5 Sustainability and Socio-Economic Aspects

It is well-known that in pulp mills, both the fibers and the dissolved organic matter in the pulp slurry consume bleaching chemicals. Still, most pulp mills usually determine the total bleaching chemical demand by measuring only the kappa number of well-washed pulp samples, i.e. not considering the bleaching agent demand of the dissolved organic matter, predominantly lignin.

Mills also assume that the content of dissolved organic matter (per ton of pulp) is constant with respect to time. However, the content of dissolved organic matter in the pulp slurry varies considerably, and presuming that it is constant will lead to either over- or undercharging of bleaching chemicals, resulting in uneven, and thus poorer, pulp quality and higher overall chemical costs.

The recent development of a sensor that continuously determines the dissolved lignin content in a fiberline has offered a solution to many earlier process control issues. The sensor will enable mills to accurately measure and account for the variability in the dissolved lignin content.

Mills currently estimate the dissolved lignin content indirectly by measuring e.g. conductivity and/or the refractive index. These measurements are however sensitive to changes in pH or ionic strength, as seen in Figure 34.

Thus, neither conductivity nor refractive index is suitable parameters to use when monitoring the dissolved lignin content in filtrates. The sensor signal was however unaffected by changes in both pH and ionic strength, thus making it a good option for measurement of dissolved lignin content.

Note that the absolute changes in the refractive index are usually very small. A difference of only 0.001 units corresponded to 3.0 filtrate kappa number units in the position from which the liquor sample was taken (Installation 1 in Figure 30).

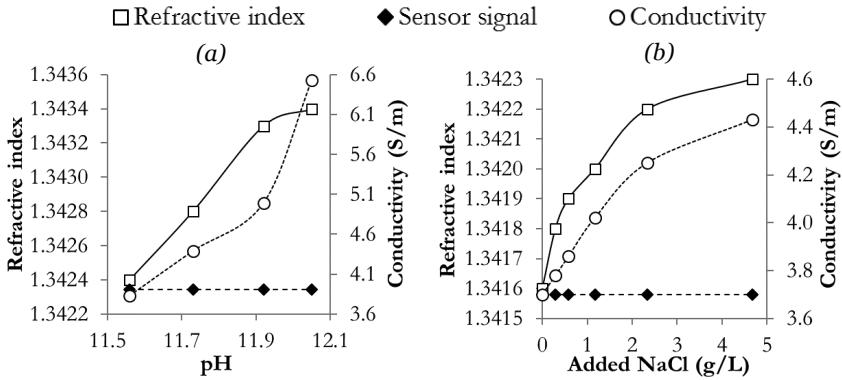


Figure 34: Impact of pH (a) and ionic strength (b) to mill filtrate samples on refractive index, sensor signal and conductivity. pH and ionic strength were altered by additions of NaOH and NaCl respectively. Note that the sensor signal is normalized. The filtrate samples were collected at Installation 1 in Figure 30. (Paper I)

Investigations have shown that the sensor signal correlates very well with filtrate kappa number, light absorption and COD (Figure 35). All three measurements can be used to estimate the dissolved lignin content (cf. Figure 31b), so the sensor can thus be calibrated to any of these three parameters.

Furthermore, the good linear correlation between the sensor signal and COD means that the time-consuming and the environmentally problematic COD test could be replaced by the signal from the new sensor. Thus, the deviation from the target dissolved matter content could be detected continuously without long time delays when measured by the sensor.

The possibility to receive a continuous signal is a major benefit of the sensor. The sensor thus provides new opportunities in optimizing fiberline operations with two major applications: (i) improving the efficiency in washing stages and (ii) optimizing chemical charges.

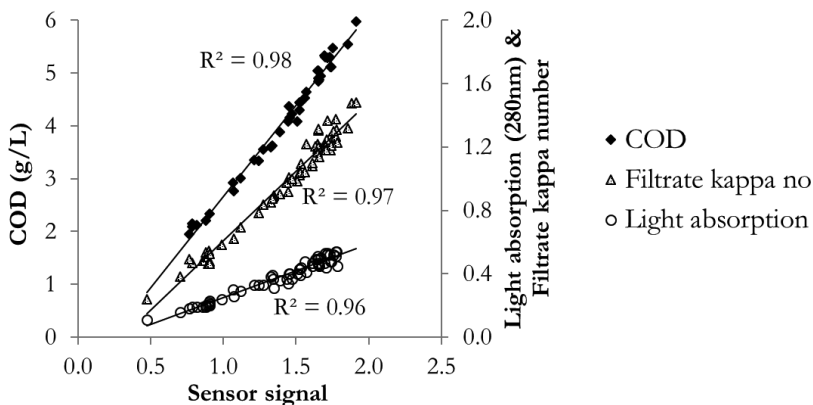


Figure 35: COD, filtrate kappa number and light absorption (at 280 nm) vs. the sensor signal (unscaled). Note that light absorption is shown for diluted values so that it can be plotted together with filtrate kappa number. The sensor was installed and the filtrate samples were collected at Installation 2 in Figure 30. (Unpublished data, but similar results are presented in Paper I)

## 5.1 Optimized washing

Implementing a sensor that can measure the dissolved lignin content will enable mills to act preventively, by e.g. optimizing the brown stock washing system. The information gathered from the sensor can be used to calculate the desired dilution factor in a specific washer. Due to restrictions in the evaporator, many mills already run the washers at the highest possible dilution factor. When the content of dissolved lignin is low, the dilution factor could, however, be decreased, thus reducing the water consumption.

The fresh water consumption may not be reduced significantly by optimizing the dilution factor since a considerable part of the wash water used in pulp mills is recycled filtrates. However, the decreased volume of wash water will have a significant impact on the evaporation load, thus reducing the energy demand and costs. The reduced evaporation load may also lead to increased production since the evaporators often are bottlenecks in a pulp mill. Thus, both environmental and economic benefits are plausible.

The results from the oxygen delignification study suggested that washing prior to the O<sub>2</sub>-stage is critical for obtaining high delignification and small viscosity loss at moderate alkaline charges. A lower degree of delignification in the O<sub>2</sub>-stage results in higher chemical consumption in the bleach plant to obtain the target kappa number and/or brightness. If possible, it may thus be worth increasing the dilution factor in the wash prior to the O<sub>2</sub>-stage to reduce the content of unoxidized dissolved matter, thus increasing the degree of delignification, despite the higher evaporation load due to the increased wash water volume.

Instead of increasing the dilution factor, an additional washer prior to the O<sub>2</sub>-stage could be installed. It may not be possible to install a new washer due to the high investment cost, but it may be possible to move one of the existing washers. For a mill with two washers prior to the O<sub>2</sub>-stage and two washers after the O<sub>2</sub>-stage, the washing sequence could be altered to three washers before and one washer after the O<sub>2</sub>-stage. As in the case of an increased dilution factor, the content of unoxidized dissolved matter into the O<sub>2</sub>-stage would be reduced by such an alteration. The fibers entering the bleach plant would likely have a lower lignin content due to the more efficient O<sub>2</sub>-stage, thus requiring less bleaching chemicals to obtain the target kappa number and/or brightness. However, implementing only one washer after the O<sub>2</sub>-stage would also result in a higher content of dissolved matter entering the bleach plant, thus requiring additional bleaching chemicals to obtain the target kappa number and/or brightness.

The balance between the positive and negative effects of increased dilution factor in the washer prior to the O<sub>2</sub>-stage or an additional washer prior to the O<sub>2</sub>-stage would determine if these scenarios are suitable options. Each choice leading to optimization needs to be carefully considered. For instance, there must be sufficient post-O<sub>2</sub> washing for the recovery of dissolved matter, thus resulting in both the environmental and economic benefits associated with the O<sub>2</sub>-stage, so fewer washers after the O<sub>2</sub>-stage may not be sufficient from that perspective.

Due to the positive impact of oxidized dissolved matter, it may also be a suitable option to install a washer that has a high outgoing pulp consistency prior to the O<sub>2</sub>-stage. The high outgoing pulp consistency would require large dilutions prior to a medium consistency O<sub>2</sub>-stage, and the dilution medium would be a recycled oxidized filtrate due to the countercurrent washing system. The content of oxidized dissolved matter entering the O<sub>2</sub>-stage would thus be increased.

According to Figure 36, in the case of a filter, the filtrate volume entering the O<sub>2</sub>-stage will be 7.3 m<sup>3</sup>. This filtrate will be a mixture of unoxidized and oxidized filtrates, where the distribution between the two will depend on the washing prior to the O<sub>2</sub>-stage. However, due to countercurrent washing, a significant part will be oxidized filtrate.

In the case of a press, 5.2 m<sup>3</sup> of the total filtrate volume will be oxidized filtrate due to the dilution after the press with recycled O<sub>2</sub>-filtrate. The remaining 2.1 m<sup>3</sup> filtrate will be a mixture of unoxidized and oxidized filtrate, where the distribution between the two will depend on the washing prior to the O<sub>2</sub>-stage. However, due to countercurrent washing, a significant part of this filtrate will be oxidized.

Thus, at equal volumes, the share of oxidized dissolved matter will be higher in the case of a press instead of a filter prior to the O<sub>2</sub>-stage, and this may influence the delignification positively in the O<sub>2</sub>-stage.

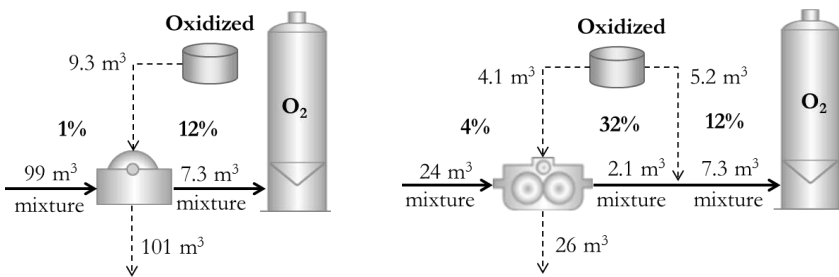


Figure 36: An illustration of the volumes and the origins of the filtrates entering an O<sub>2</sub>-stage from a filter (left) and a press (right).

## 5.2 Chemical savings

Determination of the dissolved lignin content by the new sensor in combination with measurement of the fiber-bound lignin enable pulp mills to directly determine the total lignin content, and thus the total chemical demand by the lignin, into the bleach plant. The dissolved lignin content varies significantly more than the fiber-bound lignin content so the information gathered from the sensor will be paramount for optimization of bleaching chemicals, thus resulting in reduced chemical costs in the bleach plant.

Using a feedforward control strategy based on the total kappa number has proven to be very effective in saving chemicals and maintaining high final brightness. The optimization of bleaching chemical charges will further facilitate bleach plant stability, minimize final product variability and optimize product quality. Furthermore, indirect environmental improvements are plausible due to the lower chemical consumption.

Chemical savings for six mill cases, where the dissolved lignin content was measured with the sensor prior to the D<sub>0</sub>-stage, are shown in Table 18. It is clear that not only savings of chlorine dioxide could be achieved, but also savings of sodium hydroxide. The chlorine dioxide demand in the D<sub>0</sub>-stage was reduced by 6-15% in the mills, and with approximately the same amount in the D<sub>1</sub>-stage.

For mills 1 and 6, the total cost of bleaching chemicals was reduced by 7% and 10% respectively. Apart from sodium hydroxide, Mill 4 also saved 20% hydrogen peroxide in the (EOP)-stage. Mill 4 further reported total chemical savings equivalent to 4 USD/ton of pulp, where almost half of it originated from chlorine dioxide savings in the D<sub>0</sub>-stage. With a daily production of 1 000 ton, the yearly savings amounted to approximately 1.4 million USD. Furthermore, Mill 5 reported savings of 1 kg ClO<sub>2</sub>/ton of pulp, equivalent to approximately 1 900 tons of chlorine dioxide per year.

Table 18: Chemical savings of six actual mill cases, where the dissolved lignin content was measured continuously with the sensor prior to the D<sub>0</sub>-stage and the chemical charges were adjusted accordingly. (Unpublished data)

Mill, raw material	Bleaching sequence	Production (t/day)	ClO <sub>2</sub> in D <sub>0</sub> (%)	ClO <sub>2</sub> in D <sub>1</sub> (%)	NaOH (%)
1 SW	D(EO)D	2 000	6.3	8	7.5
2 SW	D(EOP)DD	1 000	n.d.	8 <sup>b</sup>	10
3 SW	D(EOP)DD	800	n.d.	15	n.d.
4 SW/ HW <sup>a</sup>	D(EOP)DD	1 000	8.1	6.7	8.8
5 HW	D(EOP)DD	5 500	15	n.d.	10
6 HW	C/D(EOP)DD	3 000	n.d.	15 <sup>b</sup>	10

n.d.: Not determined by the mill.

<sup>a</sup>: Campaigns were run with either softwood or hardwood.

<sup>b</sup>: Total chlorine dioxide savings in D<sub>0</sub>-, D<sub>1</sub>- and D<sub>2</sub>-stages.

In general, the estimated chlorine dioxide savings for the mills were 1-2 kg ClO<sub>2</sub>/ton pulp, and the economic savings depended on several factors, e.g. production and chemical prices. A hardwood mill with bleaching sequence D(EOP)DD and a production of 1 000 ton/day (not shown in Table 18) reported yearly savings of 600 000 USD for chlorine dioxide in the D<sub>0</sub>-stage alone. Another hardwood mill, with bleaching sequence D(EOP)DD and a production of 3 000 ton/day (not shown in Table 18), reported a reduction of the total bleaching chemical cost by 12%.

Not only chemical savings were achieved by measuring the dissolved lignin content into the D<sub>0</sub>-stage. Mill 4 increased the final brightness from 87.1% ISO to 90.1% ISO, and for Mill 5, the brightness stability after the (EOP)-stage was improved. Mill 6 reported an improvement in yield by 0.7% and a significant reduction in off-grade pulp, both of which resulted in economic savings.

Thus, when the dissolved lignin content is determined in addition to the content of fiber-bound lignin, the consumption of bleaching chemicals, water and energy can be reduced while also improving quality and reducing costs.

## 6 Conclusions

- The presence of unoxidized dissolved matter in an oxygen delignification stage decreased the delignification and increased the carbohydrate degradation. In case of increasing the sodium hydroxide charge to achieve the same degree of delignification, the selectivity was further impaired due to even higher carbohydrate degradation.
- The presence of oxidized dissolved matter in an oxygen delignification stage increased both the delignification and the carbohydrate degradation. The selectivity was affected in the same way as when using a higher sodium hydroxide charge. The relatively high carbonate content in the oxidized filtrate was the main reason for the improved delignification, and the positive impact of carbonate ions may partly be due to their pH buffering effect.
- The presence of dissolved organic matter in a hot acid stage had a negative impact on the efficiency of the stage. The chlorine dioxide demand in a following chlorine dioxide stage was higher when bleaching to the same degree of delignification. At the same chlorine dioxide charge, washing between a hot acid stage and a chlorine dioxide stage only had a small impact on delignification since the degraded hexenuronic acid residues from a hot acid stage appeared not to be further degraded in a chlorine dioxide stage.
- The presence of dissolved organic matter in a chlorine dioxide stage decreased the delignification, both when originating from an oxygen delignification stage and recycled from a chlorine dioxide stage. The additional chemical demand required to compensate for this reduction was proportional to the content of dissolved organic matter, measured as filtrate kappa number. Thus, the total chemical demand was proportional to the total kappa number of the pulp.
- The presence of dissolved organic matter in a hydrogen peroxide reinforced alkaline extraction stage decreased both the delignification and the brightness when originating from a chlorine dioxide stage. Compensating for these reductions by increasing the sodium

hydroxide charge improved the brightness significantly less than the delignification.

- Filtrate kappa number, COD and light absorption correlated well with each other and with the signal from a new sensor. The dissolved lignin content varied significantly over time in several field trials, at different mill positions. Thus, the dissolved lignin content could be measured continuously and its variability could be accounted for by implementing the new sensor. Furthermore, basing the chemical charge in a chlorine dioxide stage on the sum of the fiber-bound lignin and the dissolved lignin enabled mills to optimize the chlorine dioxide charge.

## 7 Future Work

- Further investigate the reason for the positive impact on oxygen delignification by the presence of oxidized dissolved matter and determine why carbonate ions, apart from their pH buffering effect, improved the delignification.
- Determine if dissolved organic matter, measured as filtrate kappa number, is a good estimation of the additional chemical demand in the D<sub>1</sub>- and D<sub>2</sub>-stages.
- Investigate the impact of dissolved organic matter in the bleach plant on final brightness.
- Determine the optimum positions of a sensor in a pulp mill for optimized bleaching and washing performance.

## 8 Summary of Papers

### Paper I

An optical sensor, that continuously measures the dissolved lignin content in pulp slurries, was recently developed. The sensor has two major applications: (i) improving the efficiency in washing stages, and (ii) optimizing chemical charges.

Results from several mill trials have shown that the contribution from dissolved lignin in the filtrate portion of the pulp, measured as filtrate kappa number, was up to 30% of the total kappa number, i.e. the sum of the fiber and filtrate kappa numbers. It would thus be possible to achieve chemical savings by taking this component into account compared to only measuring the fiber kappa number.

The study also showed that the dissolved lignin content could be measured as filtrate kappa number, COD or light absorption, with high correlation between the parameters. Those analyses also correlated with the signal from the sensor, thus enabling mills to determine those parameters with the new sensor.

### Paper II

The impact of dissolved matter in O<sub>2</sub>- and D<sub>O</sub>-stages was investigated for softwood kraft pulps. Experiments were conducted with different levels of carryover, measured as filtrate kappa number. It was concluded that dissolved matter in an O<sub>2</sub>-stage reduced the delignification and the final pH.

In a D<sub>O</sub>-stage, the filtrate kappa number correlated with the additional ClO<sub>2</sub> charge required due to dissolved lignin. By measuring the total kappa number prior to a D<sub>O</sub>-stage, mills could use a feedforward strategy to accurately charge the amount of chlorine dioxide required to obtain a certain degree of delignification.

Mill trials showed that the variations in dissolved lignin content into a D<sub>0</sub>-stage were large. The chemical consumption was reduced significantly when the mills measured the total kappa number, and thus charged the chemicals accordingly.

### **Paper III**

The impact of dissolved matter in an O<sub>2</sub>-stage was further investigated for softwood kraft pulps. Unoxidized dissolved matter from the cooking stage and oxidized dissolved matter recycled from the post-O<sub>2</sub> washer were added in various amounts, measured as COD, to well-washed pulp samples, thus simulating different levels of carryover.

After laboratory O<sub>2</sub>-experiments, the degree of delignification for the well-washed pulp samples and for those pulp samples containing dissolved matter was very different. Pulp containing unoxidized dissolved matter reduced the degree of delignification compared to a well-washed pulp while pulp containing oxidized dissolved matter surprisingly increased the degree of delignification. The delignification efficiency of laboratory experiments thus depended on both the amount of dissolved matter and its origin.

Experiments containing the actual mixture of dissolved matter that enters an O<sub>2</sub>-stage, i.e. both unoxidized and oxidized dissolved matter, were also conducted. It was concluded that even though that pulp contained some unoxidized dissolved matter, the degree of delignification was increased compared to a well-washed pulp due to the presence of oxidized dissolved matter.

Both intrinsic viscosity and final pH decreased with increasing dissolved matter content, irrespective of its origin. However, at higher COD, both intrinsic viscosity and final pH were reduced more in the case of unoxidized dissolved matter compared to oxidized dissolved matter. Regarding selectivity, the oxidized filtrate had a similar impact as increasing the NaOH charge.

## **Paper IV**

The differences obtained in terms of delignification and selectivity in an O<sub>2</sub>-stage between unoxidized and oxidized dissolved matter were further investigated for softwood kraft pulps. Laboratory O<sub>2</sub>-experiments with additions of unoxidized and oxidized filtrates were carried out, and the results were compared at constant NaOH charge, constant degree of delignification and constant final pH.

The results showed that a pulp sample containing unoxidized dissolved matter consumed more sodium hydroxide than a well-washed pulp sample, thus requiring a higher NaOH charge to obtain the same degree of delignification.

A pulp sample containing oxidized dissolved matter, on the other hand, increased the delignification compared to a well-washed pulp sample, thus requiring less NaOH charge to obtain the same degree of delignification.

The impact of carbonate ions in the oxidized filtrate and thiosulfate ions in the unoxidized filtrate were also investigated. It was concluded that carbonate ions increased the degree of delignification, partly due to their pH buffering effect. Thiosulfate ions only had a minor negative impact on the degree of delignification.

## **Paper V**

The impact of dissolved matter in A- and D<sub>0</sub>-stages was investigated for hardwood kraft pulps. Since recycling of bleaching filtrates is common in mills, the impact on delignification was investigated with recycled D<sub>0</sub>-filtrates as well.

It was concluded that basing the ClO<sub>2</sub> charge on the total kappa number instead of the fiber kappa number would enable mills to obtain the desired degree of delignification, irrespective of dissolved matter content and origin, i.e. O<sub>2</sub>-filtrates or recycled D<sub>0</sub>-filtrates.

It was further concluded that dissolved matter reduced the efficiency of an A-stage, probably due to competing reactions between dissolved organic matter (predominantly lignin residues), fiber-bound lignin and HexA. Different kappa number reductions between the well-washed pulp and the pulp containing dissolved matter in an A-stage resulted in different chlorine dioxide demand in a following D<sub>0</sub>-stage.

Washing between A- and D<sub>0</sub>-stages only had a small impact on delignification since the HexA residues after an A-stage appeared not to be further degraded in a D<sub>0</sub>-stage, i.e. not consuming chlorine dioxide. At the same degree of delignification, the chlorine dioxide demand was significantly lower for an AD-sequence, with or without intermediate washing, than a hot D\*-stage.

## **Paper VI**

The impact of dissolved matter on delignification and brightening in an (EP)-stage was investigated for softwood kraft pulps. The impact of dissolved matter originating in a previous D<sub>0</sub>-stage and dissolved matter recycled from an (EP)-stage was investigated in laboratory experiments.

Dissolved matter from a previous D<sub>0</sub>-stage reduced the delignification and the brightness in an (EP)-stage. The final pH was also reduced, i.e. indicating that dissolved matter consumed sodium hydroxide, thus decreasing the delignification. The recycled (EP)-filtrate did not affect delignification, brightness or final pH.

It was concluded that it was possible to compensate for the reduced delignification by significantly increasing the NaOH charge, but the reduced brightness could only partly be compensated for by the same additional NaOH charge.

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# The Impact of Dissolved Matter on Fiberline Processes

Pulp mills employ different control strategies to decrease the consumption of raw materials while still maintaining high product quality. To operate a kraft pulp mill in an efficient manner, it is essential to identify the key process parameters. Residual lignin is one of the most important parameters in chemical pulping and most mills base their process control on measurements of the lignin content, analyzed as kappa number. However, they typically only determine the content of the fiber-bound lignin while the dissolved lignin in the pulp slurry is merely seen as a disturbance.

Dissolved matter, especially dissolved lignin, consumes bleaching chemicals, and any variability of the dissolved lignin content will lead to non-optimal chemical charges and subsequently higher production cost. By measuring the dissolved lignin content as well as the fiber-bound lignin content, pulp mills can however apply chemicals based on the actual total bleach load. The impact of dissolved matter was investigated in four different process stages and it was concluded that both the content and the type of dissolved matter affected the performance of the stages. Furthermore, increasing the chemical charges in the process stages could only partly compensate for the negative impact of the dissolved matter.

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