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**School of Chemical Technology
Degree Programme of Chemical Pulping Technology**

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**REPLACING SULFURIC ACID IN PULP BLEACHING WITH INTERNALLY
FORMED ORGANIC ACIDS**

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Tiivistelmä

Sellutehtaiden ympäristövaikutusten minimointi ja prosessin tehokkuuden maksimointi ovat muun muassa olleet tekijöitä, jotka ovat johtaneet valkaisuun vesikierron sulkemiseen. Rikkihapon hinnan sekä kuljetuskustannusten jatkuva nousu ovat nyt saaneet huomion kiinnittymään valkaisuun A-vaiheeseen. Tehtailla, joilla on A-vaihe käytössä, ei ole esiintynyt merkittäviä saostumisongelmia. Näiden seikkojen ansiosta A-vaiheen suodoksen kierrättäminen on herättänyt lisääntyvää kiinnostusta. Tämän tutkimuksen tavoitteena oli tutkia kierrättämisen aiheuttamat vaikutukset A-vaiheelle ja muulle valkaisulle. Lisäksi haluttiin selvittää, millainen kierrätetty suodos on ominaisuuksiltaan ja voidaanko kierrätyksellä vähentää rikkihapon kulutusta.

Työn kirjallisuusosassa käydään aluksi valkaisuulinja läpi, minkä jälkeen keskitytään suodoksiin sekä aiempiin tutkimuksiin niiden kierrättämisessä. Lisäksi kuvataan erilaisia vierasaineita, joita suodokset sisältävät ja erityisesti metallien käyttäytymistä sekä niiden aiheuttamia mahdollisia ongelmia.

Kokeellisessa osassa suoritettiin ensin kaksi valkaisuusekvenssiä (A-E_{OP}-D-P, A-E_{OP}-Z/D-P) referenssiksi. Tämän jälkeen A-vaiheen suodos otettiin talteen ja sillä suoritettiin uudelle massalle uusi A-vaihe käyttäen apuna myös rikkihappoa. Tämä toistettiin yhteensä kolme kertaa, minkä jälkeen tästä saatu massa valkaistiin samoilla sekvensseillä loppuun. Kierrätetystä suodoksesta mitattiin muun muassa vierasainepitoisuudet sekä ajettiin UVRR-spektrit.

Ensimmäiselle sekvenssille kierrätyksellä ei havaittu olevan minkäänlaisia haittavaikutuksia. Toisessa sekvenssissä Z/D-vaihe aiheutti kuitenkin eron kierrätetyn ja ei-kierrätetyn massan välille: heksenuronihappopitoisuudessa oli selkeä ero, joka näkyi myös kappaluvussa ja vaaleudessa. Lisäksi P-vaiheessa muodostui vaaleudelle 89 %:n maksimitaso, jota ei ylitetty vaikka kemikaaliannosta kasvatettiin. Tällöin myös viskositeetti aleni. Itse suodoksessa suurin osa liuenneesta orgaanisesta aineksesta oli 2-furaanihappoa ja ligniiniä sekä sen johdannaisia ja hajoamistuotteita. Rikkihappoa kierrätyksellä säästyi noin 20 %. Kriittisistä vierasaineista kloori oli pitoisuudeltaan korkein, mutta sitä ei esiintynyt kuitenkaan kohtuuttomasti. Mangaanipitoisuus niin ikään oli melko korkea. Barium-pitoisuutta ei pystytty selvittämään.

A-vaiheen suodoksen kierrättämiselle ei tässä tutkimuksessa löydetty esteitä. Tärkeimmät säästöt saataisiin jäteveden määrän pienenemisenä ja sitä kautta myös ympäristövaikutusten vähenemisenä, eikä niinkään välttämättä rikkihapon säästönä. Tutkimusta on kuitenkin jatkettava vielä mahdollisten säästöjen maksimoimiseksi sekä varmistamiseksi, ettei vierasaineista aiheudu ongelmia.

Avainsanat A-vaihe, heksenuronihappo, ECF-valkaisu, suodos, kierrätys

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Abstract

The minimization of environmental impacts and maximization of process efficiency are issues that have led to the closing of water cycles in the bleach plant. The increases in the price of sulfuric acid and transportation costs have now evoked interest in A-stage. The mills having A-stage have not reported on any significant precipitation problems. Due to these facts the reuse of A-stage filtrate has become more interesting. The goal of this research was to investigate the effects the reuse has for the operation of A-stage and final bleaching. In addition, the aim was to find out if the consumption of sulphuric acid can be decreased with the circulation of the filtrate and what are its characteristic properties.

In the literature the operation of bleach plant is first explained after which the focus is on filtrates and earlier studies about their circulation. Additionally, different non-process elements, which are found in filtrates, are described. Especially metals, their behaviour and problems they cause are explained.

In the beginning of the experimental part two reference bleaching sequences (A-E_{OP}-D-P, A- E_{OP}-Z/D-P) were performed. The A-stage filtrate was recovered and used with fresh pulp and some additional sulfuric acid to carry out the next A-stage. This was repeated three times after which the obtained pulp was bleached with the same sequence as the reference pulps. The reused filtrate was analysed among other characteristics for the non-process elements and UVR_R spectra.

For the first sequence no harmful effects caused by the recirculation of the A-stage filtrate were found. However, the Z/D-stage in the second sequence brought on a difference between the two pulps. There was a significant difference in hexenuronic acid content which was reflected on kappa number and brightness. In addition, during P-stage a brightness ceiling of 89 % ISO was formed. This also caused a decrease in viscosity. The reused filtrate contained large amounts of 2-furoic acid, lignin, its derivatives and degradation products. The savings of sulfuric acid were about 20 %. Chlorine is the most critical non-process element but its concentration was not excessive. However, the concentration of barium could not be determined and the manganese concentration was quite high.

In this research no obstacles were found for reusing the A-stage filtrate. However, the most important advantages would be rather in lower effluent volume than in saving of sulfuric acid. Further research is still required in order to maximize the savings and ensure that non-process elements do not cause any problems.

Keywords A-stage, hexenuronic acid, ECF bleaching, filtrate, circulation

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Table of Contents

Acknowledgements	4
List of abbreviations	8
Introduction.....	10
1 Background on chemical pulping	11
1.1 Pulp mill overview	11
1.2 Principles of bleaching.....	12
Literature part	14
2 Hexenuronic acid	14
2.1 Xylan in hardwood.....	14
2.2 The formation of hexenuronic acid	15
2.3 Basic information about HexA.....	16
2.4 HexA and metals.....	17
2.5 Degradation of HexA	18
2.6 Possibilities of formic acid	19
3 Non-process elements in pulp bleaching	20
3.1 Metals.....	20
3.1.1 Metals as elements.....	20
3.1.2 Metal compounds.....	22
3.1.3 Donnan theory.....	25
3.1.4 The interaction between metals and fibers in practice	26
3.2 Other non-process elements.....	28
4 Bleach plant operations.....	30
4.1 A-stage.....	30
4.2 Chlorine dioxide bleaching	32
4.3 Ozone bleaching	35
4.4 Alkaline bleaching stages.....	37
4.4.1 Alkaline extraction.....	37
4.4.2 Peroxide stage	39
4.4.3 Metal control in alkaline stages.....	41
5 Washing and its filtrates	42
5.1 Pulp washing.....	42
5.1.1 Washing principles and concepts	42
5.1.2 Brown stock washing.....	44

5.1.3 Washing stages in oxygen delignification and bleaching	44
5.1.4 Practice of pulp washing.....	47
5.2 Filtrates of pulp bleaching	49
5.2.1 Motivation for filtrate processing	49
5.2.2 The development of filtrate processing	50
5.2.3 Challenges in filtrate circulation	51
5.2.4 Composition of filtrates in general.....	52
5.2.5 Composition of A-stage filtrates.....	55
5.2.6 Reuse of A-stage filtrates.....	56
6 Conclusions of the theoretical part	60
Experimental part.....	62
7 Materials and methods.....	63
7.1 Initial pulp.....	63
7.2 Preliminary tests.....	63
7.3 Bleaching procedures	64
7.3.1 Conditions of bleaching stages.....	64
7.3.2 Performance of pre-bleaching.....	66
7.3.3 Performance of final bleaching	66
7.3.4 Sequences using filtrate circulated pulp	68
7.4 Measurements from pulps and filtrates.....	68
8 Results	69
8.1 Preliminary tests.....	69
8.2 Performance of A-stage.....	69
8.3 Performance of E _{OP} -stage	71
8.4 Performance of D-stage.....	73
8.5 Performance of Z/D-stage	74
8.6 Performance of P-stage in A-E _{OP} -D-P sequence	75
8.7 Performance of P-stage in A-E _{OP} -Z/D-P sequence.....	77
8.8 Properties of A-stage filtrates	78
8.8.1 Non-process elements in the filtrates	80
8.8.2 Organic compounds in the filtrates.....	81
9 Discussion	83
9.1 Development of pulp properties	83
9.1.1 A-stage pulp properties	84

9.1.2 E _{OP} -stage pulp properties	84
9.1.3 D-stage pulp properties	84
9.1.4 Z/D-stage pulp properties	85
9.1.5 P-stage pulp properties	85
9.2 Comparison between the D- and Z/D- sequences.....	86
9.2.1 Brightness	86
9.2.2 Kappa number	88
9.2.3 Viscosity	89
9.2.4 Brightness reversion	90
9.2.5 UVRR spectra	90
9.3 Filtrate properties.....	92
9.3.1 Non-process elements.....	92
9.3.2 Organic compounds.....	94
10 Conclusions.....	95
References.....	97
List of Appendices.....	107
Appendix 1: The methods for determination of pulp and filtrate properties.....	108
Appendix 2: Standard method for determination of HexA content	109
Appendix 3: UVRR Spectra.....	112

List of abbreviations

A	acid hydrolysis
A _{HT}	hot acid hydrolysis
A/D	acid hydrolysis and chlorine dioxide bleaching without an intermediate washing
ADT	air dry ton
AOX	adsorbable organic halogens
BDT	bone dry ton
BOD	biochemical oxygen demand
CaCO ₃	calcium carbonate
CaO	calcium oxide
Ca(OH) ₂	calcium hydroxide
ClO ₂	chlorine dioxide
CO ₂	carbon dioxide
COD	chemical oxygen demand
D	chlorine dioxide bleaching
D ₀	first chlorine dioxide bleaching
D ₁	second chlorine dioxide bleaching
D ₂	third chlorine dioxide bleaching
D _{HT}	hot chlorine dioxide bleaching
DTPA	diethylene triamine pentaacetic acid
E	alkaline extraction bleaching
E _O	alkaline extraction bleaching that also uses oxygen

E _{OP}	alkaline extraction bleaching that also uses oxygen and hydrogen peroxide
E _P	alkaline extraction bleaching that also uses hydrogen peroxide
ECF	elemental chlorine-free bleaching
EDTA	ethylene diamine tetraacetic acid
HexA	hexenuronic acid
HMW	high molecular weight
ISO	International Organization for Standardization
LMW	low molecular weight
M	mass flow of pulp (BDT/h)
meq	milliequivalent
MgSO ₄	magnesium sulfate
Na ₂ CO ₃	sodium carbonate
Na ₂ SO ₄	sodium sulfate
NaOH	sodium hydroxide
NPE	non-process element
OX	organically bound chlorine
P	hydrogen peroxide bleaching
Paa	peracetic acid bleaching
TCF	totally chlorine-free bleaching
TOC	total organic carbon
UVRR	ultraviolet resonance raman
Z	ozone bleaching

Introduction

The capacities of modern pulp mills continue increasing all the time. However, simultaneously the emissions of the plant must be kept under control. In addition, the limits of global environmental emissions keep getting stricter. Furthermore, new requirements and legislation are born. These facts require that all existing solutions should be taken into operation. The closing of the water circulations among other new technologies is therefore more and more interesting.

Bleach plant produces the largest amount of effluents in the whole pulp mill. Thus, bleaching is involved in most of the research and development projects, especially concerning eucalyptus pulp. (Bajpai, 2012) Lately, a bleaching sequence A-E_{OP}-D-P, that is here investigated, has been more and more intriguing. With this sequence it could be possible to decrease the use of chlorine dioxide to very low levels and continue closing the bleach plant.

The increasing price of sulfuric acid, which is an important chemical, and the long transportation distances especially to some areas in Brazil have aroused interest in decreasing the need of sulfuric acid. Because the mills using A-stage have not reported any significant problems about scaling this work focuses on A-stage filtrate reuse. The decrease of sulfur compounds in the filtrates would also make the filtrates more suitable for recovery cycle. First, in literature part the A-stage and the rest of the bleaching plant are discussed as well as the challenges and possibilities that the filtrate reuse arouses. The target of the thesis is to find out if the consumption of sulfuric acid in A-stage could be decreased by circulating the filtrate. Another aim is to define the composition of this filtrate and find out how the circulation effects the operation of A-stage, other bleaching stages, properties of pulp and chemical consumption.

1 Background on chemical pulping

1.1 Pulp mill overview

The principle of kraft pulping process is to chemically dissolve the components of wood that are holding the wood cells together with the least possible damage. A rough block diagram of the process is shown in Figure 1. The process starts when the wood logs are being debarked and chipped. After that the chips are being screened which ensures that the pulp will have an even quality. Then the chips are being prepared for the cooking process with air removal, steaming, heating and impregnation with liquor that contains hydroxide and hydrosulfide ions. With these actions the pulp will be more uniform, the cooking time is decreased and the fiberline production eased. The chips will end up in digester where the pulp will be cooked in high temperature, pressure and liquor. After the cooking phase the pulp will be discharged from the digester. At this point pulp contains significant amounts of impurities (organic and inorganic) and has darker color due to remaining lignin. The impurities and rejects are being removed by screening and washing. Oxygen delignification and bleaching continue the partial removal of lignin. In bleaching also brightness is increased by removing chromophores and hexenuronic acids in several different stages. (Gullichsen, 2000c)

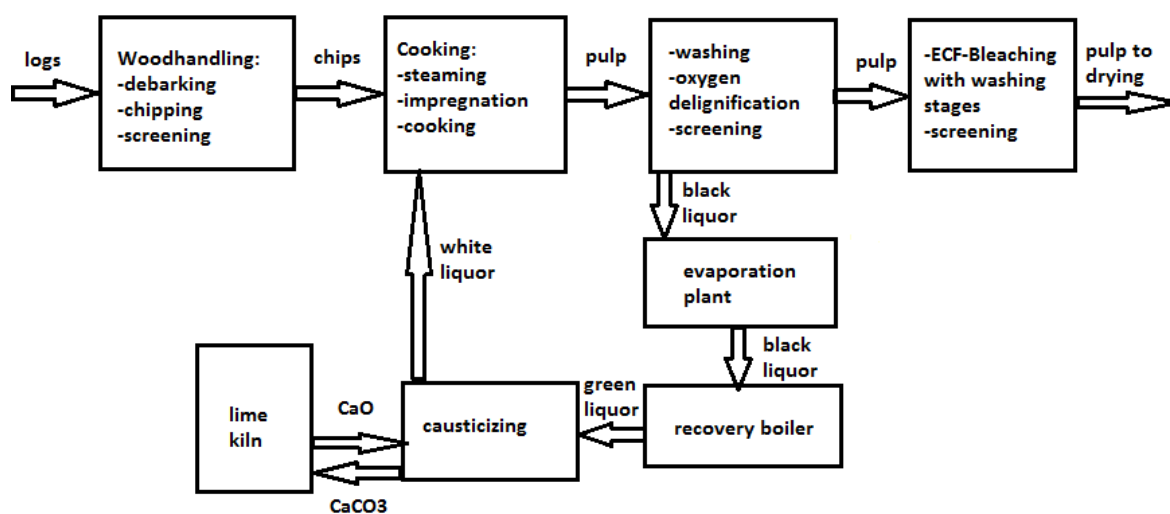


Figure 1. Block diagram of kraft process.

Black liquor from the washing stage after cooking is sent to the recovery boiler as shown in the Figure 1. This spent liquor includes cooking chemicals and a lot of organic matter which has high economic value. However, it is too dilute to be used directly. Thus, the liquor goes through a multistage evaporation plant where the dissolved solid content is raised to about 80 %. Concentrated black liquor is being burned in a recovery boiler so that energy is recovered in form of steam and electricity and green liquor is formed from sodium and sulfur chemicals.

Green liquor, which contains mostly Na_2CO_3 and Na_2S , goes to the white liquor plant, where white liquor for the cooking process is made. First, the lime is being slaked which means that CaO will be transformed to $\text{Ca}(\text{OH})_2$. After that it is used to convert sodium carbonate to sodium hydroxide which is then purified and used in cooking plant as a cooking chemical. CaCO_3 is separated from this solution and the lime kiln produces CaO from it for the causticizing process, and so a more economical process is possible. Chemical recovery system is for sodium and sulfur while the rest of the chemicals end up as dregs or cause problems in the process like potassium, chlorine and silica. (Gullichsen, 2000c)

1.2 Principles of bleaching

Bleaching process has traditionally been very little connected to the chemical cycle. It can be divided into two parts on an industrial scale: pre-bleaching and final bleaching. In pre-bleaching the removed substance is mainly lignin with a relatively large chemical dosage. The brightness at this stage remains still quite low. In the final bleaching the main target is to raise the brightness to about 88 – 94 % ISO and increase the purity of the pulp. (Gullichsen, 2000b)

Bleaching is used because it is a more selective way to remove lignin from pulp compared to cooking. Thus, the degradation of polysaccharides is reduced. In addition, shives, dirt particles, extractives and other undesired components are

removed. Nowadays bleaching is performed mainly with ECF (elemental chlorine free) but also partly with TCF (total chlorine free) bleaching. (Gullichsen, 2000b)

The most used bleaching chemicals are sulfuric acid, chlorine dioxide, sodium hydroxide, hydrogen peroxide, ozone, oxygen and peracetic acid. In mill processes the bleaching is performed in towers except for ozone bleaching and pulp is washed between the stages. It can be simplified, that the wash water for the washers comes from the washing stage of the following stage in which the pulp is cleaner. Finally from the first bleaching stages the effluent is led to the effluent treatment. Before the pulp is being fed to drying machine or paper mill, there is still a final screening that removes the rest of the impurities. (Gullichsen, 2000b)

The focus of bleaching development is not only in reducing chlorine dioxide consumption in bleaching stages but also in reducing the amount of sulfur components in bleaching filtrates. This would make the A-stage filtrate reuse in bleaching more attractive.

Literature part

2 Hexenuronic acid

2.1 Xylan in hardwood

There is about 15 – 30 % xylan in hardwood, depending on the species. Other compounds found in wood are other hemicelluloses, lignin and cellulose. Hardwood xylan is O-acetyl-4-O-methylglucuronoxylan, which means that the main chain consists of β -D-xylopyranosyl groups that are bound together with (1 \rightarrow 4)-glycosidic bonds. This chain is substituted by 4-O-methyl- α -D-glucuronic acid groups (Figure 2). These acid groups are bound in about every tenth xylose unit with (1 \rightarrow 2)-glycosidic bonds. Part of the xylose units of the main chain are also acetylated. In addition, in the reduced end of the xylan chain small amounts of L-rhamnose and galacturonic acid groups can be found. (Jääskeläinen and Sundqvist, 2007)

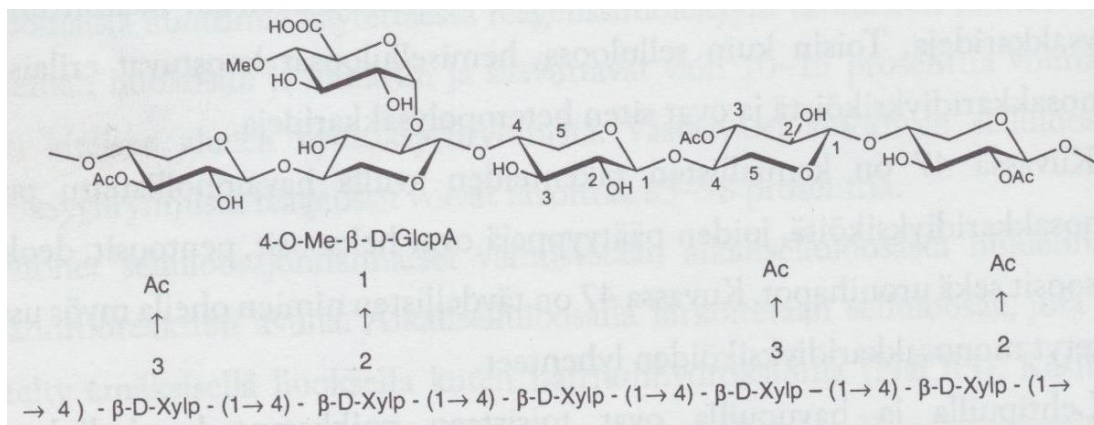


Figure 2. The structure of hardwood xylan (Jääskeläinen and Sundqvist, 2007).

2.2 The formation of hexenuronic acid

During kraft pulping in alkaline conditions some of the xylan's 4-O-methylglucuronic acid groups are degraded with the β -elimination of methanol (Johansson et al. 1977). The formed 4-deoxy-4-hexenuronic acid groups produced are better known as hexenuronic acid. This β -elimination is presented in Figure 3. After methanol has been eliminated from the uronic acid, a double bond between two carbon atoms is formed. (Teleman et al. 1995)

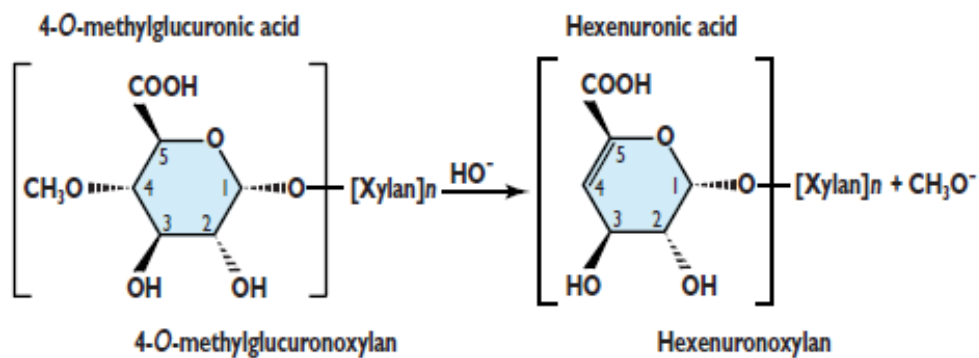


Figure 3. The transformation of 4-O-methylglucuronic acid into hexenuronic acid during the kraft pulping (Jiang Z. et al. 2000).

The amount of hexenuronic acids formed during cooking depends on cooking time, temperature, method, concentration and ionic strength of hydroxyl-ions and used raw material. (Buchert et al. 1995). As Figure 4 shows, when the cooking temperature is achieved, the HexA concentration is at its highest. When the cooking proceeds, the HexA content starts to decrease.

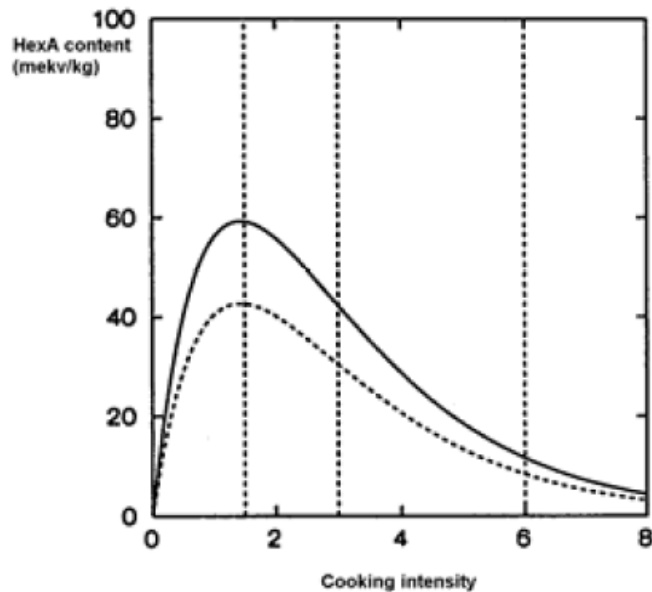


Figure 4. Development of HexA content in pulp during kraft cooking process (Vuorinen, 2011).

2.3 Basic information about HexA

There is a carbon-carbon double bond in the structure of HexA. When the kappa number is measured, potassium permanganate reacts with carbon-carbon double bonds that are located in lignin structure. Naturally, also the double bonds in HexA react with permanganate. (Buchert et al. 1995) In hardwood pulps HexA is responsible for from 3 up to 7 units of kappa number. In practice 10 meq of HexA equals to one unit in kappa number meaning that hardwood pulps contain about 30 – 70 meq HexA/kg. In softwood pulps the amount of HexA is about half of this. (Vuorinen et al. 1999) (Henricson, 1997)

One kappa unit of HexA is known to consume as much bleaching chemicals as one kappa unit of lignin. The chemicals which react with HexA are chlorine dioxide (*in situ* formed HOCl is responsible for the reaction), chlorine, ozone and peracids, although it was found that in D-, Z-stages HexA and lignin were equally reactive (Vuorinen et al. 1997) (Vuorinen et al. 1999). In chlorine dioxide bleaching HexA was converted into for example tetratic, pentaric, 2-chloro-2-

deoxypentaric and 3-deoxy-3,3-dichloro-2-oxohexaric acids. The formation of all these compounds consumes a considerable amount of chlorine dioxide. However, HexA does not react with alkaline peroxide or oxygen and therefore other chemicals are needed to produce thermally stable HexA-free pulps. (Vuorinen et al. 1997) In order to decrease the consumption of bleaching chemicals, the most economical way would be to decompose the HexA with a mild acid hydrolysis, i.e. A-stage. (Vuorinen et al. 1999) (Buchert et al. 1995) (Vuorinen et al. 1997)

Furthermore, HexA binds heavy metals, increases the amount of AOX (organically bound halogens) and causes yellowing in the course of time (Buchert et al. 1995) (Vuorinen et al. 1997) (Vuorinen et al. 1999) (Clavijo et al. 2012) (Kawae et al. 2010). The effect of HexA on brightness reversion is shown in Figure 5.

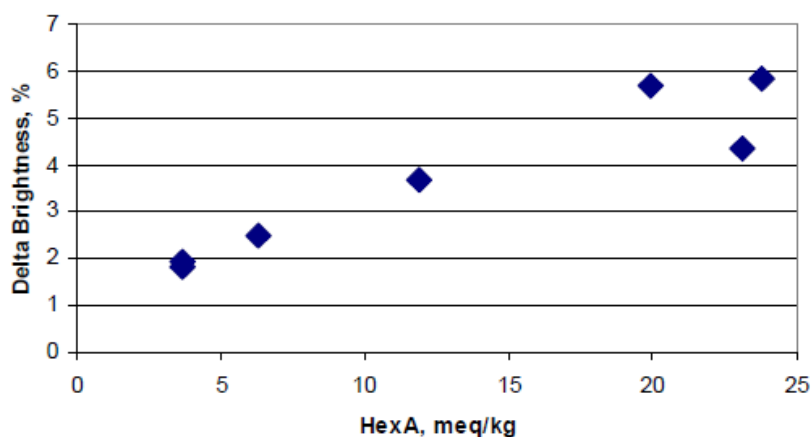


Figure 5. Effect of HexA content on brightness reversion (Pikka and Vehmaa, 2007).

2.4 HexA and metals

Positively charged metal ions like potassium, manganese and iron easily bind to carboxyl acid groups that have a negative charge. These carboxyl acid groups can be found in the uronic acid groups of hemicelluloses. Uronic acid groups not only have electric interaction with metal ions but they also have a tendency to twist and

fold so that they could also interact chemically with the ions. The carbon-carbon double bonds that HexA contains enhance the ability to bind metals substantially compared to other uronic acids. (Devenyns and Plumet, 1994) (Devenyns and Chauveheid, 1997)

In acidic conditions H^+ -ions adhere to carboxyl groups releasing metal ions that HexA has bound (Devenyens et al. 1998). This means that with acid hydrolysis it is also possible to remove metals from pulp even though 2-furancarboxylic acid and formic acid that are the main products of the hydrolysis of HexA do not form a significant amounts of complexes with Ca^{2+} , Mg^{2+} or Mn^{2+} (Räsänen et al, 2001). Especially manganese can be removed almost as effectively as with EDTA or DTPA (Vuorinen et al. 1999) (Henricson, 1997) (Devenyns et al. 1998). This is thought to be due to hot and acidic conditions because the manganese ions are found to sorb into fibers just like any other divalent ion (Räsänen et al. 2001). In addition, the iron concentration has been found to decrease significantly. Unfortunately also the amount of magnesium decreases due to A-stage unless chelates are being used. (Henricson, 1997)

It has also been proven, that HexA can cause formation of oxalic acid, especially when reacting with ozone (Rodrigues da Silva and Colodette 2002) (Pikka and Vehmaa 2007).

2.5 Degradation of HexA

Most common process in degrading HexA is the mild acid hydrolysis, A-stage, in which H_2SO_4 or HCl is used. During this acid hydrolysis the HexA degrades according to Figure 6. Acyclic form of HexA (1) is formed during the hydrolysis. It easily undergoes a β -elimination reaction, which produces substance (2) and its cyclic form (3). These compounds stabilize either via elimination of water (HD-2) or via elimination of both water and formic acid (HD-1) depending on if the

aldehyde group is hydrated or not. Elimination of water produces 5-carboxy-2-furaldehyde (5-formyl-2-furoic acid) and the elimination of water and formic acid produces 2-furancarboxylic acid (2-furoic acid). (Teleman et al. 1996) About 90 % of the eliminations happen with the latter way (Vuorinen et al. 1999).

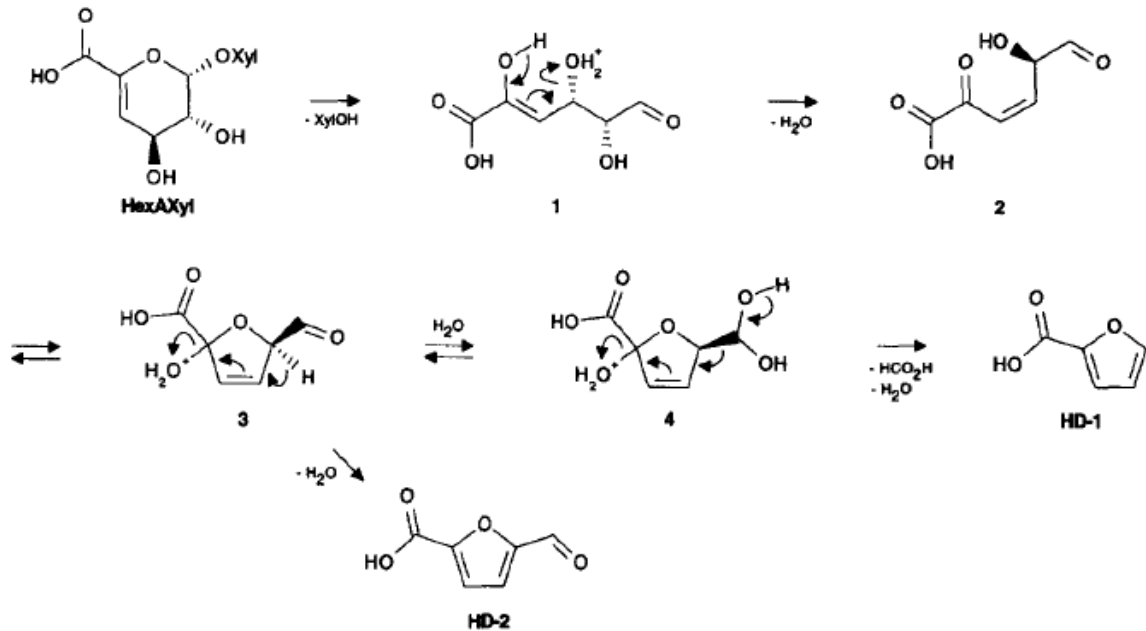


Figure 6. The degradation of HexA in acidic conditions (Teleman et al, 1996).

2.6 Possibilities of formic acid

Formic acid has recently shown potential as a biomass fractionation agent because of its ability to reach an extensive delignification simultaneously degrading hemicelluloses with a high yield. Cellulose yield has also been about 100 % when using formic acid. It has been suggested to be used in aqueous form in acid mixtures. In high temperatures formic acid treatment mostly degraded xylose and pentoses. (Dapía et al. 2002) During the process lignin is dissolved due to cleavage of β -O-4 bonds. Hemicelluloses are degraded into mono- and oligosaccharides. For delignification the acid concentration should be more than

80 %. The separation is based on the different solubilities of the components in acid, organic solvent and water, and the organic and acidic characters of formic acid. (Zhang et al. 2010) Formic acid was found to esterify hydroxyl groups of pulp during the delignification. In addition, the delignification mixture contained some acetic acid that was formed as a result of hydrolysis of acetyl groups in raw material. (Anttila et al. 2007)

3 Non-process elements in pulp bleaching

3.1 Metals

3.1.1 Metals as elements

Most of the metals that are found in the process enter with wood, but some elements, like silicon and aluminum enter with make-up lime (Ulmgren, 1997). Additionally, some metals can derive from the process equipment and end up in filtrates due to corrosion (Dahl et al. 1996). Naturally, most metals are unwanted in the process because they will cause different problems. These problems are shown in Table 1.

Table 1. Negative effects caused by metals.

Plugging in recovery boiler	K
Corrosion	K, Mg, Fe
Inert in lime cycle	Al, Mg
Scales and deposits	Al, Ca, Ba
Impact on the environment	Pb, Cd
Effect on pulp properties or bleaching	Mn, Mg, Fe

Transition metals such as iron, copper and manganese cause radical reactions. These reactions cause degradation of carbohydrate chains in oxygen-based chemical system, especially peroxide bleaching (Chirat et al. 2011). Iron is the most intractable of these and usually remains in pulp at the concentration of 10 – 20 ppm. In the mill water iron content of 0.1 mg/l will not only decrease the quality and the brightness of the pulp but also cause corrosion (Dahl et al. 1996). In addition, some brightness reversion can happen which causes increase in bleaching chemicals. Iron can for example be produced by corrosion or come with the mill water. (Boffardi, 1992)

Manganese has a detrimental impact on the brightness of the pulp. Therefore, the content of manganese should be less than 0.5 g/ADT. (Dahl et al. 1996)

Magnesium and calcium inhibit the radical reactions. Therefore, the removal of transition metals and the retaining magnesium is necessary for effective pulp bleaching. (Räsänen, 2003) (Lapierre et al. 1997) However, under some conditions magnesium can also cause corrosion. (Ulmgren, 1997)

Potassium can cause corrosion and plugging for example in the recovery boiler same way as chlorides (Ulmgren, 1997). It can accumulate in the sodium cycle and will end up in electrostatic precipitator dust. (Colodette et al. 2008) (Dahl et al. 1996) Normally potassium content is about 1 - 5 % of dry weight of concentrated black liquor solids. (Costa et al. 2005)

Normal values for NPE's in softwood processes are shown in Table 2. The values of wood can vary due to species, age and location (Ulmgren, 1997).

Table 2. Non-process elements in softwood process, units are g/ADT (Ulmgren, 1997)

	Input wood	After O	Bleached pulp
Al	12 -35	5 – 20	2 – 5
Si	2 – 25	40 – 100	1 – 5
P	50 – 100	15 – 50	2 – 5
Mg	75 – 250	100 – 200	10 – 40
Ca	500 – 1000	400 – 800	50 – 100
K	300 – 800	20 – 150	-
Cl	300 – 800	-	-
Mn	50 – 200	30 – 70	<1
Cu	1 – 2	0.5	0.1 – 0.3

3.1.2 Metal compounds

In pulping process, the metals can form also different harmful compounds. Precipitated oxalates are the most common ones in pulping process. They are formed when metal ions, mostly calcium, adhere with oxalic acids. (Rodrigues da Silva and Colodette 2002) Calcium mostly originates from wood and white liquor, in hardwood pulp the amount can be as high as 2 – 6 kg/BDT (Rudie and Hart, 2005) (Rodrigues da Silva and Colodette 2002). Main sources of oxalic acid are the cooking and especially the bleaching (Z- and D-stages) processes where up to 90 mg/l of oxalate is formed (Ulmgren and Rådeström, 2001) (Rudie and Hart, 2005).

In the cooking calcium precipitates as calcium carbonate while oxalate remains in the solution and is removed by the brownstock washing. Later in the bleach plant calcium dissolves when pH drops below 7 and is capable of reacting with oxalic acid forming calcium oxalate. (Rudie and Hart, 2005) Especially in ozone bleaching, HexA is oxidized and oxalate is formed in the next E_{OP}-stage where the highest oxalate content is found (Henricson, 1997). The formation of oxalates is

harmful because of the scaling problems in equipment and problems when closing water circulations (Sixta et al. 2006) (Rodrigues da Silva and Colodette 2002).

Ulmgren and Rådeström (2001) found out that the solubility of calcium oxalate was increased when pH decreased below 4 and when the temperature, ionic strength and magnesium ion concentration were increased. This means that by adding magnesium sulfate, the amount of deposits can be reduced. The amount of deposits can also be reduced by decreasing HexA content. The solubility of calcium oxalate in the D-stage filtrates was higher than in solutions with no organic substance. This can be explained by the fact that D-stage filtrate contained both mono- and dihydrates of calcium oxalate whereas the filtrate-free solution consisted only of the monohydrate. (Ulmgren and Rådeström, 2001) If the pH is lowered to 2.5 in a chlorine dioxide stage, the precipitation of calcium oxalate is decreased because carbonate is in form of carbonic acid which degrades into water and CO₂ which will be released to atmosphere. However, this will increase the risk of barium sulfate scaling. (Rudie and Hart, 2005) (Rudie and Hart, 2006)

Low temperature increases the formation of precipitates, except for calcium carbonate. Therefore, calcium oxalate can be found e.g. on reactor walls and pumps. These deposits are extremely difficult to remove: a very strong acid or high pressure washing is needed. (Ulmgren and Rådeström, 2001) (Ulmgren, 1997)

In addition, barium forms deposits as barium sulfate (Ulmgren and Rådeström, 2001). Barium enters the mill with wood and exits the digester as barium carbonate, mostly bound with fibers. When the pH decreases below 7, barium ions are released and they can start precipitating as barium sulfate. When the pH decreases to 2, barium starts to be released significantly more. The concentration of barium is low compared to calcium: only about 20 – 60 g/BDT in unbleached pulp and 1 – 2 g/BDT in the acid sewer. (Rudie and Hart, 2006)

The summary for the solubilities of calcium oxalate, calcium carbonate and barium sulfate is shown in Figure 7. The intervals in which the precipitation occurs are marked on the top of the picture.

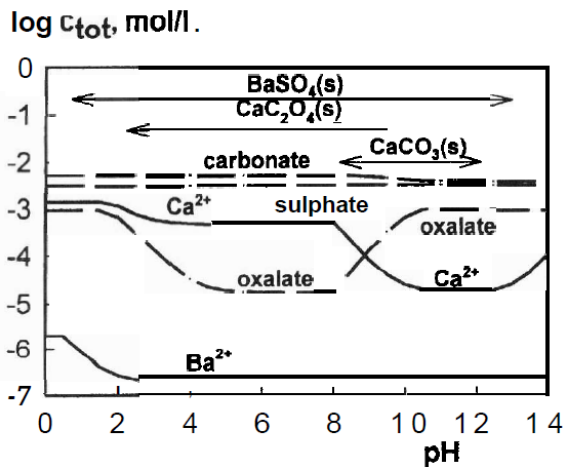


Figure 7. The effect of pH on the precipitation of BaSO_4 , CaC_2O_4 and CaCO_3 (Ulmgren, 1997).

Magnesium, as well as aluminum, can also form alkali insoluble compounds with carbonate which are removed by sedimentation and filtration of dregs. (Costa et al. 2005) Furthermore, aluminum can cause scales and deposits (Ulmgren, 1997).

There is research going on about so called “kidneys”, such as ion exchange and precipitation. Calcium oxalate and non-process elements could be separated from the system thus hindering the scaling and other problems by using “kidneys”. (EIPPCB, 2001) Metal ions found in acidic effluents can be removed by adjusting the pH to 10 – 12. Thus, many non-process elements would be precipitated as insoluble inorganic compounds. (Ulmgren, 1997)

The solubilities of different compounds are also affected by ionic strength, dissolved organic substance, solubility product of the compound, solvent, acidity and chelating agents (Ulmgren, 1997) (Dahl et al. 1996). The dissolved organic substance significantly increases the solubility of the compounds mentioned above because of interactions between these two components. In addition, the formation of these bleach plant deposits depends on the bleaching stages. In acidic stages such as acidic hydrolysis, chlorine dioxide and ozone stages the metal ions including calcium and barium are released from the fibers. In oxidative stages e.g. peroxide and ozone stages oxalate ions are formed and in stages that contain a high pH (E- and P-stages) carbonate ions are formed. In acidification sulfate ions are added. (Ulmgren, 1997)

3.1.3 Donnan theory

Water in the fiber suspension can be divided into two parts: the liquid surrounding fibers and the liquid inside the highly porous and negatively charged fiber wall. The schematic representation of this system is shown in Figure 8. The cellulose fibers act as a polyelectrolyte gel. The metal cations that are in the liquid can interact with the functional groups of fibers by two different ways: non-specifically and specifically. Non-specific interactions are electrostatic attraction and repulsion between the ions and fiber cell wall, which Donnan theory describes. Specific interactions include for example complexation of metal ions with functional groups and the adsorption of cations on to polarized surfaces. (Räsänen, 2003)

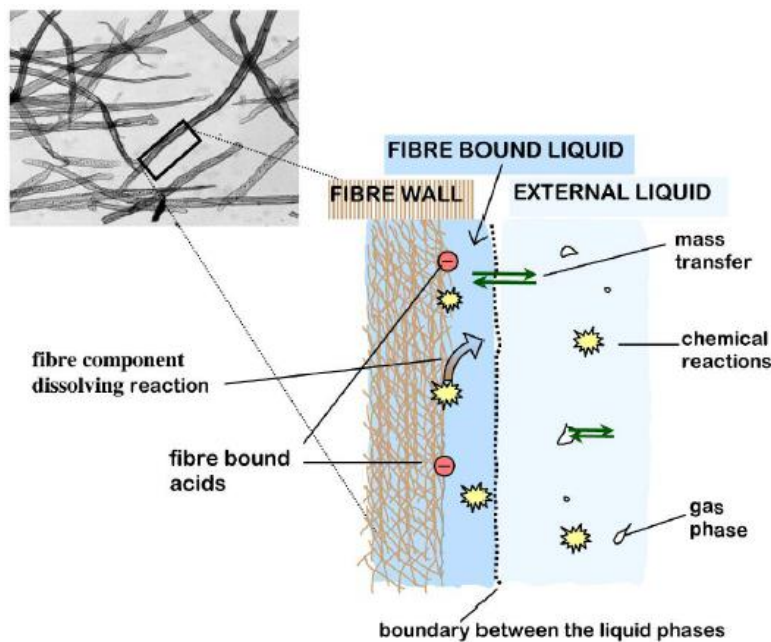


Figure 8. A schematic representation of the fiber suspension (Tarvo et al. 2008).

In a situation where pulp fibers are placed in a solution of electrolytes, anionic acid groups located within the fiber wall cause an uneven distribution of ionic species between the solutions inside the fiber wall and outside fibers (Räsänen et al. 2001) (Nordberg et al. 2001). In other words, an immobile or impermeable charge excess is located in one phase. In order to maintain the electroneutrality in both phases, the freely moving ions will move from one phase to another causing

this uneven distribution because of the immobile charge excess. (Räsänen, 2003) Donnan theory describes this distribution of ions between the fibers and the surrounding liquor. With this theory it is possible to predict the build-ups and other problems caused by non-process elements caused by system closure and identify the need for different separation technologies in order to prevent this accumulation (Neale, 1929) (Towers and Scallan, 1996) (Laivins and Scallan, 1997).

3.1.4 The interaction between metals and fibers in practice

The strength of the interactions between ions and fiber cell wall depends strongly on the charge properties of the fibers (Räsänen, 2003). According to Donnan theory, when the acidic groups in the pulp deprotonate the negative charge arises. This causes the cations to enrich in the fiber wall while the anions are expelled. Therefore, it can be said that the concentration of metal ions in the solution is dependent on the amount of acid groups on fibres and their degree of dissociation. (Athley and Ulmgren, 2001)

In addition, the charge of the metal ion and the concentrations of other components have an effect on the metal concentration. Sodium is the most general ion in the process solution of kraft pulping process thus affecting the distribution of other metal ions between the fibres and external solution. (Athley and Ulmgren, 2001) The amount of sodium bound by pulp is affected by sodium content in the filtrates and pH. Sodium is the most abundant metal in the system and even though its binding is not as strong as with divalent ions, it is bound with significant amounts to fibres. (Gu et al. 2004) The increasing concentration of sodium will decrease Donnan effect (Haglund et al. 1989).

The delignification process decreases the total charge of pulp (Räsänen, 2003). Calcium carbonate is formed already in the digester whereas magnesium carbonate presumably during oxygen delignification. These carbonates are located inside or on the fibre wall. When acid is added to the oxygen delignified pulp, a

considerable amount of acid is consumed by metal carbonates in the fibre. Therefore, the solids will dissolve and magnesium and calcium will exist as cations in the suspension. The other divalent ions are found in the suspension liquor. Sodium and potassium are found in their ionic forms because they cannot form any solid phases at these conditions. Because a part of sodium ions corresponding to the ion exchange capacity of the pulp is bound to the fibre, this part of sodium cannot be washed away but it will travel with pulp to the bleach plant. However, when magnesium sulfate is added, Mg^{2+} -ions replace Na^+ -ions in the pulp. Manganese, which exists as solid magnesium-manganese carbonate, is formed in low concentrations. (Nordberg et al. 2001)

At very low pH the internal and the external concentrations are identical for all the metals. The reason for this is that at low pH the acid groups are not dissociated which means that no basic condition for a Donnan equilibrium exists and no metals are bound to fibres, i.e. metals are easy to wash. When the pH increases, so does the internal concentration at the expense of external one. In this situation there is a larger amount of acid groups dissociated inside the fiber wall and the amount of metals bound to fibres increase. (Towers and Scallan, 1996) This is due to increase of negative charge on the fibres caused by deprotonation. Therefore, positively charged metal ions are more and more attracted and they cannot be removed by physical means. (Athley and Ulmgren, 2001) (Towers and Scallan, 1996) In addition, there is a larger imbalance in the concentrations of mobile ions between the fiber wall and suspension liquor when pH increases (Towers and Scallan, 1996).

The pH inside the fibers is always lower than in the external solution (Haglund et al. 1989). The biggest change in the metal distribution occurs when the pH is 3 - 5. This is in correlation with the dissociation of carboxylic acid groups that have pK_a of 4 (Towers and Scallan, 1996). The major part of charge in unbleached pulps is, however, caused by hexenuronic and methylglucuronic acids which have pK_a -values of about 3.1-3.3 (Räsänen et al. 2001) (Laine et al. 1994) (Teleman et al. 1995). At pH 5 – 6 various acids in residual lignin and extractives will dissociate (Laine et al. 1994). At neutral pH all the acid groups are dissociated

thus allowing λ to reach its maximum. The pK_a value of phenolic groups of lignin is about 10. All these groups mentioned are able to bind ions. (Towers and Scallan, 1996)

3.2 Other non-process elements

There are several other non-process elements that can accumulate in filtrates. A large part of them enters the mill with wood chips but the amount of non-process elements in the pulp depends also on the cooking conditions and washing efficiency (Gu et al. 2004). The silicon and phosphorous compounds present are alkali soluble. Their removal happens with equipment that removes green liquor dregs, lime mud, bleach plant effluents and precipitator dust. Table 3 presents the negative effects that are caused by elements that are not metals.

Table 3. Negative effects caused by non-process elements.

Plugging in recovery boiler	Cl
Corrosion	Cl, SO_4^{2-}
Inert in lime cycle	Si, P
Scales and deposits	Si, SO_4^{2-} , CO_3^{2-}
Impact on the environment	N, P
Dissolving in white liquor	Si

Most critical non-process elements that are not metals are chlorides and potassium. They have a tendency to accumulate in the sodium cycle causing corrosion. Usually they will end up there with different liquors. (Costa et al. 2005) Chlorine originates from wood itself – especially high chlorine content is found in eucalyptus (Vehmaa et al. 2011). Chlorides will end up in fly ash in electrostatic precipitator where it can be removed. Otherwise chlorides will cause plugging and corrosion in recovery boiler. Plugging happens on heat surfaces of the boiler due to lowered sticky temperature caused by chloride concentration. The corrosion

caused by chlorides in the equipment has been substantial and the level for chloride concentration should be less than 10 g/l depending on the temperature so that the problems in the recovery plant would be avoided (Colodette et al. 2008) (Dahl et al. 1996). Increasing temperature also increases corrosion (Dahl et al. 1996). Decreasing pH increases the corrosion caused by chlorides. In strongly alkaline pH the corrosion is known to be insignificant. (Ulmgren, 1997)

When circulating filtrates it is crucial to remove chloride or otherwise totally closed circulation of bleaching waters would be difficult to be performed. This is because the acidic bleaching filtrates contain too much chlorine for example for the recovery boiler (Jaretun and Aly, 2000). A trouble-free operation for recovery boiler requires less than 1 wt-% in black liquor and in precipitator dust (not NaCl). However, even values up to 10 wt-% can be found in fly ash. (Pfromm, 1999) Chloride can also react with water and form hypochlorous and hydrochloric acid, thus increasing steel corrosion and iron staining.

Sulfate ions are found to also cause corrosion. No impact on the pulp quality has been found for both sulfate ions and chlorides. (Boffardi, 1992)

Other ions that can be found in effluents are for example nitrates, phosphates, silicates and acetates. The main part of the inorganics found in effluents originates from the pulp or from chemicals used in bleaching. (Dahl et al. 1996) Sulfates can be removed by improving brown stock washing. Another possibility is to decrease the addition of sulfur as sulfuric acid in the bleach plant. (Rudie and Hart, 2006) Sulfates and carbonates can also cause scaling.

Non-process elements can also accumulate somewhere else in the pulp mill cycle. Silicon and phosphorous accumulate in calcium cycle. This will result in increased dead load in lime mud and deteriorating reaction efficiency in lime kiln. Already one percent of these elements will decrease the efficiency by about 5 – 6 %. Silicon can also dissolve in white liquor due to its high solubility. At higher concentrations calcium silicate can be formed. Calcium phosphate dissolves better in green liquor than in white liquor. (Costa et al. 2005) Silicon can also cause some scales and deposits (Ulmgren, 1997).

4 Bleach plant operations

After cooking, oxygen delignification is used for removing the phenolic lignin that is left in pulp. It is more selective way to decrease the kappa number to the range 12 – 20 with hardwood pulps, than by continuing cooking. Due to the reduced kappa number, oxygen delignification decreases the bleaching chemical consumption later on. The use of oxygen delignification also enables the circulation of effluents to recovery and therefore lowers the COD (Chemical Oxygen Demand) and BOD (Biochemical Oxygen Demand) emissions in bleaching effluents. (Sixta et al. 2006) The removal of HexA is, however, not possible because HexA does not react with oxygen. Thus, in principle the order of oxygen delignification and A-stage does not matter. (Vuorinen et al. 1999)

4.1 A-stage

As mentioned, HexA is degraded in A-stage which is the first bleaching stage after oxygen delignification in the modern hardwood pulp mills. The conditions of A-stage are shown in Table 4. (Vuorinen et al. 1999) At pH higher than 3.5 the hydrolysis of cellulose becomes independent of pH due to catalysis of water and therefore pH should be lower than this (Vuorinen et al. 1997). Nevertheless, if the end pH drops to 2.5, the degree of polymerization decreases significantly. The harsher the conditions are, the more HexA can be removed. However, this also leads to degradation of glycosidic bonds in cellulose chains that lowers the viscosity. Thus, it is important to control the conditions carefully during the hydrolysis. (Vuorinen et al. 1999) Vuorinen et al. (1997) found that when hydrolyzing hardwood pulps, the dissolved part was mainly xylose and its polymers whereas for softwood mainly arabinose was liberated.

Table 4. The industrial process conditions of acid hydrolysis (Henricson, 1997) (Clavijo et al. 2012).

Temperature (°C)	80 - 95
End pH	3 – 3.5
Retention time (h)	2 - 4
Consistency (%)	9 – 14
H ₂ SO ₄ (kg/BDT)	7 - 11

In Figure 9 the influence of temperature for the hydrolysis is shown. It can be seen that at some point the kappa number is no more decreasing because nearly all HexA has been degraded. Nevertheless, the viscosity continues decreasing when the A-stage proceeds. Additionally, the higher the temperature is, the faster the viscosity decreases. Vuorinen et al. (1999) found that when 90 % of the HexA was removed, the viscosity decreased an average of 50 – 100 dm³/kg. When the temperature of the hydrolysis is 120 °C, begins the zero-span tensile index to suffer. Although HexA is removed in A-stage the brightness of the pulp does not increase (Eiras and Colodette, 2003).

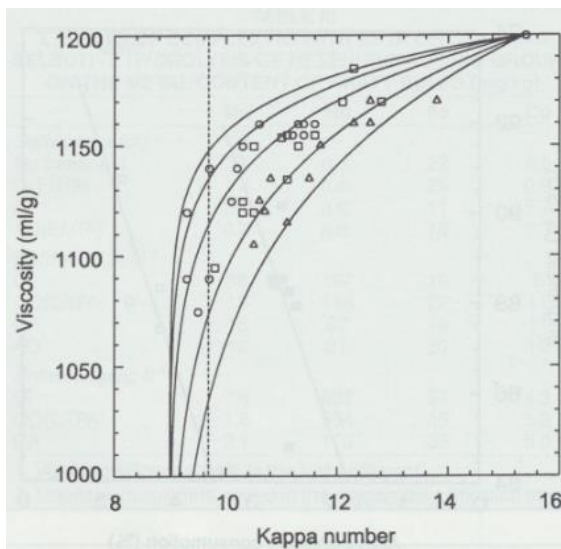


Figure 9. The change in viscosity as a function of kappa number during the A-stage, (Δ , 115 °C; \square , 105 °C; \circ , 95 °C) (Vuorinen et al, 1999).

4.2 Chlorine dioxide bleaching

In the modern hardwood pulp mills the use of chlorine dioxide as a first bleaching stage after oxygen delignification is no longer very common. It is more economical to first remove HexA with acid hydrolysis. Earlier D₀-stage used to start the bleaching sequence.

However, nowadays the modern mills that are using eucalyptus as their raw material have added a D₀-stage right after the A-stage without an intermediate washing (Pikka and Vehmaa 2007). One reason for this has been that if a stand-alone A-stage was installed, both a tower and a washer would be required. It has been found that the kappa number after the D₀-stage can be even lower when no washer is used between the stages. This is due to the fact that pH and temperature are similar to both stages and the organic products formed in the A-stage consume only slightly D₀-stage chemicals. (Sixta et al. 2006) (Henricson, 1997)

It is also possible to combine A- and D₀-stage effect into one, D_{HT}-stage. This means that both hydrolysis and D₀-stage would happen at the same time. In the beginning of D_{HT}-stage HexA and lignin are equally reactive but after few minutes only HexA is degraded. (Vuorinen et al. 1999) (Vuorinen et al. 1997) D_{HT}-stage required less chlorine dioxide thus producing less AOX in the effluent than conventional D-stage. This was thought to be due to the harsh conditions of the D_{HT}-stage. (Eiras and Colodette, 2003) In a lengthened A-stage it is the opposite: first only HexA is degraded but after some time HexA and lignin are removed at the same rate. However, when A/D-stage is used the removal of both components is more efficient. (Vuorinen et al. 1999) (Vuorinen et al. 1997) In Medina's study (2007) A/D-stage produced less overall AOX (OX values were higher for A/D-stage) than D_{HT} while the chemical consumption was on the same level. In addition, the active chlorine dosage can be lower for A/D-stage (Eiras and Colodette, 2003).

In the final bleaching chlorine dioxide can be used in one or two different stages. It can also be followed by P-stage. Nowadays the trend is to use fewer stages so

that the investment costs could be lowered although the operating costs tend to increase. However, the use of only one final bleaching stage leads to lower brightness stability. (Colodette et al. 2008) Other factors that have to be taken into consideration are final brightness, emissions, costs and chemicals used. (Pikka and Vehmaa, 2007)

In D₀-stage the main objective is to reduce or eliminate residual lignin and in latter D-stages to brighten the pulp by removing chromophores. Typical industrial process conditions for these stages are shown in Table 5.

Table 5. Typical industrial process conditions for chloride dioxide bleaching (Gullichsen, 2000b) (Chirat et al. 2011).

	D ₁	D ₂
Temperature	60 – 80	60 - 85
Final pH	3.5 - 5	3.5 - 5
Retention time (h)	1.5 - 4	2 - 4
Consistency (%)	10 - 13	10 - 15
Residual oxidant concentration (g/l)	trace - 0.05	trace – 0.03
ClO₂ (kg act. Cl/BDT)	13 – 42	5 - 21

The chemical consumption in each stage depends on the kappa number, but normally a small ClO₂ residual is maintained (10 – 50 mg ClO₂/l). The pH of the stage will decrease rapidly as soon as chlorine dioxide reacts with pulp. Therefore, an addition of sodium hydroxide is used to adjust the pH. (Gullichsen, 2000b) An optimum final pH of D₁-stage is shown in Figure 10. With increasing pH more chlorite is formed. As the pH rises above 4, the reactivity of chlorite with pulp drops rapidly. (McDonough, 1996)

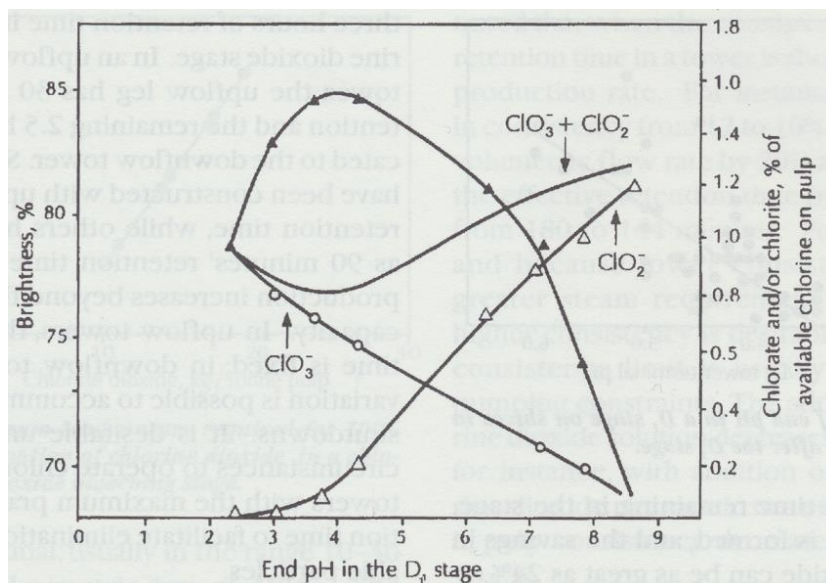


Figure 10. The dependence of brightness on the final pH in D₁-stage (McDonough, 1996).

Recent study by Tamminen (2010) stated that retention time of 60 minutes is sufficient for maximal brightness values. However, the brightness reversion would decrease when retention time is increased. When the temperature is increased, the rate of bleaching increases as well as the consumption of chlorine dioxide. Normally D₁- and D₂-stages are separated with alkaline extraction or short neutralizing in order to make D₂-stage more efficient – higher brightness with less chemicals will be achieved. If only one D-stage is used, the chemical dosage has to be significantly higher. (McDonough, 1996)

If the pH of the chlorine dioxide stage is adjusted with hydrochloric acid, the delignification process can be enhanced. This is due to the fact that hydrochloric acid increases the content of chloride ions which can lead to beneficial changes in pulp properties when the delignification is performed with 100 % chlorine dioxide. When the chloride concentration is higher, the chlorate formation is reduced. Chlorate is unwanted because it decreases the amount of oxidizing chemicals available for delignification. However, the AOX values were increased when using hydrochloric acid in initial bleaching. (Medina, 2007)

4.3 Ozone bleaching

The use of ozone is possible with or without chlorine dioxide stage. Z- and D-stage can be united because they both utilize acidic conditions. Acid conditions are chosen due to the better dissolution of ozone in low pH, normally between 2 and 3. This way the viscosity of the obtained pulp is higher and kappa number lower as shown in Figure 11.

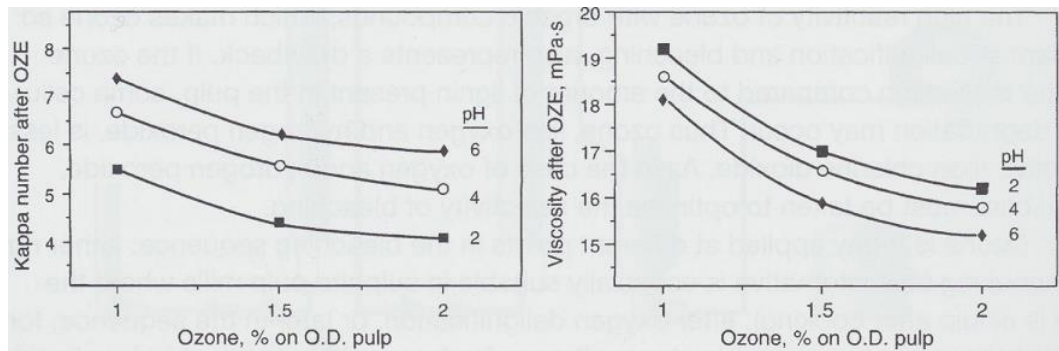


Figure 11. The effect of pH on the pulp properties in ozone stage (Chirat et al. 2011)

Ozone is known for its high reactivity and ability to react with almost any organic material. In addition, the effluent of Z-stage contains no chlorine compounds and can therefore be circulated to the chemical recovery system. (Sixta et al. 2006) The OX content of the effluent is also low as well as the brightness reversion of the pulp, when ozone is used (Colodette et al. 2008). The negative side of using ozone is that due to its gas form it has to be produced on-site which increases the plant investment costs. Ozone also attacks on carbohydrates and heavy mixing is required due to the fast reactivity. (Sixta et al. 2006)

The operating conditions of a Z-stage vary. Low consistency has been proven to require too much energy in mixing, but also medium consistency has been considered difficult due to high energy consumption. In practice ozone stage is performed in high or medium consistency. Temperature in the industrial practice is 50 – 80 °C because higher temperatures cause ozone decomposition. However, temperatures up to 80 °C are possible. Ozone can also be decomposed forming radicals due to presence of transition metals. Thus, chelation could be in theory combined with Z-stage. However, in practice no industrial solutions exist. The

reaction time of ozone with a pulp suspension is usually just seconds which means that in an industrial scale ozone bleaching is generally combined with a mixer or a small reactor. (Sixta et al. 2006)

Ozone can cause degradation of cellulose especially in final bleaching because the lignin content is too low. Selectivity is better for hardwood pulp due to the HexA content. (Sixta et al. 2006) Ozone as a matter of fact prefers to react with HexA rather than lignin (Pikka and Vehmaa, 2007). Thus, ozone is mainly used for removing HexA and lignin in prebleaching (Colodette et al. 2008).

However, it can also be used after an A-stage. Even though A-stage lowers the selectivity of Z-stage by removing HexA, it has been proved that A-stage can lower the bleaching costs in the sequence. (Colodette et al. 2008) Z-stage can also be located in the middle of the sequence or as a final bleaching stage (Sixta et al. 2006) (Andrew et al. 2013). Andrew et al. (2013) found that applying ozone immediately after A-stage is more beneficial than applying it right after oxygen delignification. In obtaining final brightness ozone has been proven to be better than chlorine dioxide. When ClO_2 reacts with lignin fragments, new colored groups were formed while an excess of ozone degraded these kinds of groups that were formed during Z-stage. In addition, chlorine dioxide did not have any effect on quinones whereas ozone easily destroyed them. (Lachenal et al. 2009)

When medium consistency ozone and chlorine dioxide stage are joined together, no intermediate washing is used. The most common solution is to use this combined stage as a first bleaching stage. (Lachenal and Muguet, 1992) Both Z/D- and D/Z-stage have been studied and Chirat et al. (1997) found that D/Z was superior for unbleached pulp whereas Z/D was superior for oxygen-delignified pulp. However, no reference is found for D/Z bleaching stage and the discussion of it is only based on laboratory experiments. After the oxygen delignification stage one kilogram of ozone can replace up to 3 kilograms of active chlorine without causing any adverse effect on pulp characteristics. Chirat and Lachenal (1997) discovered in their laboratory tests that D/Z-stage in the end of the bleaching sequence was efficient in increasing brightness. Addition of 0.6 % of

ozone saved 1.5 % of chlorine dioxide thus lowering AOX levels. In addition, the viscosities were even higher when ozone was used compared to the process where only chlorine dioxide was used.

4.4 Alkaline bleaching stages

4.4.1 Alkaline extraction

Usually in an industrial bleaching sequence there is at least one alkaline extraction stage. This so-called E-stage is in the modern eucalyptus pulp mills used as the second bleaching stage and the most critical one. (Pikka et al. 2000b) The aim of the extraction is to dissolve and remove the lignin that has reacted in the previous D-stage; it converts quinone moieties to polyphenols (Brogdon and Lucia, 2005a). Alkaline extraction also degrades lignin into smaller fragments therefore making the lignin removal easier. (Pikka et al. 2000b)

During extraction the main part of alkali is consumed for neutralizing the dissolved acidic reaction products, acidic groups of pulp, acid carryover and activating remaining lignin (Colodette et al. 2008). During the first few minutes of extraction the kappa number decreases rapidly. This is presumably caused by neutralization. The slower stage, which happens afterwards, is related to the ionization and slow mass transfer within the fibers. (Gullichsen, 2000b)

For many years the extraction had been enhanced with an addition of oxygen and/or hydrogen peroxide. This enables the kappa number to decrease further and the brightness to increase. With these oxidants it is possible to increase the ionization of phenolic groups of lignin and thus improve solubility. For eucalyptus pulp the E_O-stage is rather inefficient but E_P- and E_{OP}-stages are more often used. (Colodette et al. 2008) E_O-stage does not remove more lignin than E-stage but oxidizes polyphenols to hydroxyquinones which is shown as a slightly lower

kappa number. E_O-stage pulp also has somewhat better bleachability. (Brogdon and Lucia, 2005a) E_P- and E_{OP}-stages provide a lower kappa number and Klason lignin content than extraction stages without peroxide. This is due to the fact that use of peroxide eliminates quinonoid and muconic acid moieties. Because oxygen oxidizes polyphenols to quinones and peroxide then eliminates them, the E_{OP}-stage is proved to be the most efficient one. (Brogdon and Lucia, 2005b)

As mentioned before, the chemicals used for alkaline extraction are sodium hydroxide, oxygen and hydrogen peroxide. The industrial process conditions for extraction are given in Table 6.

Table 6. The industrial process conditions of alkali extraction (Gullichsen, 2000b).

Temperature (°C)	70 – 90
End pH	10.5 – 11
Retention time (min)	60 – 120
Consistency (%)	9 – 16
NaOH (kg/BDT)	10 - 12
O₂ (kg/BDT)	0 – 6
H₂O₂ (kg/BDT)	0 - 6

Sodium hydroxide charge is influenced by several factors: lignin content of pulp entering the bleach plant, oxygen delignification and cooking conditions, carryover from previous stage, washing filtrate circulation and E-stage conditions. (Gullichsen, 2000b) Addition of even a small amount of oxygen can cause a significant decrease in kappa number and increase in final brightness. When 5 kg/BDT oxygen is used, about 3.5 kg/BDT of chlorine dioxide is saved. This results in considerable savings in the chemical costs. (Reeve, 1989) Oxygen requires a pressurization of some kind – it is possible to pressurize only a pre-reactor or the whole tower. The pressure of an upflow tower is usually 2 – 3 bar at the top while downward flow tower uses atmospheric pressure. Already a dosage of 1.5 kg/BDT of hydrogen peroxide decreases chlorine dioxide consumption by about 3 kg/BDT. (Gullichsen, 2000b) (Chirat et al. 2011)

The consumption of hydrogen peroxide could be as high as 6 kg/BDT, as can be seen in the Table 6. This usually happens when the bleach plant is short in chlorine dioxide and usually requires pressurized conditions. The effect of temperature is significant in the extraction: it will also have an effect on the brightening agent consumption later on in bleaching. (Colodette et al. 2008)

If A_{HT}/D- or D_{HT}-stage is the first stage, it is reasonable to take advantage of the high temperature of the pulp and run the extraction at higher temperatures. However, the washing in between also affects temperature. With temperatures of over 90 °C in E-stage the consumption of peroxide increases while the yield and viscosity decrease. Oxygen is, however, not always needed if the hardwood pulp has been already treated with A_{HT}/D- or D_{HT}-stage. Oxygen can even attenuate the effect of peroxide during the extraction. However, for softwood pulp the use of oxygen in the extraction is advantageous. (Colodette et al. 2008)

4.4.2 Peroxide stage

P-stage is used normally as the final stage in the ECF bleaching sequence. Lately, it has been attracting more interest than D₂-stage due to the achieved higher final brightness, better brightness stability and beatability (Süss et al. 1999) (Carvalho et al. 2008). Although the kappa number was higher for peroxide using sequence compared to the use of chlorine dioxide in study performed by Eiras and Colodette (2005), the brightness stability was better.

In P-stage the reducing groups of carbohydrates and lignin such as oxidized cellulose and xylans are removed. Additionally, peroxide can remove o- and p-quinoid structures that are formed by side-reactions and only partially removed in preceding chlorine dioxide stage. These structures in addition to other reduced groups would react with HexA causing more brightness reversion. (Colodette et al. 2008) Quinone structures are an important part of color causing systems in lignin in the final bleaching. Peroxide, however, forms perhydroxyl anions in

alkaline conditions. These anions react easily with certain types of chromophores, especially carbonyl structures, such as quinones. (Carvalho et al. 2008)

The alkaline conditions allow the reaction products to be removed (Süss et al. 2004). It can be said that the more chlorine dioxide is used in bleaching before P-stage, the higher the consumption of peroxide should be in order to remove these formed quinones. (Carvalho et al. 2008) Furthermore, the changing the pH of pulp from acidic to alkaline environment and the fact that remaining chromophores are more prone to react with peroxide than with chlorine dioxide have an influence on the better performance of peroxide. However, still some mills oppose the idea of replacing D-stage with P-stage if process waters and wood contains large amounts of potassium. (Carvalho et al. 2008)

Perhydroxyl anion is a strong nucleophile and responsible for the most bleaching reactions in P-stage. Peroxide can also decompose and form oxygen which can react with lignin. The reactions taking place during the P-stage are generally slow. However, using pressurizing reactors will allow higher reaction temperatures, shorter reaction times and result in a higher brightness with an equal chemical consumption. The typical reaction conditions of an industrial P-stage are presented in Table 7. (Gullichsen, 2000b)

Table 7. The typical industrial process conditions for P-stage (Gullichsen, 2000b) (Chirat et al. 2011).

Temperature (°C)	80 - 90
Final pH	10.5 – 11
Retention time (min)	30 – 180
Consistency (%)	10 – 15
H₂O₂ (kg/BDT)	2 - 40
MgSO₄ (kg/BDT)	0 - 2

Peroxide is not as efficient as chlorine dioxide in removing shives and dirt. Thus, P-stage requires extra attention to screening and pre-delignification compared to D-stage as the final stage in order to reach comparable cleanliness of the final pulp. However, the AOX amounts will decrease when using peroxide instead of

chlorine dioxide although peroxide residuals in effluents are detrimental to microbial activity in biological treatment. (Gullichsen, 2000b)

4.4.3 Metal control in alkaline stages

A well-known problem with bleaching stages using peroxide is its ability to be catalyzed by transition metal ions. These reactions produce hydroxyl radicals and superoxide anions which both can react with polysaccharides by degrading them and lowering the viscosity of the pulp. Therefore, it is normal to decrease the amount of metals by using chelants and/or adding magnesium sulfate both in alkaline extraction that uses peroxide and in peroxide stage. Even a low level of transition metals can cause this degradation, thus making it important to design the metal control. Even a small addition of magnesium sulfate was found to decrease the viscosity loss and lowered peroxide consumption. (Carvalho et al. 2008) A normal charge is up to 2 kg/BDT.

The protective characteristic of magnesium is shown in Figure 12. The addition can be either as magnesium sulfate or hydroxide. Studies have shown that the ratio Mg/Mn should be over 30 in normal P-stage conditions but when the temperature increases, the ratio should be increased as well. However, an excessive addition of $MgSO_4$ may suppress the bleaching reaction. (McDonough, 1996) Even though the viscosity will be lower for peroxide treated pulp than for chlorine dioxide bleached pulp, the physical and optical properties will be better for peroxide bleached pulp. In addition, the study made by Carvalho et al. (2008) showed that the brightness before the last P-stage should be around 87 %.

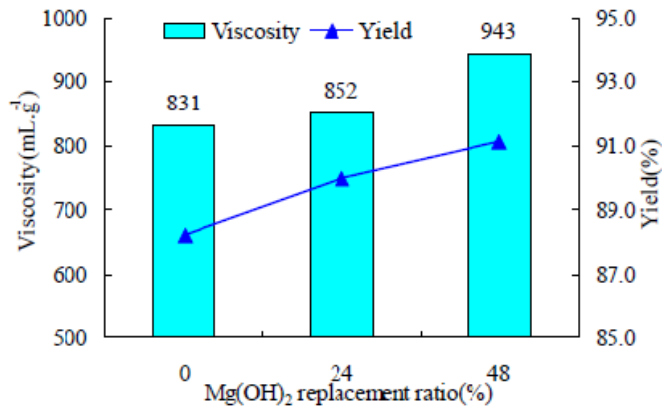


Figure 12. The protective attribute of magnesium on pulp viscosity (Liu et al. 2014)

Süss et al. (1999) found out that also an addition of sodium silicate increased the brightness and decreased the heat aging tendency. It works the same way as magnesium sulfate and complexes the transition metals through oxygen or hydroxyl bridges (McDonough, 1996).

5 Washing and its filtrates

5.1 Pulp washing

5.1.1 Washing principles and concepts

Pulp washing can be mainly performed with three different ways: by diluting and thickening, displacing and pressing. Dilution-thickening is the simplest way of them all. In principle it means that first the pulp suspension is being diluted by adding wash liquor, the suspension is mixed, the filtrate is removed and the pulp is discharged like in Figure 13. This technique is not very efficient, so it should be performed several times in series. In practice this principle is found in some bleach plant wash presses, like screw or roll presses. (Krotscheck, 2006)

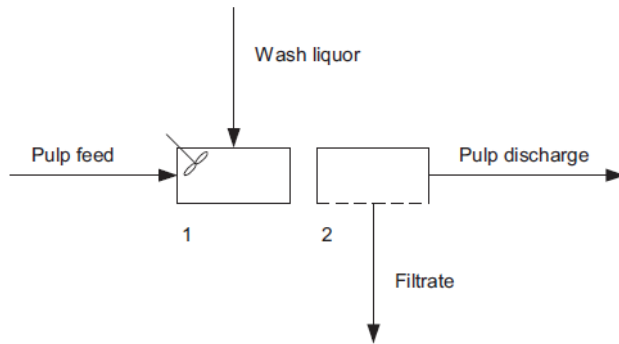


Figure 53. Dilution-thickening (Krotscheck, 2006, p. 524).

Displacement washing means that clean wash liquor is fed on top of the pulp cake and the liquor pushes away the dirty liquor that enters with pulp. The dirty liquor becomes filtrate and finally all that is left outside the fibers, is the washing liquor. So in this case there is no mixing of any kind. After the displacement there might also be need for some thickening. In theory all of the dirty liquor outside the fibers would be removed, but in reality there is always some kind of un-wanted mixing involved. Theoretical scheme is shown in Figure 14. (Krotscheck, 2006)

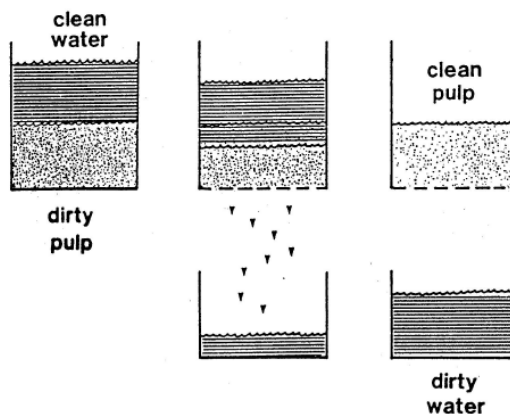


Figure 6. Displacement washing (Ruuttunen, 2010).

Pressing is about pressing the dirty liquor entering with the pulp mechanically into filtrate. The pressure causes the filtrate to go through wire or screen. Firstly, only the impurities outside the fibers are being removed, but it is also possible that when the pressure increases also the liquor trapped inside the fibers is moved to the filtrate. (Krotscheck, 2006)

The most important concepts for pulp washing are dilution factor, displacement ratio and Nordén's E-factor. Dilution factor signifies the difference between the

incoming wash liquor and the liquor leaving with pulp, divided by the pulp flow. Displacement ratio means the actual washing efficiency compared to the ideal displacement washing efficiency. (Krotscheck, 2006) The most common parameter in Scandinavia, however, is Nordén's E-factor. It expresses the amount of ideal dilution-thickening stages that are required to attain a similar washing efficiency as in certain equipment. It can be presented also as E_{10} -value which means E-factor in a consistency of 10 %. (Nordén, 1966) (Gullichsen, 2000a)

5.1.2 Brown stock washing

The purpose of brown stock washing is to remove the impurities and recover cooking chemicals with designed dilution factor and equipment. Pulp should be clean for bleaching so that the chemical consumption would be as low as possible, the runnability would not suffer and no degradation of carbohydrate chains would happen. Usually the impurities in the pulp after cooking consist of black liquor. Normally the organic and inorganic substances are separated: when talking about organic matter, the term used is COD and when it is about inorganics, usually sodium is used (mostly Na_2SO_4). (Krotscheck, 2006)

Generally, one brown stock washing stage is insufficient because the washing does not normally happen like in theory and efficiency requirement for pulp washing is quite high. Therefore, multiple washers should be installed in series or a washer should have several washing stages. The filtrate of the first washing stage has the highest concentration of impurities and it is sent to the evaporation plant. (Krotscheck, 2006)

5.1.3 Washing stages in oxygen delignification and bleaching

In washing stages between bleaching stages and after oxygen delignification the goal is to remove the unwanted components before the next bleaching stage.

These components cause increase in chemical consumption and harm the pulp properties. (Gullichsen, 2000b) (Krotscheck, 2006) After an ECF bleaching stage these components are mainly of organic matter including chlorinated organic compounds, residuals of oxidant and other non-process elements (NPE), such as metals (Costa et al. 2005). In addition, washing decreases scaling problems and adjusts other conditions, such as pH, suitable for the next bleaching stage (Gullichsen, 2000b) (Krotscheck, 2006).

Usually the optimum has to be found between the purity of the pulp and the amount of water used (Gullichsen, 2000b). The washing stage after oxygen delignification should have the best washing efficiency in the bleach plant. This is because of the large amount of dissolved organic material that consumes bleaching chemicals. E-value of 8 is necessary. (Krotscheck, 2006) (Pikka et al. 2000b)

Lately the focus in different mills has been in decreasing the water consumption of bleaching. That is why countercurrent washing is used. It means that the cleanest wash liquor is used in the last washing stage in which the pulp is also the cleanest. This wash liquor can be white water from drying machine, fresh water or condensates from the evaporation plant (Histed and Nicolle, 1973). The filtrate of this stage is used as the washing liquor of the second last stage and so on until all the washing stages have been gone through (Figure 15) (Krotscheck, 2006). Some fresh or white water can also be added to the second last washing stage (Costa et al. 2005). When the amount of filtrate out from a washing stage is lower, also the quantity of heat is lower and therefore energy efficiency of the washing stage is higher. (Krotscheck, 2006)

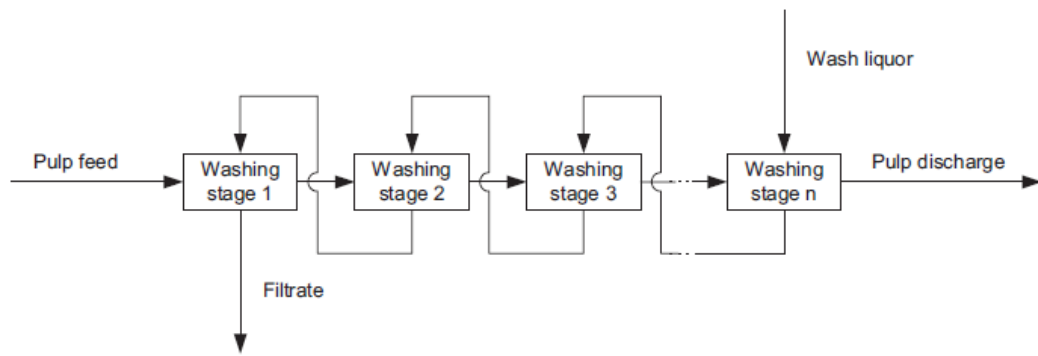


Figure 7. Countercurrent washing (Krotscheck, 2006).

Countercurrent washing is nearly always performed like shown in Figure 15. However, for example in bleaching some mills use so-called split-flow and jump-stage countercurrent washing. In split-flow countercurrent washing the filtrate flows are divided into two streams (acidic and alkaline). Before a bleaching stage pulp is washed with a filtrate that has a similar pH and that has been formed in a latter bleaching stage. After this bleaching stage the pulp is washed with a filtrate that has pH close to the one in the next stage in the sequence. (Pikka and Vehmaa, 2007) (Histed et al. 1996) Split-flow countercurrent washing is presented in Figure 16.

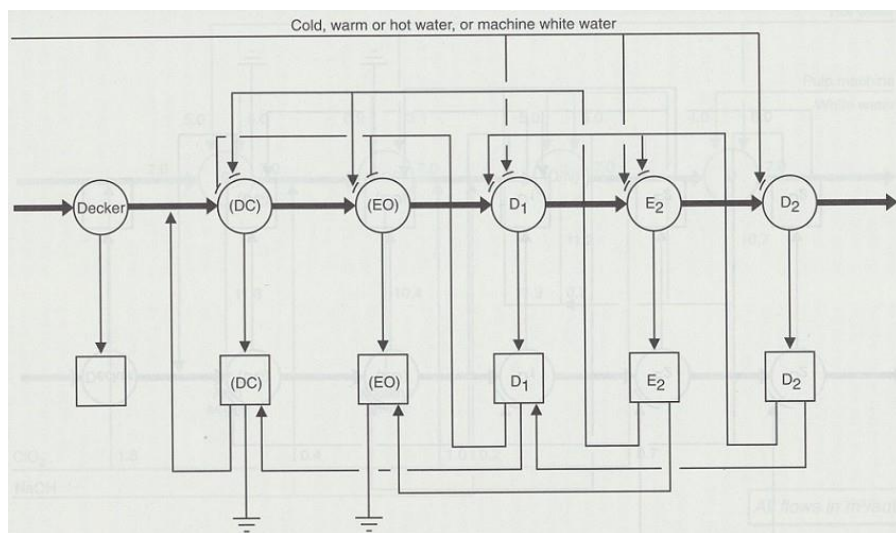


Figure 8. Split-flow countercurrent washing (Histed et al. 1996).

In jump-stage countercurrent washing the acidic and alkaline filtrates are kept apart. For example the D_1 -stage filtrate is sent to D_0 -stage washer. (Pikka and

Vehmaa, 2007) (Histed et al. 1996) Jump-stage countercurrent washing is shown in Figure 17.

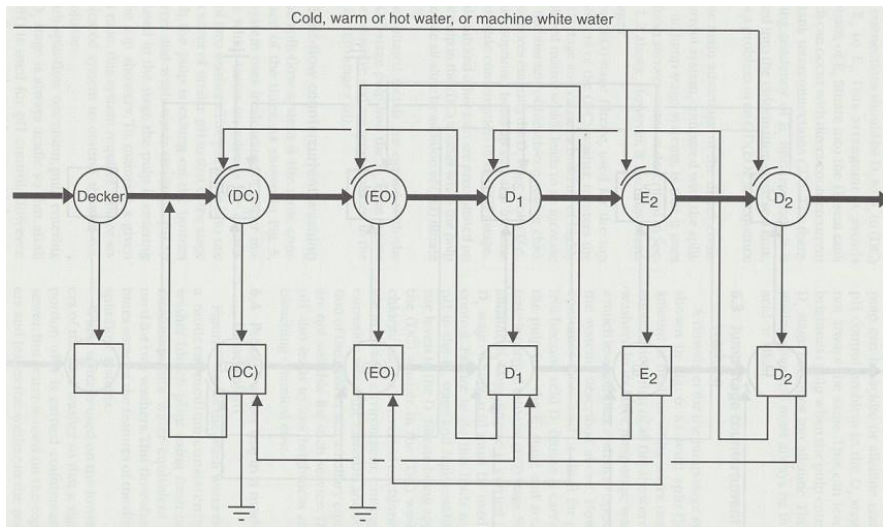


Figure 9. Jump-stage countercurrent washing (Histed et al. 1996).

When the filtrates were first being circulated and the filtrate circulations closed, fractional washing was established. This way it is possible obtain significantly lower COD content in the bleaching stages. The only washing equipment that uses fractional washing is a drum displacer. It enables the use of two or more different filtrates in a single washer at the same time. The liquids are being supplied separately and the formed filtrates are kept apart. Thus, these filtrates can be sent further to different locations of the mill: the dirtier can for example be removed from the process and the cleaner sent to another washing stage. (Pikka et al. 2000b)

5.1.4 Practice of pulp washing

In practice pulp washing is based on displacement, just like in Figure 18. First the dirty pulp with its liquor enters on top of the screen or wire forming a cake. After this the wash liquor is fed on top of the cake and forced to flow through it. The wire or screen under the cake separates the cake from the filtrate, with the impurities, that passes through. (Krotscheck, 2006)

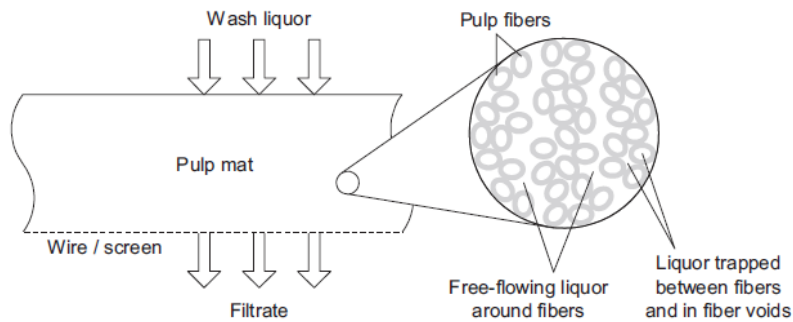


Figure 10. The washing of a pulp cake (Krotscheck ,2006, p. 512).

It is also easy to notice the three phases in which the suspension can be divided: the solid fibers, the mobile liquor that moves freely around the fibers and the liquor trapped inside and between the fibers. (Gullichsen and Östman, 1976) The free-flowing liquor is easy to displace with the wash liquor, drain or press it from the fiber suspension. The liquor inside the fibers can only be removed according to Donnan theory. On the other hand, when the dirtier liquor has been replaced with a cleaner one, the impurities can also transfer to the outside of the fibers by diffusion. This means that the molecules randomly move to the outside of the fibers due to diffusion in order to balance the concentration differences. (Krotscheck, 2006)

Some of the impurities can also be attached on the fibers themselves. When the impurities are accumulated like this, the phenomenon is called sorption. (Gullichsen and Östman, 1976) Sorption includes both terms adsorption and absorption. The cations that usually attach to fibers are sodium, potassium, magnesium and calcium. Sorption is not only affected by pH but also temperature. In acidic conditions especially carboxylic groups but also other acidic groups cause sorption. The sorption, however, reduces when the pH is lower than 3 due to the pK_a of acidic groups. In alkali conditions hydroxyl groups are the main reason for the sorption. Generally, the higher the pH is, the larger is the amount of sodium. Temperature has only a slight effect on the adsorption of metals: when the temperature is higher, the ions are more weakly adsorbed by the fibers. This means also that in higher temperatures the adsorption of metals is lower. (Eriksson and Grén, 1996)

5.2 Filtrates of pulp bleaching

5.2.1 Motivation for filtrate processing

In addition to the countercurrent washing, mills have taken extended cooking, oxygen delignification and external effluent treatment into operation. The size of mills has increased causing the degree of closure of mills to grow. These improvements enable new mills to be built on sites that have only limited resources of fresh water and makes the operation of mills located in the environmentally sensitive areas possible. It also might give an advantage on the market due to the environmentally sustainable solutions. (Bajpai, 2012) Furthermore, the requirements of environmental permits have become stricter on e.g. AOX and inorganic matter. For example in Paraiba, near Rio de Janeiro, Brazil, legislation has established fees for expenditure of fresh water and discharge of used water. (Costa et al. 2005) The sizes of some pulps mills are too large, especially because they are located close to big cities.

The reuse of effluents can also benefit economically the sodium recovery as well as decrease chemical costs. (Bajpai, 2012) Additionally, the heating and cooling costs of water will decrease significantly when the reduction in water use is utilized (Vehmaa et al. 2011).

The reason for the large interest in countercurrent washing and filtrate circulation is that bleach plant is responsible for the largest amount of effluents in the pulp mill. This is because brownstock side and oxygen delignification are connected to the recovery circle as a closed cycle whereas bleaching, wood handling and drying operate separately. The sources of effluent in a pulp mill are shown in Table 8. Due to the harmful composition of effluents, the volume should be kept as low as possible. (Bajpai, 2012) (Lindberg et al. 1994) (Vehmaa et al. 2011)

Table 8. The effluent volumes from each department of a mill (VTT, 2011).

Department of mill	Effluent volume (m ³ /ADT)
Woodhandling	2.0
Fiberline and oxygen delignification	0.3
Bleaching	15.6
Drying machine	0.3
Recausticizing and lime kiln	0.4
Evaporation	0.1
Recovery boiler and power boiler	2.3
Sealing water	0.3
Total	21.3

5.2.2 The development of filtrate processing

Nowadays the environmental impact of a modern pulp mill is almost negligible. The comparison to the situation few decades ago is shown in Figure 19. Not only the amount of effluents derived from bleach plant has decreased from 40 – 70 m³/ADT to about 10 – 15 m³/ADT but also the amount of solid waste and air emissions have decreased. (Pikka and Vehmaa, 2007) (Crăciun et al. 2010) (Axegård et al. 1997) However, it should be noticed that although the effluent amounts per ton of pulp are decreasing, the increase in the size of the mills has caused the absolute amount of effluents per mill even to rise. In addition, the concentrations of the effluents have increased. The ultimate target for the closure of the circuits would eventually be that mills do not either discharge or take in any water from the water reserves (Vehmaa et al. 2011).

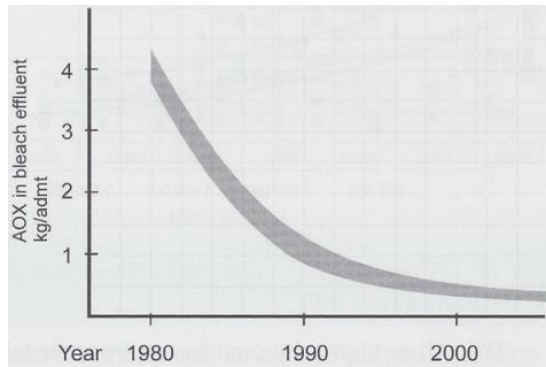


Figure 19. The development of AOX amounts in bleach effluents (Germgård et al. 2011).

At the moment it is possible to decrease the effluent discharge to about 5 m³/BDT, but a complete closure and reutilization of effluents is not yet in use. In addition, having a degree of closure this high might not always be cost effective and the washing efficiency becomes significantly important. (Bajpai, 2012) If the washing is not sufficient, the carryover becomes a problem. Thus, the closure of the filtrate circulation has caused growing interest in efficient washers (Pikka and Vehmaa, 2007). When the degree of closure is on this level, the alkaline filtrates are reused but the acidic ones are usually excluded due to their heavy metal content. Alkaline filtrates can even be used for the washing of unbleached pulp which leads to significant reduction of water flows and discharges in the system. (Bajpai, 2012)

5.2.3 Challenges in filtrate circulation

The reuse of filtrates is however demanding: The non-process elements can accumulate in the process causing scaling and corrosion in the equipment, increase the chemical consumption of oxygen derived chemicals, increase the load of dregs and sand, and decrease pulp quality (Costa et al. 2005) (Bajpai, 2012) (Pikka et al. 2000a). The deposits and problems caused by metals are explained more detailed in the chapters 3.1.1 and 3.1.2.

The closing of the bleach plant circulation to recovery causes also an excess of sulfur and sodium in the liquor loop. Therefore, some of the caustic should possibly be replaced with oxidized white liquor and occasionally some sulfur

should be removed from the system. Without the circulation the bleaching sequences require an addition of sulfuric acid and caustic. (Bajpai, 2012)

Due to the filtrate circulation also the COD of washing liquor increases (Pikka et al. 2000a) (Viirimaa et al. 2002). This COD affects both kappa number and brightness due to the organic matter that decreases the effect of bleaching chemicals. Thus, the chemical consumption is increased (Figure 20). The chemical consumption can also increase due to the pH adjustments and the buffer capacity of the pulp.

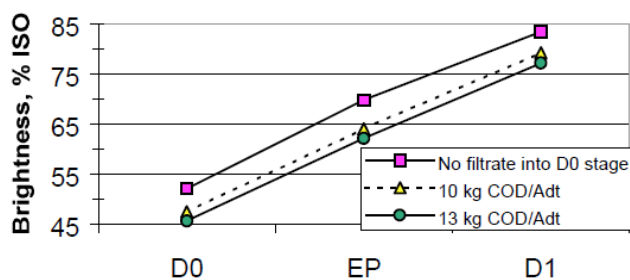


Figure 20. Addition of post oxygen stage filtrate into D₀ stage (Pikka et al. 2000a).

However, different kinds of filtrate circulations for example in D-stage have been investigated (Pikka et al. 2000a) (Vehmaa et al. 2011). These studies show that the reuse of filtrates can be totally possible. In the study of Vehmaa et al. (2011) the obtained brightness was even higher after D-stage due to a higher Cl⁻-content in effluent when lignin was removed. The color of this effluent was dark brown but inert and did not have any effect on the pulp properties. Thus, color does not tell everything about the possibilities of reusing filtrates – lignin increases the color of the filtrate but there are also other components that increase the color, e.g. iron and manganese. (Dahl et al. 1996) (Vehmaa et al. 2011)

5.2.4 Composition of filtrates in general

In addition to lignin, carbohydrates and non-process elements there are a lot of different compounds in the filtrates. The compounds in effluents are separated normally to low molecular weight (LMW) and high molecular weight (HMW)

materials. The limit between these two categories is usually 1000 Da. (Martin et al. 1995) This classification is required because the biological effluent treatment can remove mainly LMW substances. The compounds vary between monomeric compounds and large molecules. (Lehtinen, 2004) Dahlman et al. (1995) discovered that the carbohydrates dissolved in the filtrate from hardwood bleaching were mostly xylan. In addition, the carbohydrate content in the filtrate was higher for hardwood than for softwood.

HMW components are the ones that carry a considerable part of AOX and COD in the bleach effluents although the effluent mainly consists of LMW (Lehtinen, 2004). BOD content is mainly caused by LMW simple organic compounds (Dahl et al. 1996). In ECF bleaching the D₀-stage produces a significant amount of COD in the effluent. Thus, if D₀-stage is open, the wastewater amount and water usage increase but the COD level is low in the system and the chemical consumption can be minimized. If the stage is closed, brightness loss can be minimized by fractional washing but still more chemicals are required. (Pikka et al. 2000a)

The modern ECF hardwood pulp mills use less and less chlorine containing chemicals for bleaching. This is presented in Figure 21. Thus, the amount of chlorine components in the bleaching effluents has decreased significantly. (Vehmaa et al. 2011) Chlorinated compounds that are formed during the bleaching process cause serious environmental problems, such as death of algae and bioaccumulation in organisms (Lehtinen et al. 1991) (Lehtinen et al. 2004).

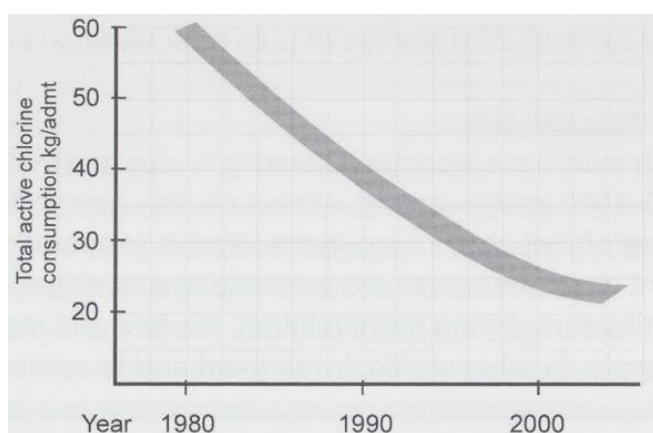


Figure 21. The consumption of active chlorine in pulp bleaching in last decades (Germgård et al. 2011).

Different types of compounds and their numbers in different bleaching effluents are presented in Table 9. It is easy to see how much less different compounds, especially chlorinated ones, ECF filtrates have compared to chlorine-based.

Table 9. Types and numbers of compounds found in different types of bleach effluents. Number of chlorinated compounds is in brackets. (Mckague et al. 1998)

	Chlorine-based	ECF	TCF
Acids and derivatives	120 (70)	83 (18)	71
Phenols and phenyl ethers	54 (51)	27 (22)	3
Alcohols	35 (19)	11 (0)	2
Aldehydes and ketones	87 (64)	41 (13)	19
Hydrocarbons	99 (84)	38 (24)	4
Dioxins and furans	24 (24)	2 (2)	0
Miscellaneous	23 (17)	11 (8)	4 (1)
Total	442 (329)	213 (87)	103 (1)

HMW substances contained much more carboxylic acid groups compared to the amount found in kraft lignin (Dahlman et al. 1995). The presence of carboxylic acids is beneficial to bleaching because they make it easier for residual lignin to dissolve (Dahlman et al. 1995).

Low molecular weight compounds can be divided into three different classes: phenolic compounds, acids and neutral compounds. The neutral compounds include e.g. resin acids, fatty acids, terpenes and sterols of which the first two are neutral only in acidic conditions. The compounds are usually non-organochloric compounds in the filtrates. (Lehtinen, 2004) The most common non-organochloric compounds are palmitic and stearic acids but also simple straight chain dicarboxylic acids were present (Mckague et al. 1998)

5.2.5 Composition of A-stage filtrates

The A-stage filtrate contains a high concentration of metals, other non-process elements, sulfuric acid and reaction products of HexA (Räsänen et al. 2005). Table 10 presents the characteristics of A-stage filtrate of an eucalyptus pulp (Costa et al. 2005).

Table 10. Characteristics of A-stage filtrate from eucalyptus kraft pulp (Costa et al. 2005).

Effluent volume (m³/t)	0.11
Acute toxicity - MICROTOX (EC_{50%})	>100
COD (mg O₂/l) / (kg O₂/t)	1297 / 11.67
BOD₅ (mg O₂/l)	670
Biodegradability (BOD₅/COD)	0.52
Color (mg Pt/l)	1356
AOX (mg Cl⁻/l) / (kg Cl⁻/t)	0.6 / 0.005
Volatile Dissolved Solids (mg/l)	968
Na (mg/l)	594
SO₄²⁻ (mg/l)	1172
Cl (mg/l)	66.5
K (mg/l)	54.7
Ca (mg/l)	31.3
Mg (mg/l)	2.42
Fe (mg/l)	0.04
Cu (mg/l)	0.04
Mn (mg/l)	0.86
P (mg/l)	4.66
Al (mg/l)	1.02
HCl Insoluble (mg/l)	9.33

This filtrate was reused 9 times, so the composition should be stabilized. The study showed that this A_{HT}-stage filtrate contained a higher organic load of COD,

BOD and color than filtrate of D-stage. Thus, if the filtrate is reused somewhere in the mill the organic load of effluents in the effluent treatment will decrease significantly.

Surprisingly, the load of the filtrate produced in this study is actually lower than in the currently discharged streams (COD = 20.9 kg O₂/t, AOX = 0.67 kg Cl⁻/t) at the mill. The toxicity of this filtrate was again higher than in the mill (EC_{50%} = 20.3). (Costa et al. 2005) Costa et al. (2005) also studied the whole sequence A_{HT}(EOP)D(PO) and the AOX content of the final effluent was quite low. The factors causing this were low dose of chlorine dioxide in the sequence, very low kappa number of pulp entering D-stage and removal of HexA, that is the responsible for a large amount of AOX, already in A_{HT}-stage (Costa et al. 2005) (Costa and Colodette, 2002). In the study of Costa et al. (2005) the filtrate reuse caused only a slight decrease in brightness, but otherwise no other impact was seen.

Gomes et al. (2007) found out that the pre-bleaching produces up to 80 % of the whole effluent load when the sequences begin with A/D or D_{HT}-stages. These sequences produce effluents with higher loads of COD, BOD and TOC than sequences without A/D and D_{HT}-stages. Nevertheless, the effluents of a sequence starting with A/D_{HT}-stage had similar loads of COD and BOD and even lower in TOC.

5.2.6 Reuse of A-stage filtrates

Costa et al. (2005) suggested the use of A-stage filtrate in the causticizing plant which can tolerate this high organic load. Thus, a significant amount of sodium could be recovered.

According to Teleman et al. (1995) the hydrolysis should only happen in acidic conditions because the degradation proceeds formally through the undissociated pK_{a,HexA} 3.1. However, the findings stated below show that this hydrolysis can

also be initiated when the pH of the external solution is close to neutral: The acidic groups in the fiber wall consist mainly of uronic acids and lignin-bound ionizable groups. At $\text{pH} > 7$ the acids exist as neutral salts. Acidification and washing the metal ions attached to fibers neutralize the acidity of the pulp. Acidification and washing remove the counter ions while the fiber bound acids stay in their protonated form. Simultaneously the pH is lowered enough to conduct the hydrolysis. (Räsänen et al. 2011) (Räsänen et al. 2005)

In addition to the reuse of A-stage filtrate in causticizing plant, Räsänen et al. (2005) have suggested the circulation of the filtrate in the A-stage. This scheme is presented in Figure 22. The arrangement required acidifying pulp by using acidic solution and then washing it before the hydrolysis. Here the fiber charge decreases and cations are released from the pulp and bound anionic groups are converted into their acid forms. The lower the pH is the better is the removal of metals. Next the acid hydrolysis takes place: It is performed without use of any acid addition like sulfuric acid because the fibers are already acidic due to washing. In other words the external solution has significantly higher pH than the fibers. This happens only when the ion concentrations are low in the pulp suspension.

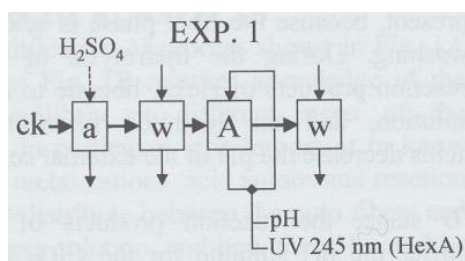


Figure 22. The circulation of filtrate back to A-stage. ck means cellulose kraft, w stands for washing, a for acid addition and A for A-stage. (Räsänen et al. 2005)

In the study pH of 2 – 3.5 was enough to initiate and sustain selective hydrolysis. However, when the HexA content is decreased the formed carboxylic acids that are liberated to the external solution starting to lower the pH of the solution. In the experimental part the removal of HexA was about 70 % when the hydrolysis was performed for 2.5 hours at 80-95 °C. In addition, the pH of the washing had an impact on the removal efficiency of HexA. The higher the pH was the lower was

the removal of HexA. Removal of about 60 % of the cationic charge resulted in sufficient HexA removal. (Räsänen et al. 2005)

Another solution that is based on the same idea by Räsänen et al. (2005) is presented in Figure 23. First the pulp is being washed with acidic filtrate in order to remove the metals and non-process elements from the pulp and then the washing with water changes the ionic form of the pulp. After the washing stage the acid hydrolysis is performed but again without any added acid. The reaction products of HexA buffer the pH of the pulp solution suitable for the D-stage that is combined with A-stage without any intermediate washing. The removal of metals also allows the direct addition of chlorine dioxide. This formed filtrate contains reaction products of HexA and chlorine dioxide bleaching but only a small amount of non-process elements is present. Hence, this filtrate could be reused in the acidification stage before AD-stage to remove the metals and NPE's from the pulp. Additionally, this way the metals could cause less damage to the pulp quality during bleaching. (Räsänen et al. 2005)

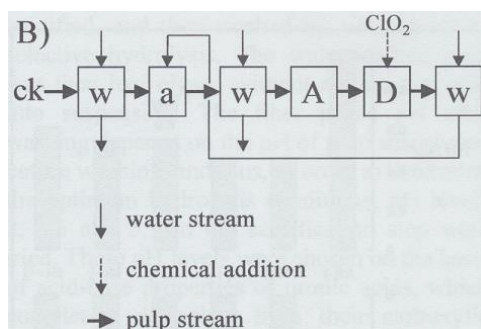


Figure 23. Combined A- and D-stage with a circulation of AD-stage filtrate to acidification of the pulp. D refers to D-stage. (Räsänen et al. 2005)

If this kind of continuous recycling of the filtrate would be taken into use, the addition of sulfuric acid to A-stage could be significantly reduced or even eliminated totally although the properties of the pulp are not improved by this circulation (Räsänen et al. 2005).

The same idea as in processes mentioned is also used in producing microcellulose by using the own acidity of the pulp. The process is similar to the ones already presented but the pH of the acidification step is lower: preferably between 1.5 and

2.5. This pH can be reached with different mineral acids but also the use of formic acid or other organic acids was suggested. (Räsänen et al. 2011) This could enable the reuse of hydrolysis filtrate since it contains formic acid among other organic acids that are formed due to the degradation of HexA.

6 Conclusions of the theoretical part

The limits of environmental emissions have globally become tighter and nowadays market demands favor environmental friendliness. These changes together with increasing mill sizes have caused the industry to look for different options in decreasing emissions. This objective is relevant especially in building new mills in highly populated areas.

Bleach plant is responsible for the largest volume of effluents. Thus, one of these process developments has been closing the water circulation in the washing stages of bleaching. The effluent discharges have decreased to about a fourth in few decades and the target is to decrease them further – even to zero. At the moment the lowest effluent discharges are about 5 m³/BDT but the economical side has to be also taken into consideration.

Currently in the pulp mills using eucalyptus as their raw material, it is necessary to have a stage to hydrolyze HexA formed in cooking. This happens in acidic conditions where formic acid, 2-furoic acid and some 5-carboxy-2-furaldehyde are formed from HexA.

Reusing the filtrate formed in the A-stage is now under observation because the price of sulfuric acid has been increasing and because of the long transportation distances to the mills increase the price even more. It has been proven that using the own acidity of pulp, it is possible to sustain autohydrolysis. Thus, circulating A-stage filtrate back to A-stage should decrease the use of sulfuric acid.

However, the transition metals can build up in the filtrate because significant amount of metals is released during the degradation of HexA. The accumulation causes different kinds of problems such as precipitation, corrosion and degradation of cellulose chains. Degradation in most cases takes place when peroxide is used and radicals are formed. Thus, magnesium sulfate is usually added in order to prevent the degradation. The most significant metals barium and calcium can form problematic compounds like calcium oxalate, calcium carbonate

and barium sulfate. Other harmful non-process elements are for example potassium and chlorine. The higher the pH is, the more metals are bound to fibres. Therefore, in acidic conditions metals are released to the liquid phase. Donnan theory is used to describe the uneven distribution of ionic species between the solution inside the fiber wall and outside fibers. Thus, it is possible to predict how the metal cations would act during the process. In addition to the compounds mentioned above, also lignin is present in the filtrates in large quantities.

For now, according to different studies A-stage filtrate could be used at least as washing liquor prior to A-stage, reused before a washing stage and hydrolysis and possibly in causticizing plant.

The most harmful effluent comes from D₀-stage, which produces a significant amount of COD. In addition, the chlorine compounds are the most harmful ones. In general, it can be said that the whole pre-bleaching generates up to 80 % of the effluent load of the whole sequence. In one study A-stage filtrate was found to have even higher organic load than D-stage filtrate, so if the reuse can be performed the load in effluent treatment would decrease significantly.

Due to the harmfulness of D-stage effluents, environmental emissions and their limits, mills are trying to decrease the use of chlorine dioxide. For example the use of peroxide stage as the last bleaching stage in the sequence is nowadays a popular choice. In addition, peroxide stage will e.g. decrease the brightness reversion. Peroxide is also used in an E_{OP}-stage that is proven to be the most efficient of alkali extractions and thus it is in most cases chosen.

Experimental part

The objective of the experimental part was to see if the sulfuric acid consumption could be decreased in A-stage by the formed A-stage filtrate. The goal was to attain a filtrate that would be similar to one to be produced at a mill non-stop. An aim was also to see what the properties of the filtrate are and how the recirculation would affect the operation of both A-stage and the following bleaching stages. The sequences containing A-stage filtrate circulation are compared to similar sequences not having filtrate circulation with differences in chemical consumptions and properties of pulp. On these grounds the industrial possibilities of A-stage filtrate circulation can be assessed.

The experimental part consisted of preliminary tests and two different reference bleaching sequences (A-E_{OP}-D-P and A-E_{OP}- Z/D-P) that were compared. These two sequences were carried out with a clean A-stage and an A-stage using 3 times circulated filtrate. The properties of A-stage filtrates and pulps after each stage were analyzed. The first sequence was chosen because it has been lately attracting interest in research and it has been taken into use in modern pulp mills, such as one in Brazil (Clavijo, 2010) (Vianna, 2013) (Pöyry Corporation). In addition, the pulp used in this experiment was received from a mill that could use this bleaching sequence. The second sequence is just a small modification of the first one using the chemicals mentioned in the literature part. The experimental layout is presented in Figure 24.

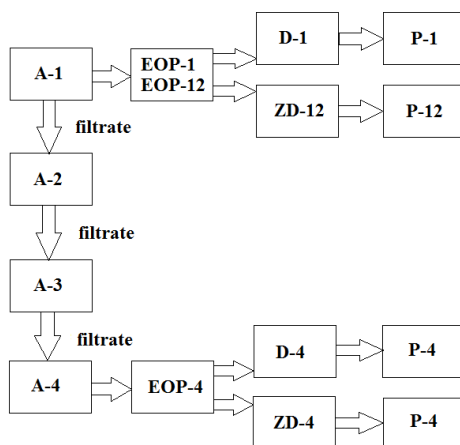


Figure 24. The experimental layout of bleaching.

7 Materials and methods

7.1 Initial pulp

Pulp used for the experimental part was eucalyptus pulp after oxygen delignification from a Brazilian mill. The initial pulp properties are shown in Table 11 and the methods in Appendix 1. Sheets that were used for brightness measurement were also used for ultraviolet resonance Raman (UVRR) measurements.

Table 11. The properties of the initial pulp.

Viscosity (ml/g)	1010
Brightness (% ISO)	62.6
Kappa number	10.7
HexA (meq/kg)	60.2

7.2 Preliminary tests

The preliminary tests were performed for oxygen delignified pulp. The main point of the tests was to find out the optimum retention time of acid hydrolysis. A-stage was performed for 2, 3 and 4 hours in an air bath digester shown in Figure 25. The temperature was chosen as 90 °C because a higher temperature would probably lead to a lower viscosity. 200 grams of oven dry pulp was measured in each autoclave, the consistency was adjusted with deionized water and pH with sulfuric acid. The digester temperature was raised to 90 °C in 55 minutes while rotating the autoclaves continuously. This continued for the whole retention time. After the A-stage the autoclaves were cooled down in cold water for 20 minutes and the filtrate was recovered by pressing the pulp in a cloth. Then, the pH of the filtrate was measured and pulp was washed using deionized water: 4 liters of deionized water was added to pulp suspension and after short mixing, excess water was

pressed out of the suspension by hand, that is the washing was done as dilution-thickening. This was repeated four times after which the dry matter content was increased to about 33 %. Eventually the pulp was homogenized. Kappa number and brightness were measured according to Appendix 1.



Figure 25. Air bath digester used for preliminary tests, A- and EOP-stages.

7.3 Bleaching procedures

7.3.1 Conditions of bleaching stages

The conditions of each stage were chosen according to the literature part and preliminary tests. The conditions were close to the optimum and similar to those used in the study of Clavijo (2010). The conditions of the sequences are shown in Tables 12 and 13. Alkaline extraction was to be carried out with peroxide and oxygen because E_{OP} is the first brightening stage, and they have been proven to enhance the brightness. Use of magnesium sulfate is obligatory in achieving a high viscosity (Clavijo, 2010). Retention time in D-stage was only 60 minutes due the fact that it was reported to be long enough (Tamminen, 2010). In addition, the final pH was lower so that enhanced brightness would be achieved. The acid/base addition was chosen so that the final pH of each stage would be achieved. For

parallel samples the dosages of sodium hydroxide and sulfuric acid were kept the same.

Table 12. The bleaching conditions for the first reference sequence.

	A	E _{OP}	D	P
Temperature (°C)	90	85	75	85
Retention time (min)	180	90	60	100
Consistency (%)	10	10	10	10
Final pH	3.1 – 3.5	10.5 - 11	3.1 – 3.6	10.5
H ₂ SO ₄ (kg/BDT)	4.8	-	-	-
NaOH (kg/BDT)	-	5.8 - 7	1.3	5.7 - 6
H ₂ O ₂ (kg/BDT)	-	6.0	-	5 - 8
O ₂ (kPa)	-	300	-	-
MgSO ₄ (kg/BDT)	-	1.2	-	1.8
ClO ₂ (kg act. Cl/BDT)	-	-	14	-

Table 13. The bleaching conditions for the second sequence.

	A	E _{OP}	Z	D	P
Temperature (°C)	90	85	75	75	80
Retention time (min)	180	90	-	60	100
Consistency (%)	10	10	10	10	10
Final pH	3 – 3.5	10.5 - 11	3	-	10.5 – 11
H ₂ SO ₄ (kg/BDT)	4.8	-	2.4 – 4.6	-	-
NaOH (kg/BDT)	-	5.8 - 7	-	0.5	9 - 11
H ₂ O ₂ (kg/BDT)	-	6.0	-	-	5 - 9
O ₂ (kPa)	-	300	-	-	-
MgSO ₄ (kg/BDT)	-	1.2	-	-	1
O ₃ (kg/BDT)	-	-	1.7	-	-
ClO ₂ (kg act. Cl/BDT)	-	-	-	7.5	-

Ozone stage was performed so that the retention time could not be precisely determined. The objective was to use 3 kilograms of ozone in the Z/D-stage but

due to a small amount of pulp only 1.7 kg was consumed. To keep the bleaching sequences comparable, only 1.7 kg of ozone was applied for the second sample. The final pH of the chlorine dioxide stage was let to decrease with ClO₂ usage and again the NaOH addition for P-stage was determined so that the correct final pH was achieved.

7.3.2 Performance of pre-bleaching

Both A- and E_{OP}-stages were carried out in an air bath digester which was shown in Figure 25. A-stage was performed just like preliminary tests but the time 3 hours for all the autoclaves.

In E_{OP}-stage the pulp amount for each autoclave was 150 grams of oven dry pulp. After the pulp, deionized water, magnesium sulfate, sodium hydroxide and hydrogen peroxide were put into the autoclave. Then 300 kPa of oxygen was added to the autoclave and then depressurized. This was repeated twice but after oxygen was added third time it was left in the autoclave and the autoclave was placed into the digester. The digester was heated rapidly to 85 °C while rotating the autoclaves. After 85 minutes the autoclaves were again cooled down, filtrate was recovered and pulp was washed similarly to post A-stage except that the volume of washing water was each time 3 liters. This way the washing effect was the same as in the A-stage washing. After this the dry matter content of the pulp was again increased and homogenized.

7.3.3 Performance of final bleaching

D-stage was performed in a MC-mixer that is shown in Figure 26. 100 grams of oven dry pulp was first warmed up in a microwave oven with deionized water and sodium hydroxide. The suspension was then put into the mixer. Once the suspension was properly mixed, chlorine dioxide was added while mixing was continued at about 1800 rpm. After that the mixing was performed every 5

minutes with 360 rpm for 20 seconds until the retention time reached 60 minutes. Then pulp was removed from the mixer using vacuum cleaner and washed like previously, but now with 2 liters of water each time, following an increase of dry matter content and homogenization.



Figure 26. MC-mixer used in D-stage.

P-stages were carried out using plastic bags in a water bath. Each bag contained 30 grams of oven dry pulp. Before placing the bags containing pulp, water and chemicals the suspension was warmed up in a microwave oven. The correct peroxide dose was determined by doing the stage with multiple different peroxide dosages and interpolation so that the desired brightness (89 % ISO) was achieved. The plastic bags were mixed by pressing them with hands every 8 minutes for 20 seconds. After 100 minutes the pulp was again washed, but this time only with 1 liter of deionized water each time, and homogenized. The 89 % ISO brightness target level was chosen because the selected chemical charges supported it the best.

The second reference sequence started with A- and E_{OP}-stages that were performed under the same conditions as in the first reference sequence. Z/D-stage was performed in the laboratory of Andritz in Glens Falls as well as the peroxide stage after it. Quantum Mark MC bleaching reactor was used as the bleaching equipment.

7.3.4 Sequences using filtrate circulated pulp

The contaminated filtrate that was used for A4-stage (A-stage in which the 3 times circulated filtrate was used) was produced according to Figure 24. This meant that first the filtrate of a normal A-stage was recovered and then reused instead of deionized water for adjusting the consistency of a new A-stage. The pH was adjusted to about 3.4 with sulfuric acid. Another A-stage was then performed as before. This procedure was repeated three times in total after which the pulp was bleached normally. Pulp was divided in two parts: the first part was bleached as mentioned in the Table 12 and the other part like in the Table 13.

7.4 Measurements from pulps and filtrates

The properties of pulp after each stage were measured similarly to determinations shown in the Appendix 1, except for HexA content which was not measured. In addition, kappa number after the P-stages was not measured. Brightness and kappa number were measured also from A-2 and A-3 pulps in order to see how the properties change when the filtrate is more and more circulated. The brightness reversion was measured according to TAPPI UM 200.

On the filtrates of each stage, the pH was measured first. The methods for the other determinations of filtrates are shown in the Appendix 1. Non-process elements were measured by Department of Chemistry of Aalto University except for chlorine.

Both the A1- and A4-stage filtrates were also later titrated using sodium hydroxide to see how the pH would change. The volume of each filtrate sample was 50 ml and the concentration of added NaOH was 76.9 mmol/l. After every 0.5 ml the pH was re-measured. In addition, UVRR spectra were measured on A1- and A4-filtrates.

8 Results

8.1 Preliminary tests

The preliminary tests were not as successful as expected (Table 14). The final pH was below the optimum for all the retention times. The target pH was between 3 and 3.5. However, this was not a serious failure because the main interest was to see how well HexA is degraded. On the grounds of the results 3 hours was decided as the retention time of the A-stage.

Table 14. The results of the preliminary tests.

	2 hours	3 hours	4 hours
Final pH	2.53	2.52	2.56
Kappa number	6	5.6	5.3
Brightness (% ISO)	62.0	61.2	60.7

8.2 Performance of A-stage

The differences between the A-stage pulps were not considerable as shown in Table 15. When comparing the brightness values between the samples it is easy to see that the brightness gets slightly lower when the filtrate is reused. The decrease, however, is not substantial and all the values are on a quite high level. Kappa number of A1-stage was somewhat higher than with other samples although the final pH was lower than in other stages. When comparing the viscosities of pulps A-1 and A-4 there was a difference of only 20 ml/g which is not significant enough to show any distinction between them.

Table 15. Properties of pulp after each A-stage.

	A-1	A-2	A-3	A-4
Final pH	3.09	3.19	3.25	3.31
Viscosity (ml/g)	980	-	-	960
Brightness (% ISO)	60.3	60.3	59.4	58.8
Kappa number	7.3	6.8	7.0	6.8

Although the removal of HexA during A-stage was not the best possible, it was noted that the brightness seldom increases during A-stage (Eiras and Colodette, 2003). The kappa number remained quite high when compared to other studies even though the duration of A-stage was 3 hours (Clavijo, 2010) (Costa et al. 2005) (Vuorinen et al. 1999). Nevertheless, this somewhat lower removal of HexA enabled the good preserving of fibres: the viscosity barely decreased unlike in the study of Clavijo (2010).

An interesting fact is that although the pH in the beginning did not change between A-stages, the final pH increased. However, although the final pH of the A4-stage was higher than in A1, it only had a slight impact on HexA removal and kappa number. The target pH was achieved for every stage.

The least intense removal of both lignin and HexA occurred with A4-stage although the difference was not considerable (Figure 27). This is in agreement with the fact that no significant differences were found between different A-stage pulps. The HexA content decreased to only about half (peak at 1655 cm^{-1}) which means that 35 meq/kg was still left. The lignin content barely decreased (peak at 1609 cm^{-1}) which is in agreement with previous studies.

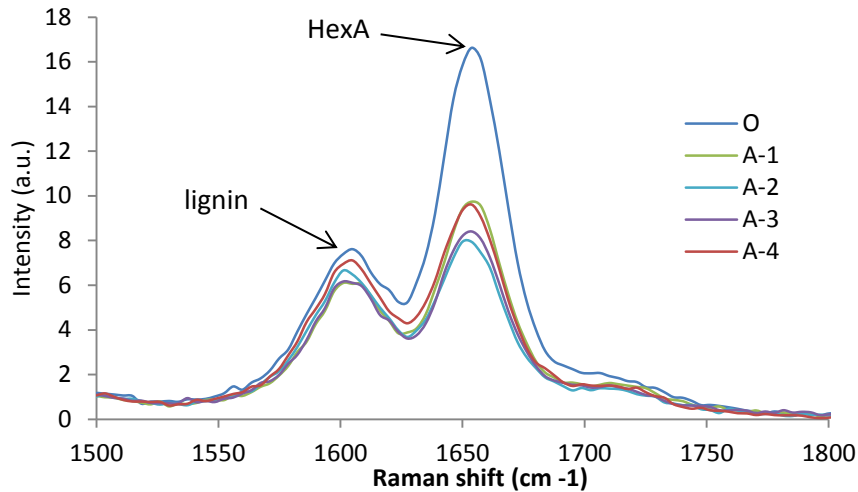


Figure 27. UVRR spectra of pulps obtained after A-stages compared to pulp before A-stage.

8.3 Performance of E_{OP}-stage

After the E_{OP}-stage still no considerable differences between the pulps can be seen as Table 16 shows. Although kappa number before E_{OP}-stage was quite high, it did not decrease more than in other studies but stayed on high level. The brightness increased significantly even though it was already on a great level before the stage (Clavijo, 2010) (Costa et al. 2005). It is an advantage that there is some residual peroxide because otherwise the easily oxidized lignin structures could still be present. The pH for EOP-1 and EOP-4 were somewhat higher than desired, but show that the viscosity still did not suffer significantly from the too high dose. From the results it can be seen that the higher the pH is, the lower is the residual peroxide concentration.

Table 16. Properties of pulps after EOP-stages. EOP-12 is the pulp that was later used in Z/D-stage and which was attained without the circulation. The difference in final pH values can be explained by differing additions of sodium hydroxide.

	EOP-1	EOP-12	EOP-4
NaOH charge (kg/BDT)	7.0	5.8	7.0
Final pH	11.11	10.55	11.33
Residual peroxide (mg/l)	3.2	51	1.9
H ₂ O ₂ consumed (kg/BDT)	5.97	5.49	5.98
Viscosity (ml/g)	930	920	910
Brightness (% ISO)	73.2	73.5	72.6
Kappa number	6.4	5.6	5.8

All of the properties of A-12 pulp were not measured but the viscosity and brightness of EOP-12 are on the same level as with EOP-1. Kappa number, however, is lower which can be a result of slightly lower A-stage pH (2.95).

As can be seen from Figure 28, the biggest cause for the reduced kappa number is decreased lignin content, as was expected. Surprisingly, the HexA content was lower for pulp number 4 than for 1.

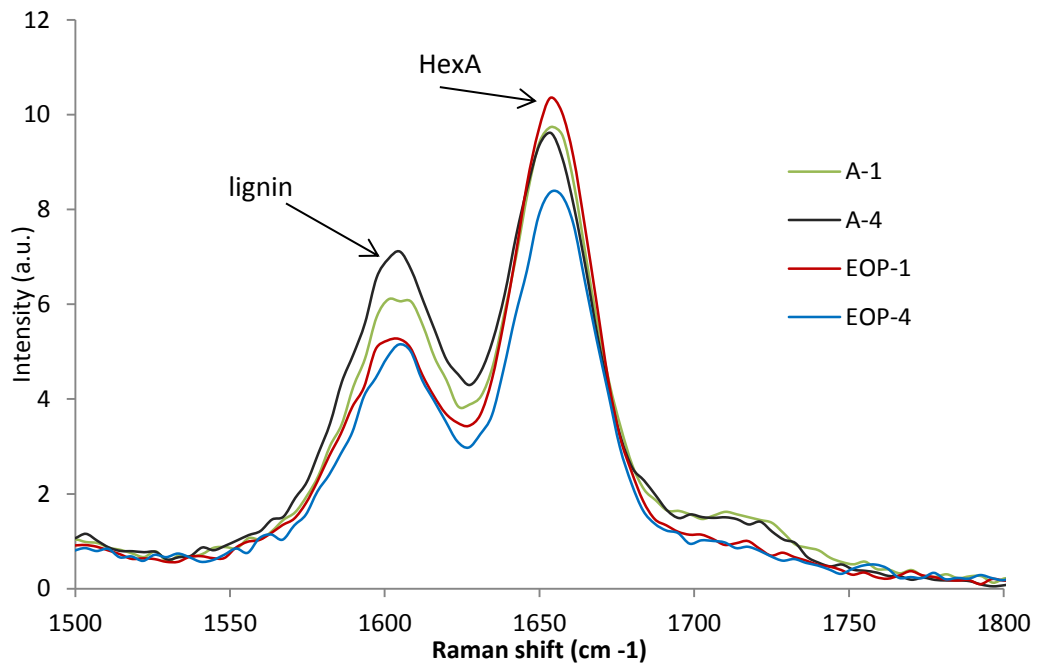


Figure 28. UVRR spectra of pulps after E_{op}-stage.

8.4 Performance of D-stage

Both of the pulps had similar properties after D-stage. These properties are shown in Table 17. During the D-stage viscosity did not decrease, kappa number decreased about 4 units just like in other studies and brightness increased by 12 % ISO (Clavijo, 2010) (Costa et al. 2005). After D-stage the brightness values were on a good level. The final pH values were somewhat higher than the target, but the properties of pulp after the D-stage show that the conditions were satisfying. This can be partly explained with the fact that after the D-stage it was noticed that some chlorine dioxide was left in the pipeline when dosing, but the amount was roughly estimated to be only 0.3 – 0.6 kg act. Cl/BDT and on a similar level for both parallel samples. The usual residual chlorine dioxide in the literature part was reported to be 10 – 50 mg ClO₂/l (Mckague and Carlberg, 1996). According to that, the residuals of this study are normal.

Table 17. Properties of pulps from the first sequence after D-stages.

	D-1	D-4
Final pH	3.98	4.15
Residual chlorine (mg ClO ₂ /l)	27.2	52.8
ClO ₂ consumed (kg act Cl/BDT)	13.68	13.37
Viscosity (ml/g)	920	900
Brightness (% ISO)	85.0	84.7
Kappa number	2.1	2.2

There seemed to be no distinction either between the UVRR spectra of pulps as shown in Figure 29. The HexA content after D-stage can be estimated to be about 15 - 20 meq/kg. This estimation is done by comparing the intensities of UVRR spectra of this stage and the initial pulp. A slightly high final pH and thus lower ClO₂ consumption could have resulted in somewhat lower removal of HexA and lignin.

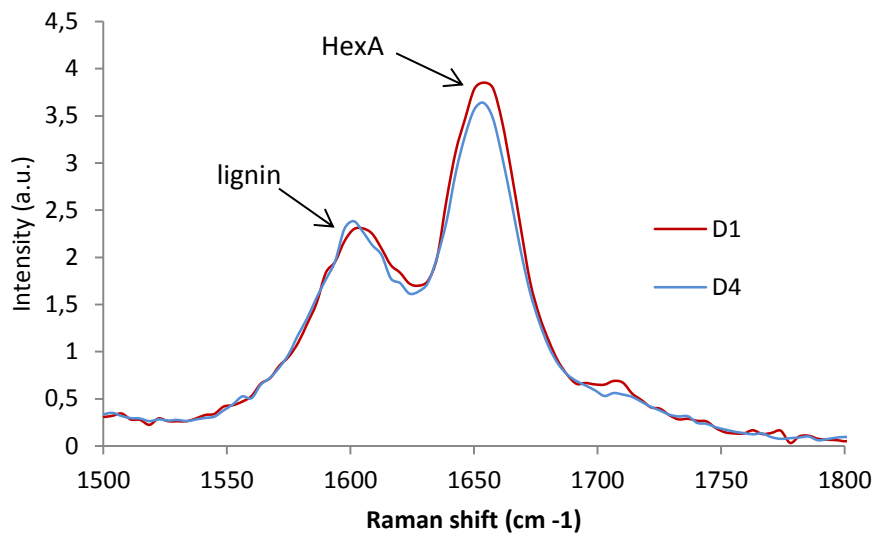


Figure 29. UVRR spectra of pulps after D-stage.

8.5 Performance of Z/D-stage

As stated before, the amount of pulp for this Z/D-stage was too small causing a low consumption of ozone. This is clearly seen as very low brightness in Table 18. In addition, the viscosity decreased considerably and the kappa numbers between the pulps differed. The final pH after adding ozone, however, was as desired but the pH after D-stage was about 2.5 which was somewhat too low. Due to this low pH the viscosity decreased.

Table 18. Properties of pulps from the second sequence after Z/D-stage.

	ZD-12	ZD-4
Final pH	2.8/2.7	2.6/2.3
Ozone consumed (kg/BDT)	1.6	1.7
ClO ₂ consumed (kg act. Cl/BDT)	7.5	7.5
Viscosity (ml/g)	790	790
Brightness (% ISO)	82.9	82.1
Kappa number	1.7	2.6

A clear difference is seen in Figure 30 between the two pulps: ZD-12 has half of the HexA amount of ZD-4. The quantity of lignin is roughly the same for both samples. HexA content for ZD-4 barely decreased. In addition, the lignin amounts for both pulps stayed on the same level.

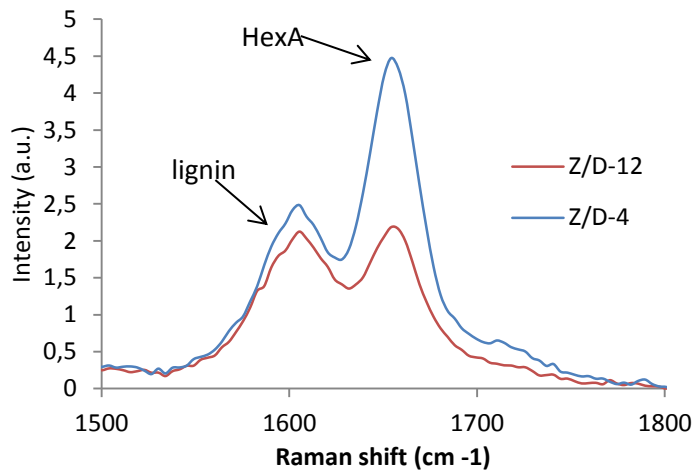


Figure 30. The UVR spectra of Z/D-pulps.

8.6 Performance of P-stage in A-E_{OP}-D-P sequence

P-stage did not cause any significant differences in P-stage performance between the pulps as shown in Table 19. Viscosities dropped significantly for all the pulps and the final viscosity remained low despite the use of magnesium sulfate. Higher peroxide dose caused larger decrease in viscosity. When there is still some residual peroxide present, the lignin structures that are easily oxidized, are absent. However, if the residual peroxide is high, the viscosity can suffer, especially when temperature is high and pH closer to neutral. (Filho and Süß, 2002) Again, it can be noticed, that the higher the pH is, the lower is the residual peroxide concentration. Final pH for all the samples was as wanted.

Table 19. Properties of pulps from the first sequence (A-E_{OP}-D-P).

	P-1	P-1	P-4	P-4
H ₂ O ₂ dosage (kg/BDT)	6	8	5	8
MgSO ₄ dosage (kg/BDT)	1.85	1.84	2	1.84
NaOH dosage (kg/BDT)	5.7	5.7	5.9	5.95
Final pH	10.79	10.77	11.01	10.93
Residual peroxide (mg/l)	208	288	120	158
H ₂ O ₂ consumed (kg/BDT)	4.13	5.40	3.92	6.58
Viscosity (ml/g)	750	700	770	700
Brightness (% ISO)	88.4	90.1	87.7	90.0
Brightness after heating (% ISO)	85.3	87.1	84.6	87.0
Brightness reversion (%)	3.5	3.4	3.5	3.4

UVRR spectra after P-stage in Figure 31 show that no HexA was degraded during the P-stage. The lignin content was decreased only slightly. There was no distinction in the spectra caused by the different dosages of hydrogen peroxide or filtrate reuse. The brightness reversion values between the samples are identical and therefore the filtrate reuse does not have any effect on the brightness stability.

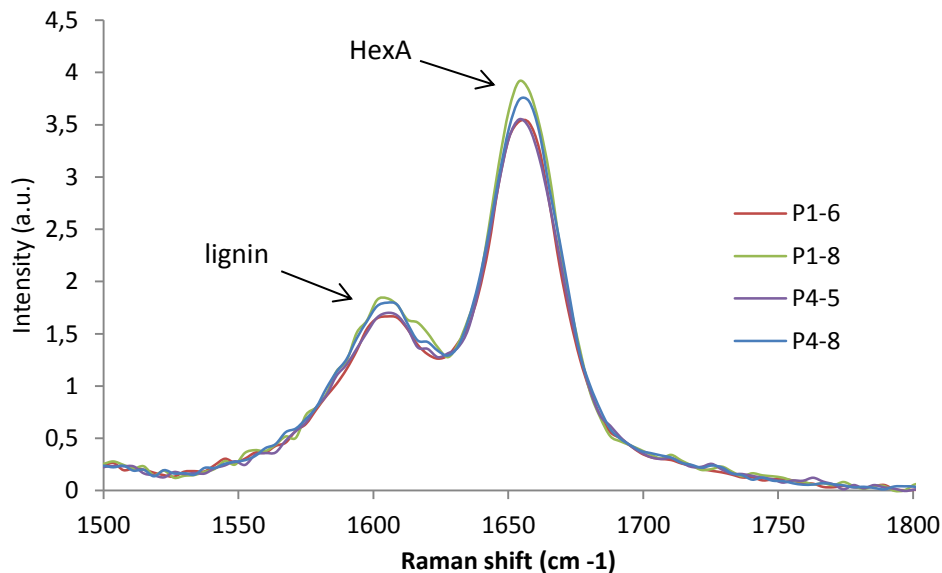


Figure 31. UVRR spectra of the pulps after P-stages.

8.7 Performance of P-stage in A-E_{OP}-Z/D-P sequence

After P-stage there were differences between the pulps as shown in Table 20. For P-4 sample the brightness had a ceiling and thus the bigger consumption of hydrogen peroxide did not have any impact on the brightness. This could have been caused by Z/D-stage that slightly failed due to insufficient mixing. For P-12 sample there was no brightness ceiling in 89 % ISO. This 89 % ISO brightness was achieved with only a consumption of about 3.1 kg H₂O₂/BDT. The brightness reversion was for both pulps on a good level which is quite the same as in previous studies (Clavijo, 2010) (Andrew et al. 2013). There were no differences in viscosity between the parallel samples which had different dosages of peroxide. Residual peroxide amounts were again also high but the final pH was within the target in every case.

Table 20. Bleaching results and properties of pulps from the sequence containing Z/D-stage.

	P-12	P-12	P-4	P-4
H ₂ O ₂ dosage (kg/BDT)	5	7	7	9
MgSO ₄ dosage (kg/BDT)	1	1	1	1
NaOH dosage (kg/BDT)	9	10	10	11
Final pH	10.6	10.8	10.7	11.0
Consumed H ₂ O ₂ (kg/BDT)	3.3	3.5	5.3	7.6
Viscosity (ml/g)	750	740	710	720
Brightness (% ISO)	89.3	89.7	88.8	88.9
Brightness after heating (% ISO)	87.7	88.1	87.0	87.0
Brightness reversion (%)	1.8	1.8	2.0	2.1

The UVRR spectra of P-stage pulps show that no differences are found due to different chemical charges (Figure 32). However, for both cases the lignin content had decreased slightly after the E_{OP}-stage. The content of HexA remained the same during the stage but ended up higher than in the study of Clavijo (2010)

even though the brightness reversion was practically the same, which is not in agreement with the literature part.

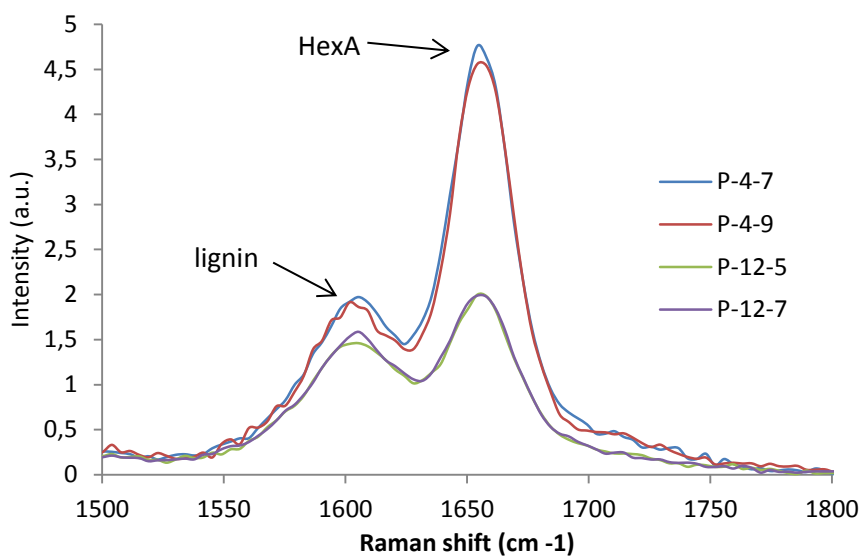


Figure 32. The UVRR spectra of P-stage pulps.

8.8 Properties of A-stage filtrates

The amount of sulfuric acid to be added, after the previous filtrate was combined with pulp, decreased after each A-stage. In addition, it was easily notable that when more filtrate was circulated, the pH decreased less and less, when sulfuric acid was added before the next stage. These facts mean that the acidity of the filtrate increased and that the filtrate acted as a buffer. As a proof of this, the titration curves of both A1- and A4-sample show that A4-sample requires more sodium hydroxide than A1 before reaching pH 7. This can be explained with increasing content of organic acids in the A4-filtrate. The pH curve is presented in Figure 33.

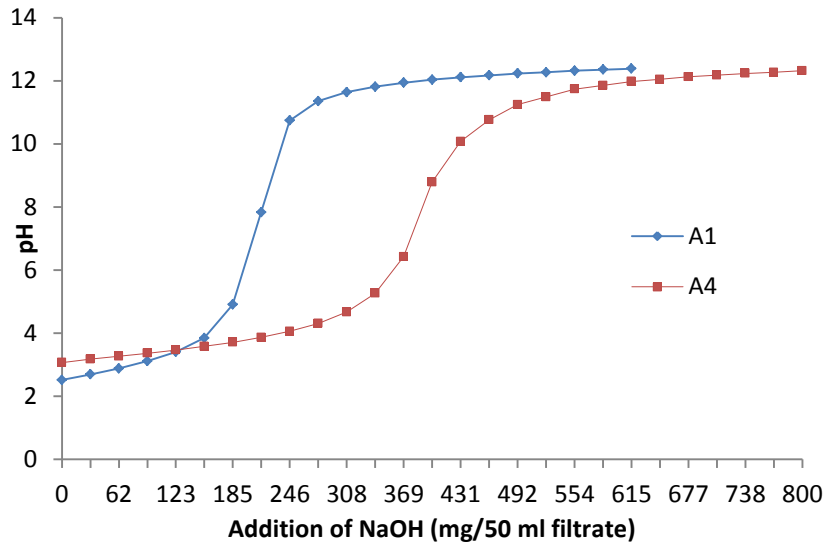


Figure 33. The titration curve for A1- and A4-filtrates.

The curve shows that about twice as much sodium hydroxide had to be added in A4-filtrate than in A1-filtrate in order to reach neutral pH. Although the start pH was already higher for A4-sample, A1-sample required 210 mg NaOH/l and A4-sample 380 mg/l for pH 7. In addition, the steepness of the slope is much lower for A4-filtrate which also refers to the fact that the acidity is higher for A4-filtrate.

In addition, when the new pulp was introduced to filtrate, the pH before adding any acid decreased every time: with A1-filtrate pH was 5.3, with A2-filtrate 4.5 and with A3-filtrate 4.3. Naturally, there also was a clear difference in the color between the filtrates: A4 had significantly darker color than A1 which according to literature can be due to lignin (Vehmaa et al. 2011).

The sulfuric acid addition did not decrease significantly after each A-stage as shown in Figure 34. The initial pH in every case was 3.4 ± 0.05 . The results were somewhat surprising compared to the fact that the acidity was so high and pH of pulp with the filtrate without any acid addition was under 5 for A3- and A4-pulp suspensions. However, the buffer properties of the filtrate explain this behavior.

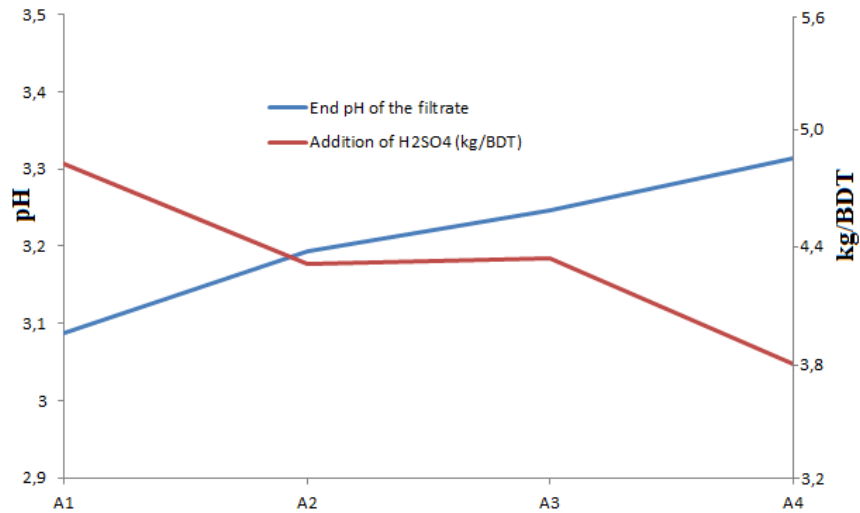


Figure 34. The dose of sulfuric acid for each stage and the final pH of the filtrate.

8.8.1 Non-process elements in the filtrates

The differences in the composition between the A4- and A1-filtrates were relatively quite similar for NPE's and TOC. The concentrations for most elements were 2.7 - 3.3 –fold in the A4-filtrate, as shown in Table 21. This finding is logical because there is a certain concentration of each NPE in the A1-filtrate and when the filtrate is reused in A-stage, the NPE's naturally accumulate in the filtrate. However, the concentrations of Ba, Cu and Fe were unaffected while the concentrations of Al and Mn in the filtrate decreased due to the circulation. Obviously these two elements were retained more strongly on the pulp.

Table 21. Non-process elements found in the filtrates. Values are in mg/l.

	A1	A4	A4/A1
P	1.0	3.3	3.3
S	223	530	2.4
Si	0.7	2.2	3.1
Fe	2.3	2.0	0.9
Mn	2.4	0.8	0.3
Cu	0.1	0.1	1
Al	0.5	0.2	0.4
Ba	0.4	0.4	1
Mg	17	54	3.2
Ca	138	450	3.3
Na	290	835	2.9
K	4.2	11.8	2.8
Cl	59	164	2.8
TOC	493	1400	2.8

8.8.2 Organic compounds in the filtrates

The UVRR spectra of both A1- and A4-filtrates have several emission bands at the same wavenumbers but the band intensities vary significantly between the samples, as can be seen in Figure 35. Most of the peaks are more intense for the A4-filtrate. The different peaks are specified in Table 22 and the UVRR spectrum of 20 g/l of 2-furoic acid, which is utilized in defining the peaks, is presented in Appendix 3. The whole spectrum of both filtrates are shown in Appendix 2.

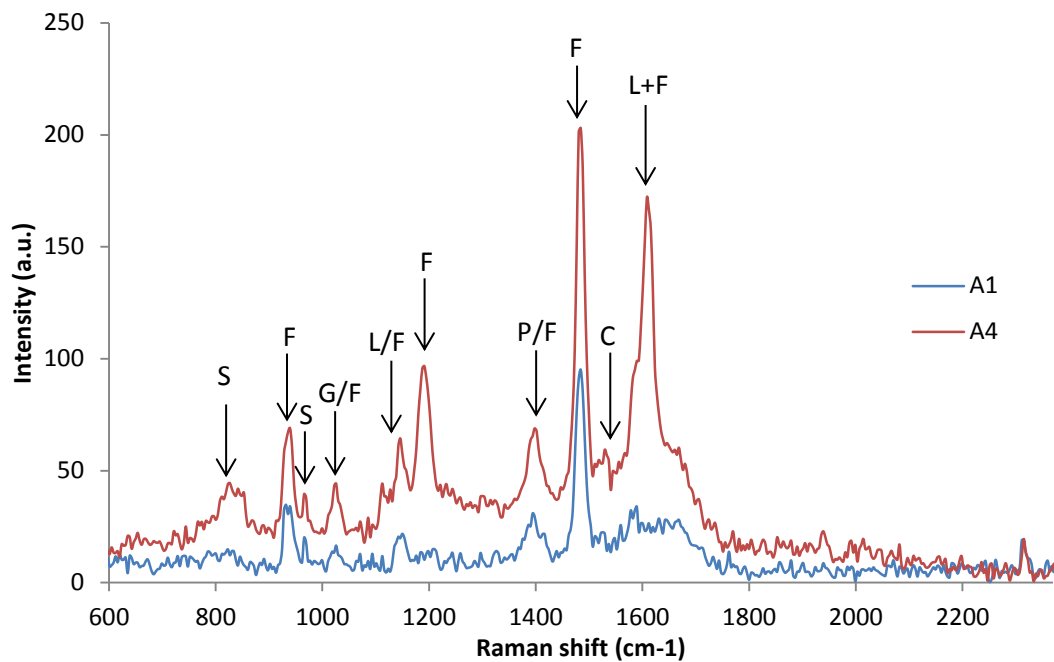


Figure 35. UVRR spectra of A1- and A4-filtrates. S stands for syringyl compounds, F for 2-furoic acid, G for guaiacyl compounds, L for lignin, P for phenolic structures and C for 5-formyl-2-furancarboxylic acid.

Table 22. Specified UVRR peaks for A4- and A1-filtrates.

Shift of the peak (cm ⁻¹)	Specific for the peak
805 - 830	Only for A4-filtrate, caused by syringyl units (Saariaho et al. 2005)
930 - 940	A4 intensity is double compared to A1, caused by 2-furoic acid
970 - 980	More intense for A4, caused by syringyl compounds (Saariaho et al. 2005)
1020 - 1030	A4 intensity is double compared to A1, caused by guaiacyl units (Saariaho et al. 2005) or 2-furoic acid
1145 - 1150	A4 intensity is triple to A1, caused by lignin derivatives (Saariaho et al. 2005) (Pandey and Vuorinen, 2008) or 2-furoic acid
1191	Only for A4-filtrate, caused by 2-furoic acid
1394 – 1399	A4 intensity is double to A1, caused by phenolic units (Wang, 2012) or 2-furoic acid

1482	Highest peak for both, A4 intensity is double to A1, caused by 2-furoic acid (Loureiro et al. 2010)
1525	Only for A4- filtrate, caused by 5-formyl-2-furancarboxylic acid
1580 – 1650	Much more intense for A4-filtrate, caused by lignin and its derivatives but also 2-furoic acid

9 Discussion

9.1 Development of pulp properties

First, the initial properties of the oxygen delignified pulp were determined. These properties are shown in Table 11. The amount of HexA in reality is somewhat higher because TKK procedure quantifies only 80 – 90 % of the HexA (Tenkanen et al. 1995). Just like mentioned in the literature part, about 10 meq/kg is equivalent to one kappa unit. Thus, HexA in pulp used for this work is responsible of even about 6.5 kappa units of total 10.7.

In comparison with the values reported in the literature, the viscosity and kappa number were on the average level. HexA content and brightness were on the higher end of average values. (Vuorinen et al. 1999) (Clavijo, 2010) (Gomes et al. 2007) (Clavijo et al. 2012)

9.1.1 A-stage pulp properties

Even though the brightness did suffer slightly from the filtrate reuse in A-stage, the viscosity was unaffected and the kappa number was even somewhat lower than without the filtrate circulation. These slight differences could not be confirmed by the UVRR spectra because they were almost identical for both pulps.

9.1.2 E_{OP}-stage pulp properties

After E_{OP}-stage the difference between the pulps in kappa number was the same as after A-stage, but the brightness values were now closer to each other. The viscosities of the samples were again identical. For EOP-1 sample the HexA content did not decrease at all while EOP-4 had a slight decrease in HexA content. HexA was not expected to degrade during E_{OP}-stage as mentioned in the literature part.

9.1.3 D-stage pulp properties

The differences in pulp properties caused by the filtrate reuse disappeared in this stage. The viscosities were again practically the same between the pulps but now so were also brightness and kappa number. So during D-stage the change in brightness was superior for D-4 sample whereas the decrease in kappa number was significantly higher for D-1 sample. After D-stage the HexA contents of the pulps were now similar and there seemed to be no distinction between the UVRR spectra. During the D-stage both HexA and lignin content decreased to about half of what they were before the D-stage.

9.1.4 Z/D-stage pulp properties

Z/D-stage caused a significant difference between the two pulps. ZD-4 had twice as much HexA as ZD-12 but the lignin content was roughly the same for both of the pulps. Some of this difference in lignin and HexA content can be explained by the low A-stage pH for ZD-12. This difference explains also the difference formed in kappa number. Viscosities were again same and the difference in brightness values remained the same as after E_{OP}-stage.

9.1.5 P-stage pulp properties

After the P-stage of the sequence containing the D-stage, the UVRR spectra of the pulps were about the same. In addition, the viscosity, brightness values and brightness reversion were the same. Thus, neither the filtrate reuse nor accumulation of harmful metals did seem to have any effect on the end properties of pulp. This could be caused by D- and Z/D-stages which remove metals due to their acidity. However, when compared to the studies of Clavijo (2010) and Andrew et al. (2013) the brightness reversion for all the samples was quite high.

The desired brightness was 89 % ISO so that the results obtained with circulation could then be easier assessed. Therefore, using Figure 36 the required hydrogen peroxide dose can be estimated: For both P-1 and P-4 samples this dose was about 6.7 kg/BDT. However, there is a slight difference in the amounts of consumed peroxide: P-4 sample consumes about 1 kg H₂O₂/BDT more which is at least partly caused by higher pH during the stage. This may not surely be significant also in mill scale.

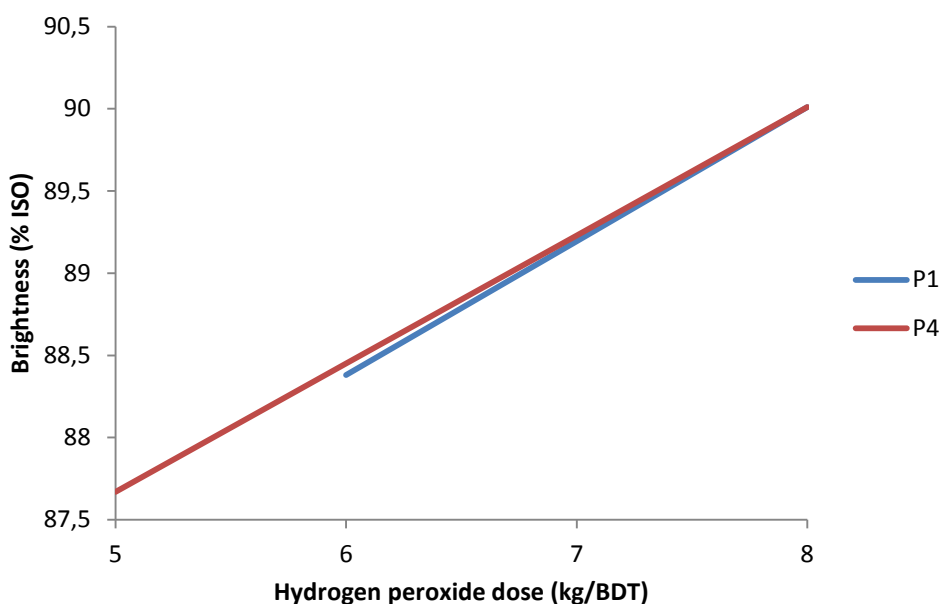


Figure 36. Brightness in relation to hydrogen peroxide dose in bleaching sequence 1.

P-stage for Z/D-pulp did not change the UVRR spectra which means that the final pulp without the circulation had half of the HexA amount compared to the pulp with circulation. The lignin content remained slightly lower for the pulp without reuse. These dissimilarities explain the differences in brightness values but the dissimilarities in brightness reversion are surprisingly small as compared to the differences in spectra. In this sequence the reversion values were on the same level as in other studies (Clavijo, 2010) (Andrew et al. 2013). The viscosities dropped significantly for both pulps but no considerable differences were found.

9.2 Comparison between the D- and Z/D- sequences

9.2.1 Brightness

Brightness levels of whole D- and Z/D-sequences are shown in Figure 37. The brightness levels after the P-stage cannot be directly compared because the dosages of hydrogen peroxide differ. Thus, test points were chosen with different dosages so that comparison could be made between the sequences. Because the D-sequence had similar final brightness levels for both pulps, the value closest to 89

% ISO was chosen (6 kg/BDT of which 4.1 was consumed) although the consumption of peroxide varied slightly. For the P-1 sample of the Z/D-sequence, again closest point to the 89 % ISO was chosen (5 kg/BDT of which 3.3 kg/BDT was consumed). Lastly, for the P-4 sample, the point of comparison was chosen as the brightness which was achieved with 7 kg/BDT (5.3 kg/BDT consumed) because of the brightness ceiling obtained.

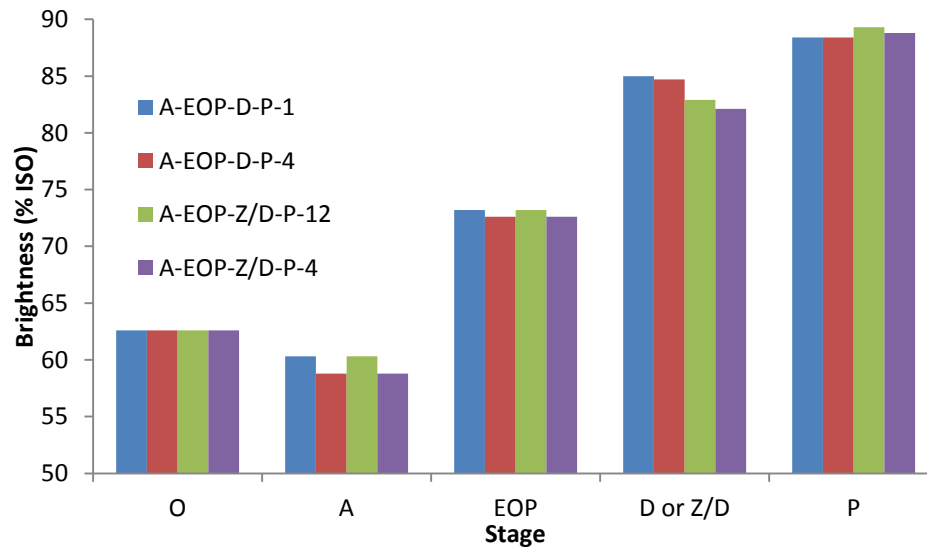


Figure 37. The brightness levels after each stage.

The clearest distinction between the sequences is after D- and Z/D-stages: Due to the low consumption of ozone the brightness values are significantly lower for Z/D-pulps before P-stage. The beginning of the sequences was similar and for both sequences the situation is the same: after A-stage the brightness for the sample without circulation is higher. The difference formed in A-stages is already smaller after E_{OP}-stage. The difference no longer exists after the P-stage. In fact, the final brightness for the P-12 sample was surprisingly achieved with a lower dosage of H₂O₂ than for P-1 and also for P-4 sample, even though the brightness after Z/D-was several units lower.

No reason for the differences in peroxide doses was found. In the study of Clavijo (2010) the brightness after D-stage was about 82 % ISO which is close to the values obtained with Z/D-pulp. The peroxide dosage to reach 90.4 % ISO in that study was 7 kg/BDT. Too big dosage of MgSO₄ could inhibit the peroxide

reactions but the dosage was even slightly lower than in the study of Clavijo (2010). The P-4 sample of the second sequence reached 88.8 % ISO quite easily when considering the low brightness after D-stage although it reached a brightness ceiling. The ceiling may have been caused by the imperfect mixing. The final brightness is somewhat harder to achieve for the second sequence when the filtrate is circulated but not for the first sequence. For the first sequence the consumption of peroxide is only slightly lower if filtrate is not circulated. Additionally, pH also has an effect on the peroxide consumption.

9.2.2 Kappa number

There was not much variation between the kappa numbers of the sequences as shown in Figure 38. An exception was EOP-1 pulp which had quite high kappa number. In addition, the kappa numbers after D-stage were the same but the ones after Z/D-stage differed significantly. The kappa number for A-12 was not measured because the conditions of the A-stage were kept constant. However, the pH of A12-stage was slightly lower than that of A1-stage and the kappa after E_{OP}-stage was lower than even for EOP4-sample. Thus, the kappa number was chosen to be 7 in Figure 38. This is between the kappa numbers of A1- and A4-samples. Kappa numbers after P-stage were not measured.

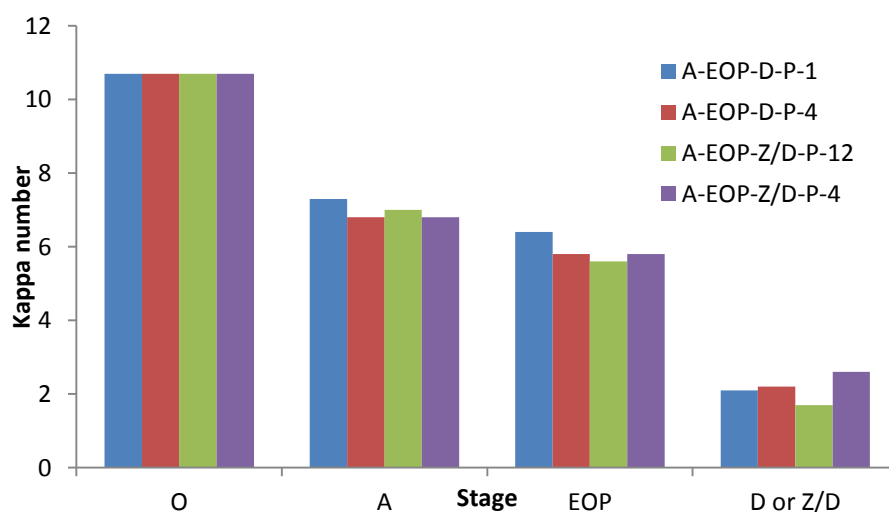


Figure 38. Kappa numbers after each stage for each sequence.

9.2.3 Viscosity

The viscosity of each sample is presented in Figure 39. The P-stage viscosities are matching the test points chosen for Figure 37. The viscosity of A-12 was to be 970 ml/g, which is between the values of pulps 1 and 4. This was again due to the lower final pH of the A-12 stage.

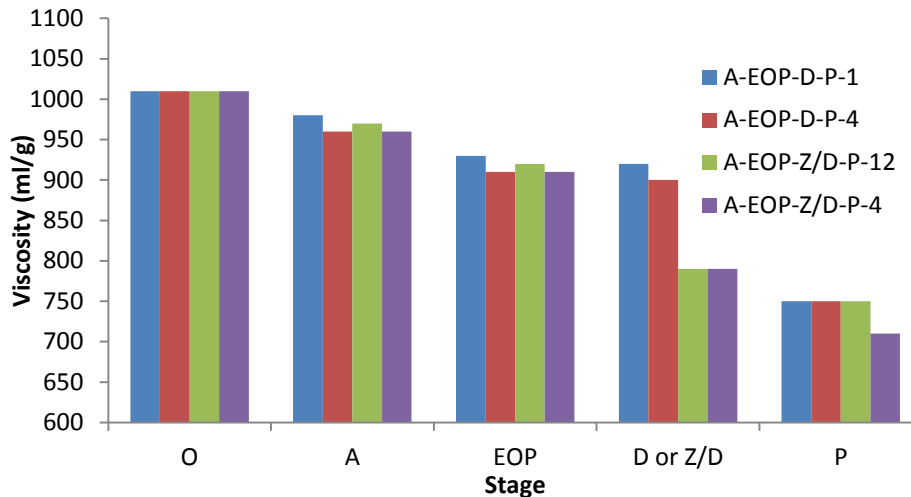


Figure 39. Development of pulp viscosity during the bleaching sequences.

In the beginning of sequences no significant variation is seen but during the Z/D-stage the viscosities dropped more than 100 units while during the D-stage the decrease in viscosity was negligible. The use of ozone is known to decrease the viscosity (Andrew et al. 2013). After the P-stage the viscosities of both sequences were practically the same except for P4-sample of the Z/D-sequence. Thus, the viscosity of Z/D-sequence pulps decreased less than the viscosity of Z/D-sequence pulps during the P-stage. This could be caused by the fact that in the P4-pulp of the second sequence the H₂O₂ dosage was higher. The viscosity of the second sequence did not decrease as much as the one of the first sequence during P-stage because the viscosity was already notably lower after the Z/D-stage.

All in all, the final viscosities were low at least compared to values at pulp mills. In laboratory the proportion of pulp in contact with metallic reactors and walls is significantly higher than in mill scale bleaching reactors and towers. In addition, the process conditions were not optimized according to viscosity loss. It is not

unusual that the sequences performed in the laboratory result in low viscosity. In accordance with the study of Costa et al. (2005) no significant differences in viscosity were found between the filtrate circulated pulps and pulps with reference sequences.

9.2.4 Brightness reversion

The difference of brightness reversion between the sequences is significant as presented in Figure 40: The value of the first sequence is almost double the one for the second sequence. The differences in brightness reversion values are discussed more detailed in the next chapter.

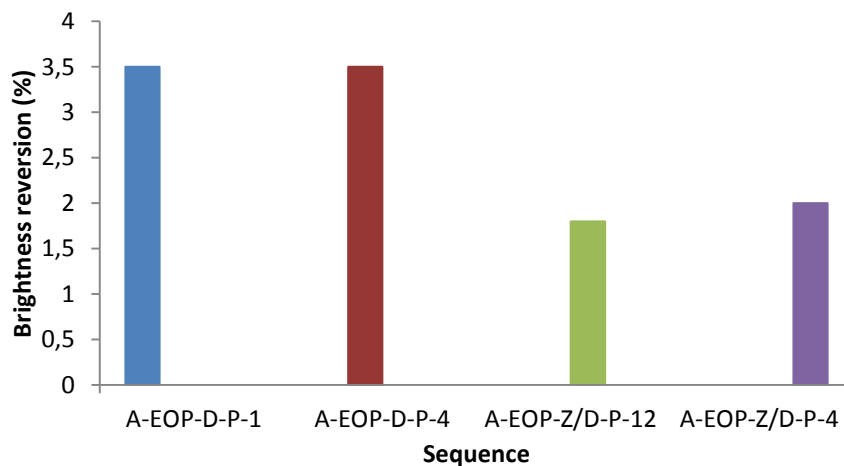


Figure 40. Brightness reversion (% ISO) for each sequence.

9.2.5 UVRR spectra

Figures from 41 - 44 show the UVRR spectra of all the sequences in this study. The spectra are the same for 1 and 4 samples in A- and E_{OP}-stages even though EOP-12 could have somewhat lower contents of lignin and HexA.

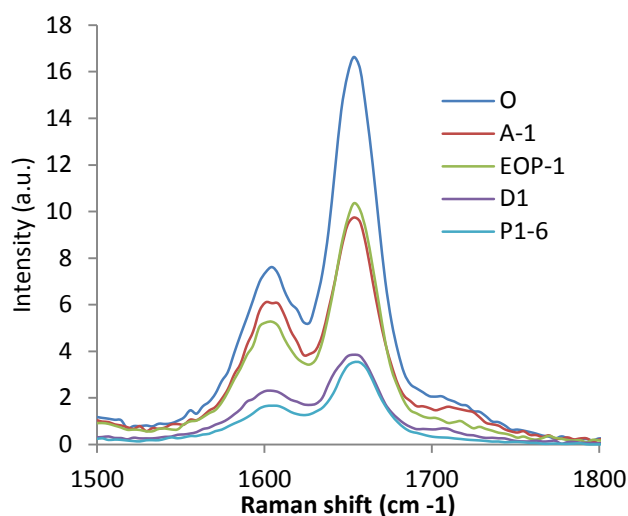


Figure 41. The UVRR spectra of the D-sequence without filtrate circulation.

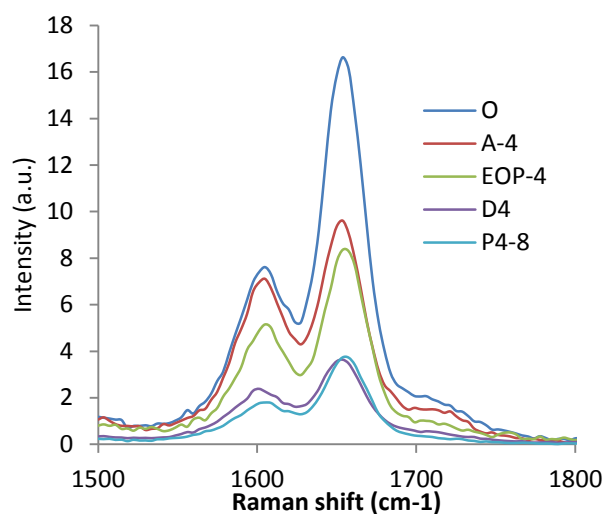


Figure 42. The UVRR spectra of the D-sequence with filtrate circulation.

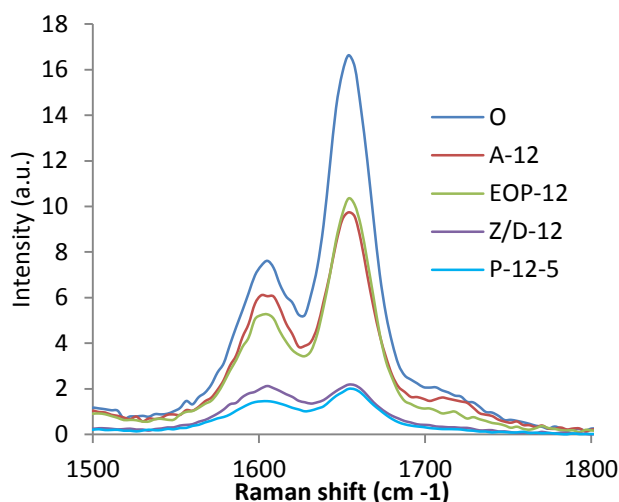


Figure 43. The UVRR spectra of the Z/D-sequence without filtrate circulation.

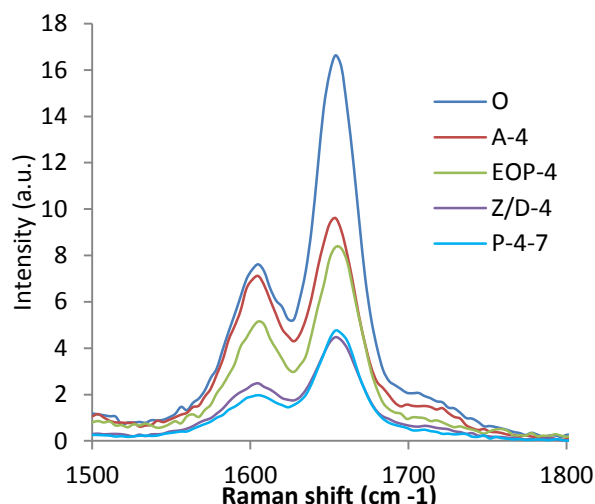


Figure 44. The UVRR spectra of the Z/D-sequence with filtrate circulation.

The HexA level of ZD-12 pulp is about twice lower than of all the others. ZD-12 pulp is the pulp obtained without circulation and used for Z/D-sequence. ZD-4 has slightly higher HexA content than the both pulps of the first sequence. After the P-stage all the pulps have similar spectra as before the stage. Lignin contents of all the pulps in every stage are practically the same regardless of the sequence or filtrate circulation. Thus, the only difference is caused by the Z/D-stage without circulation in relation to HexA content. Ozone is known to react preferentially with HexA than with lignin (Andrew et al. 2013). However, the ozone charge and even the total chemical charge in both Z/D-stages were low when talking about

active chlorine. Hence, it is surprising how low the lignin and HexA contents are in both pulps compared to the other sequence. However, the lignin and HexA amounts remain quite high compared to the study of Clavijo (2010). This is due to inefficient removal of HexA during all A-stages.

HexA content does not explain the difference in brightness reversion levels because P-12 has lowest quantity of HexA but still the same brightness reversion as P-4 of the second sequence. Thus, Z/D-stage must cause something that lowers the brightness reversion. As stated in the literature part, using ozone decreases brightness reversion. It is also known that carbonyl groups can also cause brightness reversion, but they can be removed using for example chlorine dioxide and hydrogen peroxide (Wennerström, 2005). In addition, they are mostly formed during Z-stage. According to Clavijo (2010) both the use of peroxide and the use of $MgSO_4$ with peroxide decrease brightness reversion, but there was almost no difference at all in using them between the sequences.

The cause for brightness ceiling of P-4 in the second sequence cannot either be explained with UVRR spectra. It can be concluded of these two sequences the Z/D-P one was somehow more efficient, even though the ozone consumption of the Z/D-stage was also very low. However, when having filtrate circulation this efficiency was slightly decreased although it still remained on a somewhat same level as the one of D-P sequence.

9.3 Filtrate properties

9.3.1 Non-process elements

The concentrations of some elements in the filtrates did not increase as expected: The small differences in copper and aluminum concentrations between A1- and A4-samples could possibly be explained with measurement errors or inaccuracies. For example in case of copper the device could have rounded a concentration of 0.05 mg/l to 0.1 mg/l. The amount of copper in the study of Costa et al. (2005)

was on the similar level as in this one. As stated in the literature part, barium is known to dissolve better when pH is about 2 thus making the filtrates already saturated. Thus, the rest of barium could be attached to pulp. The higher the barium concentration in the filtrate is the higher is naturally the probability for barium deposits in the bleaching equipment. In addition, iron is also poorly soluble when pH is above 2. However, the concentration of iron in this study was significantly higher than in the study of Costa et al. (2005) although the variation is largely caused by raw material. However, it can be concluded that as the accumulation of NPE's increased almost 200 %, the acidity of the filtrate also nearly tripled.

Other elements that had a higher concentration in this study were magnesium and calcium that were mentioned to be both good in preserving fibres. Therefore, it is a disadvantage that the concentration of these is higher in the filtrate. In addition, the amounts of chlorine and sodium are somewhat higher than in the study made by Costa et al. (2005). As mentioned in the literature part, chlorine is one of the most problematic elements in the recovery cycle and hence its concentration should be as low as possible.

Compared to the study of Costa et al. (2005) lower concentrations of phosphorous, aluminum and potassium were found in this study. The most significant difference was with potassium. This is beneficial because Costa et al. proposed that potassium is the most problematic inorganic element, and phosphorous another important one. For some reason the manganese concentration in A4-filtrate is one third of the one in A1-filtrate but appears to be on a similar level compared to the study of Costa et al. For preserving the fibres the more manganese is removed in A-stage, the less stays with the pulp causing polymerization, especially with peroxide. However, when recirculating the filtrate less manganese should be present in the filtrate. Thus, the concentration should be lower.

The content of sulfur is somewhat high due to the added sulfuric acid. However, when the filtrate is reused the Na/S balances of the mill do not change. Na and S are both of high economic value and thus they should be recovered. In addition,

from environmental point of view, the recovery of sodium and sulfur is important. Costa et al. (2005) had about 400 mg/l of sulfur in their filtrate. The main reason for the differences in concentrations is the NPE content of pulp entering the A-stage and the whole mill.

The TOC level was 50 % lower compared to the study by Clavijo (2010). The difference was probably caused by the less extensive removal of HexA in the A-stage. The moderate decrease in kappa number during A-stage confirms this interpretation.

9.3.2 Organic compounds

Most of the Raman bands originating from 2-furoic acid in A4-filtrate were twice higher than in A1-filtrate. This also fits well with the fact that the titrable acid content was about two times higher for A4-filtrate. Another degradation product of HexA, 5-formyl-2-furancarboxylic acid shows Raman band at 1525 cm^{-1} which is present in UVRR spectrum of A4-filtrate whereas in the spectrum of A1-filtrate the peak is not that clear. This tells that the most of the formed degradation products are found as 2-furoic acid as it was already mentioned (Vuorinen et al. 1999). Another fact that can be seen from the spectra is that there is no peak at about 1098 cm^{-1} which would belong to cellulose.

There is also a surprisingly significant difference in the intensity of lignin band (1600 cm^{-1}) between the filtrates. The significantly higher lignin content in A4-filtrate explains its darker color. In addition, the intensities of the peak at 1191 cm^{-1} between the filtrates varied significantly. The UVRR spectrum of 2-furoic acid, however, showed peaks in these both wavelengths, although no lignin was present that could have explained the peak at 1650 cm^{-1} . The intensities between 2-furoic acid and the filtrates are not comparable because UVRR spectrum of 2-furoic acid was not normalized. Yet, some of the differences between these 2 peaks can be explained with 2-furoic acid.

10 Conclusions

The effect of circulating the A-stage filtrate on the operation of A-stage and subsequent final bleaching was studied. The experimental work consisted of bleaching the pulp, with and without the filtrate circulation, using two different sequences (A-E_{OP}-D-P and A-E_{OP}-Z/D-P). In addition, the properties of circulated filtrate were determined.

The operation of A-stage did not suffer from the reuse of the filtrate. The only disadvantage was a slight decrease in brightness after A-stage – even the UVRR spectrum of the pulp barely affected by the circulation. In addition, the small difference had already almost disappeared after the E_{OP}-stage.

When reusing the A-stage filtrate and adjusting the pH every time to 3.4 the use of sulfuric acid could be decreased by 20 %.

The filtrate circulation had no effect on the final bleaching in D-P sequence, properties of the pulp and chemical consumption.

Nevertheless, the filtrate reuse was found to have some impact on Z/D-stage. The residual content of HexA and lignin remained higher while the brightness gain was lower, and the viscosity decreased more extensively. Full final brightness was harder to achieve when A-stage filtrate was circulated prior to the Z/D-stage. However, the residual lignin content of the fully bleached pulp was always on the same level irrespective of the bleaching sequence and the filtrate circulation.

Circulation of the A4-filtrate led to accumulation of organic acids among which 2-furoic acid and formic acids (not analyzed) were the most important ones. Thus, a double amount of NaOH was required to neutralize the A4-filtrate compared to A1-filtrate. A4-filtrate also had significantly stronger color and higher lignin content than A1-filtrate had.

In general, the filtrate circulation led to enrichment of soluble non-process elements. Typically their concentration was tripled. The most critical one is

chlorine whose concentration was not excessive. However, the manganese concentration was quite high and the total content of barium could not be determined. Thus, a risk of barium sulfate scaling could not be assessed.

All in all, the reuse of the filtrate in A-stage still looks promising. No disadvantages for the D-P sequence were found although the filtrate contained significant amounts of lignin and the NPE content was increased compared with A1-filtrate. Thus, in future, a solution in which part of the filtrate would be removed from the circulation should be investigated. This way the excessive accumulation of harmful components could be prevented. Another possibility would be still to try decreasing the addition of sulfuric acid. Because the circulated filtrate has high acidity, the process proposed by Räsänen et al. (2005, 2011) could help to induce the hydrolysis. It would also be good to know what causes these kinds of NPE amounts have and if they harm the operation in the long run.

References

- Andrew, J. E., Johakimu, J., & Ngema, N. E. (2013). Ozone bleaching of South African *Eucalyptus grandis* kraft pulps containing high levels of hexenuronic acids. *Tappi Journal*, *12*(8), 9-16.
- Anttila, J. R., Rousu, P. P., & Tanskanen, J. P. (2007). Modelling of multistage washing systems: Application in the design of pulping processes based on organic acids. *Paperi Ja Puu*, *89*(2), 95-101.
- Athley, K., & Ulmgren, P. (2001). Interaction between divalent metal ions and oxygen-delignified kraft pulps. *Nordic Pulp And Paper Research Journal*, *16*(3), 204-214.
- Axegård, P., Carey, J., Folke, J., Gleadow, P., Gullichsen, J., Pryke, D., Reeve, D., Swan, B. & Uloth, V. (1997). Minimum Impact Mills: Issues and Challenges. *Tappi Proceedings – Environmental Conference & Exhibition, Part 1*. 529-541.
- Bajpai, P. (2012). Closed-cycle bleach plant. *Environmentally Benign Approaches For Pulp Bleaching*. Elsevier. 329-372.
- Bergnor-Gidnert, E., Tomani, P. E., & Dahlman, O. (1998). Influence on pulp quality of conditions during the removal of hexenuronic acids. *Nordic Pulp And Paper Research Journal*, *13*(4), 310-316.
- Boffardi, B. P. (1992). Corrosion and deposit control in mill supply water. *Tappi Engineering Conference* (3). 953-974.
- Brogdon, B. N., & Lucia, L. A. (2005a). New insights into lignin modification during chlorine dioxide bleaching sequences (III): The impact of modifications in the (EO) versus E stage on the D1 stage. *Journal Of Wood Chemistry And Technology*, *25*(3), 133-147.
- Brogdon, B. N., & Lucia, L. A. (2005b). New insights into lignin modification during chlorine dioxide bleaching sequences (IV): The impact of modifications in the (EP) and (EOP) stages on the D1 stage. *Journal Of Wood Chemistry And Technology*, *25*(3), 149-170.

Buchert, J., Teleman, A., Harjunpää, V., Tenkanen, M., Viikari, L., & Vuorinen, T. (1995). Effect of cooking and bleaching on the structure of xylan in conventional pine kraft pulp. *Tappi Journal*, 78(11), 125-130.

Cabrera, M. N. (2009). Composición química y tratamiento de los effluents generados en las nuevas secuencias de blanqueo A-E_P-D_ND y A-E_P-D-P. Universidad de la República, Facultad de Ingeniería. Master's Thesis.

Carvalho, M. G. V., & Carvalho, N. M. (2008). Performance of a final hydrogen peroxide stage in the ECF bleaching of Eucalypt D₀E_{OP}D₁ kraft pulps. *Tappi Journal* 7(8). 8-13.

Chirat, C., Lachenal, D., Angelier, R., & Viardin, M. T. (1997). (ZD) bleaching: fundamentals and application. *Journal Of Pulp And Paper Science*, 23(6), J289-J292.

Chirat, C., & Lachenal, D. (1997). Other ways to use ozone in a bleaching sequence. *Tappi Journal*, 80(9), 209-214.

Chirat, C., Hostachy, J-C., Paloniemi, J., Pelin, K., Pohjanvesi, S., Nordén, S., Vesala, R. & Wennerström, M. (2011). Bleaching. *Chemical Pulping Part 1, Fibre Chemical And Technology*. Second edition. Ed. Fardim, P. Publ. Paper Engineer's Association/Paperi ja Puu Oy. 460-587.

Clavijo, L. (2010). Optimización de las secuencias de blanqueo A(E_{OP})DD y A(E_{OP})DP. Universidad de la República, Facultad de Ingeniería. Master's Thesis.

Clavijo, L., Cabrera, M.N., Kuitunen, S., Liukko, S., Rauhala, T., Vuorinen, T. (2012). Changes in eucalyptus kraft pulp during a mild acid treatment at high temperature. *O Papel*, 73(4), 59-64.

Colodette, J. L., Gomes, C. M., Rabelo, M. S., Eiras, K. M. M., De Fatima Gomes, A., & Oliveira, K. D. (2008). Eucalyptus kraft pulp bleaching: state-of-the-art and new developments. *Tappi Journal*, 7(2), 18.

Costa, M. M., & Colodette, J. L. (2002). The effect of kraft pulp composition on its bleachability. *Tappi International Pulp Bleaching Conference*. 195-213.

Costa, M. M., Landim, A., Colodette, J., Silva, C. M., & Ventrórim, G. (2005). A novel bleaching technology adapted to partial bleach plant closure. *Paperi Ja Puu*, 87(7), 442-448.

Crăciun, G., Duțuc, G., Botar, A., Puițel, A. C., & Gavrilesco, D. (2010). Environmentally friendly techniques for chemical pulp bleaching. *Environmental Engineering & Management Journal (EEMJ)*, 9(1), 73-80.

Dahl, O., Tirri, T., & Niinimäki, J. (1996). Sulfaattisellun valkaisuissa käytettävän kierrätysveden laatuvaatimukset. University of Oulu.

Dahlman, O. B., Reimann, A. K., Stromberg, L. M., & Morck, R. E. (1995). High-molecular-weight effluent materials from modern ECF and TCF bleaching. *Tappi Journal*, 78(12), 99-109.

Dapía, S., Santos, V., & Parajó, J. C. (2002). Study of formic acid as an agent for biomass fractionation. *Biomass And Bioenergy*, 22(3), 213-221.

Devenyns, J., & Chauveheid, E. (1997). Uronic acids and metals control. 9th *International Symposium On Wood And Pulping Chemistry*. M5-1.

Devenyns, J., Chauveheid, E. & Mårtens, H. (1998). Uronic acids and metals control. *International Pulp Bleaching Conference*, 151-157.

Devenyns, J., Plumet, L. (1994). The importance of the magnesium to manganese ratio in alkaline peroxide bleaching. *European Workshop On Lignocellulosics And Pulp*, 139-144.

EIPPCB (2001), BREF document for the Pulp and Paper Industry, http://eippcb.jrc.ec.europa.eu/reference/BREF/ppm_bref_1201.pdf, Referred on 25.2.2014.

Eiras, K. M. M., & Colodette, J. L. (2003). Eucalyptus kraft pulp bleaching with chlorine dioxide at high temperature. *Journal Of pulp And Paper Science*, 29(2), 64-69.

Eiras, K. M. M., & Colodette, J. L. (2005). Investigation of eucalyptus kraft pulp brightness stability. *Journal Of Pulp And Paper Science*, 31(1), 13-18.

Eriksson, G., & Grén, U. (1996). Pulp washing: sorption equilibria of metal ions on kraft pulps. *Nordic Pulp & Paper Research Journal* 11(3), 164-170+176.

Filho, C. L. & Süß, H. U. (2002). Hydrogen peroxide in chemical pulp bleaching – an overview. *Iberoamerican Congress On Pulp And Paper Research*. 1-27.

Germgård, U., Annergren, G. & Olsson, B. (2011). Fiberlines. *Chemical pulping part 1, Fibre chemical and technology*. Second edition. Ed. Fardim, P. Publ. Paper Engineer's Association/Paperi ja Puu Oy. 675-728.

Gomes, C. M., Colodette, J. L., Mounteer, A. H., Del'Antonio, N., & Silva, C. M. (2007). Characterization and biodegradability of effluents derived from hot acid hydrolysis and hot chlorine dioxide bleaching of eucalyptus pulp. *Appita Journal: Journal Of The Technical Association Of The Australian And New Zealand Pulp And Paper Industry*, 60(1), 65-69+73.

Gu, Y., Malmberg, B., & Edwards, L. (2004). Prediction of metals distribution in mill processes, Part 1: Metals equilibrium model. *Tappi Journal*, 3(1), 26-32.

Gullichsen, J. (2000a). Chemical engineering principles of fiber line operations. *Chemical Pulping*. Eds. Gullichsen, J. & Fogelholm, C. Publ. Fapet Oy. 245-330.

Gullichsen, J. (2000b). Fiberline operations. *Chemical Pulping*. Eds. Gullichsen, J. & Fogelholm, C. Publ. Fapet Oy. 19-244.

Gullichsen, J. (2000c). Introduction. *Chemical Pulping*. Eds. Gullichsen, J. & Fogelholm, C. Publ. Fapet Oy. 14-18.

Gullichsen, J., & Ostman, H. (1976). Sorption and diffusion phenomena in pulp washing. *Tappi Journal*, 59(6), 140-143.

Haglund, I. A. K., Kringstad, K. P., & Almin, K-E. Donnan equilibria in pulping and bleaching; some considerations. *International Symposium On Wood And Pulping Chemistry Part 2*. 635-640.

Henricson, K. (1997). AHL stage: Improved pulp bleachability by mild acid treatment. *Paperi Ja Puu*, 79(8), 546-550.

Histed, J., McCubbin, N. & Gleadow, P. L. (1996). Bleach plant operations, equipment and engineering. *Pulp Bleaching – Principles And Practice*. Eds. Dence, C. W. & Reeve D. W., Tappi press. 513-674.

Histed, J. A., & Nicolle, F. M. A. (1973). Water reuse and recycle in kraft bleacheries. *Pulp And Paper Magazine Of Canada*, 74(12), 80-91.

Jaretun, A., & Aly, G. (2000). Removal of chloride and potassium from kraft chemical recovery cycles. *Separation Science and Technology*, 35(3), 421-438.

Jiang, Z. H., Van Lierop, B., & Berry, R. (2000). Hexenuronic acid groups in pulping and bleaching chemistry. *Tappi Journal*, 83(1), 167-175.

Johansson, M. H., & Samuelson, O. (1977). Epimerization and degradation of 2-O-(4-O-methyl- α -D-glucopyranosyluronic acid)-D-xylitol in alkaline medium. *Carbohydrate Research*, 54(2), 295-299.

Jääskeläinen, A. S., & Sundqvist, H. (2007). *Puun Rakente ja Kemia*. Otatieto. 142.

Kawae, A. & Uchida, Y. (2010). Relationship between hexenuronic acid and brightness reversion of ECF-bleached hardwood Kraft Pulp: Part 1. *Japan Tappi Journal*, 64(2), 60-69.

Krotscheck, A. W. (2006). Pulp Washing. *Handbook of pulp*. Ed. Sixta, H. WILEY-VCH Verlag GmbH & Co. KGaA. 511-559.

Lachenal, D. & Muguet, M. (1992). Degradation of residual lignin in kraft pulp with ozone. Application to bleaching. *Nordic Pulp And Paper Research Journal*, 1(7), 25-29.

Lachenal, D., Pipon, G., & Chirat, C. (2009). Final pulp bleaching by ozonation: chemical justification and practical operating conditions. *Journal Of Pulp And Paper Science*, 35(2), 53-56.

Laine, J., Lövgren, L., Stenius, P., & Sjöberg, S. (1994). Potentiometric titration of unbleached kraft cellulose fibre surfaces. *Colloids And Surfaces A: Physicochemical And Engineering Aspects*, 88(2), 277-287.

Laivins, G. V. & Scallan, A. M. (1998). The Exchange And Removal Of The Metal Cations In Pulps. *The Fundamentals Of Papermaking Materials, Vol 2*. Ed. Baker, C. F. Publ. Pira International. 837-858.

Lapierre, L., Paleologou, M., Berry, R. M., & Bouchard, J. (1997). The limits of metal removal from kraft pulp by acid treatment. *Journal Of Pulp And Paper Science*, 23(11), J539-J542.

Lehtinen, K.-J., (2004). Relationship of the Technical development of pulping and bleaching to effluent quality and aquatic toxicity. Eds. Borton L., Hall, T., Fisher, R. & Thomas, J. *Pulp & Paper Mill Effluent Environmental Fate & Effects*. DESTech Publications Inc.

Lehtinen, K.-J., Axelsson, B., Kringstad, K., & Strömberg, L. (1991). Characterization of pulp mill effluents by the model ecosystem technique. SSVL-investigations in the period 1982-1990. *Nordic Pulp And Paper Research Journal* 6(2). 81-88.

Lindberg, H., Engdahl, H., & Puumalainen, R. (1994). Strategies for metal removal control in closed cycle mills. *International Pulp Bleaching Conference*. 293-302.

Liu, Y. L., Chen, K. F., & Lin, B. P. (2013). The Use of Mg (OH) 2 in the Final Peroxide Bleaching Stage of Wheat Straw Pulp. *Bioresources*, 9(1), 161-170.

Loureiro, P. E., Fernandes, A. J., Furtado, F. P., & Carvalho, D. V. (2010). New insights into chromophore chemistry of eucalyptus pulps assessed by UV-resonance raman micro-spectroscopy. *XXI TECNICELPA Conference and Exhibition*.

Martin, V. J., Burnison, B. K., Lee, H., & Hewitt, L. M. (1995). Chlorophenolics from high molecular weight chlorinated organics isolated from bleached kraft mill effluents. *Holzforschung* 49(5), 453-461.

McDonough, T. J. (1996). The Technology of Chemical Pulping. *Pulp bleaching – Principles and Practice*. Eds. Dence, C. W. & Reeve D. W., *Tappi Press*. 213-456.

Mckague A. B. & Carlberg, G. (1996). Pulp bleaching and the environment. *Pulp bleaching – Principles and Practice*. Eds. Dence, C. W. & Reeve D. W., *Tappi Press*. 749-846.

Mckague, A. B., Chew, W., Zhu, S. & Reeve, D. W. (1998). Compounds identified in effluents from bleaching wood pulp. *Proceedings Of The International Pulp Bleaching Conference Vol. 1*. 205-212.

Medina, J. (2007). Characterization of efficient ECF bleaching parameters of Eucalyptus pulp. Universidad de la República, Facultad de Ingeniería. Master's Thesis.

Neale, S. M. (1929). 30—The Swelling Of Cellulose, And Its Affinity Relations With Aqueous Solutions, Part I—Experiments On The Behaviour Of Cotton Cellulose And Regenerated Cellulose In Sodium Hydroxide Solution, And Their Theoretical Interpretation. *Journal Of The Textile Institute Transactions*, 20(12), T373-T400.

Nordberg, C., Lidén, J., & Öhman, L. O. (2001). Modelling the distribution of free, complexed and precipitated metal ions in a pulp suspension using Donnan equilibria. *Journal Of Pulp And Paper Science*, 27(9), 296-301.

Nordén, H. V. (1966). Analysis of a pulp washing filter. *Kemian Teollisuus*, 23(4), 344-351.

Pandey, K. K., & Vuorinen, T. (2008). UV resonance Raman spectroscopic study of photodegradation of hardwood and softwood lignins by UV laser. *Holzforschung*, 62(2), 183-188.

Pfromm, P. H., (1999). Chloride and potassium in the kraft recovery cycle: A practical guide. *Institute Of Paper Science And Technology*. Project F01706, report 4. 11.

Pikka, O., Vehmaa, J. (2007). Advances in eucalyptus pulp bleaching technology. 3rd ICEP. Referred on 4.2.2014. Available at: <http://www.eucalyptus.com.br/icep03/80Pikka.text.pdf>.

Pikka, O., Vehmaa, J., Alastalo, J., & Gullichsen, J. (2000a). Improved bleaching by means of fractional washing. *Proceedings Of Tappi Pulping/Process & Product Conference*, [CD-ROM].

Pikka, O., Vesala, R., Vilpponen, A., Dahllöf, H., Germgård, U., Norden, S., Bokström, M., Steffes, F., Gullichsen, J., (2000b). Bleaching applications. In *Chemical Pulping*. Eds. Gullichsen, J. & Fogelholm, C. Publ. Fapet Oy. 617-666.

Pöyry Corporation. Pöyry homepage [Online]. Sharing success – Fibria, Brazil Referred on 26.6.2014. Available: http://www.poyry.com/sites/default/files/poyry_fibria_a4_client_success_story.pdf.

Ragnar, M., & Backa, S. (2004). Hot chlorine dioxide bleaching-A modified approach. *Nordic Pulp & Paper Research Journal*, 19(4), 417-419.

Reeve, D. W. (1989). Delignification process variables. *Pulp And Paper Manufacture: Alkaline pulping (Vol. 5)*. Eds. Kocurek, M. J., Grace, T. M., & Malcolm, E. Tappi Pr. 448-460.

Rodrigues da Silva, M., & Colodette, J. (2002). Mill experience using a hot acid stage for eucalyptus kraft pulp bleaching. *Tappi International Pulp Bleaching Conference*, 287-297.

Rudie, A. W., & Hart, P. W. (2005). Managing calcium oxalate scale in the bleach plant. *Solutions!*. 45-46.

Rudie, A. W., & Hart, P. W. (2006). Modeling and minimization of barium sulfate scale. *Tappi Engineering, Pulping & Environmental Conference Proceedings*. p. 10.

Ruuttunen, K., Selluloosatekniikan perusteet – slides. [online]. Massan pesun periaatteet ja pesulaitteet, 23.09.2010, https://noppa.aalto.fi/noppa/kurssi/puu-23.2000/luennot/Puu-23_2000_19_massan_pesu_2010.pdf, Referred on 12.02.2014.

Räsänen, E. (2003). Modelling ion exchange and flow in pulp suspensions. VTT Technical Research Centre of Finland.

Räsänen, E., Laitinen, A., van Heiningen, A. R., & Koukkari, P. (2005). Application of Donnan equilibrium theory for improved bleaching process chemistry. *59th Appita Annual Conference And Exhibition: Incorporating The 13th ISWFPC (International Symposium On Wood, Fibre And Pulping Chemistry)*. 321-327.

Räsänen, E., Robertsén, L., Vuorenalo, V., Karppi, A., Parviainen, K., Dahl, O. & Vanhatalo K. (2011). Manufacturing of Microcellulose. WO 2U11/154597 A1.

Räsänen, E., Stenius, P., & Tervola, P. (2001). Model describing Donnan equilibrium, pH and complexation equilibria in fibre suspensions. *Nordic Pulp & Paper Research Journal*, 16(2), 130-139.

Saariaho, A. M., Argyropoulos, D. S., Jääskeläinen, A. S., & Vuorinen, T. (2005). Development of the partial least squares models for the interpretation of the UV resonance Raman spectra of lignin model compounds. *Vibrational Spectroscopy*, 37(1), 111-121.

Sixta, H., Süß, H., Potthast, A., Schwanninger, M. & Krottscheck, A. W. (2006). Pulp Bleaching. *Handbook Of Pulp*. Ed. Sixta, H. WILEY-VCH Verlag GmbH & Co. KgaA. 609-932.

Süß, H. U., Schmidt, K., Del Grosso, M., & Mahagaonkar, M. (1999). Peroxide application in ECF sequences - a description of the state-of-the-art. *Proceedings Of The 53rd Appita Annual Conference*. 129-136.

Süss, H. U., Schmidt, K., & Hopf, B. (2004). How to improve brightness stability of ECF bleached softwood and hardwood kraft pulp. *58th Appita Annual Conference Proceedings* (2). 493-499.

Tamminen, T. (2010). Final Bleaching of Kraft Pulp: The Optimization of the First Chlorine Dioxide Stage (D₁). Helsinki University of Technology, Department of Forest Product Technology. Master's Thesis.

Tarvo, V., Kuitunen, S., Lehtimaa, T., Tervola, P., Räsänen, E., Tamminen, T., Aittamaa, J., Vuorinen, T., & Henricson K. (2008). Modelling of chemical pulp bleaching. *Nordic Pulp And Paper Research Journal*, 23(1). 91-101.

Teleman, A., Harjunpää, V., Tenkanen, M., Buchert, J., Hausalo, T., Drakenberg, T., & Vuorinen, T. (1995). Characterisation of 4-deoxy- β -l-threo-hex-4-enopyranosyluronic acid attached to xylan in pine kraft pulp and pulping liquor by ¹H and ¹³C NMR spectroscopy. *Carbohydrate Research*, 272(1), 55-71.

Teleman, A., Hausalo, T., Tenkanen, M., & Vuorinen, T. (1996). Identification of the acidic degradation products of hexenuronic acid and characterisation of hexenuronic acid-substituted xylooligosaccharides by NMR spectroscopy. *Carbohydrate Research*, 280(2), 197-208.

Tenkanen, M., Gellerstedt, G., Vuorinen, T., Teleman, A., Perttula, M., Li, J., & Buchert, J. (1999). Determination of hexenuronic acid in softwood kraft pulps by three different methods. *Journal Of Pulp And Paper Science*, 25(9), 306-311.

Towers, M., & Scallan, A. M. (1996). Predicting the ion-exchange of kraft pulps using Donnan theory. *Journal of pulp and paper science*, 22(9). 332-337.

Ulmgren, P. (1997). Non-process elements in a bleached kraft pulp mill with a high degree of system closure-state of the art. *Nordic Pulp And Paper Research Journal*, 12(1). 32-40.

Ulmgren, P., & Rådeström, R. (2001). Solubility and mechanisms of precipitation of calcium oxalate in D (chlorine dioxide stage) filtrates. *Journal Of Pulp And Paper Science*, 27(11), 391-396.

Vehmaa, J., Pikka, O., Tervola, P. & Poulin, T. (2011) Reuse of purified process water in fiberline – laboratory results. *Tappi Peers Conference Vol. 1*. 13-34.

Vianna, V. Reduction of solid waste from pulp mill fiberline. 6th ICEP – November 24th – 27th, 2013, Colonia Del Sacramento, Uruguay. Slide 5. Available

at:

http://www.6thicep.org.uy/styles/inc4/downloads/Slides/12_Vianna%20Viridiane.pdf

Viirimaa, M., Dahl, O., Niinimäki, J., Ala-Kaila, K., & Perämäki, P. (2002). Identification of the wash loss compounds affecting the ECF bleaching of softwood kraft pulp. *Appita Journal*, 55(6), 484-488.

VTT. (2011). KnowPulp [online]. Version 10.0. Referred on 8.10.2014. Available at: http://know.aalto.fi/pulp/latest/english/raw_materials/2_water/1_usage/vesitase_img.htm?zoom_highlightsub=effluent.

Vuorinen T., Chemistry of pulping and bleaching – slides. [online]. Formation of hexenuronic acid, 04.04.2011. Referred on 31.1.2014. Available at: https://noppa.aalto.fi/noppa/kurssi/puu-19.3000/luennot/Puu-19_3000_hexa.pdf.

Vuorinen, T., Fagerström, P., Buchert, J., Tenkanen, M., & Teleman, A. (1999). Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps. *Journal Of Pulp And Paper Science*, 25(5), 155-162.

Vuorinen, T., Fagerström, P., Räsänen, E., Vikkula, A., Henricson, K., & Teleman, A. (1997). Selective hydrolysis of hexenuronic acid groups opens new possibilities for development of bleaching processes. *9th International Symposium Wood And Pulping Chemistry (ISWPC)*, M4-1 – M4-4.

Wang, C. (2012). Photonanocatalyst aided alkaline pretreatment and Raman spectroscopic characterization of corn stover biomass. Iowa State University. Master's Thesis.

Wennerström, M. (2005). Decreasing brightness reversion with powerful ozone bleaching. *Pulp And Paper Canada*, 106(1). 41-44.

Zhang, M., Qi, W., Liu, R., Su, R., Wu, S., & He, Z. (2010). Fractionating lignocellulose by formic acid: characterization of major components. *Biomass And Bioenergy*, 34(4), 525-532.

List of Appendices

Appendix 1: The methods for determination of pulp and filtrate properties

Appendix 2: Standard Method for determination of HexA content

Appendix 3: UVRR Spectra

Appendix 1: The methods for determination of pulp and filtrate properties

Table 1. The methods for pulp determinations.

HexA content	TKK procedure (Appendix 2)
ISO brightness	SCAN-CM 11:95 and SCAN-P 3:93
Kappa number	SCAN-C 1:00
Viscosity	SCAN-CM 15:99

Table 2. The methods for filtrate determinations.

Residual peroxide	iodometric titration	E _{OP} - and P-stage filtrates
Residual chlorine	iodometric titration	D-stage filtrates
TOC	SFS-EN 1484, Shimadzu TOC-V total organic carbon analyzer	A1- and A4-filtrates
Chloride content	ion chromatography	A1- and A4-filtrates
Alkali metals	AAS-device (Varian 240)	A1- and A4-filtrates
Other NPE's	ICP-OES-device (Perkin-Elmer 7100 DV)	A1- and A4-filtrates

Appendix 2: Standard method for determination of HexA content



TEKNILLINEN KORKEAKOULU

TYÖOHJE C/6

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Hexenuronic Acid content of Sulphate Pulps

0 Introduction

During kraft pulping a major part of the 4-O-methylglucuronic acid groups of the native wood xylans are converted to 4-deoxyhex-4-enuronic acid groups (HexA). Because of its ene functionality, HexA reacts with several bleaching chemicals, such as chlorine, chlorine dioxide, ozone and peracids, thus consuming these chemicals. Also permanganate attacks HexA which therefore contributes to the κ -number of the pulps. The removal of HexA groups reduces the consumption of bleaching chemicals in all bleaching sequences and increases the brightness stability of the pulps.

1 Scope

The method is used to determine the amount of hexenuronic acid groups in sulphate pulps by mild, selective acid hydrolysis.

The amount of hexenuronic acid groups in the pulp depends on the cooking temperature, time, hydroxyl ion concentration and ionic strength.

2 References

Vuorinen, T., Buchert, J., Teleman, A., Tenkanen, M. and Fagerström, P., Selective hydrolysis of hexenuronic acid groups and its application in ECF and TCF bleaching of kraft pulps, International Pulp Bleaching Conference, April 14-18, 1996, pp. 43-51.

3 Definitions

80-90 % of the HexA groups can be selectively hydrolyzed with this method.

4 Principle

In acid hydrolysis the hexenuronic acid groups are selectively converted to formic acid and furan derivatives (2-furoic acid and 5-carboxy-2-furaldehyde). The quantification of HexA groups is based on the quantification of formed furan derivatives by UV-spectroscopy.

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5 Reagents

All solutions are prepared in a laboratory, thermostated at 25 °C.

5.1 De-ionized water

5.2 1 M sodium formate buffer

37.7 ml strong formic acid and 200 ml 1 M sodium hydroxide diluted to 1 liter with deionized water.

5.3 10 mM sodium formate buffer.

The ratio of 1 M sodium formate buffer and ion exchanged water is 1:100 (or 8mM formic acid + 2 mM sodium formate).

6 Apparatus

6.1 Rotating autoclaves (8x220ml) of stainless steel with valves in the captures, oil-bath digester (Haake).

6.2 Oven, adjustable to (105±3)°C

6.3 Vacuum filter assembly consisting of a Büchner funnel and vacuum flask

6.4 UV Spectrophotometer

6.5 Gas bottle (nitrogen)

7 Preparation of the sample

The pulp is washed well with deionized water. The pulp suspension is filtered to ~30 % dry matter content and homogenised. The dry weight of the pulp is measured according to a standard procedure (SCAN-C 3:78).

8 Procedure

Add approximately 2.5 g (dry matter content) homogenized pulp to an autoclave (volume 220 ml) with 0.01 M sodium buffer (150 ml). The pH should be ~3.5. After closing the autoclave the oxygen is replaced with nitrogen. The autoclave is circulated in a preheated oil-bath (110°C) for one hour. After the heating period the autoclave is cooled with cold, running water in order to stop the reaction.

After opening the autoclave carefully (some pressure is inside) the pulp is filtered with vacuum on a Büchner funnel and washed with deionized water (~500 ml). The hydrolyzate and the washing waters are combined and diluted to one liter with deionized water.

The UV-spectrum of the diluted hydrolyzate is measured at 200-500 nm. A blank solution is prepared by diluting 150 ml of 0.01 M sodium formate buffer to 1000 ml with deionized water. UV spectrum of the blank solution is subtracted from the sample spectrum. The absorbance is determined at the absorption maximum of 2-furoic acid at 245 nm. If necessary, baseline correction is made at 400-500 nm (generally at 480 nm). If the absorbance at 245 nm is greater than 1.5, the sample must be diluted.

9 Calculation

The amount of HexA in pulp (c; meq/kg) is determined from the equation

$$c = (A_{245} - A_{480}) / (8.7xm) \quad (1)$$

where,

A_{245} = absorbance at 245 nm

A_{480} = absorbance at 480 nm

m = dry-weight of the pulp (kg)

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$\epsilon = 8,7 \text{ mM}^{-1}\text{cm}^{-1}$ = Molar absorption coefficient at 245 nm in respect to the hexenuronic acid. If further dilution has been used, the result must be divided with the dilution factor (<1). Eq. 1 assumes that the cell length in the absorption measurement is 1 cm. If other cell lengths are used, the result must be divided by the cell length (cm).

e.g. 90 % conversion of the hexenuronic acid groups.

10 Quantitativity

11 Evaluation of bleaching potential

Under these standard conditions ~90 % of the hexenuronic acid groups are removed. The actual hexenuronic acid content is thus ~10 % higher than the value obtained with this standard method.

The conditions of the standard method have been selected so that they approximately correspond to an *optimal degree of hexenuronic acid removal* (~90 %) in an A-stage of bleaching sequences. In addition, the method has made to be fast and practical in laboratory work. This means that the conditions are not optimal for the viscosity of the pulp. Thus, the standard conditions should only be used for fast screening of the potential of the A-stage for different pulps.

The absorption at ~245 nm derives from 2-furoic acid which is the major (~90 %) hydrolysis product. The absorption maximum of 5-carboxy-2-furaldehyde is at ~280 nm. The absorption coefficient ($8,700\text{M}^{-1}\text{cm}^{-1}$) at ~245 nm has been determined for the conversion of hexenuronic acid group in an isolated hexenuronoxyl-oligosaccharide and it thus takes into account both degradation products.

Typically a reduction of 10 meq/kg in the hexenuronic content corresponds to 1 unit reduction in κ -number determination in a 50 or 75 % reduced scale. A separate dry weight determination after the A-treatment is unnecessary because the yield of the treatment is very high (>99 % for softwood pulps, >98 % for hardwood pulps). TOC of the hydrolyzate is recommended for the yield determinations when necessary.

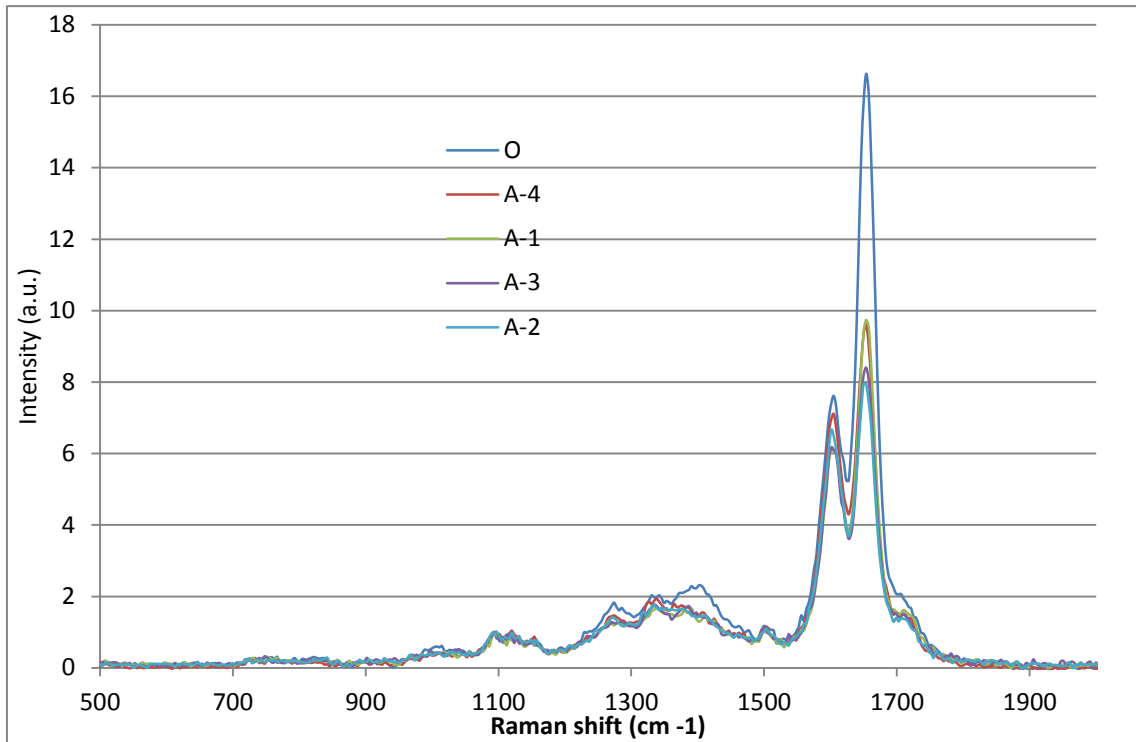
If other conditions are used, it is better first to study the liberation of the hydrolysis products as a function of time. Checking of the time-dependence is also recommended when the standard method is adopted for a certain reactor for the first time because different reactors may have different heating up times and temperature calibrations. The hydrolysis follows first-order kinetics (exponential decay) and from this time-dependence it is possible to evaluate how long reaction time is needed for

12 Kappa number

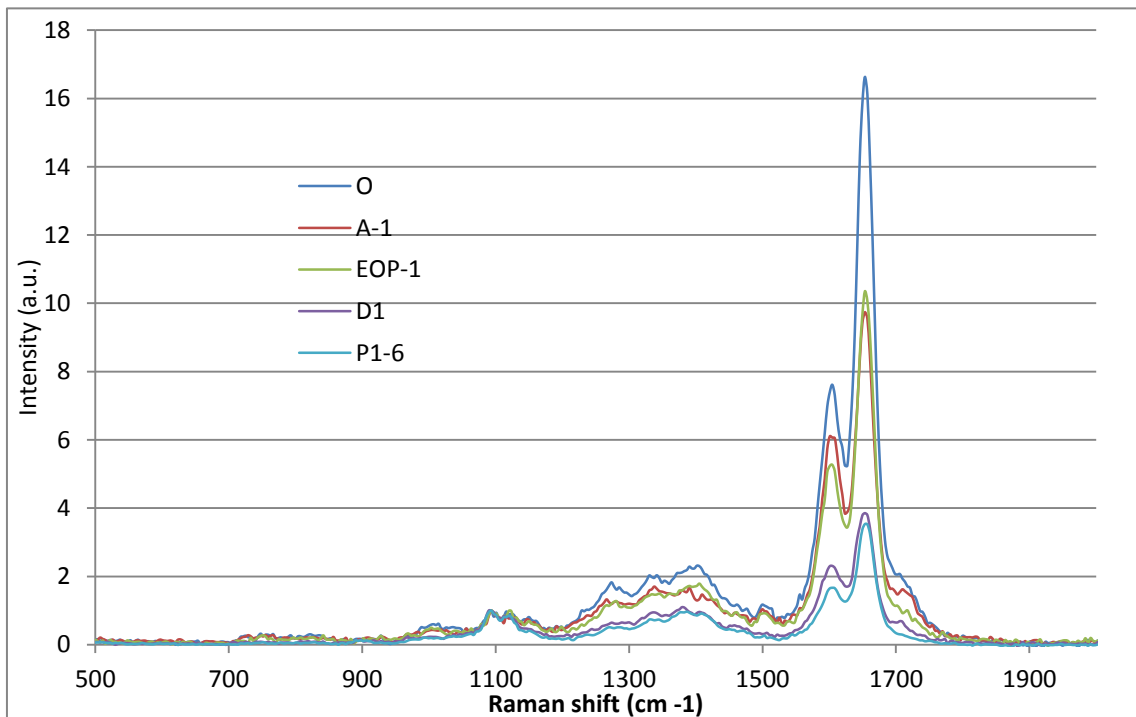
The kappa number of kraft pulps correlates with the total content of lignin and hexenuronic acid groups. The kappa number after the selective hydrolysis of hexenuronic acid groups (κ_A) gives a better measure of lignin content. The decrease in kappa number ($\Delta\kappa$) in the selective hydrolysis of HexA approximately corresponds to the hexenuronic acid content of the pulp (Eq. 2).

$$\begin{aligned} \kappa &= \kappa_A + \Delta\kappa \\ &\equiv \kappa_{\text{lignin}} + \kappa_{\text{HexA}} \end{aligned} \quad (2)$$

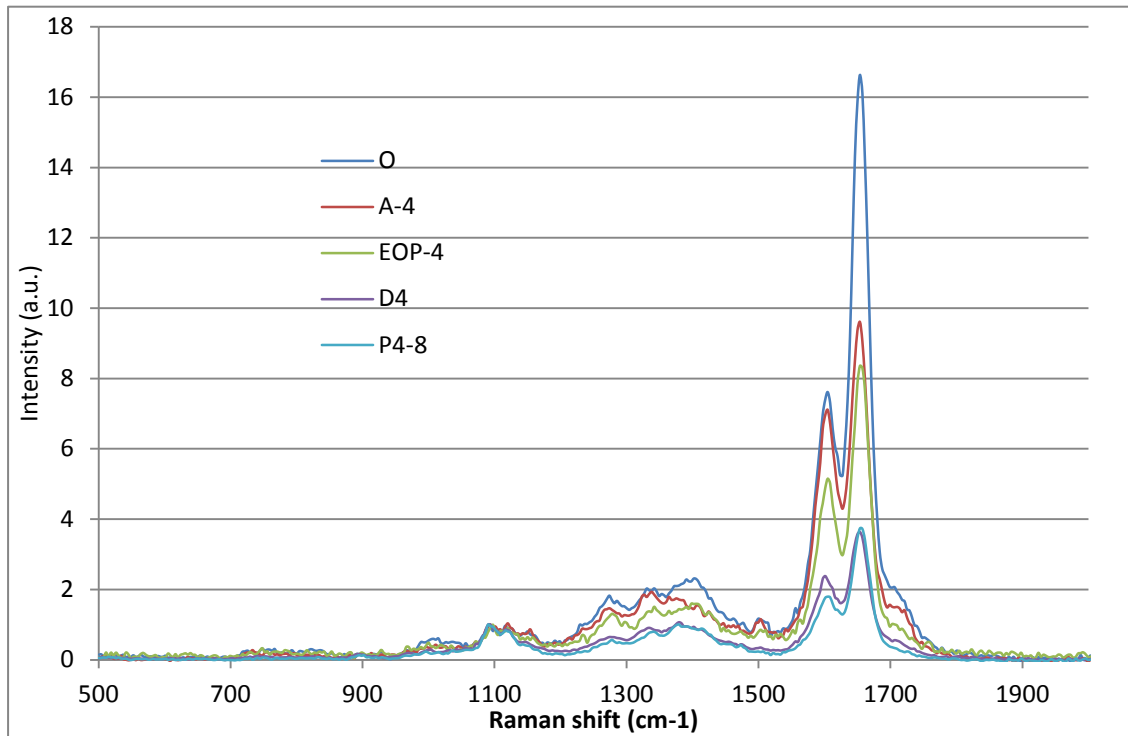
Appendix 3: UVRR Spectra



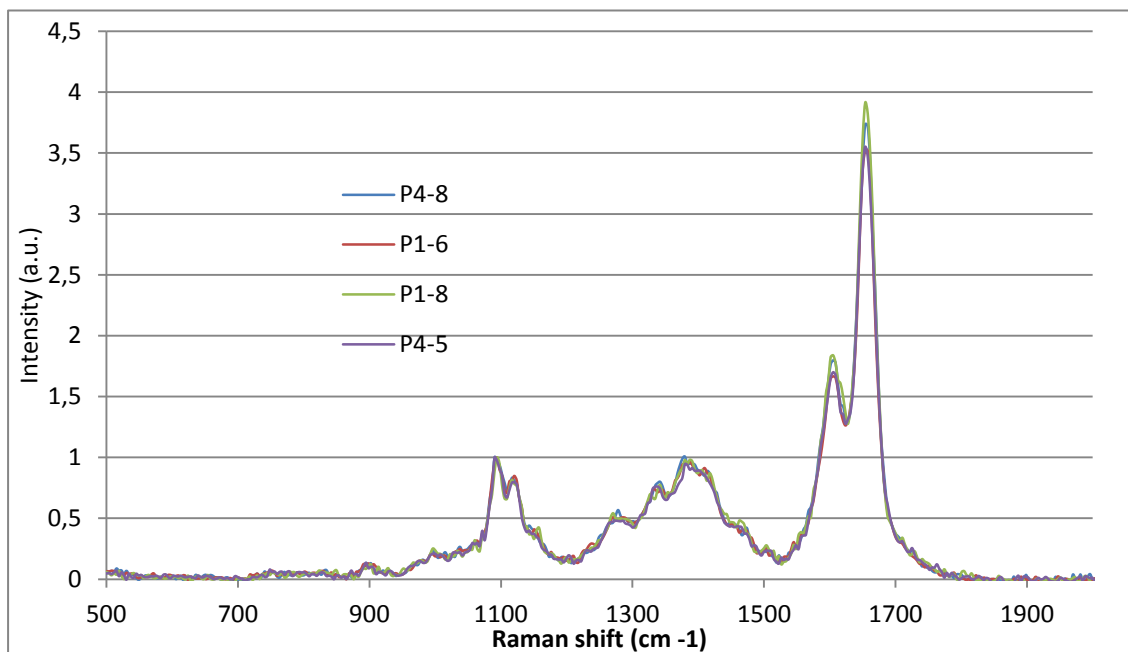
UVRR spectra of pulps after oxygen delignification and different A-stages.



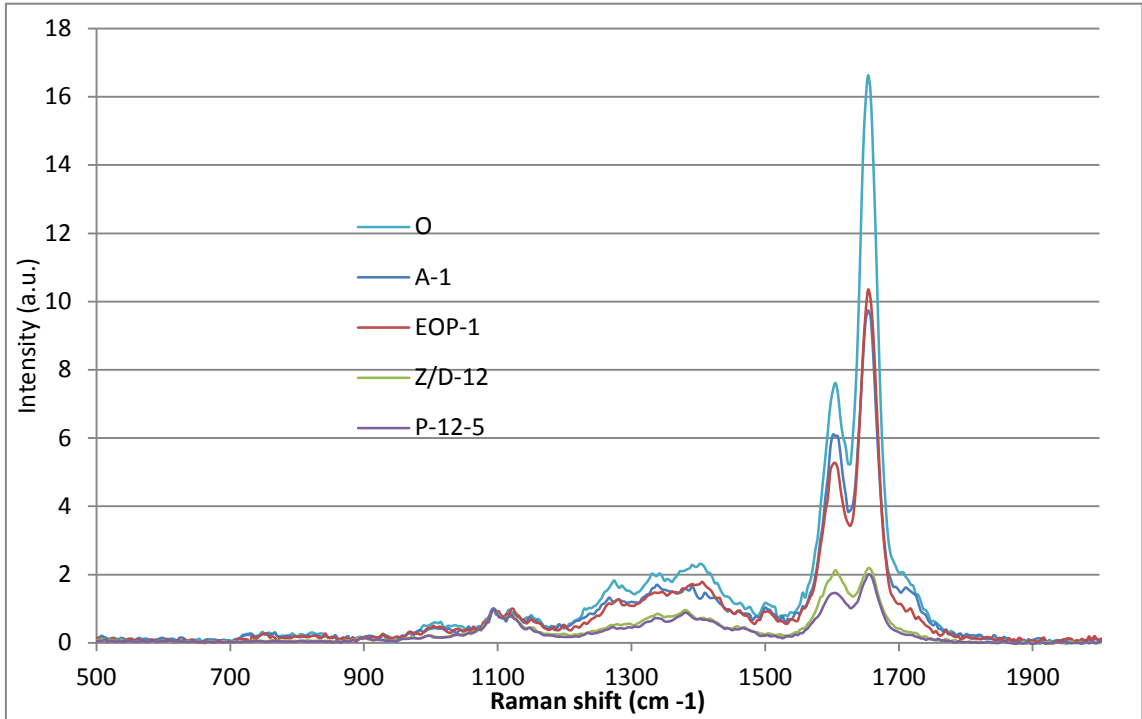
UVRR spectra of pulp after each stage in the first sequence without filtrate circulation.



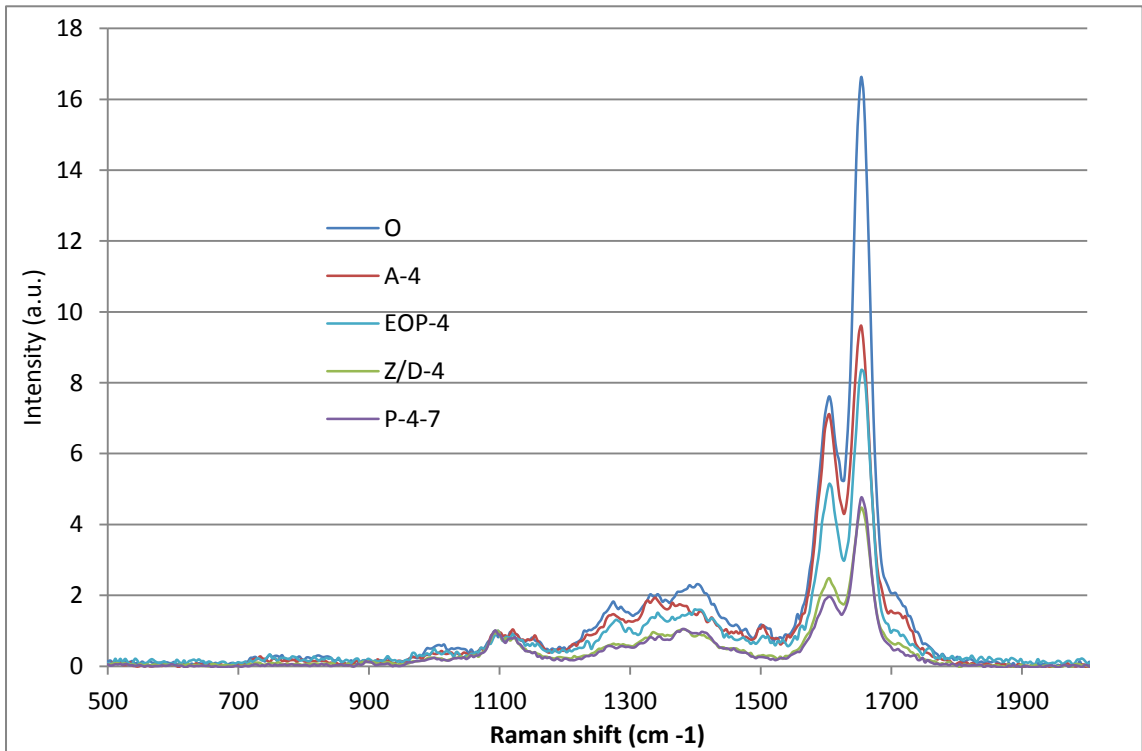
UVRR spectra of pulp after each stage in the first sequence with filtrate circulation.



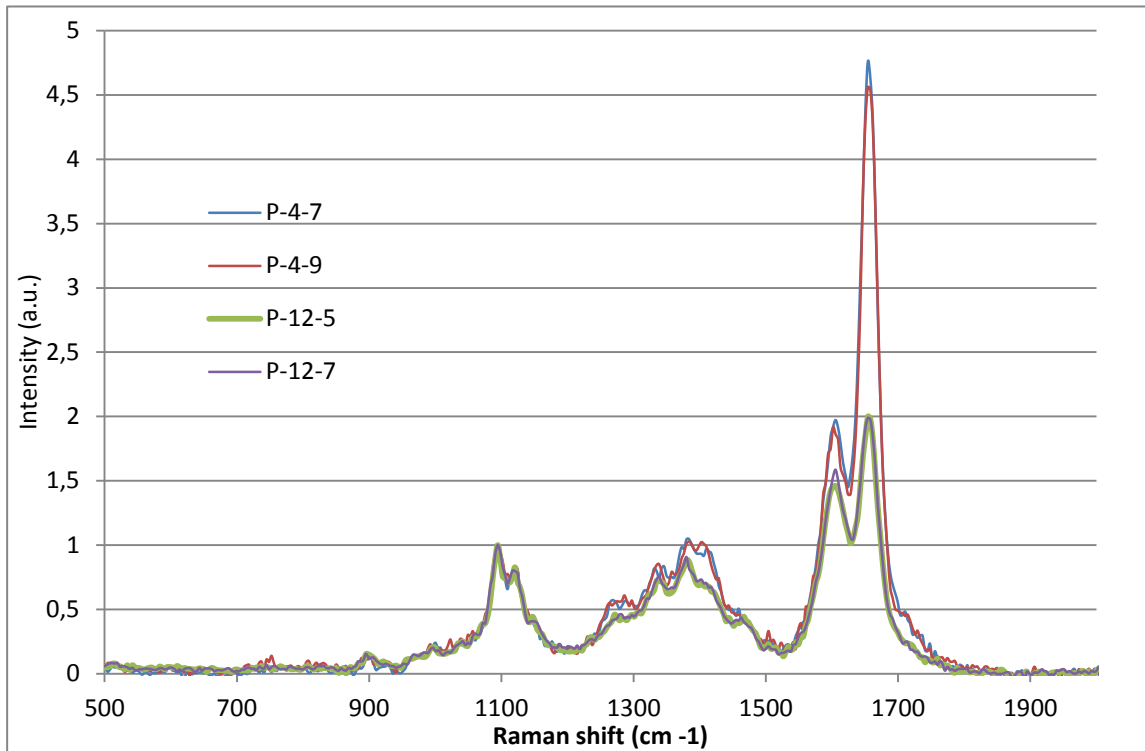
UVRR spectra of pulps after different P-stages in the first sequence.



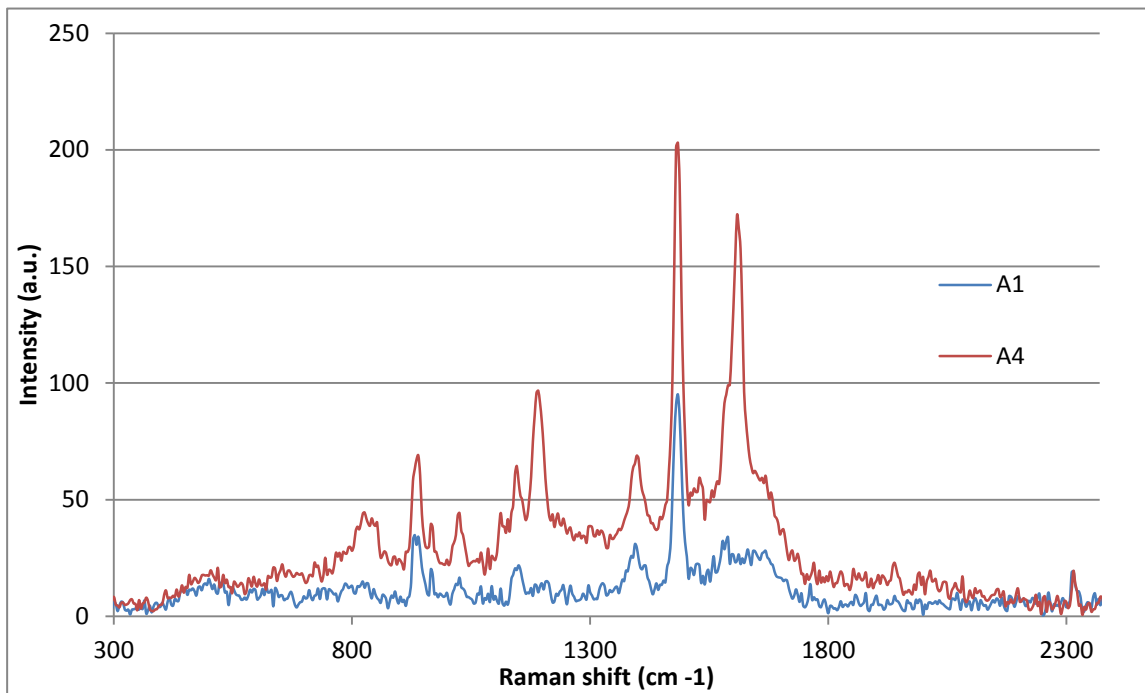
UVRR spectra of pulp after each stage in the second sequence without filtrate circulation.



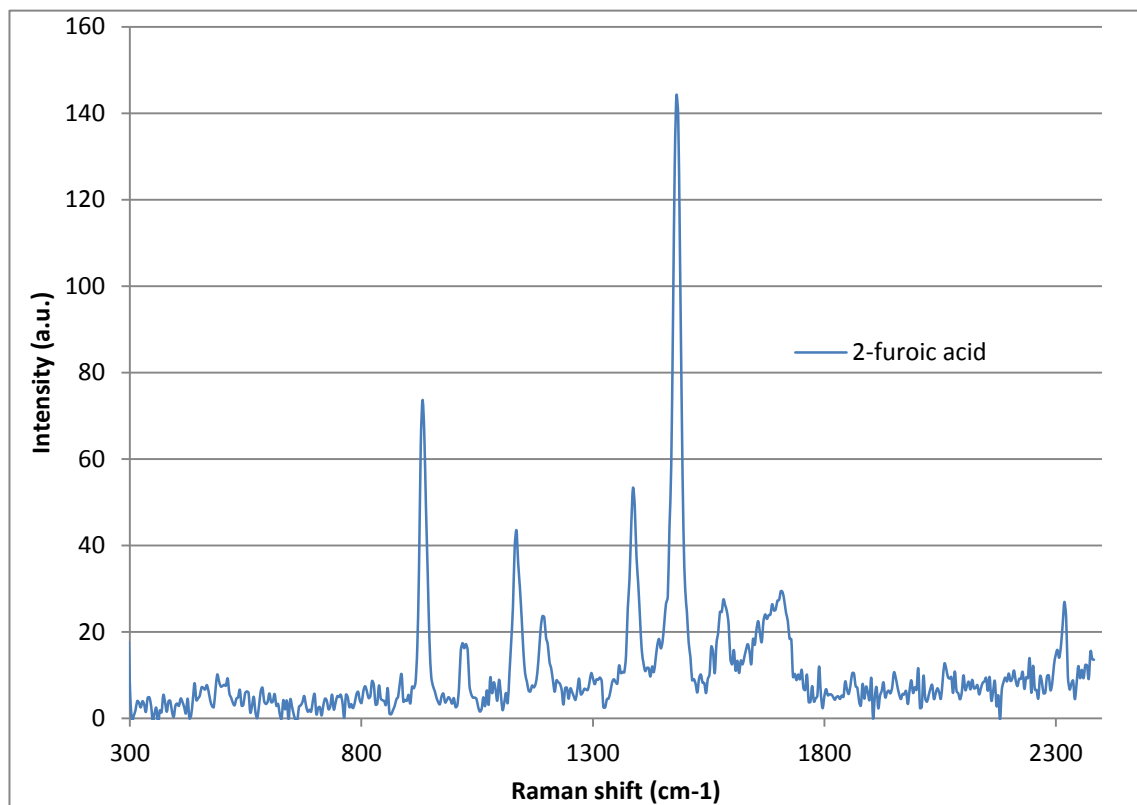
UVRR spectra of pulp after each stage in the second sequence with filtrate circulation.



UVRR spectra of pulps after different P-stages in the second sequence.



UVRR spectra of both filtrates.



UVRR spectrum of 2-furoic acid.