Brightness reduction of peroxide-bleached mechanical pulp and fillers in the wet end of a paper machine

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Abstract

This study examined the brightness reduction of peroxide-bleached mechanical pulp and paper fillers in the wet end of a paper machine. The effect of different process variables was studied on a laboratory scale using a device that simulates the short circulation of a paper machine. The fines-containing wire water was circulated in the device and wire water samples were taken during this circulation. Fines sheets were prepared from the samples and their optical properties were measured to explore the darkening of the fines fraction during the circulation. In addition, the darkening of the fiber fraction and paper fillers was studied.

The results indicated that the brightness reduction of the peroxide-bleached mechanical pulp in the wet end of a paper machine was partly due to the formation of light-absorbing chromophores in the fibers and fines and partly due to the adsorption of light-absorbing substances to the surfaces of fibers and fines from the water phase. Paper fillers do not contain lignin or other structures with a high darkening tendency and their brightness reduction was caused by the adsorption of light-absorbing dissolved and colloidal substances (DCS).

Pulp washing was found to be an efficient way to reduce the tendency for darkening of the pulp itself and also the fillers, because it removes light-absorbing substances from the pulp suspension. In addition to the wood-based DCS, the most important factors affecting the brightness reduction of peroxide-bleached mechanical pulp were the residence time of the pulp in the wet end and the iron concentration of the white water. Other factors decreasing the brightness notably, but to a lesser extent, were high shear rate generated to the pulp, carbon dioxide gas, chloride ions, and calcium ions. No change was noted in the light absorption of the peroxide-bleached mechanical pulp between acidic and neutral test conditions. Thus, from brightness point of view, paper grades from peroxide bleached mechanical pulp can be manufactured equally well at neutral or at acidic process conditions. The Precipitated Calcium Carbonate (PCC) fillers were found to have somewhat higher tendency for darkening than the Precipitated Calcium Sulfate (PCS) filler.

Tiivistelmä

Tässä työssä tutkittiin peroksidivalkaistun mekaanisen massan ja paperin täyteaineiden vaaleuden alenemista paperikoneen märässä päässä. Eri prosessimuuttujien vaikutusta tummumiseen tutkittiin laboratoriomittakaavassa käyttämällä laitetta, joka simuloi paperikoneen lyhyttä kiertoa. Hienoainepitoista viiravettä kierrätettiin laitteessa ja viiravesinäytteitä otettiin kierrätyksen aikana. Näytteistä valmistettiin hienoainearkkeja ja niiden optiset ominaisuudet mitattiin, jotta hienoaineen tummumista kierrätyksen aikana voitiin tutkia. Myös kuitufraktion ja täyteaineiden tummumista tutkittiin.

Testitulokset osoittivat, että peroksidivalkaistun mekaanisen massan tummuminen johtui osittain valoa absorboivien kromoforien muodostumisesta hienoaineeseen ja kuituihin ja osittain kiertovedestä niiden pinnoille kiinnittyneistä valoa absorboivista aineista. Paperin täyteaineet eivät sisällä ligniiniä tai muita rakenteita, jotka ovat alttiita tummumiselle, joten niiden vaaleuden aleneminen johtui ainoastaan valoa absorboivien liuenneiden ja kolloidaalisten aineiden kiinnittymisestä.

Massan pesu todettiin tehokkaaksi tavaksi ehkäistä massan ja täyteaineiden tummista, koska se poistaa massasuspensiosta valoa absorboivia aineita. Puusta peräisin olevien liuenneiden ja kolloidaalisten aineiden lisäksi merkittävimmät peroksidivalkaistun mekaanisen massan tummumista aiheuttavat tekijät olivat massan viipymäaika märässä päässä ja kiertoveden rautapitoisuus. Muita merkittäviä vaaleutta alentavia tekijöitä olivat massaan kohdistuva korkea leikkausnopeus, hiilidioksidi, kloridi- ja kalsiumionit. Peroksidivalkaistun mekaanisen massan valon absorptiokertoimessa ei havaittu eroa happamien ja neutraalien testiolosuhteiden välillä. Niinpä, paperin vaaleuden kannalta, paperia voidaan valmistaa yhtä hyvin neutraaleissa ja happamissa prosessiolosuhteissa. Saostetulla kalsiumkarbonaatti –täyteaineella oli jokseenkin suurempi taipumus tummua kuin saostetulla kalsiumsulfaatilla.

PREFACE

Espoo, October 10th , 2013

Pekka Varhimo

LIST OF SYMBOLS AND ABBREVIATIONS

Al^{3+}	Aluminum ion
$AlCl_3$	Aluminum chloride
ANS	Polyaluminum nitrate sulfate
Ar^+	Argon ion
B	Boron
Ba^{2+}	Barium ion
BDDJ	Britt dynamic drainage jar
BMcN	Bauer McNett fractionator
c_{HB}	Consistency in the headbox
c_{WW}	Consistency of the wire water
C=C	Carbon-carbon double bond
Ca^{2+}	Calcium ion
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
$Ca(OH)_2$	Calcium hydroxide
$CaSO_4$	Calcium sulfate
$CaSO_4 \cdot ½H_2O$	Hemihydrate
$CaSO_4 \cdot 2H_2O$	Dihydrate
Cl^-	Chloride ion
Co	Cobalt
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate ion
Cr	Chromium
CSF	Freeness
Cu^{2+}	Copper ion
DCS	Dissolved and colloidal substances
DDJ	Dynamic drainage jar
DIP	Deinked recovered paper pulp
DORT2002	Discrete Ordinate Radiative Transfer model
Fe^{2+}	Ferrous ion
Fe^{3+}	Ferric ion
$Fe(OH)_3$	Ferric hydroxide
$FeSO_4$	Ferrous sulfate
g	gravitational acceleration constant
GCC	Ground calcium carbonate
GCS	Ground calcium sulfate
GW	Stone groundwood
H_2SO_4	Sulfuric acid
HCl	Hydrogen chloride
ICP	Inductively Coupled Plasma
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ISO	International organization for standardization

k	Specific light absorption coefficient
K	Potassium
KBr	Potassium bromide
KCl	Potassium chloride
KOH	Potassium hydroxide
LWC	Lightweight coated paper, coated magazine paper
Mg	Magnesium
Mn^{2+}	Manganese ion
$MnCl_2$	Manganese chloride
mesh	The number of openings per linear inch of a screen or wire
N_2	Nitrogen
Na^+	Sodium ion
NaCl	Sodium chloride
NaOH	Sodium hydroxide
Ni^{2+}	Nickel ion
NTU	Nephelometer Turbidity Units
O_2	Oxygen
P52	Fiber material passed the 52 mesh wire
P200	Fiber material passed the 200 mesh wire
PAC	Polyaluminum chloride
Pb^{2+}	Lead ion
PCC	Precipitated calcium carbonate
PCS	Precipitated calcium sulfate
PVam	Polyvinyl amine
R52	Fiber material retained on the 52 mesh wire
RDF	Recycling Device of Fines
rpm	Revolutions per minute
s	Specific light scattering coefficient
S	Sulfur
SC	Supercalendered paper, uncoated magazine paper
Si	Silicon
SO_4^{2-}	Sulfate ion
Sr	Strontium
TMP	Thermomechanical pulp
UV	Ultra-violet
UV-Vis	Ultraviolet-Visible
XRF	X-Ray Fluorescence
Zn^{2+}	Zinc ion

LIST OF PUBLICATIONS

Paper I   Varhimo, P., Konn, J., Lillandt, M. and Paltakari J. (2012): Brightness reduction of mechanical pulp in the wet end of a paper machine: Method development and validation, *Nordic Pulp and Paper Research Journal* 27(3), 542-549.

Paper II   Varhimo, P., Konn, J., Lillandt, M. and Paltakari J. (2013): Brightness reduction of mechanical pulp in the wet end of a paper machine: The effect of pH, pulp washing and shear rate, *Nordic Pulp and Paper Research Journal* 28(1), 51-58.

Paper III   Varhimo, P., Konn J., Lillandt M. and Paltakari J. (2013): Brightness reduction of calcium carbonate and calcium sulfate fillers in the wet end of a paper machine, *Nordic Pulp and Paper Research Journal* 28(1), 59-67.

Paper IV   Varhimo, P., Konn J., Lillandt M. and Paltakari J. (2013): Brightness reduction of mechanical pulp in the wet end of a paper machine: The effect of different ions in the circulation water, *BioResources* 8(3), 4117-4133.

AUTHOR'S CONTRIBUTION

I, II, IV

Pekka Varhimo was responsible for the experimental design with the co-authors, performed all experimental work, analyzed the results and wrote the first versions of the manuscripts.

III

Pekka Varhimo was responsible for the experimental design with the co-authors, performed main part of experimental work, analyzed the results and wrote the first version of the manuscript.

CONTENTS

1 INTRODUCTION AND OBJECTIVES OF THE STUDY

Peroxide-bleached mechanical pulp is used as raw material for printing papers, such as newsprint, supercalendered (SC), and light-weight-coated (LWC) magazine papers. Paper fillers are fine, white pigment powders that are used in various mechanical paper grades at levels up to 20–35 % of the paper furnish. The brightness demands for improved newsprint and many magazine paper grades have been raised in recent years. Therefore, it is important to be able to produce mechanical pulps with high brightness in an ecofriendly and cost-effective way (Enberg et al. 2009; Ohlsson, Federer 2002; Luoma et al. 2004). Brightness reduction of mechanical pulp in paper machine water circulations is a well-known phenomenon. In a typical case, the brightness of mechanical pulp straight after the peroxide bleaching stage is 75 %, but only 70 % after the web forming. The reasons behind the darkening are not fully known.

The aim of this dissertation was to determine the mechanisms and phenomena behind the brightness reduction of peroxide-bleached mechanical pulp and fillers in the wet end of a paper machine.

The main research questions were: How to create a method and apparatus to study the brightness reduction? Why the brightness of peroxide-bleached mechanical pulp decreases in the wet end and what are the factors that affect it? Do also fillers darken? What are the factors that affect the brightness reduction of fillers?

In order to assess the mechanisms and phenomena causing the brightness reduction, it was necessary to develop a suitable method. For this purpose, a new laboratory scale device, the Recycling Device of Fines (RDF), was constructed. In **Paper I**, the main target was the validation of the new experimental method used for studying the brightness reduction. In **Papers II** and **IV**, the effect of the different process variables on the brightness reduction of peroxide-bleached mechanical pulp was examined using the experimental method developed in **Paper I**. In **Paper II**, the focus was on the pulp washing, process pH and the shear rate generated to the pulp in the wet end. The effect of different ions in the circulation water was explored in **Paper IV**. In **Paper III**, the brightness reduction of fillers was studied. The process variables in the filler tests were the type of filler used, the amount of wood-based dissolved and colloidal substances in the circulation water and process pH. In addition, the effect of carbon dioxide gas on the brightness reduction of the fines fraction of peroxide-bleached TMP was studied in **Paper III**.

2 TASKS OF RESEARCH

2.1. Construction and validation of applicable apparatus and methodology to study the brightness reduction (Paper I)

In order to simulate the short circulation of a paper machine, a laboratory scale methodology was developed. The experimental procedure was developed in terms of controlled consistencies, flow rates, shear forces, temperature, and pH. For this purpose, a new laboratory scale device, the Recycling Device of Fines (RDF), was constructed. The requirement for the validation was a high repeatability of the experimental procedure. In addition, the brightness reduction should be due to an increase in the light absorption of the pulp, not due to a change in the structure (light scattering relating to changes in bonding between the fibers or formation based changes) of the produced sheets and reached in a reliable and sufficiently short residence time.

2.2. To determine the effect of the following factors on the brightness reduction of peroxide-bleached mechanical pulp

2.2.1 Pulp washing (Paper II)

Mechanical pulps are usually not thoroughly washed. The amount of dissolved and colloidal substances (DCS) in the pulp suspension typically decreases during washing. The aim was to study whether this pulp washing and the decrease in the DCS content decreases the darkening tendency of peroxide-bleached mechanical pulp.

2.2.2 pH (Paper II)

Paper grades containing mechanical pulp are produced typically either at acidic (pH 4.0–5.5) or neutral-alkaline (pH 6.5–8.5) conditions. The aim was to determine whether alkaline darkening happens when the papermaking pH is increased from 4.8 to 7.3.

2.2.3 Shear rate (Paper II)

Several elements in the stock and approach systems and in the wet end of a paper machine generate high shear rates. The aim was to study if the shear rate generated on the pulp affects the brightness reduction.

2.2.4 Carbon dioxide gas (Paper III)

The use of carbon dioxide gas for the adjustment of paper machine pH has increased dramatically over the past years. In addition, calcium carbonate fillers form CO_2 gas while dissolving. The aim was to determine whether carbon dioxide gas affects the brightness reduction of peroxide-bleached mechanical pulp.

2.2.5 Different ions in circulation water (Paper IV)

The white water of a paper machine contains various amounts of different ions. The aim was to resolve which ions affect the brightness of the pulp.

2.3 To determine the effect of the following factors on the brightness reduction of PCC and PCS fillers (Paper III)

2.3.1 The type of filler

The aim was to determine whether PCC and PCS fillers have differences in their tendencies to darken in the wet end of a paper machine.

2.3.2 Wood-based dissolved and colloidal substances

In the production of mechanical pulps approximately 2–5% of the wood material is dissolved or dispersed into the process waters of the paper mill. The aim was to conclude whether these wood-based dissolved and colloidal substances (DCS) affect the brightness reduction of PCC and PCS fillers.

2.3.3 pH

The aim was to determine whether the process pH affects the brightness reduction of PCC and PCS fillers.

3 SCOPE OF RESEARCH

In respect to pulps and fillers, this work focused on the brightness reduction of peroxide-bleached mechanical pulp (mainly TMP) and Precipitated Calcium Carbonate (PCC) and Precipitated Calcium Sulfate (PCS) fillers. The brightness reduction of the fines and fiber fraction of the pulps was studied separately. The brightness reduction was verified by measuring the optical properties of the produced fines and fiber sheets from test series with diverging process variables. The effects of the process variables on the strength properties of the produced sheets was not studied in this work with the exception of some tensile strength measurements that were carried out to resolve the reasons for differences in the light scattering values of the fines sheet.

The studied brightness reduction was limited to the wet end of a paper machine comprised of the processes between the peroxide bleaching stage and the web forming. The brightness reduction was studied on a laboratory scale using a device that simulates the darkening phenomena in the short circulation of a paper machine. The studied temperature and pH ranges were 58–60 °C and 4.8–8.7, because these conditions are typical in the wet end of an actual paper machine. Also, the shear rates generated to the pulp, the wire retention and the consistency of the wire water were typical for the wet end of an actual paper machine. However, this method did not inclusively simulate the short circulation of an actual paper machine with the additions of different chemical additives, such as fixatives or retention aids, but concentrated only on the brightness reduction of the pulp components and fillers. In addition, in the wet end of an actual paper machine, the fresh pulp flow is continuous from the machine chest to the short circulation. This could not have done with the laboratory-scale device i.e. it was impossible to remove the fibers from the wire section and replace them with new fibers during the circulation. Thus, the residence time of fibers that remained on the top of the wire section was as long as that of the fines passing the wire and circulating in the device. The brightness reversion or yellowing of the final paper caused by light-, heat-, or moisture-induced ageing was not included in this work.

4 BACKGROUND

4.1 Peroxide-bleached mechanical pulp

Mechanical pulps are produced by defibering wood mechanically either by grinding the wood logs or by refining the wood chips (*Fig 1*). The production of mechanical pulp is an efficient way of utilizing the virgin wood resources since the yield from these production methods is high, normally 97–98 % for Norway spruce (Sundholm 1999), and the environmental effect is relatively low. In addition, the high opacity, bending stiffness, and ink absorptivity make mechanical pulps suitable as raw material for printing papers, such as newsprint, supercalendered (SC), and light-weight-coated (LWC) magazine papers. The bulkiness and compressibility of mechanical fibers are also appreciated properties (Enberg et al. 2009; Rundlöf et al. 2000a, 2000b; Bobacka 2001).
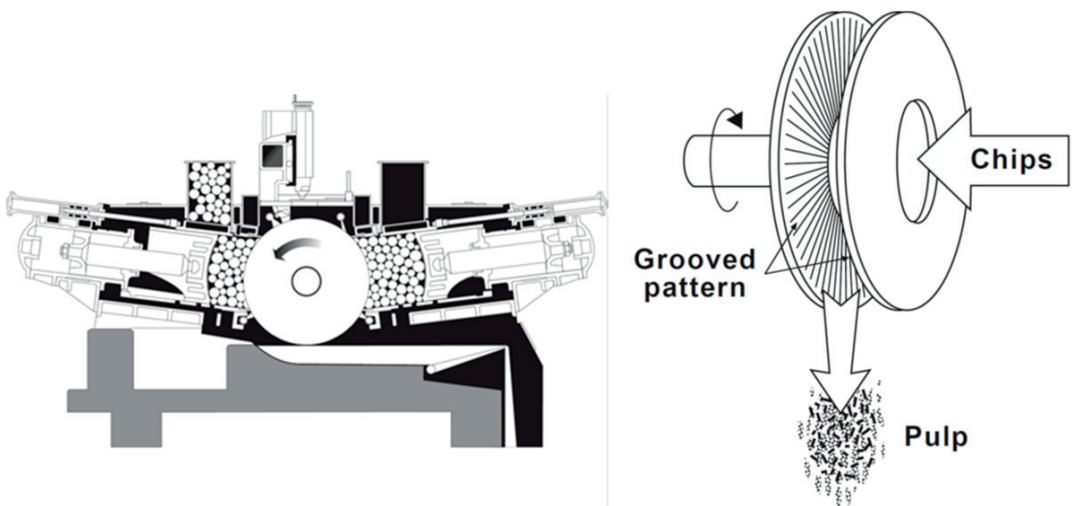
Fig 1. Principles of grinding (left, Liimatainen et al. 1999) and refiner-based mechanical pulping (right, Tienvieri et al. 1999).

The structure of softwood fiber cell wall and the composition of the major constituents in it are shown in *Fig 2*. As the yield from the mechanical pulping processes is high, the pulp composition is approximately the same as in wood. The bleaching of mechanical pulps is referred to as lignin-retaining bleaching and, therefore, the chemical composition does not change that much either during the bleaching. The brightness typically improves by 15–20%-units (from ~60 % to ~75–80 %) during the peroxide bleaching and the yield is 97–98 % (Lindholm 1999).
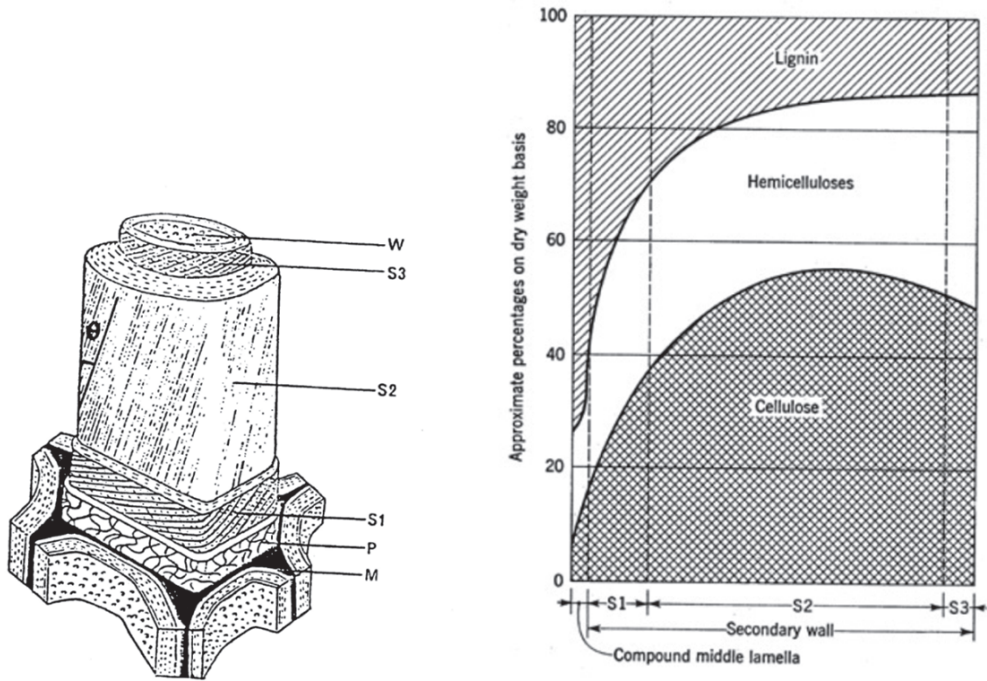
Fig 2. Structure of softwood fiber cell wall (left, Salmén et al. 1999; Ilvessalo-Pfäffli, Laamanen) composed of the middle lamella (M) and the four fiber walls (P, S1, S2 and S3) and distribution of the major chemical components in the softwood fiber cell wall (right, Salmén et al. 1999; Panshin, DeZeeuw 1970).

A typical pulping line for peroxide-bleached thermomechanical pulp (TMP) is shown in *Fig 3*. The process starts with debarking and chipping of wood logs or handling of saw mill chips. The chips are washed and preheated before fed to the refiners. After the refining stages, the latency of the fibers is removed, the pulp is screened, the rejected material is re-refined, the pulp consistency is increased by pre-dewatering and pressing, the pulp is bleached and pressed, and finally stored before fed to the paper machine.

Fines have traditionally been defined as the fraction of a fiber suspension that passes a 200-mesh wire (Luukko 1998). The fines content of mechanical pulps is relatively high. In a very coarse TMP (CSF 700 ml), the fines content (proportion of the pulp that passes the 200 mesh wire i.e. proportion of P200 fraction) is approximately 15 %, and the subsequent mechanical treatment can increase the fines content to above 30 %. The typical fiber length distributions of mechanical pulps are shown in *Fig 4*. The specific surface area of shorter fractions is higher than that of longer fractions (*Fig 4*).
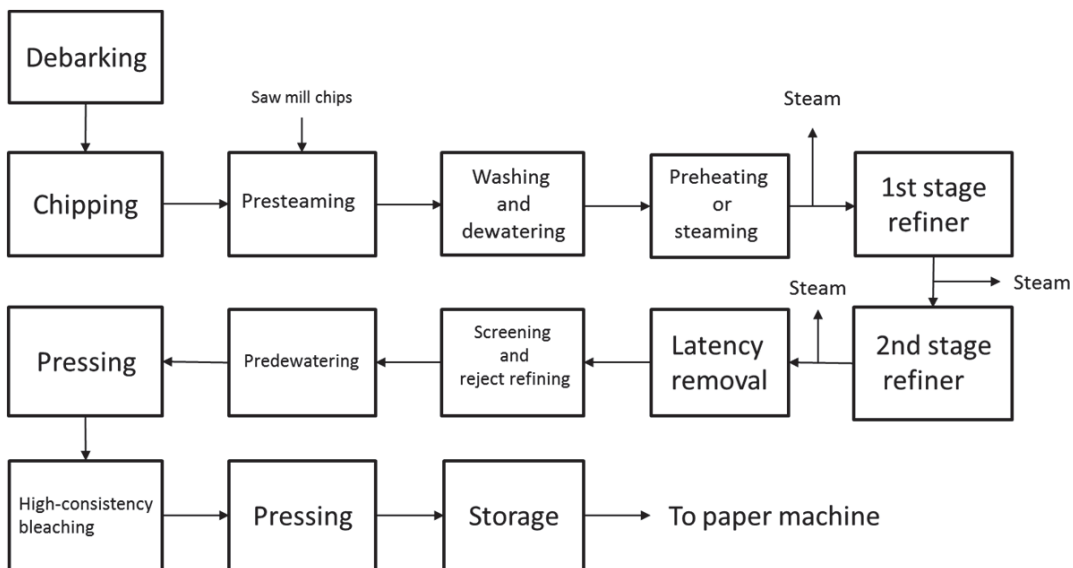
Fig 3. A typical pulping line for peroxide-bleached thermomechanical pulp (TMP). (Drawn based on Jussila et al. 1999; Tienvieri et al. 1999).
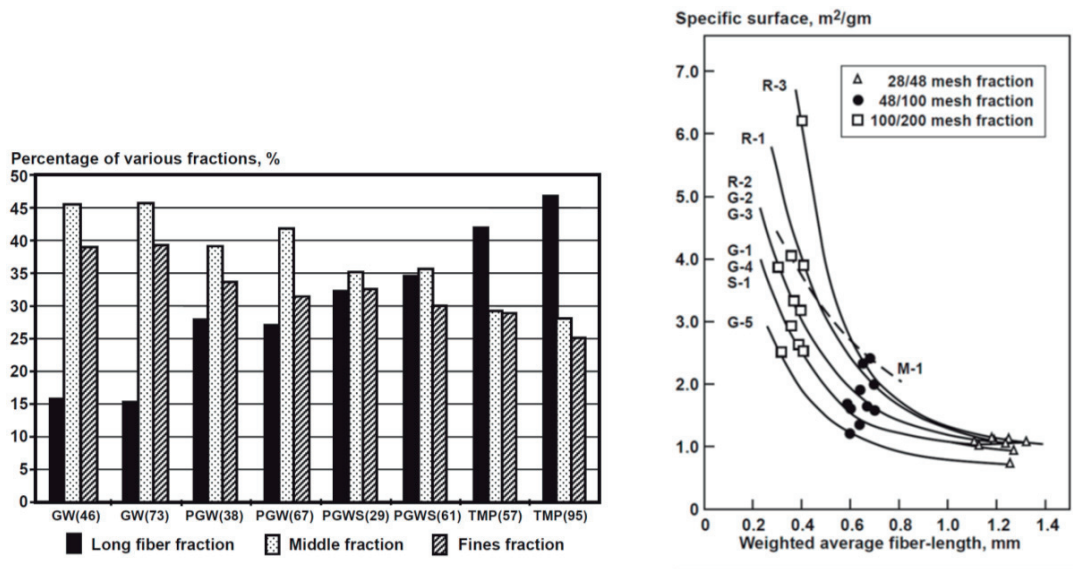
Fig 4. Typical fiber length distributions (left, Vanninen 1996; Heikkurinen, Leskelä 1999) and the specific surface of fractions (right, Forgacs 1963; Heikkurinen, Leskelä 1999) of different mechanical pulps. Freeness values of the pulps are shown inside the parantheses (left). From the ten pulps (right), three are refiner mechanical pulps (R) and the rest are groundwood pulps (G, S, M).

The fines fraction of mechanical pulps is important for both the optical and mechanical paper properties. The brightness is determined by the balance between the light scattering and light absorption coefficient. The fines particles increase the light scattering ability and, thereby, opacity and in most cases brightness by

providing a large specific surface area in the sheet. On the other hand, the fines fraction usually has a higher lignin content (Chang et al. 1979; Sundberg et al. 2003; Kangas, Kleen 2004) than the fiber fraction and, therefore, a higher light absorption coefficient and it is also more susceptible towards darkening. In addition, fines collect light-absorbing dissolved and colloidal substances from the circulation water very effectively due to their large specific surface area. Usually, the increased light scattering dominates and the net contribution of the fines to the brightness is, in most cases, positive (Rundlöf et al. 2000a, 2000b).

In the production of mechanical pulp approximately 2–5 % of the wood material is released from the fiber material and become dissolved or dispersed in the process waters (Holmbom 1996). These dissolved and colloidal substances (DCS) in mechanical pulp waters are mainly lipophilic extractives, hemicelluloses, lignin, and lignans (Sundberg et al. 1994b). Although the chemical composition of the fiber material does not change drastically during the peroxide bleaching, the dissolved and colloidal substances released from peroxide-bleached mechanical pulp have a totally different composition than those from unbleached mechanical pulp. Most of these changes are due to alkaline conditions. The major changes that alkaline conditions cause are the release of acetic acid from deacetylation of dissolved glucomannans, formation of pectic acids from demethylation of pectins, an increased amount of anionic groups both in pulp surfaces and in water phase, loss of steric stabilization and an increased amount of extractives that are removed from fibers into the water (Holmbom et al. 1991; Sundberg et al. 2000; Holmbom, Sundberg 2003; Sundberg 2004). The change in dissolved and colloidal substances caused by peroxide bleaching is shown in *Fig 5*.
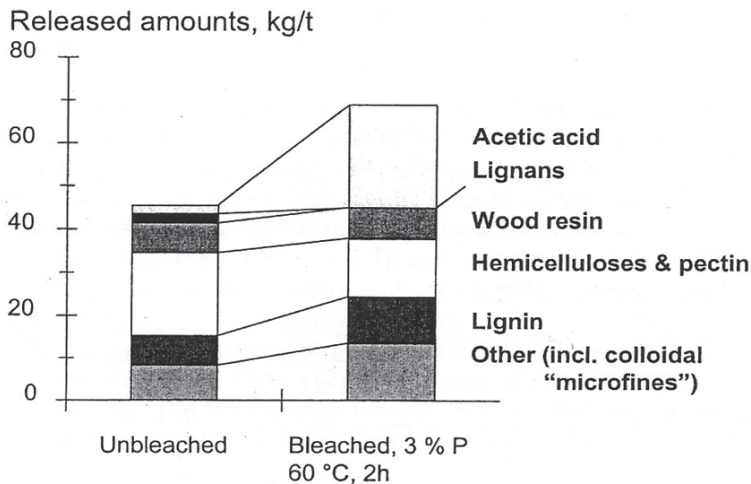
Fig 5. The change in dissolved and colloidal substances caused by alkaline peroxide bleaching. (Holmbom, Sundberg 2002).

The changes in lignin structure during peroxide bleaching are not fully known. Peroxide bleaching decreases light absorption in the whole visible range, especially in the 300 nm range. The change in the range of 300

nm is probably due to the destruction of quinoid groups and coniferyl aldehyde groups (Heitner, Schmidt 1991). It is not fully known which chromophores are able to resist peroxide bleaching. It is assumed that ortho- and para-quinoid groups are mainly responsible for the light absorption and color of peroxide-bleached mechanical pulp (Holmbom et al. 1991).

The colloidal extractives occur in process waters mainly as droplets with a diameter in the range of 0.1–2 μm. Peroxide bleaching does not affect extractives notably. Lipophilic extractives that occur in hydrophobic aggregates do not react with peroxide. Only dissolved components, e.g. resin acids, lignans, and stilbenes, react with peroxide, consume it, and are oxidized/degraded (Ekman, Holmbom 1989; Holmbom et al. 1991). Although the extractives are only slightly changed during peroxide bleaching, their colloidal stability is completely changed. In unbleached mechanical pulps dissolved glucomannans act efficiently as sterical stabilators for the wood pitch. As the concentration of dissolved glucomannans decreases in the peroxide bleaching, the extractives are easily flocculated in the presence of salts, and especially in the presence of multivalent ions e.g. calcium and aluminum (Sundberg et al. 1994a, 1994b; Sundberg 1995; Holmbom, Sundberg 2003). Norway spruce (*Picea abies*) does not contain a large enough amount of colored extractives to affect the pulp brightness, but the removal of the wood pitch from the fibers into the water and possible re-adsorption on the fiber surfaces can reduce the bonding capacity of the fibers (Lindholm 1999).

4.2 Fillers

4.2.1 General

Paper fillers are fine, white pigments powders. The purposes of using fillers are to improve optical properties and printability of paper and to cut manufacturing costs. Fillers fill the spaces between fibers, smoothen the surface and improve formation, opacity, dimensional stability, gloss, and usually also brightness. Most fillers are cheaper than fibers, which reduces the manufacturing costs. They are added at levels up to 20–35 % of the paper furnish. Exceptions are specialty pigments, which are expensive and added in lower amounts, approximately 5–10 %, in order to achieve specific paper properties (Krogerus 2007).

Fillers have also undesirable effects on paper and papermaking relating to the loss of bonding between fibers. This leads to lowered strength properties and stiffness as well as increased linting in printing. Furthermore, the consumption of chemical additives increases and the poor retention of fillers may cause two-sidedness of the paper. In addition, abrasion on the paper machine may increase, which, for example, decreases the operating life of fabrics. Due to their large density, fillers can settle in the water systems. Therefore, the agitation in the paper machine chests has to be intensive enough and the flow rates in large piping systems high. Settled filler easily forms deposits and can thus cause problems in the circulation waters.

Calcium carbonate and kaolin are the main fillers used in paper making. Also calcium sulfate has been used on some paper machines. Fillers are usually manufactured from natural minerals, but calcium carbonate and calcium sulfate can also be made synthetically by precipitation.

4.2.2 Precipitated Calcium Carbonate (PCC)

Precipitated calcium carbonate is mostly used in North America, because the resources of natural calcium carbonate are insufficient in that part of the world. The properties of PCC differ notably from natural calcium carbonates. The specific mineral properties of PCC particles (e.g. crystal form, size, shape) can be tailored by the manufacturing conditions to improve certain paper properties. The crystal forms of PCC are aragonite and calcite. Aragonite particles are typically needles and aggregates of needles, whereas calcite is precipitated as scalenohedral or rhombohedral agglomerates, or prismatic particles (Krogerus 1999, 2007). In contrast to most of the other fillers used in paper making, the surface of PCC can possess a cationic charge.

The starting material of the precipitation process of PCC is usually crushed limestone. It is burned in an oven at temperatures around 1000 °C to form calcium oxide, CaO. CaO is slaked with water to form a calcium hydroxide ($Ca(OH)_2$) slurry. Carbon dioxide (CO_2) gas is introduced into the slurry under controlled conditions to form the precipitated calcium carbonate crystals. The flowsheet of the precipitation process is shown in *Fig 6*.
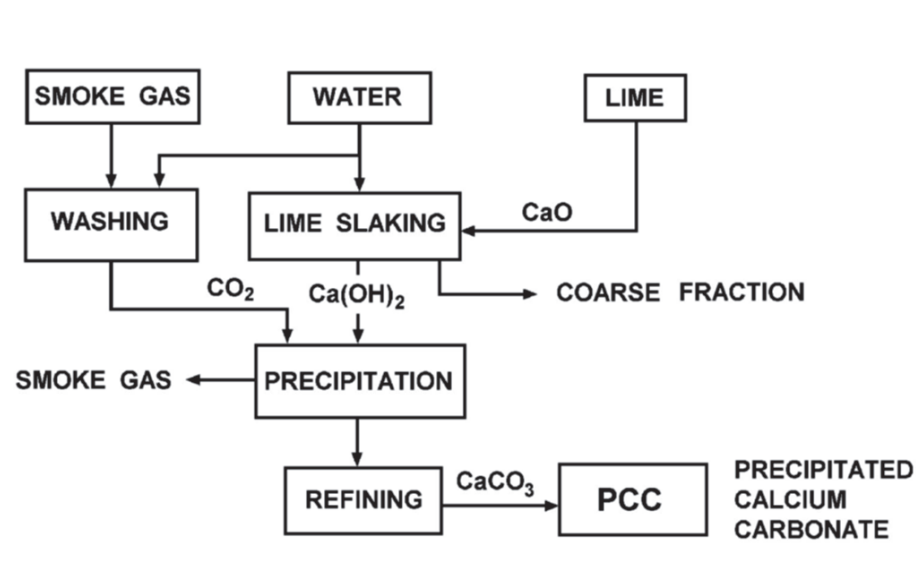
Fig 6. Flowsheet of the manufacture of precipitated calcium carbonate (PCC). (Krogerus 1999).

The solubility and the rate of decomposition of calcium carbonate fillers depends mainly on their acidity, particle size, amount of dissolved CO_2, and temperature. At acidic pH, the dissolved carbonate ions decompose forming CO_2 gas which accelerates the dissolution of solid calcium carbonate (Jaakkola, Manner 2001). The solubility of calcium carbonate fillers as such is very small, only 25 mg/l, but significantly higher in carbon dioxide containing waters, even 1500 mg/l (Krogerus 2007). If the pH level drops below 6.5–7.0, the solubility increases dramatically while the increasing temperature decreases the solubility. The solubility of calcium carbonate as a function of pH is shown in *Fig 7*.
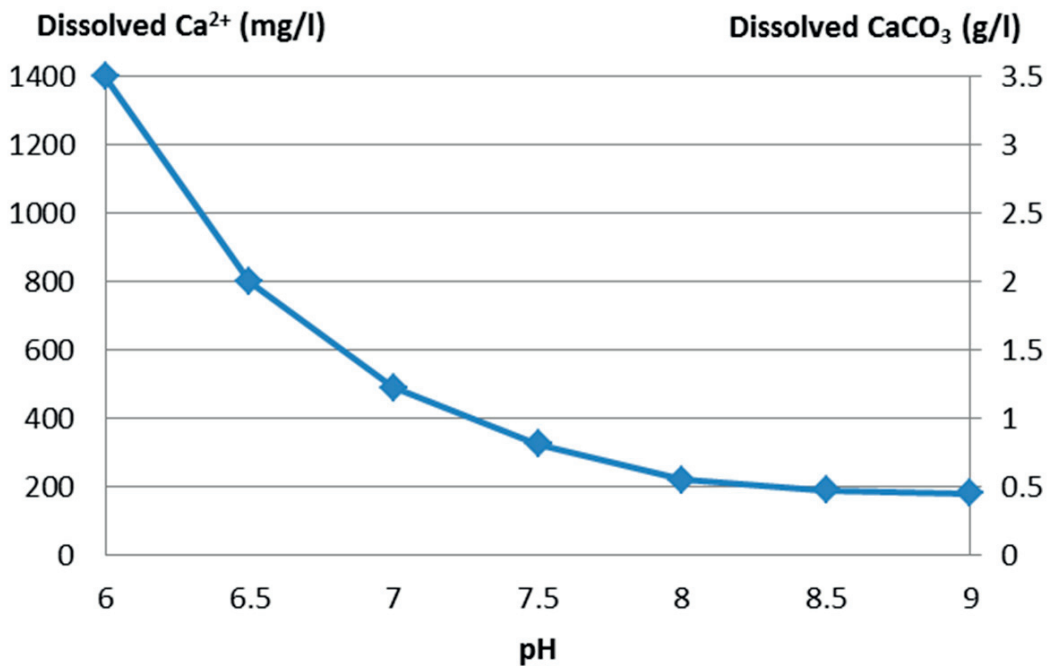
Fig 7. Solubility of calcium carbonate as a function of pH at 20 °C. (Drawn based on Lehtinen 2000).

4.2.3 Precipitated Calcium Sulfate (PCS)

Calcium sulfate, often called gypsum, can be manufactured from natural minerals by mechanical grinding (GCS) or synthetically by precipitation process (PCS). The crystallization process of precipitated calcium sulfate (PCS) resembles that of PCC. In the manufacturing process, hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) is used as raw material and the final product is precipitated as dihydrate ($CaSO_4 \cdot 2H_2O$) in water. The particle size and shape can be tailored with the process conditions. Usually, the PCS particles are needle-shaped or platy but also other particle shapes can be obtained. The final product is sold as slurry or dried powder. The flowsheet of the manufacture of PCS is shown in *Fig 8*.
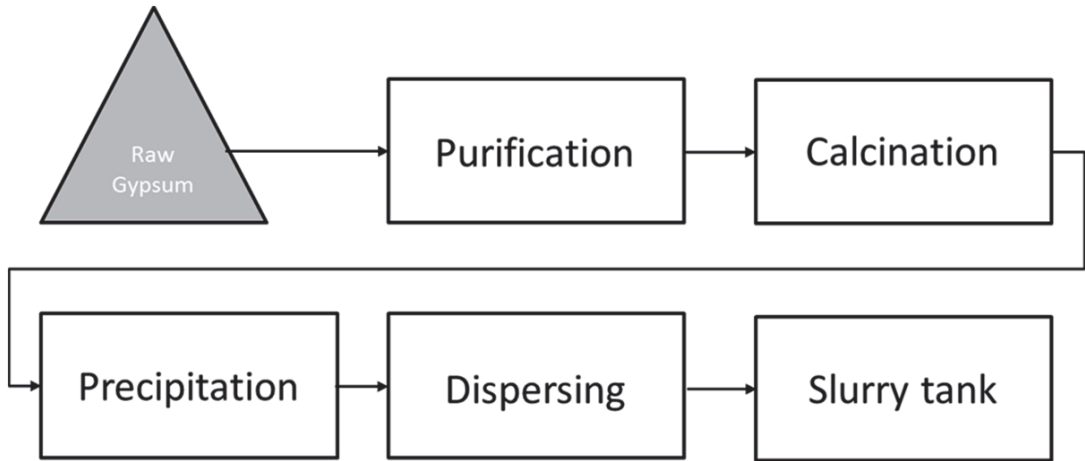
Fig 8. Gypsum pigment process based on precipitation. (Aarni, Turkki 2009).

The solubility of gypsum in water is rather extensive. The rate of solubility depends on the particle size: the finer the particles, the faster the dissolution. A saturated calcium sulfate solution contains approximately 2.1 g of $CaSO_4/l$. This solubility equilibrium is easily reached in the water circulations of a paper machine and it raises the calcium concentration of circulation water to the level of approximately 580 mg/l. When it comes to solubility, it makes no difference whether gypsum pigment is used in acidic or neutral papermaking processes (*Fig 9*). The dependency on the temperature of the solubility of gypsum is also fairly low (*Fig 9*). Gypsum itself is a neutral salt that, unlike carbonate, does not buffer the pH of circulation water. As gypsum is dissolved, gas is not released as when carbonate is decomposed (Lehtinen 2000).
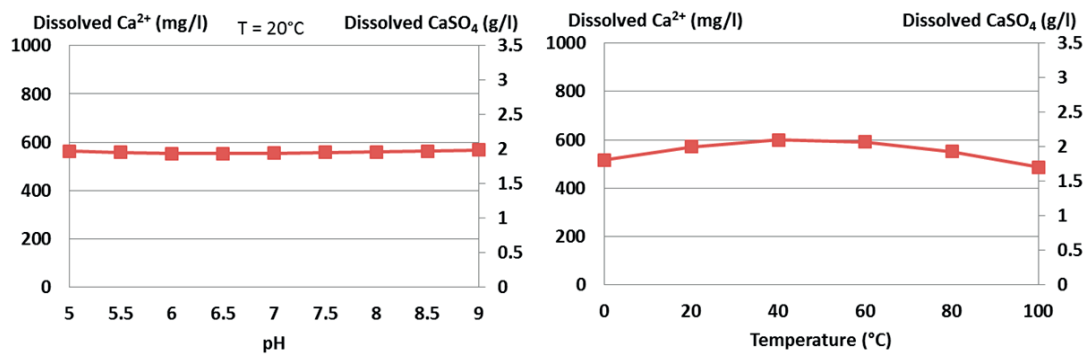
Fig 9. Solubility of gypsum as a function of pH (left) and temperature (right). (Drawn based on Lehtinen 2000).

4.2.4 Interactions between fillers and DCS

The interactions between fillers and wood-based dissolved and colloidal substances (DCS) comprise a complex system. The increase in the pH increases the degree of dissociation of carboxylic groups in DCS, thus enhancing the anionic charge (Saarimaa et al. 2006). The surface chemistry of the filler depends on pH, electrolyte concentration, the dissolution of ions from the particle surfaces, and the adsorption of hydrophilic or hydrophobic substances.

Both polysaccharides and extractives can be adsorbed onto the fillers. They can also be adsorbed as aggregates on the filler surface (Willför et al. 2000). The amphoteric surface of the fillers makes it possible for the filler pigments to form aggregates of their own. In contrast to most of the other fillers used in papermaking, the surface of PCC can possess a cationic charge. According to Miyanishi et al. (2000), anionic DCS in bleached TMP filtrate will adsorb on PCC until the anionic demand of PCC has been neutralized. Adsorption of DCS on different fillers at pH 5 and 8 has been studied by Willför et al. (2000). Compared to kaolin or talc, PCC or GCC do not adsorb DCS very well from peroxide-bleached TMP water. Kaolin adsorbs glucomannans and anionic pectins. Kaolin and talc adsorb extractives, but significantly only at pH 5. The most possible adsorption mechanism of lipophilic extractives and lignans is the adsorption to the hydrophobic areas of the filler pigments, although a co-aggregation with micro-fines and dissolved carbohydrates is also possible. According to the latter study, the amount of kaolin or talc needed to obtain a substantial adsorption of DCS was 10 g/l. According to both of these mentioned studies (Miyanishi et al. 2000; Willför et al. 2000), colloidal substances are adsorbed on the fillers more preferentially than dissolved substances.

The circulation water of a paper machine can contain high concentrations of calcium ions released from fillers. Calcium ions may interact with DCS. The lipophilic extractives and carbohydrates containing galacturonic acid (e.g. anionic pectins) of peroxide bleached mechanical pulp are flocculated in the presence of multivalent cations e.g. calcium (Sundberg et al. 1994a, 1994b; Sundberg 1995; Holmbom, Sundberg 2003; Saarimaa et al. 2006). Hence, in the circulation water of a paper machine using calcium sulfate or calcium carbonate as filler, the colloidal wood pitch in the circulation water is at least partly aggregated. Uncontrolled aggregation of lipophilic extractives can impair the runnability of the paper machine and the quality of produced paper.

4.3 The wet end of a paper machine

4.3.1 Definitions

The wet end of a paper machine is officially limited to the mixing chest, machine chest and a wet pressing section as well as the processes between them (*Fig 10*). In practice in paper mills, the wet end is comprehended to include only the headbox, the wire section, and the short circulation (Häggblom-Ahnger, Komulainen 2000). The short circulation refers to the system in which paper machine wire water is separated from the stock in web forming and used for dilution of the thick stock to be delivered to the headbox (Weise et al. 2008).
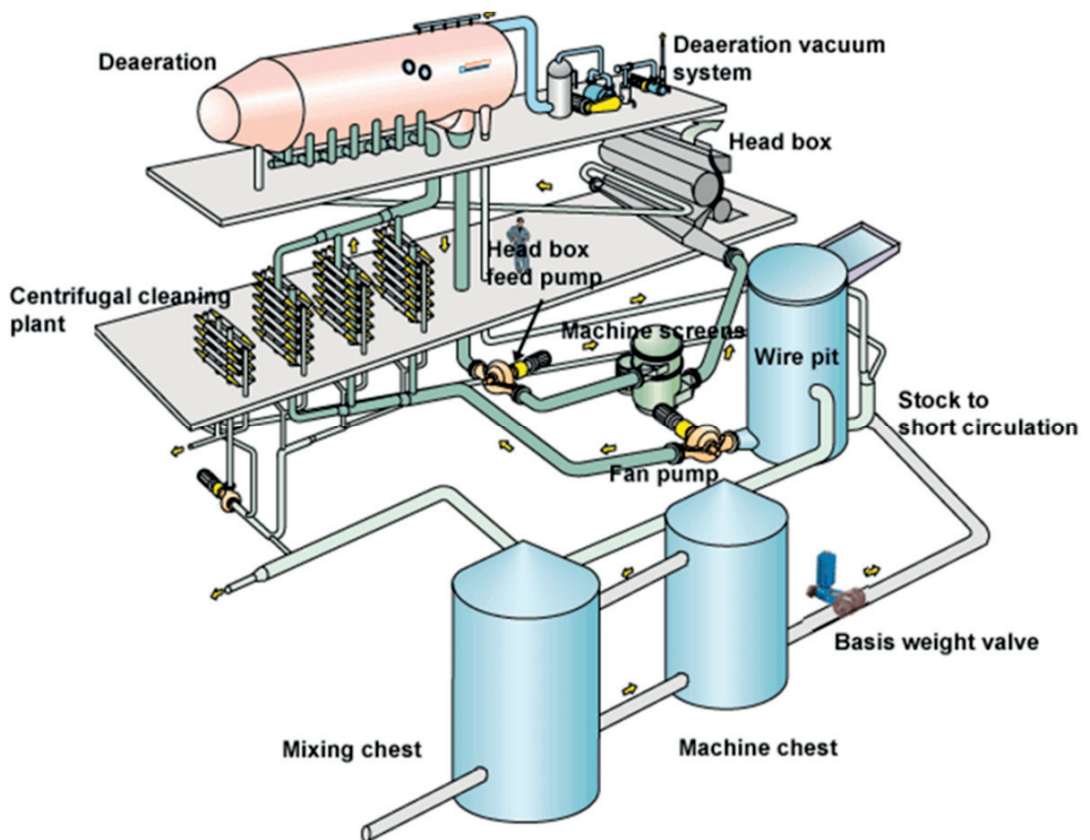
Fig 10. The wet end of a paper machine. (KnowPap 2013).

4.3.2 Retention

Retention is a measure to describe the proportion of the stock that is retained in the paper web from the flow from the headbox to the wire on a paper machine wire section. A rough estimate for the retention can be calculated using *Eq. 1* (Häggblom-Ahnger, Komulainen 2000):

$$\text{Retention}=\frac{c_{HB}-c_{WW}}{c_{HB}}\cdot100\%$$
(1)

where:

c_{HB} is consistency in the headbox,

c_{WW} is consistency of the wire water.

When it comes to avoiding darkening, a high retention is desirable, because it shortens the residence time of the stock components in the short circulation. However, a maximum retention is not usually the primary target, because it can cause poor formation of paper and problems in dewatering and needs a high dose of retention chemicals. Retention can be divided into mechanical and chemical retention. Chemical retention occurs primarily already immediately after the headbox before the web forming and it is most important for the small particles (e.g. fillers and fines material) that are chemically agglomerated with the fiber material using different retention aids. Mechanical retention plays a more important role at the end of the wire section where the wet paper web is already formed. Retention can be determined individually for the different stock components. As the particle size of the fillers and fines is smaller than that of the long fibers, their mechanical retention is also lower. This leads to large filler and fines concentrations in the short circulation. Usually fiber retention is 50–90 % while the filler retention can be as low as 20–30 % (Huuskonen, Eiroma 1983).

4.3.3 Temperature and pH

The temperature and the pH level are two of the most important basic measurements in the wet end. The temperature is typically at a range 40–60 °C (Sharp, Bennett 1997). Increasing the temperature increases the rate of chemical reactions and the dissolution of substances. In contrast, a decreased temperature causes precipitation of dissolved substances. Therefore, it is very important to stabilize the process temperature and to avoid temperature shocks. The typical pH ranges for acid and neutral-alkaline white waters are 4–5 and 6.5–8, respectively (Sharp, Bennett 1997). Increasing the pH level increases the solubility of wood

components and, thus, the amount of anionic trash. In addition, the surface charge of the fiber material increases and bacterial activity escalates. The decrease in the pH may cause precipitates that are practically insoluble and disturb the process significantly. Whether the process is acidic or neutral-alkaline, a constant pH is always desirable and pH shocks should be avoided. The pH control of the wire pit is developed to balance the chemical conditions in the wet end. The monitoring system of the wire pit controls the feed flow of pH chemicals, such as sodium hydroxide, sulfuric acid or aluminum sulfate automatically on the basis of the measured data. Over the past years, carbon dioxide gas has been used to replace sulfuric acid or aluminum sulfate as the chemical of choice (Grist, Canty 2006). The benefit of carbon dioxide is that it leaves no residual sulfate or aluminum ions in the wet end allowing the water to be circulated longer before its treatment is required.

4.3.4 Conductivity, turbidity and cationic demand

Conductivity describes the salt concentration of the suspension and dissolved inorganic matter increases it. It is sufficient as a measuring method when only monovalent cations (e.g. H^+, Na^+) are present. The white water may contain relatively large amounts of polyvalent cations (e.g. Ca^{2+}, Al^{3+}) and therefore the specific measurement of different cations may be reasonable, especially, if they cause problems.

Turbidity describes the amount colloidal substances suspended in a liquid. It requires that fibers and fillers are removed from the suspension before the measurement. The measurement is based on light scattering. The higher the amount of colloidal substances, the higher the turbidity. The amount of lipophilic extractives in the water has been shown to correlate well with turbidity at low pH levels, where lipophilic extractives are mostly present in a colloidal state (Holmbom, Örså 1993; Käyhkö 2002).

The stock contains many solid particles, such as fibers, fines, and fillers that usually all have a negative charge. In addition, the DCS usually have a large capacity of negative charge. The cationic demand is a measure of the amount of anionic polymers in the suspension. It can also be used to determine the amount of anionic trash. Examples of total consistency, ash consistency, pH, conductivity, turbidity, and cationic demand of the centrifuged wire water samples of different paper grades containing mechanical pulp are shown in *Table 1*.

Table 1. Properties of wire water samples of different paper grades containing mechanical pulp. (Nguyen 1997).

	Newsprint	SC	LWC
Total consistency (mg/l)	4719	6665	3094
Ash consistency (mg/l)	70	4341	1133
pH	6.54	4.54	6.47
Conductivity (mS/m)	37.5	117.4	118.6
Turbidity (NTU)	307	3.6	6.2
Cationic demand (µmeq/l)	47.1	7.6	7.7

4.3.5 Ion concentrations

The white water of a paper machine contains relatively large amounts of different ions. These ions can be carried into the water flows with pulps, fresh water, fillers and chemical additives or they can be dissolved from the process equipment. Ion concentration examples of the wire waters of different paper grades containing mechanical pulp are shown in *Table 2*.

Table 2. Ion concentrations (mg/l) of wire water samples of different paper grades containing mechanical pulp. (Nguyen 1997).

	Newsprint	SC	LWC
Cl	19.4	9.1	8.0
Ca	10	6	17
Si	0.7	0.7	0.2
Na	45	200	200
K	19	4	10
Mg	2.3	1.7	5.5
Al	0.225	0.240	0.550
Mn	1.0	0.067	1.3
Ba	0.065	0.020	0.12
Fe	0.055	0.36	0.63
Cu	0.030	0.037	0.045

4.3.6 Shear rate

There are several elements in the wet end of a paper machine that generate high shear rates (d´Incau 1983). Pumps can generate a very large shear rate, especially at the inlet in the eye of the impeller (10^5 s^{-1}). A high shear rate is also created in the slice and in the turbulence generator of a headbox (10^4 s^{-1}). The mean shear rate at the center of a centricleaner, inside the perforations of a screen basket, and at the discharge side of a pump impeller has a typical value of 10^3 s^{-1}. Drainage elements, such as drainage foils and table rolls, create a comparatively low shear rate (10^2 s^{-1}). The time of residence of particles in the various stock approach system elements and their regions varies considerably. For example, the fluid will experience a shear rate of 10^4 s^{-1} for 2–3 ms in the headbox slice, whereas it will undergo a shear rate of 10^3 s^{-1} for approximately 50-100 ms at the discharge side of the impeller in a pump. The longest residence times, on the order of 10 s depending on the length of the pipe, are found in the piping system, where the shear rate is relatively low

(10^2 s^{-1}). Furthermore, the percentage of the flow that is affected by the shear rates changes from one point to another. For instance, at the headbox slice approximately 5–10 % of the flow experiences a shear rate of 10^4 s^{-1}, whereas in a centricleaner 100 % of the flow is strained by a shear rate higher than 10^3 s^{-1}. Increasing running speed of a paper machine increases the shear rates generated to the pulp (Tam Doo et al. 1984).

4.4 Measurement of optical properties of paper

4.4.1 Measurement principles

In the measurement of optical properties of paper, the intrinsic reflectance factor (R_∞) and the reflectance factor over a black background (R_0) are measured. The intrinsic reflectance factor, R_∞, is the reflectance factor of a layer or pad of material of opaque thickness (transmission = 0), i.e. such a thickness that the reflectance factor stays constant when the thickness of a pad is increased by adding more sheets in the pad. R_0 is a measure of non-transparency of the material. The measurement principles of R_∞ and R_0 are shown in *Fig 11*.

R_∞ — Opaque pad of paper

R_0 — A single sheet over a black background
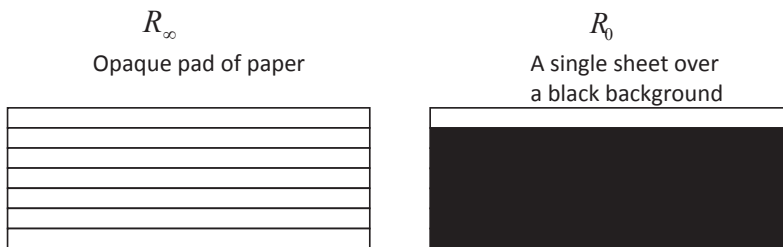
Fig 11. The principles of optical measurement of paper. R_∞ is the reflectance factor for an opaque pad of paper (left) and R_0 is the reflectance factor for a single sheet over a black background (right). (Pauler 2002).

4.4.2 The most common parameters describing the paper brightness

To characterize the brightness of a material, which is almost totally white, such as paper, is quite problematic. A color is a three dimensional property and, therefore, it is impossible to describe the difference between color and white (colorless) using only one measure. The fact that paper is naturally yellowish helps somewhat. The two most common standardized measurement methods of brightness are ISO brightness (ISO 2470) and Y-value (ISO 5631). (Aaltonen 1985).

ISO brightness, R_{457}, is the intrinsic reflectance factor of paper measured with $d/0^O$ geometry. The peak of the sensitivity spectrum corresponds to a wavelength of 457 nm. ISO brightness is a good measure

determining the effects of bleaching on the brightness of pulp because the bleaching operation increases reflectance particularly at the blue end of the spectrum. ISO brightness is not a good measure of lightness because the measurement disregards a large portion of the visible spectrum of light. ISO brightness does not correlate the impression of whiteness but it indicates how slightly yellow the pulp is. The reflectance factors including ISO brightness, R_{457}, is defined as percentages. The ISO brightness of a black, nonreflecting material is 0 % and that of a perfect diffuser 100 %. (Vaarasalo 1999).

The Y-value, which is one of the three tristimulus values X,Y,Z, is often used as a single measure of the reflectivity of the material (Pauler 2002). The Y-value is the intrinsic reflectance factor measured with an instrument whose response to the wavelengths of light corresponds to the response of healthy eye. The center of the response is at 557 nm and the spectrum covers the entire visible range of light of 400–700 nm. Even though the Y-value is related to the sensitivity of the eye to light, it is not sufficient to measure the concept of whiteness. Y-value is an indicator of the perceived lightness (Vaarasalo 1999). *Fig 12* shows the sensitivity spectrum of ISO brightness and Y-value.
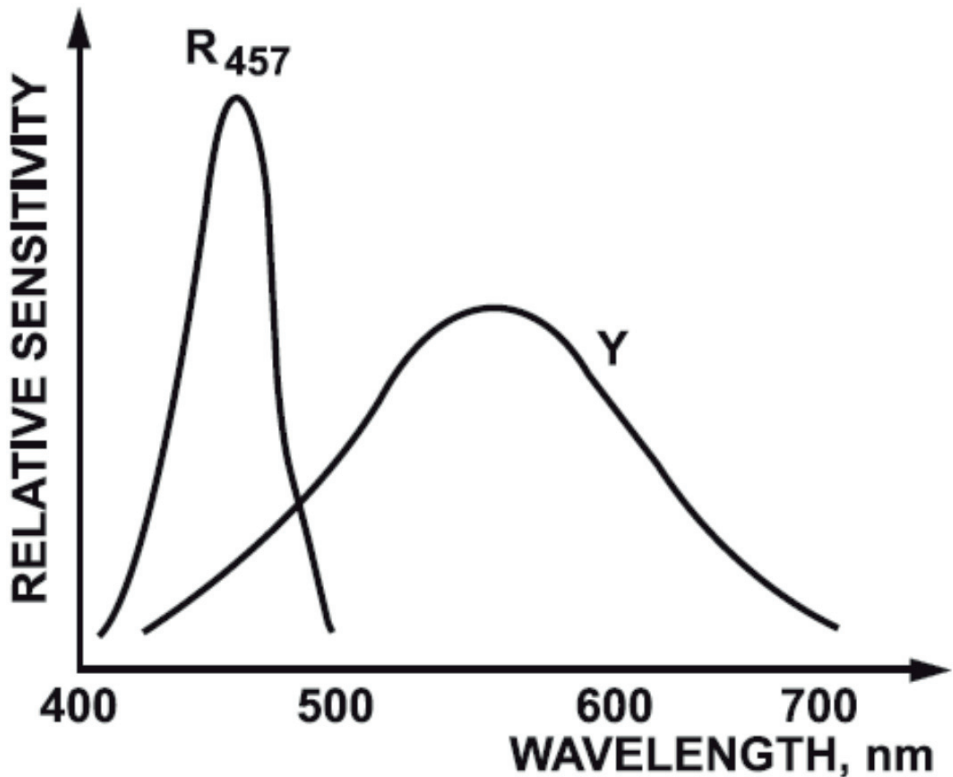
Fig 12. Sensitivity distribution of ISO brightness (R_{457}) and Y-value (R_{557}). (Vaarasalo 1999).

4.4.3 Light scattering and light absorption

The light scattering coefficient, s (m^2/kg), and the light absorption coefficient, k (m^2/kg), are the theoretical quantities connected with the Kubelka-Munk theory (Kubelka, Munk 1931). A measure of scattering ability of an infinitely thin layer of material is signified by an s. Respectively, k indicates the ability of an infinitely thin layer to absorb light.

The light scattering coefficient depends greatly on the refractive index and on the number of internal surfaces of the material. In case of paper, the most important properties are the refractive index of all paper raw material components, the number of optical surfaces, and the number and the size distribution of particles that are smaller than half of the wavelength of incoming light. The higher the light scattering, the lighter the material appears. The most effective scattering ability is with particles which have the diameter very close to the wavelength of incoming light. From that it is easy to understand that the wavelength of incoming light also affects the light scattering coefficient. (Paulapuro 1985).

Light absorption coefficient is directly related to the nature and intensity of chromophoric structures (molecular groups which give color) present in paper. The higher the light absorption, the darker the material appears. Many paper making processes influence the light scattering and/or the light absorption of pulp or paper. For example, the light absorption of pulp decreases in bleaching, while the addition of filler usually increases the light scattering of the produced paper. The interaction between light scattering and light absorption determines how we perceive the material. (Pauler 2002).

4.4.4 Kubelka-Munk theory

The dependence of brightness (R_∞ *100, measured at 457 or 557 nm) on both light scattering (s) and absorption (k) is described by the Kubelka-Munk theory (Kubelka, Munk 1931):

$$R_\infty = 1 + \frac{k}{s} - \sqrt{\left(\frac{k}{s}\right)^2 + 2\left(\frac{k}{s}\right)}$$

(2)

or

$$\frac{k}{s} = \frac{(1 - R_\infty)^2}{(2R_\infty)}$$

(3)

and

$$s = \frac{1}{w\left(\dfrac{1}{R_\infty} - R_\infty\right)} \ln \frac{(1 - R_0 R_\infty)}{\left(1 - \dfrac{R_0}{R_\infty}\right)}$$

(4)

where:

R_∞ is the reflectance/reflectivity of paper sheet of infinitive thickness,

R_0 is the reflectance of a single paper sheet over a black backing of nil reflectance,

k is the specific light absorption coefficient (m^2/kg),

s is the specific light scattering coefficient (m^2/kg),

w is the sheet grammage (kg/m^2).

After the measurements of R_∞ and R_0, s can be calculated from *Eq* 4 and after that k from *Eq* 3. In practice, paper does not fulfill all the requirements of Kubelka-Munk theory. The most important sources of error are (Paulapuro 1985):

- The assumption that paper is an optically homogeneous material and s and k stay constant irrespective of the direction of light heading inside the paper. Material is not homogenously distributed in the z-direction of a paper, especially fines and fillers are not. s and k values calculated from the measurements are therefore averages of all local s and k values inside the paper.

- The assumption that s and k stay constant when changing the grammage of paper or coating if the paper raw material composition stays constant. In practice it has been observed that the structure of paper changes slightly when changing the grammage of paper.

- The assumption that the incoming light is monochromatic. The interaction between the material layer and light is selective regarding the wave length. In measurements, the incoming light usually includes many different wave lengths. The s and k values measured with different spectral characteristics are not comparable.

- The assumption that incoming light, as well as traveling light inside the paper, is diffuse.

- The gloss is not taken into account in the theory but it is assumed that all the interaction between light and paper takes place inside the material layer where the light scatters and is absorbed. The bigger gloss the bigger inaccuracy in the measurements.

The assumption that the Kubelka-Munk light scattering coefficient, s, can be used as a measure of the ability of a sheet structure to scatter light, independently of the light absorption properties of the same structure is not totally valid. In the Kubelka-Munk theory, the light absorption (k) is calculated from the light scattering (s) and the measured reflectances (R_∞ and R_0) using *Eq* 3 which means that the deviation in s will also affect k. It has been observed that when color was added to a sheet structure without changing it e.g. by addition of dye (Rundlöf, Bristow 1997) or by thermal ageing (Karlsson et al. 2012), light scattering (s) decreased in regions of the spectrum corresponding to the increase in light absorption (k). To overcome the errors introduced in the Kubelka-Munk modelling, advanced models have been developed. One such model is Discrete Ordinate Radiative Transfer model DORT2002 (Edström 2005), which takes anisotropic scattering into account and can calculate the optical response given almost any illumination and detection geometry. However, due to its ease of use and the sufficient accuracy, Kubelka-Munk theory is still widely used for practical purposes.

The effect of unit changes in the light scattering or light absorption coefficient on brightness depends on the current level of brightness, as illustrated in *Fig 13*, for which the curves were drawn using *Eq 2*. The effect of small changes in the specific light scattering coefficient is the greatest at low values of brightness, while small changes in the light absorption coefficient have only a small effect. On the contrary, at high values of brightness the light absorption coefficient plays a more important role.
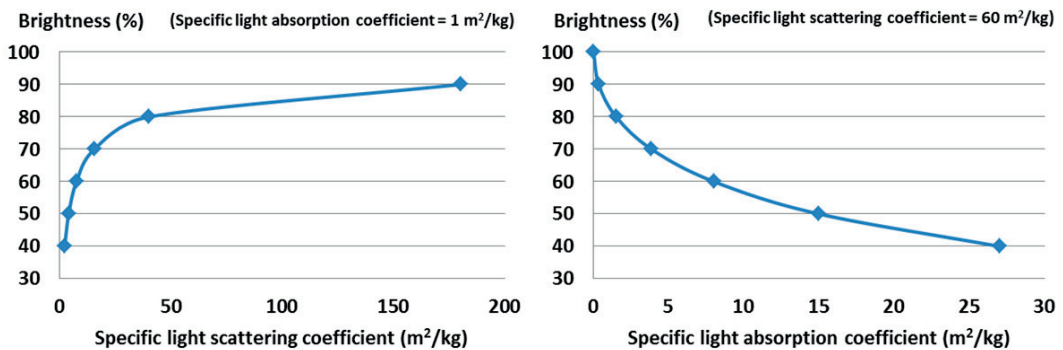
Fig 13. The effect of unit changes in the specific light scattering coefficient (left) and specific light absorption coefficient (right) on brightness. Values calculated using Kubelka-Munk equation.

Calculation of the optical behavior of paper is possible when the *s* and *k* of the raw material components are known. The overall optical properties are equal to the weighted sum of the optical properties of the raw material components comprising the sheet (Parsons 1942; Allison, Graham 1989):

$$P_{wp} = \sum (P_i X_i) \tag{5}$$

where:

P_{wp} is optical property (*k* or *s* value) of a sheet of whole pulp,

P_i is optical property of sheet of pure component *i*,

X_i is mass fraction of *i* in the whole pulp sheet

This additivity rule is inadequate. The rule is valid if the components do not react optically with each other. For example, the ratio of raw material components should not influence the fiber bonding ability. The components should also be evenly distributed. Nevertheless, in many cases the additivity rule is sufficiently accurate to determine the optical properties of the final product (Anjala 1985; Allison, Graham 1989).

4.5 Brightness reduction

Due to the reuse of white water and the fact that mechanical pulps are usually not thoroughly washed, the amount of DCS in the water systems of paper machine can rise high. In addition to reduced paper strength properties and paper machine runnability, these substances can also reduce paper brightness. According to many studies, dissolved lignin and its derivatives are responsible for the brightness decrease while colloidal extractives influence the reduced paper strength (Rundlöf et al. 2000c; Holmbom 1992; Kokko et al. 2004; Back et al. 2000; Lee et al. 2006; Rundlöf 2002). However, according to some studies (Francis, Ouchi 2001; Zhang 2000), the colloidal fraction is also responsible for the decrease in brightness whereas the dissolved fraction lowers the strength properties of paper.

The fraction of peroxide-bleached mechanical pulp that most interacts with DCS is the fines fraction. This is due to the large specific surface area of the fines that enhances the interaction ability. Because of smaller dimensions, most of the fines material ends up in the white water of a paper machine. According to Rundlöf (2002), the fines that have been recirculated for a period of time in the white water system have a higher light absorption than the fresh fines. The fines were fractionated from the white water using a Britt Dynamic Drainage Jar (BDDJ). In this fractionation, the amount of water needed was relatively low and the DCS were

not washed away. DCS could be removed by an acetone extraction or by a Bauer McNett (BMcN) fractionation. The acetone extraction and washing (BMcN) decreased the light absorption of the white water fines, but they were still darker than the fresh fines. This indicates that part of the darkening was attributed to the adsorption of DCS and part to the darkening of the fines, as such, during the circulation. The contribution of the addition of different types of fines to the light absorption coefficient of the handsheet is shown in *Fig 14*.
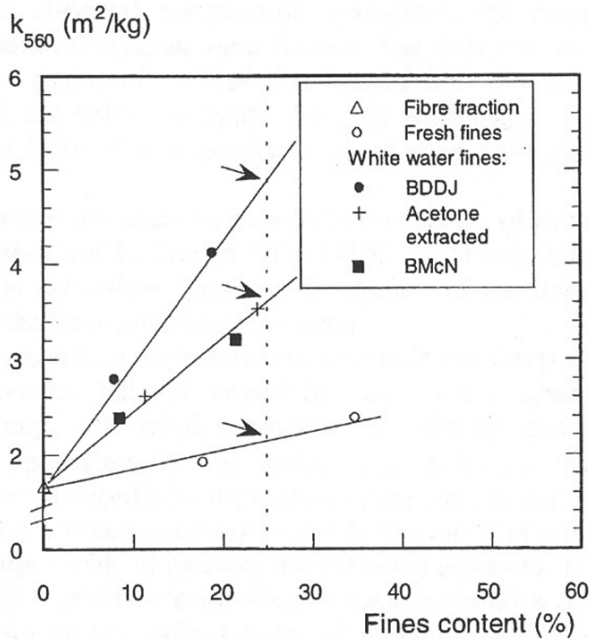
Fig 14. The light absorption coefficient (k_{560}) of handsheets prepared from fresh fines and differently treated white water fines added to the same fresh fiber fraction. The procedure used to fractionate the fines from the white water sample is shown as "BDDJ" for Britt Dynamic Drainage Jar and "BMcN" for Bauer McNett fractionator. (Rundlöf 2002).

The contributions of different types of fines in *Fig 14* to the Y-value of a sheet containing 25 % of these fines added to the fresh fiber fraction are shown in *Table 3*. The assumption was that the light scattering stays constant during the circulation and extraction (50 m²/kg). The increase in light absorption of the fines reduced the brightness of the sheet significantly.

Table 3. Calculated $R_{560} \approx$ Y-values of sheets containing 25 % of different types of fines added to the same fresh fiber fraction. (Rundlöf 2002).

	Fresh TMP fines	White water fines	White water fines, extracted
s_{560} (m²/kg)	50	50	50
k_{560} (m²/kg)	2.1	5.0	3.6
$R_{560} \approx$ Y-value (%)	74.9	64.2	68.5

In addition to wood-based dissolved and colloidal substances, white water contains also other detrimental substances. The most problematic fresh water compounds are humic acids, algae and transition metals. Humic acids, which are very similar to lignin containing phenolic groups, and metal ions are harmful to the brightness as well as to the brightness stability, because they are readily adsorbed on various pulp fibers and fines.

In addition to transition metal ions, also other ions can be carried into the system with fresh water, pulps, fillers and chemical additives or they can be dissolved from the process equipment. The effect of metal ions on the brightness of mechanical pulp has been studied to some extent (Forskåhl 2000; Janson, Forskåhl 1989; Ni et al. 1997; Konn 1998). According to Ni et al. (1997), Fe^{2+} and Fe^{3+}-ions have a significantly negative effect on the brightness of bleached mechanical pulps, while copper and aluminum ions have a smaller negative effect at the same concentration. The effect of calcium, magnesium, and manganese ions was found negligible in the same study. The brightness loss with metal ions present at concentrations typical for tap water can be as high as 4 %-units (Ni et al. 1997). The darkening is explained by the formation of colored complexes between lignin functional groups and metal ions. Other reasons for darkening could be metal ion-catalyzed oxidation of functional groups on fiber surfaces or oxidation of dissolved and colloidal substances such as lignin, lignans, carbohydrates, and extractives present in the water phase (Styan 1975). Dissolved aromatic structures can also form complexes with metal ions (Konn 1998). The thermal yellowing could be accelerated by transition metal ions, especially iron (Read et al. 1968; Gupta 1970; Ni et al 1997). Precipitation of metal ions as highly colored compounds is also possible. The negative effect of metal ions on the brightness of bleached mechanical pulps is stronger than that of unbleached mechanical pulps; this can be attributed to new functional groups, such as phenolic hydroxyl and carboxyl groups, being generated during alkaline peroxide bleaching (Ni et al. 1997).

The relatively high temperature of white water can accelerate the darkening (thermal darkening). For sheets made from mechanical pulp, the increase of pH from acidic towards alkaline levels has been reported to lead to an increase in the light absorption coefficient and a decrease in the light scattering coefficient resulting in a brightness loss (alkaline darkening) (Hua, Laleg 2009; Hubbe 2007). The increase in light absorption is due to the formation of light-absorbing chromophores and the decrease in light scattering due to fiber swelling, which makes fibers more conformable. For dry paper made from extensively swollen fibers, a greater proportion of the total surface is in optical contact and less surface is available for light scattering (Hua, Laleg 2009; Hubbe 2007). Microbial activity can increase the amount of the colored compounds in white water. Furthermore, some paper chemicals, e.g. shading dyestuff, from the white water can decrease the brightness (Bouchard et al. 2000). If de-inked pulp is used, white water can contain residual ink that also darkens the pulp (Ricard, Dorris 2007; Hua, Laleg 2009).

5 EXPERIMENTAL

5.1 Materials

5.1.1 Pulps

The pulps used in this study were peroxide-bleached thermomechanical (TMP) and groundwood (GW) pulps from Norway spruce (*Picea abies*), see *Table 4*. Washed TMP pulps were sampled after the bleaching and washing stages from two different Nordic paper mills producing LWC- and SC-paper. Washed TMP SC 1, 2 and 3 were from the same mill but their properties differed slightly from each other. Unwashed TMP SC was sampled prior to bleaching from the same mill as washed TMP SC pulps and it was later chelated and bleached in the laboratory. Industrial unbleached GW pulp was chelated and bleached in the laboratory and split into two portions. One portion (washed GW) was washed after the laboratory bleaching and the other was not (unwashed GW). The laboratory chelation, bleaching and washing are presented in more detail in **Paper II**.

Table 4. Properties of the pulps used.

	Dry content (%)	CSF Freeness (ml)	pH	ISO Brightness (%)	Fines content P200 (%)	Used in Paper
Standards used	ISO 638-1978 (E)	ISO 5263, ISO 5267-2	-	SCAN-CM 11:95, ISO 2470	SCAN-CM 66:05	
Washed TMP LWC	31.7	31	7.5	75.3	28	I (TMP 1), IV (TMP LWC)
Washed TMP SC 1	32.7	39	7.3	73.0	30	I (TMP 2a), III (TMP 1), IV (TMP SC 1)
Washed TMP SC 2	31.3	70	7.7	75.9	20	I (TMP 2b), II (Washed TMP), III (TMP 2), IV (TMP SC 2)
Washed TMP SC 3	30.8	23	7.7	76.1	25	I (TMP 2c)
Unwashed TMP SC	11.0	34	5.7	75.4	32	II (Unwashed TMP)
Washed GW	10.0	33	7.0	78.5	36	II (Washed GW)
Unwashed GW	10.0	30	7.0	78.5	36	II (Unwashed GW)

5.1.2 Fillers

The properties and dosage of the fillers used are shown in *Table 5*. All the fillers were commercially available products. The particle size of fillers was measured using Micromeritics Sedigraph 5100 Particle Size Analyzer. For the particle size measurement, the fillers were silted with deionized water and a small amount of dispersant was added if needed.

Table 5. The fillers that were used in the experiments.

Filler	Brightness (%)	Median particle size (μm)	Dosage (g/l)
Precipitated Calcium Carbonate 1 (PCC 1)	Y-value: 97 ISO: 95	1.9	1.5
Precipitated Calcium Carbonate 2 (PCC 2)	Y-value: 97 ISO: 95	2.1	1.5
Precipitated Calcium Sulfate (PCS)	Y-value: 96 ISO: 95	1.4	3.6 (1.5)*
*2.1 g/l of added PCS dissolved			

The crystal form of the PCC fillers was calcite precipitated as scalenohedral agglomerates and the particle shape of the PCS filler was platy (*Fig 15*). The PCC 2 filler was chemically modified to enable use at close to neutral pH with only minor dissolution. The PCC fillers were delivered as dry pigment powders and PCS as 28 wt% slurry. PCC fillers were silted with deionized water to form 21 wt% slurries before use.
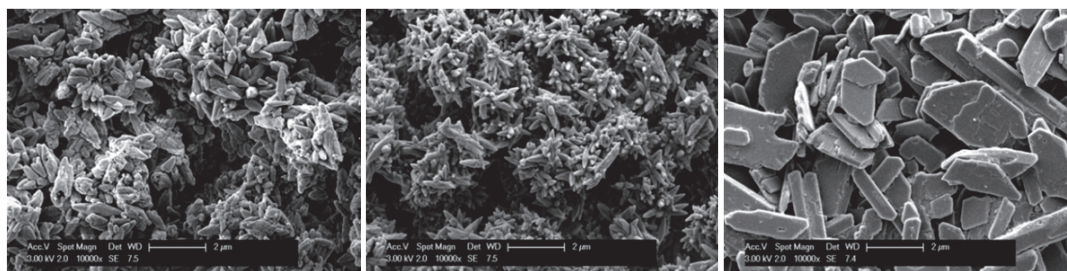
Fig 15. Scanning electron micrographs of the fillers: PCC 1 (left), PCC 2 (middle) and PCS (right).

The zeta potential of the PCC 2 and PCS fillers at pH ranges used in this study was measured using Malvern Zetasizer ZS. The samples were prepared in 1 mM KCl solution (1 ml of sample in 250 ml of solution) and the pH was adjusted with KOH or HCl. The pH did not affect the zeta potentials of the fillers notably. The zeta potential of PCC 2 was between -13 and -15 mV at pH range 7.3–8.3 and that of PCS -21 mV at pH range 5.7–7.8. The zeta potential of the PCC 2 was negative probably due to the surface modification and the zeta potential of the PCS due to the dispersant used in the delivered PCS slurry. The zeta potential of the PCC 1 was not measured, but it was probably positive at the used pH range 7.3–8.7. Ono and Deng (1997) used a very similar PCC grade as the PCC 1 in their study. In that study, the zeta potential changed from

positive to negative at pH 10.5. The zeta potential change of the PCC from positive to negative as the pH increases was due to the decrease of Ca^{2+} concentration in the solution. Although the average zeta potential of the PCC 1 particles was probably positive at pH 7.3–8.7, the surface was actually amphoteric because of the presence of CO_3^{2-} and Ca^{2+} ions.

5.1.3 Chemicals

In all publications (**Papers I-IV**), the pH of the pulp was adjusted before the hot disintegration, controlled after 10000 revolutions and after the hot disintegration (30000 revolutions) by a drop wise addition of 1M NaOH or H_2SO_4. The pH of the fines-containing wire water was also controlled during the circulation in the RDF by drop wise additions of 1M NaOH or H_2SO_4. Furthermore, carbon dioxide gas was slowly bubbled into the wire pit of the RDF during the circulation in **Paper III** to study its effect on the brightness reduction of the fines fraction of the peroxide-bleached TMP.

All the other chemicals used were dissolved in the dilution waters before the experiments to study the effect of different cations and anions on the brightness reduction (*Table 6*). These tests were conducted in **Paper IV**. The effect of transition metal ions (Fe^{2+}, Mn^{2+}) that are often carried into the water flows of a paper machine with pulps and act as disturbing agents in the peroxide bleaching was studied by using ferrous sulfate and manganese chloride. The dosages of these chemicals were low because the concentrations of ferrous and manganese ions is typically relatively low in the white water of a paper machine and ferrous ions were supposed to darken the fines and fiber fraction already at low concentrations. The effect of sulfate and chloride ions was assumed to be negligible at these low dosage levels.

The effect of ions that are often carried in the system with different chemical additives, fillers, and coating pigments (Al^{3+}, Ca^{2+}, Na^+, Cl^-, SO_4^{2-}, CO_3^{2-}) was studied at higher dosage levels (*Table 6*). The effect of sulfate, chloride, and carbonate ions was studied using calcium sulfate, calcium chloride, and calcium carbonate. The dosage of each chemical was calculated in order for the amount of added calcium ions to be constant. Calcium chloride, aluminum chloride, and sodium chloride were used to study the effect of calcium, aluminum, and sodium ions. The dosage of each chemical was calculated in order for the amount of the added chloride ions to be constant. All the chemicals were analytical grades with very low impurity contents (iron content max 5 ppm) except calcium carbonate which was a dry, synthetically precipitated filler pigment powder with a $CaCO_3$-content of 98 % and iron content (as Fe_2O_3) of 0.06 %. The same PCC was also used as a filler in **Paper III** (PCC 1).

Table 6. The chemicals that were used to study the effect of different ions on the darkening of the fines and fiber fraction of peroxide-bleached TMP.

Chemical	Dosage (mg/l)	
	Cation	Anion
Ferrous sulfate (FeSO$_4$ · 7 H$_2$O)	Fe^{2+}: 0, 0.3, 0.5, 1.0, 2.5, or 5.0	SO$_4^{2-}$: 0, 0.5, 0.9, 1.7, 4.3, or 8.6
Manganese chloride (MnCl$_2$ · 4 H$_2$O)	Mn^{2+}: 0 or 1.0	Cl$^-$: 0 or 1.3
Calcium sulfate (CaSO$_4$ * 2 H$_2$O)	Ca^{2+}: 0 or 250	SO$_4^{2-}$: 0 or 599
Precipitated calcium carbonate, PCC (CaCO$_3$)	Ca^{2+}: 0 or 250	CO$_3^{2-}$: 0 or 374
Calcium chloride (CaCl$_2$ * 2 H$_2$O)	Ca^{2+}: 0, 125, or 250	Cl$^-$: 0, 221, or 442
Aluminum chloride (AlCl$_3$)	Al^{3+}: 0, 56, or 112	Cl$^-$: 0, 221, or 442
Sodium chloride (NaCl)	Na$^+$: 0, 143, or 286	Cl$^-$: 0, 221, or 442

5.2 Methods

5.2.1 Experimental procedure

In order to simulate the short circulation of a paper machine and to reach a realistic brightness reduction in a sufficiently short residence time, a laboratory scale methodology was developed. The experimental procedure was developed in terms of controlled consistencies, flow rates, shear forces, temperature, and pH. A laboratory scale circulation device was constructed (Recycling Device of Fines, RDF), see *Fig 16*. It was set up of a DDJ-type drainage jar and a heated stainless steel sink combined by a peristaltic pump circulating the fines-containing wire water back to the drainage jar.

The pulp was hot disintegrated at a consistency of 20 g/l and thereafter diluted with deionized water to a consistency of 5 g/l. The pulp suspension (5 g/l) was added into the wire section of the RDF (*Fig 16*). It was agitated for 30 seconds before the drain valve of the wire section was opened. The fines-containing wire water passed through the wire and the drain valve into the wire pit of the RDF. After the first fractionation the fibers (fraction above the wire) were removed from the system. Another portion of pulp suspension (5 g/l) was added into the wire section and the fractionation was repeated and the fiber fraction was removed. The purpose of the two first fractionations was to fill the wire pit with enough fines-containing water to make the circulation procedure possible. The actual circulation test was started by adding a third portion of pulp suspension into the wire section. The drain valve was opened and the circulation started by continuously pumping the fines-containing water back from the wire pit into the wire section. A 52 mesh wire was chosen

to be used in the wire section to keep the drainage time short and the amount of the fines circulating high enough. The fines-containing wire water of peroxide-bleached mechanical pulp was circulated in the device for various residence times and samples were taken during the circulation.
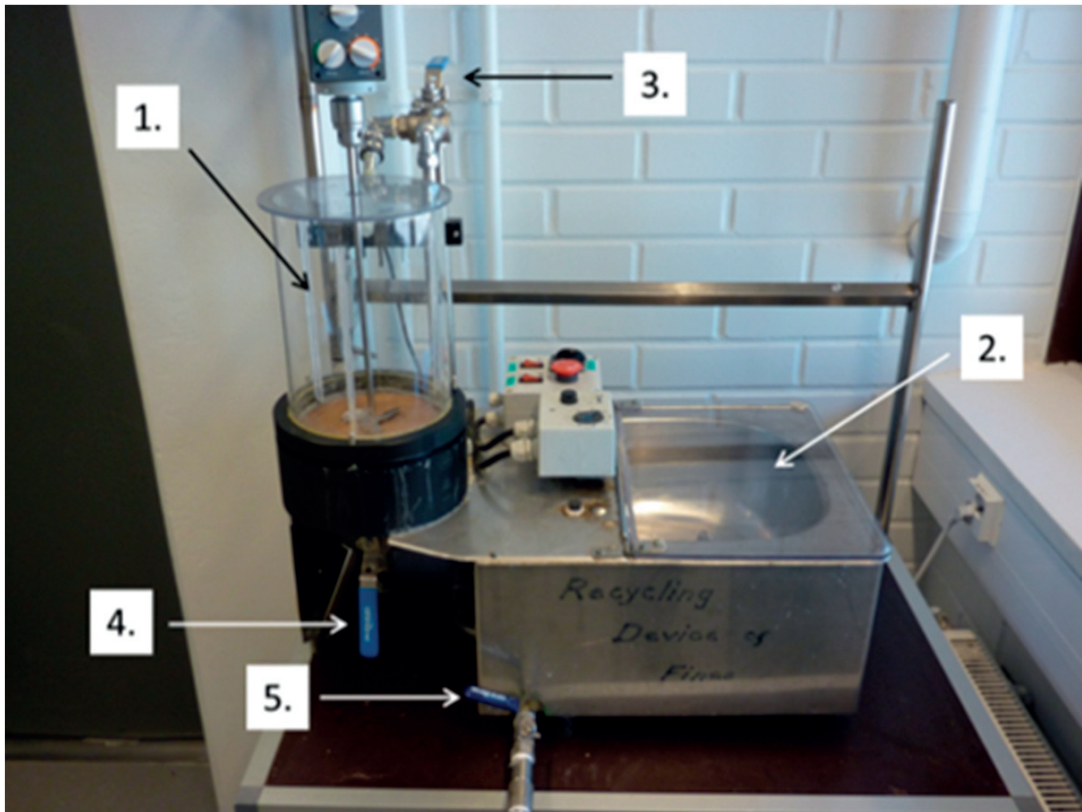
Fig 16. The Recycling Device of Fines (RDF). 1.Wire section, 2.Wire pit, 3.Inlet valve of wire section, 4.Drain valve of wire section, 5.Sampling valve.

Laboratory sheets were formed from the fines and fiber samples using a special vacuum sheet former with a 150 mesh wire (**Paper I**). The most notable benefit achieved by using the special sheet former compared to a conventional sheet former (ISO 5269-1) was that the samples needed not to be diluted in the sheet former enabling a fast sheet forming. In addition, it has been shown in a recent study (Karlsson et al. 2012) that the brightness of mechanical pulp decreases more during the sheet forming when sheets are formed at a low consistency using a conventional sheet former compared to a vacuum sheet former with a higher sheet forming consistency. Therefore, the use of the special sheet former was necessary to avoid extra darkening. The optical properties of the produced sheets were measured. Hence, the darkening of the fines and fiber fractions could be determined as a function of the circulation time.

In this study, the fraction that passed the 52 mesh RDF wire is called fines fraction and the fraction that remained on top of the RDF wire is called fiber fraction. The fiber fraction was not further washed to remove all fines since this could have also washed out colored substances from the fibers. The high fines content makes this fraction resemble the original pulp composition more than a pure long fiber fraction. The flow sheet of the whole experimental procedure is shown in *Fig 17*. The subprocesses of the experimental procedure (hot disintegration, Recycling Device of Fines, sheet former) are presented in more detail in **Paper I**.
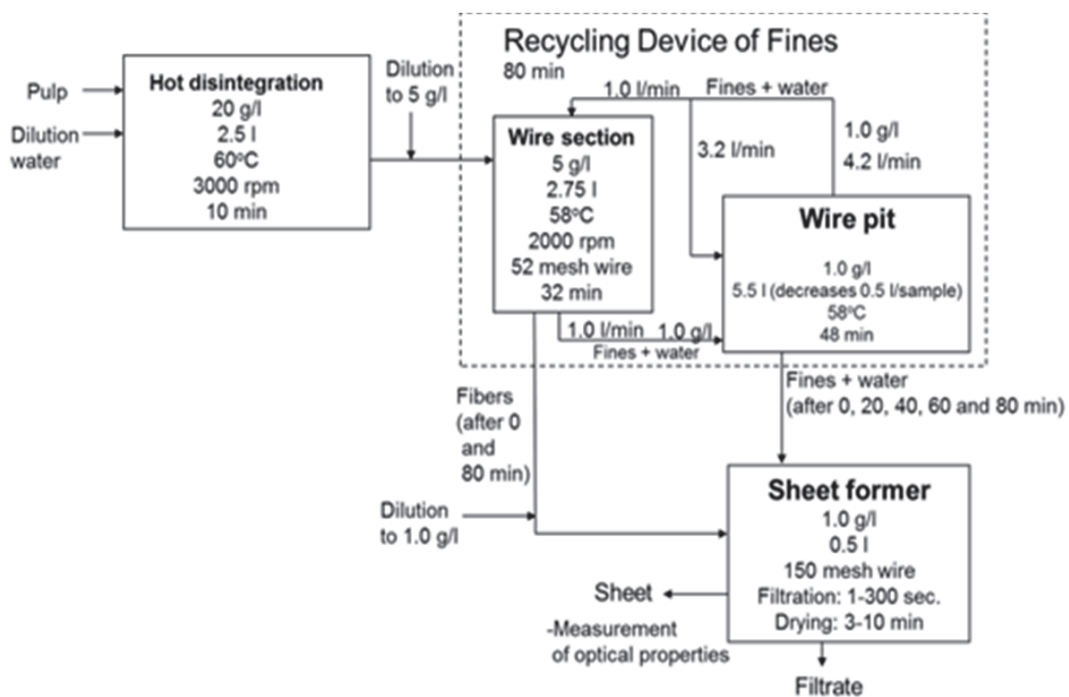
Fig 17. The flow sheet and values of the parameters of the experimental procedure.

The repeatability of the experimental method was considered to be an important factor. Repeatability or test-retest reliability is the variation in measurements taken by a single person or instrument on the same item and under the same conditions. Repeatability conditions include: the same measurement procedure, the same observer, the same measuring instrument used under the same conditions, the same location, and the repetition over a short period of time. These conditions were fulfilled in this study. Precision indicates the proximity of measurements to the repeatability, accuracy to the reference (true) value of the measurement (*Fig 18*). A measurement is called valid if it is both accurate and precise. In this study, there were no reference values for the optical properties of the fines or fiber fraction of peroxide-bleached TMP and, therefore, only the precision (repeatability) of the experimental procedure was tested.
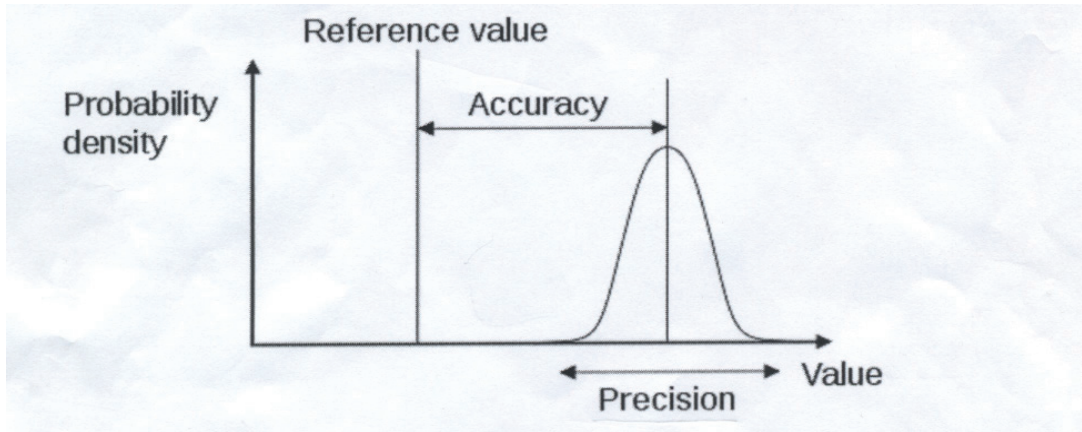
Fig 18. Precision and accuracy define the accuracy of the measurement.

The repeatability of the experimental method was examined using washed TMP SC 3. The circulation time was 80 min, pH 7.3, and temperature 58 °C. The fines-containing wire water samples were taken after 0, 40, and 80 min circulation and the fiber samples at the beginning (0 min) and at the end of the circulation (80 min). The number of parallel circulation runs was 6 and the number of parallel sheets prepared in each circulation time in a run was 2. Variation in the optical properties measured between the parallel circulation runs and parallel sheets in the same run was studied. The variation in the optical properties measured from the sheets of the parallel circulation runs described the variation caused by the RDF while the variation between the parallel sheets in the same circulation run described the variation caused by the sheet former. The variations caused by the RDF and the sheet former constituted the variation of the experimental method. Standard deviation was used as a measure of variation. The methodology of repeatability tests is also presented in **Paper I**.

The effect of pulp washing on the amount of dissolved and colloidal substances (DCS) of the pulp was studied as follows: washed and unwashed pulps were diluted with deionized water to a consistency of 20 g/l and hot-disintegrated at 60 °C. The wood material was separated from the water phase by a laboratory centrifuge (60 min, 6500 g) and the supernatant was carefully pipetted off. The following properties were measured from the supernatants directly after centrifugation: pH, conductivity, and cationic demand. The cationic demand was analyzed by titrating with 2.867 meq/l polybrene solution using a Methrom 715 Dosimat titrator and Mütek PCD03 pH Particle Charge Detector. The turbidity of the supernatants was measured after the adjustment of the pH to 5. An Analite Nephelometer Model 156 NPS was used, which gives the results in NTU units (Nephelometer Turbidity Units). The pH adjustment was completed because the turbidity measurement requires that extractives should be mainly in a colloidal state in order to produce

representative values, and at a high alkalinity, the resin and fatty acids are dissolved and are not present as colloidal substances (Ruohomäki 2003; Sundberg et al. 2009).

The effect of pulp washing on the amount of different metals and other elements in the pulp was studied from dried washed and unwashed pulps by an X-Ray Fluorescence (XRF) analysis. The amount of different ions in the water phases of disintegrated pulps was also determined by an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis.

The experimental procedure (*Fig 17*) was used to study the effect of pulp washing and the process pH on the brightness reduction of the fines and fiber fractions of peroxide-bleached mechanical pulp. The fines fractions of washed and unwashed pulps were circulated at acidic (4.8) and neutral (7.3) pH levels. **Paper II** discusses these experiments in more detail.

The effect of shear rate on the brightness reduction of the fines and fiber fraction of washed TMP SC 2 was studied by agitating the pulp (5 g/l; 2.75 l) for 80 min in a hot disintegration container at 60 °C. The agitation speeds were 100, 2000, and 3000 rpm. The agitation speeds were chosen to correspond to the shear rates generated to the pulp in the stock approach system of an actual paper machine. After the agitation the fines fraction was separated from the fiber fraction using the wire section of the RDF and a 52 mesh wire, sheets from both fractions were formed and their optical properties measured. The brightness reduction of the fines fraction during the circulation in the RDF (*Fig 16*) can be considered to consist of two phases: brightness reduction in the high-shear wire section and brightness reduction in the low-shear wire pit and pipelines. The brightness decrease in the wire section and in the wire pit and pipelines was simulated to study the quantity of the brightness reductions in these two regions of the device. During a normal 80 minute circulation procedure, the fines on average remain 48 min in the wire pit and pipelines (low shear) and on average 32 min in the wire section at 2000 rpm agitation (high shear). The brightness reduction in the wire section was simulated by agitating the pulp in a hot disintegration container at 2000 rpm for 32 min. The wire section of the RDF could not be used for the wire section simulation, because the heating elements of the RDF are located in the wire pit. The brightness reduction in the wire pit and pipelines was simulated by fractionating the pulp (5 g/l; 5.5 dm^3) using the wire section of the RDF and a 52 mesh wire and then circulating the fines fraction (about 1.2 g/l) in the RDF for 48 min so that the wire section was bypassed and the fines-containing wire water was circulated only through the pipelines to and from the wire pit. The flow rate of the fines-containing wire water in the pipelines generated by the peristaltic pump of the RDF was 4.2 l/min. Although pumps usually generate high shear rates, the shear in the peristaltic pump of the RDF was relative low due to the low flow rate. In addition, the residence time of the fines in the pump was short compared to the total time in the wire pit and pipelines during the circulation. The brightness reduction of the fines fraction during

a normal 80 min circulation procedure could be compared to the combination of the brightness reduction results of the wire section and wire pit simulations. These experiments are discussed in more detail in **Paper II**.

The effect of CO_2 gas on the brightness reduction of the fines fraction of the peroxide-bleached TMP (washed TMP SC 1) was studied by introducing carbon dioxide gas into the wire pit of the RDF during the circulation. The gas was slowly bubbled (measured to be ~30 cm^3/min, which is equal to 0.054 g/min) through the suspension (8.25 l) during the 80 min circulation. The total amount of added gas per liter (~0.524 g/l) was slightly lower than its solubility (~0.625 g/l) into water at 58 °C. A lid was used to limit the escape of the gas from the wire pit. These tests are also presented in **Paper III**.

The experimental procedure (*Fig 17*) was used to study the effect of different ions on the brightness reduction of the fines and fiber fraction of washed peroxide-bleached TMP. Different chemicals were dissolved in the dilution water before the experiments to act as the model substances of disturbing cation and/or anion. These tests are discussed in more detail in **Paper IV**. The different ions were always added as chemical compounds including both cations and anions. To separate these pairs from each other and clearly see the effect of each cation and anion, multiple linear regression analyses were performed from the results in **Paper IV** using MINITAB 16 Statistical Software. The fluorescence of the fines sheets of the test points including dissolved $CaCl_2$ and $CaSO_4$ were measured at the wavelength range 400–600 nm with a Perkin Elmer LS-50B luminescence spectrometer (**Paper IV**) to determine the effect of chloride ions on the fluorescence of the sheets. The number of the parallel measurements per test point was 3.

PCC and PCS fillers were circulated in the RDF (*Fig 16*) with and without the fines fraction of the peroxide-bleached TMP to study the darkening of the fillers. In addition, the adsorption of wood-based dissolved and colloidal substances on the fillers during the circulation was examined using the UV Raman spectrometry. The methodology of filler tests is discussed in more detail in **Paper III**. Additivity rule (*Eq 5.*) was used in the interpretation of the results of **Paper III** to eliminate the effect of the variation in the filler content of the produced sheets.

5.2.2 Measurement of optical properties of the sheets in this study

The optical properties of the produced sheets were measured in order to study the brightness reduction of the raw materials and the effect of different process variables on the brightness. The sheets were conditioned (ISO 187:1990 (E); 23 °C, 50 % RH) and the grammage measured (ISO 536:1995 (E)). A 070R Elrepho Spectrophotometer was used to measure the following optical properties: ISO brightness (R_{457}) according to ISO 2470, Y-value (R_{557}), specific light absorption coefficient (k_{557}), and specific light scattering coefficient (s_{557}) according to ISO 5631:2000 (E). All the optical properties were measured from the top side of the sheets using 5 parallel measurements per sheet. As the light absorption and light scattering coefficients were determined at the wavelength 557 nm, they were related to the Y-value, not to the ISO brightness. However, the development of ISO brightness and Y-value was almost identical between the different test points and, therefore, the light absorption and light scattering coefficients correlated well with ISO brightness.

6 RESULTS AND DISCUSSION

6.1 Evaluation of the brightness reduction (Paper I)

The brightness of the fines fraction was found to decrease during the circulation (*Fig 19*). The brightness reduction was quite similar for the fines fractions of the different washed peroxide-bleached TMP pulps. The brightness minimum was not reached during 6.5 hours circulation, but the rate of darkening appeared to decrease towards the end of the circulation. Samples of the fiber fraction were taken at the beginning and at the end of the circulation. The fibers darkened at almost the same rate as the fines (*Fig 20*). The brightness reduction during the circulation was probably partly due to the formation of light-absorbing chromophores in the lignin structures of fibers and fines (e.g. thermal darkening) and partly due to the adsorption of the light-absorbing dissolved and colloidal substances (e.g. lignin and its relatives) to their surfaces from the water phase. The fines fraction was expected to be more susceptible towards darkening than the fibers. Reasons for that are the high lignin content and a large specific surface area of the fines leading to a high tendency for collecting light-absorbing substances from the circulation water. However, the fast darkening of the fibers was considered to be due to the high shear rate in the wire section. The fibers remained in the wire section of the RDF during the whole circulation time, while the fines were, on average, 60 % of the circulation time in the wire pit, where the shear rate was low. The effect of the shear rate on the brightness reduction is later discussed in Section 6.4. The average rate of darkening, approximately 2 %-units (ISO) per hour that was reached using the method, was considered to be acceptable and reliable.
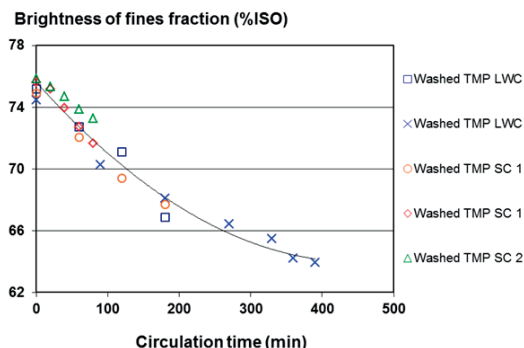
Fig 19. The effect of circulation time in the RDF on the brightness reduction of the fines fraction of peroxide-bleached TMP at pH 7.3 and 58 °C.
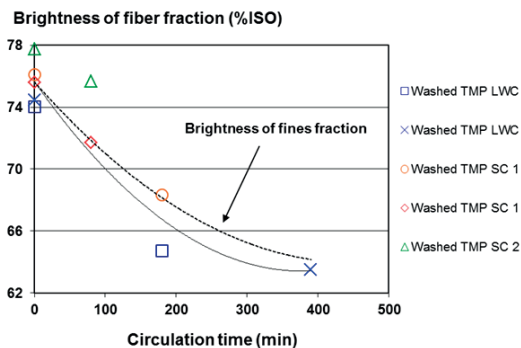
Fig 20. The effect of circulation time in the RDF on the brightness reduction of the fiber fraction of peroxide-bleached TMP at pH 7.3 and 58 °C. The dotted trend line illustrates the darkening of the fines fraction.

The brightness reduction of the fines fraction was mostly due to the increased light absorption (*Fig 21*). The light scattering of the fines fraction changed during the circulation, but the change was occasional and no

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systematic change with respect to circulation time was seen (*Fig 22*). The darkening of the fiber fraction was also mainly due to the increased light absorption (*Fig 23*). However, also the light scattering of the fiber fraction decreased during the circulation in most cases, especially at the short circulation times (*Fig 24*).
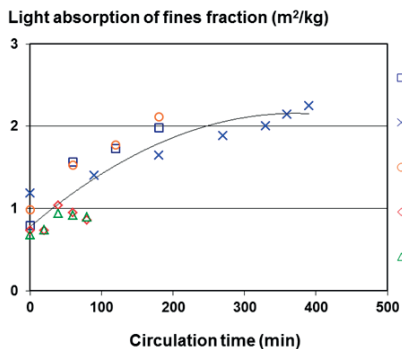
Fig 21. The effect of circulation time in the RDF on the light absorption of the fines fraction of peroxide-bleached TMP at pH 7.3 and 58 °C.
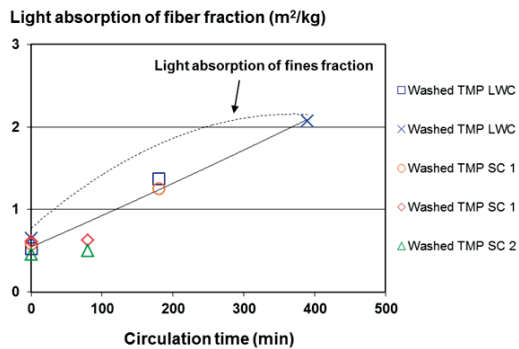
Fig 23. The effect of circulation time in the RDF on the light absorption of the fiber fraction of peroxide-bleached TMP at pH 7.3 and 58 °C. The dotted trend line illustrates the light absorption of the fines fraction.
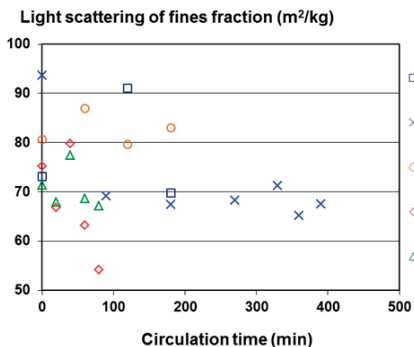
Fig 22. The effect of circulation time in the RDF on the light scattering of the fines fraction of peroxide-bleached TMP at pH 7.3 and 58 °C.
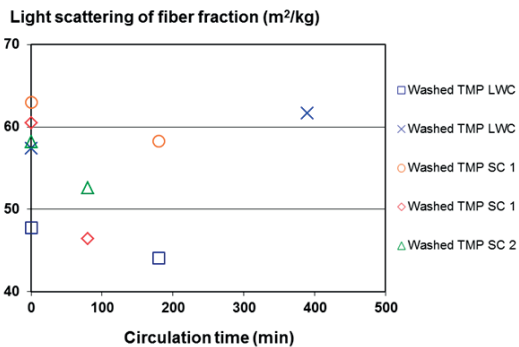
Fig 24. The effect of circulation time in the RDF on the light scattering of the fiber fraction of peroxide-bleached TMP at pH 7.3 and 58 °C.

6.2 Repeatability of the method (Paper I)

The brightness results of the repeatability test of the experimental method are shown in *Fig 25*. The number of parallel circulation runs was 6 and the number of parallel sheets prepared in each circulation time in a run was 2 (A and B in *Fig 25*). The variations of the optical properties were calculated for each circulation time (*Table 7*). The total variation in the ISO brightness was ± 0.2–0.3 %-units for the fines sheet and ± 0.1–0.2

%-units for the fiber sheet. The brightness reduction results were repeatable and the new method was found suitable for studying the darkening phenomena of mechanical pulps.
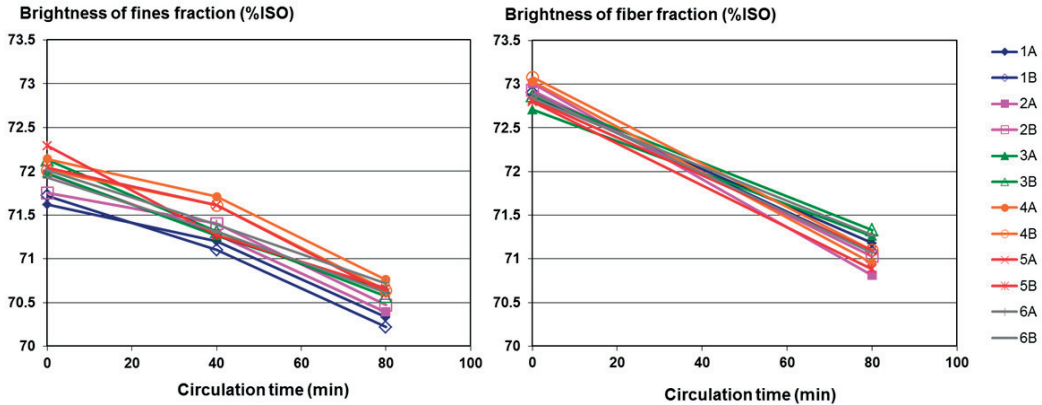
Fig 25. The effect of circulation time on the brightness reduction of the fines (left) and fiber fraction (right) of peroxide-bleached TMP (washed TMP SC 3). These tests were carried out to study the repeatability of the experimental method.

Table 7. Variation in the optical properties of the fines and fiber fraction of peroxide-bleached TMP (washed TMP SC 3). k = specific light absorption coefficient, s = specific light scattering coefficient.

Source of variation	Circulation time (min)	Fines fraction			Fiber fraction		
		ISO bright. (%)	k (m^2/kg)	s (m^2/kg)	ISO bright. (%)	k (m^2/kg)	s (m^2/kg)
RDF (between circulation runs)	0	72.0±0.3	1.13±0.10	53.5±4.1	72.9±0.1	0.77±0.05	40.8±2.6
	40	71.4±0.2	1.16±0.06	50.8±2.4			
	80	70.6±0.2	1.27±0.05	52.3±3.6	71.1±0.2	0.88±0.07	39.5±3.1
Sheet former (between parallel sheets)	0	72.0±0.1	1.13±0.09	53.5±4.1	72.9±0.1	0.77±0.06	40.8±2.9
	40	71.4±0.1	1.16±0.12	50.8±5.0			
	80	70.6±0.1	1.27±0.08	52.3±3.2	71.1±0.1	0.88±0.04	39.5±2.0
Within single sheet	0	72.0±0.1	1.13±0.14	53.5±6.6	72.9±0.1	0.77±0.07	40.8±3.6
	40	71.4±0.1	1.16±0.14	50.8±5.9			
	80	70.6±0.1	1.27±0.18	52.3±6.6	71.1±0.1	0.88±0.06	39.5±2.6
Total*	0	72.0±0.3	1.13±0.13	53.5±5.8	72.9±0.1	0.77±0.08	40.8±3.9
	40	71.4±0.3	1.16±0.14	50.8±5.5			
	80	70.6±0.2	1.27±0.10	52.3±4.8	71.1±0.2	0.88±0.08	39.5±3.7
Total**	0	72.0±0.3	1.13±0.20	53.5±8.8	72.9±0.2	0.77±0.10	40.8±5.3
	40	71.4±0.3	1.16±0.20	50.8±8.1			
	80	70.6±0.3	1.27±0.20	52.3±8.2	71.1±0.2	0.88±0.10	39.5±4.5
*Total variation in the optical properties if measured using 5 parallel measurements according to ISO 2470 and ISO 5631:2000(E). **Total variation in the optical properties of single measurement with 070R Elrepho Spectrophotometer.							

Elrepho Spectrophotometer measures the different reflectance factors (e.g. ISO brightness and Y-value) and the opacity of the sheet. After that, the device calculates the light scattering and light absorption values from Kubelka-Munk equations. In practice, paper does not fulfill all the requirements of Kubelka-Munk theory (Paulapuro 1985). For example, when applying Kubelka-Munk theory, the light scattering and light

absorption coefficients are not supposed to change when the grammage of paper is changed. In reality, the structure of paper changes slightly when the grammage is changed, which may affect the light scattering coefficient. In these tests, the grammage varied only slightly between the sheets, but quite a lot within a sheet due to its uneven structure. This could have been a source of error. This also explains the large variations in the light scattering results. Light scattering is very sensitive to small changes in the structure of the sheet. It is very difficult to produce a sheet with an even structure from the fines fraction alone, especially without dilution to a very low consistency in the sheet former. The same problem of non-uniform light scattering within sheets produced from fiber fractions is also observed before (Granberg, Béland 2004). The filtration of the sheets in the special vacuum sheet former was carried out at a relatively high consistency (1.0 g/l) for the following reasons: dilution could have washed away colored substances from the surfaces of the fines and fibers and the drainage time of the sheet forming was aimed to be constant and as short as possible to avoid extra darkening. Therefore, the light scattering and light absorption values are indicative.

6.3 The effect of pulp washing and pH (Paper II)

GW pulp was chelated and bleached in laboratory and split into two portions. One portion (washed GW) was washed after the laboratory bleaching with deionized water and the other was not (unwashed GW). The washed TMP pulps were sampled after the bleaching and washing stages from two different Nordic paper mills producing LWC- and SC-paper. The washed TMP SC 1, 2 and 3 were from the same mill but their properties differed slightly from each other. The unwashed TMP SC was sampled prior to bleaching from the same mill as the washed TMP SC pulps and it was later chelated and bleached in the laboratory. Thus, the difference in the results of the washed and the unwashed TMP described the effect of mill washing, and the difference of the washed and unwashed GW indicated the effect of laboratory washing. As the washed TMP pulps were bleached in a mill and the unwashed TMP in the laboratory, the TMP pulps were not as comparable as the GW pulps.

Pulp washing did not seem to affect the metal contents of the pulp very much (*Table 8*). The effect of pulp washing on the amount of different ions released from the pulp into the water phase during the hot disintegration was also rather minute (*Table 9*). The concentrations of most of the ions were below the detection limit, 1 mg/l. In the experiments, the pulps were diluted with deionized water after the hot disintegration from 20 g/l to 5 g/l before the circulation and, hence, the ion concentrations of the circulation water can be assumed to be ¼ of the concentrations in the water phases of the hot disintegrated pulps.

Lillandt (2003) has studied the effect of washing on the amount of DCS in the water phase of peroxide-bleached TMP. In his study, the washing removed more than 50 % of DCS. The amount of water used

(g water/g o.d. pulp) in a washing step was approximately the same as in this study with washed GW pulp. In Lillandt (2003), the pulp was washed once while in this work twice. In Lillandt (2003) the washing was carried out in a Perti-tester at 60 °C while in this study it was completed in Büchner funnel at 90 °C. These differences in the washing procedure and conditions are not supposed to affect the washing result much. Thus, the decrease of the DCS in the present study with GW pulp can be assumed to be at least as high as in Lillandt (2003). In addition, *Table 9* presents decreased conductivity, turbidity, and cationic demand of the water phases of disintegrated pulps after washing, indicating that the amount of DCS in the pulp suspension decreased.

Table 8. The metal contents of the pulps analyzed by X-Ray Fluorescence (XRF) spectrometer.

	Ca (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Mg (mg/kg)	S (mg/kg)	Na (mg/kg)
Washed TMP LWC	480	2	12	7	100	320	4690
Washed TMP SC 1	400	2	6	3	30	480	5290
Washed TMP SC 2	470	2	6	4	35	570	7720
Unwashed TMP SC	390	2	7	6	45	960	5510
Washed GW	610	3	14	2	60	580	3860
Unwashed GW	600	3	16	3	65	350	8720

Table 9. Properties of the water phases of disintegrated pulps. The concentrations of Al, B, Ba, Co, Cr, Fe, Mg, Ni, Sr, and Zn were < 1 mg/l in all water phase samples.

	pH	Conductivity (µS)	Turbidity (NTU) at pH 5	Cationic demand (meq/l)	Ca (mg/l)	Cu (mg/l)	K (mg/l)	Na (mg/l)
Washed TMP LWC	7.7	291	63	0.28	< 1	< 1	< 1	58
Washed TMP SC 1	7.3	390	63	0.33	< 1	< 1	1.6	74
Washed TMP SC 2	6.7	523	57	0.90	< 1	< 1	< 1	102
Unwashed TMP SC	5.6	1113	88	1.17	1.4	1.8	1.3	220
Washed GW	6.6	133	194	0.20	1.7	< 1	< 1	23
Unwashed GW	7.1	1070	327	2.03	2.2	< 1	1.8	237

Laboratory washing clearly reduced the tendency to darkening of the fines and fiber fraction of GW pulp (*Fig 26*). The initial brightness values of the washed and unwashed GW pulps were essentially the same, but the darkening during the circulation was faster with unwashed pulp. The faster darkening during the circulation with unwashed GW was because of the faster increase of the light absorption of the fines and fiber fraction (*Fig 27*). This was probably due to the wood-based light-absorbing substances (e.g. lignin and its derivatives) the amount of which in the pulp suspension decreased during the washing (see *Table 9*). These substances have a high tendency to darken and they were probably adsorbed onto the surfaces of the fines and fibers during the circulation. The washing had a relatively small effect on the metal content of GW pulp (*Table 8*) and its water phase (*Table 9*) with the exception of sodium (Na), whose amounts decreased

notably during the washing. However, sodium is not tend to darken the pulp as later will be shown in Section 6.6.3. Therefore, the faster darkening of unwashed GW was not due metal ions. In addition, ferrous ions, for instance, have a tendency to darken the fines and fiber fractions very fast, but do not affect the rate of darkening during the circulation as later will be shown in Section 6.6.1.
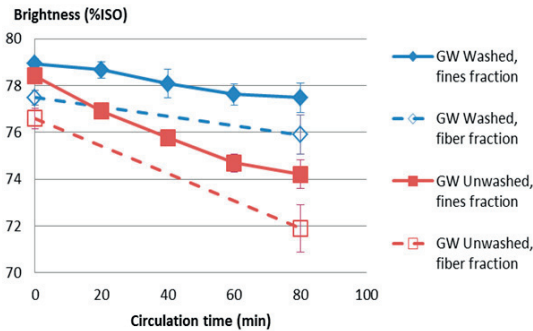
Fig 26. The effect of pulp washing on the brightness of the fines and fiber fraction of peroxide-bleached groundwood (GW) during the circulation in the RDF at 58 °C and pH 7.3. Brightness values were calculated as average of two circulations in parallel. Standard deviation was used as a measure of variation.

Fig 27. The effect of pulp washing on the light absorption of the fines fraction of peroxide-bleached groundwood (GW) during the circulation in the RDF at 58 °C and pH 7.3. Light absorption values were calculated as average of two circulations in parallel. Standard deviation was used as a measure of variation.

The effect of the pH on the brightness reduction of the fines and fiber fraction was studied at acidic (4.8) and at neutral pH (7.3) using the washed and unwashed peroxide-bleached TMP. The brightness of the fines fraction of both washed and unwashed pulps was higher at the acidic pH already after the hot disintegration and remained higher during the whole circulation (*Fig 28*). When the unwashed TMP was used, the brightness after the hot disintegration was notably lower at neutral pH, but the difference in brightness decreased during the circulation. The brightness reduction of the fines fraction of the unwashed TMP was notably faster than that of washed TMP indicating that in addition to the laboratory washing (GW pulps), also the mill washing reduced the tendency to darkening.

Fig 28. The effect of pH on the brightness of the fines fraction of washed and unwashed peroxide-bleached TMP during the circulation in the RDF at 58 °C. Brightness values were calculated as average of three circulations in parallel except for the washed TMP at pH 7.3 which values were calculated as average of two parallel circulations. Standard deviation was used as a measure of variation.

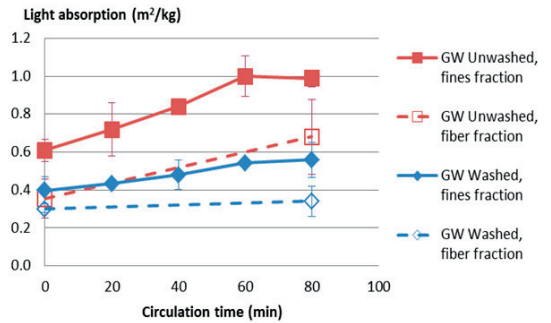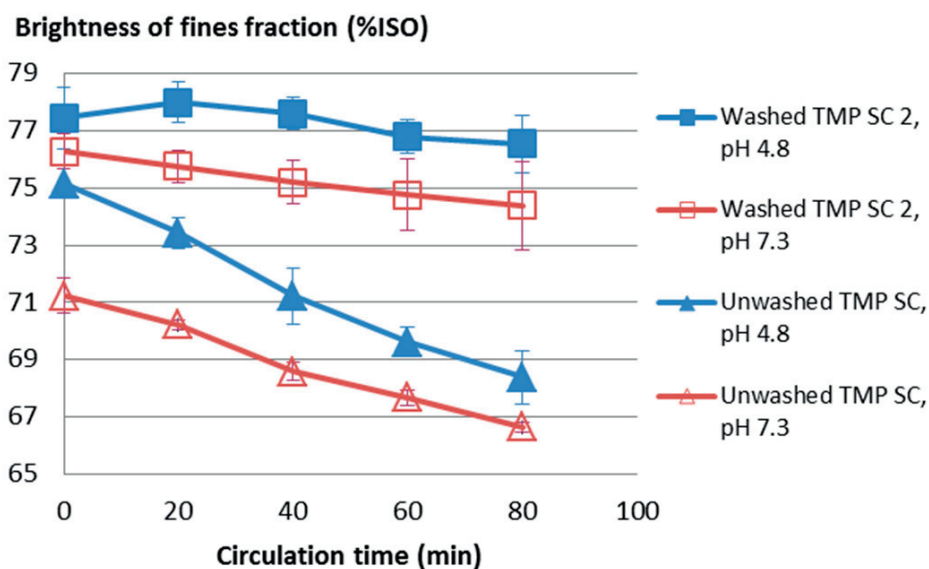The light absorption of the fines fraction was not affected by the pH levels in the tested range (*Fig 29a*). The light absorption of the fines fraction of the unwashed TMP after the hot disintegration was higher and the increase in light absorption during the circulation notably faster than that of the washed TMP resulting in a larger brightness decrease as seen in *Fig 28*. The reason for the higher brightness values at the acidic pH was the higher light scattering (*Fig 29b*). With the unwashed TMP at acidic pH, the light scattering decreased during the circulation (*Fig 29b*) resulting in a larger brightness decrease in *Fig 28* compared to neutral pH. It seems that the fines lost their high light scattering ability during the circulation, when the amount of dissolved and colloidal substances of the suspension was high. As mentioned earlier in section 4.4.4, the increase in light absorption may decrease light scattering even if the structure of the produced sheet is unchanged (Rundlöf, Bristow 1997; Karlsson et al. 2012), because the light scattering and light absorption coefficients are theoretical quantities that are dependent of each other in the Kubelka-Munk theory. However, as this decrease was not seen at neutral pH using the same pulp and was relatively large (~20 m^2/kg) and occurring in all three parallel circulation runs at acidic pH, it was most likely real. This decrease in light scattering did not affect the tensile strength of the fines sheet (results shown in **Paper II**). It seems that the number of optical contacts in the sheet decreased, but the bonding ability of the sheet did not change. No correlation between the light scattering and tensile index of the fines sheet was shown. The tensile index was higher for the washed TMP fines indicating that the dissolved and colloidal substances reduced the

bonding ability of the fines sheet. The tensile strength was slightly higher at higher pH. Hence, it seems that the lower light scattering at the neutral pH was at least partly the result of the increased bonding ability of the fines sheet. The relatively large variations in light scattering and light absorption results are due to uneven sheet structures.
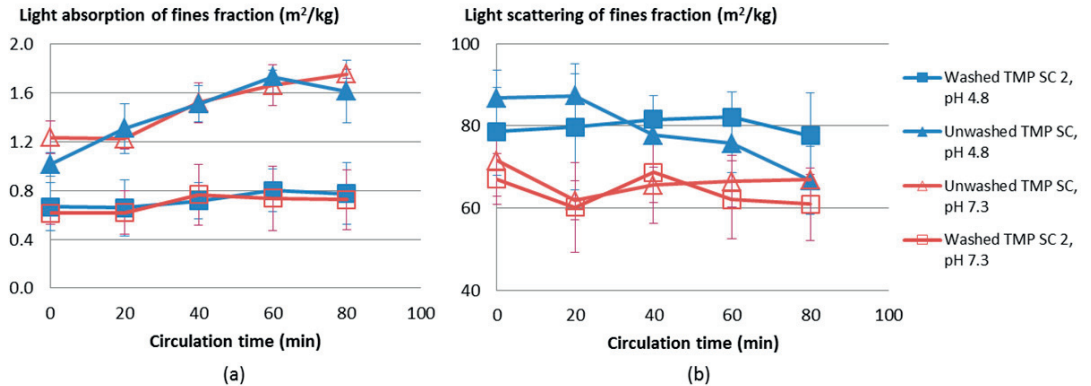
Fig 29. The effect of the pH on (a) the light absorption and (b) the light scattering of the fines fraction of washed and unwashed peroxide-bleached TMP during the circulation in the RDF at 58 °C. Light absorption and light scattering values were calculated as average of three circulations in parallel except for the washed TMP at pH 7.3 which values were calculated as average of two parallel circulations. Standard deviation was used as a measure of variation.

The brightness, light absorption or light scattering of the fiber fraction was not affected by the pH during the circulation. However, the pH during the sheet forming of the fiber sheet was close to neutral also in the acidic circulation test points. The light scattering of the fiber sheet would probably have been higher at the acidic pH, if the sheet forming had been carried out at the acidic pH. It seems that the brightness reduction of the fines fraction was not due to the formation of alkali-catalyzed chromophores, but the brightness reduction was likely the result of the ionization of acidic groups that decreased the light scattering. This could have been avoided by the acidification of the suspension before the sheet preparation to pH 4.8 in all test points. An increase in the light absorption of the fiber and fines fraction was to be expected due to the increased pH through alkaline darkening. However, the pH did not seem to affect the light absorption notably in the tested range.

According to the study of Lai et al. (1992), the pH does not affect the brightness of peroxide-bleached TMP at pH range 5–8, but the brightness decreased sharply at pH > 10. In that study, the pulp was stirred under ambient conditions at different pH values for 1 h before sheet preparation. According to the present study, the darkening of the washed and unwashed peroxide-bleached TMP fines exposed to typical shear rates in the wet end at 58 °C caused by the pH increase from 4.8 to 7.3 is purely due to the decreased light scattering. This indicates that the brightness reduction is not an obstacle for neutral papermaking.

6.4 The effect of shear rate (Paper II)

The agitation speeds (rpm) of a Britt Dynamic Drainage Jar has earlier been converted to shear rates (s^{-1}) (Tam Doo et al. 1984). The agitation parameters in the tests of the present study were very similar to those in a Britt Dynamic Drainage Jar agitation. Hence, the approximated shear rates in the present study were: 100 rpm $\approx 4 \cdot 10^2$ s^{-1}, 2000 rpm $\approx 1.4 \cdot 10^4$ s^{-1}, and 3000 rpm $\approx 2.2 \cdot 10^4$ s^{-1}. These agitation speeds correspond quite well with the shear rates generated to the pulp in the various elements in the wet end of an actual paper machine, for example in the piping system (low shear) and in the headbox or pump (high shear).

According to the tests results in *Fig 30*, the increased shear rate (agitation speed) increased the rate of darkening of both the fines and the fiber fraction. Thus, it can be assumed that the brightness reduction rate in the wet end of an actual paper machine is higher in the high shear elements (e.g. pumps, headbox) than in the low shear elements (e.g. piping system). However, the brightness decrease was notable also under low shear (100 rpm) and, thus, the total darkening can be suspected to depend greatly on the time of residence of pulp in the various elements in the wet end.
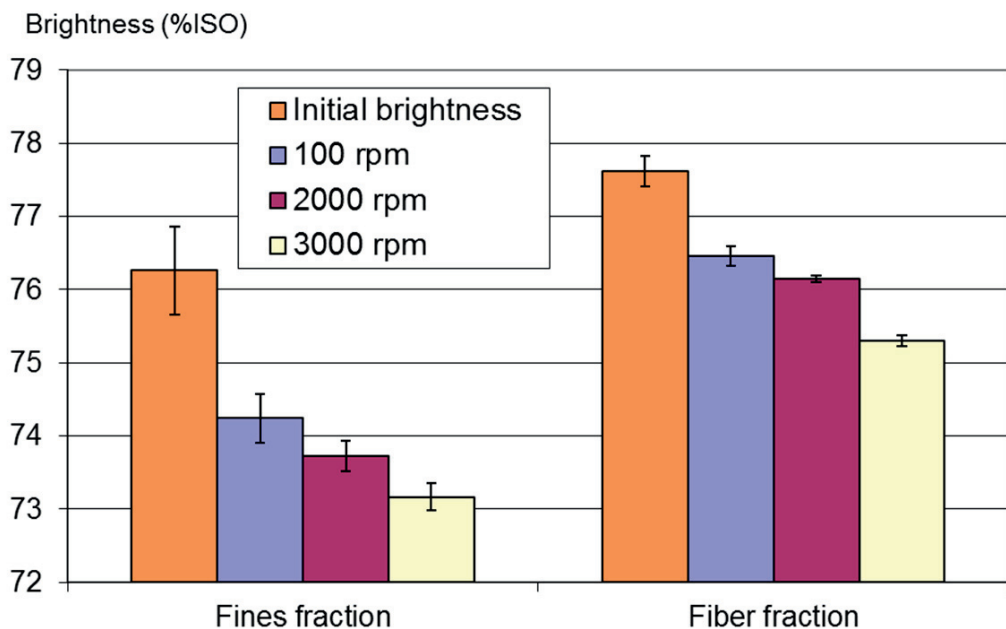

Fig 30. The effect of shear rate on the brightness reduction of the fines and fiber fraction of washed TMP SC 2. Agitation time was 80 min, pulp consistency 5 g/l, temperature 60 °C and pH 7.3. The initial brightness is the brightness before the agitation (= agitation time 0 min).

The brightness reduction as a function of agitation speed in *Fig 30* is evident, but the changes in the light absorption or light scattering results were somewhat inconsistent (results shown in **Paper II**). Due to the large variations in the light absorption and light scattering results caused by an uneven structure of the sheets, the differences between the agitation speeds were not statistically significant. However, it seemed that the brightness reduction was due to the increased light absorption of both the fines and the fiber fraction. The light scattering of the fines and fiber sheet decreased during the agitation at all the agitation speeds, but the difference between the agitation speeds was minute.

There are several possible reasons for the increased rate of darkening when increased shear forces are present. It is possible that the increased shear exposes new surfaces of the fines and fibers that are more susceptible towards darkening. It is also possible that the fines and fibers adsorb light-absorbing substances from the water phase more efficiently due to the new surfaces. In addition, the adsorption rate of the light-absorbing substances from the water phase may increase due to the increased collision rate of the particles as a function of the increased shear.

At the same shear rate levels, the rate of darkening was higher for the fines fraction than for the fiber fraction. Probable reasons for the higher brightness reduction of the fines fraction are a high lignin content and a large specific surface area of the fines leading to a high tendency for collecting light-absorbing substances from the water phase.

The brightness reduction of the fines fraction during the circulation in the RDF can be considered to consist of two phases: brightness reduction in the high-shear wire section and brightness reduction in the low-shear wire pit and pipelines. During the normal 80 min circulation in the RDF, the fines fraction is, on average, 32 min in the wire section and 48 min in the wire pit and pipelines. By adding the brightness reduction during 32 min in 2000 rpm agitation (wire section simulation) and the brightness reduction during 48 min in the wire pit and pipelines (wire pit simulation,) the result should correspond to the brightness reduction occurring during the 80 min circulation in the RDF.

The results were compared and the simulation results matched well with the actual brightness reduction results during the circulation in the RDF (*Fig 31*). Most of the brightness reduction of the fines fraction (approximately 66 %) occurred in the wire section. According to the results in Section 6.1, the rate of darkening of the fines and fiber fraction during the circulation in the RDF was almost identical. The fast darkening of the fibers was probably due to the higher shear applied to the fiber fraction than to the fines fraction. The fibers remained in the wire section of the RDF during the whole circulation time, while the

fines were on average 60 % of the circulation time in the wire pit and pipelines, where the shear rate was low.
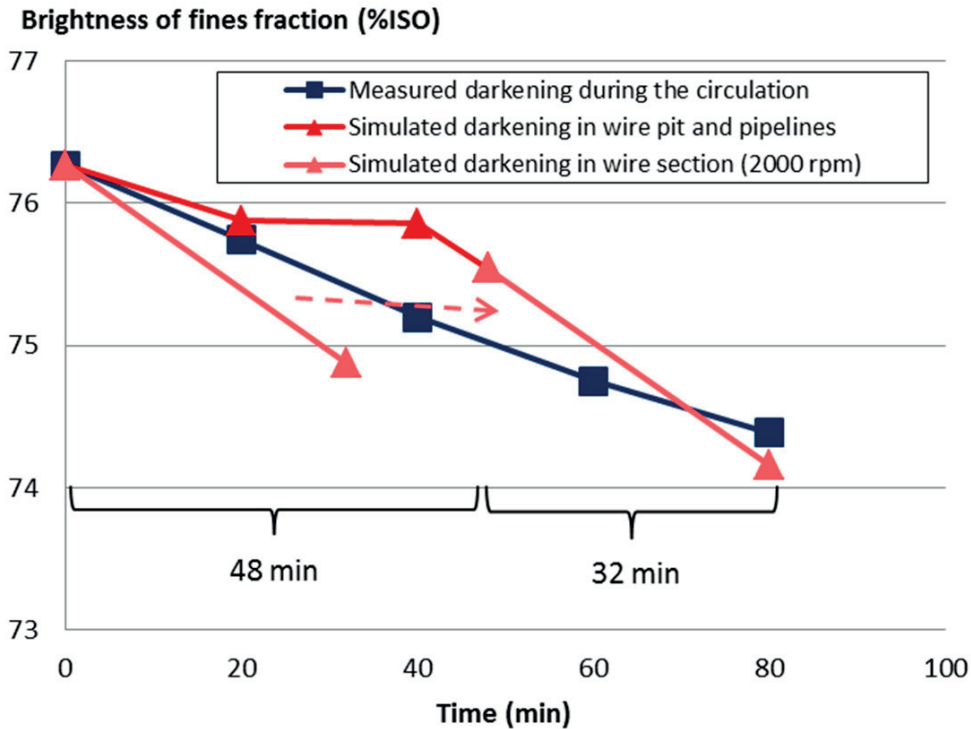
Fig 31. The comparison of the measured (dark blue squares) and simulated (triangles) rate of darkening of the fines fraction of washed TMP SC 2 during the 80 min circulation in the RDF at 58 °C and pH 7.3. The simulated rate of darkening combines the darkening effects of the circulation in the wire pit and pipelines of the RDF for 48 min (dark red triangles) and the agitation of the pulp for 32 min in a DIAF agitator (light red triangles) simulating the darkening in the wire section.

6.5 The effect of carbon dioxide gas (Paper III)

The effect of carbon dioxide gas on the brightness of the fines fraction of peroxide-bleached TMP (washed TMP SC 1) was studied. Carbon dioxide was slowly bubbled into the wire pit of the RDF during the circulation and the brightness decrease of the fines fraction was determined. The lowered brightness was due to the increased light absorption of the fines fraction (*Fig 32*). The light scattering of the fines fraction also increased. It was not possible to keep the pH at 7.3 due to the strong buffering effect of CO_2 and, therefore, the circulation was carried out at pH 5.3. As shown earlier in Section 6.3, the decrease in the pH from 7.3 to 4.8 does not affect the light absorption of the fines fraction of the peroxide-bleached TMP, but increases its light scattering. This change in the light scattering was seen with added CO_2 gas too. However, when CO_2

gas was added, the increased light absorption dominated and the brightness of the fines fraction decreased. Similar circulation tests were also carried out with added N_2 gas, O_2 gas and air. These gases did not decrease the brightness of the fines fraction and, hence, the darkening was due to particularly CO_2. Carbon dioxide gas can be used for the pH control in the wet end of a paper machine and also the dissolution of calcium carbonate fillers releases it. From brightness point of view, the use of carbon dioxide gas for paper machine pH control is questionable in the wet end of a paper machine and the dissolution of calcium carbonate fillers should be avoided.
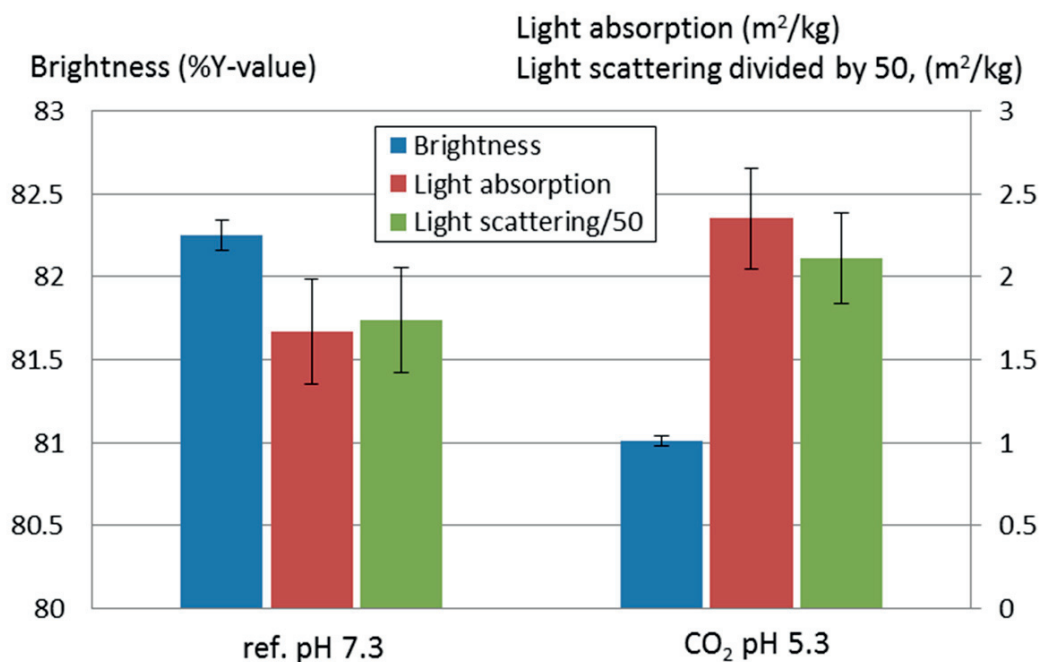
Fig 32. The effect of carbon dioxide gas on the brightness, light absorption, and light scattering of the fines fraction of peroxide-bleached TMP (washed TMP SC 1). The circulation time was 80 min and temperature 58 °C. The initial brightness (circulation time 0 min) of the fines fraction at pH 7.3 was 87.0 %Y-value.

6.6 The effect of different ions in circulation water (Paper IV)

6.6.1 Ferrous and manganese ions

Ferrous ions decreased the brightness of the fines fraction substantially already at low concentrations (*Fig 33a*). The brightness reduction was due to the increased light absorption (*Fig 33b*). Fe^{2+} -ion concentration of 0.3 mg/l decreased the brightness of the fines fraction by approximately 2 %-units. Fe^{2+}-ions darkened the fines fraction already during the hot disintegration (before the circulation), but the rate of darkening during

the circulation was the same as without ferrous ions. Thus, the mechanism for darkening during the circulation with added Fe^{2+} concentrations of 0.3–1.0 mg/l seemed to be the same as without added ions. Manganese ions did not affect the brightness at the dosage level of 1.0 mg/l (*Fig 33a*).
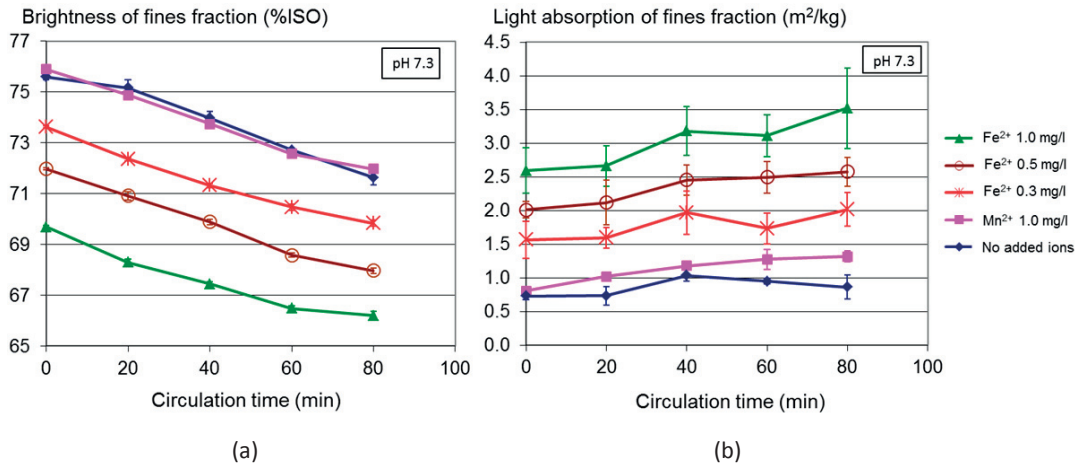
Fig 33. The effect of Fe^{2+}- and Mn^{2+}-ion concentrations of the wire water on the (a) brightness and (b) light absorption of the fines fraction of peroxide-bleached TMP (Washed TMP SC 1) during the circulation in the RDF at pH 7.3 and 58ºC. Fe^{2+}-ions were added as $FeSO_4$ and Mn^{2+}-ions as $MnCl_2$. The values of the test points are from single circulations.

When the Fe^{2+}-ion concentration of the circulation water was very high (2.5–5.0 mg/l), major part of the brightness reduction occured already before the circulation and the circulation time did not have as large effect on the darkening (results shown in **Paper IV**).

Ferrous ions also decreased the brightness of the fiber fraction. Ferrous ions increased the light absorption of the fiber fraction less than that of the fines fraction. The stronger darkening of the fines fraction resulted probably from the typically higher lignin content of the TMP fines than TMP fibers (Chang et al. 1979; Sundberg et al. 2003; Kangas, Kleen 2004) and ferrous ions probably formed strongly colored complexes with lignin. In addition, ferrous ions could have formed complexes with the dissolved and colloidal substances in the water phase and the fines could have collected these complexes more effectively than the fibers due to their larger specific surface area.

6.6.2 Chloride, sulfate, and carbonate added with calcium

The effect of chloride, sulfate, and carbonate ions on the brightness of the fines and fiber fraction of peroxide-bleached TMP was studied by dissolving $CaCl_2$, $CaSO_4$, and $CaCO_3$ in the circulation water. The dosage of each chemical was calculated for the amount of the added Ca^{2+}-ions to be 250 mg/l. The fines-

containing wire water was circulated in the RDF for 80 min. When the wire water contained dissolved $CaCl_2$, the brightness of the fines fraction of the peroxide-bleached TMP decreased both at neutral and at the acidic pH (*Fig 34*). The darkening effect was instant, because the brightness was decreased already at the beginning of the circulation. At acidic pH, the darkening was also faster during the circulation, while at the neutral pH the rate of darkening during the circulation was the same as without the added ions. $CaSO_4$ and $CaCO_3$ decreased the brightness slightly during the circulation, but notably less than $CaCl_2$. $CaCO_3$ was tested only at the acidic pH because it does not dissolve at the neutral pH level. Because of the effect of $CaCl_2$ was substantially higher than that of $CaSO_4$ or $CaCO_3$, the chloride ions appeared to be, therefore, notably more harmful to the brightness of the fines fraction than sulfate or carbonate ions.

(a)   (b)
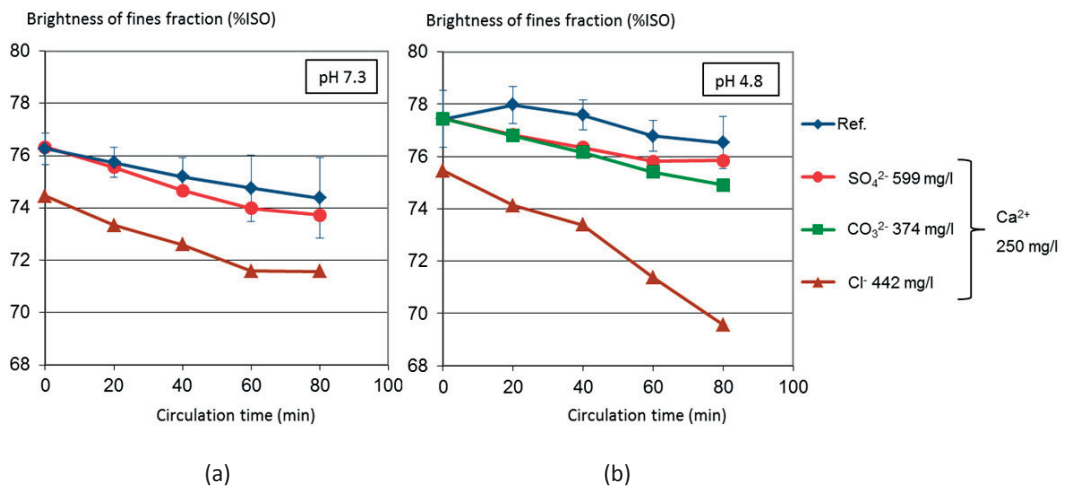
Fig 34. The effect of SO_4^{2-} -, CO_3^{2-} -, and Cl^- -ions added with calcium on the brightness of the fines fraction of peroxide-bleached TMP (Washed TMP SC 2) during the circulation at 58 °C in the RDF at (a) pH 7.3 and (b) pH 4.8. The dosage of each chemical was calculated for the amount of the added Ca^{2+}-ions to be 250 mg/l. The values of Ref. -test point at pH 7.3 were calculated as an average of two circulations in parallel, the values of Ref. -test point at pH 4.8 as average of three circulations in parallel and the values of all the other test points were from single circulations. Standard deviation was used as a measure of variation.

When $CaCl_2$ was added, the brightness reduction of the fines fraction was due to the increased light absorption both at neutral and acidic pH (*Fig 35*). $CaSO_4$ or $CaCO_3$ did not increase the light absorption as much. Calcium increased the light scattering of the fines fraction regardless of whether it was added as sulfate, carbonate, or chloride. It seemed that the calcium ions flocculated the fines which resulted in a porous sheet that had a greater surface available for light scattering. Due to the increased light scattering that compensated the increased light absorption, $CaSO_4$ did not affect the brightness of the fines fraction negatively at neutral pH (*Fig 34a*). The relatively large variations in light scattering and light absorption results can be attributed to the uneven sheet structures.
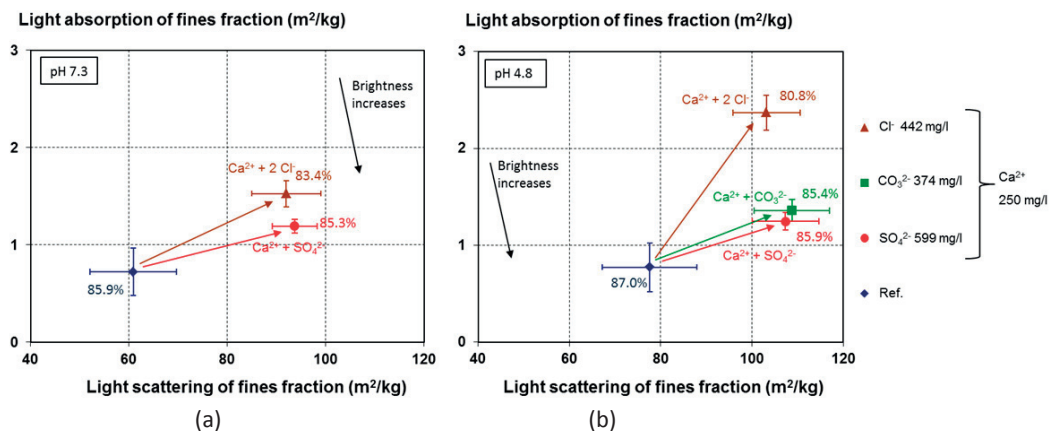
Fig 35. The effect of SO_4^{2-}-, CO_3^{2-}-, and Cl^- -ions added with calcium on the light absorption and light scattering of the fines fraction of peroxide-bleached TMP (washed TMP SC 2) at (a) pH 7.3 and (b) pH 4.8. The circulation time was 80 min and temperature 58 °C. The dosage of each chemical was calculated for the amount of the added Ca^{2+}-ions to be 250 mg/l. The brightness values (Y-values) of the test points are shown next to the data points. The values of Ref. -test point at pH 7.3 were calculated as average of two circulations in parallel, the values of Ref. -test point at pH 4.8 as average of three circulations in parallel and the values of all the other test points were from single circulations. Standard deviation was used as a measure of variation.

Calcium chloride also decreased the brightness of the fiber fraction of peroxide-bleached TMP both at neutral and acidic pH. At neutral pH, $CaSO_4$ decreased the brightness too, but to a lesser extent than $CaCl_2$. The brightness decrease was because of the increased light absorption of the fibers. The chemicals did not affect the light scattering of the fibers. This was probably because the calcium ion concentration of the water phase during the fiber sheet forming was low due to the dilution with deionized water before the sheet preparation. The fines fraction was not diluted before the sheet forming and the calcium ion concentration of the water phase was higher resulting in higher light scattering. At acidic pH, $CaSO_4$ or $CaCO_3$ did not affect the light absorption, light scattering, or brightness of the fiber fraction.

Chloride itself does not absorb light in the visible region of the spectrum. Chloride ions among other halides have a tendency to extinguish fluorescence of materials (Geddes 2001). The decrease in fluorescence can generate radicals that cause darkening. Chloride ions and the increased circulation time decreased the fluorescence of the fines sheet at pH 4.8 (*Fig 36*). However, although the chloride ions decreased the brightness of the fines fraction also at pH 7.3 (*Fig 34a*), no significant differences in fluorescence of those sheets were found. Thus, the decreased fluorescence cannot explain the chloride ion caused brightness reduction alone.
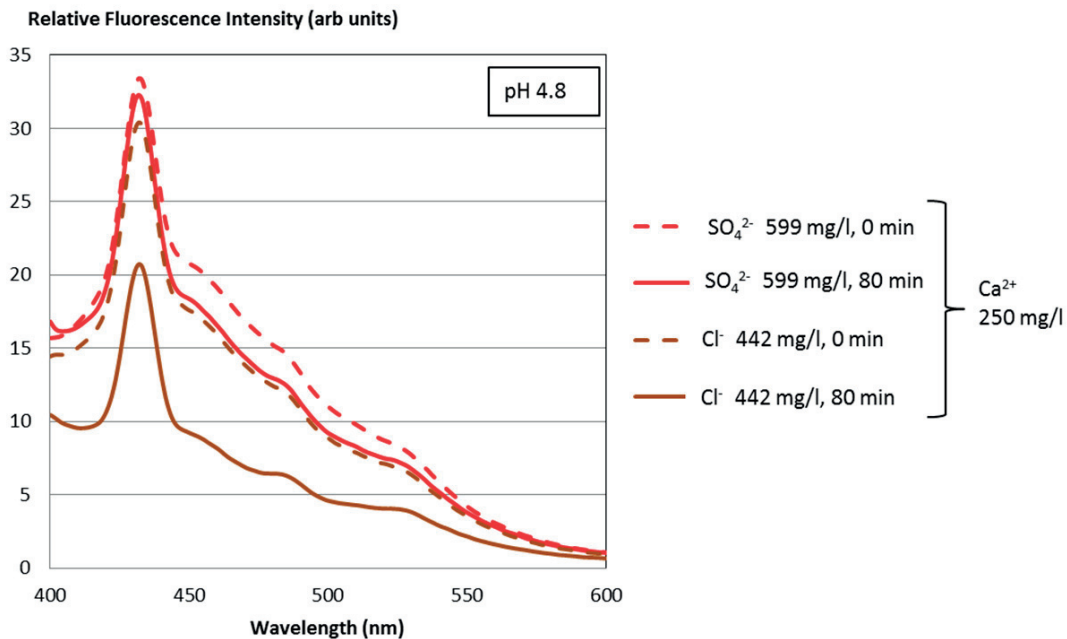
Fig 36. Relative fluorescence intensities of the fines fraction of peroxide-bleached TMP (washed TMP SC 2) circulated in the RDF at pH 4.8 and 58 °C. CaSO₄ or CaCl₂ was dissolved in the circulation water so that the amount of added Ca^{2+}-ions was 250 mg/l. The circulation time was 0 or 80 min. The brightness values of the same fines sheets were shown in Fig 34b.

6.6.3 Aluminum, calcium, and sodium added with chloride

The effect of aluminum, calcium, and sodium ions on the brightness of the fines and fiber fraction of peroxide-bleached TMP was studied by dissolving $AlCl_3$, $CaCl_2$, and NaCl in the circulation water. The dosages of each chemical were calculated for the amount of the added Cl^--ions to be 221 or 442 mg/l. At neutral pH, $CaCl_2$ and NaCl decreased the brightness of the fines fraction to some extent while $AlCl_3$ slightly increased the brightness (*Fig 37a*). At acidic pH, all the chloride chemicals decreased the brightness of the fines fraction (*Fig 37b*). $CaCl_2$ decreased the brightness most and $AlCl_3$ least. The increase in the chemical dose decreased the brightness with all the chloride chemicals. The chloride chemicals also decreased the brightness of the fiber fraction.

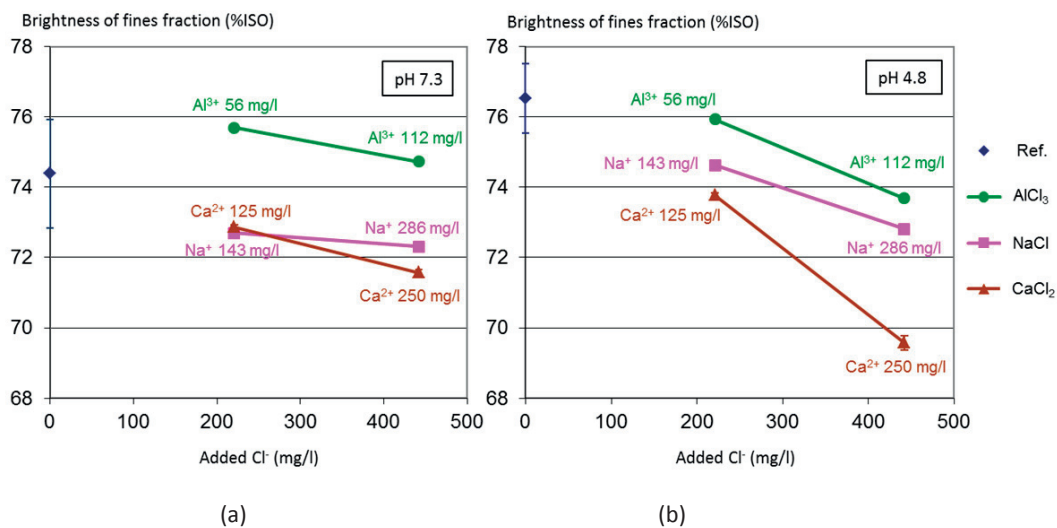**Fig 37.** The effect of added AlCl₃, CaCl₂, and NaCl on the brightness of the fines fraction of peroxide-bleached TMP (Washed TMP SC 2) at (a) pH 7.3 and (b) pH 4.8. The circulation time was 80 min and temperature 58 ℃. The value of Ref. -test point at pH 7.3 was calculated as average of two circulations in parallel, the value of Ref. -test point at pH 4.8 as average of three circulations in parallel and the values of all the other test points were from single circulations. Standard deviation was used as a measure of variation.

The decrease in brightness was due to the increased light absorption of the fines fraction (*Fig 38*). CaCl₂ increased the light absorption more than NaCl or AlCl₃. Hence, it seems that in addition to chloride ions, also calcium ions increased the light absorption. Chloride chemicals increased the light absorption of the fines fraction during the circulation more at acidic than at neutral pH indicating that chloride ions were more harmful to the brightness at acidic pH. In addition to Ca^{2+}-ions, Al^{3+}-ions increased the light scattering of the fines fraction. There was a clear change in the formation of the fines sheets, when aluminum or calcium ions were added. Aluminum and calcium ions seemed to flocculate the fines, which resulted in a porous sheet that had a greater surface available for light scattering. The sheet structure change resulted probably because at high concentrations of cations, the ionizable groups (e.g. carboxylic groups) of fines surfaces were in a dissociated form and the fines were not as swelled and softened as in pure water. This same effect of cations on pulp has been observed in many earlier studies too and the swelling has been reported to decrease with increasing cation valence (Scallan, Grignon 1979; Scallan 1983; Hammar et al. 1995; Salmén 1995). The utilization of the positive effect of Al^{3+} -ions on the light scattering on an actual paper machine is somewhat questionable, because the formation and the strength properties of the produced paper would probably worsen. In addition, it is unclear if the light scattering of the paper containing all pulp fractions (and possibly also filler) increases as much as that of the laboratory sheets from fines fraction.

It is possible that calcium ions fixed light-absorbing substances from the water phase on the surface of the fines and fiber fractions and the light absorption increased that way. However, this is uncertain because aluminum ions would have expected to fix the light absorbing substances too, but aluminum did not increase the light absorption of the fines or fiber fraction.
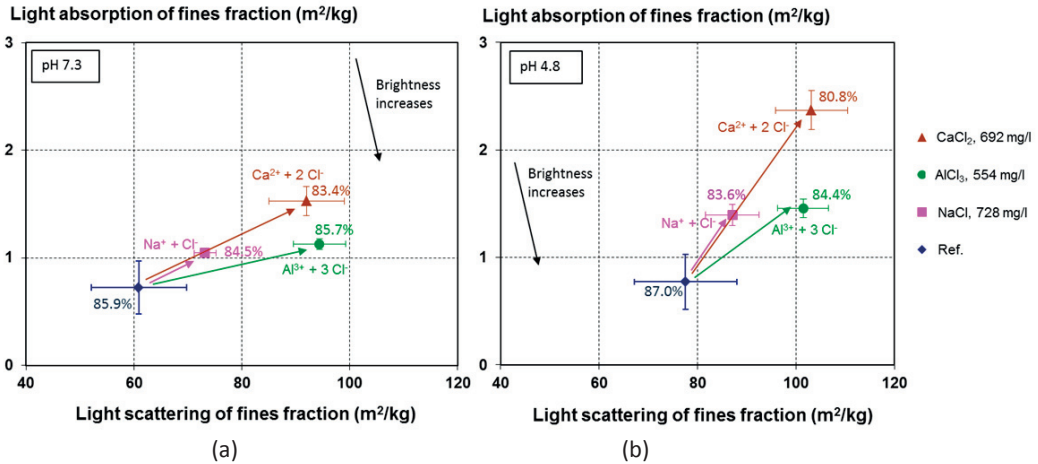
Fig 38. The effect of Na^+-, Ca^{2+}-, and Al^{3+} -ions added with chloride on the light absorption and light scattering of the fines fraction of peroxide-bleached TMP (Washed TMP SC 2) at (a) pH 7.3 and (b) 4.8. The circulation time was 80 min and temperature 58 ℃. The dosage of each chemical was calculated for the amount of the added Cl^--ions to be 442 mg/l. The values of Ref. -test point at pH 7.3 were calculated as average of two circulations in parallel, the values of Ref. -test point at pH 4.8 as average of three circulations in parallel and the values of all the other test points were from single circulations. Standard deviation was used as a measure of variation.

6.7 Brightness reduction of calcium carbonate and calcium sulfate fillers (Paper III)

6.7.1 Circulation of filler-containing wire water

PCC 1 and PCS were circulated in the RDF for 80 min in diluted filtrate of peroxide-bleached TMP at pH 7.3 and 58 °C. For comparison, the fillers were also circulated in deionized water. Sheets were formed from the peroxide-bleached TMP and circulated filler for the target filler content of the sheet to be 75 %. The light absorption and light scattering coefficients were calculated for the filler components using *Eq 5*.

The light absorption of fillers increased more during the circulation when they were circulated in the filtrate than in deionized water (*Fig 39*). This indicates that the wood-based light-absorbing substances were attached from the water phase onto the surface of the fillers during the circulation. The light absorption of the PCC 1 increased more than that of the PCS indicating that the PCC 1 adsorbed these substances more than the PCS. In addition, the light absorption of the PCC 1 was much higher already at the beginning of the

circulation in the filtrate than in deionized water, which indicates that part of the adsorption took place rapidly. The light scattering of the PCS (*Fig 40*) was somewhat higher when it was circulated in the filtrate indicating that the wood-based dissolved and colloidal substances probably changed the way the PCS flocculated. The light scattering is very sensitive to small changes in the structure of the sheet. Small unit changes in the light absorption affect the brightness notably, while the light scattering has to change substantially more to have similar effects on brightness. The change in the light scattering of both fillers during the circulation was occasional and no systematic change with respect to circulation time was observed.

Fig 39. The light absorption of fillers during the circulation in the RDF at pH 7.3 and 58 °C in water containing wood-based dissolved and colloidal substances (TMP filtrate) and in pure water (deionized water). The light absorption values of the fillers were calculated from the light absorption values of the sheets comprising about 75 % filler and 25 % peroxide-bleached TMP. PCC = Precipitated Calcium Carbonate, PCS = Precipitated Calcium Sulfate.

Fig 40. The light scattering of fillers during the circulation in the RDF at pH 7.3 and 58 °C in water containing wood-based dissolved and colloidal substances (TMP filtrate) and in pure water (deionized water). The light scattering values of the fillers were calculated from the light scattering values of the sheets comprising about 75 % filler and 25 % peroxide-bleached TMP. PCC = Precipitated Calcium Carbonate, PCS = Precipitated Calcium Sulfate.

The brightness values of the fillers (*Fig 41*) were calculated from the light absorption (*Fig 39*) and light scattering (*Fig 40*) values using Kubelka-Munk equation (*Eq 2*). The brightness of the fillers decreased more during the circulation when they were circulated in the filtrate than in deionized water and the brightness of the PCC 1 decreased more than that of the PCS. The brightness reduction (*Fig 41*) was due to the increased light absorption of the fillers (*Fig 39*).
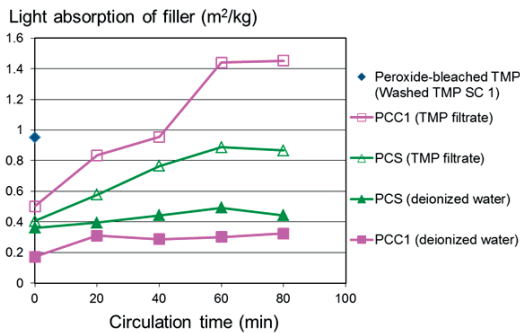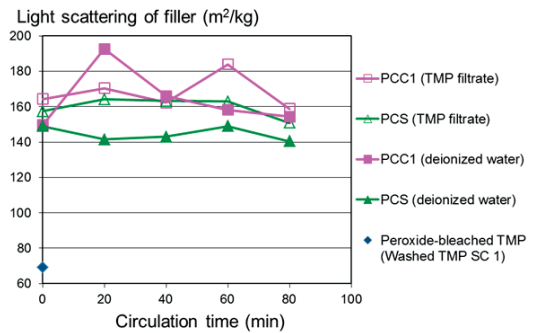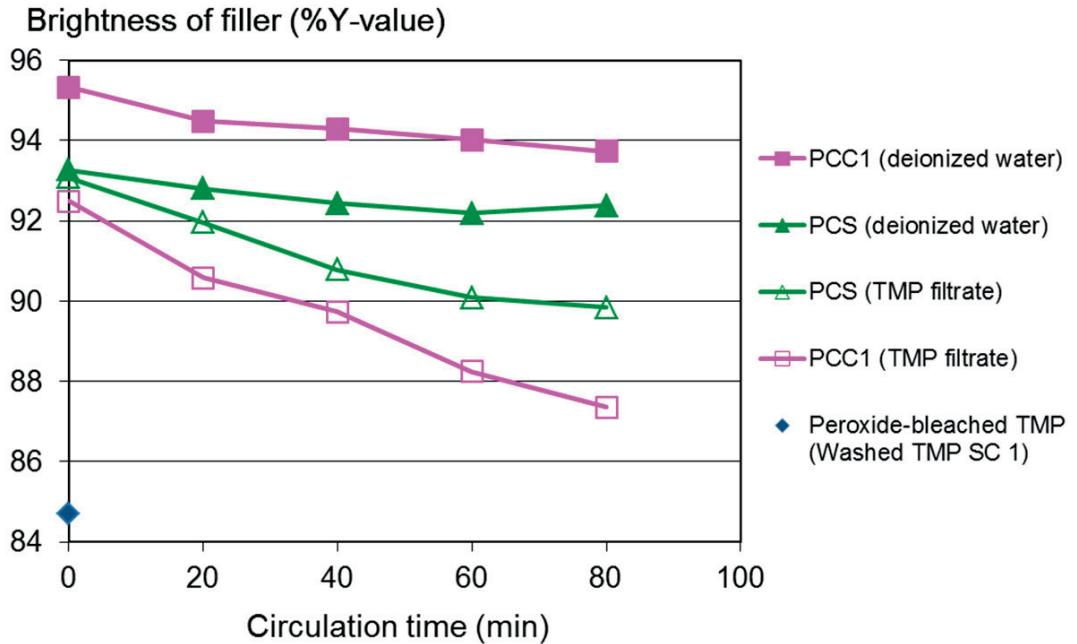
Fig 41. The brightness reduction of fillers during the circulation in the RDF at pH 7.3 and 58 °C in water containing wood-based dissolved and colloidal substances (TMP filtrate) and in pure water (deionized water). The brightness values of the fillers were calculated from the light absorption and light scattering values using Kubelka-Munk equation. PCC = Precipitated Calcium Carbonate, PCS = Precipitated Calcium Sulfate.

The filler consistency of the wire water decreased to some extent during the circulation. The effect of the decreasing filler content on the light absorption and light scattering was eliminated by calculating these coefficients for the filler components (values in *Fig 39 and 40*) from the optical properties of the produced sheets using *Eq 5* and, after that, the brightness values (*Fig 41*) using *Eq 2*. As the target filler content (75 %) of the sheets was identical in all test points and the variation less than 11 %-units (between 63.6 and 74.2 %), the elimination of the filler content variation did not skew the results. According to the calculations, in the filler content range of 63–75 %, a decrease of 1 %-unit in the filler content of a sheet decreased the brightness less than 0.1 %-units.

The extrapolation of filler content of the sheet from 75 % to 100 % increased the brightness values (*Fig 41*), because the brightness of the peroxide-bleached TMP was only 84.7 %Y-value. However, the extrapolated brightness values at the beginning of the circulation in deionized water in *Fig 41*, especially with PCS, were still much lower than the inherent brightness values of the fillers in *Table 5*. This was probably due to the fact that the inherent brightness values were measured from pure filler pellets and the values in *Fig 40* calculated from the optical properties of sheets containing approximately 25 % TMP. Although the

extrapolation was useful for the elimination of filler content variation, it did not necessarily provide very accurate brightness values for the filler components.

The adsorption of wood-based dissolved and colloidal substances on the fillers during the circulation was supported by the UV Raman spectrometry analyses. The UV Raman spectra from KBr-pellets produced from the PCC 1 and PCS samples are shown in *Fig 42* and *Fig 43*. The results depict that the same aromatic and unsaturated compounds were attached on both fillers during the circulation. The band at 1605 cm^{-1} is derived from the aromatic structures. These aromatic structures appear in lignin, lignans, and in some resin acids. The band at 1642 cm^{-1} is derived from C=C bond, which appears only in few lignin structures but is very general in extractives. The most probable extractives appearing at 1642 cm^{-1} are resin and fatty acids, according to Nuopponen (2005). The intensities of the spectra were normalized so that the amounts of carbonate (1100 cm^{-1}) in *Fig 42* and sulfate (1000 cm^{-1}) in *Fig 43* were assumed to be constant between the samples and the amount of different compounds could be compared relative to the amount of carbonate or sulfate. The shape of the bands was similar between 0 min and 80 min samples showing that the same compounds were attached on the fillers already at the beginning of the circulation, but to a lesser extent. The relatively large amount of compounds in the 0 min samples was not necessarily only due to the adsorption from the wire water, but they could also be attached on the fillers during the filtration of the filler-containing wire water sample.

The amount of compounds attached on the PCC 1 during 80 min circulation was about three times as high and the amount of compounds attached on the PCS about twice as high as the amount at the beginning of the circulation indicating that the dissolved and colloidal substances were adsorbed on the filler surfaces during the circulation. No absolute values of the amount of compounds adsorbed (mg/g filler) could be determined by the analysis. Neither the absolute amount of the adsorbed compounds on the PCC 1 and the PCS could be compared. However, it was noted that the relative difference of the adsorbed amount between the beginning and the end of the circulation was higher for PCC 1 than for PCS. UV Raman measurement is not sensitive for hemicelluloses and, therefore, the adsorption of hemicelluloses on the surface of the fillers cannot be excluded.
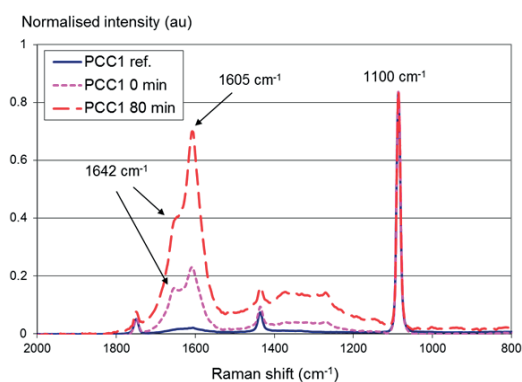
Fig 42. The UV Raman spectra from the filler samples of Precipitated Calcium Carbonate 1 (PCC 1). PCC 1 was circulated in the RDF at pH 7.3 and 58°C in the diluted filtrate of hot disintegrated peroxide-bleached TMP (Washed TMP SC 1). The heights of the bands indicate the amount of wood-based dissolved and colloidal substances adsorbed on the filler surface. Measurements were conducted from the KBr-pellets produced from the samples. PCC1 0 min = Sample taken at the beginning of the circulation, PCC1 80 min = Sample taken after 80 min circulation, PCC1 ref. = Untreated PCC1 powder. The intensity of the spectra was normalized so that the amount of carbonate (at 1100 cm^{-1}) was assumed to be constant between the samples.
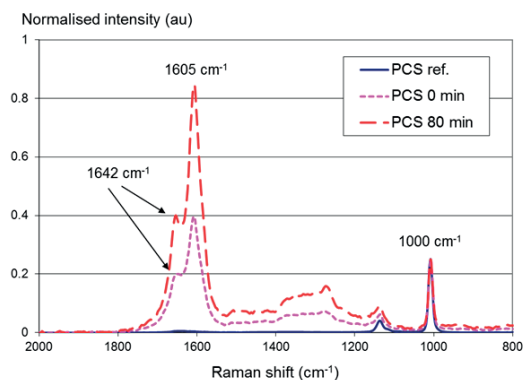
Fig 43. The UV Raman spectra from the filler samples of Precipitated Calcium Sulfate (PCS). PCS was circulated in the RDF at pH 7.3 and 58°C in the diluted filtrate of hot disintegrated peroxide-bleached TMP (Washed TMP SC 1). The heights of the bands indicate the amount of wood-based dissolved and colloidal substances adsorbed on the filler surface. Measurements were conducted from the KBr-pellets produced from the samples. PCS 0 min = Sample taken at the beginning of the circulation, PCS 80 min = Sample taken after 80 min circulation, PCS ref = Untreated oven dried PCS slurry. The intensity of the spectra was normalized so that the amount of sulfate (at 1000 cm^{-1}) was assumed to be constant between the samples.

Raman spectrometry was also used for surface measurements of the fines and fiber sheets that did not contain any filler. However, the measurements did not give any further information about the adsorption of DCS on the surfaces of fines and fibers during the circulation. It was very difficult to determine the differences in adsorbed amounts of different types of DCS because also the uncirculated fiber material contained these same substances.

6.7.2 Circulation of wire water containing filler and the fines fraction of peroxide-bleached TMP

The fillers were circulated in the wire water of the RDF with the fines fraction of peroxide-bleached TMP (washed TMP SC 2) to study the brightness reduction of the fillers in the presence of the fines. The target composition of the produced sheets was 50 % filler and 50 % fines. The variation in the filler content of the sheets was small (45.7–54.2 %). The filler content during 80 min circulation decreased by 6.3 %-units for PCC 1; 2.3 %-units for PCC 2; and 1.9 %-units for PCS. When the PCC 1 was used, the amount of the dissolved Ca^{2+}-ions in the filtrate of the sheet former was 75 mg/l at the beginning of the circulation and 210 mg/l after 80 min circulation. This dissolution corresponds to a decrease in the filler content of about 7.3 %-units. The decrease in the filler consistency of PCC 1 was, hence, mainly due to dissolution. Fillers were also visually observed to attach to the bottom of the wire pit during the circulation. This may explain the filler

consistency decrease for PCC 2 and PCS. The variation was eliminated by extrapolating the filler content to 50 % in every test point using *Eq 5*.

When the PCS was used, the light absorption (*Fig 44*) increased very little, indicating that the PCS adsorbed light-absorbing substances less than the PCC fillers. With PCC 2 the increase in light absorption during the circulation was about the same as without filler and with PCC 1 the light absorption increased the most. The fillers did not affect the light absorption of the sheet notably at the beginning of the circulation. Fillers increased the light scattering of the sheet (*Fig 45*), but the light scattering did not change substantially during the circulation. The PCC fillers increased the light scattering of the sheet more than the PCS, since the light scattering ability of aggregates (PCC) is typically higher than that of the platy particles (PCS) (Imppola 2009).

Fig 44. The effect of circulation time in the RDF at pH 7.3 and 58 °C on the light absorption of sheets prepared from the wire water of the RDF containing filler and the fines fraction of peroxide-bleached TMP (washed TMP SC 2). PCC = Precipitated Calcium Carbonate, PCS = Precipitated Calcium Sulfate. The actual filler content of the produced sheets was in the range of 45.7-54.2 % and the values were calculated from the measured values of the produced sheets by extrapolating the filler content to 50 %.

Fig 45. The effect of circulation time in the RDF at pH 7.3 and 58 °C on the light scattering of sheets prepared from the wire water of the RDF containing filler and the fines fraction of peroxide-bleached TMP (washed TMP SC 2). PCC = Precipitated Calcium Carbonate, PCS = Precipitated Calcium Sulfate. The actual filler content of the produced sheets was in the range of 45.7-54.2 % and the values were calculated from the measured values of the produced sheets by extrapolating the filler content to 50 %.

The brightness values of the sheets (*Fig 46*) were calculated from the light absorption and light scattering values using the Kubelka-Munk equation (*Eq 2*). Compared to the sheets made of only fines, fillers increased the brightness of the sheet because of the higher light scattering (*Fig 45*) of the fillers. The rate of darkening during the circulation was notably lower when the wire water contained PCS due to the smaller increase in the light absorption of the sheet (*Fig 44*). In addition to the adsorption of the light-absorbing substances from the water phase, part of the increase in the light absorption of the fines fraction during the circulation is believed to be due to the formation of the light-absorbing chromophores in the lignin structures of the fines. Fillers do not contain lignin and their light absorption increase was probably only due to the adsorption of the light-absorbing substances.
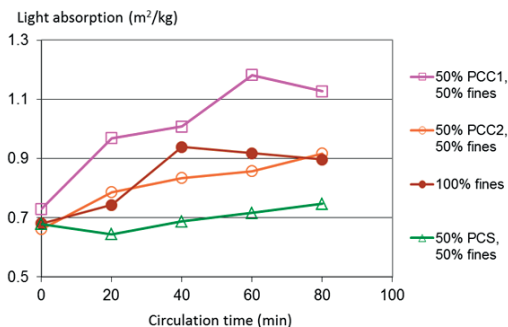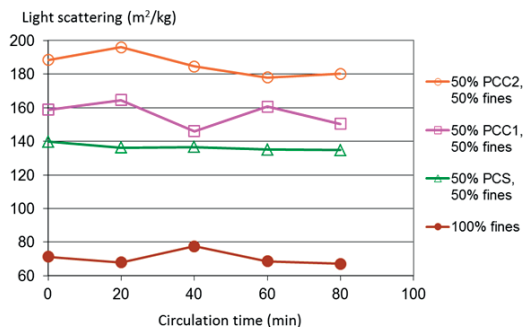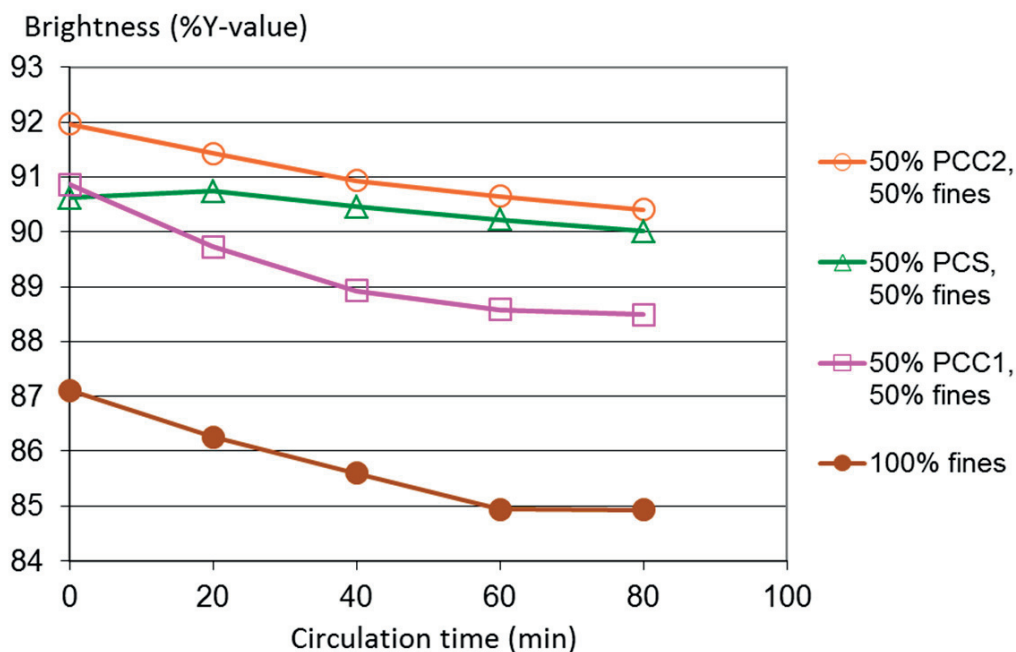
Fig 46. The effect of circulation time in the RDF at pH 7.3 and 58 °C on the brightness of sheets prepared from the wire water of the RDF containing filler and the fines fraction of peroxide-bleached TMP (washed TMP SC 2). PCC = Precipitated Calcium Carbonate, PCS = Precipitated Calcium Sulfate. The values were calculated from the light absorption and light scattering values using Kubelka-Munk equation.

The dissolution of PCS and PCC 1 increased the calcium ion concentration of the water phase significantly. The lipophilic extractives and galacturonic acid containing carbohydrates (e.g. anionic pectins) of the peroxide-bleached mechanical pulp are flocculated in the presence of multivalent cations (e.g. calcium, aluminum) (Sundberg 1995; Saarimaa et al. 2006). When $CaCl_2$ is added to the peroxide-bleached TMP water, the coagulation of resin starts at the dosage of 1 mmol/l and all the resin is aggregated at the dosage of 10 mmol/l (Sundberg et al. 1994a, 1994b, 1996). This is equivalent to Ca^{2+} concentrations of 40–400 mg/l. Hence, the colloidal wood pitch was probably fully aggregated when the PCS was used and also at least partly aggregated when the PCC 1 was used. However, the brightness reduction was lowest with PCS and, hence, it appears that the increased Ca^{2+} concentration or the aggregation of wood pitch did not have a major effect on the darkening. In addition, as was seen in Section 6.6.2, the dissolved SO_4^{2-} or CO_3^{2-} ions did not have a notable effect on the brightness of the fines fraction of the peroxide-bleached TMP.

The effect of the pH on the brightness of the sheets containing approximately 50 % filler and 50 % fines is shown in *Fig 47*. The actual filler contents of the sheets are shown next to the data points. The effect of the variation in the filler content on brightness could not be eliminated, because the optical properties of the fines

fraction were known only at pH 7.3. The variation in the filler content did not affect the brightness that much, as, for example the brightness of the sheet containing PCC 1 at pH 7.3 would have been less than 0.2 %-units higher, if the filler content had been extrapolated from 45.7 % to 50 %. The brightness losses seen for PCC 2 and PCS were minute indicating that the effect of the pH was practically insignificant for PCC 2 and PCS.
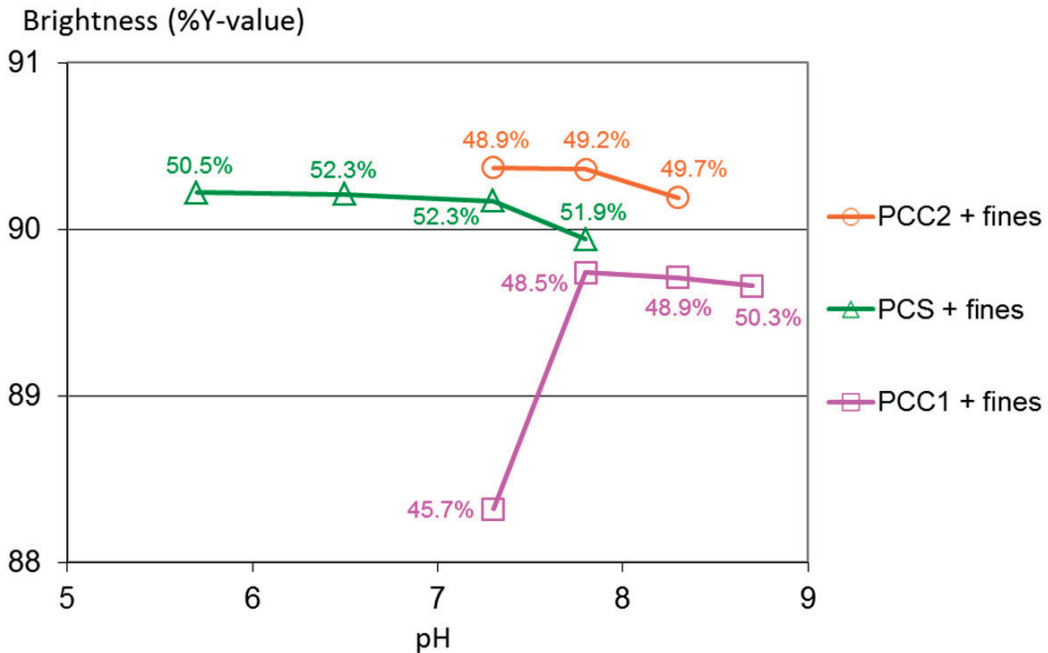
Fig 47. The effect of pH on the brightness of the sheet containing about 50 % filler and 50 % the fines fraction of peroxide-bleached TMP (washed TMP SC 2). The circulation time was 80 min and temperature 58 °C. The filler contents of the sheets are shown next to the data points. PCC = Precipitated Calcium Carbonate, PCS = Precipitated Calcium Sulfate. The brightness values of the sheets from the fines fraction of peroxide-bleached TMP were: At pH 4.8: 87.0 %Y-value and at pH 7.3: 84.9 %Y-value.

For PCC 2 and PCS the filler content was close to 50 % at all pH levels. When PCC 1 was used, the filler content was close to 50 % at pH 7.8–8.7, but notably lower at pH 7.3. With PCC 1 at pH 7.3, the amount of dissolved Ca^{2+}-ions in the water phase was 75 mg/l at the beginning of the circulation and 210 mg/l after 80 min circulation indicating that PCC 1 dissolved. $CaCO_3$ fillers form CO_2 gas while dissolving. CO_2 decreases the brightness of the fines fraction of the peroxide-bleached TMP as was shown in Section 6.5. At pH 7.3, PCC 1 released carbon dioxide while dissolving and it probably darkened the fines fraction of the peroxide-bleached TMP causing the low brightness values in *Fig 46* and *47*.

6.8 Summary of the effects of different process variables

The effect of different process variables on the optical properties of the fines and fiber fraction of peroxide-bleached mechanical pulp at circulation time 80 min at 58 °C is collected in *Table 10*.

Table 10. The effect of process variables on the optical properties of the fines and fiber fraction of peroxide-bleached mechanical pulp at circulation time 80 min at 58 °C. k = specific light absorption coefficient. s = specific light scattering coefficient. Notice that a positive effect (+) in light absorption-column (k) has a negative effect on brightness.

Variable (Circulation time 80 min)	Fines fraction				Fiber fraction			
	Brightness (%ISO)	Y-value (%)	k (m^2/kg)	s (m^2/kg)	Brightness (%ISO)	Y-value (%)	k (m^2/kg)	s (m^2/kg)
Pulp washing (unwashed→washed)	+++	+++	- - -	±0	+++	+++	- - -	±0
pH (7.3→4.8)	+	±0	±0	+	±0	±0	±0	±0
Shear rate (10^2 s^{-1}→10^4 s^{-1})	-	-	+	±0	-	-	+	±0
CO_2 gas (0 g/l→0.524 g/l)	-	-	++	+	n.a.	n.a.	n.a.	n.a.
Fe^{2+} (0 mg/l→1 mg/l)	- - -	- - -	+++	±0	- - -	- - -	+++	±0
Ca^{2+} (0 mg/l→250 mg/l)	-	-	++	++	±0	-	+	±0
Al^{3+} (0 mg/l→112 mg/l)	+	+	±0	++	±0	±0	±0	±0
Cl^- (0 mg/l→442 mg/l)	- -	- -	++	±0	-	-	+	±0
Mn^{2+} (0 mg/l→1 mg/l)	±0	±0	±0	±0	±0	±0	±0	±0
SO_4^{2-} (0 mg/l→599 mg/l)	±0	±0	±0	±0	±0	±0	±0	±0
CO_3^{2-} (0 mg/l→374 mg/l)	±0	±0	±0	±0	±0	±0	±0	±0
+++/- - - = Variable increases/decreases the optical property very much. ++/- - = Variable increases/decreases the optical property much. +/- = Variable increases/decreases the optical property a little. ±0 = Variable has no effect on the optical property. n.a. = not analysed								

The effect of the wood-based dissolved and colloidal substances on the brightness reduction of PCC and PCS fillers is collected in *Table 11*. The rate of brightness reduction during the circulation was notably faster when fillers were circulated in TMP filtrate indicating that the DCS were adsorbed on the filler surfaces and thus lowered their brightness. The PCC adsorbed more DCS from the water phase than the PCS and was, therefore, more susceptible towards darkening. PCC fillers were more susceptible towards darkening also when circulated with the fines fraction of the washed peroxide-bleached TMP (*Table 12*). The pH of the wire water did not affect the darkening of the mixture of filler and the fines fraction as long as the pH was high enough to avoid the dissolution of PCC.

Table 11. The effect of circulation time on the optical properties of the fillers during the circulation in deionized water and in the filtrate of washed peroxide-bleached TMP at pH 7.3 and 58 °C. PCC = Precipitated Calcium Carbonate. PCS = Precipitated Calcium Sulfate.

Variable	100% filler			
	Brightness (%ISO)	Y-value (%)	k (m^2/kg)	s (m^2/kg)
Circulation time in deionized water (0 min→80 min):				
PCC 1	-	-	+	±0
PCS	-	-	+	±0
Circulation time in TMP filtrate (0 min→80 min):				
PCC 1	- - -	- - -	+++	±0
PCS	- -	- -	++	±0
+++/- - - = Variable increases/decreases the optical property very much.				
++/- - = Variable increases/decreases the optical property much.				
+/- = Variable increases/decreases the optical property a little.				
±0 = Variable has no effect on the optical property.				

Table 12. The effect of circulation time and pH at 58 °C on the optical properties of sheets produced from circulation water containing 50 % filler and 50 % fines fraction of washed peroxide-bleached TMP. PCC = Precipitated Calcium Carbonate. PCS = Precipitated Calcium Sulfate.

Variable	50% filler, 50% fines fraction of washed peroxide-bleached TMP			
	Brightness (%ISO)	Y-value (%)	k (m^2/kg)	s (m^2/kg)
Circulation time at pH 7.3 (0 min→80 min):				
PCC 1	- - -	- - -	+++	±0
PCC 2	- -	- -	++	±0
PCS	-	-	+	±0
pH:				
PCC 1 (8.7→7.8)	±0	±0	±0	±0
(7.8→7.3)	- - -	- - -	+++	±0
PCC 2 (8.3→7.3)	±0	±0	±0	±0
PCS (7.8→5.7)	±0	±0	±0	±0
+++/- - - = Variable increases/decreases the optical property very much.				
++/- - = Variable increases/decreases the optical property much.				
+/- = Variable increases/decreases the optical property a little.				
±0 = Variable has no effect on the optical property.				

7 CONCLUSIONS

In order to simulate the short circulation of a paper machine and to reach a realistic brightness reduction in the fines and fiber fraction of peroxide-bleached mechanical pulp in a sufficiently short residence time, a laboratory scale methodology was developed. For this purpose, a new laboratory scale device, the Recycling Device of Fines (RDF), was constructed. The rate of darkening reached using the new device was acceptable and reliable, the brightness reduction was due to the increased light absorption, the results were repeatable and the method was found suitable for studying the darkening phenomena in the wet end of a paper machine.

The results indicated that the brightness reduction of peroxide-bleached mechanical pulp in the wet end of a paper machine was partly due to the formation of light-absorbing chromophores in the fibers and fines and partly due to the adsorption of light-absorbing substances to the surfaces of fibers and fines from the water phase. Fillers do not contain lignin or other structures with high darkening tendency and their brightness reduction was caused by the adsorption of light-absorbing DCS. Pulp washing removes the light-absorbing substances from the pulp suspension and is, therefore, an efficient way to reduce the darkening tendency of the pulp itself as well as that of the fillers.

In addition to the wood-based DCS, the most important factors affecting the brightness reduction of peroxide-bleached mechanical pulp were the residence time of the pulp in the wet end and the iron concentration of the white water. Other factors decreasing the brightness notably, but to lesser extent, were high shear rate generated to the pulp, carbon dioxide gas, chloride ions, and calcium ions. No change was noted in the light absorption of the peroxide-bleached mechanical pulp between acidic and neutral test conditions. Thus, from brightness point of view, paper grades from peroxide-bleached mechanical pulp from Norway spruce can be manufactured equally well at neutral or at acidic process conditions.

UV Raman measurements indicated that the wood-based DCS were adsorbed on both PCC and PCS fillers resulting in their decreased brightness. PCC filler was more prone to adsorb these substances and was therefore more susceptible towards darkening. The pH of the wire water did not affect the darkening of the fillers. However, a too low pH can cause dissolution of calcium carbonate fillers and formation of carbon dioxide gas that may decrease the brightness of wood material. The use of PCS as filler or coating pigment in paper mills is minimal currently, but relative to brightness reduction tendency it could give somewhat better results than the PCC fillers.

This study provides important knowledge for papermakers as well as filler and chemical suppliers. If a paper mill has problems with paper brightness, an installation of an efficient pulp washing stage after the peroxide

bleaching could be beneficial. The cost-effectiveness of the installation of a pulp washing stage should be calculated thoroughly. Another possibility to reduce the detrimental effect of the DCS could be an internal purification system of the circulation water, but it would probably be more reasonable to remove the detrimental substances already in an earlier stage, e.g. in a pulp washing stage. A high retention is also desirable, because it shortens the residence time of the stock components in the short circulation. Hence, the optimization of the retention systems is very important. It is essential to ensure that the iron content of the pulp and white water is as low as possible because already low contents of iron have a negative effect on the brightness of the produced paper. The high shear rates are very difficult to be avoided in the flows of an actual paper machine. They are needed, for example, to keep an even stock consistency and to ensure an optimal working of different chemical additives. From brightness point of view, the use of carbon dioxide gas for paper machine pH control is questionable in the wet end of a paper machine and the dissolution of calcium carbonate fillers should be avoided.

Although the chloride ions darkened the fines and fiber fraction, the chloride ion concentration of the white water in actual paper machines is very rarely as high as in these tests. However, chloride chemicals are used very commonly as model chemicals for different cations in laboratory tests. This study showed that chlorides are not suitable model chemicals for cations, if darkening phenomena are studied, because chloride ions decrease the brightness.

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