

Brightness Reduction of Mechanical Pulp in the Wet End of a Paper Machine: The Effect of Different Ions in the Circulation Water

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Darkening of the fines and fiber fraction of peroxide-bleached thermo-mechanical pulp (TMP) was studied on a laboratory scale using a device that simulates the short circulation of a paper machine. Selected chemicals were dissolved in the circulation water to study the effect of different cations and anions. Ferrous ions darkened the fines and fiber fraction by increasing the light absorption. It is very important to keep the iron content of the pulp and white water as low as possible because even low contents of iron have a negative effect on the brightness of produced paper. Also, chloride ions decreased the brightness by increasing the light absorption of the fines and fiber fraction. Calcium ions increased both the light absorption and light scattering of the fines fraction. The increased light absorption dominated and the brightness decreased. Calcium chloride is used very commonly as a model chemical for calcium ions in laboratory tests, but the use of it is not recommended, if the darkening phenomena are studied, because chloride ions decrease the brightness. Aluminum ions increased the brightness of the fines fraction by increasing the light scattering. Manganese, sodium, sulfate, or carbonate ions did not affect the optical properties.

Keywords: Brightness reduction; Fines; Thermomechanical pulp; Mechanical pulp; Wet end; Water circulation; Cation; Anion

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INTRODUCTION

The brightness demands for improved newsprint and for 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 and Federer 2002; Luoma *et al.* 2004). The white water of a paper machine contains relatively large amounts of various ions that can decrease the brightness of the produced paper.

Different ions can be carried into the water flows of a paper machine with pulps, fresh water, fillers, and chemical additives or they can be dissolved from the process equipment. Iron and manganese are typical disturbing metal ions in peroxide bleaching processes of mechanical pulps (Lindholm 1999; Johns 1996; Kappel and Sbaschnigg 1991; Colodetto *et al.* 1988). Because iron and manganese decompose peroxide, it is important to remove them before a peroxide bleaching stage. The removal can be carried out by acidifying the pulp to pH levels of 2 to 3 or by treating the pulp with a chelating agent.

Acidification and the chelating agent release the metal ions from the fibers, but they still have to be washed out of the system in a washer ahead of the bleaching stage. Because the chelation and washing are usually incomplete, the metal ions can be carried with the pulp to the circulation waters of a paper machine. In addition, fillers and coating pigments used in paper making, especially kaolin, can contain relatively large amounts of iron.

The main sources of the other metal ions (Na^+ , Ca^{2+} , and Al^{3+}) and anions (Cl^- , SO_4^{2-} , and CO_3^{2-}) studied in this paper are different chemical additives, fillers, and coating pigments used in the papermaking process. Sodium hydroxide used for controlling the pH of the stock is the main source for Na^+ ions, while calcium carbonate used as filler or coating pigment is the main source of Ca^{2+} and CO_3^{2-} ions. Al^{3+} ions mainly come from inorganic fixatives.

Different dry-strength additives *e.g.* Polyvinyl Amine (PVAm) and fixatives *e.g.* polydiallyldimethylammonium chloride (poly-DADMAC) and polyaluminum chloride (PAC) contain chloride. The sources of sulfate ions are *e.g.* sulfuric acid that is used for pH control and fixatives *e.g.* aluminum sulfate (papermaker's alum), and polyaluminum nitrate sulfate (ANS).

The effect of metal ions on the brightness of mechanical pulp has been studied to some extent (Forskåhl 2000; Janson and Forskåhl 1989; Ni *et al.* 1997; Konn 1998), while, to our knowledge, the effect of different anions has yet to be studied. 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). In addition to the effect of different anions, this study gives additional information on the metal ion-caused brightness reduction of both the fines and the fiber fraction of peroxide bleached TMP as a function of time when the pulp is exposed to typical shear rates in the wet end of a paper machine.

The darkening is explained by the formation of colored complexes between lignin functional groups and metal ions (Ni *et al.* 1997). 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). 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 (Ni *et al.* 1997; Read *et al.* 1968; Gupta 1970). Precipitation of metal ions as highly colored compounds is also possible.

The aim of this study was to clarify the effects of Fe^{2+} , Mn^{2+} , Na^+ , Ca^{2+} , Al^{3+} , Cl^- , SO_4^{2-} , and CO_3^{2-} ions on the brightness reduction of the fines and fiber fractions of peroxide bleached TMP in the short circulation. This is part of a broader research on mechanisms and phenomena causing the brightness reduction of mechanical pulp and fillers in the wet end of a paper machine.

EXPERIMENTAL

Materials

Pulps

The pulps used in this work were washed peroxide bleached thermomechanical pulps from Norway spruce (*Picea abies*), sampled after bleaching and washing stages of two different Nordic paper mills producing SC- and LWC-paper. The properties of the pulps are shown in Table 1.

Table 1. Properties of the Pulps Used

	Dry content (%)	CSF (mL)	pH	ISO Brightness (%)	Fines content P200 (%)
Standards used	ISO 638-1978 (E)	ISO 5263, ISO 5267-2	-	SCAN-CM 11:95, ISO 2470	SCAN-CM 66:05
TMP LWC	31.7	31	7.5	75.3	28
TMP SC 1	32.7	39	7.3	73.0	30
TMP SC 2	31.3	70	7.7	75.9	20

The amounts of different metals in the pulps were studied from dried pulp samples by an X-Ray Fluorescence (XRF) analysis (Table 2). Also the concentrations of different ions in the water phases of hot disintegrated pulps (at 60 °C and 20 g/L) were studied by an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis. The concentrations of Al^{3+} , Ca^{2+} , and Fe^{2+} were below the detection limit, 1 mg/L. The Na^+ concentrations were 58 mg/L (TMP LWC), 74 mg/L (TMP SC 1), and 102 mg/L (TMP SC 2). In the experiments the pulps were diluted after hot disintegration from 20 g/L to 5 g/L before circulation, and hence the ion concentrations of the circulation water without added ions can be assumed to be 1/4 of the concentrations in the water phases of the hot disintegrated pulps. As the ion concentrations of the water phases of hot disintegrated pulps were low, the major part of the ions in the circulation water came from the ion additions, and the initial metal content of the pulp did not have a notable effect on the ion-caused darkening.

Table 2. Metal Contents of the Pulps Analyzed by X-Ray Fluorescence (XRF) Spectrometer

	Ca (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Na (mg/kg)
TMP LWC	480	12	7	4690
TMP SC 1	400	6	3	5290
TMP SC 2	470	6	4	7720

Chemicals

Different chemicals were used to study the effect of different ions on the darkening of the fines and fiber fraction of peroxide bleached TMP (Table 3). The chemicals were dissolved in dilution water before the experiments to act as model substances of disturbing cations and/or anions.

Ferrous sulfate and manganese chloride were added to study the effect of Fe^{2+} - and Mn^{2+} -ions, respectively. The dosages of these chemicals were low because the concentrations of ferrous and manganese ions is typically 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 effects of sulfate, chloride, and carbonate ions were studied at higher dosage levels using calcium sulfate, calcium chloride, and calcium carbonate, respectively. The dosage of each chemical was calculated so that the amount of added calcium ions was constant. Calcium chloride, aluminum chloride, and sodium chloride were used to study the effect of calcium, aluminum, and sodium ions, respectively. The dosage of each chemical was calculated so that the amount of added chloride ions was constant.

All the chemicals were analytical grades with very low impurity contents (iron content max 5 ppm) except calcium carbonate, which was a dry filler pigment powder with a CaCO_3 -content of 98% and iron content (as Fe_2O_3) of 0.06%. In addition to chemicals in Table 3, 1 M NaOH and H_2SO_4 were used for pH control of the pulp and fines-containing wire water (circulation water) during the experimental procedure.

Table 3. Chemicals 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 ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$)	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 ($\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$)	Mn^{2+} : 0 or 1.0	Cl^- : 0 or 1.3
Calcium sulfate ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$)	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 ($\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$)	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

Methods

The short circulation of a paper machine was simulated on a laboratory scale using the Recycling Device of Fines (RDF); see Varhimo *et al.* 2012 for details. It is set up like a DDJ-type drainage jar (wire section) and a heated stainless steel sink (wire pit) combined with a peristaltic pump circulating the fines-containing wire water back to the drainage jar. A 52-mesh wire screen was used in the drainage jar. Peroxide-bleached TMP was diluted with deionized water to a consistency of 20 g/L and hot-disintegrated at 60 °C. The pH of the pulp was adjusted before the hot disintegration, controlled at 10,000 revolutions, and, after the hot disintegration (30,000 revolutions), by drop-wise addition of 1 M NaOH or H_2SO_4 . The hot-disintegrated pulp was diluted with deionized water to a consistency of 5 g/L and transferred into the RDF. Different chemicals (see Table 2) were dissolved in the dilution waters. The fines-containing wire water was circulated at 58 °C, and the wire water samples were taken during the circulation. The fiber samples were taken before and after the circulation. The pH of the fines-containing wire water was measured and controlled during the circulation by drop-wise additions of 1 M NaOH or H_2SO_4 . The chemical additions did not affect the consistency of the fines-containing wire water, and therefore the separation of the fines and fiber fraction during the circulation

was not disturbed by the added ions. 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 fractionated or washed to remove all fines since this could have also washed colored substances away from the fibers. The high fines content makes this fraction resemble the original pulp composition more than a pure long fiber fraction. The fractions were similar to the fractions generated in Varhimo *et al.* 2012.

The sheets (target grammage 50 g/m²) were prepared from the samples using a special vacuum sheet former with a 150-mesh wire (Varhimo *et al.* 2012), and the optical properties of the sheets were measured. Hence, darkening of fines and fiber fractions could be determined as a function of the circulation time at acidic (4.8) and neutral (7.3) pH levels. The fines suspension, about 1.0 g/L, was transferred as such into the sheet former, and no dilution was used in the sheet former. The fiber samples were diluted with deionized water to a consistency of 1.0 g/L without pH adjustment before being transferred into the sheet former. So, the pH during the sheet forming of fiber sheets was close to neutral both in acidic and neutral circulation test points. In addition, the ion concentrations of the water phase were low during the sheet forming of fiber sheets.

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 in different test points and therefore the light absorption and light scattering coefficients correlated well with ISO brightness. The fluorescence of the fines sheets of test points including dissolved CaCl₂ and CaSO₄ were measured within the wavelength range 400 to 600 nm with a Perkin Elmer LS-50B luminescence spectrometer to find out the effect of chloride ions on the fluorescence of the sheets. The measurement parameters were: emission slit 10 nm, excitation slit 10 nm, scan speed 100 nm/min, emission filter 390 nm, and excitation wavelength 375 nm. The number of parallel measurements per test point was 3. A flow sheet of the experimental procedure is shown in Fig. 1.

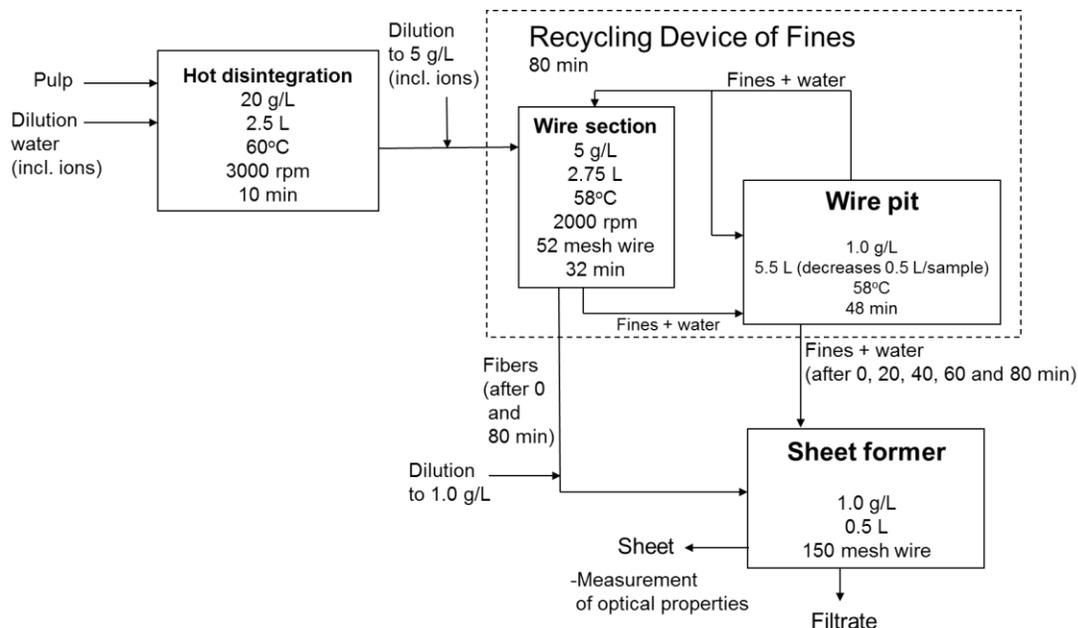


Fig. 1. The flow sheet and values of the parameters of the experimental procedure

With a typical circulation time of 80 min, the retention time of the fines was 32 min on average in the wire section where the shear forces were high (2000 rpm agitation) and 48 min on average in the wire pit where the shear forces were low. The fiber fraction remained in the wire section for the whole circulation time.

Mathematical models used in interpretation of results

The different ions were always added as chemical compounds including both cations and anions. To mathematically separate the individual effects of these pairs from each other and to characterize the effect of each cation and anion separately, multiple linear regression analyses were performed based on the results. The variables were: Fe^{2+} , Mn^{2+} , Al^{3+} , Ca^{2+} , Na^+ , Cl^- , SO_4^{2-} , CO_3^{2-} , pH, circulation time, and the pulp used. The levels of the variables in the different runs were too irregularly distributed to be used in a classical analysis of variance. In a multiple linear regression analysis the linear model that minimizes the difference between the measured responses and the predicted values is found. The minimization is made in the least square sense. Because of the linearity, there is a unique solution. The analysis also produces statistics where the significance of the different variables is estimated. One value that can be used to estimate the significance of the variables is the p-value, a number between 0 and 1, which can be interpreted as a probability. A level of 0.01 was chosen as significance limit; a p-value higher than that was interpreted to indicate no statistical significance of the variable. If some of the variables were found to have higher p-values than 0.01, they were then removed from a subsequent regression analysis.

In the case of the ion-variables there is bound to be multicollinearity between the variables since they are always added in the form of certain chemical compounds. According to the results, it could be assumed that the effect of the carbonate ion is negligible. Then, the multicollinearity was lifted and the analysis can be performed. After removing the not statistical significant variables, the carbonate ion can be taken back into the analysis. So, finally the effect of carbonate ion was also tested. The regression analysis was made for the main effects using MINITAB 16 Statistical Software.

RESULTS AND DISCUSSION

The Effect of Ferrous and Manganese Ions

Ferrous ions were found to decrease the brightness of the fines fraction substantially at low concentrations (Fig. 2). A Fe^{2+} -ion concentration of 0.3 mg/L decreased the brightness of the fines fraction by about 2%-units. Fe^{2+} -ions already darkened the fines fraction during the hot disintegration (before the circulation), but the rate of darkening during the circulation was the same as without ferrous ions. The brightness reduction during the circulation without added ions 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 adsorption of light-absorbing dissolved and colloidal substances (e.g. lignin and its relatives) to their surfaces from the water phase. The mechanism for darkening during the circulation with added Fe^{2+} concentrations of 0.3 to 1.0 mg/L seemed to be the same. According to Varhimo *et al.* (2013a), a pH change from 4.8 to 7.3 did not affect the light absorption of the fines or fiber fraction of peroxide bleached TMP during the circulation, and hence the darkening was not due to alkaline

conditions. Manganese ions did not affect the brightness at the dosage level of 1.0 mg/L (Fig. 2).

When the Fe^{2+} -ion concentration of the circulation water was very high (2.5 or 5.0 mg/L), a major part of the brightness reduction happened already before the circulation, and the circulation time did not have as large effect on the darkening (Fig. 3). The brightness actually increased in the beginning of the circulation, which was probably caused by de-sorption of iron from the surfaces of the fines due to the high shear rate (2000 rpm agitation) in the wire section of the RDF.

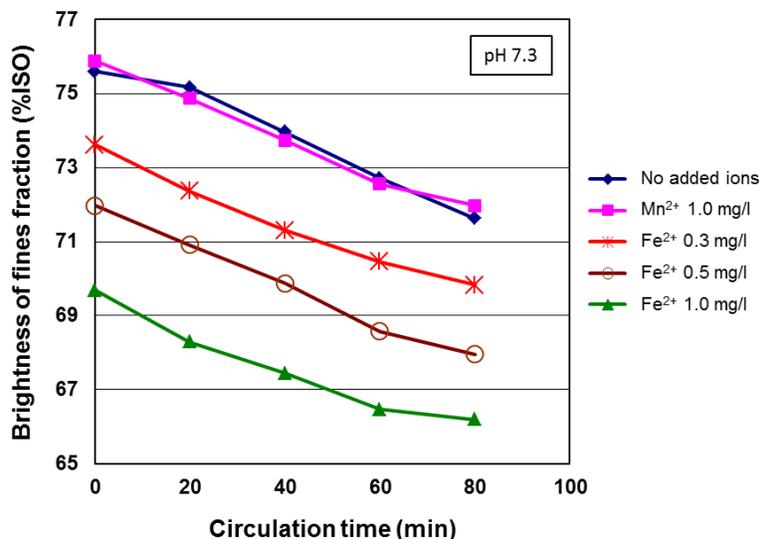


Fig. 2. The effect of Fe^{2+} - and Mn^{2+} -ion concentrations of the wire water on the darkening of the fines fraction of peroxide bleached TMP (TMP SC 1) during the circulation in the RDF at pH 7.3 and 58 °C. Fe^{2+} -ions were added as FeSO_4 and Mn^{2+} -ions as MnCl_2 . The values of the test points are from single circulations.

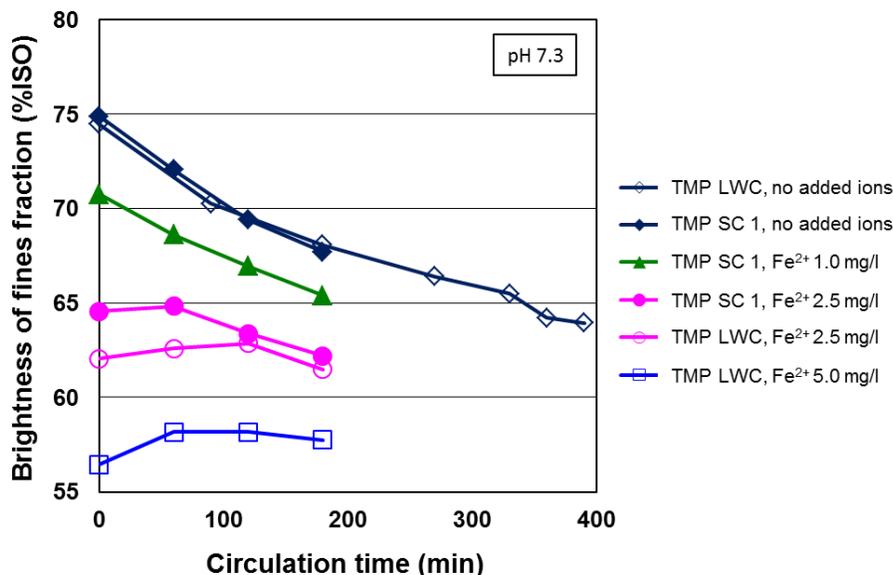


Fig. 3. The effect of Fe^{2+} -ion concentration of the wire water on the darkening of the fines fraction of peroxide bleached TMP during the circulation in the RDF at pH 7.3 and 58 °C. Fe^{2+} -ions were added as FeSO_4 . The values of TMP SC 1, no added ions-test point were calculated as average of two circulations in parallel and the values of all the other test points were from single circulations.

Two similar test series were carried out with TMP SC 1, and the results are shown in Figs. 2 and 3: no added ions and Fe^{2+} 1.0 mg/L. The brightness values at the same circulation times (0 and 60 min) in these test series were from different runs and therefore not precisely the same, yet quite close to each other.

Ferrous ions also decreased the brightness of the fiber fraction. The darkening of fines and fiber fractions caused by ferrous ions is due to increased light absorption. Ferrous ions increase the light absorption of the fiber fraction less than that of the fines fraction. The brightness of the fines and fiber fraction is compared in Fig. 4. When Fe^{2+} -ions were not added in the process, the brightness of the fines fraction was about the same as that of the fiber fraction. When the Fe^{2+} -ion concentration of the circulation water was 1.0 mg/L, the brightness of the fines fraction was slightly lower than that of the fiber fraction. At the Fe^{2+} -ion concentration of 2.5 mg/L, the brightness of the fines fraction was notably lower than that of the fiber fraction. The difference in brightness between the fines and the fiber fraction was especially large at the beginning of the circulation. At longer circulation times, the difference in brightness was smaller.

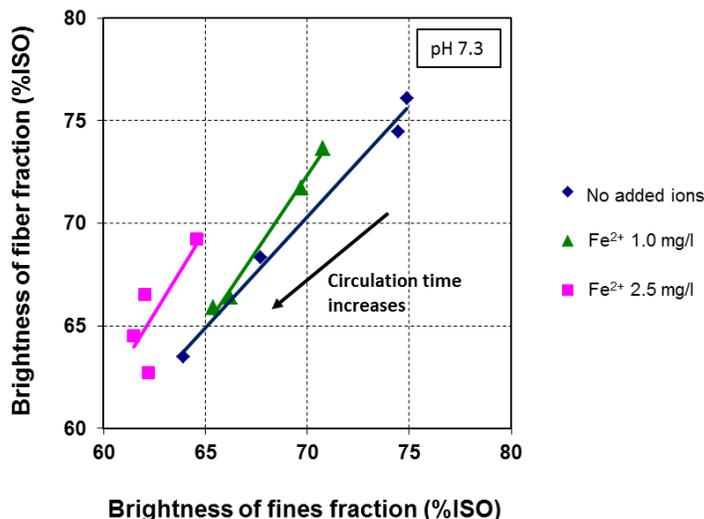


Fig. 4. The brightness of the fines fraction compared to the brightness of the fiber fraction of peroxide bleached TMP. Fe^{2+} -ions were added as FeSO_4 .

The stronger darkening of the fines fraction is probably due to the fact that fines of refiner-based mechanical pulps typically have a higher lignin content than the corresponding fibers (Chang *et al.* 1979; Sundberg *et al.* 2001; Kangas and Kleen 2004) and ferrous ions probably formed strongly colored complexes with the lignin. In addition, ferrous ions could have formed complexes with dissolved and colloidal substances in the water phase and fines could have collected these complexes more effectively than fibers due to their larger specific surface area.

The Effect of Chloride, Sulfate, and Carbonate Added with Calcium

The effects of chloride, sulfate, and carbonate ions on the brightness of the fines and fiber fractions 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 so that the amount of added Ca^{2+} -ions was 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 peroxide bleached TMP decreased both at neutral and at acidic pH levels (Fig. 5). The darkening effect was instant because the brightness was already lower at the beginning of the circulation. At an acidic pH level, the darkening was also faster during the circulation, while at a neutral pH level, the rate of darkening during the circulation was the same as without 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 an acidic pH level because it does not dissolve at neutral pH levels. Because CaCl_2 decreased the brightness much more than CaSO_4 or CaCO_3 , chloride ions seemed to be much more harmful to the brightness of the fines fraction than calcium, sulfate, or carbonate ions.

In the authors' previous study (Varhimo *et al.* 2013b), it was found that carbon dioxide gas decreases the brightness of the fines fraction of peroxide TMP. Calcium carbonate fillers form carbon dioxide gas while dissolving (Jaakkola and Manner 2001). However, in the present study, the PCC filler was dissolved in the dilution water on the day before the experiments, and therefore the water phase probably did not contain free carbon dioxide gas during the experimental procedure.

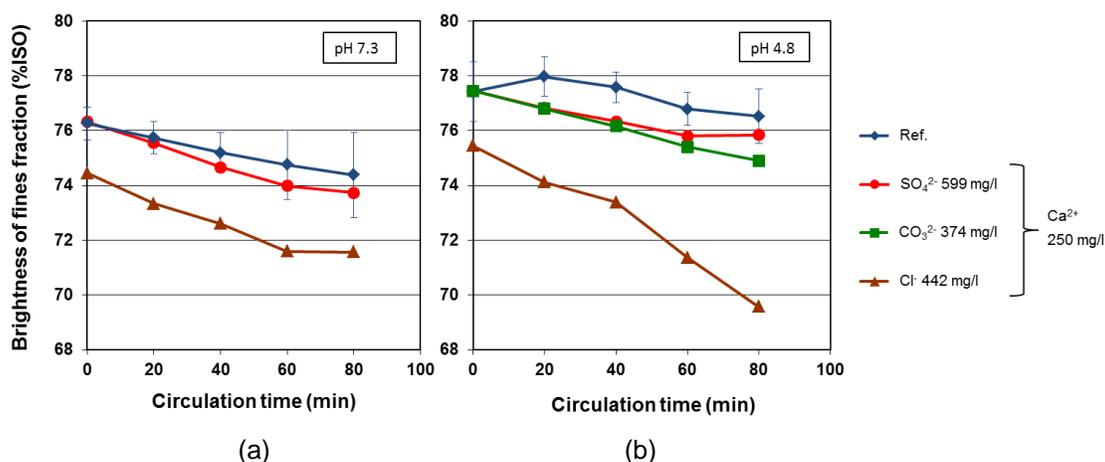


Fig. 5. The effect of SO_4^{2-} , CO_3^{2-} , and Cl^- ions added with calcium on the brightness of the fines fraction of peroxide bleached TMP (TMP SC 2) during the circulation at 58°C in the RDF at (a) pH 7.3 and (b) pH 4.8. The dosage of each chemical was calculated so that the amount of added Ca^{2+} ions was 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 an 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 increased light absorption both at neutral and acidic pH levels (Fig. 6). 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. The relatively large variations in light scattering and light absorption results can be attributed to uneven sheet structures. The grammage varied only slightly between the sheets, but quite a lot within a sheet due to its uneven structure. This explains the large variations in light scattering results. The 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 filtration of the sheets in the sheet former was carried out at 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. So, the light scattering and light absorption values are indicative.

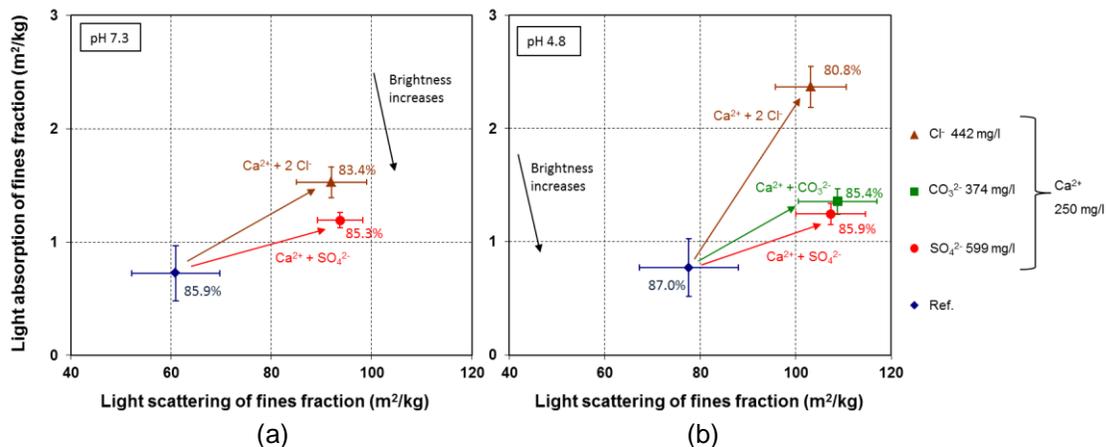


Fig. 6. The effect of SO_4^{2-} , CO_3^{2-} , and Cl^- ions added with calcium on the light absorption and light scattering of the fines fraction of peroxide bleached TMP (TMP SC 2) at (a) pH 7.3 and (b) pH 4.8. The circulation time was 80 min and temperature 58 °C. The dosage of each chemical was calculated so that the amount of added Ca^{2+} -ions was 250 mg/L. The reflectivity 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 an average of two circulations in parallel, the values of Ref. -test point at pH 4.8 as an 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.

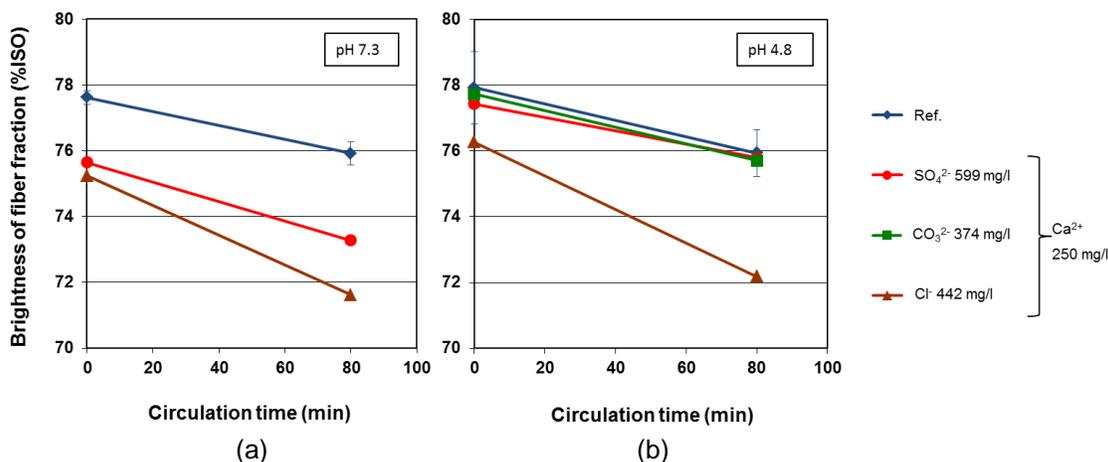


Fig. 7. The effect of SO_4^{2-} , CO_3^{2-} , and Cl^- ions added with calcium on the brightness of the fiber fraction of peroxide bleached TMP (TMP SC 2) during the circulation at 58 °C in the RDF at (a) pH 7.3 and (b) pH 4.8. The dosage of each chemical was calculated so that the amount of added Ca^{2+} -ions was 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 an 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 levels (Fig. 7). At a neutral pH level, CaSO_4 also decreased the brightness. The brightness decrease was due to the increased light absorption of the fibers. The chemicals did not affect the light scattering of the fiber sheets. This is 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. Due to the increased light scattering that compensated the increased light absorption, CaSO_4 did not negatively affect the brightness of the fines fraction at a neutral pH level (Fig. 5a). At an acidic pH level, 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. 8). However, although the chloride ions decreased the brightness of the fines fraction also at pH 7.3 (Fig. 5a), no significant differences in fluorescence of those sheets were found. Thus, the decreased fluorescence cannot by itself explain the extent of brightness reduction caused by the chloride ion.

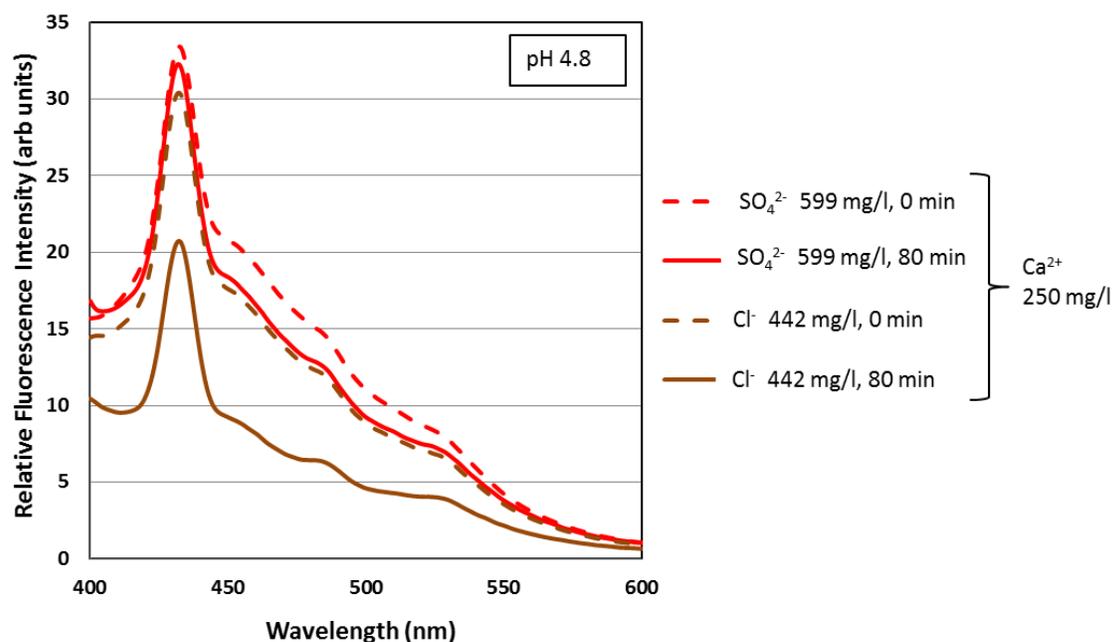


Fig. 8. Relative fluorescence intensities of the fines fraction of peroxide bleached TMP (TMP SC 2) circulated in the RDF at pH 4.8 and 58 °C. CaSO_4 or CaCl_2 was dissolved in the circulation water so that the amount of added Ca^{2+} -ions was 250 mg/L. The circulation time was 0 or 80 min. The brightness values of the same fines sheets were shown in Fig 5b.

The Effect of Aluminum, Calcium, and Sodium Added with Chloride

The effects of aluminum, calcium, and sodium ions on the brightness of the fines and fiber fractions of peroxide bleached TMP were studied by dissolving AlCl_3 , CaCl_2 , and NaCl in the circulation water. The dosages of each chemical were calculated so that

the amount of added Cl^- -ions was 221 or 442 mg/L. At a neutral pH level, CaCl_2 and NaCl decreased the brightness of the fines fraction to some extent, while AlCl_3 slightly increased the brightness (Fig. 9a). At an acidic pH level, all of the chloride chemicals decreased the brightness of the fines fraction (Fig. 9b). CaCl_2 decreased the brightness the most and AlCl_3 the least. The increase in chemical dose decreased the brightness with all of the chloride chemicals. The chloride chemicals also decreased the brightness of the fiber fraction.

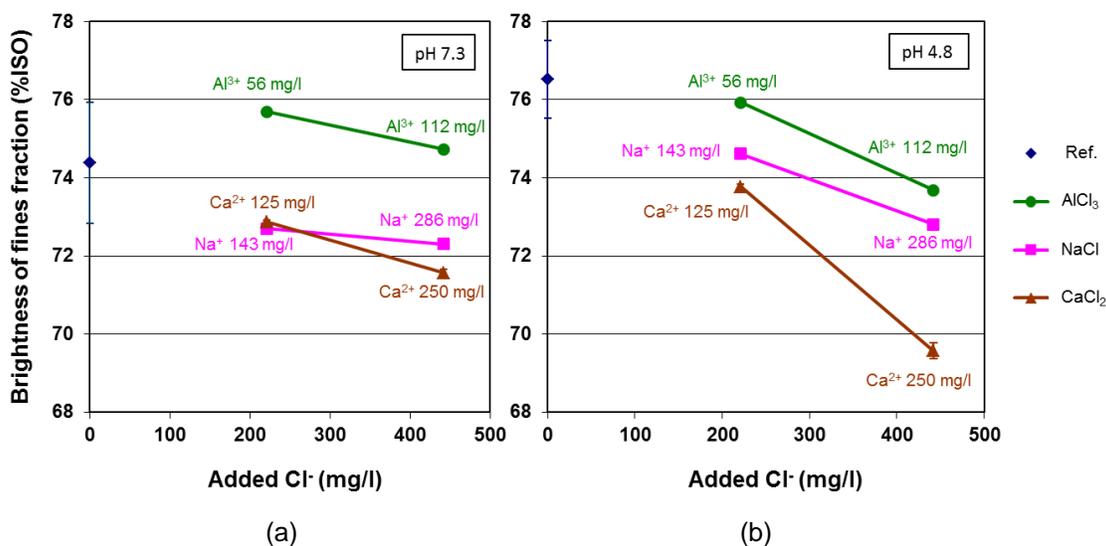


Fig. 9. The effect of added AlCl_3 , CaCl_2 , and NaCl on the brightness of the fines fraction of peroxide bleached TMP (TMP SC 2) at (a) pH 7.3 and (b) pH 4.8. The circulation time was 80 min and temperature 58 °C. The value of Ref. -test point at pH 7.3 was calculated as an average of two circulations in parallel, the value of Ref. -test point at pH 4.8 as an 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 can be attributed to the increased light absorption of the fines fraction (Fig. 10). CaCl_2 increased the light absorption more than NaCl or AlCl_3 . Hence, in addition to chloride ions, calcium ions also increased the light absorption. Chloride chemicals increased the light absorption of the fines fraction during the circulation more at acidic than at neutral pH levels, indicating that chloride ions are more harmful for the brightness at acidic pH levels. In addition to Ca^{2+} -ions, Al^{3+} -ions also increased the light scattering of the fines fraction. Regardless of large variations in the measured values, the increase in the light scattering of the fines sheet was significant, from 61 to 93 m^2/kg at pH 7.3 and from 78 to 102 m^2/kg at pH 4.8, when CaCl_2 or AlCl_3 was added. If the light absorption of the fines fraction had remained the same, 0.72 m^2/kg at pH 7.3 m^2 and 0.77 m^2/kg at pH 4.8, in Fig. 10, the reflectivity (Y-value) would have increased from 85.9 to 88.3% at pH 7.3 and from 87.0 to 88.5% at pH 4.8. However, Cl^- and Ca^{2+} -ions increased the light absorption and hence the brightness decreased. If Al^{3+} -ions were added with anions that do not affect the light absorption of the fines, the brightness would have increased.

There was a clear change in the formation of the fines sheets, when aluminum and calcium ions were added. Aluminum and calcium ions seemed to flocculate the fines, which resulted in a porous sheet that had a greater unbounded surface area available for

light scattering. This change in the sheet structure was probably because at high concentrations of cations, the ionizable groups (*e.g.* carboxylic groups) of fines surfaces were in dissociated form and the fines were not as swelled and softened as in pure water. This same effect of cations on pulp has also been observed in many earlier studies and the swelling has been reported to decrease with increasing cation valence (Scallan and Grignon 1979; Scallan 1983; Hammar *et al.* 1995; Salmén 1995). Utilization of the positive effect of Al^{3+} -ions on the light scattering on a real 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.

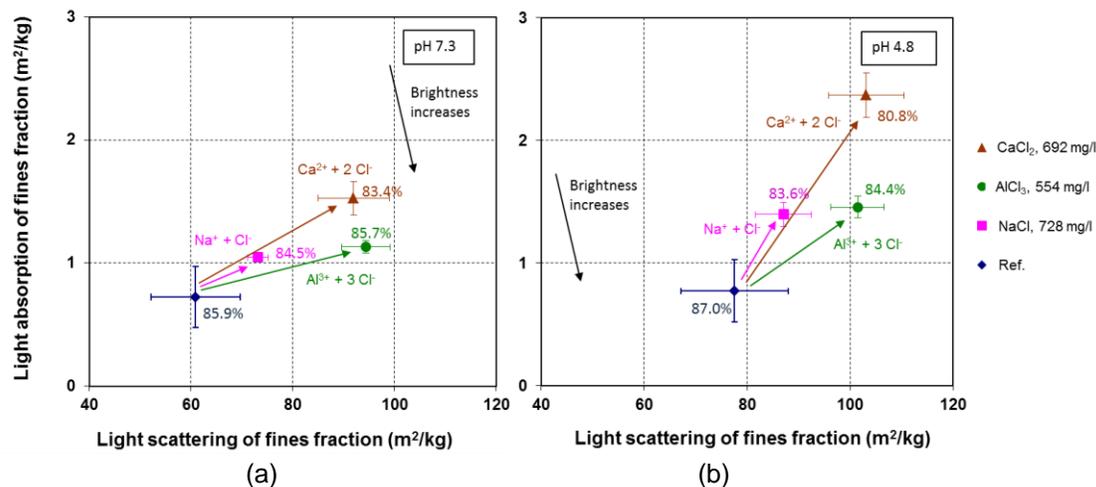


Fig. 10. The effect of Na^+ -, Ca^{2+} -, and Al^{3+} -ions added with chloride on the light absorption and light scattering of the fines fraction of peroxide bleached TMP (TMP SC 2) at (a) pH 7.3 and (b) 4.8. The circulation time was 80 min and temperature 58 °C. The dosage of each chemical was calculated so that the amount of added Cl^- -ions was 442 mg/L. The reflectivity 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 an average of two circulations in parallel, the values of Ref. -test point at pH 4.8 as an 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.

Mathematical Models Based on Results

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 separately multiple linear regression analyses were performed based on the results. A linear mathematical model was calculated for ISO brightness, Y-value, specific light absorption coefficient (k), and specific light scattering coefficient (s) of the fines and fiber fractions of peroxide bleached TMP (Table 4). The results of the regression analyses supported the results shown in this paper quite well. However, the linear mathematical model predicted too low initial brightness values for the fines

fraction of TMP LWC and TMP SC 2 (73.2%) compared to those of the measured values (74.5% for TMP LWC and 74.9-75.6% for TMP SC 1). According to the results shown in Fig. 2, the measured brightness values with added Mn^{2+} were very close to those of the reference, indicating no significant effect of manganese ions. But when fitting the mathematical model there is, compared to the reference, an additional parameter to describe the brightness value where Mn^{2+} has been added – the coefficient of the Mn^{2+} -variable. As a consequence and because of the fact that the addition of Mn^{2+} was conducted only at one level (1 mg/L), the model spuriously affiliated a significant positive effect to the addition of manganese ions.

Table 4. Effect of Different Ions in the Circulation Water, pH, and Circulation Time at 58 °C on the Optical Properties of the Fines and Fiber Fraction of Peroxide Bleached TMP

Initial Values	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)
TMP LWC*	73.2	84.9	0.58	74.5	74.4	85.4	0.63	56.5
TMP SC 1*	73.2	83.2	1.26	82.3	74.4	85.4	0.63	56.5
TMP SC 2*	77.0	88.1	0.58	74.5	77.7	88.8	0.35	56.5
Change in...								
Mn^{2+} (0 mg/L → 1 g/L)**	(+1.7) [^]	(+3.2) [^]	±0	±0	±0	±0	±0	±0
Fe^{2+} (0 mg/L → 1 mg/L)**	-2.9	-3.0	+0.97	±0	-2.3	-3.0	+0.53	±0
Na^+ (0 mg/L → 286 g/L)	±0	±0	±0	±0	±0	±0	±0	±0
Ca^{2+} (0 mg/L → 250 g/L)	-1.0	-1.2	+0.44	+23.2	±0	-1.4	+0.17	±0
Al^{3+} (0 mg/L → 112 g/L)	+1.8	+1.3	±0	+26.3	±0	±0	±0	±0
Cl^- (0 mg/L → 442 g/L)	-2.6	-2.3	+0.39	±0	-1.5	-1.5	+0.17	±0
SO_4^{2-} (0 mg/L → 599 g/L)	±0	±0	±0	±0	±0	±0	±0	±0
CO_3^{2-} (0 mg/L → 374 g/L)***	±0	±0	±0	±0	±0	±0	±0	±0
pH (7.3 → 4.8)	+1.3	±0	±0	+8.4	±0	±0	±0	±0
Circulation time (0 min → 80 min)	-2.0	-1.6	+0.31	±0	-2.4	-1.6	+0.22	±0
Adjusted R Square	0.95	0.93	0.88	0.52	0.93	0.93	0.94	0.00
* Initial values: pH 7.3, circulation time 0 min, no added ions								
** Studied only at pH 7.3								
*** Studied only at pH 4.8								
[^] the model spuriously affiliated a significant positive effect								
k = specific light absorption coefficient; s = specific light scattering coefficient.								
Notice that the positive values (+) in light absorption-column (k) have a negative effect on brightness.								

Fe^{2+} -ions decreased the brightness of both fractions by increasing the light absorption. Al^{3+} -ions increased the brightness of the fines fraction by increasing the light scattering. When Ca^{2+} -ion concentration of the circulation water increased from 0 to 250

mg/L, both the light absorption and the light scattering of the fines fraction increased. The effect of increased light absorption dominated and Ca^{2+} -ions decreased the brightness of the fines fraction by 1%-unit. Cl^- -ions decreased the brightness by increasing the light absorption of the fines and fiber fractions. Decreased pH increased the brightness of the fines fraction by increasing the light scattering. Increased circulation time decreased the brightness of both fractions by increasing the light absorption. Na^+ , SO_4^{2-} , or CO_3^{2-} -ions had no effect on the optical properties of the fines or fiber fractions.

Adjusted R Square (Table 3) expresses the accuracy of the model. The bigger (or closer to 1) the Adjusted R Square, the more accurate the model is. The accuracies of the models of ISO brightness, Y-value, and light absorption (k) were quite high. The accuracy of the fines fraction model of light scattering (s) was relatively poor. The light scattering of the fines sheet could not be predicted very accurately by the variables because the sheet structure was uneven and the changes in light scattering were quite occasional. None of the variables had a significant effect on the light scattering of the fiber sheet. This was probably because the ion concentrations of the water phase were low and the pH was close to neutral in all test points during the fiber sheet forming due to the dilution using deionized water before the sheet preparation.

CONCLUSIONS

1. Ferrous ions darkened the fines fraction of peroxide bleached TMP already at low concentrations. The effect was instant, which means that iron darkened the fines fraction already at the beginning of the circulation, but did not increase the rate of darkening during the circulation. Ferrous ions also darkened the fiber fraction of peroxide bleached TMP, though not as much as they darkened the fines fraction. The darkening caused by ferrous ions was attributed to increased light absorption of the fines and fiber fraction. It is very important to keep the iron content of the pulp and white water as low as possible because already low contents of iron have a negative effect on the brightness of produced paper.
2. Calcium ions increased both the light absorption and light scattering of the fines fraction. The increased light absorption dominated, and the brightness decreased.
3. Chloride ions decreased the brightness by increasing the light absorption of the fines and fiber fraction. Chloride ions were more harmful to the brightness at acidic pH levels than at neutral pH levels. Although the chloride ions darkened the fines and fiber fractions, the chloride ion concentration of the white water in real paper machines is very rarely as high as in these tests. Calcium chloride is used very commonly as a model chemical for calcium ions in laboratory tests. This study showed that calcium chloride is not a suitable model chemical for calcium ions, if the darkening phenomena are studied, because chloride ions decrease the brightness.
4. Aluminum ions increased the brightness of the fines fraction by increasing the light scattering.
5. Manganese, sodium, sulfate, or carbonate ions did not affect the optical properties of the fines or fiber fraction.

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