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High consistency hydrogen peroxide bleaching of mechanical pulps with varying amounts of fines

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KEYWORDS: Mechanical pulps, Brightness, Light scattering, Light absorption, Fines, Bleaching, Hydrogen peroxide, Temperature

SUMMARY: Hydrogen peroxide is a widely used bleaching chemical for mechanical pulps and is particularly useful when high brightness levels are required. The objective of this work was to study fines as a limiting factor for reaching higher brightness levels in high consistency hydrogen peroxide bleaching of Norway spruce (*Picea abies*) thermomechanical (TMP) and stone groundwood (SGW) pulps. The hydrogen peroxide bleaching efficiency (i.e. light absorption coefficient reduction) was studied as a function of temperature, alkali charge and fines content using an experimental design based on MODDE software (Umetrics AB).

It is known that all types of fines contain more lignin, hemicelluloses, pectins, metals and less cellulose than long fibres. The light absorption coefficient was greater for unbleached TMP than for unbleached SGW pulp and an increased quantity of fines increased the light absorption coefficient for both pulp types. The increase was, however, most pronounced for the TMP. Furthermore, the data suggests that both the fibre fraction and the fines fraction are more coloured in the thermomechanical pulp. In most cases, increased amounts of fines in the pulp had a negative impact on the bleached pulp brightness in spite of the improved light scattering ability accompanying the addition of fines. A level of fines exceeding 50% was especially detrimental resulting in lower pulp brightness due to a higher light absorption coefficient.

Increasing the bleaching temperature did not improve the bleaching efficiency. The optimal bleaching temperature at a hydrogen peroxide charge of 4.5% was found to be 70°C within the tested interval of 70–110°C. For a fines content of 25%, the stone groundwood pulp displayed a brightness of 83% whereas the thermomechanical pulp achieved a brightness of 79%.

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The demand for higher brightness in newsprint and high quality printing papers, such as LWC (lightweight coated) paper and SC (super-calendered) paper, has increased over a number of years. For these applications, the brightness of mechanical pulps, the main components of such papers, must be improved. Hydrogen peroxide is a

widely used bleaching chemical that is particularly useful when high brightness levels are required however there is a limit to the brightness gain that can be achieved by increasing the amount of hydrogen peroxide applied to a pulp (Presley, Hill 1996). One limiting factor for the bleaching efficiency could be the mechanical pulp fines.

Fines have traditionally been defined as the fraction of a pulp that passes through a 200-mesh wire (see e.g. Luukko 1998). All types of fines contain more lignin, hemicelluloses and pectins, and less cellulose than long fibres (Kleen et al. 2003; Sundberg et al. 2003; Kangas, Kleen 2004; Haugan, Gregersen 2006). Furthermore, the chemical structure of lignin has been shown to vary depending on its morphological origin in wood (Boutelje, Eriksson 1984; Sorvari et al. 1986), which might imply that fibre and fines could behave differently when subjected to bleaching. Mechanical pulp fines have been found to lower the hydrogen peroxide bleaching efficiency and metals such as iron, manganese and copper were accumulated in the fines fraction (Roick et al. 1991; Leduc, Daneault 2007). Metal ions, especially transitions metal ions such as iron can form strongly coloured complexes with lignin and extractives that contribute to the darkening of mechanical and chemimechanical pulps (Gupta 1970; Polcin, Rapson 1972; Janson, Forsskåhl 1989; Ni et al. 1997; Ni et al. 1999; Yoon et al. 1999).

Petit-Conil and Laurent (2003) found that fibre could be bleached to a higher brightness level when bleached separately, whereas fines had better bleachability when bleached in the entire pulp. The fines fraction consumed almost all the hydrogen peroxide and the consumption by the fines was explained by higher lignin and wood extractive contents than those of the corresponding fibres. However, Allison and Graham (1989) studied hydrogen peroxide bleaching of mechanical pulp fractions from Radiata pine. Kinetic rate laws for peroxide bleaching were found to be similar for fibres and fines, indicating similar chromophore reactivity and thus structure.

Fines are not homogeneous and are generally divided into lignin-rich flake-like particles originating from the middle lamella and primary cell wall, and fibrillar-like particles originating from the cellulose-rich secondary wall of the fibres (Honkasalo et al. 1983; Luukko 1998). The flake-like fines have been found to have a higher

bleachability compared to the fibrillar-like fines (Haugan, Gregersen 2006).

The brightness response in the bleaching stage is dependent on the initial pulp brightness. Generally, a higher initial unbleached brightness results in higher bleached brightness under similar bleaching conditions (Kouk et al. 1989). Several factors influence the hydrogen peroxide bleaching performance such as alkalinity, temperature, retention time, consistency, and hydrogen peroxide stability. Hydrogen peroxide bleaching is performed under alkaline conditions in order to produce the perhydroxyl anion that is considered to be the active bleaching species. It is important to optimize the alkali charge as an alkali charge that is too high may lead to pulp darkening, whereas an alkali charge that is too low may lead to inefficient bleaching. pH levels that are too high may lead to hydrogen peroxide decomposition and exceed the rate of the bleaching reaction resulting in a reduced brightness response. The formation of the perhydroxyl anion is also enhanced by increasing the temperature (Presley, Hill 1996) due to the decrease of the pK_a value of the hydrogen peroxide anion with increased temperature (Andersson, Amini 1996). Temperature and retention time are closely related, an increase in temperature accelerates the hydrogen peroxide bleaching reactions but also hydrogen peroxide decomposition. The combination of temperature and retention time have to be chosen so that a reasonable portion of the charged hydrogen peroxide is consumed (Lindholm 1999), however a retention time that is too long can consume all the hydrogen peroxide and induce yellowing due to alkaline and thermal darkening reactions (Leary, Giampaolo 1999). Furthermore, the bleaching consistency influences the bleaching response that increases continuously as pulp consistency is increased up to a level of about 40% (Kappel, Sbaschnigg 1989). Hydrogen peroxide is decomposed by transition metals such as iron, manganese and copper (Colodette et al. 1988), which is undesirable. To reach higher brightness levels, a conventional hydrogen peroxide bleaching process therefore often includes a chelating stage where detrimental metal ions are removed before bleaching. Hydrogen peroxide bleaching of mechanical pulps is often performed at 30% pulp consistency at temperatures of between 60 and 75°C, and the pulp is retained in a tower for 1-3 hours (Meyer et al. 1990; Dessureault et al. 1994; Presley, Hill 1996; Dietz et al. 2009).

High temperature hydrogen peroxide bleaching could offer some advantages over conventional hydrogen peroxide bleaching. With increasing bleaching temperatures, less time was required to

reach the maximum brightness level (Liebergott et al. 1987; Kappel, Sbaschnigg 1991). The alkali charge could be reduced when the temperature was increased (Kappel, Sbaschnigg 1991), but at higher hydrogen peroxide charges the brightness became more sensitive to the caustic charge (Liebergott et al. 1987). Contradictory results have been reported regarding the brightness obtained at high temperature bleaching compared to conventional bleaching with both lower (Kappel, Sbaschnigg 1991; Hill et al. 1996; Logenius 2008) and higher (Liebergott et al. 1987) final brightness values having been reported.

The present work aims to develop a better understanding of the factors limiting the bleachability of fibre and fines to high brightness levels. The effect of temperature and alkali charge during high consistency hydrogen peroxide bleaching of spruce thermomechanical and stone groundwood pulps containing different amounts of fines will be presented and thoroughly discussed.

Materials and Methods

Pulps

Commercially produced pulps, an unbleached thermomechanical pulp (TMP) and a stone groundwood (SGW) pulp produced from Norway spruce (*Picea abies*) were used in the experiments described in this paper. The TMP was metal chelated in the mill. Pentanatriumdietylenetriaminpentaacetat (Na_5DTPA) was added after the disc filter and before the first dewatering press. The pulp was collected after the dewatering press at the blowline from the secondary stage refiner. The SGW pulp was collected from a double wire press before bleaching and was not treated with a chelating agent in the mill.

Metal management

A chelating stage was carried out in order to reduce the metal content of the pulps prior to the oxidative bleaching with hydrogen peroxide. The TMP was chelated in the mill with a commercial Na_5DTPA solution (Versenex 80 from Dow, Sweden) at a charge of 0.40%. The pulp was Na_5DTPA treated at ~60°C, pH~5.5 at 8% pulp consistency. After a retention time of 15-30 minutes the pulp was dewatered to about 30% consistency. The fractionated TMP with a fibre/fines ratio of 25/75 and the SGW pulp was treated in the laboratory with 0.40% Na_5DTPA at room temperature and at 5% pulp consistency. After a retention time of 30 minutes, the pulp was dewatered on a polyamide wire (125 µm) in a Büchner funnel to about 25% consistency, the filtrates being recirculated twice

through the filter cake to avoid the loss of fibres and fines material. To wash out the water-soluble metal-DTPA complexes, 1 litre deionised water was added to 200 g pulp in the funnel, repeated twice (a total of 3 litres), and pressed to a consistency of approximately 40%. The iron and manganese contents of the pulps are stated in *Table 1*. The addition level for Na₅DTPA is given as commercial product. The chelated pulps were stored in a freezer at -24°C until use.

Preparation of pulps with different amounts of fines

Unbleached TMP and SGW pulps were disintegrated in deionised water, diluted to 10 g/l, and fractionated into a fibre and a fines fraction using a Britt dynamic drainage jar with a metal plate wire with 76 µm hole diameter (ca. 200 mesh, from PRM Inc., USA). One litre of the pulp suspension was poured into the drainage jar with the agitator at low speed. The agitation was increased to 900 rpm and the outlet was opened. The pulp was drained until the level in the jar sank below the stirrer after which 1 litre deionised water was added, this was repeated 3 times (a total of 4 litres). The fibre and fines fractions were mixed in controlled portions to obtain pulps with different fibre/fines ratios. The pulps were dewatered on a polyamide wire of 125 µm in a Büchner funnel, the filtrates being recirculated twice through the filter cake and pressed to a consistency of approximately 40%. The target fines contents of the fractionated pulps were 0, 25, 50 and 75 weight%. Characteristic data for unfractionated and fractionated pulps is stated in *Table 1*.

Hydrogen peroxide bleaching

High consistency hydrogen peroxide bleaching was performed at a pulp consistency of 30%. Five g (oven-dry) pulp was mixed with the bleaching chemicals at room temperature for one minute using a stainless steel coffee grinder. The pulp was thereafter immediately placed into a polyethylene plastic bag (thickness 90 µm from Genpack A/S, Denmark), which was sealed and immersed into thermostatic water or glycol bath. The hydrogen peroxide charge was 4.5% and the sodium hydroxide charge was optimised and varied between 0.9 and 3.6% with the purpose of reaching the highest possible brightness. The sodium silicate (S38 with a weight ratio between SiO₂ and Na₂O of 3.25, supplied by PQ Europe, Sweden) charge was kept constant at 2.9%. The bleaching trials were performed at 70°C and 90°C at a retention time of 120 minutes and at 110°C at a retention time of 5, 10, 15 and 120 minutes. After the bleaching stage, the pulp was cooled to room temperature and further used for determination of optical properties. One gram of pulp (oven-dry) was diluted with 50 gram deionised water. After five minutes, the pulp suspension was dewatered in a Büchner funnel on a Munktell 3 filter paper. The filtrate was collected and used to determine residual hydrogen peroxide. The addition level for sodium silicate is given as commercial product. Hydrogen peroxide and sodium hydroxide are given as 100% active components.

Table 1. Freeness, fines content and optical properties together with metal, extractive and lignin contents for unbleached TMP and SGW pulp at different fibre/fines ratios.

Pulp	Freeness ml CSF	Fines content wt%	Brightness ¹ % ISO	S _{457nm} m ² /kg	k _{457nm} m ² /kg	Fe mg/kg	Mn mg/kg	Extractive content wt%	Lignin content wt%
<i>TMP</i>									
Reference	55	31	62.1	64	7.4	1	42	0.9	28.8
Fractionated		5	59.2	43	6.1	1	9	0.2	26.0
Fractionated		28	60.2	63	8.3	2	11	0.8	28.5
Fractionated		49	60.2	80	10.5	3	11	1.2	31.3
Fractionated		75	59.9	90	12.1	6	20	1.8	34.2
Fractionated and DTPA washed		75	60.5	86	11.1	4	<0.05		
<i>SGW pulp</i>									
Reference	50	32	67.6	69	5.4	7	2	1.1	29.8
Fractionated		5	66.1	52	4.5	3	1	0.3	27.5
Fractionated		27	67.1	68	5.5	7	1	0.8	29.0
Fractionated		55	67.6	83	6.5	10	2	1.2	30.7
Fractionated		77	67.5	92	7.3	16	3	1.8	33.0

¹Brightness determined on laboratory sheets (65 g/m²) according to ISO standard method 9416.

Preparation of laboratory sheets for evaluation of optical properties

Laboratory sheets (60 g/m², oven-dry) were formed in a laboratory sheet former using a 76- μ m (ca. 200 mesh) polyamide wire (from Derma, Sweden). The optical properties (brightness, light scattering (*s*) and light absorption (*k*) coefficients) were determined according to ISO standard method 9416. In this paper the *s*- and *k*-values were determined with the brightness function, R_{457} .

Brightness pads (approximately 200 g/m², oven-dry) for ISO brightness determination were prepared according to ISO standard method 3688 (using funnel and filter paper) and the ISO brightness was determined according to ISO standard method 2470.

Experimental design

One part of the experimental work presented in this paper was designed using the MODDE 5.0 software (Umetrics AB, Umeå, Sweden). The factors examined (temperature, sodium hydroxide charge and fines content) were varied simultaneously over a set of planned experiments; the results were then connected by means of a mathematical model. The model is used for interpretation, predictions and optimization of the process. The data collected by the experimental design is used to estimate the coefficients of the model. The model represents the relationship between the response [brightness, light scattering coefficient (s_{457nm}), light absorption coefficient (k_{457nm}) and hydrogen peroxide consumption] and the factors (temperature, sodium hydroxide charge and fines content). Data gathered using a central composite and face-centred (CCF) design was used to generate prediction models. All responses were modeled together using multiple linear regressions (MLR). The experiments were conducted using factors at three levels, i.e. low, medium and high. The following factors were varied: temperature (70°C, 90°C and 110°C), sodium hydroxide charge (0.9%, 1.8% and 2.7%) and fibre/fines ratio (TMP: 72/28, 51/49, 25/75 and SGW pulp: 73/27, 45/55, 23/77). The experimental design for hydrogen peroxide bleaching of TMP and SGW pulp with different fibre/fines ratios is shown in Table 4.

Other analyses

Analyses and methods not mentioned elsewhere in the experimental section are as follows: freeness (ISO standard method 5267-2), fines content (SCAN standard method CM 66:05) and metal ion content (SCAN standard method CM:38:96). The pulps were extracted with dichloromethane to determine the extractive content according to SCAN standard method C7:62. The lignin content of the pulps is given as the sum of acid-insoluble lignin (Klason

lignin) and acid-soluble lignin. The acid-insoluble lignin was determined gravimetrically according to TAPPI method T 222. The acid-soluble lignin was determined using UV-spectroscopy at 205 nm ($\epsilon = 128 \text{ dm}^3\text{g}^{-1}\text{cm}^{-1}$) according to the procedure described by Dence (1992). Residual hydrogen peroxide was determined by iodometric titration where the liberated iodine was titrated with 0.1 M sodium thiosulphate.

Results and discussion

Light absorption coefficient (k_{457nm}) for unbleached pulps with various fines content

In the pulping process, elevated temperatures in the defibering stage can cause discoloration by reactions of chromophores and leucochromophores located in the lignin (Gellerstedt, Pettersson 1980; Gellerstedt et al. 1983; Gratzl 1985; Chong et al. 1991). Colour reversion induced by heat could also involve the pulp carbohydrates (Polcin, Rapson 1971; Luo et al. 1988; Holmbom et al. 1992; Grossmann, Ott 1994; Beyer et al. 1995; Fischer et al. 1995; Tylli et al. 1997). Metal ions, especially transition metal ions such as iron can form strongly coloured complexes with lignin and extractives which contribute to the darkening of mechanical and chemimechanical pulps (Gupta 1970; Polcin, Rapson 1972; Janson, Forsskåhl 1989; Ni et al. 1997; Ni et al. 1999; Yoon et al. 1999).

In an unpressurized groundwood process, the grinding temperature will not exceed 100°C (Liimatainen et al. 1999), whereas in a TMP process the temperature in the first refiner can be 143°C–158°C (Tienvieri et al. 1999), although the temperature can exceed 170°C in a temperature peak (Härkönen et al. 2003). The typical brightness of unbleached Norway spruce pulps produced in the TMP process is 57–60% ISO and in the stone ground wood process 60–65% ISO (Lindholm 1999). Previous results indicate that steaming native spruce wood at temperatures below 120°C causes no brightness losses (Logenius et al. 2005). However, when steaming TMP from spruce at higher temperatures, above 165°C, the brightness declined by several units (Koskinen et al. 1997).

The light absorption coefficient (k_{457nm}) for unbleached TMP and SGW pulp at various fines content is shown in Fig 1 and listed in Table 1. The light absorption coefficient was higher for unbleached TMP than for unbleached SGW pulp and an increased amount of fines increased the light absorption coefficient for both pulp types. The increase was, however, most pronounced for the TMP. The data also suggests that both the fibre fraction and the fines fraction are more coloured in the thermomechanical pulp. One reason for the

higher light absorption coefficient for TMP could be the higher temperatures during processing. The light absorption coefficient is known to increase during refining and coloured metal ion complexes are suggested to be formed (Johansson, Gellerstedt 2000; Johansson et al. 2002). The brightness of the wood raw material may also differ depending on how fresh it is, the ratio of sapwood (brighter) and heartwood (darker), the growth conditions of the wood (fast growth gives brighter wood than slow growth) and the bark content that is detrimental for the brightness (Brill 1985; Hartler 1986; Höglund, Wilhelmson 1993).

Fig 1. The light absorption coefficient (k_{457nm}) as a function of fines content for unbleached TMP and SGW pulp.

The metal (iron, manganese), extractive and lignin contents increased with increased amount of fines (see *Table 1*) as expected, despite the fact that the fractionation procedure and re-addition of fines to the pulp includes extensive washing of the pulp (see experimental section and discussion below). The manganese content of SGW pulp was lower probably due to better chelating conditions in the laboratory compared to the conditions prevailing in the mill. The main source of metals in mechanical pulp is the wood raw material and the mill water (Read et al. 1968; Christiansen, Michalowski 1989). The SGW pulp contained 3-4 times more iron than the TMP, even though it is known that the level of iron may increase during the refining process (Colodette, Dence 1989). The iron was accumulated in the fines fraction (*Table 1*).

Light-scattering coefficient (s_{457nm}) for unbleached pulps with various fines content

The properties of the fractions larger than the fines set the initial level of light scattering. The addition of fines will increase the light scattering coefficient and fines from different types of pulps all improve the light scattering coefficient in a similar way and are directly additive up to a certain fines level (Lindholm 1980). The light scattering coefficient of unbleached SGW fibres was 52 m²/kg and 9 units higher than

that for the TMP fibres (5% fines content), see *Table 1*. However, at high fines concentrations above 50%, the initial differences in light scattering between the two pulps were reduced, and the pulps exhibited a similar light scattering coefficient. This was also shown by Lindholm (1980).

Hydrogen peroxide bleaching at 70°C

In hydrogen peroxide bleaching, it is important to optimize the alkali charge in order to reach the highest possible brightness level and to avoid too high alkali charges which will result in yellowing due to the prevailing alkaline conditions (Leary, Giampaolo 1999). Unbleached TMP with different fibre/fines ratios were bleached using 4.5% hydrogen peroxide at a pulp consistency of 30% and at a temperature of 70°C for 120 minutes. The sodium hydroxide charge was varied between 0.9 and 3.6%. In most cases, the highest brightness was about 79% and was achieved at an alkali charge of 2.7%. Increasing the sodium hydroxide charge to 3.6% did not increase the brightness any further for most of the pulps (*Fig 2*). The brightness was somewhat increased however for the pulp with the lowest amount of fines (5% fines). An alkali interval between 0.9 and 2.7% was therefore suitable for further bleaching trials since an alkali charge of 3.6% was too high and some alkali darkening reactions occurred for the pulp with the highest amount of fines (75% fines). The fibre/fines ratio of 51/49 reached the highest brightness of about 80%.

Fig 2. The brightness (ISO 2470) of TMP with different fibre/fines ratios as a function of sodium hydroxide charge. The charge of hydrogen peroxide was 4.5%.

It is known that heat and light induces yellowing of lignin-rich mechanical pulps (Gratzl 1985; Schmidt, Heitner 1993; Leary 1994; Paulsson, Ragauskas 1998; Forsskåhl 2000). Furthermore, transition metal ions such as iron and copper can cause discoloration, either directly (upon ion exchange) or after subsequent ageing (Gupta 1970; Janson, Forsskåhl 1989). High iron content has been reported in fibre and fines fractions (Allison, Graham 1989; Haugan, Gregersen 2006). Allison and Graham (1989)

ascribed the high content to the fractionation process. The light absorption coefficient of the unbleached fractionated pulp (28% fines) was higher than the reference pulp (31% fines), *Table 1*. Great care was taken to reduce possible sources of contaminants of the samples in the fractionation procedure by using deionised water (low metal content), and by storing the samples in cold and dark conditions, but the cause of the differences cannot be explained. Nevertheless, the fractionated pulp (28% fines) showed a similar bleaching response as the reference pulp (31% fines) (*Fig 2*).

High levels of transition metals, particularly manganese, iron and copper, will catalyse the decomposition of hydrogen peroxide and reduce the possibility for reaching high brightness levels (Andersson, Amini 1996). Manganese is loosely bound to the wood matrix and can be removed by a chelating agent (e.g. DTPA). Manganese can also be removed by cation exchange with calcium or magnesium. Furthermore acidic conditions will liberate the manganese ions. Iron and copper are strongly attached to the wood matrix and are considerably more difficult to remove (Sundén et al. 2000).

The TMP reference (31% fines), which was chelated and washed in the mill, had a manganese content of 42 mg/kg. The fractionated TMP and remixed pulp (28% fines) were exposed to a considerable amount of deionised water during fractionation and had a manganese content of 11 mg/kg (see *Table 1*). This difference in manganese content indicated that a part of the manganese in the reference pulp was to a large extent water-soluble and complexed with DTPA. As can be seen in *Table 2*, the water-soluble complexed manganese did not interfere in the bleaching under the conditions and metal levels tested; no significant difference in

hydrogen peroxide consumption between the two pulps was seen (*Table 1*).

The TMP fractionated and remixed pulps contained more manganese, as is shown in *Table 1*, than the SGW pulps.

To see how this difference influenced the bleaching response for further trials, a DTPA wash was performed on the highest manganese containing pulp (TMP, fibre/fines ratio 25/75) and the manganese content was reduced from 20 mg/kg to <0.05 mg/kg. The brightness of the pulps after hydrogen peroxide bleaching for the DTPA-treated and the untreated pulp was essentially the same, 78.6% vs. 79.0%, although the DTPA-treated pulp consumed less peroxide, 57% compared to 74%, probably due to the decreased manganese-induced decomposition of hydrogen peroxide (cf. Presley, Hill 1996). Increased amount of residual hydrogen peroxide did not contribute to higher brightness.

Hydrogen peroxide bleaching at 110°C

The perhydroxyl anion is generally accepted as the active bleaching species in alkaline hydrogen peroxide systems. The formation of the anion can be regulated by increasing or decreasing the pH and temperature at a constant hydrogen peroxide concentration. Hydrogen peroxide bleaching at higher temperatures of mechanical pulps will increase the reaction rates of both the bleaching and hydrogen peroxide decomposition reactions. Because of the increased reaction rates, it is necessary to make the appropriate adjustments in retention time (Presley, Hill 1996). Logenius (2008) studied high temperature hydrogen peroxide bleaching of TMP and revealed that a retention time of 5-10 minutes was optimal at 105°C. Too long a time can consume all the hydrogen peroxide and induce yellowing due to alkaline and thermal darkening reactions.

Table 2. The brightness and hydrogen peroxide consumption for TMP at different fibre/fines ratios. Bleaching conditions: 70°C, 120 minutes, 30% pulp consistency. Chemical charges: 4.5% H₂O₂, 0.9-3.6% NaOH, 2.9% sodium silicate.

NaOH charge %	Fractionated TMP Fibre/fines 72/28		Reference TMP Fibre/fines 69/31		Fractionated TMP Fibre/fines 25/75		Fractionated TMP Fibre/fines 25/75 DTPA washed	
	Brightness ¹ %	Peroxide consumption %	Brightness ¹ %	Peroxide consumption %	Brightness ¹ %	Peroxide consumption %	Brightness ¹ %	Peroxide consumption %
0.9	76.3	39	76.3	38				
1.8	78.3	53	78.5	54				
2.7	79.0	66	79.1	69	79.0	74	78.6	57
3.6	79.3	79	79.0	85				

¹Brightness determined on brightness pads (200 g/m²) according to ISO standard method 2470.

The hydrogen peroxide bleaching efficiency (i.e. light-absorption coefficient reduction) is probably due to the balance between the chromophore-reducing reactions of hydrogen peroxide and the chromophore-creating reactions initiated by alkali. When the hydroxide ion concentration increases more than the perhydroxyl anion concentration, the alkaline chromophore-creating reactions start to prevail over the bleaching reactions. A temperature increase will favour hydrogen peroxide decomposition rather than bleaching reactions due to the higher activation energy (Moldenius, Sjögren 1982).

Hydrogen peroxide bleaching of TMP (fibre/fines ratio 25/75) and SGW pulp (fibre/fines ratio 23/77) at 110°C for 120 minutes with an alkali charge of 2.7% was too long, as expected, since all the hydrogen peroxide was consumed resulting in low brightness of 70.3% and 67.2% respectively. Hydrogen peroxide bleaching trials using different retention times at 110°C revealed that 10-15 minutes was optimal (Table 3). Increased retention time was not expected to give any higher brightness since 3/4 of the hydrogen peroxide was consumed. A retention time of 10 minutes was therefore chosen for further bleaching trials.

Table 3. Optical properties and hydrogen peroxide consumption for TMP at 25/75 fibre/fines ratio. Bleaching conditions: 110°C, 5-15 minutes, 30% pulp consistency. Chemical charges: 4.5% H₂O₂, 2.7% NaOH, 2.9% sodium silicate.

Time min	Brightness ¹ %	S _{457nm} m ² /kg	k _{457nm} m ² /kg	Peroxide consumption %
5	76.0	87	3.2	67
10	76.4	82	3.0	76
15	76.4	82	3.0	77

¹Brightness determined on laboratory sheets (65 g/m²) according to ISO standard method 9416.

Hydrogen peroxide bleaching at various temperatures evaluated with experimental design

The TMP and SGW pulp bleaching trials were evaluated using the MODDE 5.0 software. Table 4 shows the experimental design and basic data analysed.

When fitting a model the most important diagnostic tool consists of the two companion parameters R^2 and Q^2 . R^2 is a measure of fit, i.e. how well the model fits the data whereas Q^2 indicates how well the model predicts new data. R^2 varies between 0 and 1, where 1 indicates a perfect model. Similarly to R^2 , Q^2 has the upper limit of 1. A $Q^2 > 0.5$ should be regarded as good and $Q^2 > 0.9$ as excellent.

Table 4. The MODDE experimental design and responses (optical properties and hydrogen peroxide consumption) for hydrogen peroxide bleaching of TMP and SGW pulp with different fibre/fines ratios. Chemical charges: 4.5% H₂O₂, 2.9% sodium silicate.

Temperature °C	NaOH %	Fines content %		Brightness ¹ %		S _{457nm} m ² /kg		k _{457nm} m ² /kg		Peroxide consumption %	
		TMP	SGW	TMP	SGW	TMP	SGW	TMP	SGW	TMP	SGW
70	0.9	28	27	76.5	79.4	63	69	2.3	1.8	39.4	44.4
70	0.9	75	77	76.9	78.1	98	93	3.4	2.9	44.6	81.1
70	1.8	49	55	79.0	81.4	77	80	2.2	1.7	50.0	69.1
70	2.7	28	27	79.2	82.8	57	65	1.5	1.2	65.9	61.1
70	2.7	75	77	78.7	80.9	85	86	2.5	2.0	73.8	85.1
90	0.9	49	55	77.1	76.5	80	85	2.7	3.1	35.6	76.0
90	1.8	28	27	77.4	79.2	60	67	2.0	1.8	60.6	68.9
90	1.8	49	55	77.9	78.1	75	81	2.3	2.5	57.7	81.8
90	1.8	49	55	78.4	78.2	75	82	2.2	2.5	53.9	80.9
90	1.8	49	55	78.7	78.1	76	81	2.2	2.5	54.3	81.1
90	1.8	75	77	77.0	76.6	86	94	2.9	3.4	65.5	90.9
90	2.7	49	55	79.3	80.0	67	73	1.8	1.8	71.5	89.3
110	0.9	28	27	75.1	78.8	63	71	2.6	2.0	33.1	42.4
110	0.9	75	77	75.8	77.7	94	98	3.6	3.1	36.4	74.2
110	1.8	49	55	77.4	79.9	79	79	2.6	2.0	46.0	64.7
110	2.7	28	27	77.3	81.2	55	63	1.9	1.4	59.4	68.0
110	2.7	75	77	76.4	78.7	82	85	3.0	2.4	75.6	85.6

¹Brightness determined on laboratory sheets (65g/m²) according to ISO standard method 9416.

From the MODDE model used in this work, the R^2 values for the responses were >0.90 and the Q^2 values >0.84 which is considered to be very good.

Fig 3 shows the regression coefficients of the interaction model and their 95% confidence intervals. The first three coefficients, also called linear terms, reveal the real effects of the three factors (temperature, NaOH charge, fines content). The last coefficient shows whether there is any interaction among the factors. The uncertainty of the coefficients is given by the confidence intervals.

Fig 3. Hydrogen peroxide bleaching of TMP and SGW pulp with different fibre/fines ratios. Scaled and centred regression coefficients of the interaction model for the light absorption coefficient with 95% confidence interval as error bars.

The coefficient plot displays the impact for each factor for a response. The MODDE model coefficient plot indicates that the main effects, i.e. temperature, alkali (NaOH) charge, and fines content, were important for the light absorption coefficient (Fig 3). It can be seen that fines content had the strongest impact on the light absorption coefficient. When the fines content was increased from the medium level, 50%, to its high level, 75%, and the other factors remained fixed at their medium levels, the light absorption coefficient increased by 0.5 units. The second most influential factor was the sodium hydroxide charge, where an increased caustic charge decreased the light absorption coefficient. The third factor, temperature, had the lowest impact on the light absorption coefficient with increased temperature increasing the light absorption coefficient to some extent. The interaction term “Temperature x NaOH” was statistically insignificant as the confidence interval included zero and no interaction between sodium hydroxide and temperature was seen, meaning that it was not beneficial to lower the sodium hydroxide charge when the temperature was increased in the chosen intervals. The chosen interval for the NaOH charge was 0.9, 1.8 and 2.7% and the difference in level was probably too large to see any NaOH charge reduction when the temperature increased. In Logenius (2008)

work it was shown that an approximate 30% decrease in NaOH charge resulted in unchanged brightness but still lower than that obtained at 70°C. Kappel and Sbaschnigg (1991) reported a 30% reduction in optimum NaOH charge (i.e. at optimal brightness) when the temperature was increased from 60 to 95°C but the higher temperature resulted in lower brightness than that obtained at 60°C.

The MODDE model coefficient plot indicates that alkali charge and fines content were important for the light scattering coefficient (Fig 4). It can be seen that fines had the greatest impact on the light scattering; increased fines content increased the light scattering coefficient. The second most influential factor was the NaOH charge. Increased sodium hydroxide charge decreased the light scattering coefficient, probably due to the improved bonding resulting in increased sheet density (Engstrand, Sjögren 1991). The temperature and the interaction term “Temperature x NaOH” did not affect the light scattering coefficient as the confidence interval included zero and was statistically insignificant.

Fig 4. Hydrogen peroxide bleaching of TMP and SGW pulp with different fibre/fines ratios. Scaled and centred regression coefficients of the interaction model for the light scattering coefficient with 95% confidence interval as error bars.

The following charts in this paper are based on the predicted values from the MODDE 5.0 model. The predicted values of optical properties and hydrogen peroxide consumption are also given in Table 5, Appendix.

Hydrogen peroxide bleaching of TMP and SGW pulp at 70, 90 and 110°C revealed that the highest brightness and lowest light absorption coefficient was obtained at an alkali charge of 2.7% irrespective of the fines content of the pulp or the bleaching temperature (see Table 5, Appendix). Haugan and Gregersen (2006) reported that hydrogen peroxide bleaching of fines needed quite high sodium hydroxide charges to reach the lowest light absorption coefficients. The bleaching was performed at 3% pulp consistency which is different from the high consistency conditions (30%) used in

this investigation and those prevalent in industrial processes. The lowest light absorption coefficients were obtained at a bleaching temperature of 70°C (NaOH charge 2.7%), see *Figs 5 and 6*.

Fig 5. The light absorption coefficient ($k_{457\text{nm}}$) as a function of temperature for hydrogen peroxide bleached TMP with fibre/fines ratio of 25/75, 50/50 and 75/25%. Bleaching conditions: 4.5% H_2O_2 , 2.7% NaOH, 2.9% Silicate, 70°C, 120 minutes, 30% consistency. Predicted values.

Fig 6. The light absorption coefficient ($k_{457\text{nm}}$) as a function of temperature for hydrogen peroxide bleached SGW pulp with fibre/fines ratio of 25/75, 50/50 and 75/25%. Bleaching conditions: 4.5% H_2O_2 , 2.7% NaOH, 2.9% Silicate, 70°C, 120 minutes, 30% consistency. Predicted values.

Increased temperature did not reduce the k -value to the same extent. In the case of SGW pulp with the highest fines content (75%), hydrogen peroxide bleaching at 90°C for 120 minutes seemed to be too long as almost all peroxide (97%) was consumed resulting in a light absorption coefficient that was probably too high (*Fig 6*). The SGW pulp seemed to be more sensitive for the 90°C temperature and 120 minutes retention time compared to TMP (cf. *Fig 5* and *Fig 6*) where the light absorption coefficient and the hydrogen peroxide consumption were higher (*Table 5, Appendix*), although the SGW pulp contained a small amount of manganese.

The iron content was, however, somewhat higher as shown in *Table 1*. Increasing the temperature from 70°C up to 110°C decreased the brightness by 2

units for both pulps (*Table 5, Appendix*). The divergent difference in the light absorption coefficient between unbleached TMP and SGW pulp towards higher fines content (*Fig 1*) was, after hydrogen peroxide bleaching (at optimal conditions), rather constant and the difference after bleaching was about 0.5 units (*Fig 7*).

Fig 7. The light absorption coefficient ($k_{457\text{nm}}$) as a function of fines content for hydrogen peroxide bleached TMP and SGW pulp. Bleaching conditions: 4.5% H_2O_2 , 2.7% NaOH, 2.9% Silicate, 70°C, 120 minutes, 30% consistency. Predicted values, 95% confidence interval as error bars.

The SGW pulp reached a higher final brightness than the TMP (*Fig 8*) due to a lower light absorption coefficient (*Fig 7*). Although increased fines content increased the light absorption coefficient, the TMP brightness was increased when the fines content increased from 25% to 50% (*Fig 8*). This was due to the increase in the light scattering coefficient (*Fig 9*). Increasing the fines content further from 50% to 75% decreased the brightness for both pulps since the increased light scattering coefficient (*Fig 9*) could not compensate for the increased light absorption coefficient (*Fig 7*).

Fig 8. The brightness as a function of fines content for hydrogen peroxide bleached TMP and SGW pulp. Bleaching conditions: 4.5% H_2O_2 , 2.7% NaOH, 2.9% Silicate, 70°C, 120 minutes, 30% consistency. Predicted values, 95% confidence interval as error bars.

Fig 9. The light scattering coefficient (s_{457nm}) as a function of fines content for hydrogen peroxide bleached TMP and SGW pulp. Bleaching conditions: 4.5% H₂O₂, 2.7% NaOH, 2.9% Silicate, 70°C, 120 minutes, 30% consistency. Predicted values, 95% confidence interval as error bars.

Conclusions

The objective of this work was to study fines as a limiting factor for reaching higher brightness levels in hydrogen peroxide bleaching of mechanical pulps. For unbleached TMP and SGW pulps, an increased amount of fines in the fractions increased, as expected, the light absorption coefficients and the amounts of extractives, lignin and transition metals (Fe, Mn). Unbleached TMP had a higher light absorption coefficient than unbleached SGW pulp, and both the fibres and fines were more coloured.

The bleaching temperature in the interval 70–110°C did not affect the light scattering coefficient of the pulps. The light scattering coefficients decreased, as expected, for all TMP and SGW pulp fibre/fines fractions with an increased charge of sodium hydroxide. The hydrogen peroxide bleaching efficiency (i.e. light absorption coefficient reduction) in the 70–110°C temperature interval was found to be best at the lowest bleaching temperature, when residence time and alkali charge were also taken into consideration. In most cases increased amounts of fines in the pulp had a negative effect on the bleached pulp brightness. This was to some extent compensated with an increased light scattering coefficient. The SGW pulp displayed a better final brightness level, 2–4 brightness units higher than the brightness of the TMP under similar bleaching conditions. However, the SGW pulp seemed to be more sensitive to the 90°C temperature and longest (120 minutes) retention time compared to the TMP. At a hydrogen peroxide charge of 4.5% and at a fines content of 25%, the stone groundwood pulp displayed a brightness of 83% whereas the thermo-mechanical pulp reached a brightness of 79%.

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Appendix

Table 5. The predicted (MODDE 5.0) optical properties and consumed hydrogen peroxide for hydrogen peroxide bleached TMP and SGW pulp with different fibre/fines ratios.

Temperature °C	NaOH %	Fines %	Brightness ¹ %		S _{457nm} m ² /kg		k _{457nm} m ² /kg		Peroxide consumption %	
			TMP	SGW	TMP	SGW	TMP	SGW	TMP	SGW
70	0.9	25	76.1	79.4	62	68	2.3	1.8	41.2	45.2
70	1.8	25	77.6	81.3	58	66	1.9	1.4	53.6	54.0
70	2.7	25	79.1	83.2	55	64	1.5	1.0	65.9	62.8
70	0.9	50	77.8	79.5	83	79	2.6	2.1	34.9	60.5
70	1.8	50	79.0	81.2	78	76	2.2	1.6	49.3	65.9
70	2.7	50	80.2	82.9	73	74	1.8	1.2	63.7	71.3
70	0.9	75	76.9	78.2	97	94	3.4	2.9	43.7	78.0
70	1.8	75	77.7	79.7	90	90	2.9	2.4	60.1	80.1
70	2.7	75	78.6	81.1	84	86	2.5	1.9	76.6	82.1
90	0.9	25	75.6	77.0	59	71	2.3	2.5	45.8	56.1
90	1.8	25	76.9	78.5	55	68	1.9	2.1	59.4	66.9
90	2.7	25	78.2	80.1	51	65	1.5	1.7	73.0	77.7
90	0.9	50	77.3	77.1	81	83	2.7	2.8	39.5	71.3
90	1.8	50	78.3	78.5	75	78	2.3	2.4	55.1	78.8
90	2.7	50	79.2	79.8	70	74	1.9	1.9	70.8	86.2
90	0.9	75	76.4	75.8	94	97	3.4	3.6	48.3	88.8
90	1.8	75	77.1	76.9	87	92	3.0	3.1	65.9	92.9
90	2.7	75	77.7	78.0	80	86	2.6	2.7	83.6	97.0
110	0.9	25	74.9	78.8	61	70	2.6	2.0	34.1	40.0
110	1.8	25	75.9	80.0	57	66	2.3	1.7	48.9	52.8
110	2.7	25	77.0	81.2	53	62	1.9	1.3	63.8	65.7
110	0.9	50	76.6	79.0	83	82	3.0	2.3	27.8	55.2
110	1.8	50	77.3	80.0	77	77	2.6	1.9	44.7	64.7
110	2.7	50	78.0	80.9	72	71	2.2	1.5	61.5	74.2
110	0.9	75	75.7	77.6	96	97	3.7	3.1	36.6	72.8
110	1.8	75	76.1	78.4	89	90	3.3	2.7	55.5	78.9
110	2.7	75	76.4	79.1	82	83	2.9	2.3	74.4	85.0

¹Brightness determined according to ISO standard method 9416.