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# High consistency hydrogen peroxide bleaching of a Norway spruce stone groundwood pulp: Influence of heat treatment and iron content

Anette Karlsson

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

**SUMMARY:** The objective of this work was to improve the understanding on how thermal treatments of mechanical pulps containing iron influence the unbleached brightness and hydrogen peroxide bleachability at high brightness levels. An unbleached Norway spruce stone groundwood (SGW) pulp was subjected to heat and iron ( $\text{Fe}^{3+}$ ) treatments followed by a chelating stage and a high consistency hydrogen peroxide bleaching stage. The hydrogen peroxide bleachability was studied on pulps as a function of pre-treatment at elevated temperatures and strongly bound iron content prior to bleaching and the alkali charge during bleaching. The evaluation was done using an experimental design based on the MODDE software (Umetrics AB).

Heat treatment of the unbleached SGW pulp at 110 or 140°C did not induce a significant increase in light absorption coefficient. Increasing the heat treatment temperature to 170°C did, however, result in an increased light absorption coefficient corresponding to a brightness loss of 3.5% ISO. The light scattering coefficient was found to be essentially unchanged regardless of the heat-treatment conditions applied. The brightness loss resulting from the heat treatment could only partly be regained by hydrogen peroxide bleaching.

An increased amount of strongly bound iron in the unbleached SGW pulp increased the light absorption coefficient. This increase was slightly higher when heat pre-treatment was performed at 140 and 170°C compared to when heating at 110°C. Hydrogen peroxide bleaching was found to reduce the iron content of the pulps and thus regain some of the brightness that was lost. This effect was most pronounced at the higher alkali charge levels. It is thus important to minimise the processing temperature, the time at high temperature and the iron content of the pulp in order to improve the unbleached brightness and bleachability of mechanical pulps.

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The temperature during fibre separation and development will be lower when producing a stone groundwood (SGW) pulp than when producing a thermomechanical pulp (TMP). In nonpressurised processes as the SGW process, the grinding zone temperature will most probably exceed 100°C only for a very short moment (Liimatainen et al. 1999).

During pressurised grinding processes (PGW), the temperature in the grinding zone may reach about 140°C (Salmén et al. 1999). In the TMP processes the temperature is higher both due to preheating of the wood chips (140-160°C for 5-180 seconds) and can exceed 190°C at a steam peak in the refining zone (Engstrand et al. 1995; Tienvieri et al. 1999; Härkönen et al. 2003). The brightness levels of Norway spruce SGW pulps and TMPs are in the range of 60-65% ISO and 57-60% ISO, respectively (Lindholm 1999). Previous results suggest that both fibre and fines fractions have higher chromophore content in TMP compared to SGW pulp (Petit-Conil, Laurent 2003; Karlsson, Agnemo 2010). The reason for higher chromophore content and thus lower brightness for TMP compared to SGW pulp is the higher temperature during the pulping process. Under mechanical pulping conditions the elevated temperatures initiate reactions in the lignin resulting in chromophores and leucochromophores (Gellerstedt, Pettersson 1980; Gellerstedt et al. 1983; Gratzl 1985; Chong et al. 1991). Chromophores induced by heat could also involve reactions of extractives and 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). Moreover, heat treatments of carbohydrates have been found to induce yellowing (Forsskåhl 2000). The brightness loss was attributed to the hemicellulose components and pectic substances and also cellulose gave rise to some colour on heating. 5-Hydroxymethyl-2-furaldehyde has also been proposed to interact with pulp components such as lignin or hemicelluloses leading to colour formation (Forsskåhl et al. 2000).

The lower brightness level of TMP compared to SGW pulp is also influenced by the lower light scattering coefficient (Höglund, Wilhelmson 1993; Varhimo, Tuovinen 1999).

Metal ions and 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. 1999a; Yoon et al. 1999). The light absorption coefficient has been reported to increase during refining and coloured metal ion complexes are suggested to be

formed (Johansson, Gellerstedt 2000; Johansson et al. 2002). The main source of metals ions is the wood raw material, the amount depending on the species and place of growth and the mill process waters may also contribute with large amounts of metals (Read et al. 1968; Christiansen, Michalowski 1989; Presley, Hill 1996). Further, the process equipment could introduce metals and, for instance in thermomechanical pulping, the level of iron may increase during the refining process (Colodette, Dence 1989). Friman et al. (2003) reported an iron content increase through the thermomechanical pulping process from about 2 to 40 mg/kg where the metal ions were derived from process additives present in the paper machine water. Iron contents of 20-30 mg/kg in thermomechanical and groundwood pulps have also been reported by e.g. Ni et al. (1999b, 2000). Further, transition metals such as iron, manganese and copper decompose hydrogen peroxide under bleaching conditions leading to lower bleached pulp brightness (Colodette et al. 1988). The presence of traces of ferrous ( $\text{Fe}^{2+}$ ) or ferric ( $\text{Fe}^{3+}$ ) ions in the pulp has a detrimental effect on both the brightness and the brightness stability (Gellerstedt et al. 1983; Chong et al. 1991). Ferric ions were the most detrimental of all metal ions examined whereas ferrous ions have substantially less effect on colour (Polcin, Rapson 1971; Styan 1975; Peart, Ni 2001). Iron participates in redox cycles which may result in severe discoloration of the pulp (Janson, Forsskåhl 1989; Grönroos et al. 1998). The importance of maintaining a low iron content during the entire pulping process is thus important; minimising the transition metal ion content by e.g. the use of chelating agents may both improve the brightness and the heat-induced brightness stability of pulps, both before and after bleaching with dithionite or hydrogen peroxide (Presley, Hill 1996; Ni et al. 1997).

Hydrogen peroxide is a widely used bleaching chemical that is particularly useful when high brightness levels are required. There is, however, a limit to the brightness gain that can be achieved by increasing the amount of hydrogen peroxide applied to a pulp where the maximum brightness is achieved at a hydrogen peroxide charge of about 4-5%. Stone groundwood pulps respond better to hydrogen peroxide bleaching than do thermomechanical pulps. At hydrogen peroxide charges of 4-5%, the maximum brightness of Norway spruce produced in the stone groundwood process is about 82-83% ISO and in the thermomechanical process 79-80% ISO (Presley, Hill 1996). One limiting factor for reaching higher brightness levels is the fines which have a negative impact on the bleached pulp brightness in spite of the improved light-scattering

ability of fines (Karlsson, Agnemo 2010). Other contributing factors could be heat-induced chromophores formed during fibre separation and development and the presence of strongly bound iron in the unbleached pulp.

The objective of this work was to improve the understanding of and investigate the possible synergistic effects of high temperature level and high iron content on the brightness development in the mechanical pulping and hydrogen peroxide bleaching processes. The bleachability of a Norway spruce (*Picea abies*) stone groundwood pulp subjected to thermal treatments and containing varying amounts of strongly bound iron is presented and discussed.

## Material and Methods

### Pulps

A commercially produced unbleached Norway spruce (*Picea abies*) stone groundwood (SGW) pulp with a freeness value of 79 ml CSF was used in the experiments described in this paper. The pulp was collected after the dewatering press prior to bleaching.

### Metal ion management

A chelating stage was carried out in order to reduce the metal content of the pulp prior to the oxidative bleaching with hydrogen peroxide. The SGW pulp was chelated in the laboratory with a commercial diethylenetriaminepentaacetic acid, sodium salt ( $\text{Na}_5\text{DTPA}$ , Versenex 80 from Dow, Sweden) solution at a charge of 0.5% at room temperature, 5% pulp consistency and the pH adjusted to pH 5.0-5.5 with 0.05 mol/l sulphuric acid ( $\text{H}_2\text{SO}_4$ , p.a.) or 0.1 mol/l sodium hydroxide ( $\text{NaOH}$  p.a.). After a retention time of 30 min, the pulp was dewatered on a polyamide wire (125  $\mu\text{m}$ ) in a Büchner funnel to about 25% consistency, the filtrate being recirculated twice through the filter cake to avoid losses of fibres and fines material. The water-soluble metal-DTPA complexes were washed out by adding 1 l deionised water to 200 g pulp in a funnel and dewatered to about 20% pulp consistency. The procedure was repeated twice (a total of 3 litres), and thereafter pressed to a pulp consistency of approximately 35-40%. The copper and manganese contents of the pulp were below 0.05 mg/kg after the chelating stage. The iron content was 6 mg/kg. The added amount of  $\text{Na}_5\text{DTPA}$  is given as commercial product. The chelated pulp was stored in a freezer at  $-24^\circ\text{C}$  until use.

### Preparation of pulps with different amounts of iron

The SGW pulp was diluted with deionised water to 4% consistency and mixed with different amounts of an iron (III) chloride solution ( $\text{FeCl}_3 \cdot x \text{H}_2\text{O}$ ,

p.a. from Merck Chemicals) at room temperature. The metal ion solution was freshly prepared prior to use. Three levels of iron were added to the pulp; 30, 70 and 110 mg/kg. After a retention time of 30 min, the pulps were dewatered on a polyamide wire (125  $\mu\text{m}$ ) in a Büchner funnel to about 25% consistency, the filtrate being recirculated twice through the filter cake to avoid losses of fibres and fines material.

### Heat treatment

The unbleached SGW pulps containing different amounts of iron were subjected to heat, using a double-mantled stainless steel vessel that was pressurised with steam (detailed description of the experimental equipment is given in Logenius 2008). The desired temperature was reached within a few seconds. After treatment, the steam was stopped, the outlet was opened, and the temperature dropped immediately to below 100°C. The pulp sample was taken out of the vessel within 20 sec and immediately cooled to room temperature in a plastic bucket standing in a cold-water bath where the pulp was once again chelated with Na<sub>5</sub>DTPA and treated as described above (see *Metal ion management*). This was done to retain only strongly bound iron in the pulp. The heat treatment procedure was performed at three temperature levels (110, 140 and 170°C) and at three retention times (1, 2 and 5 min).

### Hydrogen peroxide bleaching

High consistency hydrogen peroxide bleaching was performed at a pulp consistency of 30%. Five grams of pulp (oven-dry) 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  $\mu\text{m}$ , from Genpack A/S, Denmark), which were sealed and immersed into a thermostatic water bath. The hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) charge was 4.5% and the sodium hydroxide (NaOH) charge was optimised and varied between 0.9 and 2.7% with the purpose to reach the highest possible brightness. The sodium silicate (S38 with a weight ratio between SiO<sub>2</sub> and Na<sub>2</sub>O of 3.25, supplied by PQ Europe, Sweden) charge was kept constant and was 2.9%. The manganese and copper contents were less than 1 mg/kg and the iron content was 51 mg/kg in the sodium silicate used. The bleaching trials were performed at 70°C with a retention time of 120 minutes. After the bleaching stage, the pulp was cooled to room temperature. One gram of pulp (oven-dry) was diluted with 50 g de-ionised water and after 5 min, 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 charges are given as 100% active component.

### Preparation of laboratory sheets and evaluation of optical properties

Laboratory sheets (62 g/m<sup>2</sup>, oven-dry) were formed in a laboratory sheet former using a 76- $\mu\text{m}$  (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 methods 2470 and 9416. In this paper, the *s*- and *k*-values were determined with the brightness function,  $R_{457}$ .

### Experimental design

A part of the experimental work presented in this paper was designed using the MODDE 5.0 software (Umetrics AB, Umeå, Sweden). The factors examined (heat treatment temperature, sodium hydroxide charge and iron content of the pulp prior to H<sub>2</sub>O<sub>2</sub> bleaching) were varied simultaneously over a set of planned experiments; the results are then connected by means of a mathematical model. The model is used for interpretation, predictions and optimisation 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 responses (brightness,  $S_{457\text{nm}}$ ,  $k_{457\text{nm}}$ , iron remaining in the pulp after H<sub>2</sub>O<sub>2</sub> bleaching and hydrogen peroxide consumption) and the factors (heat treatment temperature, sodium hydroxide charge and iron content of the pulp prior to H<sub>2</sub>O<sub>2</sub> bleaching). Data gathered using a central composite and face-centred (CCF) design was used to generate prediction models. All responses were modelled 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 (110, 140 and 170°C), sodium hydroxide charge (0.9, 1.8 and 2.7%) and iron content (25-27, 36-41 and 53-57 mg/kg). The experimental design is shown in *Table 3*.

### Other analyses

Analyses and methods not mentioned elsewhere in the experimental section are as follows: freeness (ISO standard method 5267-2) and metal ion content (SCAN standard method CM:38:96) measured on laboratory sheets. The residual hydrogen peroxide, i.e., the hydrogen peroxide that was not consumed during bleaching, was determined by iodometric titration where the liberated iodine was titrated with 0.1 M sodium thiosulphate. The carboxylic group content was determined by conductometric titration according to Katz et al. (1984).

## Results and discussion

The influence of heat treatment and ferric ( $\text{Fe}^{3+}$ ) ions on brightness and bleachability of mechanical pulps was studied using a model pulp. The pulp used was an unbleached and DTPA-chelated Norway spruce (*Picea abies*) stone groundwood (SGW) pulp. This model pulp was chosen since SGW pulp has a rather low content of heat-induced chromophores. The iron content of the unbleached pulp was 6 mg/kg pulp and was considered to be strongly bound.

It has been reported that a large part of the iron (and copper) are strongly attached to the wood matrix (as precipitates or present in ray cells) and are therefore considerably more difficult to remove (Sundén et al. 2000). Further, adding ferric ions to a pulp suspension and thereafter heating to 100°C did result in strongly bound iron in the form of crystalline goethite which was not removable from the pulp with an acidic water wash (Rothenberg, Robinson 1980). In grinding and refining operations, the ferric ions present in the system might be converted to goethite due to the heat generated during processing. Goethite is also known to decompose hydrogen peroxide (Lin, Gurol 1998) which lowers the hydrogen peroxide bleaching efficiency.

The SGW pulp, containing various amounts of strongly bound iron, was subjected to thermal treatments and thereafter hydrogen peroxide bleached to high brightness levels (~80% ISO). This was done in order to get a better understanding of the differences between groundwood and thermo-mechanical pulps with respect to unbleached and bleached brightness.

### The influence of heat treatment on the optical properties of unbleached SGW pulps containing varying amounts of strongly bound iron

Experiments were conducted in which the SGW pulp was subjected to heat treatment before bleaching with various amount of iron. This was performed at three temperature levels: 110, 140 or 170°C and at three retention times: 1, 2, or 5 minutes. The optical properties and the strongly bound iron content of untreated, heat and iron+heat-treated unbleached SGW pulps are listed in *Table 1*. The iron content for the pulps only treated with heat varied between 6-11 mg/kg. The variations can probably be explained by inhomogeneity in the wood raw material, contamination during heating and/or variation in the iron analyses.

The light scattering coefficient ( $S_{457\text{nm}}$ ) was essentially unaffected by the heat treatment regardless of the conditions applied (*Table 1*).

Table 1. Optical properties and iron content of untreated and heat-treated unbleached Norway spruce SGW pulps containing different amounts of strongly bound iron.

Treatment	Heating temperature, °C	Heating time, min	Brightness <sup>1</sup> % ISO	$S_{457\text{nm}}$ , m <sup>2</sup> /kg	$k_{457\text{nm}}$ , m <sup>2</sup> /kg	Fe content, mg/kg
None, ref			65.9	69	6.1	6
Heat	110	1	65.5	66	6.0	7
Heat	110	2	65.7	69	6.2	
Heat	110	5	65.3	65	6.0	11
Heat+iron	110	1	64.2	67	6.6	27
Heat+iron	110	1	63.6	67	7.0	41
Heat+iron	110	1	63.0	67	7.3	57
Heat	140	1	65.7	67	6.0	11
Heat	140	2	64.8	65	6.2	
Heat	140	5	64.4	66	6.5	6
Heat+iron	140	1	63.4	67	7.1	25
Heat+iron	140	1	62.6	67	7.5	41
Heat+iron	140	1	62.0	68	7.9	56
Heat	170	1	62.4	66	7.5	8
Heat	170	2	60.9	63	7.9	
Heat	170	5	57.0	66	10.7	8
Heat+iron	170	1	59.9	65	8.7	27
Heat+iron	170	1	59.4	65	9.1	36
Heat+iron	170	1	59.0	65	9.3	53

<sup>1</sup>Brightness determined on laboratory sheets (65 g/m<sup>2</sup>) according to ISO standard method 2470.

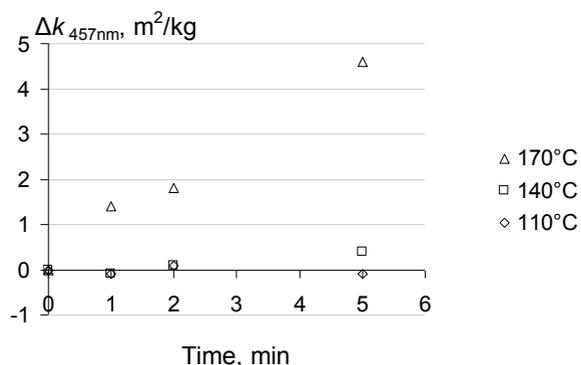


Fig 1. The change in light absorption coefficient,  $\Delta k_{457nm}$ , as a function of retention time for Norway spruce SGW pulp subjected to heat treatment up to 5 minutes at 110, 140 and 170°C. The strongly bound iron content was 6-11 mg/kg (cf. Table 1).

Within the time and temperature span evaluated, the light absorption coefficient ( $k_{457nm}$ ) increased provided that the heat treatment was performed at minimum 140°C. The increase in light absorption was most pronounced for the highest heating temperature (170°C) and already after one minute, the increase in  $k$ -value was considerable and corresponded to approximately 3.5% ISO lower brightness (Table 1). This is in agreement with previous results, i.e. steaming native spruce wood at temperatures below 120°C for up to six minutes causes no significant discoloration while in the temperature interval 140-160°C, the elevated temperature resulted in a brightness reduction (Logenius et al. 2005). Furthermore, Koskinen et al. (1997) reported a brightness reduction by several units when steaming spruce TMP at temperatures above 165°C for 25 sec. At longer residence time, i.e. up to 60 min it has, however, been shown by means of experiments on spruce wood meal that the chromophore content will increase to some extent even at 70 °C, it was also shown that the rate of chromophore content increased rapidly with increasing temperature (Engstrand et al. 1987).

The kinetics of the chromophore content increase is shown in Fig 1 as  $\Delta k_{457nm}$ , where  $\Delta k_{457nm}$  is final  $k$ -value for heat-treated pulp minus  $k$ -value for the untreated pulp.

The colour generated when heating the unbleached groundwood pulp containing different amounts of strongly bound iron, for one minute at 110, 140 or 170°C is shown in Fig 2 (cf. Table 1). It is evident that an increased amount of iron in the pulp increased the rate of chromophore creating reactions. The increase in  $k$ -value was slightly higher at 140 and 170°C (about 0.5 units) compared to 110°C. At the highest heating temperature and highest iron content, i.e., 170°C and 53 mg/kg, the light absorption coefficient increased with 1.8 m<sup>2</sup>/kg

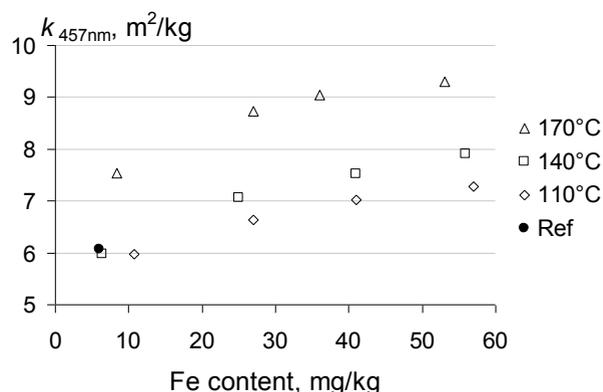


Fig 2. The light absorption coefficient of Norway spruce SGW pulp subjected to heat treatment for one minute at 110, 140 and 170°C as a function of the strongly bound iron content.

compared to the heat-treated reference pulp and with about 3.2 m<sup>2</sup>/kg compared to the untreated reference pulp. This corresponds to a brightness loss of approximately 3.5 and 7% ISO, respectively.

#### The influence of heat treatment and strongly bound iron content on the hydrogen peroxide bleachability of SGW pulps

The untreated reference SGW pulp was bleached using 4.5% hydrogen peroxide at a pulp consistency of 30% at 70°C for 120 min and with varying alkali charges (0.9-2.7%) in order to find the optimal conditions for further bleaching trials. Sodium silicate was added as stabiliser and the charge was kept constant at 2.9% for all bleaching trials reported in this paper. In addition, the SGW pulps heat-treated for one minute were hydrogen peroxide bleached at the highest alkali charge (2.7%). The hydrogen peroxide consumption was about 60% for both untreated and heat-treated pulps at an alkali charge of 2.7%. Further increase in the alkali charge would have increased the hydrogen peroxide consumption, but the increase in brightness was expected to be limited (cf. Karlsson, Agnemo 2010).

Heat treatment for one minute at 110 or 140°C did not increase the  $k$ -value for the unbleached pulps as discussed above (see Table 1). Hydrogen peroxide bleaching of the heat-treated pulps resulted in approximately the same  $k$ -values (1.2 and 1.3 m<sup>2</sup>/kg), which were in the same region as for the untreated reference pulp (Table 2). Heat treatment at 170°C increased the  $k$ -value of the unbleached pulp by about 1.4 units and lowered the brightness with about 3.5 %ISO (see Table 1). The chromophores created by means of heat treatment could only to a limited extent be removed when the pulp was subsequently bleached with 4.5% hydrogen peroxide. The heat-treated pulp had a brightness of 79.7% ISO while the brightness of the untreated

Table 2. Optical properties, hydrogen peroxide consumption and iron content of untreated and heat-treated bleached Norway spruce SGW pulps. Chemical charges: 4.5% H<sub>2</sub>O<sub>2</sub> and 2.9% sodium silicate.

Treatment	Heating temp., °C	Heating time, min	NaOH, %	Brightness <sup>1</sup> , %ISO	S <sub>457nm</sub> , m <sup>2</sup> /kg	k <sub>457nm</sub> , m <sup>2</sup> /kg	H <sub>2</sub> O <sub>2</sub> consum., %	Fe remain. <sup>2</sup> , mg/kg
None, ref			0.9	79.5	68	1.8	30	6
None, ref			1.8	81.3	65	1.4	42	6
None, ref			2.7	82.2	62	1.2	55	6
Heat	110	1	2.7	82.3	61	1.2	54	7
Heat	140	1	2.7	81.8	62	1.3	57	7
Heat	170	1	2.7	79.7	61	1.6	59	9

<sup>1</sup>Brightness determined on laboratory sheets (65 g/m<sup>2</sup>) according to ISO standard method 2470.

<sup>2</sup>Iron content of the pulp after hydrogen peroxide bleaching.

Table 3. The MODDE experimental design with responses (optical properties, hydrogen peroxide consumption and iron remaining in the pulp after H<sub>2</sub>O<sub>2</sub> bleaching) for Norway spruce SGW pulps bleached with hydrogen peroxide. The SGW pulps containing different amounts of iron and were heat-treated for one minute at 110, 140 or 170°C. Chemical charges: 4.5% H<sub>2</sub>O<sub>2</sub> and 2.9% sodium silicate.

Treatment	Heating temp., °C	Fe content <sup>1</sup> , mg/kg	NaOH, %	Brightness <sup>2</sup> , % ISO	S <sub>457nm</sub> , m <sup>2</sup> /kg	k <sub>457nm</sub> , m <sup>2</sup> /kg	H <sub>2</sub> O <sub>2</sub> consum., %	Fe remain. <sup>3</sup> , mg/kg
Heat+iron	110	27	0.9	78.9	68	1.9	34	19
Heat+iron	110	27	2.7	81.9	61	1.2	67	11
Heat+iron	110	41	1.8	80.7	66	1.5	57	29
Heat+iron	110	57	0.9	77.7	68	2.2	38	46
Heat+iron	110	57	2.7	80.6	62	1.5	82	23
Heat+iron	140	25	1.8	80.8	66	1.5	49	15
Heat+iron	140	41	0.9	77.6	69	2.2	35	32
Heat+iron	140	41	1.8	80.2	66	1.6	58	24
Heat+iron	140	41	1.8	80.2	66	1.6	58	22
Heat+iron	140	41	1.8	80.1	67	1.7	56	22
Heat+iron	140	41	2.7	80.9	63	1.4	75	16
Heat+iron	140	56	1.8	79.8	67	1.7	61	31
Heat+iron	170	27	0.9	76.2	69	2.6	34	17
Heat+iron	170	27	2.7	80.1	62	1.5	65	13
Heat+iron	170	36	1.8	78.2	67	2.0	52	29
Heat+iron	170	53	0.9	75.0	68	2.8	33	46
Heat+iron	170	53	2.7	78.4	63	1.9	74	25

<sup>1</sup>Iron content of the pulp prior to hydrogen peroxide bleaching.

<sup>2</sup>Brightness determined on laboratory sheets (65 g/m<sup>2</sup>) according to ISO standard method 2470.

<sup>3</sup>Iron content of the pulp after hydrogen peroxide bleaching.

reference pulp was 82.2% ISO, i.e., a brightness difference of 2.5%ISO (Table 2).

Heating wood at elevated temperatures is known to partly degrade the carbohydrates resulting in organic acids as degradation products (Alén et al. 2002). Heat treatment at 170°C for one minute increased the carboxylic acid group content with about 10% from about 110 mmol/kg to about 120 mmol/kg. The alkali optimum was, however not expected to be displaced to higher charges due to organic acid formation as a consequence of the thermal treatment since the heat-treated pulps were DTPA washed prior to bleaching. An alkali interval between 0.9 and 2.7% was therefore judged to be sufficient for the bleaching trials described below.

Norway spruce SGW pulps containing various amounts of iron in the interval 25-57 mg/kg were subjected to thermal treatments (one minute at 110, 140 or 170°C) and thereafter hydrogen peroxide bleached. The MODDE 5.0 software was used as a tool to design and evaluate the bleaching trials. Table 3 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. From the MODDE model used in this

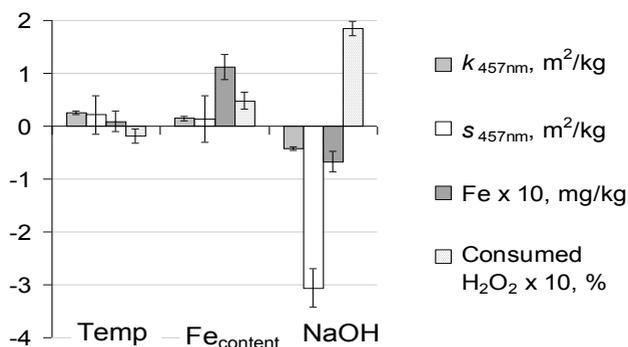


Fig 3. Hydrogen peroxide bleaching of heat-treated Norway spruce SGW pulps with different amounts of strongly bound iron. Scaled and centred regression coefficients of the interaction model for the iron content remaining in the pulp after bleaching (Fe, scale x 10), light scattering coefficient ( $s_{457nm}$ ), light absorption coefficient ( $k_{457nm}$ ) and consumed hydrogen peroxide ( $H_2O_2$ , scale x 10) with 95% confidence interval as error bars.

work, the  $R^2$  values for the responses were  $>0.95$  and the  $Q^2$  values  $>0.85$ , which is considered to be very good.

Fig 3 shows the regression coefficients of the interaction model and their 95% confidence interval. The MODDE model coefficient plot indicates that the main effects, temperature, iron content of the pulp prior to bleaching and alkali charge were all important for the light absorption coefficient. An increased alkali charge (within the tested interval) decreased the light absorption coefficient whereas the heat treatment and the strongly bound iron content increased the  $k$ -value. The alkali charge had the strongest impact on the light absorption coefficient followed by the heat treatment and the iron content of the pulp prior to bleaching.

The alkali charge was important for the light scattering coefficient (Fig 3). An increased sodium hydroxide charge decreased the light scattering coefficient as expected (cf. Karlsson, Agnemo 2010).

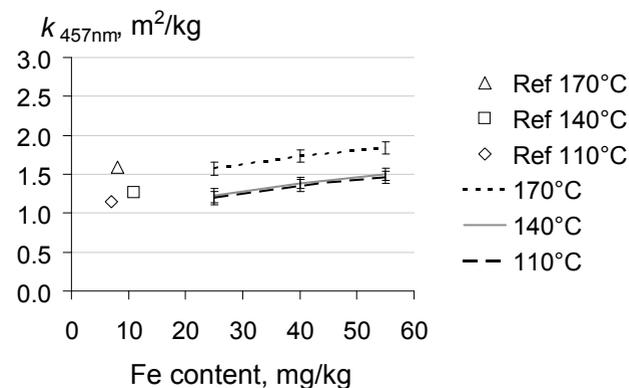
Carboxylic acid groups may be formed in lignin as a consequence of hydrogen peroxide bleaching at alkaline conditions (Gellerstedt et al. 1980; Sjöström 1989; Sundberg et al. 2000). The carboxylic acid group content increased to 230 mmol/kg when the alkali charge was 2.7%, which will increase density and thus lower the light scattering ability (cf. Engstrand, Sjögren 1991). It can further be seen that heat treatment and iron content prior to bleaching had no impact on the light scattering ability as the confidence interval included zero and was statistically insignificant. Further, the MODDE model coefficient plot indicates that the main effects, iron content of the pulp prior to bleaching and NaOH charge, were important for the iron content that remains in the pulp after hydrogen

peroxide bleaching. The iron content of the pulp prior to bleaching had the strongest impact, as expected (Fig 3). The second most influential factor was the sodium hydroxide charge. The third factor, heating temperature, was statistically insignificant as the confidence interval included zero. This means that the iron content that remains in the pulp after hydrogen peroxide bleaching was independent of the heat treatment temperature in the interval 110–170°C.

The alkali charge had the strongest impact on the hydrogen peroxide consumption followed by the iron content of the pulp prior to bleaching. Treatment with heat had the lowest impact on the hydrogen peroxide consumption and was barely significant.

Hydrogen peroxide bleaching of the SGW pulp revealed that the highest brightness and lowest light absorption coefficient was obtained at an alkali charge of 2.7% irrespective of the iron content of the pulp or the heating temperature prior to bleaching in the interval examined (Table 4, Appendix).

The heat-treated (110, 140 or 170°C) SGW pulps with an iron content of 25 mg/kg prior to bleaching had, after bleaching, a light absorption coefficient similar to the corresponding heat-treated reference SGW pulps (cf. Fig 4, Table 2). The approximately one unit increase in  $k$ -value (Fig 2) for the unbleached heat-treated pulps with an iron content of 25 mg/kg was eliminated after bleaching (Fig 4). Hydrogen peroxide bleaching could not restore the brightness at higher amounts of strongly bound iron in the pulps (Table 4, Appendix).



110°C, Ref 140°C, Ref 170°C) and heat- and iron-treated alkali optimised hydrogen peroxide bleached Norway spruce SGW pulps as a function of the iron content of the pulps prior to bleaching. Bleaching conditions: 4.5%  $H_2O_2$ , 2.7% NaOH, 2.9% Silicate, 70°C, 120 minutes and 30% pulp consistency. Measured (reference pulps) and predicted values. The 95% confidence interval is given as error bars.

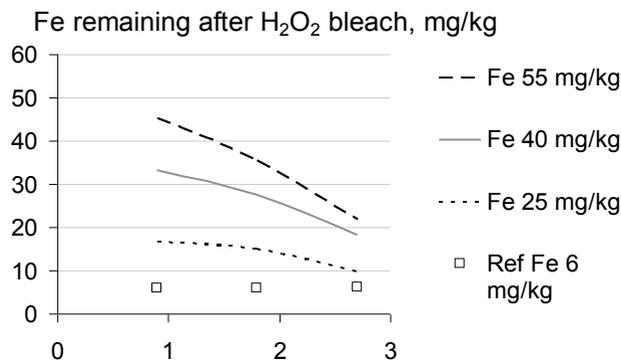


Fig 5. Iron remaining in the Norway spruce SGW pulp after hydrogen peroxide bleaching of untreated and heat-treated (one minute at 110°C) Norway spruce SGW pulps containing various amounts of strongly bound iron as a function of alkali (NaOH) charge. The reference pulp (Ref) was not heat-treated and no Fe was added. Bleaching conditions: 4.5% H<sub>2</sub>O<sub>2</sub>, 2.9% Silicate, 70°C, 120 minutes and 30% pulp consistency. Measured (Ref) and predicted values. See also Table 4 in Appendix.

It was noted that the iron content in the pulp was lowered after hydrogen peroxide bleaching and that the decrease was more pronounced at higher alkali charges. The hydrogen peroxide action on the insoluble iron might be the reason why it solubilizes and gets removed. It was reported by Colodette et al. (1988) that the catalytic activities of iron were greatly enhanced at pH values above 10.8. In Fig 5, bleaching of the 110°C heat-treated SGW pulp is shown. As discussed above, the heating temperature was statistically insignificant and consequently similar trends were found for the pulps heat-treated at 140 or 170°C (see Table 4, Appendix). As can be seen in Fig 5 the iron content was reduced from 25 mg/kg to approximately the initial iron level (6 mg/kg) after bleaching and the *k*-value was recovered (Fig 4). Hydrogen peroxide bleaching did not reduce the iron content to the same extent at higher iron levels in the interval tested, which resulted in higher *k*-values after bleaching (cf. Figs 4 and 5). The reduction in iron content was, however, still extensive with a reduction degree of about 50-60%.

The hydrogen peroxide consumption was to some extent lower at a treatment temperature of 140 or 170°C, although the differences were small (cf. Fig 3). In Fig 6, the hydrogen peroxide consumption is shown for the untreated reference pulp (Ref) and the lowest treatment temperature (110°C) with various iron contents as a function of alkali charge. Increased iron content in the pulp increased the hydrogen peroxide consumption, probably due to iron-induced hydrogen peroxide decomposition (cf.

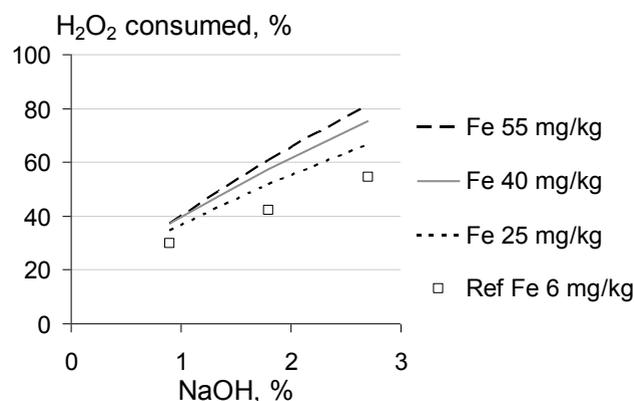


Fig 6. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) consumption of untreated (Ref) and heat-treated (one minute at 110°C) Norway spruce SGW pulps containing various amounts of strongly bound iron as a function of alkali (NaOH) charge. Bleaching conditions: 4.5% H<sub>2</sub>O<sub>2</sub>, 2.9% Silicate, 70°C, 120 minutes and 30% pulp consistency. Measured (Ref) and predicted values. See also Table 4 in Appendix.

Colodette et al. 1988; Lin, Gurol 1998). This was especially pronounced at high alkali charges. The hydrogen peroxide consumption was about 80% at an iron content of 55 mg/kg while the reference pulp consumed 55% at an alkali charge of 2.7% (Fig 6 and Table 2).

High temperature during fibre separation and development, as in a thermomechanical pulping process, will introduce chromophoric material that results in a lower unbleached brightness compared to a groundwood pulp. An increased iron content of the pulp will further lower the brightness. It is known that a higher initial unbleached brightness often results in higher bleached brightness under similar bleaching conditions (Kouk et al 1989). Conventional groundwood (SGW) pulps as well as pressurised groundwood (PGW) pulps typically have both a higher unbleached brightness and responds better to hydrogen peroxide bleaching than thermomechanical pulps (Presley, Hill 1996). The chromophores generated by the thermal pre-treatment could only partly be removed by hydrogen peroxide bleaching resulting in a reduced brightness ceiling. Hydrogen peroxide bleaching was found to reduce the iron content of the pulps and thus regain some of the brightness that was lost, this effect was most pronounced at the higher alkali charge levels. It is thus important to minimise the unit process stage temperatures, residence times and the iron content of the pulp in order to improve the unbleached brightness and bleachability of mechanical pulps.

## Conclusions

The heat induced increase in chromophore content in Norway spruce (*Picea abies*) stone groundwood (SGW) pulp was small at temperatures of up to 140°C when heat treatment was performed for one minute. Heat treatment at 170°C was, however, detrimental and the brightness loss was about 3.5 %ISO after heating for one minute. The light scattering coefficient of the pulp was essentially unaffected by heat treatment. The brightness reduction at 170°C could only partly be regained during high consistency hydrogen peroxide bleaching. At a hydrogen peroxide charge of 4.5%, the stone groundwood pulp displayed a brightness of 82.3% ISO whereas the heat-treated (170°C) pulp reached a brightness of 79.7% ISO.

The chromophore content of the spruce SGW pulp increased when the amount of strongly bound iron in the pulp increased. Hydrogen peroxide bleaching was found to reduce the iron content of the pulps and thus regain some of the brightness that was lost, this effect was most pronounced at the higher alkali charge levels. The chromophores generated due to heat treatment (110, 140 or 170°C) with an iron content of 25 mg/kg, was eliminated after bleaching. The light absorption coefficient was similar to the corresponding heat-treated reference SGW pulps. The bleachability (measured as a reduction in the light absorption coefficient) of the SGW pulp was, however, reduced when the iron content of the pulp increased. Increased iron content in the pulp increased the hydrogen peroxide consumption especially at high alkali charges.

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## APPENDIX

Table 4. The predicted (MODDE 5.0) optical properties, consumed hydrogen peroxide and iron content remaining after hydrogen peroxide bleaching of Norway spruce SGW pulps.

Heating temperature <sup>1</sup> °C	Fe content <sup>2</sup> mg/kg	NaOH %	Brightness <sup>3</sup> % ISO	$S_{457nm}$ m <sup>2</sup> /kg	$k_{457nm}$ m <sup>2</sup> /kg	H <sub>2</sub> O <sub>2</sub> consumption %	Fe remaining <sup>4</sup> mg/kg
110	25	0.9	79.0	68	1.9	35	17
110	25	1.8	81.4	66	1.4	52	15
110	25	2.7	82.1	61	1.2	67	10
110	40	0.9	78.3	68	2.1	37	33
110	40	1.8	80.6	66	1.5	57	28
110	40	2.7	81.2	62	1.4	75	18
110	55	0.9	77.8	68	2.2	37	45
110	55	1.8	80.1	66	1.6	61	35
110	55	2.7	80.6	62	1.5	81	22
140	25	0.9	78.4	69	2.1	34	12
140	25	1.8	81.0	66	1.5	51	11
140	25	2.7	81.9	62	1.2	65	7
140	40	0.9	77.7	69	2.2	36	29
140	40	1.8	80.2	66	1.6	56	24
140	40	2.7	81.0	63	1.4	74	15
140	55	0.9	77.2	68	2.3	37	41
140	55	1.8	79.7	66	1.7	59	32
140	55	2.7	80.4	63	1.5	80	19
170	25	0.9	76.2	68	2.5	32	17
170	25	1.8	79.0	66	1.9	48	17
170	25	2.7	80.0	62	1.6	62	13
170	40	0.9	75.5	68	2.7	34	34
170	40	1.8	78.2	66	2.0	54	29
170	40	2.7	79.1	63	1.7	71	21
170	55	0.9	75.0	68	2.8	34	46
170	55	1.8	77.6	66	2.1	57	37
170	55	2.7	78.5	63	1.8	77	25

<sup>1</sup>Heating time: one minute.

<sup>2</sup>Iron content of the pulp prior to hydrogen peroxide bleaching.

<sup>3</sup>Brightness determined on laboratory sheets (65 g/m<sup>2</sup>) according to ISO standard method 2470.

<sup>4</sup>Iron content of the pulp after hydrogen peroxide bleaching.