Low dosage sulfite pretreatment in a modern TMP-line

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KEYWORDS: Chip pretreatment, double disc refining, energy reduction, Impressafiner, low dosage, Norway spruce, mill scale, pulp properties, sulfite, TMP

SUMMARY: The effects of low dosage sulfite pretreatment combined with modern high consistency double disc refining were evaluated for production of thermomechanical pulp in a mill scale trial using Norway spruce wood at the Braviken paper mill (Holmen Paper AB, Sweden). Spruce wood chips were mechanically pretreated in an Impressafiner before impregnation with different dosages (0-1.2%) of sodium sulfite (Na_2SO_3) at pH 9. Approximately 23% of the added sulfite was converted to sulfonate groups in pulp, resulting in a sulfonate content of 0-0.28% (as Na_2SO_3).

The low dosage sulfite addition increased tensile index, elongation, density, brightness and decreased shive content, light scattering and light absorption coefficients when compared at equal specific energy consumption (SEC). The increase in tensile index was proportional to dosage of sulfite.

Further analyses showed that low dosage sulfite addition did not affect the distribution of the Bauer-McNett fractions nor the fibre length for pulps refined with equal SEC. However, the low dosage sulfite addition increased fibre delamination/internal fibrillation (D/IF).

With the addition of 1.2% Na_2SO_3, it was possible to produce pulp with a tensile index of 47 Nm/g using ~320 kWh/bdt (~15%) lower refining energy, compared with pulps produced without sulfite addition.

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In the production of newsprint and improved newsprint grade papers it is desirable to reach high opacity at sufficient paper strength. For this purpose, the thermomechanical pulp (TMP) process provides pulp with a suitable combination of light scattering and strength (Höglund, Wilhelmsson 1993). However, the use of electrical energy in this process is high. In this study we investigated the possibility to reduce the specific energy consumption (SEC) in a modern TMP-line by increased wood softening through the use of low dosage sulfite pretreatment.

Wood softening is related to the transition of lignin from a brittle glass-like to an elastic rubber-like form. This transition occurs as the temperature is increased but is also dependent on loading frequency (Becker et al. 1977). The temperature interval for glass transition has been calculated to lie between 100 to 170°C at the frequency of a commercial refiner (10 kHz) (Irvine 1985). Refining at temperatures below the glass transition range will lead to fractures both parallel and transverse to the fibre direction, resulting in reduced fibre length. As the temperature is increased, fractures parallel to the fibre direction will be favored. A further increase in temperature towards the higher end of the glass transition phase will promote fractures to occur predominantly in the compound middle lamella region resulting in lignin capsulated fibres (Irvine 1985; Lai, Iwamida 1993; Johansson et al. 1997).

Wood softening can also be affected by sulfonation of lignin. The deprotonated form of the sulfonic acid will be highly hydrated in the wet state which will increase the mobility of lignin molecules. In the sulfur content range 0.3 to 3.0% (as Na_2SO_3), sulfonation decreased the softening temperature of black eastern spruce by about 2°C for every 0.1% increase in sulfur content (as Na_2SO_3) (Atack et al. 1978).

Low dosage sulfonation (i.e. sulfite pretreatment to a sulfonate content <0.5% as Na_2SO_3) prior to refining has been shown to affect pulp properties differently compared to the effects seen in the dosage range of the chemithermomechanical pulp (CTMP) process. Axelson and Simonson (1982a) found a maximum for both tensile index and light scattering at a sulfur content of 0.2% (as Na_2SO_3) when compared at certain SEC. Similar results regarding the maximum in tensile index have later been reproduced several times (Axelson, Simonson 1982b, 1983a, 1983b; Westermark et al. 1987; Svensson et al. 1994).

The maximum for both tensile index and light scattering at a sulfur content of 0.2% (as Na_2SO_3) may be explained by the selective sulfonation of the primary cell wall for low sulfite dosages (Westermark et al. 1987). Low dosage sulfonation also affects the softening temperature of the middle lamella- and primary cell wall layers differently. The softening temperature of the middle lamella is decreased by sulfonation while the softening temperature of the primary cell wall layer is increased from a value below that of the middle lamella (Östberg, Salmén 1988). Östberg and Salmén (1988) suggested that the higher protein content of the primary cell wall may explain the different effect on the primary cell wall and middle lamella layers.

By comparing the microscopic appearance of fibre-fibre fractures for wood with different sulfur contents, it was possible to relate the maximum in tensile index at a sulfur content of 0.2% (as Na_2SO_3) to fibre surfaces where the middle lamella was almost completely removed. These surfaces also had very thin, thread-like fragments which were not present at higher sulfonation levels (Westermark et al. 1987; Johansson et al. 1997).

To our knowledge, there is only one prior study of low dosage sulfonation in mill scale (Axelson, Simonson 1983b), with some additional information presented by Axelson (1984). In that mill scale study, tensile index was increased from 23 to 28 Nm/g at 1700 kWh/bdt when chips were impregnated with cold sulfite liquid to a sulfonate content of 0.2% (as Na_2SO_3). The study was performed at the Göta mill in a two stage single disc TMP-line where chips were preheated at 126°C for 3 min and thereafter refined with a pressurized first stage and an atmospheric second stage. Pulps with different energy input were produced by changing the refining energy in the second stage while the refining conditions in the first stage were kept constant.

The design of a modern TMP-line has some important differences compared to the TMP-line in Göta mill. In today's designs, chips are usually only preheated under pressurized conditions for a few seconds prior to refining and the first stage refining is normally performed at higher temperature and intensity. This type of design is found both in Valmet's double disc lines and in Andritz's RTS lines, which are two of the most frequently installed TMP-processes for printing grade paper since the end of the nineties. It is therefore of great interest to also evaluate the effect of low dosage sulfite pretreatment in a modern TMP-line. One question is how the different preheating conditions in a modern TMP-line affect the degree of sulfonation. Another question is whether low dosage sulfonation show a similar effect on pulp properties when refined in one stage at higher temperature and intensity.

The present study is part of a series of studies aimed at demonstrating reduced energy consumption in mechanical pulping by combining chip pretreatment and increased refining intensity. An earlier study in this series described the effect of pure mechanical pretreatment in the same TMP-line (Nelsson et al. 2012). This part is focused on wood softening using low dosage sulfonation.

Materials and Methods

A full scale trial was conducted in the double disc TMP line (production rate 720 bone dry metric ton per day (bdt/d)) at the Braviken mill (Holmen Paper AB, Norrköping, Sweden), outlined in, *Fig 1*. The raw material used was a mixture of round wood and saw mill chips from Norway spruce (*Picea abies* (L.) Karst.).

Chips were fed from a conventional chip washer to a steaming bin (90°C, ~15 min) and then through a rotary valve to a pressurized RT-conveyor (1.8 bar(g), 3 to 10 s). Thereafter chips were compressed in an Impressafiner MSD 500 (Andritz) with a compression ratio of 2.7:1 and SEC of 18 kWh/bdt.

Directly after compression, chips were submerged in the impregnation liquid where different dosages of Na_2SO_3 were added. Fresh water (1.3 m^3/bdt) was used for the impregnation and sulfite was added by mixing concentrated solutions of $NaHSO_3$ (sodium bisulfite, 37.5%, Brenntag Nordic AB, Malmö, Sweden) and NaOH (sodium hydroxide, 45%, Brenntag Nordic AB, Malmö, Sweden) into the continuous flow of the impregnation liquid.

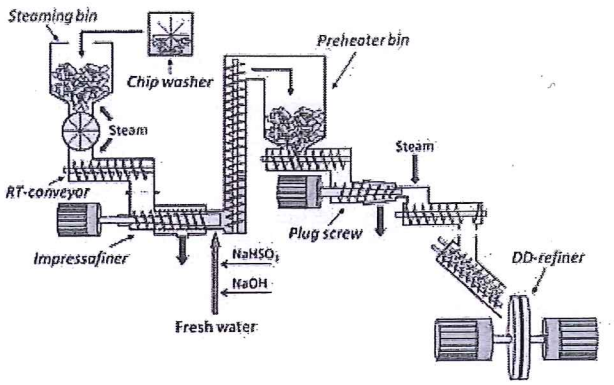

Fig 1 - Process overview.

The impregnation solution was passed through a static mixer after which the pH was measured. The solution was then absorbed by the chips in the impregnator. Addition of $NaHSO_3$ was calculated using the Impressafiner production rate to render additions of 0, 1, 2, 5 and 10 kg $NaHSO_3$/bdt of wood chips. Addition of NaOH was adjusted to render an impregnation solution of pH 9. This gave sodium sulfite dosages of 0, 0.12, 0.24, 0.61 and 1.2% as percent Na_2SO_3 on oven dried basis of wood chips, which corresponds to sulfite dosages of 0, 9.5, 19, 48 and 95 mmol/kg wood and at the liquor to wood ratio of about 2:1 (33% consistency) sulfite concentrations of 0, 4.8, 9.5, 24 and 48 mmol/l.

After impregnation, the temperature of the chips was 62°C. The chips were retained in an atmospheric preheater bin (no steam added) for ~8 min and thereafter fed through a plug screw to the pressurized refiner feeding system where they were preheated at 4.5 bar(g) (~155°C) for ~8 seconds prior to refining.

Pulps were sampled from one of three parallel DD refiners (RGP68DD, Valmet). The 72" refiner discs were counter rotating at 2x1500 rpm, including p-(DN72N816-817) and c-segments (DO52B036-037). The refiner production rate was calculated from flow and consistency measurements after the individual stand pipe following each refiner. The production rate over the refiner was 8.6 bdt/h and the blow line consistency after refining 30-32%. The refining energy was changed by adjusting the hydraulic pressure acting on the refiner discs. The hydraulic pressure was in turn controlled by the disc gap measurement. The disc gap distance control system was set at a certain distance before start of sampling. Pulp samples were collected from the blow line directly after the double disc refiner for different refining energy consumptions (~1750-2100 kWh/bdt) and dosage of Na_2SO_3 (0, 0.12, 0.24, 0.61 and 1.2%). SEC is presented as "total SEC" which is the sum of the specific energy consumption in the pretreatment and refining.

Five pulp samples were collected during a period of 12 min for each chemical dose and refining energy. The samples were mixed and analysed three times with the following methods: Hot disintegration (ISO 5263-3), fibre length and shives (PulpEye AB), Canadian standard freeness (ISO 5267-2), Rapid Köthen lab sheet (ISO 5269-2, DIN 54358), density (ISO 534), tensile index and elongation (ISO 1924-2), tear index (ISO 1974), specific light scattering coefficient and light absorption

coefficient at an effective wavelength of 557 nm (ISO 9416) and brightness (ISO 2470).

Six pulps were chosen for additional analyses including total sulfur content of unwashed pulp (SCAN-CM 57:99), fibre charge of whole pulp (SCAN-CM 65), Bauer McNett fractionation (SCAN-CM 6:05) and internal fibre development according to Fernando and Daniel's (2010) method of Simons' staining. The pH was also measured for these pulps by the following method: 12 g high consistency pulp (~30% dry content) was diluted with 60 ml deionised water. The sample was dewatered in a Büchner funnel after 15 min and the pH measured on the eluate.

The sulfonate content of pulps was measured in two later repetitions of the trial. Two different types of sulfonate contents were determined: 1) Sulfonate content directly after sampling: 200 g of the pulp was immediately submerged in 10 l of cold water after collection from the blow line in order to stop further sulfonation. Afterwards, the pulps were dewatered and dried; 2) Sulfonate content of pulps for lab sheets: Pulps were not cooled after sample collection. After hot disintegration, pulps were dewatered and dried. The sulfonate content was measured by SCAN-CM 57:99 for both 1) and 2). To describe how much of the added sodium sulfite that formed sulfonate groups in the pulp we calculated a conversion ratio. This was calculated by dividing the amount of formed sulfonate groups with the amount of added sodium sulfite in moles per weight unit of dry wood chips or pulp. The conversion ratio for 2) was used to calculate the sulfonate content of the pulps produced in this study.

Results and discussion

Low dosage sodium sulfite pretreatment was applied in a modern mill scale TMP-line using an Impressafiner to impregnate chips with sulfite. Pulps were produced in a high intensity double disc refiner where pulps were refined to low freeness (60–190 ml) in one stage.

Approximately 49% of the sulfur added as sodium sulfite in the impregnator was present in the pulp after refining, *Fig 2*. The other 51% was removed in the plug screw feeding the pressurised refiner. The dry content of chips was increased from approximately 33 to 50% in the plug screw, removing about 50% of the impregnation liquor. Some sulfur was also present in pulps (0.07% as Na_2SO_3) even when no sulfite was added. This sulfur originates from sulfur containing compounds in the refiner dilution water.

From added sulfite, about 18% was converted to sulfonate groups in the pulp, when measured on pulps that were cooled directly after sample collection, *Fig 2*. Due to the high temperatures in subsequent process stages after refining, the conversion ratio will increase a few percentage points. Therefore, it is more relevant to look at the conversion ratio of 23%, which was measured for pulps used to produce lab sheets, *Fig 2*. These pulps were allowed to cool at room temperature after refining, which caused post sulfonation of pulps.

Using a conversion ratio of 23% also enables comparison with earlier studies of low dosage sulfonation

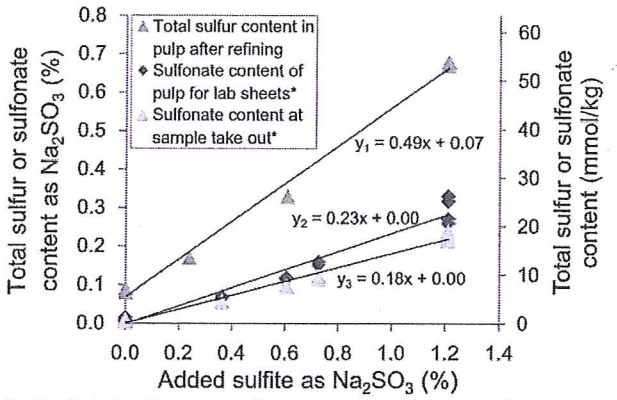

Fig 2 - Total sulfur and sulfonate content in pulps after refining vs. added sodium sulfite. From added sulfur, 49% was present in pulp after refining (y_1), 18% was present as sulfonate content in the pulp when collected from the blow line (y_3) and 23% was present as sulfonate content in pulps prepared for lab sheets (y_2). *The sulfonate contents were measured for two repetitions of the trial (see Materials and Methods section).

since pulps were handled in a similar manner in these studies (Axelson, Simonson 1982b, 1983a, 1983b; Svensson et al. 1994).

Our conversion ratio of 23% is rather low compared to the conversion ratio range of 60-95% reported by Axelson and Simonson (1983b) for the trial at the Göta mill. The difference can be attributed to the removal of ~50% of the impregnation liquor in the plug screw. Axelson and Simonson (1983b) disregarded this type of loss when calculating their conversion ratio. Furthermore, the lower conversion ratio can also be attributed to the much shorter preheating time in the modern TMP-line in our study.

Compared to the amount of sulfite available after the plug screw (~49%) the conversion ratio was about 47%. Even though the conversion ratio was low it was still possible to reach a sulfonate content of ~0.28% as Na_2SO_3 (22 mmol/kg) for the highest sulfite addition (1.2%), *Fig 2*. This sulfonate content lies within the range where Axelson and Simonson (1983b) found a maximum for tensile index in mill scale.

Engstrand et al. (1985) performed studies concerning the effects of sulfite concentration and temperature on the kinetics of wood sulfonation reactions at pH 9. The studies were performed under ideal conditions using wood meal and very high liquor to wood ratio. Engstrand et al. (1985) showed that a sulfite concentration of 20 mmol/l would give a sulfonate content in wood after 15 min of about 0.19% as Na_2SO_3 (15 mmol/kg) at 70°C and about 0.40% as Na_2SO_3 (32 mmol/kg) at 130°C.

A sulfite concentration of 20 mmol/l equals an addition of 0.50% as Na_2SO_3 (40 mmol/kg) in our study since we had a liquor to wood ratio of 2:1 at the chemical addition point. Given the results presented by Engstrand et al. (1985) for ideal conditions, the maximum conversion ratio after 15 min would be 38% at 70°C and 80% at 130°C. The lower conversion ratio in our study can be explained by the different reaction conditions, i.e. ~50% of the liquor was removed after 8 minutes at 62°C; the use of wood chips instead of wood meal caused longer diffusion distances; the lower liquor to wood ratio led to a

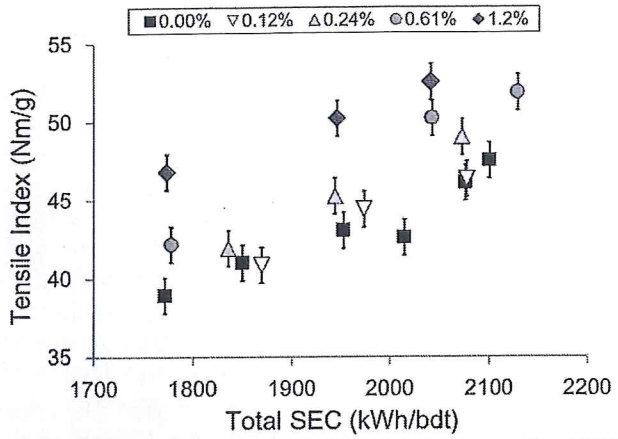

Fig 3 - Tensile index vs. total specific energy consumption (SEC) for pulps pretreated with different amounts of sodium sulfite (shown in legend).

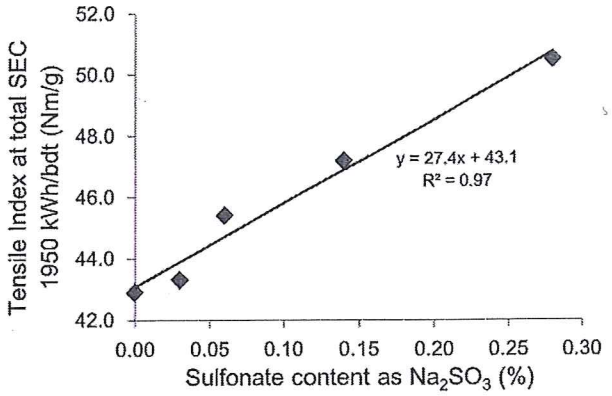

Fig 4 - Tensile index vs. sulfonate content at a constant total SEC of 1950 kWh/bdt.

reduction in sulfite concentration of the liquor as sulfonation of wood occurred.

Ferritsius and Moldenius (1985) studied the effect of different chip impregnation techniques on the degree of sulfonation for sodium sulfite additions in the range of 0.6-2.7%. They found that even with preheating of wood chips for 3 min at 125°C after the sulfite addition it was not possible to reach a conversion ratio higher than 25%. This conversion ratio also included the post sulfonation of pulp after refining. For an addition of 0.6% Na_2SO_3 they reached a sulfonate content of about 11 mmol/kg which is very similar to our result when post sulfonation is included, *Fig 2*.

The most apparent effect of sulfite pretreatment was an increase in tensile index when the pulps were compared at similar SEC, *Fig 3*. The increase in tensile index was proportional to the amount of sodium sulfite added and was 7.6 Nm/g (~18%) for the highest dosage (1.2% Na_2SO_3), *Fig 4*.

In *Table 1*, pulp properties for different sulfite additions are interpolated to a total SEC of 1950 kWh/bdt. The most prominent effects of sulfite addition were increases in tensile index, elongation and density along with decreases in freeness, shives content and light absorption. The reduction in light absorption led to an increase in brightness. The sulfite addition also slightly reduced light scattering. Fibre length and tear index was not affected by addition of sulfite when compared at similar SEC, *Table 1*.

The increase in tensile index in relation to the sulfonate content of pulp found in this study is comparable to the effects seen in other studies of low dose sulfonation (Axelson, Simonson 1982a, 1982b, 1983a, 1983b; Westermark et al. 1987; Svensson et al. 1994). The highest sulfonate content reached in our study was 0.28% (as Na_2SO_3). This is close to the sulfonate content of ~0.2% (as Na_2SO_3), where the maxima in tensile index were reported earlier (Axelson, Simonson 1982a, 1982b, 1983a, 1983b; Westermark et al. 1987; Svensson et al. 1994). The linear trend shown in *Fig 4* may therefore be consistent with the earlier studies showing a maximum at a sulfonate content of approximately 0.2% (as Na_2SO_3).

Table 1 - Refining conditions and pulp properties for different dosages of Na_2SO_3 interpolated to total SEC 1950 kWh/bdt. The two bottom rows show total SEC and light scattering coefficient at tensile index 47 Nm/g.

Na_2SO_3 added (%)	0.00	0.12	0.24	0.61	1.2
Total SEC (kWh/bdt)	1950	1950	1950	1950	1950
Hydraulic force (t)	58.4	57.4	58.9	57.4	56.5
Disc gap (mm)	0.77	0.77	0.75	0.74	0.71
Sulfonate content[a]	0.00	0.03	0.06	0.14	0.28
Sulfonate content[b]	0	2	4	11	22
Fibre length (mm)	0.94	0.94	0.92	0.92	0.92
CSF (mL)	136	134	122	127	116
Shives (sum/g)	400	400	370	330	270
Density (kg/m³)	461	465	469	477	490
Tensile index (Nm/g)	42.9	43.3	45.4	47.2	50.5
Tear index (Nm²/kg)	7.0	7.0	7.0	7.0	7.0
Elongation (%)	1.9	1.9	2.0	2.1	2.1
Light scattering[c] (m²/kg)	60.1	59.2	60.6	59.2	58.5
Light absorption[c] (m²/kg)	1.72	1.59	1.54	1.45	1.37
Brightness (% ISO)	64.3	64.7	65.5	66.1	66.7
Total SEC at tensile index 47 Nm/g (kWh/bdt)	2110	2090	2000	1950	1790
Light scattering[c] at tensile index 47 Nm/g (m²/kg)	64.3	63.2	62.4	59.0	55.0

[a]Sulfonate content as Na_2SO_3 (%), calculated values based on measurements from two repetitions of the trial. [b]Sulfonate content as mmol/kg. [c]Specific coefficient at 557 nm.

The studies of Axelson and Simonson (1982a) and Svensson et al. (1994) reported results where the light scattering coefficient was increased at sulfonate contents below 0.2%, when compared to unsulfonated pulp at certain SEC. Such an increase in light scattering coefficient was not seen in our study. Reasons for this may be the differences between our study and the two studies outlined above; i.e. mill vs. pilot scale, 8 s vs. 3 min preheating time, one vs. two stage refining.

The effect of low dosage sulfonation on pulp properties differs from the effect seen for the higher degree of sulfonation used for production of chemithermo-mechanical pulp (CTMP), earlier described by e.g. Atack

et al. (1978). Therefore we have chosen not to compare the results in our study with studies regarding sulfonation in typical CTMP-processes for softwoods where 2-4% Na_2SO_3 is normally used and where the sulfite is allowed to react a few minutes at 130-150°C before chip-refining.

In the bottom of *Table 1*, refining energy and light scattering coefficient at a tensile index of 47 Nm/g are shown for the different additions of sulfite. For the highest sulfite dosage, total SEC was reduced by ~320 kWh/bdt (i.e. ~15%) when compared to pulp with equal tensile index produced without sulfite addition. However, the reduction in energy consumption achieved led to a reduction in light scattering when compared at certain tensile index, *Table 1*.

When studying effects of chip pretreatment it is also important to consider refining parameters to understand the full effect of the pretreatment. *Table 1*, shows that a reduction in disc gap was needed when sulfite was added in order to maintain the SEC. However, it was not required to increase the hydraulic force acting on the discs to reduce the disc gap. Assuming the addition of sulfite did not affect the distribution of pulp in the disc gap, the decrease in disc gap should reflect increased wood softening due to the sulfonation of lignin.

Miles and Omholt (2008) showed that the stress/strain relationship (which is affected by wood softening) of the refined material is one of the factors affecting the disc gap. Measurements on sulfonated white spruce wood blocks have further shown that both the stress plateau and toughness are reduced linearly with sulfonation (Mao et al. 2004). It has also been shown that sulfonation (1.6% as Na_2SO_3) of eastern black spruce wood blocks slightly reduces the storage modulus in the glass transition phase for loadings in the transverse direction (Heitner, Salmén 1994). The storage modulus describes the elastic behavior of a viscoelastic material. Although it is difficult to relate such measurements performed on wood blocks at low frequencies to the conditions in a mill scale refiner where wood is divided into individual fibres and where the frequency is much higher, the changes in the compression behavior of wood caused by sulfonation may explain the decrease in disc gap. Furthermore, in a recent study by Engberg et al. (2014) it was shown that low dosage sulfonation at pH 9 also resulted in wood softening when measured at strain rates relevant for refining by using a Split-Hopkinson device.

A reduction in disc gap due to wood softening should have led to an increase in the maximum strain of the wood material during the load cycles in the refiner, especially since other refining parameters remained unchanged. It seems reasonable therefore that this may have had an effect on the development of pulp properties during refining.

Table 2 shows properties of six individual pulps produced with different dosages of sulfite and SEC. Addition of 1.2% Na_2SO_3 at pH 9 increased the pulp pH from ~5.7 to ~7.1 after refining. The fibre charge was increased by 25-40 mmol/kg by the addition of 1.2% Na_2SO_3. A sulfonate content of 0.28% as Na_2SO_3 is equal to 22 mmol/kg and partly explains the increase in fibre charge. The further increase in fibre charge could possibly be explained by another effect of the sulfite pretreatment where demethylation of pectin leads to formation of carboxylic acids (Konn et al. 2007).

Distribution of the Bauer-McNett fractions was not affected by addition of sulfite, *Fig 5*. The most prominent effect was a decrease in the >12 fraction as the refining energy was increased. Likewise, the >16 fractions were decreased and the <30 fractions were increased when the refining energy was increased. The proportion of the 16-30 fractions did not change in response to neither increased refining energy nor degree of sulfonation.

Fernando and Daniel's (2010) method of Simons' staining of the 16-30 fraction was used to assess and statistically analyze the degree of delamination/internal fibrillation (hereafter denoted D/IF) of fibres in the pulps, *Fig 6*. The degree of D/IF is correlated with the flexibility and collapsibility of fibres. To increase the strength of printing grade papers, fibres with high D/IF are preferable since these fibres will increase the bonding area within the sheet and therefore produce a stronger paper (Paavilainen 1993, Stone et al. 1968).

Both sulfite pretreatment and an increase in SEC resulted in an effective increase in D/IF. For example, the pulp with the highest sulfite dosage in combination with

Table 2 - Pulp properties for different refining energies and dosage of Na_2SO_3.

Energy level	Low	Low	High	High	High	High
Total SEC (kWh/bdt)	1780	1780	2080	2080	2040	2040
Na_2SO_3 added (%)	0.00	1.2	0.00	0.24	0.61	1.2
Total sulfur[a]	0.08	0.67	0.09	0.17	0.33	0.68
Sulfonate content[b]	0.00	0.28	0.00	0.06	0.14	0.28
Sulfonate content[c]	0	22	0	4	11	22
Pulp pH	5.7	7.0	5.8	6.0	6.3	7.2
Fibre charge[d]	70	110	71	80	95	96
Fibre length (mm)	1.00	0.99	0.88	0.86	0.91	0.88
Tensile index (Nm/g)	38.9	46.8	46.1	49.0	50.2	52.5
Light scattering[e]	56.7	54.8	64.1	64.6	59.7	60.5

[a)]Total sulfur content in pulp after refining as Na_2SO_3 (%). [b)]Sulfonate content as Na_2SO_3 (%), calculated values based on measurements from two later repetitions of the trial. [c)]Sulfonate content as mmol/kg. [d)]Fibre charge in whole pulp (mmol/kg). [e)]Coefficient at 557 nm (m^2/kg).

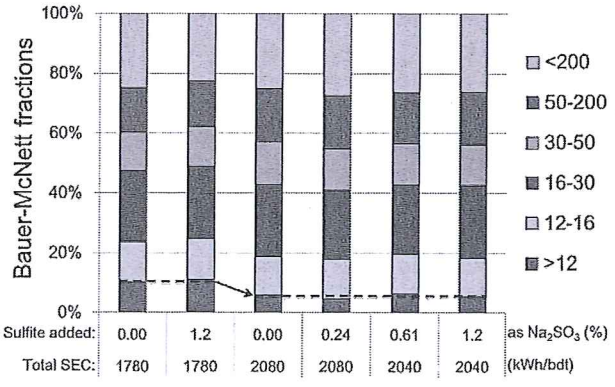

Fig 5 - Bauer-McNett fractions for pulps with different sulfite addition and total SEC.

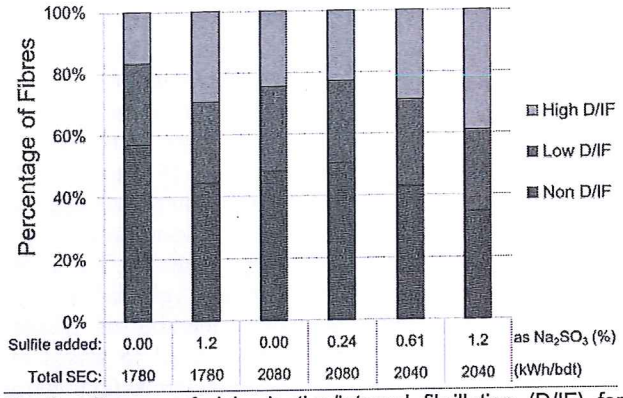

Fig 6 - Degree of delamination/internal fibrillation (D/IF) for pulps with different sulfite addition and total SEC. Two hundred fibres were analysed for each pulp.

highest energy input (i.e. 1.2(2040)), was dominated by fibres with low and high D/IF (~65%), of which the majority were "high D/IF" fibres (~39%), *Fig 6*. Here, the pulp name denoted with a number outside the bracket represents sulfite dosage and the number within bracket the SEC.

To evaluate the statistical significance of the difference in D/IF for the pulps, we used an ordinal logistic regression test (according to Fernando, Daniel 2010). The test showed that both increasing SEC and sulfite addition had very high significant influence on enhancing fibre wall D/IF (P values 0.0039 and 0.0033 respectively). The significant effect on D/IF by increasing SEC is consistent with previous studies (Fernando et al. 2011, 2013).

Further evidence for the significant effects described above was provided when the D/IF results were analysed pairwise. A significant difference can be seen between two pulps with similar SEC but increasing sulfite dosage (0.00(1780) vs 1.2(1780); P=0.0032 and 0.00(2080) vs 1.2(2040); P=0.0005). Likewise, there is also a significant difference between two pulps with similar sulfite dosage but with increasing SEC (0.00(1780) vs 0.00(2080); P=0.0351 and 1.2(1780) vs 1.2(2040); P=0.0111). Interestingly, the Simons' staining method revealed that the fibre populations of the two pulps 0.00(2080) and 1.2(1780) were more or less similar with respect of internal fibre development (P=0.3647). This shows that a low dosage sulfite pretreatment (1.2% as Na_2SO_3) can be used to produce pulp with similar degree of D/IF compared to pulp produced without sulfite pretreatment but with 300 kWh/bdt higher energy input.

Simons' staining measures accessibility of the interior surfaces in fibre cell walls through selective staining of fibres containing pores larger than 5 nm (Yu et al. 1995). This type of internal fibre development (i.e. wall D/IF) has earlier been shown to correlate positively with the whole pulp tensile index and density (Stone et al. 1968; Fernando et al. 2011; 2013). Stone et al. (1968) suggested that this correlation was a result of increased flexibility and collapsibility for fibres with increased D/IF. Fibre flexibility and collapsibility depend on fibre dimensions (fibre cell wall thickness and width) and elasticity (Young's modulus) of the fibre cell wall (Claudio-da-Silva 1983; Paavilainen 1993). An increase in the amount of pores larger than 5 nm in the fibre cell wall (as measured by Simons' staining) should correlate with a decrease in the elasticity of the fibre cell wall and thereby with increasing flexibility and collapsibility of the fibre.

In a study by Muhić et al. (2010), performed on the same TMP-line as our study, it was shown that increased refining temperature led to a reduction in the disc gap and an increase in tensile index of pulps at certain SEC. One explanation for the reduction in disc gap could be an increased wood softening due to the higher refining temperature. Fernando et al. (2011) studied the same pulps as Muhić et al. (2010) and found the increase in tensile index resulting from the higher refining temperature correlated well with an increase in D/IF of the fibres.

We therefore propose that the increase in D/IF when sulfite was added in our study could have been a result of wood softening which led to a reduction disc gap. The link between the reduction in disc gap and the increase in D/IF may be the increase in maximum strain of the wood material in the refiner when the disc gap was reduced, as described above.

The increase in tensile index as a result of low dosage sulfite pretreatment in our study may be explained by a number of different effects. One explanation may be the effect of low dosage sulfonation on fibre separation mechanism as described by Westermark et al. (1987) and Johansson et al. (1997). This type of fibre separation may have increased the external fibrillation of fibres.

Another explanation may be the increase in fibre charge (Zhang et al. 1994). However, based on measurements by Zhang et al. (1994), the increase in fibre charge seen in our study would only explain a minor part of the increase in tensile index.

A third explanation to the increase in tensile index concerns the increase in D/IF, which implies more flexible fibres. An increase in fibre flexibility will increase the proportion of bonded area in relation to total area inside the sheet and therefore increase the tensile index (Paavilainen 1993, Stone et al. 1968). We suggest that the increase in D/IF is an important factor for increasing the tensile index of the low dosage sulfite pretreated pulps in this study.

The sulfite pretreatment did not affect fibre length, *Table 1*, or distribution of Bauer-McNett fractions, *Fig 5*, when compared at equal SEC, hence the increase in tensile index was not a result of changes in fibre dimensions or the amount of fines. Furthermore, the increase in density could be a reason for the slight reduction in light scattering for sulfonated pulps when compared to non-sulfonated pulps at similar SEC.

This study presents a basis for future studies on how to further optimize low dosage sulfonation in combination with changes in other refining parameters. One interesting combination that has already been shown is low dosage sulfonation together with further increased refining intensity (Nelsson et al. 2014).

This study has also demonstrated an effective and robust application of low dosage sulfonation in mill scale. In the ranges applied here, both the degree of sulfonation and the effect on pulp properties was linear with the amount of added sulfite. This is an attractive feature for a pretreatment concept since it facilitates easy process control.

Conclusions

Low dosage sulfite pretreatment of wood chips were performed in a modern state of the art TMP-line. The increase in tensile index of ~7.6 Nm/g at a sulfonate content of 0.28% (as Na_2SO_3), compared with unsulfonated pulps at similar SEC, was of the same magnitude as shown in earlier reports regarding the effect of low dose sulfonation. However, in our study there was no increase in light scattering as a result of low dosage sulfite pretreatment, rather a reduction. The SEC needed to produce pulp with a tensile index of 47 Nm/g was reduced by ~320 kWh/bdt (~15%) when wood chips were pretreated with 1.2% Na_2SO_3 compared with pulps without sulfite addition. The amount of added sulfite gave a proportional effect on pulp properties, i.e. the addition of 1.2% Na_2SO_3 gave approximately a double increase in tensile index compared with addition of 0.61% Na_2SO_3.

Low dosage sulfite pretreatment of chips with 1.2% Na_2SO_3 resulted in a sulfonate content of pulps of 0.28% (as Na_2SO_3). The addition of sulfite did not affect the distribution of Bauer-McNett fractions or fibre length when compared at certain SEC. However, the low dosage sulfite pretreatment increased both fibre charge and the degree of delamination/internal fibrillation (D/IF) of fibres. Furthermore, statistical analysis on the degree of fibre wall D/IF showed that similar internal fibre development can be obtained with an energy input of 1780 kWh/bdt after low sulfite dosage (1.2%) pretreatment as for untreated chips refined with 2040 kWh/bdt. Increase in D/IF is suggested to have improved the flexibility and collapsibility of the pulp (fibres) and thereby the tensile index.

The reduced disc gap at certain SEC due to wood softening by sulfonation is suggested as an explanation for the increase in D/IF.

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