

PAPER I

**Effect of cell wall thickness
and fines on bleaching of
softwood kraft pulp**

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Effect of cell wall thickness and fines on bleaching of softwood kraft pulp

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SUMMARY

The effectiveness of various bleaching chemicals on softwood kraft pulp fibres of different cell-wall thickness was studied and the effect of primary fines on bleaching was investigated. Softwood kraft pulps of different average cell-wall thickness were obtained by fractionating with hydrocyclones. After the fractionation unbleached softwood kraft pulp fractions were treated with oxygen, chlorine dioxide, hydrogen peroxide and ozone. In the oxygen stage, kappa reduction increased and the consumption of sodium hydroxide per unit decrease in kappa number decreased with cell wall thickness at a given primary fines content. The consumption of hydrogen peroxide per unit decrease in kappa number increased with cell wall thickness at the same primary fines content. The consumption of chlorine dioxide and ozone per brightness unit gained decreased with cell wall thickness. In addition, the results showed that primary fines adversely affected the hydrogen peroxide bleaching of the pulp.

KEYWORD

Fractionation, hydrocyclone, cell wall thickness, primary fines, bleaching

INTRODUCTION

The cell wall thickness of softwood varies within the tree, along the stem from butt to top, and also with age. In addition the proportion of different cell wall layers varies between latewood (thick-walled

fibres) and earlywood (thin-walled fibres) (Table 1 (1)).

The differences in chemical composition between thick-walled latewood and thin-walled earlywood are due to differences in the distribution of components in the cell wall (Table 2). Thick-walled latewood fibres have a lower content of lignin due, indirectly, to the difference in cell wall thickness. At the beginning of the cell wall thickening process, the first 4-6 lamellae of the secondary wall form a 0.1-0.2 µm thick lignin-rich S1 layer (2). In temperate softwoods, the S2 layer of the secondary wall varies widely in thickness. In latewood cells, the secondary wall consists of approximately 30-40 lamellae and contains more cellulose and less lignin than the P and S1 layers. In earlywood walls, the S2 layer is considerably thinner. Hence the content of lignin is higher in thin-walled earlywood cells than in thick-walled latewood cells (2). The compound middle lamella (M+P) contains up to 0.88 g/g lignin, whereas the lignin content of the secondary cell wall of conifer tracheids ranges from 0.22 to 0.25 g/g (3).

Besides fibres, softwood pulp also contains a small amount, approximately 1 to 3 percent of the o.d. pulp, of primary fines. The primary fines consist of ray

cells, some broken fibres and thin sheets from the fibre surface (4,5). The fines fraction differs from the fibre fraction in that it has higher contents of lignin, metal ions and extractives. Fines have also been found to contain slightly more xylan and glucomannan (4). The lignin in primary fines has a high molar mass and few phenolic hydroxyl groups (5). The lignin in ray cells, the main constituent of primary fines, has more "condensed" lignin, with more aromatic carbon-carbon linkages than in other pulp fractions (6,7).

It is also known that various bleaching chemicals differ in the way they react with different lignin structures and also their location across the cell wall (8,9). The powerful oxidants, like ozone, react more rapidly with outer cell wall material, P+S1 and S3 layers, while reaction with lignin in the interior wall S2 appears to be slowed down by mass transfer limitations. According to Wang (8) hydrogen peroxide and chlorine dioxide produce uniform residual lignin distributions. However, according to Laine (10) only a small reduction in the surface lignin is obtained by hydrogen peroxide treatment. Kleen *et al.* (11) found that hydrogen peroxide removes surface lignin from kraft pulp effectively and that hydrogen peroxide cannot penetrate the fibre wall as well

Table 1.
Proportions of different cell wall layer in spruce tracheids (1).

Layer	Earlywood		Latewood	
	Thickness µm	Proportion %	Thickness µm	Proportion %
P	0.1	6	0.1	2
S1	0.2	13	0.3	7
S2	1.4	79	4.0	90
S3	0.03	2	0.04	1
Total	1.7		4.4	

Table 2.
Proportion and distribution of cellulose and lignin in earlywood and latewood of softwood (3).

Layer	Cellulose, % of total cellulose		Lignin, % of total lignin	
	Earlywood	Latewood	Earlywood	Latewood
M+P	4	3	27	18
S1	9	5	10	8
S2+S3	87	92	63	74

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as chlorine dioxide does. After oxygen delignification, the content of residual lignin in the P+S1 and S3 layers is higher than in the S2 layer (8). According to Wang (8) oxygen delignification maintains the nonuniform lignin distribution created in the pine kraft pulping, with the P+S1 and S3 layers containing about 30-35% more lignin than the S2 layer. According to Laine (10) oxygen delignification reduced the total lignin content by about 50%, while the surface lignin, originating from the remnants of the middle lamella and lignin reprecipitated during cooking, decreased only about 15%. On the other hand, Kleen *et al.* (11) found that oxygen delignification removed a higher fraction of the surface lignin (30%) than of the total lignin (20%) from the softwood kraft pulp.

The objective of this study was to investigate the overall effectiveness of various bleaching chemicals (i.e. bleaching chemical consumed per kappa number reduction and bleaching chemical consumed per brightness units gained) on softwood kraft pulp fibres of different cell-wall thickness, and to also study the effect of primary fines on bleaching.

MATERIALS AND METHODS

Raw material and fractionation

Unbleached softwood kraft pulp from a Finnish mill (66% pine, *Pinus sylvestris* and 34% Norway spruce, *Picea abies*) was fractionated using Noss Ab hydrocyclones to obtain pulps of different cell wall thickness. It is known from the literature (12) that hydrocyclone separation takes place on fibre wall thickness so, that thick-walled fibres are directed to the reject fraction and thin-walled fibres to the accept fraction. Prior to the hydrocy-

clone trials the pulp was screened to reduce its shive content. The hydrocyclone trials were carried out as a two-stage system, in which the rejects from the primary stage were fed to the secondary stage and the accepts from the secondary stage were fed back to the primary stage (Fig. 1). Five different mass reject rates (RRm) were used (19%, 27%, 45%, 72% and 91%) and the feed consistency of the primary stage was varied from 0.12 to 0.68%.

For a portion of the accepts, about 57 to 70% of the fines were removed before the bleaching trials to obtain approximately the same fines content as in the reject fractions. This permitted further investigation of the effect of fines content. Primary fines (4%) were removed using a rotating wire drum, Attisholz laboratory filter, with a 200-mesh (76 µm) wire. After the fines removal, the pulps had a fines content of 1 to 2% and kappa number was about 26.

In summary the pulps available for bleaching were as follows

- Feed
- Feed with excess fines removed: Feed'
- Thick walled pulps (rejects): Rm19r, Rm27r, Rm45r, Rm72r, Rm91r
- Thin walled pulps (accepts): Rm19a, Rm27a, Rm45a, Rm72a, Rm91a
- Thin walled pulps (accepts) with excess fines removed: Rm19a', Rm27a', Rm45a', Rm72a', Rm91a'

Bleaching

The unbleached fibre pulps: feed pulp, reject pulp, accept pulp containing all the fines and accept pulp from which fines were removed, were treated with oxygen,

chlorine dioxide, hydrogen peroxide and ozone. Oxygen delignification was performed in steel autoclave bombs with air bath heating. Ozone treatment was carried out in a plastic flow-through reactor. The chelation, chlorine dioxide, alkaline extraction and hydrogen peroxide treatments were carried out using sealed polyethylene bags in a thermostatically controlled water bath. Standard laboratory washing was carried out between stages: Pulp was diluted to 5% consistency with deionised water of the same temperature as that of the preceding stage. After dewatering, the pulp was washed twice with cold deionised water of an amount equivalent to ten times the absolutely dry pulp amount.

The bleaching chemical treatments were carried out under the following conditions:

- Chelation (Q) before oxygen and hydrogen peroxide treatments: 70 °C, 3% consistency, 60 min reaction time, EDTA 0.2% on pulp, initial pH adjusted to 4.3.
- Oxygen treatment (O): 90 °C, 8% consistency, 30 min temperature increase time, 60 min reaction time, NaOH charge (% on pulp) 0.07*incoming kappa number, 0.5% MgSO₄, oxygen pressure 8 bar. Final pH was from 10.8 to 11.6. Residual sodium hydroxide was determined by titration with hydrochloric acid.
- Chlorine dioxide treatment (D): 50 °C, 8% consistency, 60 min reaction time, active chlorine charge (% on pulp) 0.2*incoming kappa number, initial pH adjusted to ~ 3. Residual chlorine dioxide was determined by titration with sodium thiosulphate.
- Alkaline extraction (E) after chlorine dioxide and ozone treatments: 60 °C, 10% consistency, 60 min reaction time, initial pH~11.
- Hydrogen peroxide treatment (P): 90 °C, 10% consistency, 60 min reaction time, 2.0% NaOH on pulp, 0.25% MgSO₄ on pulp, 0.2% DTPA on pulp, 3.0% hydrogen peroxide on pulp. Final pH was from 9.4 to 9.6. Residual hydrogen peroxide was determined by titration with sodium thiosulphate.
- Ozone treatment (Z): 50 °C, 12.5% consistency, 0.35% ozone on pulp, initial pH adjusted to 3. The ozone formation was determined from potassium iodide solution by titration with sodium thiosulphate.

Kappa number (ISO 302), viscosity (ISO 5351) and brightness (brightness was

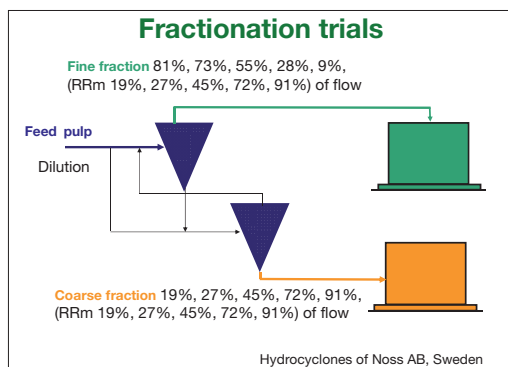


Fig. 1 Trial configuration for hydrocyclone fractionation.

measured from the split sheet, ISO 2470) were determined after the bleaching chemical treatments. In addition to routine analyses, a chemical analysis based on total solubilisation of pulp by enzymatic hydrolysis was used (13). The lignin content, the content of phenolic hydroxyl groups and the content of conjugated groups were determined from the sample solution. Fines content was determined using a Dynamic Drainage Jar (DDJ) with a wire hole diameter corresponding to a 200-mesh (76 µm) wire. Cell wall thickness measurement was performed according to Lammi (14), and Simons' staining according to Simons (15).

RESULTS AND DISCUSSION

Fibre properties

After the hydrocyclone treatment pulps of different cell wall thickness were obtained. Cell wall thickness varied from 3.9 µm to 6.2 µm (Fig. 2).

Fines accumulated during fractionation in the thin-walled accept pulp. The accumulated fines in the accept fraction had a higher lignin content and it increased the kappa number of the pulp (Fig. 3).

Despite the higher kappa numbers, the pulps having thin-walled fibres and a high fines content was brighter than the pulp having thick-walled fibres (Fig. 4) in agreement with Brännvall *et al.* (16). One reason for this is that the hand sheets made from the pulp with thin-walled fibres and high fines content contained more fibres for a given weight, and as a result this sheet had more light-reflecting surfaces and consequently had a higher

Table 3

Simons' staining.

	Cell wall thickness, µm	Yellow, %	Blue, %	Undyed, %
Feed (original pulp)	4.7	79	21	1
Thick-walled	6.2	45	54	1
Thin-walled	3.9	73	25	1

light scattering coefficient.

The structure of the thin-walled and thick-walled fibres was significantly different as indicated by Simons' staining (Table 3). Simons' staining reveals the structure of the fibre, the internal fibrillation and the looseness of the fibre wall. Simons' stain is a mixture of two dyes, which have different molecular size. Orange dye is assumed to absorb to the fibre wall if there is enough space, and if the fibre wall is denser (smaller pores) the fibre is dyed blue since the blue dye have a smaller particle size (15).

The proportion of yellow-dyed fibres

was 45% for the pulp containing thick-walled fibres, and 73% for the pulp containing thin-walled fibres (Table 3). This means that the structure of the thick-walled fibres is denser than that of the thin-walled fibres. The structure of the feed pulp was about the same as that of the pulp containing thin-walled fibres, because the average cell wall thickness of the feed pulp was closer to that of the pulp containing the thin-walled fibres. The feed pulp contained more thin-walled fibres than thick-walled fibres.

Bleaching chemical treatments

In the oxygen stage kappa reduction increased (Fig. 5a) and the consumption

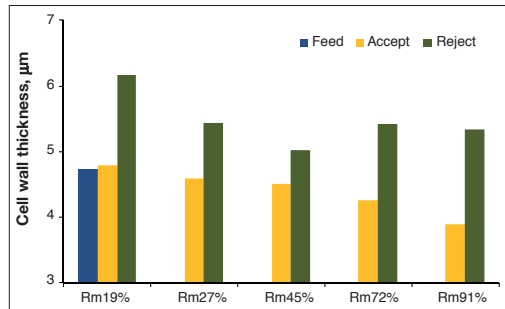


Fig. 2 Cell wall thickness of the feed (original pulp), accept (thin-walled) and reject (thick-walled) pulp for different mass reject ratios.

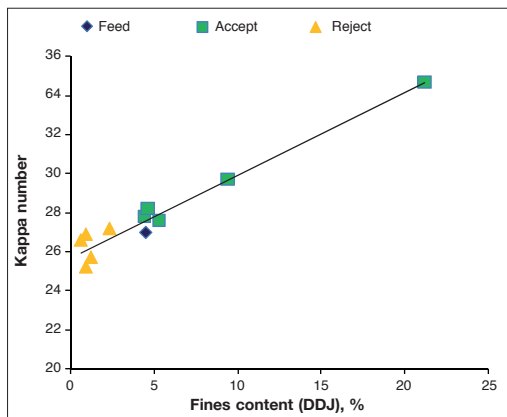


Fig. 3 Kappa number of the feed, accept and reject pulps plotted against fines content.

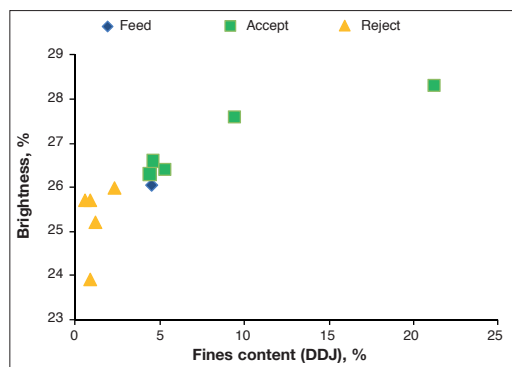


Fig. 4 Brightness of the feed, accept and reject pulps plotted against fines content.

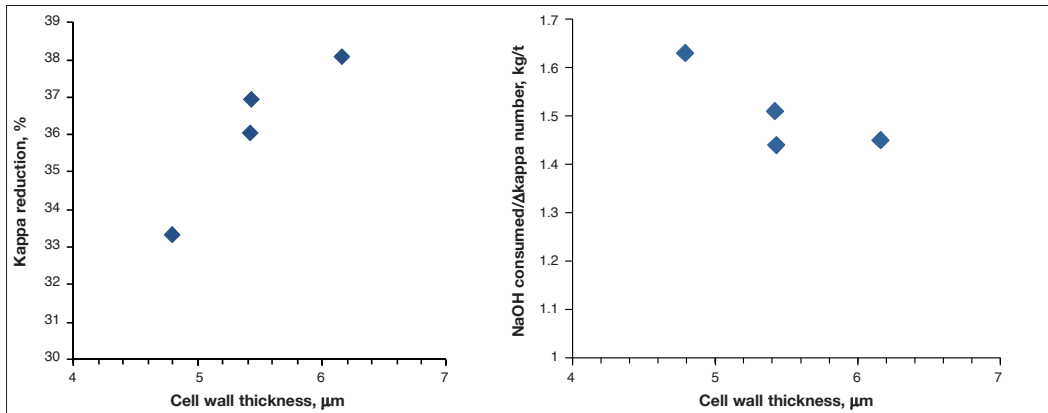


Fig. 5. a) Kappa reduction in oxygen delignification as a function of cell wall thickness. Fines content was from 1 to 1.9%. b) NaOH consumption per kappa number reduction as a function of cell wall thickness. Fines content was from 1 to 1.9%. Points in figure are for pulps: Rm19a', Rm19r, Rm27r, Rm72r.

of sodium hydroxide per unit decrease in kappa number decreased (Fig. 5b) with the cell wall thickness at a given fines content. One possible explanation for these findings is that the proportion of S2 layer is greater in thick-walled fibres than in thin-walled fibres (1).

According to the literature, the dissolution of lignin by oxygen is more effective from the S2 layer than from the (P+S1) or S3 layers (8,10). It is known that oxygen predominantly reacts with lignin structures containing a free phenolic hydroxyl group. The concentration of phenolic

hydroxyl groups in the lignin of the secondary wall of the fibres is more than double that found in the middle lamella and primary wall lignin (6). The pulp with thick-walled fibres contained more phenolic groups, which were formed during the cooking (Fig. 6). After the oxygen treatment, the number of phenolic groups was lower in the pulp containing thick-walled fibres than in the pulp containing thin-walled fibres. This indicates that the phenolic groups are possibly more stable in pulp containing thin-walled fibres. There may also be differences in how

they are morphologically located, i.e. differences in accessibility, phenolic groups in thick-walled fibres being more accessible than those in thin-walled fibres. Correlation between the sodium hydroxide consumption and fines content of the pulp was not found. It is known that the lignin in primary fines has a high molar mass and few phenolic hydroxyl groups, which could explain the poor reactivity of the pulp with high fines content towards oxygen (5).

No correlation was found between the cell wall thickness and the chlorine dioxide consumption per unit decrease in kappa number after the chlorine dioxide treatment. A small correlation was seen

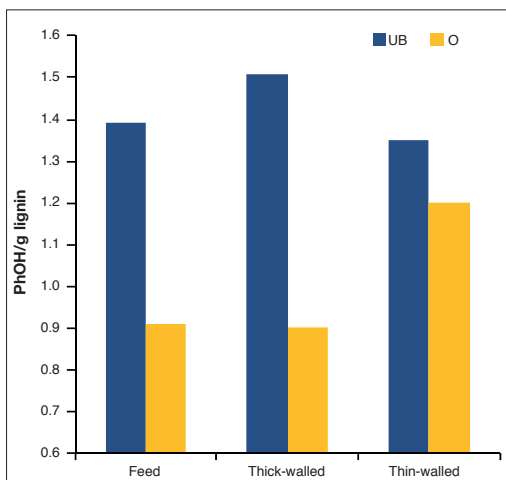


Fig. 6 Concentration of phenolic groups in unbleached and oxygen-treated pulps. UB – unbleached, O – oxygen delignified. Cell wall thicknesses: Feed 4.7 μm, Thick-walled 6.2 μm, Thin-walled 3.9 μm.

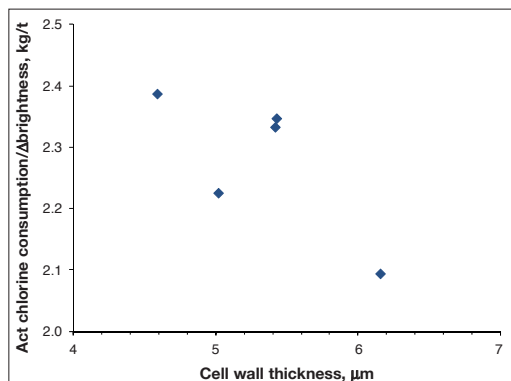


Fig. 7 Active chlorine consumption kg/Δ brightness as a function of cell wall thickness. Brightness was measured after alkaline extraction stage. Fines content was from 1 to 1.7%. Points in Figure are for pulps: Rm19r, Rm27a', Rm27r, Rm45r, Rm72r.

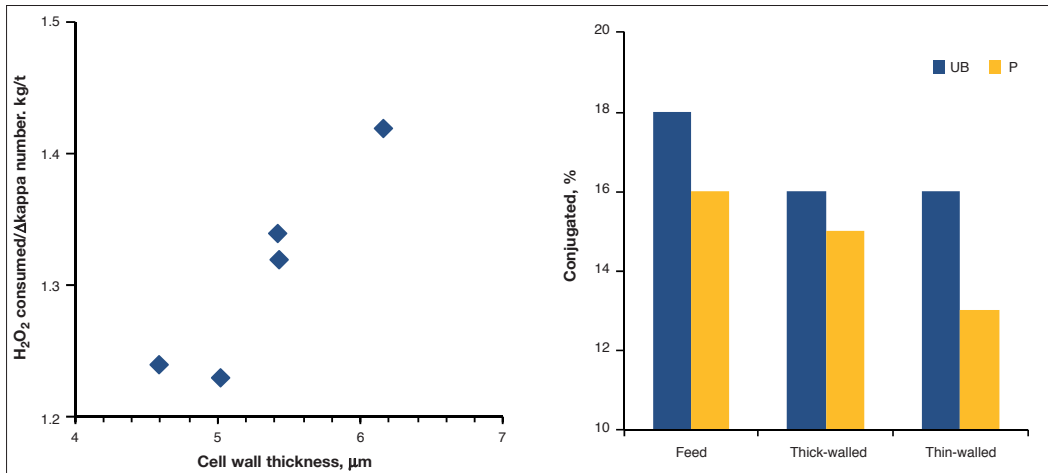


Fig. 8. a) Hydrogen peroxide consumption / Δ kappa number as a function of cell wall thickness. Fines content was from 1 to 1.7%. Points in Figure are for following pulps: Rm19r, Rm27a', Rm27r, Rm45r, Rm72r. b) Amount of conjugated groups in unbleached and hydrogen peroxide-treated pulps. Pulp was chelated before hydrogen peroxide treatment. Cell wall thicknesses: Feed 4.7 μm, Thick-walled 6.2 μm, Thin-walled 3.9 μm.

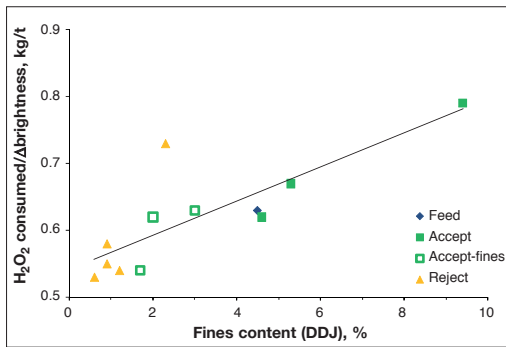


Fig. 9. Consumption of hydrogen peroxide as a function of primary fines content.

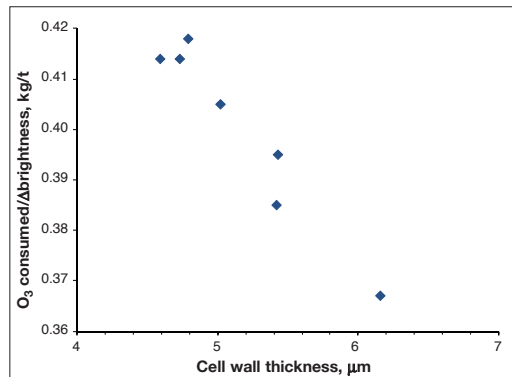


Fig. 10 Ozone consumption / Δ brightness as a function of cell wall thickness. Brightness was measured after alkaline extraction stage. Fines content was from 1 to 1.9%. Points in Figure are for following pulps: Feed', Rm19a', Rm19r, Rm27a', Rm27r, Rm45r, Rm72r.

between the cell wall thickness and the chlorine dioxide consumption per brightness unit gained (Fig. 7), the latter decreasing with cell wall thickness. Laine *et al.* (10) found surface lignin played a significant role with regard to brightness development during bleaching. They suggested that surface lignin is very probably more coloured than lignin in the other regions of the fibres. Also, Abe (17) found that a prebeating, i.e. removal of surface lignin, improved bleachability of unbleached kraft pulp. Thin-walled fibres probably contain more lignin characteristic of surface lignin i.e. middle lamella lignin and precipitated lignin and this explains their poorer bleachability with chlorine dioxide. In addition, both Laine

et al. (10) and Kleen *et al.* (11) found that chlorine dioxide does not remove surface lignin effectively.

Consumption of hydrogen peroxide per unit decrease in kappa number increased with cell wall thickness at the same fines content (Fig. 8a). In addition, the number of conjugated groups, containing a carbonyl group, was reduced more by hydrogen peroxide treatment of the pulp containing thin-walled fibres than of the pulp containing thick-walled fibres (Fig. 8b).

This also indicates that the hydrogen

peroxide treatment was more effective on the pulp with thin-walled fibres. Thinner fibres have a higher fraction of the lignin on the surface; and the increased removal of conjugated structures from thinner fibres seems to be because the surface lignin is more accessible. Kleen *et al.* (11) also found that peroxide cannot penetrate the fibre wall as well as chlorine dioxide and that hydrogen peroxide removes surface lignin effectively.

The consumption of hydrogen peroxide per brightness unit gained increased with increasing fines content (Fig. 9),

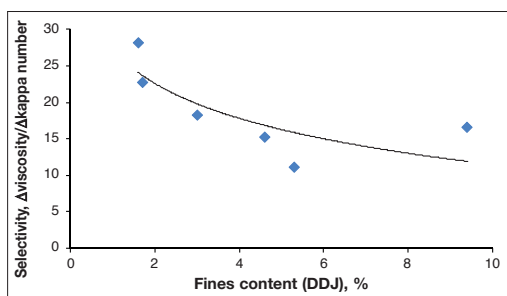


Fig 11. Selectivity (Δ viscosity/ Δ kappa number) in ZE stage plotted against fines content of the pulp.

while metal content of the pulps was about the same. This might be caused by the differences in lignin content and structure (18). According to Bäckström *et al.* (18) the better brightness gain achieved with no primary fines is due to the removal of chromophores.

The ozone consumption per brightness unit gained decreased with cell wall thickness (Fig. 10). The (P+S1) and S3 layers are said to react more quickly with ozone than the S2 layer (8). In the thin-walled fibres the proportions of (P+S1) and S3 layers are greater (1) and probably as a result of this the consumption of ozone was higher in the pulp containing thin-walled fibres.

The fines content seemed to have a slight influence on the selectivity (Δ viscosity/ Δ kappa number) values after the ozone treatment, so that the pulp containing a high amount of fines had a better selectivity (Fig 11.). The fines might have preserved the fibres, because, as mentioned earlier, ozone reacts more rapidly with outer cell wall material, (P+S1) and S3 layers, while reaction with lignin in the interior wall S2 appear to be slowed down by mass transfer limitations (8).

CONCLUSIONS

The results showed that the morphological features of the fibres influence the bleaching of the pulp. Results support earlier hypotheses that oxygen predominantly reacts with lignin in S2 layer, because the kappa reduction in the oxygen stage increased with the cell wall thickness. No correlation was found

between the cell wall thickness and the chlorine dioxide consumption per unit decrease in kappa number. However, the consumption of chlorine dioxide per brightness unit gained decreased with the cell wall thickness. In the hydrogen peroxide stage the bleachability of the pulp deteriorated due to the primary fines. The consumption of hydrogen peroxide per unit decrease in kappa number increased with the cell wall thickness. Ozone as a powerful oxidant reacted preferably with the surface lignin. This was seen in the higher consumption of ozone per brightness unit gained in the case of the pulp containing thin-walled fibres.

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