

Helsinki University of Technology Laboratory of Paper Technology

Reports, Series A 14

Espoo 2002

**IMPROVING THE COMBINATIONS OF CRITICAL PROPERTIES
AND PROCESS PARAMETERS OF PRINTING AND WRITING
PAPERS AND PAPERBOARDS BY NEW PAPER-FILLING METHODS**

Petri Silenius

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Forest Products Technology, for public examination and debate in Auditorium E at the Helsinki University of Technology (Espoo, Finland) on the 14th of February 2003 at 12 noon.

Helsinki University of Technology
Department of Forest Products Technology
Laboratory of Paper Technology

Teknillinen korkeakoulu
Puunjalostustekniikan osasto
Paperitekniikan laboratorio

Distribution:

Helsinki University of Technology
Department of Forest Products Technology
Laboratory of Paper Technology
P.O. Box 6300
FIN-02015 HUT

ISBN 951-22-6007-7

ISSN 1237-6248

Picaset Oy
Helsinki 2002

Digitally printed on M-real SuperFill paper 80 g/m²
No optical brighteners were used

ABSTRACT

The present study focused on improving the property combinations of printing and writing papers that become critical when lowering grammage. The target was to clarify whether improved combinations can be achieved through structuring precipitated pigments, pulps, and pulp fines in a new way. A kinetic model for diffusion of ions within the fiber wall was developed and used to interpret data from diffusion experiments in order to clarify the limitations of fiber loading, which was also briefly studied. Fiber loading, however, failed to provide paper with adequate properties. A new composite filler produced by precipitating calcium carbonate on pulp fines (SuperFill) was introduced and a mechanism for the paper filler suggested.

Based on the diffusion coefficients obtained and a general knowledge of crystallization, it can be concluded that the tendency of calcium carbonate to precipitate into the lumen or deeper within the fiber wall during fiber loading is minor, when precipitation is performed for birch fibers using the reaction between calcium hydroxide and carbon dioxide. Consequently, fiber loading did not offer significant benefits compared with fillers added normally to the stock.

SuperFill provided paper with a significantly improved combination of light scattering coefficient and strength compared with fillers added normally to the stock. The proposed mechanism for SuperFill consists of three elements. First, SuperFill provides paper with a more uniform spatial filler distribution with reduced agglomeration, which may contribute to paper light scattering coefficient through the combined effect of the pigment itself, interruption of the fiber bonded area, and reduced fines collapse. Second, the fines component of SuperFill most probably contributes to increased activation through enhanced bonding, resulting in increased paper strength. Third, it was shown that SuperFill influences paper in such a way that a more optimum pore structure with respect to paper light scattering is achieved. The combination of formation and retention was also improved with SuperFill. The economic value of SuperFill technology was estimated to be considerable.

PREFACE

The present study was initiated at the Department of Chemical Technology, Lappeenranta University of Technology, and continued at the Empire State Paper Research Institute (ESPRI), State University of New York at Syracuse, NY, USA. Finally, the thesis was completed at the Laboratory of Paper Technology, Helsinki University of Technology.

I thank Professor Hannu Paulapuro at the Helsinki University of Technology, who has been the supervisor of this thesis, for providing comments and guidance. I also thank Professors Matti Lindström and Philip Luner for their instruction during the work at their laboratories in Lappeenranta and Syracuse.

The study was financed by the M-real Corporation and the Technology Development Centre of Finland (Tekes), for which I am grateful.

I express my sincere thanks to all persons who have contributed to the study. Experimental activities such as pilot- and full-scale paper machine trials can certainly not be done alone. To mention a few, I thank Olavi Imppola and his research team, as well as the production teams at Specialty Minerals Nordic, for joining our forces to turn this into a larger scale project. Special thanks are addressed to Jari Meuronen, Marie-Louise Wallberg, Sami Haapala, and Sune Wännström at M-real Corporation, and Leena Yliniemi at Metsä-Botnia, for inspiring teamwork.

I also thank Risto Kekki and Soili Hietanen at M-real Corporation and Peter Duncan at Specialty Minerals Inc. for seeing the commercial potential of the SuperFill innovation, and Markku Leskelä together with Professor Jyrki Kettunen at M-real for commenting on the draft of the dissertation. Professor Kari Lumme at Helsinki University is acknowledged for his competent help in interpreting the results linking light scattering with paper structure.

Special thanks are expressed to Professor Jyrki Kettunen at M-real Corporation who has created the climate enabling postgraduate studies to be done along with duty, and to his successor Lars Gädda for continuing this tradition.

Finally, and most importantly, I thank my wife Minna and my parents for encouragement and patience, and especially our little daughter Veera who decided to pop up, boosting the final sprint of writing. Obviously, writing was the best excuse for avoiding changing diapers.

Lohja, December 2002

Petri Silenius

LIST OF SYMBOLS AND ABBREVIATIONS

α a root of Eq. $J_0(\alpha R) = 0$ to satisfy the boundary condition $C = 0$, when $r = R$ and $t > 0$

β_n n'th root of equation $J_0(\beta_n) = 0$ ($\beta_n = \alpha_n R$)

γ_n parameter defined by $\gamma_n = \frac{D\beta_n^2}{R^2}$

A total surface area of fibers

a_n coefficient of n'th term which can be determined from the initial condition $C = C_{max}$, when $0 \leq r \leq R$ and $t = 0$ by

$$C_{max} = \sum_{n=1}^{\infty} a_n J_0(\alpha_n r)$$

B parameter defined by $B = AC_{max} R \frac{2}{V_{H_2O}}$

C concentration within fibers

C_{max} concentration within fibers at $t = 0$

C_s^* theoretical concentration of electrolyte in the water phase of the fiber suspension

$C_s(u)$ concentration in the solution outside the fibers defined by $C_s(u) = f_{out}(u)$

$C_{s(max)}^*$ concentration in the plateau region at the end of each experiment

D diffusion coefficient within the fiber wall

E elastic modulus

$F_{in}(s)$ Laplace transform of the theoretical concentration in water phase

$f_{in}(s)$ Laplace transform of the theoretical relative concentration

in water phase defined by $f_{in}(s) = \frac{C_s^*(s)}{C_{s(max)}^*} = \frac{L(C_s^*(t))}{C_{s(max)}^*}$

$f_{in}(t)$ theoretical relative concentration, $f_{in}(t) = 1$, when $t > 0$

$F_{out}(s)$	Laplace transform of the measured concentration in water phase
$f_{out}(s)$	Laplace transform of the measured relative concentration in the water phase defined by $f_{out}(s) = \frac{C_s(s)}{C_{s(max)}^*} = \frac{L(C_s(t))}{C_{s(max)}^*}$
$f_{out}(t)$	measured relative concentration, $f_{out}(t) = 1 - e^{-(t-T)/k}$, when $t > T$
$G(s)$	transfer function which describes the system's dynamic behavior satisfactorily
J	molar flux through the fiber wall
J_0	Bessel function of order zero of the first kind
J_1	first-order Bessel function of the first kind
k	time constant
L	operator indicating Laplace transform
n	index corresponding to n 'th root of $J_0(\alpha R) = 0$
\dot{n}	molar flow through the fiber wall
r	distance from the symmetry axis of the fiber
R	fiber radius
S	bending stiffness
t	time
T	length of time delay
t_b	thickness of a rectangular beam (paper)
u	time defined by $u = t - T$
V_{H2O}	volume of the suspension

COD	chemical oxygen demand
CMC	carboxy-methyl cellulose
CSF	Canadian standard freeness
ESPRI	Empire State Paper Research Institute
EuroFEX	pilot paper machine at STFI
GCC	ground calcium carbonate
HW	hardwood
KCL	Finnish Pulp and Paper Research Institute
NPV	net present value
O.D.	oven dry
PCC	precipitated calcium carbonate
PM	paper machine
psd	particle size distribution
R&D	research and development
SEM	scanning electron microscope
SF	Short Fine (fillings for short fiber refining)
°SR	Schopper-Riegler number
SSA	specific surface area
STFI	Swedish Pulp and Paper Research Institute
SW	softwood
Tekes	Technology Development Centre of Finland
TCF	totally chlorine-free
TMP	thermomechanical pulp
XPM	experimental paper machine

CONTENTS

1	INTRODUCTION	1
1.1	Background	1
1.1.1	Changes in operational environment.....	1
1.1.2	Resource efficiency and quality requirements	1
1.1.3	New opportunities.....	2
1.1.4	Real price of products.....	3
1.2	Scope of the study	3
1.3	Review of fiber-loading techniques.....	4
1.4	Calcium carbonate, its raw materials, and production	7
1.5	Rheology of pulp suspensions	12
1.6	Objectives and structure of the thesis	14
2	POTENTIAL AND LIMITATIONS OF FIBER-LOADING TECHNIQUES	16
2.1	Diffusion-controlled kinetics of electrolyte transfer within pulp fiber wall	16
2.1.1	Mechanisms of obtaining fillers in the fibers	16
2.1.2	Theory	17
2.1.3	Experimental	26
2.1.4	Results	28
2.1.5	Discussion	31
2.2	Fiber loading and impacts of loaded fibers on paper properties	35
2.2.1	Experimental	35
2.2.2	Results and discussion.....	36
2.3	Conclusions.....	45
3	FINES-FILLER COMPOSITE: SUPERFILL TECHNOLOGY	46
3.1	The idea of fines-filler composite technology	46
3.2	Hypotheses	48

4	IMPACT OF FINES-FILLER COMPOSITE ON CRITICAL PROPERTY COMBINATIONS AND PROCESS PARAMETERS OF PRINTING AND WRITING PAPERS AND PAPERBOARDS	49
4.1	Introduction.....	49
4.1.1	Critical property combinations.....	49
4.1.2	Retention and formation.....	51
4.2	Experimental	53
4.2.1	Fines production and analyses.....	53
4.2.2	Fines-filler composite production and analyses.....	53
4.2.3	Paper production and testing	54
4.3	Results and discussion	55
4.3.1	Light scattering coefficient and tensile strength	56
4.3.2	Light scattering coefficient and Scott bond	61
4.3.3	Light scattering coefficient and burst strength.....	64
4.3.4	Light scattering coefficient and pore structure	66
4.3.5	Light scattering coefficient, density, and bending stiffness	69
4.4	Retention and formation.....	73
4.5	Impact of calcium carbonate portion of fines-filler composite on paper properties..	77
4.6	Conclusions.....	83
5	MECHANISM OF FINES-FILLER COMPOSITE IN PAPER.....	85
5.1	More uniform spatial distribution of filler particles in paper with reduced agglomeration and improved retention: The combined effect of the pigment itself, interruption of the fiber bonded area, and reduced fines collapse.....	85
5.2	Positive effect of the fines fraction of fines-filler composite on paper strength; the activation model.....	93
5.3	Improved pore structure with respect to light scattering.....	99
5.4	Conclusions.....	99
5.5	The role of specific surface area of fines and fibers with respect to the mechanism	100
5.6	Paper machine operations with respect to the mechanism	102
6	ECONOMIC POTENTIAL OF FINES-FILLER COMPOSITE TECHNOLOGY	103
6.1	Main factors influencing economic potential	103
6.2	Added value of the technology: a hypothetical paper mill case	104
7	DISCUSSION AND CONCLUSIONS.....	107
8	LIST OF APPENDICES.....	112
9	REFERENCES	113
	APPENDICES	

1 INTRODUCTION

1.1 Background

1.1.1 Changes in operational environment

During recent years the pulp and paper industry has faced considerable change in its operational environment. This change has provided papermakers with both huge challenges and opportunities. Corporations have merged strongly, enabling wider product portfolios, better customer service, and better possibilities for product rationalization. These rather fundamental changes enable wider utilization of new innovative technologies within a single corporation.

The trend in paper product development is presently directed more often by customers' needs and wishes. Printing paper customers want to cut down mailing costs and reduce waste. The relative prices of resources needed to produce a product can also vary with time and location, which controls development. Energy and environmental taxes could be added to the price of paper products. The predominant trend under these conditions is that customers want to purchase paper products with lower grammage.

1.1.2 Resource efficiency and quality requirements

Resource efficiency means that more is achieved with reduced resources. In papermaking, the main resources are materials, energy, capital, and human resources. When more printing surface with reduced grammage is produced, profit from this excess surface can be shared between the papermaking company and its customer. In this line of thinking, fixed capital and energy costs are also lower for the surface area unit produced. If the time dimension

is incorporated, it can be estimated how the new technologies maintain their competitive edge. This approach is considered as total resource efficiency.

Under the circumstances in which grammage is lowered, opacity, strength, and density of paper become the critical properties. In many applications, however, the stiffness of paper is even more critical. Opacity can be increased by using more filler in paper, but this usually decreases paper strength and stiffness. Thus, paper structure should be altered in such a way that desirable paper properties are maintained. Since competition is strong, paper properties such as printability should also rather be improved. This is a challenge in which all innovative ideas should be carefully considered.

1.1.3 New opportunities

Both pigments and cellulosic materials should be used as effectively as possible under the circumstances mentioned above. New developments such as precipitated fillers and pigments are known to offer new opportunities to improve paper properties. Improved information on synergism and interaction of precipitated pigments with fibers and fines may provide papermakers with new ways to improve paper properties. It has also been assumed that inorganic salts precipitated within fiber walls may increase fiber stiffness with positive impact on light scattering and paper stiffness.

Since low-grammage papers can also be produced by layering, the value of new developments regarding functional raw materials may be increased. Specific layers, e.g. surfaces of paper, can be enriched with functional raw material providing paper surfaces with improved properties. Other components may instead be located in the middle layer, providing paper with other properties.

1.1.4 Real price of products

It is known from experience that the real price of paper products decreases on average by approximately 2% per year. This is the minimum that should be covered by rationalization, product development, and other actions aiming at efficiency improvement. Rationalization is not enough in the long run, which makes innovative products with technological jumps crucial.

1.2 Scope of the study

The present study focuses on improving the property combinations of printing and writing papers, which become critical when lowering the grammage of paper. The approach is to clarify the opportunities originating from structuring precipitated pigments and pulp materials in a new way. The pulp materials in this study include bleached kraft pulps and pulp fines. "Fines" is used here to mean pulp fines only. In the experimental part of this thesis calcium carbonate is precipitated using the reaction between calcium hydroxide and carbon dioxide.

Fiber loading is among the more traditional techniques studied. The emphasis, however, is on an invention described in this thesis, i.e. the SuperFill technology based on the synergism between precipitated calcium carbonate and kraft pulp fines together with fibers. The feasibility and limitations of different techniques are also studied. A first insight into the product development based on SuperFill technology is also given together with rough economic estimates. The study includes laboratory-, pilot-, and mill-scale experiments. Fines properties and production are outside the scope of this thesis as are the calcium carbonate precipitation and conditions such as rheology of the pulp and fines suspensions, but can be found in the literature.

1.3 Review of fiber-loading techniques

Fillers are used in many grades of paper to improve optical and physical properties or simply to replace more expensive fibers. Due to the extensive possibilities of modifying size and shape of PCC (precipitated calcium carbonate) crystals, it is among the most attractive minerals for alkaline papers. High CaCO_3 -level papers are commonly produced.

At high filler levels, a considerable number of fine mineral particles are not retained by fiber network in the paper machine, resulting in white waters with high solids content. Novel retention aids such as microparticle systems function satisfactorily but have certain limitations, as will be clarified in more detail in Chapter 4.

Methods for incorporating fillers inside fibers have been extensively studied, not only for better filler retention but for better paper properties. The first studies, regarding titanium dioxide, were reported by Scallan and associates^{1,2}. In this method an excess of titanium dioxide was stirred with a pulp slurry, transferring titanium dioxide into the fiber lumens.

More recent studies on cell wall loading were reported by many research groups in the U.S.A. and Japan^{3,4}. Usually the approach has been to saturate pulp fibers with a soluble calcium salt and to precipitate calcium as carbonate by adding another soluble salt which contains carbonate ions. The salts used can be for example calcium chloride and sodium carbonate^{5,6}. Craig⁷ describes this method, in which pigmented fibers contained more pigment than fiber materials that were mixed with untreated pulp in papermaking. Filler retention during papermaking was good but paper strength poor.

A patent to Thomsen⁸ describes a modification of the previous method. According to this patent a 10% solution of calcium chloride was used to

saturate fibers that were then compressed to a moisture content of 50% and sprayed with ammonium carbonate solution to precipitate calcium carbonate. The soluble by-product, which in this case was ammonium chloride, was then flushed out with water. Opacity of the paper improved when loaded fibers were used in papermaking. A disadvantage of this method is the reduction in paper strength⁹. These techniques also suffer, according to the literature, from a limited ability to generate the most important form of calcium carbonate in papermaking, i.e. calcite, if seeding is not used¹⁰.

Japanese patent documents^{4,11} describe a method of fiber wall loading that yields no by-products other than water. In this method, as explained in the examples, calcium hydroxide is dispersed in a 1% slurry of beaten or unbeaten pulp. Calcium carbonate is then precipitated by bubbling carbon dioxide gas through a slurry of calcium hydroxide and pulp. According to the latter patent document, good calcium carbonate retention can be achieved in papermaking. The raw materials of calcium carbonate are relatively inexpensive as used in this technique.

Certain differences in opinion concerning the advantages of cell wall loading in papermaking and especially on paper properties exist. Allan¹² summarized the advantages both in the papermaking process and paper properties. First, white water management is facilitated due to improved retention, and the dosages of expensive polymeric retention aids can be reduced. Second, less thermal energy is required to dry fiber wall-filled paper, because the filler is impervious to water and the fiber content per unit weight of the paper is lower. The collapse of fiber voids during drying may also be reduced¹³ which may facilitate drying. Third, abrasion damage to the Fourdrinier wire should be less severe because the filler is inside the fiber.

Regarding paper properties, the following advantages are reported by Allan as well. First, fiber wall filled paper exhibits smaller two-sidedness because the filler is retained within fibers during sheet formation. Second, paper should be less dusty than conventional paper. Third, although substantial disagreement exists, Allan reported fiber wall filled paper to exhibit greater tensile, burst, and tear strength than corresponding conventional paper. Better strength properties have also been reported by other authors^{14, 15}. Indeed, if lumen loading is performed by mixing titanium dioxide with the pulp, paper strength can be increased compared with the filler added normally to the stock. This increase, however, must be questioned when precipitation methods are used.

Better strength obtained with titanium dioxide is assumed to be due to increased hydrogen bonding of fibers, because the filler is located inside the fibers. Furthermore, titanium dioxide does not change the chemistry of fiber surfaces. The optical properties of paper made of lumen- or cell wall-loaded pulp are in general equal to those of conventionally loaded paper^{1, 3}.

Fiber micropores are very small, and fiber wall pore structure naturally impacts fiber loading. Never-dried fibers typically have pore volume of 1.5 ml/g with narrow size distribution¹⁶. When never-dried kraft fibers are beaten, there is an increase in the volume of larger micropores^{17, 18}. Water flow into the fiber wall due to the osmotic pressure gradient makes fibers swell, depending on the chemical environment, which alters the pore structure of the fiber wall¹⁹.

In summary, methods of incorporating fillers inside fibers can be based on precipitation, or a filler can be mechanically stirred with a pulp slurry, transferring filler into the fiber lumen. The latter technique typically suffers from the excessive need for expensive titanium dioxide filler. In precipitation the approach has usually been to saturate pulp fibers with a soluble calcium salt and to precipitate calcium as carbonate by another soluble carbonate salt.

These techniques generate troublesome soluble by-products and obviously provide paper with poor strength, which make the methods impractical on an industrial scale.

The most interesting method used in the industry to precipitate calcium carbonate is to bubble carbon dioxide gas through a slurry of calcium hydroxide (carbon dioxide process). This technique is already widely used in commercial PCC production, but its feasibility regarding fiber loading has not been shown explicitly. Thus, fiber loading by means of this precipitation technique was limitedly incorporated into the experimental part of this thesis since it also has potential advantages over the other techniques.

1.4 Calcium carbonate, its raw materials, and production

To control the precipitation process in such a way that the right kind of product with desired crystal size and shape can be obtained, information on parameters such as solubilities must be known. Abundant literature information about calcium components and the precipitation of calcium carbonate is available. The most essential information is summarized in this chapter, followed by certain deductions.

Natural calcium carbonate exists as three anhydrous polymorphous minerals: calcite, aragonite, and vaterite. Vaterite is not stable enough to be used as a filler. Calcite and aragonite can be prepared by precipitation in industrial scale and are known as PCC. It is mainly produced by leading carbon dioxide gas into a slurry of calcium hydroxide.

The solubility of calcium hydroxide in pure water decreases with increasing temperature, as presented in Table 1.

Table 1. Solubility of calcium hydroxide in pure water (pH ~ 12.4) ²⁰.

Temperature, °C	Ca(OH) ₂ solubility, mg · kg ⁻¹ solution
20	17·10 ²
40	13·10 ²
60	11·10 ²
80	8.7·10 ²
100	6.6·10 ²

Based on the calculations of Plummer *et al.* ²¹ for the temperature range from zero to 90 °C the solubilities of both calcite and aragonite decrease with increasing temperature. The solubility of calcite is presented in Table 2.

Table 2. Solubility of calcite in pure water. ²¹

Temperature, °C	Calcite solubility, mg · kg ⁻¹ solution
10	6.24
30	5.57
50	4.67
70	3.69
90	2.75

When precipitation is performed using the carbon dioxide process, the pH value undergoes a change during the process. The precipitation reaches its end point when the calcium hydroxide runs out and calcium carbonate buffers the pH to about 8.4.

Generally, temperature is among the most important variables that control precipitation, since it typically influences solubility and supersaturation. Supersaturation means that the solution contains more dissolved solid than that represented by saturation conditions ²². The other variables include seeding, stirring rate, pH, geometry of the crystallizer, and the use of additives.

As expressed earlier, the solubilities of calcium carbonate and its raw materials can be altered by changing the temperature, which further influences the supersaturation of the solution. Generally, in precipitation the nucleation rate increases exponentially and crystal growth linearly with supersaturation ²³. It can be further concluded that particle size should decrease with increasing supersaturation, resulting in higher total amounts of particles. Regarding calcium carbonate, the percentual increase in solubilities of both calcium hydroxide and calcium carbonate are approximately equal with decreasing temperature, but the solubility of calcium hydroxide is approximately 250 times higher than that of calcium carbonate. Even though the percentual changes are the same, this large difference in solubilities causes tremendous increase in calcium carbonate supersaturation when the temperature is decreased. Thus, if general theories are valid regarding calcium carbonate precipitation by means of the carbon dioxide process, particles should become smaller with decreasing temperature. This must of course be tested experimentally, since the process may also contain other temperature-dependent ionic equilibria.

Some information on this is also available in the literature concerning manufacture of PCC. According to a Canadian patent ²⁴ the average diameter of calcium carbonate particles was 2.0 μm and 3.0 μm when the initial temperature of precipitation was 15 °C and 30 °C, respectively. Scalenohedral

calcite crystals were crystallized when the initial temperature was 55 °C or higher.

The stirring rate and supersaturation have a combined effect on particle size. At very low levels of supersaturation, the particle size of calcite is increased with stirring rate, whereas at high levels of supersaturation it is reduced.²⁵

The temperature during precipitation affects the mineral type of calcium carbonate. Calcite is precipitated at temperatures below 40 °C, whereas the amount of aragonite is increased at temperatures higher than 50 °C. However, the mineral form partly changes to calcite when the reaction time is prolonged.²⁶

Regarding calcium carbonate, the inflow and molar ratio of carbon dioxide are important. Calcium carbonate can be precipitated under different partial pressures of carbon dioxide. The total pressure can also be varied²⁷. The inflow of carbon dioxide must be in the right order of magnitude with respect to calcium hydroxide content. However, within a narrow region, carbon dioxide inflow can be used to control crystal size. Generally, higher inflow rates yield smaller crystals. According to Yamada²⁸ doubling the inflow rate of carbon dioxide under defined conditions reduced the particle size of calcite from 0.8 μm to 0.05 μm.

Seeds can be used to facilitate precipitation, especially if nucleation is limited. Regarding calcium carbonate and the carbon dioxide process, seeding is not needed since high supersaturation and nucleation rates are easily obtained. However, seeds can be used if it is desired that the amount of a certain type of particle is maximized. Reddy and Gaillard²⁹ studied the effect of seed concentration on the crystal growth rate of calcite. The growth rate decreased

with increasing seed concentration to a value of 300 mg/L. At higher concentrations growth rate was constant.

Additives can alter the rate of nucleation or crystallization, or both. If an additive is adsorbed selectively on certain faces of crystals, thus preventing the adsorption of material to be crystallized, the additive alters the shape of the crystals ³⁰.

Polymers usually decrease the average size of calcium carbonate. Verdoes *et al.* ³¹ studied the influence of several additives on the precipitation of calcium carbonate on cotton fiber surfaces. Polymers with polystyrene sulfonic acid groups retarded crystal growth, whereas polymers with polyacrylic acid groups increased the growth rate.

Suhara *et al.* ³² noted that surface active substances influenced the polymorphism of calcium carbonate. Calcium carbonate was found to precipitate as vaterite in the presence of non-ionic surface active additives. Corresponding cationic additives at low concentrations resulted in both vaterite and calcite. At higher concentrations, however, only calcite was formed. Anionic and cationic substances behaved analogously at low concentrations. The amount of amorphous calcium carbonate increased with increasing concentration of anionic additive.

Certain polymers and inorganic ions have certain effects on calcium carbonate polymorphism. It was shown by Canselier ³³ that the formation of rhombic calcite decreased and the amount of vaterite increased in the presence of stearic acid. Dalas ³⁴ reported that COCH₃ and COH groups increase the formation of calcite. The behavior of certain groups such as SO₃H is dependent on the type of polymer chain that the groups are linked to. According to Wakita and Kinoshita ³⁵ calcium carbonate precipitated

mostly as aragonite in the presence of magnesium and sodium ions. Iron makes calcium carbonate particles slim in the middle and plumper at the ends³⁶.

According to Giannimaras *et al.*³⁷ crystallization of calcite was already inhibited by orthophosphate at very low concentrations. The proposed mechanism is that orthophosphate occupies the entire surface area of each crystal, thus preventing the adsorption of calcium and carbonate ions. The crystallization rate was found to decrease drastically with increasing concentration of orthophosphate³⁸. Some other phosphates behave similarly, diphosphate ions³⁹, sodium phosphate, and polymaleic acid⁴⁰ inhibit the crystallization of calcite, while the polyphosphates often function as dispersing agents. Giannimaras *et al.*⁴¹ studied the precipitation of calcium carbonate in the presence of oxalate ions, which were found to reduce the rate of crystal growth.

1.5 Rheology of pulp suspensions

Basic information on suspension rheology is highly relevant regarding fiber loading since effective stirring and mass transfer are vital for effective precipitation. The economical range of calcium hydroxide consistency, which is by experience normally above 15% by weight of suspension, suggests also that an interesting option is to make fiber loading at medium pulp consistency, i.e. at fiber consistencies between 5% and 15% by weight. Fiber flocculation is highly relevant with respect to rheology under these conditions.

Flocculation of dilute pulp suspensions has been extensively studied since the 1950s. Mason^{42,43} demonstrated that flocculation is mainly a mechanical phenomenon which occurs when consistency of pulp suspension crosses a critical value which depends on the fiber properties. This value for pulp fibers

is very low, typically below 0.1% by weight. According to Ritala and Huiku⁴⁴ the critical concentration depends on the width and length of the fibers. Within the consistency range between 0.2% and 0.4% fibers form a network where flocs can be seen as denser areas^{45, 46, 47, 48, 49}.

Flocculation tendency of fiber suspensions depends on many factors such as fiber length and flexibility. To some degree flocculation can also be affected by chemical means^{50, 51}. The most important factor is, however, the consistency of fiber suspension. Floc strength and flocculation rate of a given pulp increase exponentially with consistency.^{52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63} The flow state, normally the turbulence, is the most important external factor. Shear forces under turbulent conditions can break flocs down but also cause them to adhere. Thus, turbulence can also contribute to flocculation under certain conditions.^{64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76} According to a recent study of Bennington and Mmbaga⁷⁷ fibers are efficient at dampening turbulence within a suspension.

The behavior of medium-consistency pulp-fiber suspensions is strongly dependent on their flow state. Under static conditions the suspension behaves as viscoelastic material. However, at high shear it behaves as a turbulent Newtonian liquid. The transition to liquidlike flow can be referred to as fluidization.^{78, 79, 80, 81, 82, 83}

Thus, pulp suspensions are normally very heavily flocculated at 10% consistency but can be fluidized under conditions of strong shear. Under these conditions the fiber flocculation is greatly reduced. The transition to the fluidized state occurs normally at power inputs of about 5 kW/L at medium pulp consistency⁸⁴. Mixers with which fluidization is obtained are available commercially.

1.6 Objectives and structure of the thesis

The main objective of the study is to clarify whether positive impacts on critical property combinations and process parameters of printing and writing papers and boards can be achieved through structuring precipitated pigments, kraft pulps, and pulp fines differently from that of traditional for commercially produced papers. This objective is further divided into four subobjectives. The subobjectives are:

1. **To critically review the literature regarding lumen loading and fiber wall loading** (together referred to as fiber loading); Chapters 1 and 7.
2. **To study the potential, feasibility, and limitations of fiber loading.** A basic task is to address whether calcium carbonate can be feasibly precipitated within pulp fibers having no pit apertures with positive impact on fiber and paper stiffness; Chapters 2 and 7.
3. **To clarify the potential and feasibility of the technique developed based on the synergism between precipitated calcium carbonate and pulp fines together with fibers** (referred to as SuperFill technology); Chapters 3, 4, 6, and 7.
4. **To study the mechanism of SuperFill effects in paper;** Chapters 3, 5, and 7.

The operational environment of the pulp and paper industry is first examined in Chapter 1 to set the right targets for the study. Even though the main focus of the study is on SuperFill technology, the fiber loading and respective literature are reviewed in Chapter 1. Since the potential for fiber loading has not been shown explicitly in the literature, a limited experimental study is summarized in Chapter 2. This chapter combines the results and deductions of the study on the mass transfer of ions within the fiber wall with the results from fiber-loading experiments to form firmer conclusions on the potential and limitations of fiber loading.

The main part of the thesis, Chapters 3 through 6, are devoted to SuperFill technology. Chapter 3 briefly presents the idea behind the technology together with the hypotheses. The impacts of SuperFill on critical property combinations and process parameters are discussed in Chapter 4 with a set of results. Chapter 4 also contains a brief introduction to critical property combinations and process parameters to put the results in perspective. The hypotheses and suggested mechanism of SuperFill on paper are discussed in Chapter 5 based on both information from the literature and results from the experimental measurements presented in this thesis. The feasibility and economic value of SuperFill technology is briefly discussed in Chapter 6.

Finally, the main findings and implications of the study as a whole are discussed and conclusions made in Chapter 7. Suggestions for follow-up work are also presented in this chapter. Some of the laboratory-scale results have been presented in previous publications and theses.^{85, 86, 87, 88, 89}

2 POTENTIAL AND LIMITATIONS OF FIBER-LOADING TECHNIQUES

2.1 Diffusion-controlled kinetics of electrolyte transfer within pulp fiber wall

2.1.1 Mechanisms of obtaining fillers in the fibers

Even though fiber loading is reviewed in Chapter 1, a brief introduction to the loading mechanisms is given here to clarify in more detail the factors relevant to loading. Lumen loading is usually done by mixing fine fillers with pulp. In this process filler particles are transferred into the lumen from the bulk solution through pit apertures. Scallan *et al.*¹ found that the kinetics of lumen loading is dependent on the stirring rate. It was suggested that turbulence causes flow through the lumen, and thus the lumen-loading rate was enhanced with the stirring rate. Petlicki *et al.*⁹⁰ proposed that fillers can diffuse into the lumen. In their model the rate of lumen loading was limited by the transport of fillers through the pit apertures in the fiber walls. The model was compared with data from Midleton⁹¹ and Alince *et al.*⁹² and was found to describe the data quite well.

The studies described above are limited only for processes in which the diameter of filler particles is smaller than the diameter of pit apertures. If we consider fiber wall loading instead of lumen loading, the filler is usually prepared by reaction of ions (*in situ* precipitation). In this case the diffusion of ions within the fiber wall is the major mechanism for obtaining the raw materials of filler through the fiber wall. Many studies concerning diffusion of different substances through wood have been published during the last 30 years. For example, diffusion of wood preservatives⁹³, water⁹⁴, and pulping chemicals⁹⁵ has been investigated. However, diffusion of ions inside the cell wall of pulp fibers, and especially the impacts of blocking material on diffusion, have not been studied extensively.

The aim of this part of the thesis is to present a theoretical model for diffusion of ions within the cell wall of pulp fibers having no pit apertures suspended in water. With the aid of this model and a modest amount of experimental data the diffusion coefficients of ions inside the fiber wall can be determined. Moreover, the experimental data interpreted by this model may help to clarify whether fibers without pit apertures can be loaded by the method using the reaction of sparingly soluble salts such as calcium hydroxide.

2.1.2 Theory

Since the fiber radius is small the diffusion through a fiber wall is rapid and the experimental method for studying this phenomenon must be fast enough to give reliable data. However, it can be imagined that handling of a single fiber is difficult due to the small dimensions of fibers. It was therefore decided to study the diffusion using known amount of fibers suspended in water and to assume that the diffusion coefficient within the fiber wall of separate fibers remains constant. Furthermore, it was desired to establish a method, that completely overlooks interfiber diffusion, unlike other methods known^{96, 97}, taking into account only intrafiber diffusion.

To perform the experiments, the fibers were thoroughly saturated with concentrated electrolyte solution and then pressed until practically no external solution was present. Pressing was done following the same procedure used with all samples to minimize the relative errors originating from possible residues of external solution. At the beginning of each experiment the fibers were placed in a small vessel of deionized water with efficient stirring. Diffusion was followed by measuring the conductivity of the solution outside the fibers as a function of time.

Since the process is rather rapid and the value $t=0$ of each measurement difficult to set accurately, it was decided to search for a transfer function to describe accurately the dynamic response of our measuring system (stirring, vessel geometry, dynamic response of the conductivity sensor, etc.). A detailed description on the application of this transfer function is presented later.

The mathematical solution of the diffusion problem for an infinite cylinder which in practice describes a fiber of arbitrary length in which diffusion takes place solely through the fiber wall can be found in the literature⁹⁸. In the model presented in this thesis, the fiber radius R is assumed to be constant and fiber length $L \gg R$.

When the fiber length is assumed to be infinite and the concentration of ions zero at the outer surface of fiber ($r=R$), the time-dependent radial diffusion through the fiber wall can be described by Fick's second law in cylindrical coordinate systems:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right), 0 \leq r \leq R \quad (1)$$

where	C	concentration of electrolyte within fibers
	t	time
	D	diffusion coefficient of electrolyte within the fiber wall
	r	distance from the symmetry axis of fiber
	R	fiber radius

Eq. (1) can be solved for the following initial and boundary conditions ⁹⁸:

$$C = C_{max}, \quad \text{when } 0 \leq r \leq R \text{ and } t = 0 \quad (2a)$$

$$C = 0, \quad \text{when } r = R \text{ and } t > 0 \quad (2b)$$

$$\frac{\partial C}{\partial r} = 0, \quad \text{when } r = 0 \quad (2c)$$

The initial condition (2a) provides homogeneous distribution of concentrated electrolyte within the fibers before each experiment is initiated. Boundary condition (2b) can be stated only if stirring of the fiber suspension is effective and/or the diffusion coefficient of the electrolyte is much larger in water than within the fiber wall. Finally, boundary condition (2c) provides that the fibers are symmetrical and unbroken.

This approach does not take into account the water phase in the lumens but can be considered reasonable since there are always also collapsed fibers present with practically no water phase in the lumens. Furthermore, the cylindrical geometry even in the presence of collapsed fibers can be considered better than the plate geometry because even collapsed fibers cannot be considered very flat due to the thickness of fiber walls. Possible errors originating from the simplifications are discussed in more detail in Section 2.1.5.

If we assume effective mixing of the fiber suspension and that the radius of the fibers is constant, we can write Fick's first law for the molar flow of electrolyte through the fiber wall as follows

$$\dot{n} = AJ = -AD \left(\frac{\partial C}{\partial r} \right)_{r=R} \quad (3)$$

where \dot{n} molar flow of electrolyte through the fiber wall
 J molar flux of electrolyte through the fiber wall
 A total surface area of fibers

If we substitute $C = e^{-D\alpha^2 t} u(r)$, where $u(r)$ is a function of r only, we obtain from Eq. (1)

$$\frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} + \alpha^2 u = 0 \quad (4)$$

which is Bessel's differential equation of order zero.

Since the solution of the second kind in Eq. (4) is infinite at $r=0$, the solution is given solely by

$$C = aJ_0(\alpha r)e^{-D\alpha^2 t} \quad (5)$$

where J_0 is the Bessel function of order zero of the first kind.

To satisfy boundary condition (2b), α must be a root of

$$J_0(\alpha R) = 0 \quad (6)$$

This equation has no complex or repeated roots, but instead an infinite number of real positive roots. Thus, the solution of Eq. (4) can be given by the series expansion

$$C = \sum_{n=1}^{\infty} a_n J_0(\alpha_n r) e^{-D\alpha_n^2 t} \quad (7)$$

where n index corresponding to the n 'th root of Eq. (6)
 a_n coefficient of n 'th term

The constants a_n in Eq. (7) can be determined from the initial condition of Eq. (2a) ⁹⁹

$$C_{\max} = \sum_{n=1}^{\infty} a_n J_0(\alpha_n r) \quad (8)$$

If we use the theorem of orthogonal functions and substitute integration for summation, we obtain for the constants a_n ⁹⁹

$$a_n = \frac{2C_{\max}}{R\alpha_n J_1(\alpha_n R)} \quad (9)$$

where J_1 is the first-order Bessel function of the first kind.

After substitution of the constants a_n into Eq. (7) and by using definition $\beta_n = \alpha_n R$ we obtain ⁹⁹

$$C = 2C_{\max} \sum_{n=1}^{\infty} \frac{J_0(\beta_n r/R)}{\beta_n J_1(\beta_n)} e^{-\beta_n^2 Dt/R^2} \quad (10)$$

where β_n according to Eq. (6) is the n 'th root of Equation $J_0(\beta_n) = 0$.

If we differentiate C with respect to r , we obtain on the fiber surface ($r = R$)

$$\left(\frac{\partial C}{\partial r} \right)_{r=R} = \frac{-2C_{\max}}{R} \sum_{n=1}^{\infty} e^{-\beta_n^2 Dt/R^2} \quad (11)$$

The concentration of electrolyte in the water phase of the fiber suspension C_s^* can now be calculated from

$$C_s^* = \frac{\int_0^t n dt}{V_{H_2O}} \quad (12)$$

where V_{H_2O} is the volume of the suspension.

If we substitute Eq. (11) into Eq. (3) and combine the resulting equation with Eq. (12), we obtain after integration

$$C_s^* = AC_{\max} R \frac{2}{V_{H_2O}} \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} (1 - e^{-\beta_n^2 Dt/R^2}) \quad (13)$$

Eq. (13) gives the theoretical concentration of electrolyte in the water phase at different times of the diffusion experiment.

As mentioned earlier, it was desired to describe the dynamics of the measuring system with a transfer function to enhance accuracy. For this the linear concept of transfer functions is used, e.g. to describe transfer function G in the Laplace plane by Eq. (14):

$$f_{out}(s) = G(s) f_{in}(s) \quad (14)$$

where $f_{in}(s)$ Laplace transform of the theoretical relative concentration

$$\text{of electrolyte in the water phase, } f_{in}(s) = \frac{C_s^*(s)}{C_{s(\max)}^*} = \frac{L(C_s^*(t))}{C_{s(\max)}^*}$$

where L is the operator indicating the Laplace transform and $C_s^*(t) \rightarrow C_{s(\max)}^*$ according to Eq. 13 when $t \rightarrow \infty$.

$f_{out}(s)$ Laplace transform of the measured relative concentration of

$$\text{electrolyte in the water phase, } f_{out}(s) = \frac{C_s(s)}{C_{s(\max)}^*} = \frac{L(C_s(t))}{C_{s(\max)}^*}$$

$G(s)$ transfer function that describes the system's dynamic behavior satisfactorily

The transfer function can be obtained with certain assumptions from an experiment in which no pulp is used in the system but concentrated electrolyte is added to the measurement vessel at $t = 0$. For this case the shapes of the functions $f_{in}(t)$ and $f_{out}(t)$ are given schematically in Fig. 1.

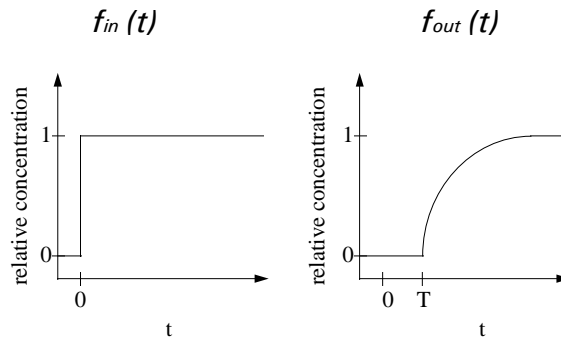


Figure 1. Shapes of functions $f_{in}(t)$ and $f_{out}(t)$ in an experiment where no pulp is used in the system and concentrated electrolyte is instead added at $t=0$.

In the above experiment the functions $f_{in}(t)$ and $f_{out}(t)$ can be expressed mathematically in a satisfactory way with Equations ¹⁰⁰

$$f_{in}(t) = 1, \text{ when } t > 0 \quad (15 \text{ a})$$

$$f_{out}(t) = 1 - e^{-(t-T)/k}, \text{ when } t > T \quad (15 \text{ b})$$

where k time constant
 T length of time delay

By finding Laplace transforms for Eqs. (15a) and (15b) and substituting the results in Eq. (14), and moreover by solving $G(s)$, we obtain

$$G(s) = \left(\frac{\frac{1}{k}}{s + \frac{1}{k}} \right) e^{-Ts} \quad (16)$$

Next we consider experiments performed by adding pulp in the measuring vessel at $t = 0$.

When we substitute $B = AC_{\max} R \frac{2}{V_{H_2O}}$ and $\gamma_n = \frac{D\beta_n^2}{R^2}$, we can find the Laplace transform for C_s^* given in Eq. (13) as follows

$$F_{in}(s) = B \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} \left(\frac{1}{s} - \frac{1}{s + \gamma_n} \right) \quad (17)$$

Substituting Eqs. (16) and (17) in Eq. (14) in the form of $F_{out} = G \cdot F_{in}$ gives

$$F_{out}(s) = B e^{-Ts} \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} \left(\frac{\frac{1}{k}}{s + \frac{1}{k}} \right) \left(\frac{\gamma_n}{s(s + \gamma_n)} \right) \quad (18)$$

Finally, if we use $u = t - T$, take the inverse Laplace transform of Eq. (18), and divide both sides of the resulting equation by the term $C_{s(\max)}^*$, we obtain for the relative concentration in the solution outside the fibers

$$\frac{C_s(u)}{C_{s(\max)}^*} = \frac{B}{C_{s(\max)}^*} \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} \left[1 + \left(\frac{\gamma_n}{\frac{1}{k} - \gamma_n} \right) e^{\left(\frac{-u}{k}\right)} - \left(\frac{\frac{1}{k}}{\frac{1}{k} - \gamma_n} \right) e^{-\gamma_n u} \right] \quad (19)$$

where $C_s(u) = f_{out}(u)$ and $C_{s(\max)}^*$ describes the concentration in the plateau region at the end of each experiment. The left-hand side of Eq. (19) can now conveniently be considered as a relative concentration.

In the present study seven first terms for Eq. (19) were found to adequately describe the experimental data. The first ten roots of equation $J_0(\beta_n) = 0$ are as follows ¹⁰¹: $\beta_1 = 2.40483$, $\beta_2 = 5.52009$, $\beta_3 = 8.65373$, $\beta_4 = 11.79153$, $\beta_5 = 14.93092$, $\beta_6 = 18.07106$, $\beta_7 = 21.21164$, $\beta_8 = 24.35247$, $\beta_9 = 27.49348$, $\beta_{10} = 30.63461$.

The diffusion coefficients can be calculated from the parameter D/R^2 which can be obtained from the curve fitting of Eq. (19). The value for time constant k can first be determined from the results of conductivity measurements with only electrolyte by fitting Eq. (15) to the experimental data.

2.1.3 Experimental

2.1.3.1 Materials

Unbeaten, never-dried Botnia Plus Birch totally chlorine-free (TCF) kraft pulp was selected for diffusion measurements and supplied by Metsä-Botnia, Kaskinen. Since birch pulp fibers do not have pit apertures diffusion occurs principally only through the fiber wall. Thus, the model presented describes the diffusion reasonably well.

Diffusion experiments were also conducted with fiber wall-loaded pulp containing 10% calcium carbonate by weight. Loading was performed for unbeaten fibers at 20 °C initial temperature using the carbon dioxide process (cf. Section 2.2).

According to scanning electron microscope (SEM) images and confocal laser microscopy the mean diameter of fibers used in this study was approximately 30 μm and 35 μm , when fibers were dried and suspended in water, respectively. The value 35 μm appears somewhat high in view of the typical average values for birch fibers but was used in this study since it was

obtained through direct observation with microscopic techniques. Whether the value is 35 μm or lower does not impact the relative order of diffusion coefficients obtained within different fibers of the same diameter. Potassium chloride (KCl; Merck, p.a.) was used in these experiments as model electrolyte.

2.1.3.2 Apparatus and measurements

All measurements were made in a thermostatted vessel at 5 $^{\circ}\text{C}$ with a liquid volume of 500 mL provided with effective stirring. A schematic view of the apparatus is shown in Fig. 2.

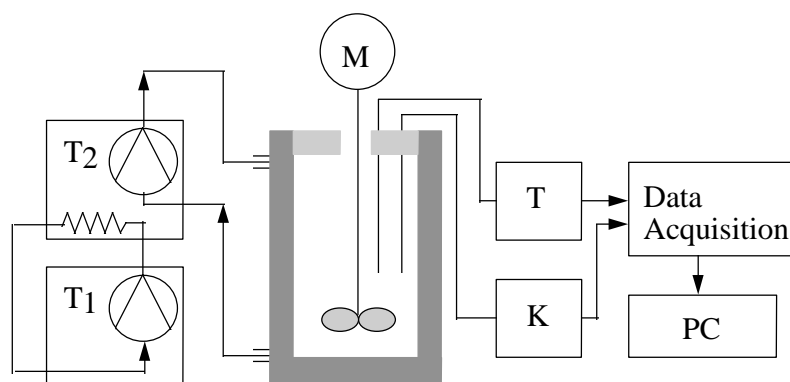


Figure 2. Schematic setup of apparatus used for the diffusion measurements. T_1 = thermostat filled with ice water for controlling temperature of the cooling circulation of thermostat T_2 , T_2 = thermostat for controlling temperature of measurement vessel to 5 $^{\circ}\text{C}$, T = temperature gauge, K = conductivity gauge.

The stirring rate was 750 1/min and the hydrodynamic conditions in each experiment were kept as constant as possible.

To determine time delay T and time constant k which originate from small errors in starting data collecting at $t = 0$ and dynamic effects of mixing and conductivity monitoring, conductivity of water in which 3 molar potassium chloride solution was added at $t = 0$ was first measured. The total amount of

potassium chloride added was set to the same level as in experiments with fibers.

To obtain the electrolyte diffusion coefficients the fibers were first thoroughly saturated with 3 molar potassium chloride solution and pressed until the fibers contained practically no external solution. At $t = 0$ a sample of fibers was placed in the measurement vessel and suspended instantly with stirring. The increase in potassium chloride concentration outside the fibers was followed by measuring the conductivity of the solution with respect to time. It is generally known that concentration and conductivity are almost directly proportional in dilute solutions. The diffusion coefficients of potassium chloride inside the cell wall were calculated from the concentration curve as described in Section 2.1.2.

Preliminary experiments showed that fiber consistency had no effect on the diffusion coefficients. In the actual measurements the amount of fibers in each measurement was 0.25 g O.D. (oven dry). Experiments were made both for fibers with and without precipitated calcium carbonate inside the cell wall.

2.1.4 Results

According to the preliminary experiments the amount of fibers did not affect the dynamics of the conductivity measurements at concentrations < 2 g dry fibers/1000 mL of suspension. The amount of fibers used in actual experiments was small enough to permit assumption of zero concentration of electrolyte at the fiber surface. The final concentration of electrolyte in the water phase at the end of each experiment was not actually zero but remained so small compared with that inside the fibers at the beginning of each experiment that this assumption could be made with reasonable accuracy. The value of time constant k was first determined to be 0.79 s

from the results of conductivity measurements using only electrolyte by fitting Eq. (15b) to the experimental data ¹⁰².

To calculate the diffusion coefficients within the fiber wall Eq. (19) was fitted to the experimental data obtained from measurements with pulp suspensions (by means of a nonlinear curve-fitting procedure)¹⁰². As a result the best-fit values for parameters B , D/R^2 , T , and the initial level of relative concentration could be solved. Fixing the initial level of relative concentration was not desired due to possible slight deviations from zero. Furthermore, the value of time delay T was impossible to control exactly. Therefore, it was not fixed but changed as a fitting parameter in each individual experiment. From the values of parameter D/R^2 we could evaluate diffusion coefficient D within the fiber wall when the mean diameter of fibers was known. The theoretical equation (solid curve) fitted quite accurately to the experimental data (dots) as can be seen from the data-fitting example presented in Fig. 3.

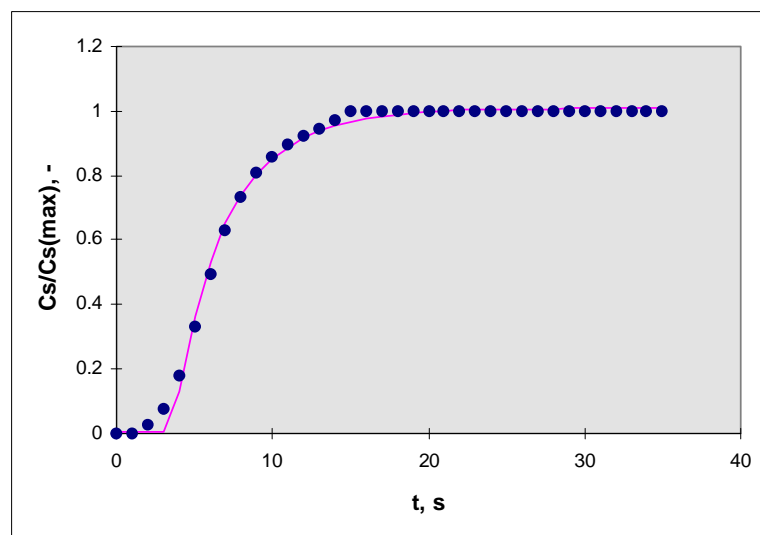


Figure 3. Results from a typical experiment, in which diffusion of KCl through fiber wall was followed by measuring the concentration (conductivity) of electrolyte outside the fibers at 5 °C. Solid curve = theoretical curve.

Measurements were repeated for filled and unfilled fibers as well as with electrolyte alone to minimize the effect of the variation. The mean relative concentration curves for each case were obtained (Fig. 4).

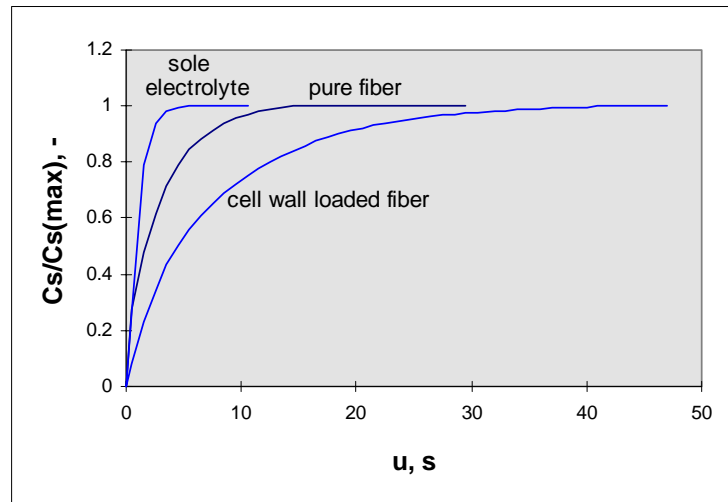


Figure 4. Results (mean curves) from diffusion experiments in which diffusion of KCl through both unfilled and CaCO_3 -filled fiber wall was followed by measuring the concentration (conductivity) of electrolyte outside the fibers at 5 °C compared with KCl alone at 5 °C. $u = t$ -length of time delay.

Diffusion coefficients were calculated as presented in Section 2.1.2 and are tabulated in Table 3 together with the values of parameter D/R^2 from the curve-fitting of Eq. (19). Confidence intervals were calculated from the variation in repetitive measurements.

Table 3. Values of diffusion coefficients of KCl at 5 °C within both unfilled and CaCO₃-filled fiber wall when the mean radius of fibers in water is taken to be 17.5 μm, and including parameters from the curve fit of Eq. (19) with confidence intervals at 95% confidence level.

	Unfilled fiber	CaCO ₃ - filled fiber (10% CaCO ₃ by weight)
$D_{\text{KCl}}, \text{m}^2/\text{s}$	$14.6 \pm 4.5 \cdot 10^{-12}$	$5.7 \pm 1.0 \cdot 10^{-12}$
$D/R^2, \text{s}^{-1}$	$47.8 \pm 14.9 \cdot 10^{-3}$	$18.6 \pm 3.2 \cdot 10^{-3}$

It can be seen from Fig. 4 that the concentration of electrolyte increases much more rapidly in experiments with unfilled fiber than with cell wall-filled fiber. This indicates that the diffusion through the unfilled fiber wall is distinctly more rapid than that through the CaCO₃-loaded fiber wall. This is also indicated as a decrease in diffusion coefficient of potassium chloride within the loaded fiber wall.

2.1.5 Discussion

A good fit for the model was obtained with data from the experiments. Information is limitedly available in the literature on diffusion coefficients within pulp fiber walls. Still, to validate the results the literature available concerning both methods and results obtained in other diffusion studies with other types of materials is briefly referred to.

Conductometry was found to be a promising method for measuring consistency of pulp suspensions since the conductance of a pulp suspension

is known to be a linear function of pulp consistency¹⁰³. However, conductometry is sensitive to the natures of both the fibers and the aqueous medium, which restricts its use for this purpose. Since the ionic diffusivities are directly proportional to the ionic mobilities, analysis of pulp suspension conductivity data may, however, give some insight into the rate of diffusion inside the fiber wall. Been and Oloman⁹⁶ estimated from the conductivity data of fiber suspensions that the ionic diffusivity in the thermomechanical pulp (TMP) fiber wall was about 50% of the corresponding value in the bulk solution. However, the brokenness of TMP fibers apparently complicated calculation of the true diffusivities inside the fiber wall.

Ostrowska et al.¹⁰⁴ calculated the concentration-dependent diffusion coefficients of a dispersed dye in anionically modified polyester fiber by using the grid method and data from experimental concentration profiles. Assuming cylindrical symmetry of the fiber, the value of the diffusion coefficient varied between $0.6 \cdot 10^{-15} \text{ m}^2/\text{s}$ and $2.0 \cdot 10^{-15} \text{ m}^2/\text{s}$, depending on the concentration.

Briggs et al.¹⁰⁵ measured diffusivities of counterions inside beet disks that were between 11 and 13 times smaller than that at infinite dilution.

According to Stamm¹⁰⁶ and Cady et al.¹⁰⁷ diffusion rates in a cross direction of wood are usually between 10% and 35% of the values in water, and the decrease is linked to the physical properties of wood, such as reduced effective cross-sectional area and mechanical blocking. Diffusion within the fibers and wood is, however, difficult to compare, because diffusion in wood also occurs through cracks and other defects. Both chemical and physical characteristics of wood and pulp are also different. Diffusion coefficients even within different types of fibers may differ appreciably, depending on the origin of the fiber and the method of cooking and bleaching.

In the present study a method was desired that completely omits the diffusion between the fibers, in contrast to many other methods, and considers only intrafiber diffusion. With the aid of this method and the theory presented here diffusion can be measured just within the fiber wall. Moreover, experimental data in this study were collected as a function of time, which is of obvious advantage in studying kinetic phenomena such as diffusion.

The value of the diffusion coefficient of potassium chloride in a very dilute aqueous solution at 5 °C extrapolated by using the data of Lobo et al.¹⁰⁸ at different temperatures is $1.0155 \cdot 10^{-9} \text{ m}^2/\text{s}$. Thus, the value of the diffusion coefficient of potassium chloride in the transverse direction of fibers within the unbeaten birch fiber wall found in this study was 1/70 of that in dilute aqueous solution. Luner¹⁰⁹ referred that swelling of fibers considerably affects diffusion in the transverse direction of fibers. As is generally known, the tendency of unbeaten fiber to swell is quite small. Furthermore, birch fibers do not have pit apertures facilitating diffusion. By considering this information and the facts discussed above, the diffusion coefficients obtained in this study appear to be of the right order of magnitude and in harmony with the results from studies with other types of cellulosic materials. Moreover, the difference between the diffusion coefficients of potassium chloride in water and within the fiber wall justifies assumption of the boundary condition (2b), i.e. diffusion in the concentration polarization layer located on the surface of the fiber is much faster compared with diffusion within the fiber wall.

The differences in diffusion coefficients of potassium chloride regarding loaded and unloaded fibers can also be assumed to reasonably well describe the differences in diffusion of the raw materials of calcium carbonate during precipitation. It is also assumed that possible waterflow pulses into the fibers originating from osmotic pressure differences when fibers were placed in the measurement vessel did not appreciably affect the diffusion coefficients

obtained. This assumption can be made with reasonable accuracy because the fibers were unbeaten with a low tendency to swell, and because attempts were made to press the fibers after saturation only until the external solution was removed. These assumptions and the diffusion coefficients obtained suggest that the concentrations of raw materials in calcium carbonate precipitation are very small inside the fiber wall compared with those in bulk solution and on the surfaces of fibers. According to Nývlt²³ crystal growth rate increases linearly and nucleation rate exponentially with supersaturation. Thus, the tendency toward precipitation is much larger on the surface and at close proximity to the surface within the fiber wall as well as in the bulk solution than deeper inside the fiber wall or in the lumen. Moreover, the diffusion coefficient within a pure fiber wall is about 3 times larger than that within a CaCO₃-loaded fiber wall. These facts can be assumed to limit considerably the loading of fibers without pit apertures.

The cylindrical geometry used in the model fairly well describes the diffusion, as long as the fibers are not badly collapsed. This idealization might have caused some errors in this study because there are always at least small fractions of collapsed fibers present. However, the geometry used better describes the diffusion compared with plate geometry because even collapsed fibers cannot be considered very flat due to the thickness of the fiber walls. In addition, possible slight errors in diffusion coefficients are apparently due to the fact that the diffusion model presented does not consider the water phase in the lumens of fibers. Once again, since there are also collapsed fibers present with practically no water phase in the lumens, this approach can also be considered fairly good.

The diameter of fibers was assumed to be constant, which also apparently caused some errors. Furthermore, the transfer function determined did not describe the dynamics originating from the possible delay in suspending fibers

at the beginning of each experiment, which could have caused slight errors. The impact of the latter was probably very small since fibers appeared to be suspended instantly when examined visually.

Although fibers in the model were treated as infinite cylinders, the impact of the ends of the actual fibers on diffusion coefficient estimation was negligible, due to very low surface area of the ends compared with the area of the entire fiber surface. Since conditions in each measurement were kept as constant as possible, these errors apparently did not affect the order of the diffusion coefficients concerning each fiber sample.

2.2 Fiber loading and impacts of loaded fibers on paper properties

2.2.1 Experimental

To obtain more explicit information on fiber loading, some precipitation experiments were performed. Loading was performed in stirred tank reactors both at low and medium pulp consistencies by leading carbon dioxide gas into a slurry of calcium hydroxide and bleached chemical pulps of different refining degrees. The hardwood (HW) pulps used in the low-consistency loading experiments were beaten (31 °SR) and unbeaten for preliminary and verification experiments, respectively. Some of the loaded samples were washed to remove the crystals outside the fibers. However, postprecipitation refining was also investigated for the same reason in the verification experiments in which loading was performed at low consistency for a 75/25 mixture of HW and softwood (SW) pulps beaten together for 2 min with no load followed by 5 min with a 2.268-kg weight. The HW pulp (20 °SR) was used in medium-consistency loading experiments.

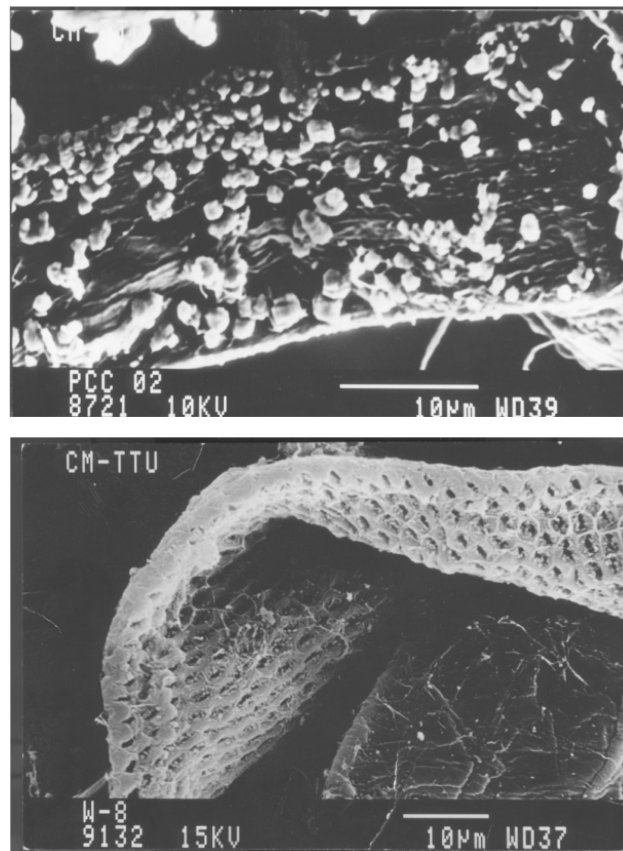
Fiber stiffness was measured with Steadman's method ¹¹⁰ in some of the loaded samples and compared with that of unloaded samples. The quality and location of calcium carbonate were estimated with SEM and the amount measured by weighing the residue of the washed fibers after burning.

A number of 60 g/m², 75 g/m², and 80 g/m² handsheets were made for paper testing with varying amounts of loaded fiber and commercial calcium carbonate. In the low-consistency experiments the furnish consisted of bleached HW and SW pulps at 55/45 and 75/25 ratios for the preliminary and verification experiments, respectively. In the medium-consistency experiments, the furnish consisted of 60% HW pulp and 40% SW pulp. With reference fillers the pulps used in sheetmaking were always treated similarly as those used in fiber loading. A more detailed description of the furnish refining degrees, sheetmaking procedures, paper testing, and other experimental conditions is presented in Appendix 1.

2.2.2 Results and discussion

2.2.2.1 Precipitation of calcium carbonate in the presence of hardwood kraft pulp fibers using the carbon dioxide process at low pulp consistency

In preliminary experiments a typical crystal size achieved on fiber surfaces was approximately 1-2 μm in diameter but smaller within the cell walls. Typical examples can be seen in the SEM micrographs presented in Fig. 5.



*Figure 5. Magnifications of calcium carbonate crystals precipitated onto fiber surfaces and within the cell wall of a vessel tracheid.*⁸⁸

It was also concluded from the SEM micrographs that calcium carbonate was basically not precipitated in the lumens of fibers. This can clearly be seen in a sample micrograph presented in Fig. 6.

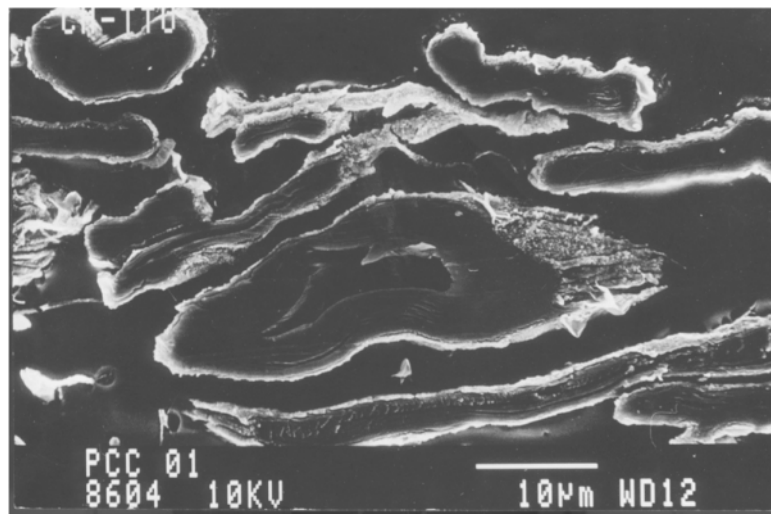


Figure 6. Cross sections of loaded fibers with no visible calcium carbonate particles in the lumen. The calcium carbonate content of the sample was 11%.⁸⁸

Pulp loading levels of up to 13% were typically achieved in these preliminary experiments. These were the typical filler levels of washed pulp samples which may also include certain amounts of calcium carbonate on fiber surfaces tightly bound to fibrils. Thus, it was assumed that the calcium carbonate in the washed samples was at least partly located within the cell walls, since it was not seen in the lumens of unbroken fibers nor considerably on the fiber surfaces. However, when examining Fig. 6 carefully there appears to be a small amount of very small particles on the fiber surfaces. Attempts to analyze the exact location of the calcium carbonate within the cell wall were not made. However, based on the results presented in Section 2.1 it can be assumed that the calcium carbonate was located in the first surface layers or on the surface of fibers rather than deeper inside. Furthermore, the calcium carbonate crystals were seen in the pores of vessel tracheids (Fig. 5). Table 4 summarizes the calcium carbonate contents of the samples.

Table 4. Calcium carbonate contents of loaded pulp samples after washing with water ⁸⁸. The amount of water used in washing is presented in parentheses. The samples selected for sheetmaking are marked with an asterisk.

	CaCO ₃ content of pulp after washing, %
Sample A *	8.4 (24 L)
Sample B *	12.3 (24 L)
Sample C	12.9 (24 L)
Sample D *	39.0 (8 L)

It can be concluded that sample D was not washed thoroughly enough to remove particles precipitated in bulk solution or on the fiber surfaces. The low loading degrees suggest that most of the calcium carbonate precipitated elsewhere from the lumen or cell wall. The additives used during carbonation basically did not alter the crystal size and morphology of calcium carbonate in those experiments from which loaded pulps were selected for sheet production.

Although the fiber loading was found to have no effect on bulk and no statistically significant impact on fiber stiffness⁸⁸ based on the paper-testing results with HW 55%/SW 45% furnish, the bending stiffness of paper appeared to slightly increase compared with commercial PCC. The light scattering coefficient of paper was similar to that of paper with PCC filler added normally to the stock. Fiber loading decreased tensile index considerably, by approximately 15% compared with commercial PCC of the same filler level in these experiments, even though fibers were washed to remove filler particles outside the fibers after precipitation. The commercial reference PCC was scalenohedral with a specific surface area (SSA) of 11 m²/g.

The increase in bending stiffness was supported by subsequent experiments in which the opacity and strength of paper with fibers including fiber-loaded calcium carbonate were lower compared with commercial PCC (Appendix 2). Depending on loading level, the stiffness increased by maximum 25% with fibers including fiber-loaded calcium carbonate at approximately 22% filler level. However, at filler levels close to 15% and 30% the increase was considerably lower. In these experiments the hardwood/softwood ratio was 75/25 and the proportion of loaded pulp between 0% and 60% of the total amount of hardwood. The commercial PCC used was prismatic (SSA 7 m²/g). Given the sensitivity of stiffness measurement to paper density, which unfortunately was not recorded in the verification experiments, the reason for the observed increase in stiffness could not be completely clarified. However, since the measurements were performed carefully using at least 3 different filler levels, and because the increase in stiffness was seen in different sets of experiments, there is a great confidence that the findings are correct. Furthermore, the paper-testing results are the mean values of replicated measurements taken to improve accuracy.

It can be assumed that the loaded fibers behaved differently, regarding the measured and effective thickness of paper, which can be considered among the most probable factors explaining the increase in bending stiffness with no increase in bulk and tensile index. Certain complicated interactions may also occur between loaded fibers and other components in the fiber network that cannot be predicted from the properties of single fibers. These types of metafiber properties ^{111, 112} may occur even though measurements of single fibers do not show statistically significant differences. A uniform z-directional filler distribution in paper may be another explanation, which can be concluded from the SEM micrograph presented in Fig. 7.

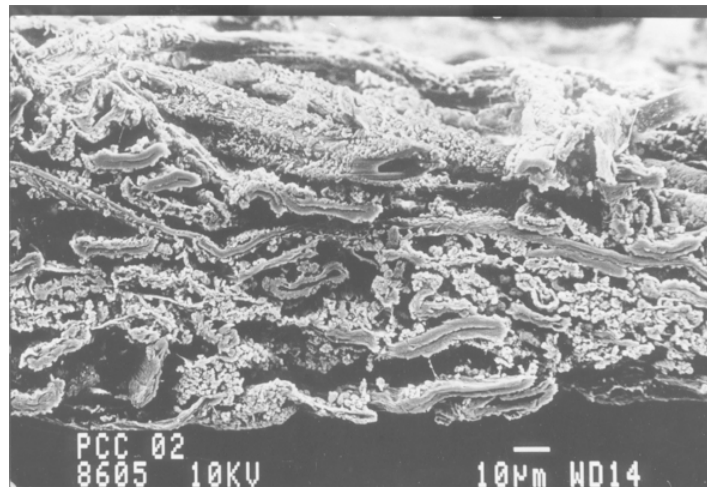


Figure 7. Cross section of paper made with unwashed loaded pulp showing uniform z-directional filler distribution. ⁸⁸

Z-directional filler distribution is known to have an impact on bending stiffness ¹¹³.

Thus, although fiber wall loading appears to have a positive impact on paper stiffness, there are also major disadvantages. First, the use of cell wall loaded pulp prepared at low pulp consistency had a negative impact on paper strength. This is probably due to the fact that precipitation occurs on fiber surfaces rather than inside the fibers, causing changes in fiber surface properties. This may reduce the hydrogen bonding ability of fibers, which was however not seen as an improved light scattering coefficient, probably due to unfavorable crystal morphology of calcium carbonate formed during loading, nor was it seen as lowered density. Possible changes in fiber structure that were not seen in the fiber stiffness measurement may also have resulted in the observed reduction in strength.

The postprecipitation refining improved paper strength, but the increase in paper stiffness was lost. In these experiments opacity and brightness were also lower compared with the reference (scalenohedral PCC with SSA 11

m²/g). SEM micrographs clearly showed that refining removed particles from fiber surfaces. Improved strength is in line with an earlier assumption that particles precipitated on fiber surfaces may have reduced paper strength through changes in fiber surface properties. It is also in harmony with the assumption that improved paper stiffness may have resulted from more uniform z-directional filler distribution, which was now lost when particles were removed from fiber surfaces by refining. Detached particles were free to relocate in sheetmaking, which perhaps resulted in a less uniform z-directional filler distribution. Alternatively, the fiber structure itself was probably altered in such a way that the increase in paper stiffness was no longer seen.

The second major disadvantage regarding fiber loading at low consistency in general is that the total volume of the slurry may become impractically large, resulting in either very large or numerous reactors. Third, the consistency of calcium hydroxide is far from the optimum considered to be much higher than that used in these precipitation experiments. Within the optimum region, precipitation can be done economically.

The results are mainly in line with those reported in the literature, supporting both advantages and disadvantages of loading by this process. The increase in paper stiffness was not mentioned in the literature cited. By considering the facts presented above, fiber loading does not appear attractive in low-consistency pulp suspensions; instead medium or high consistencies should be considered.

2.2.2.2 Precipitation of calcium carbonate in the presence of birch kraft pulp fibers using the carbon dioxide process at medium pulp consistency

Fiber loading by means of the carbon dioxide process at medium pulp consistency was limitedly studied in this part of the thesis. The feasibility of this method with respect to both the precipitation process and paper properties was compared with those of the low-consistency experiments.

The precipitation reaction was found to proceed seven times faster in the pressurized mixer (initial pressure 10 bar, 100% carbon dioxide) at 10% pulp consistency than in a normal pressure mixer (20% carbon dioxide) at low consistency. However, if it is assumed that the reaction order with respect to carbon dioxide partial pressure is approximately 1, the reaction rates become almost equal in both cases if estimated for 20% carbon dioxide. Although the total pressure was higher at medium consistency, the reaction rate was presumably limited by the smaller volume of bulk water, in which ions can transfer to the fibers.

The precipitated calcium carbonate was pure calcite, based on the x-ray diffraction measurement. The average crystal size on the fiber surfaces was approximately between 0.5 μm and 1 μm in diameter. The crystal shape was roundish. The calcium carbonate content of washed pulp samples was approximately 10%; this level may also contain certain amounts of calcium carbonate on the fiber surfaces tightly bound to fibrils, as indicated in SEM micrographs.

The paper made of cell wall-loaded fibers was between 1% and 4% stiffer and 7% bulkier than paper filled with commercial PCC at the same filler content, whereas tensile strength and brightness were equal. Although the

increase in stiffness is moderate it is not unusual, since the papers were also bulkier. Thus, the result can be considered plausible. The paper strength achieved can be considered good, since it was achieved without external washing of loaded fibers. As mentioned earlier, if loading is done at low consistency, fibers must be washed extremely well after precipitation to maintain even satisfactory paper strength.

Good strength at medium consistency was first assumed to be due to the lower amount of bulk water present in precipitation, resulting in higher probability of calcium carbonate precipitation within the fiber walls. The loading degree was, however, not higher than that achieved at low consistency. The probable explanation is that high shear within a medium-consistency mixer more effectively detaches the particles precipitated on the fiber surfaces, resulting in better fiber bonding in papermaking. High shear apparently also further fibrillates the pulp resulting in higher paper strength in the experiments.

The opacity of fiber-loaded paper was between 2% and 3% lower than that of paper filled with commercial PCC (prismatic, SSA 7 m²/g). The most relevant paper properties are presented in Appendix 3.

The experiments by Klungness *et al.*¹¹⁴ revealed that loading performed in pressurized disc refiners at medium consistency increased paper density, which was compensated for by decreasing the wet-web pressing pressure. Furthermore, wet-end starch was required to regain the strength loss associated with decreased wet pressing. Thus, in view of this information, loading performed in a medium-consistency mixer appears more advantageous.

2.3 Conclusions

Diffusion coefficients of ions within unfilled and CaCO₃-filled fiber walls were estimated to be about 1.5% and 0.5% of that in dilute aqueous solution, respectively, when experiments were done for bleached birch kraft fibers. When incorporating this result into the fiber loading, it can be pointed out, that in theory the tendency of calcium carbonate to precipitate in the lumen or at least deeper within the fiber wall during the loading process is limited, when precipitation is performed using the reaction between calcium hydroxide and carbon dioxide. This applies at least to birch fibers without pit apertures.

Paper stiffness may be slightly increased using the loaded pulp in the furnish, without considerably sacrificing other paper properties, only when loading is performed in a medium-consistency mixer. However, fiber loading appears to offer no significant benefits compared with fillers added normally to the stock. Loading at medium consistency has advantages over the same treatment at low consistency with respect to paper strength and economics of the precipitation.

The filler particles precipitated within the fiber walls may be too small for effective light scattering. Furthermore, since the refractive indices of fiber and calcium carbonates are very similar^{115, 116} (fiber 1.55, GCC 1.56, PCC 1.59), the pigment-to-fiber interfaces within fiber walls do not practically scatter light. Instead, pigment-to-air interfaces should be maximized, which cannot be achieved through fiber loading.

3 FINES-FILLER COMPOSITE: SUPERFILL TECHNOLOGY

3.1 The idea of fines-filler composite technology

Because of the major tendency of calcium carbonate to precipitate on the surfaces of fibers, it was thought that an effective filler may be achieved by precipitating calcium carbonate on fibrillar pulp fines with thicknesses of approximately the same range as the diameter of filler particles.

This idea was first tested on a laboratory scale, using kraft pulp fines produced by beating.

This new filler provided paper with a significantly improved combination of optical properties and paper strength compared with commercial PCC fillers of the same morphology and crystal size. When adding the filler to the paper the decrease in tensile strength was only approximately one half of that which occurs with the same amount of commercial PCC of the same crystal size and morphology. The new filler also provided paper with a significantly improved light scattering coefficient compared with commercial PCC of the same crystal size and morphology at the same calcium carbonate level. Under laboratory conditions it nearly doubled the light scattering coefficient of paper at constant tensile index and Scott bond compared with commercial PCC. The experimental results are illustrated in more detail in Chapter 4.

The structure of the new filler is unusual. SEM analysis revealed that calcium carbonate crystals are precipitated on fibrils, resulting in chainlike structures in which calcium carbonate crystals are supported by the fibrils. This structure can clearly be seen from the SEM micrograph presented in Fig. 8.

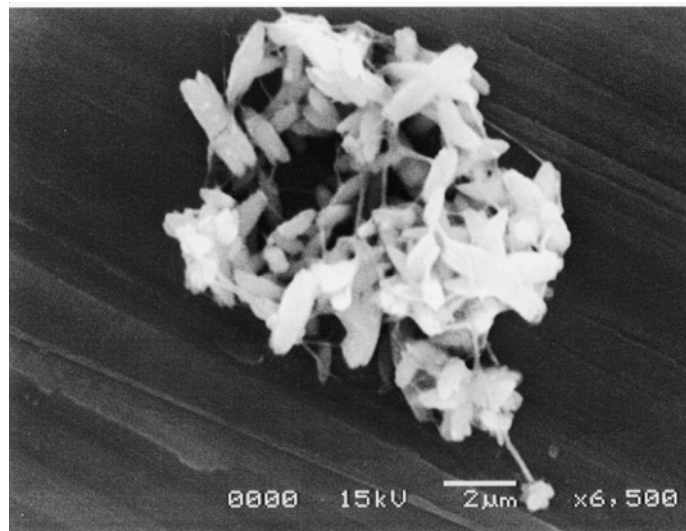


Figure 8. Calcium carbonate precipitated on filamentous SW kraft pulp fines produced by beating and fractionating (SuperFill).

The production technique can be considered as an *in-situ* precipitation, but it differs from fiber or lumen loading by the proportions of cellulosic material and calcium carbonate, and by the type of cellulosic material. The filler in question is mainly composed of calcium carbonate, whereas loaded fibers contain relatively low proportions of calcium carbonate. Moreover, the cellulosic part of the new filler is composed mainly of narrow fibrils instead of fibers. Normal principles of precipitation are valid in the production of this filler.

These results together with data presented later suggest a particular mechanism of the filler, as hypothetically presented in Section 3.2 and clarified in more detail in Chapter 5. Due to significantly improved paper properties the fines-filler composite and related technology were named SuperFill. Since this name is short and describes well the function, effect, and application of the material, it has been used later in this thesis to denote this filler. The longer term, the "fines-filler composite", is used only in headings. The rest of this thesis is devoted to explaining in detail the SuperFill technology and its benefits.

3.2 Hypotheses

The general hypothesis is that improved combinations of critical properties and process parameters of printing and writing papers and paperboards can be achieved with SuperFill. The combinations in question are presented in Section 4.1.1. In SuperFill production the hypothesis is that calcium carbonate can be precipitated on kraft pulp fines.

The improved paper quality obtained may be explained by the particular mechanism of SuperFill in paper. In view of the preliminary results presented in Section 3.1 and information from the literature (Section 4.1.2 and Chapter 5), it can be suggested that the hypothetical mechanism is composed of different elements. First, SuperFill may provide paper with a more uniform spatial filler distribution with reduced agglomeration resulting in higher paper light scattering coefficient. Second, the fines fraction of SuperFill most probably contributes to bonding, resulting in increased paper strength. Third, SuperFill may influence paper in such a way that different pore structure is achieved. The structure may be beneficial with respect to light scattering coefficient of paper. The mechanism is discussed in more detail in Chapter 5 together with the respective literature.

Experiments to verify these hypotheses are presented and discussed in Chapters 4, 5, and 7.

4 IMPACT OF FINES-FILLER COMPOSITE ON CRITICAL PROPERTY COMBINATIONS AND PROCESS PARAMETERS OF PRINTING AND WRITING PAPERS AND PAPERBOARDS

4.1 Introduction

4.1.1 Critical property combinations

Depending on the application, papers and boards have certain properties or property combinations that are critical for particular end uses. In this chapter the focus is on printing and writing papers and paperboards. The approach is to treat product- and process-state variables principally as presented by Ryti and Aaltonen ¹¹⁷ and more recently by Levlin and Paulapuro ¹¹⁸, when applicable to filler comparison. However, since exact end-use application was not desired here the approach used is more general, including rough product and process analyses on various end products. The emphasis is on critical command variables, i.e. those variables with advantageous effects on one or more of the important properties of the product and disadvantageous effects on some other product properties.

Opacity and strength normally form a critical property combination in printing and writing papers. However, under circumstances in which grammage is lowered, density and stiffness also become critical properties. As is well known, density has a very strong impact on paper stiffness. In certain applications, particularly in copying paper, opacity, brightness, and bending stiffness are the most critical properties. Opacity can be increased by using more filler in paper. This, however, changes paper structure in such a way that the strength and stiffness of paper decrease. Furthermore, paper stiffness can be maintained by methods that increase paper thickness by decreasing density. A drawback is that this usually has a negative effect on paper strength. Thus, critical properties can be considered normally more or

less as compromises. If a critical property is improved, another becomes weakened.

The pore structure of paper is a relevant property, regarding both printability and opacity. Good internal bond strength of paper is required in offset printing. In certain paperboard applications, especially in the case of white top linerboard which consists of a whiter top layer and darker backing layer, the customer requires both good brightness and burst strength. The relevance of burst strength has decreased lately, but a certain level is still required. Crush tests are also used to estimate liner behavior in the end product. Since the liner is relatively thick, opacity of the entire structure is not critical. However, opacity of the brighter top layer is critical, since it masks the darker backing layer. Thus, light scattering coefficient of the top layer has a strong impact on the brightness of the liner. For economical reasons the top layer should also be thinner, which may be possible by using SuperFill as a filler in this layer. Good formation is also important for most of the paper and board products.

In view of these facts, the measures that reasonably well describe the effect of raw materials on the performance of printing and writing papers and some boards included light scattering coefficient, brightness, tensile strength, Scott bond, burst strength, density, bending stiffness, pore size distribution, air resistance, and formation. The critical command variables are filler content of the sheet and paper grammage, when comparing SuperFill with reference fillers. Furthermore, when comparing different SuperFill qualities, the calcium carbonate portion of SuperFill is included. SuperFill qualities with different fines sources are also compared.

4.1.2 Retention and formation

Retaining of fillers by the fiber network is among the important processes in papermaking. Retention can occur right in the stock when fillers and fibers are put together, or by filtration in the wire section. Retention can be both mechanical and chemical in nature.¹¹⁹ It has been shown that mechanical retention is minor in the furnish due to high turbulence¹²⁰ and small size of filler particles. In the wire section mechanical retention is higher, but it typically results in not more than a 30% filler retention¹²¹.

The size and shape of filler particles naturally affect retention. At conditions of equilibrium in dynamic systems the amount of pigments located on fiber surfaces decreases with increasing filler size. At the same time the role of filtration increases.¹²² Simple coagulation is not sufficient to retain fillers under high-shear conditions¹¹⁹, and filler particles are normally so small that mechanisms other than simply mechanical retention are required to achieve desired filler level. Thus, specific retention agents are used to bind fillers to the fibers.

The target is to get the filler particles to attach to the fibers prior to forming section. Chemical retention is dependent on the configuration and charge of the retention polymer. A vast literature exists on retention aids and the mechanisms of retention^{123, 124}. Polymers can also be used for preflocculation of fillers¹²⁵ and coflocculation of fillers and fines¹²⁶, which can contribute to mechanical retention. These flocculation techniques, however, do not appear too attractive in terms of paper properties, as clarified later.

Since polymers also cause flocculation and agglomeration of filler particles and pulp fines^{121, 120, 127} they further tend to impair paper formation, which often limits the effective use of retention aids. Thus, retention and formation are normally more or less compromises, i.e. improvement in one impairs the

other. One consequence is that paper is typically produced with relatively low retention to achieve desired formation. This results in high white water consistency with several problems¹²⁸. Commercial retention systems are also known to be relatively sensitive to chemical changes in water circulations.

Formation is greatly affected by forming conditions as well. The novel forming concepts such as gap formers with combined roll- and blade-forming units have improved the situation regarding the combination of formation and retention. The differences in formation between the forming concepts are caused by the differences in speed-difference (shear) fields. In addition to retention, formation is typically affected by simultaneous phenomena occurring in the wire section such as drainage, shear forces due to speed difference in the stock, as well as the state of flocculation in the headbox jet.

129

There are also furnish-related quantities that are clearly correlated with formation when paper is formed with the same forming section^{130, 131}. Fiber length and coarseness, i.e. mass of a single fiber, are clearly correlated with formation potential^{132, 133, 134, 130}. Kerekes *et al.*¹³⁵ developed the so-called crowding number to describe flocculation tendencies.

SuperFill technology may offer a new route to improve both formation and retention simultaneously, since filler retention may be decreasingly dependent upon chemical retention, flocculation, and agglomeration. The following chapters summarize some examples of the most relevant results regarding critical property combinations and process parameters of printing and writing papers and some boards that can be improved with SuperFill technology.

4.2 Experimental

4.2.1 Fines production and analyses

The fines carrier of SuperFill was produced on a laboratory scale by beating with a Voith Sulzer refiner or in a Valley laboratory hollander. With the Voith Sulzer refiner the specific edge load was 0.25 Ws/m for hardwoods and 0.75 Ws/m for softwood. Highly beaten pulp produced with the hollander was fractionated with a Bauer McNett apparatus using 14-, 50-, 100-, and 200-mesh screens. The fraction that passed through the 200-mesh wire screen (P200) was allowed to settle, whereupon the aqueous phase was separated. This fraction was used to produce SuperFill. The conditions and analyses are presented in more detail in Appendix 4.

Fines were produced at pilot and mill scale with the JC-01 refiner by Metso Corporation with SF (Short Fine) fillings. The products were not fractionated. Analyses performed after each refiner stage included the Schopper-Riegler number and fiber length. Bauer McNett distributions were measured after all refiner stages, according to the standard SCAN-M6. The conditions and analyses are presented in more detail in Appendices 5 and 6.

Different bleached kraft pulps were investigated as fines sources for SuperFill, as presented in more detail in the appendices. The energy needed for reaching the appropriate refining degree with each pulp was measured.

4.2.2 Fines-filler composite production and analyses

Carbonation, i.e. precipitation to form calcium carbonate, was performed on a laboratory scale either in 4- or 30-L stirred-tank reactors in which carbon dioxide with 20% partial pressure was introduced into the reactor filled with appropriate amounts of fines and calcium hydroxide. The reaction was

followed by measuring pH and conductivity. The calcium carbonate content of SuperFill was varied to determine the optimum region in terms of paper properties.

For pilot- and mill-scale paper machine trials SuperFill was produced on-site at PCC plants. The same principles of carbonation are valid for both laboratory and mill scale. The initial temperature mainly used was 55 °C, resulting in scalenohedral crystals between 1.2 µm and 2.2 µm in size. However, for all trials references were selected so that the psd (particle size distribution) of a reference PCC was roughly the same as that seen in SuperFill. For pilot- and mill-scale paper machine trials SuperFill with 70% calcium carbonate content by weight was produced. The SuperFill was cleaned with centrifugal cleaners after carbonation to remove sand and other impurities. The structure of SuperFill was analyzed visually from SEM micrographs and the calcium carbonate portion measured by titration. The SSA of precipitated calcium carbonate in SuperFill was estimated using nitrogen adsorption and psd visually from SEM micrographs.

The conditions and analyses are presented in more detail in Appendices 4-6.

4.2.3 Paper production and testing

A number of 60-g/m² laboratory handsheets without circulation water were made for paper testing, according to the standards SCAN-C 26:76 and SCAN-M 5:76, except in the use of retention system and filler addition. Sodium silicate between 0.05% and 0.15% of fibers and starch, 0.65% of fibers were used as retention agents. In addition to commercial fillers, controls showing the impact of a simple mixture of the fines used to produce SuperFill and a PCC filler of roughly the same psd as that seen in SuperFill were also included in the first set of laboratory-scale experiments. In these controls the amounts of fines in sheets were similar to those in SuperFill. All handsheets

were dried for 24 hours with drying plates to prevent shrinkage. Papers were tested according to the respective standards (cf. Appendix 4).

SuperFill was also tested in a laboratory-scale experimental paper machine (XPM). The XPM is a small device, a schematic view is enclosed in Appendix 4, which also shows the positions at which chemicals are added. A more detailed description of the trial setup, including conditions and analyses, is presented in Appendix 4 as well.

Furthermore, SuperFill was tested in a variety of pilot-scale paper machines. Due to the excessive amount of data produced, only those trials in a paper machine with the most realistic conditions, the EuroFEX in the Swedish Pulp and Paper Research Institute (STFI), Sweden, are reported in this thesis. A more detailed description of the trial settings, conditions, and analyses is presented in Appendix 5.

A mill-scale paper machine trial was conducted in a paper machine owned by the M-real Corporation, in which runnability both in the paper machine and coater, wet-end chemistry, water circulations, dewatering characteristics, and surface properties of the paper were the topics of main interest. Description of the trial settings, conditions, and analyses is presented in Appendix 6. Furnishes with different pulp compositions and refining degrees were used in the trials.

4.3 Results and discussion

In this chapter the focus is on the most relevant results, covering typical examples of laboratory experiments as well as pilot- and mill-scale trials.

4.3.1 Light scattering coefficient and tensile strength

To start with, the light scattering coefficient and tensile index of handsheets are first considered separately as functions of filler level. These comparisons are important when considering the role played by the hypothetical mechanism of SuperFill as presented in Chapter 3. Figures 9 and 10 present these comparisons for SuperFill obtained under laboratory conditions and for three reference fillers⁸⁷. A control showing the impact of a simple mixture of the fines used to produce SuperFill and a PCC filler of roughly the same psd as that seen in SuperFill was also included. The handsheets were dried with drying plates to prevent shrinkage.

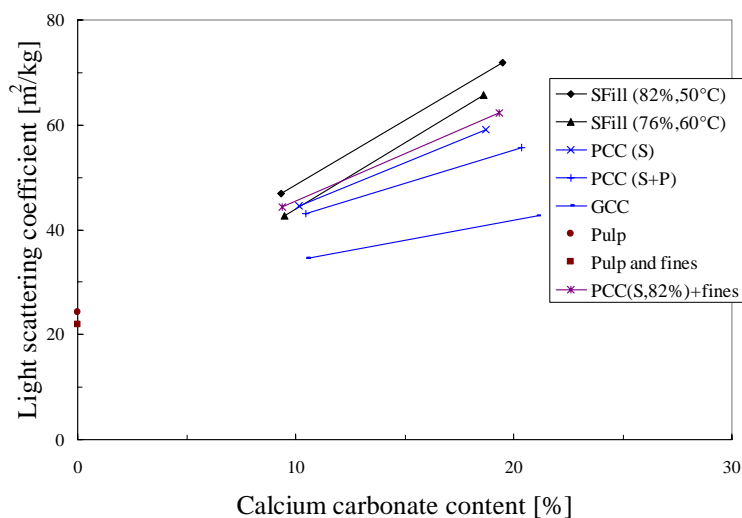


Figure 9. Light scattering coefficient of handsheets as a function of filler level for the scalenohedral SuperFill obtained under laboratory conditions and for commercial PCCs (S=scalenohedral, SSA 6 m²/g; P=prismatic, SSA 5.5 m²/g; S+P=50/50 mixture) and ground calcium carbonate (GCC=Filler L by Omya). The calcium carbonate portion of SuperFill and initial temperature of precipitation are mentioned in the legend. The psd of the scalenohedral reference PCC was roughly the same as that seen in SuperFill. The furnish consisted of 30% bleached softwood kraft pulp (27 °SR) and 70% bleached birch kraft pulp (22 °SR). Fines were produced from bleached softwood kraft pulp.

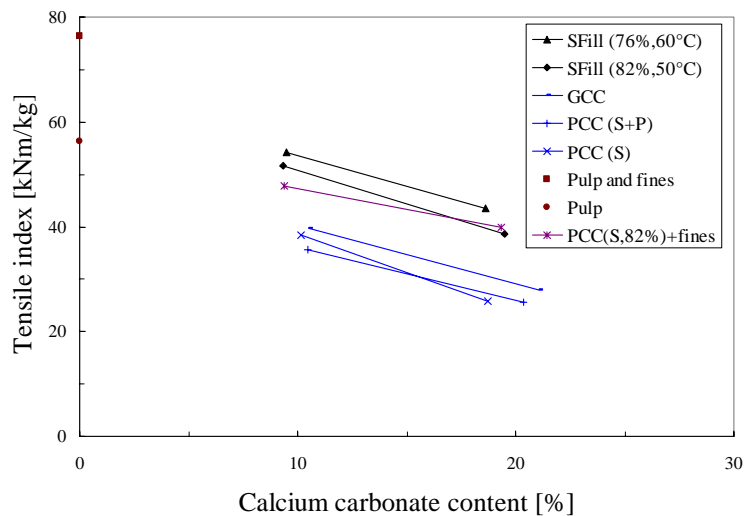


Figure 10. Tensile index of handsheets as a function of filler level for the scalenohedral SuperFill produced under laboratory conditions and for commercial PCCs (S=scalenohedral, SSA 6 m²/g; P=prismatic, SSA 5.5 m²/g; S+P=50/50 mixture) and ground calcium carbonate (GCC=Filler L by Omya). The calcium carbonate portion of SuperFill and initial temperature of precipitation are mentioned in the legend. The psd of the scalenohedral reference PCC was roughly the same as that seen in SuperFill. The furnish consisted of 30% bleached softwood kraft pulp (27 °SR) and 70% bleached birch kraft pulp (22 °SR). Fines were produced from bleached softwood kraft pulp.

Fig. 11 further presents the combination of light scattering coefficient and tensile index in the same graph for these fillers⁸⁷.

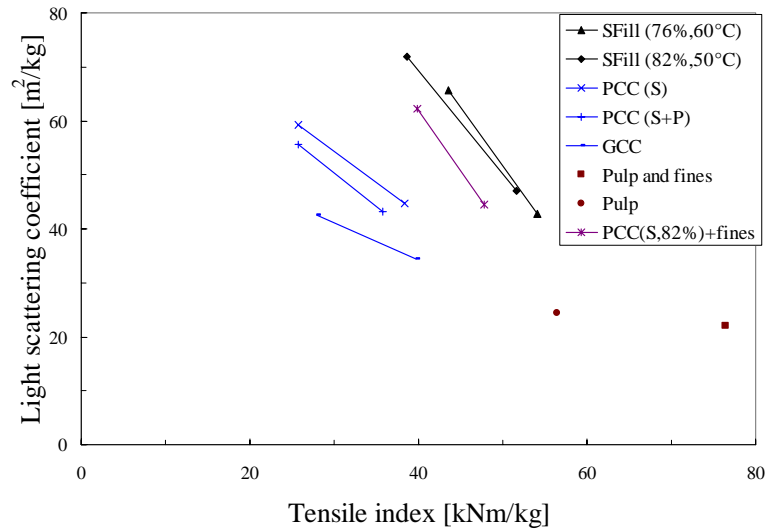


Figure 11. A combination of light scattering coefficient and tensile index of handsheets for the scalenohedral SuperFill obtained under laboratory conditions and for commercial PCCs (S=scalenohedral, SSA 6 m²/g; P=prismatic, SSA 5.5 m²/g; S+P=50/50 mixture) and ground calcium carbonate (GCC=Filler L by Omya). The calcium carbonate portion of SuperFill and initial temperature of precipitation are mentioned in the legend. The psd of the scalenohedral reference PCC was roughly the same as that seen in SuperFill. The furnish consisted of 30% bleached softwood kraft pulp (27 °SR) and 70% bleached birch kraft pulp (22 °SR). The calcium carbonate levels of the sheets were approximately 10% and 20%. Fines were produced from bleached softwood kraft pulp.

When comparing SuperFill and PCC first at the 20% filler level, SuperFill provides paper with approximately 25% and 50% higher light scattering coefficient and tensile index, respectively. However, when comparing SuperFill and PCC at the same tensile index (40 kNm/kg) in which the filler level with SuperFill and PCC is 20% and 10%, respectively, SuperFill provides paper with approximately 60% higher light scattering coefficient than does PCC. Thus, with SuperFill more filler can be used to provide paper with additional increases in light scattering coefficient. It can also be seen that the reference with added fines mixed with scalenohedral PCC provides paper with part of the benefit obtained with SuperFill. Furthermore, to compare this with pure PCC the comparison should be made with the scalenohedral PCC. Thus,

it appears that the mixture provides paper with increased tensile strength, whereas the light scattering coefficient is basically not improved compared with pure PCC of the same psd. These features are discussed in more detail in Chapter 5. It was also decided after this first set of laboratory-scale experiments (combined with some additional results on added fines presented in Appendix 7) that the focus would be on the developmental path with SuperFill in further experiments, since it appears to offer benefits over the simple mixture of the fines and PCC. Therefore, mixtures of the added fines and separate PCC fillers were not included in further papermaking experiments.

Fig. 12 presents the combination of light scattering coefficient and geometric mean of tensile index of paper produced in the XPM for SuperFill with three different fines sources and for a reference PCC filler ¹³⁶. The SSA values of the fillers were similar (Appendix 4).

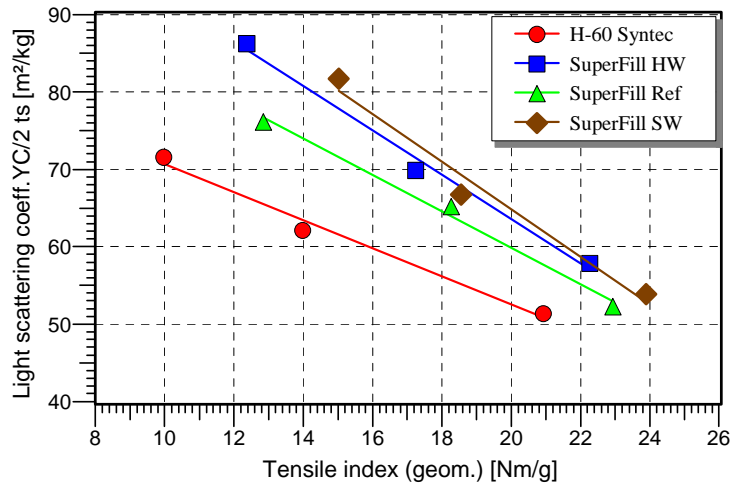


Figure 12. A combination of light scattering coefficient and tensile index of paper produced in the XPM for the scalenohedral SuperFill obtained in the laboratory and for commercial PCC (H-60 = Syntec by Omya) of roughly the same CaCO_3 psd. The fines source for SuperFill is presented in the legend (HW = mixed hardwood kraft pulp, SW = softwood kraft pulp, Ref = birch kraft pulp). The furnish consisted of 30% bleached softwood kraft pulp and 70% bleached mixed hardwood kraft pulp which were after disintegration beaten together to a level of 22.7 °SR in an Escher-Wyss conical laboratory refiner at 3.0% consistency.

It can be seen from the figure that SuperFill provides paper with even more than 30% increased light scattering coefficient compared with commercial PCC at the same tensile index.

Fig. 13 presents the same combination for a paper produced in the EuroFEX pilot paper machine at STFI, Stockholm, for SuperFill and PCC.

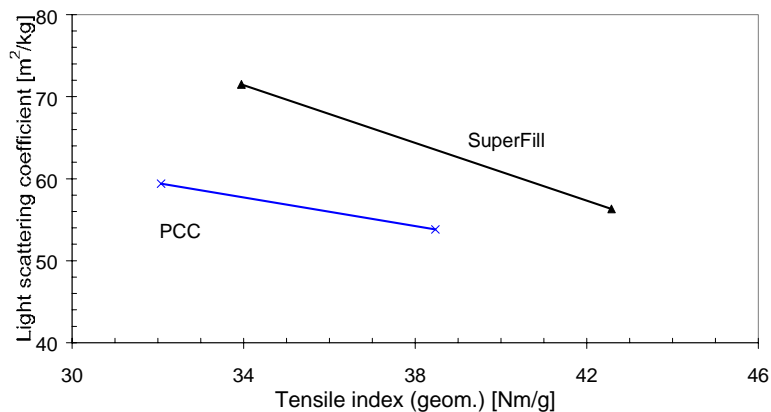


Figure 13. A combination of light scattering coefficient and tensile index of paper produced in the EuroFEX pilot paper machine for SuperFill (scalenoedral, SSA 8.7 m²/g) produced at mill scale and for commercial PCC (scalenoedral, SSA 6 m²/g) of roughly the same CaCO₃ psd. The furnish consisted of 30% bleached softwood kraft pulp (23 °SR) and 70% bleached birch kraft pulp (21 °SR). Fines for SuperFill were produced from bleached birch kraft pulp.

It can be seen from Fig. 13 that SuperFill provides paper with approximately 25% higher light scattering coefficient compared with commercial PCC at the same tensile index (34 Nm/g).

Since both light scattering coefficient and tensile index can be simultaneously improved, the results appear to agree with the hypothetical mechanism presented in Chapter 3. The actual results supporting the mechanism are presented in Section 4.3.4 and Chapter 5.

4.3.2 Light scattering coefficient and Scott bond

The Scott bond is among the quantities that can be most significantly improved by the use of SuperFill technology. Fig. 14 presents the Scott bond for handsheets as a function of filler level for SuperFill obtained under

laboratory conditions and for three reference fillers ⁸⁷. A control showing the impact of a simple mixture of the fines used to produce SuperFill and a PCC filler of roughly the same psd as that seen in SuperFill was also included.

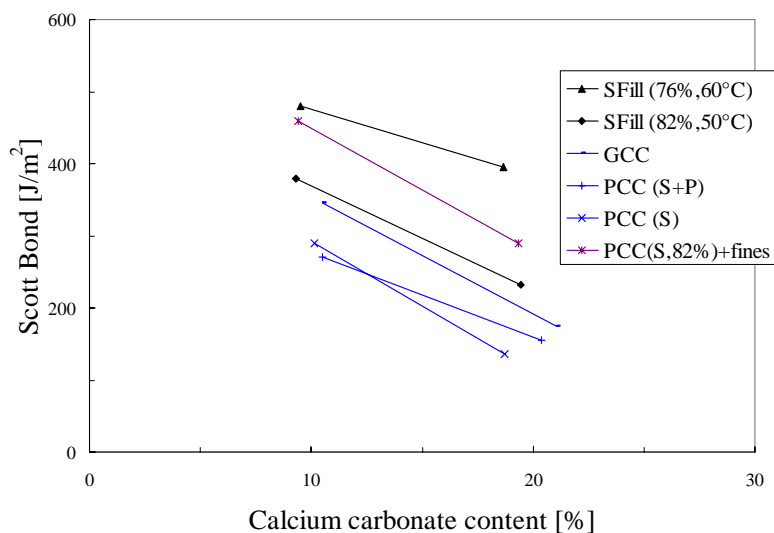


Figure 14. Scott bond for handsheets as a function of filler level for the scalenohedral SuperFill obtained under laboratory conditions and for commercial PCCs (S = scalenohedral, SSA 6 m²/g; P = prismatic, SSA 5.5 m²/g; S + P = 50/50 mixture) and ground calcium carbonate (GCC = Filler L by Omya). The calcium carbonate portion of SuperFill and initial temperature of precipitation are mentioned in the legend. The psd of the scalenohedral reference PCC was roughly the same as that seen in SuperFill. The furnish consisted of 30% bleached softwood kraft pulp (27 °SR) and 70% bleached birch kraft pulp (22 °SR). Fines were produced from bleached softwood kraft pulp.

This comparison clearly shows the impact of fines, either added separately or as a component of SuperFill, on the internal bond strength of paper. It can be seen from the figure that at higher filler contents SuperFill provided paper with almost three times higher Scott bond compared with standard commercial PCC (scalenohedral, SSA 6 m²/g).

As an example, Fig. 15 presents the combination of light scattering coefficient and Scott bond for a paper produced in the EuroFEX pilot paper machine at STFI for SuperFill and PCC.

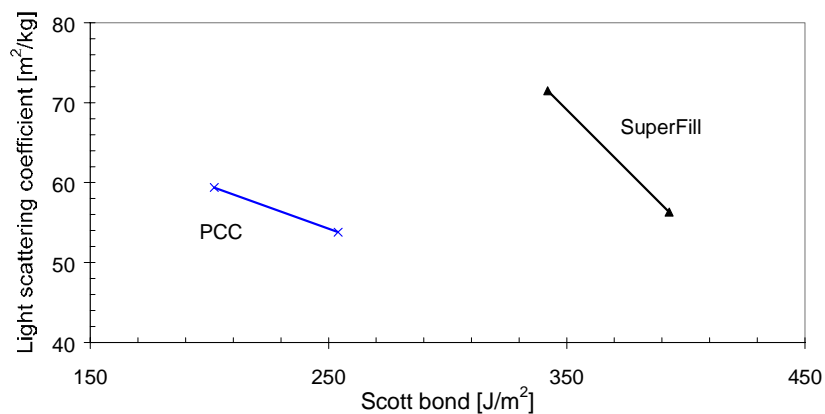


Figure 15. A combination of light scattering coefficient and Scott bond of paper produced in the EuroFEX pilot paper machine for SuperFill (scaleno-hedral, SSA 8.7 m²/g) produced at mill scale and for commercial PCC (scaleno-hedral, SSA 6 m²/g) of roughly the same CaCO₃ psd. The furnish consisted of 30% bleached softwood kraft pulp (23 °SR) and 70% bleached birch kraft pulp (21 °SR). Fines for SuperFill were produced from bleached birch kraft pulp.

The figure indicates that SuperFill provides paper with approximately 70% higher light scattering coefficient compared with standard commercial PCC (scaleno-hedral, SSA 6 m²/g) as extrapolated to the same Scott bond value (300 J/m²). In contrast, SuperFill provides paper with approximately 90% higher Scott bond at the same light scattering coefficient (59 m²/kg). The Scott bond values presented in this section are still well within measurable range with the apparatus used (lower range up to 525 J/m²).

4.3.3 Light scattering coefficient and burst strength

In this section some discussion is devoted to white top linerboards since burst strength is still important in this application. Fig. 16 presents the combination of light scattering coefficient and burst strength of paper produced in the EuroFEX pilot paper machine.

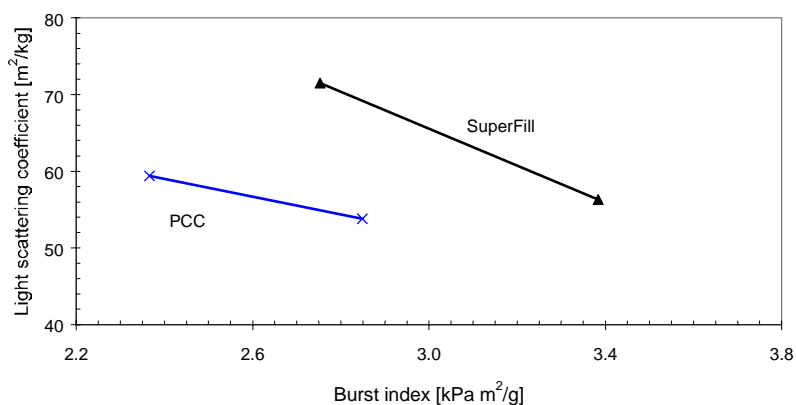


Figure 16. A combination of light scattering coefficient and burst index of paper produced in the EuroFEX pilot paper machine for SuperFill (scalenoedral, SSA 8.7 m²/g) produced at mill scale and for commercial PCC (scalenoedral, SSA 6 m²/g) of roughly the same CaCO₃ psd. The furnish consisted of 30% bleached softwood kraft pulp (23 °SR) and 70% bleached birch kraft pulp (21 °SR). Fines for SuperFill were produced from bleached birch kraft pulp.

It can be seen from Fig. 16 that the light scattering coefficient can be improved somewhat greatly with SuperFill at constant burst strength compared with standard commercial PCC; at 2.8 kPa m²/g the increase is approximately 30%. This indicates that the brightness of linerboard could be increased by incorporating SuperFill in the top layer of the board, or alternatively the top layer grammage lowered with no decrease in brightness. Fig. 17 presents the brightness of a 2-layered linerboard produced in the EuroFEX pilot paper machine at STFI for SuperFill in the top layer with two

grammages and for commercial PCC (scalenoedral, SSA 6 m²/g). The total grammage of all liners was 140 g/m².

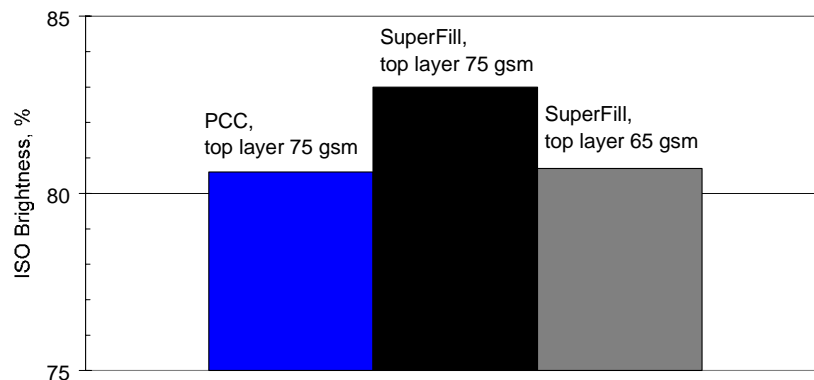


Figure 17. Brightness of 140 g/m² white top linerboard produced in the EuroFEX pilot paper machine for SuperFill (scalenoedral, SSA 8.7 m²/g) produced at mill scale and for commercial PCC (scalenoedral, SSA 6 m²/g) of roughly the same CaCO₃ psd. The fillers were used in the top layer. The top layer furnish consisted of 30% bleached softwood kraft pulp (23 °SR) and 70% bleached birch kraft pulp (21 °SR). The backing layer furnish consisted of unbleached kraft pulp (17 °SR) comprised mainly of softwood. Fines for SuperFill were produced from bleached birch kraft pulp. The burst indices of all liners were approximately 3.4 kPa m²/g.

Fig. 17 shows that SuperFill provides liner with higher brightness than commercial PCC. It is also seen from the figure that top layer grammage can be decreased by 10 g/m² using SuperFill with no decrease in liner brightness. This may have a strong positive impact on the economy of linerboard production if production capacity can be kept constant.

These results can be considered very favorable, knowing that standard PCC by itself already gives benefit over the fillers used in the linerboard business today.

4.3.4 Light scattering coefficient and pore structure

Based on earlier studies¹³⁷ pores between 0.25 μm and 0.30 μm in radius provide paper with highest light scattering coefficient. This is in line with the results by Gill *et al.*¹³⁸ and also with the light scattering theories which suggest that pores with a size close to half the wavelength of white light, increase paper light scattering effectively. As an example, Fig. 18 plots the pore size distribution within this region both for SuperFill and commercial PCC (H-60 Syntec by Omya) as measured by mercury porosimetry¹³⁶. The entire distributions are presented in Appendix 8¹³⁶.

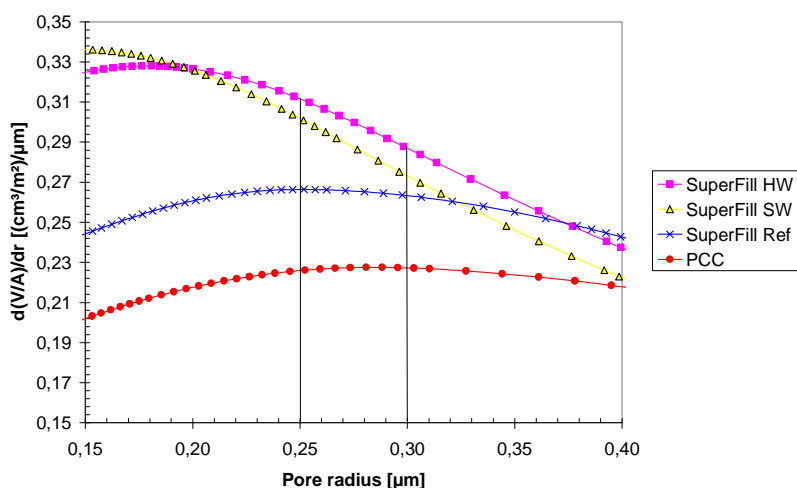


Figure 18. Pore size distributions of XPM (experimental paper machine) produced paper within the most relevant region with respect to light scattering properties both for scalenohedral SuperFill with three different fines sources and for commercial PCC (H-60 Syntec by Omya) of roughly the same CaCO_3 psd. The calcium carbonate portions of the SuperFill samples were approximately 70% by weight and calcium carbonate content of papers 20%. Fines source for SuperFill is presented in the legend: HW=bleached mixed hardwood kraft pulp, SW=bleached softwood kraft pulp, Ref=bleached birch kraft pulp.

An important finding from this comparison is that regardless of fines source SuperFill has a larger area in the region contributing to light scattering than

that with commercial PCC. Moreover, the amount of optimum pores increased more rapidly with SuperFill compared with commercial PCC when the filler level was increased, as can be seen from the figures presented in appendix 9¹³⁶. The figures also indicate, regarding the larger pores, that in the case of SuperFill the amount of larger pores decreased with increasing filler content unlike the situation in commercial PCC. This finding can be valuable in terms of printing properties. The same phenomenon was also discovered with oil porosimetry as can be seen from Fig. 19. The Coulter oil method does not measure the pores in the region considered most relevant with respect to light scattering, but gives a measure that may help to interpret and predict coated paper quality.

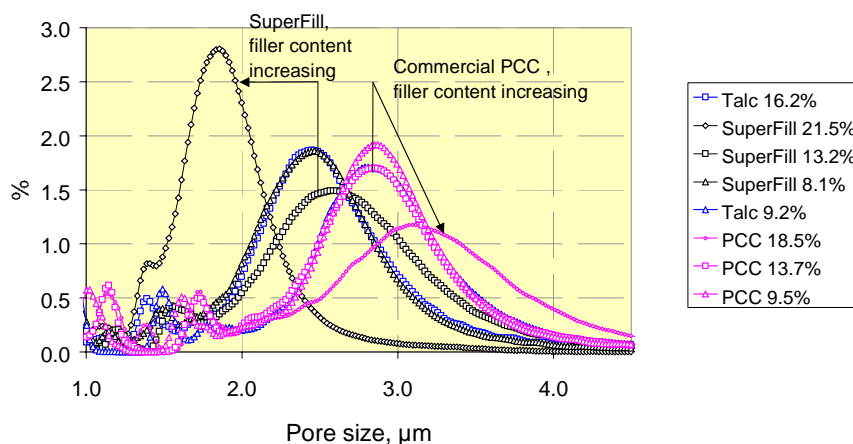


Figure 19. Pore size distributions of base papers produced at mill scale for SuperFill (scalenohedral, SSA 9.6 m²/g) and two reference fillers (PCC: scalenohedral, SSA 11 m²/g; Talc: Finntalc by Mondo Minerals). The psd of the reference PCC was close to that seen in SuperFill. Distributions were measured with a Coulter oil porosimeter. The filler content is presented in the legend. The furnish consisted of 74% bleached birch kraft pulp (22-25 °SR) and 26% bleached pine kraft pulp (22-25 °SR).

It can be seen from Fig. 19 that at lower filler levels no major differences in pore size distributions were found. However, when increasing the filler content to approximately 20%, a distinctive phenomenon can be seen. The pore size median increases with increasing filler content with PCC, and the distribution becomes wider. In this case 75% of the curve is within 2.3 μm range in width (PCC 20%). However, when filler content is increased to this level with SuperFill, the value of the pore size median becomes lower and the distribution narrower, unlike the situation with talc and PCC. In that case 75% of the values are within 0.8 μm range in width. The same effect can also be seen with talc but to a minor degree.

At higher filler contents the pore size median and width of the distribution with SuperFill are only 60% and 34% of that with PCC, respectively (75% of the curve). Thus, SuperFill provides paper with a significantly closer structure compared with commercial PCC. In the case of coated paper this may be an advantage contributing to coating and paper quality due to better coating coverage. This is supported by the results of on-line coated, calendered papers produced in the same mill trial. The results indicated that coated papers including SuperFill as a filler exhibited approximately 5% units higher gloss and 0.1 pps units better smoothness compared with papers including the same amount of talc as a filler (15%). This is a good result, considering that coat weight was lower for base paper with SuperFill as a filler (12.6 g/m^2 for SuperFill, 13.1 g/m^2 for talc).

Another distinctive finding is that the number of pores within the most relevant region in terms of light scattering can be increased with SuperFill without overall increase in porosity (Bendtsen). With SuperFill, the value of Bendtsen air permeability was approximately 67% of that with PCC.

4.3.5 Light scattering coefficient, density, and bending stiffness

Figures 20 and 21 present the bending stiffness and density of handsheets for SuperFill produced under laboratory conditions and for three reference fillers⁸⁷. A simple mixture of the fines used to produce SuperFill and a PCC filler of roughly the same psd as that seen in SuperFill was also included as a reference.

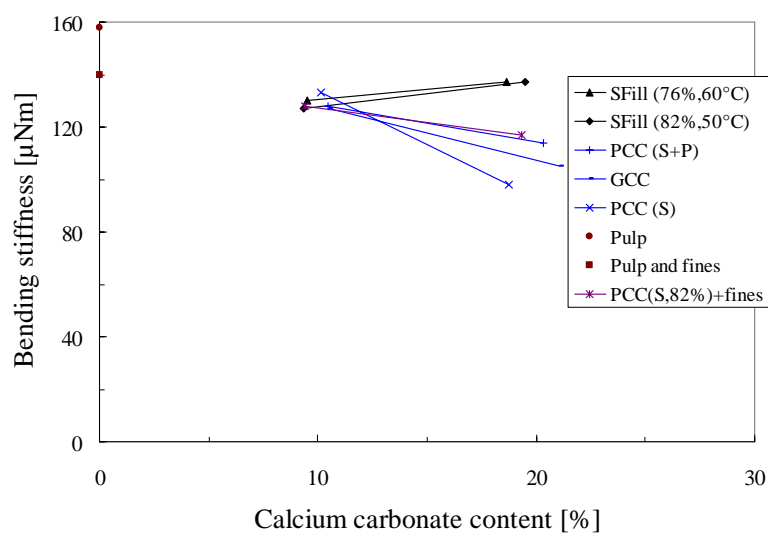


Figure 20. Normalized ($w_0=60$ g/m²) bending stiffness of handsheets as a function of filler level for the scalenohedral SuperFill obtained under laboratory conditions and for commercial PCC fillers (S=scalenohedral, SSA 6 m²/g; P=prismatic, SSA 5.5 m²/g; S+P=50/50 mixture) and ground calcium carbonate (GCC=Filler L by Omya). The calcium carbonate portion of the SuperFill and initial temperature of precipitation are mentioned in the legend. The psd of the scalenohedral reference PCC was roughly the same as that seen in SuperFill. The furnish consisted of 30% bleached softwood kraft pulp (27 °SR) and 70% bleached birch kraft pulp (22 °SR). Fines were produced from bleached softwood kraft pulp.

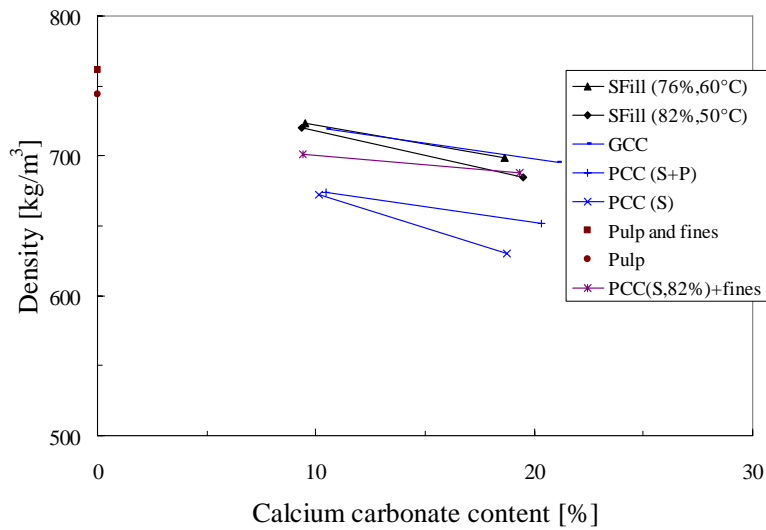


Figure 21. Density of handsheets as a function of filler level for the scalenohedral SuperFill obtained under laboratory conditions and for commercial PCC fillers (S = scalenohedral, SSA $6 \text{ m}^2/\text{g}$; P = prismatic, SSA $5.5 \text{ m}^2/\text{g}$; S + P = 50/50 mixture) and ground calcium carbonate (GCC = Filler L by Omya). The calcium carbonate portion of the SuperFill and initial temperature of precipitation are mentioned in the legend. The psd of the scalenohedral reference PCC was roughly the same as that seen in SuperFill. The furnish consisted of 30% bleached softwood kraft pulp (27 °SR) and 70% bleached birch kraft pulp (22 °SR). Fines were produced from bleached softwood kraft pulp.

It can be seen from the figures that all papers at 10% filler content exhibit stiffness values of approximately $130 \mu\text{Nm}$. When the filler content is increased to 20% SuperFill provides paper with approximately $10 \mu\text{Nm}$ additional increase in paper stiffness, whereas other fillers with or without added fines decrease paper stiffness by approximately $15\text{-}30 \mu\text{Nm}$. However, added fines with scalenohedral reference PCC increased paper stiffness compared with the same PCC without fines addition. The decrease in density was seen with all fillers studied when increasing filler content to 20%.

To clarify the reason for this phenomenon the results with the samples "SuperFill (82% PCC, 50 °C)" and "PCC (S)" are studied in more detail. These samples were selected because the grammages of papers were exactly the same at both filler levels, and because the psd of calcium carbonate is similar for these samples. The approach is to plot the values of measured actual and calculated stiffness in the same graph and examine whether they behave in the same way as a function of filler level. The calculation was performed using the measured values of paper thickness and elastic modulus according to Eq. ¹³⁹

$$S_b = \frac{E \cdot t_b^3}{12} \quad (20)$$

where S_b bending stiffness
 E elastic modulus
 t_b the thickness of a rectangular beam (paper)

The results are presented in Fig. 22.

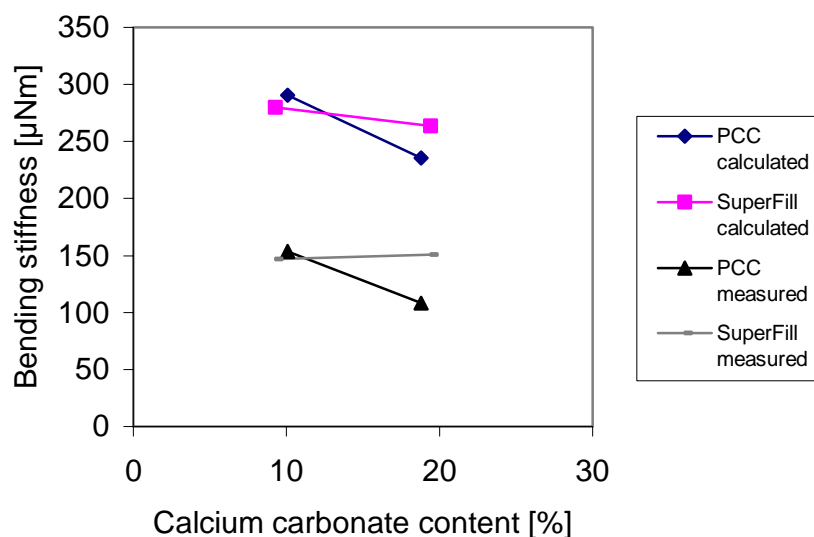


Figure 22. Measured actual and calculated stiffness of paper for the scalenohedral SuperFill and commercial PCC (scalenohedral, SSA 6 m²/g) of roughly the same CaCO₃ psd.

It can be seen from the figure, regardless of the systematic difference between measured and calculated values, that the trends are similar both for measured and calculated values. This suggests that the measured values can be considered relatively reliable. It is also evident that higher stiffness with SuperFill is due to a higher elastic modulus, since SuperFill did not decrease density (increase bulk) more than the other fillers. The systematic difference between measured and calculated values of stiffness is apparently due to the difference between the measured and effective thickness of paper, i.e. the thickness of uncalendered paper measured by normal standards is higher than the actual effective thickness resulting from roughness of the paper surface. According to Kartovaara ¹⁴⁰ this difference can typically result in as much as 80% higher values for calculated stiffness compared with measured stiffness of uncalendered papers, which is very close to that presented in Fig. 22.

The results from the XPM trials indicated the same phenomenon, i.e. the bending stiffness of papers including SuperFill as a filler was higher than that with commercial PCC, although the bulk was lower (Appendix 10) ¹³⁶. Thus, the increase in stiffness was apparently again due to increase in the elastic modulus. However, due to differences in grammages at 10% and 30% filler levels, only the results at the 20% filler level can be compared reliably. In this comparison SuperFill provided paper with approximately 8% higher stiffness compared with commercial PCC, when fines for SuperFill were produced from bleached birch kraft pulp.

The stiffness of paper produced in the EuroFEX pilot paper machine was also higher with SuperFill than that with commercial PCC. Higher stiffness can be partly explained by higher grammage, partly by increased elastic modulus and bulk. The major difference compared with previous results was that the density of SuperFill-filled paper was lower than that of commercial PCC. The

reason for this may be found from the structure of SuperFill. The results suggest that paper stiffness may further be improved by changing e.g. the calcium carbonate morphology in SuperFill in such a way that bulk is maintained.

4.4 Retention and formation

Since formation and retention are matters that can be realistically studied only under actual forming conditions, pilot- and mill-scale trials alone are reported in this section. The forming concepts and trial conditions are presented in Appendices 5 and 6.

Fig. 23 presents an example of a combination of formation and total retention measured in a EuroFEX pilot paper machine trial at STFI, where the impact of SuperFill was clearly seen. The sample points were selected so that two filler levels were represented for both fillers and one sample of both fillers was made using a polymer of 300 g/t for more precise comparison. Formation was measured using beta-radiographic recording by the method developed at STFI¹⁴¹. Lower values mean better formation.

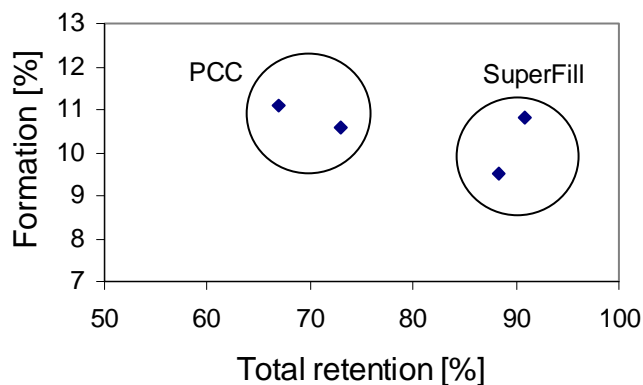


Figure 23. Formation and total retention measured in EuroFEX pilot paper machine trial at STFI with SuperFill (scalenoedral, SSA 5.5 m²/g) obtained at mill scale and with commercial PCC (scalenoedral, SSA 6 m²/g) of roughly the same CaCO₃ psd. The furnish consisted of 30% bleached softwood kraft pulp (23 °SR) and 70% bleached birch kraft pulp (21 °SR). Fines for SuperFill were produced from bleached birch kraft pulp.

The figure shows that both formation and total retention can be improved with SuperFill compared with commercial PCC. Better retention resulted in significantly lower white water consistency with SuperFill, as can be seen from Fig. 24.

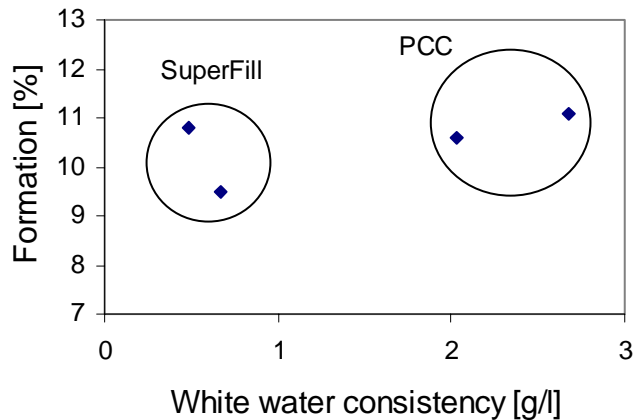


Figure 24. Formation and white water consistency in EuroFEX pilot paper machine trial at STFI with SuperFill (scaleno-hedral, SSA 5.5 m²/g) obtained at mill scale and with commercial PCC (scaleno-hedral, SSA 6 m²/g) of roughly the same CaCO₃ psd. The furnish consisted of 30% bleached softwood kraft pulp (23 °SR) and 70% bleached birch kraft pulp (21 °SR). Fines for SuperFill were produced from bleached birch kraft pulp.

These results with SuperFill can be considered very favorable since they were achieved together with improved combination of light scattering and strength properties.

In the mill-scale paper machine trial filler retention was highest with SuperFill (between 40% and 50%) even though retention polymer dosage was 30% lower than that with other fillers. Filler retention with talc and PCC was between 30% and 40%. Good retention with SuperFill also resulted in lower white water consistency compared with the other fillers as presented graphically in Appendix 11. Regarding other wet end related issues there were no major changes in white water conductivity, chemical oxygen demand (COD), pH, cationic demand, and dissolved calcium concentration with different fillers. In the mill-scale trial no major differences in beta formation were seen between different fillers.

The beneficial effect on formation can be discussed in view of the furnish-related quantities presented in Section 4.1.2. The fines component blend of SuperFill is produced by refining, which changes fiber dimensions relatively much. If the dimensions are measured as fiber length, the decrease is between 30% and 40%. When presented more explicitly, the birch fiber length was measured as 0.93 mm at 20 °SR (target for furnish birch fiber was 21 °SR) and 0.56 mm at 91 °SR (target for fines of SuperFill) for the specific pilot trial represented in Figs. 23 and 24. Thus, the decrease in birch fiber length was 0.37 mm compared with the birch fiber typically used in the furnish. The amount of this fines blend in paper is approximately 12% of the fiber material when SuperFill with 70% of calcium carbonate is added to attain a 20% calcium carbonate content of the paper. Consequently, the average fiber length in the furnish decreased by approximately 0.1 mm (assuming 2.2 mm SW fiber length), which can be considered relevant in terms of formation potential of the pulp mixture in view of the literature cited in Section 4.1.2. This feature most probably explains at least part of the improved formation with SuperFill. Another factor may be that SuperFill perhaps resulted in a denser fiber mat during the roll-forming stage of the STFI former, which further improved the function of the blade-forming section. This type of phenomenon may be possible in view of the literature¹⁴² and the experience that usage of fines typically improves formation.

The considerably improved retention of SuperFill compared with that in other fillers is presumably due to the fact that retention of chemical fines is good¹⁴³ resulting in good retention of the entire SuperFill structure. Retention is thus decreasingly dependent upon chemical retention aids and flocculation, resulting in better combination of formation and retention.

4.5 Impact of calcium carbonate portion of fines-filler composite on paper properties

The calcium carbonate portion of SuperFill is among the most essential control parameters regarding SuperFill quality and clearly impacts paper properties and phenomena in papermaking. It also impacts both SuperFill and paper production economy, which together with paper price and local conditions define the total benefit within each product segment. The economic items are clarified in Chapter 6.

Based on the experiments performed the general trend is that the combination of light scattering and paper strength is improved with decreasing PCC portion of SuperFill. This can be systematically seen in Figures 25 and 26 for which the hardwood and softwood were beaten in a Valley laboratory hollander for 7 and 5 minutes, respectively. The furnish consisted of 30% bleached softwood kraft pulp and 70% bleached birch kraft pulp. Fines for SuperFill were produced from bleached birch kraft pulp (cf. Appendix 5).

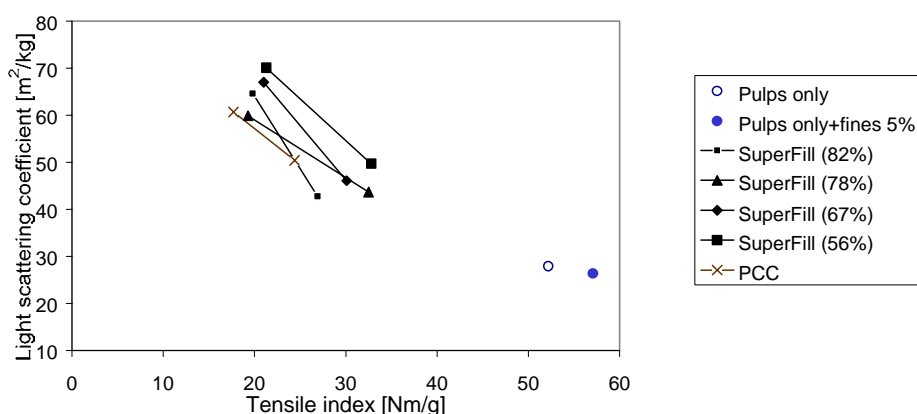


Figure 25. Combination of light scattering coefficient and tensile index for the scalenohedral SuperFill with four different calcium carbonate ratios and for commercial PCC (scalenohedral, SSA 6 m²/g) of roughly the same CaCO₃ psd. The calcium carbonate portion of SuperFill is presented in the legend.

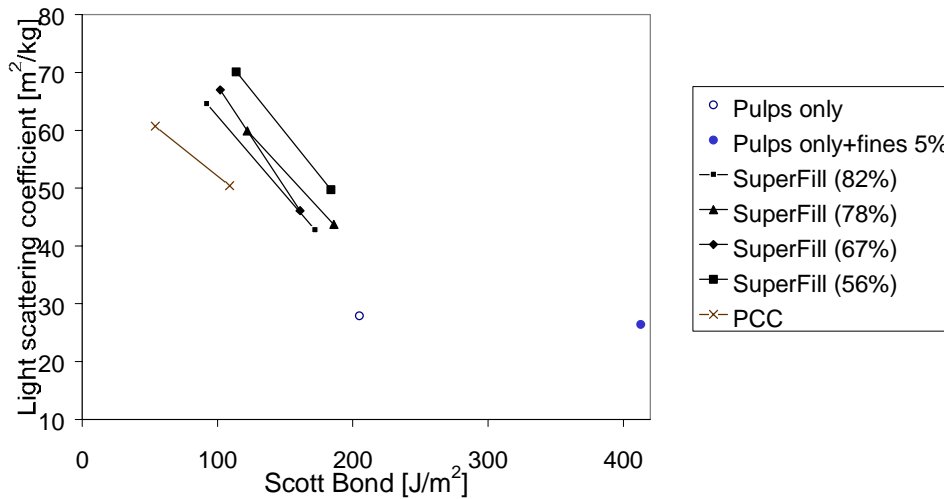


Figure 26. Combination of light scattering coefficient and Scott bond for the scalenohedral SuperFill with four different calcium carbonate ratios and for commercial PCC (scalenohedral, SSA 6 m²/g) of roughly the same CaCO₃ psd. The calcium carbonate portion of SuperFill is presented in the legend.

The results are in harmony with the hypothetical mechanism of SuperFill in paper, as is presented in Chapter 3. An increase in fines content offers more room for calcium carbonate to precipitate on. Consequently, the average number of calcium carbonate particles precipitated on a single fibril is lower, probably resulting in lower probability of neighboring particles to locate too close to each other with respect to effective light scattering, if particle size is unchanged. Furthermore, when this type of SuperFill is used in papermaking, with minimum agglomeration, the average distance of neighboring PCC particles is high enough, resulting in more uniform spatial filler distribution in paper with improved light scattering. Another explanation may be that the higher total surface area of fibrils for calcium carbonate particles to precipitate on may result in increased numbers of particles with reduced particle size and improved light scattering potential, if the particle size is not carefully controlled. Either way, the impact on light scattering is similar. These two

phenomena may also occur simultaneously. However, the SEM images in this set of experiments suggest the presence of unchanged psd and increased distance of neighboring CaCO_3 particles, as can be concluded from Fig. 27a compared with Fig. 27b. Furthermore, the increase in fines content may have resulted in enhanced activation, which can be seen as improved tensile index.

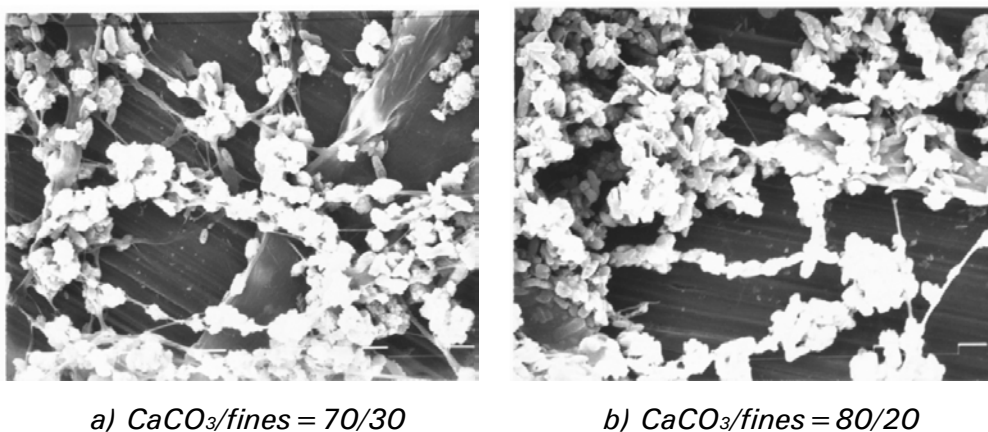


Figure 27. SEM micrographs of SuperFill samples with different $\text{CaCO}_3/\text{fines}$ ratios. The magnification is the same in both micrographs.

However, the light scattering results presented earlier in Figs. 9 and 11 somewhat disagree with those presented in Figs. 25 and 26, whereas the results on strength agree. A likely reason for this is that the SuperFill sample with the higher calcium carbonate portion in Figs. 9 and 11 was precipitated at lower initial temperatures, resulting in slightly smaller particle size, albeit similar to that of the scalenohedral reference and the other SuperFill, based on SEM analysis. Given the sensitivity of the light scattering properties to particle size, this may at least partly explain the deviation. Another explanation may be the differences in density observed in this specific set of experiments. Thus, since the trends presented in Figs. 25 and 26 are quite consistent and the experiments were performed with a number of different calcium carbonate portions, and since the particle size with different calcium carbonate portions

was shown to be basically unchanged, the results can be considered plausible.

Regarding the other relevant properties, density and air resistance of paper decrease with increasing calcium carbonate ratio of SuperFill as can be seen from Figs. 28 and 29 in which the conditions and furnish were the same as those for Figs. 25 and 26.

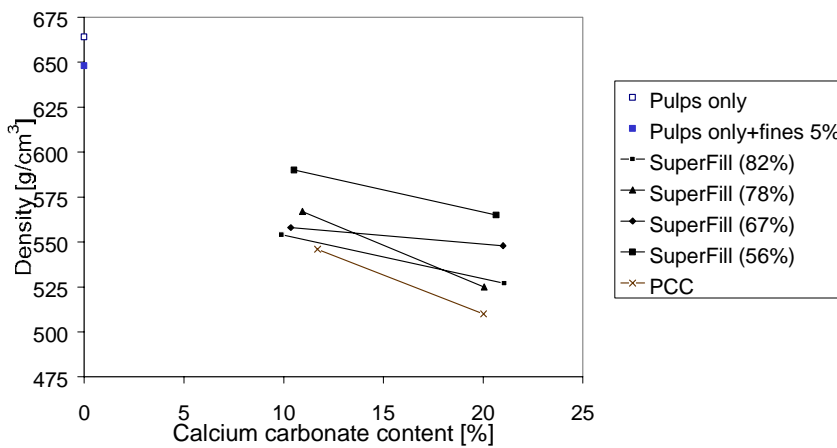


Figure 28. Density of paper filled with the scalenohedral SuperFill and commercial PCC (scalenohedral, SSA 6 m²/g) of roughly the same CaCO₃ psd. The calcium carbonate portion of SuperFill is presented in the legend.

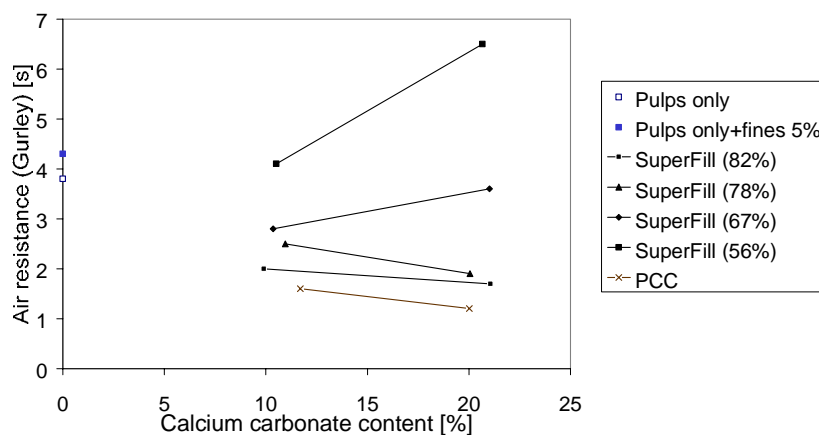


Figure 29. Air resistance of paper filled with the scalenohedral SuperFill and commercial PCC (scalenohedral, SSA 6 m²/g) of roughly the same CaCO₃ psd. The calcium carbonate portion of SuperFill is presented in the legend.

A somewhat peculiar feature of SuperFill in the experiments presented here was that the light scattering coefficient of paper increased with density in contrast to that typical for fillers added normally to the stock. The reason for this can be found from the phenomena discussed in Chapter 5.

A dramatic change in air resistance can be seen when the calcium carbonate portion of SuperFill crosses the value of approximately 75%. Above this value SuperFill behaves as fillers normally do, i.e. the air resistance decreases with increasing filler content. Below this value the air resistance increases with filler content, which may suggest that dewatering problems may be anticipated in paper machines with less effective dewatering capacity. On the other hand, this phenomenon may be successfully utilized in those applications where constant air resistance is required with different filler contents.

In conclusion, the feasible range over which the PCC ratio of SuperFill can vary originates from paper properties and production economy. High calcium carbonate portions are advantageous with respect to both SuperFill and paper production economy, as well as some paper properties such as density. On the other hand, most of the relevant paper properties are improved with decreasing calcium carbonate portions. However, calcium carbonate portions much lower than approximately 70% are generally not economical, due to increased capital and energy requirements needed to produce higher amounts of fines, and due to possible dewatering restrictions in paper machines.

The upper limit of the calcium carbonate portion originates from the fact that above a certain limit the beneficial mechanisms of SuperFill, as hypothetically presented in Chapter 3, may no longer exist. Thus, the feasible range can be considered to be between 70% and 85% of calcium carbonate as total weight of SuperFill, based on experience, when fines for SuperFill are produced from bleached birch kraft pulp. The region may be somewhat different with other types of fines sources.

Depending on paper or board grade used different product properties are relevant as clarified earlier, e.g. for white top linerboard both brightness and burst strength are important. Brightness can be increased by improving light scattering of the top layer. This can be done more effectively with lower calcium carbonate portions of SuperFill which are also beneficial with respect to relevant strength properties of the liner. Instead, a critical property combination for ambitious copying paper products with lowered grammage includes opacity and stiffness. In this case the optimum calcium carbonate portion of SuperFill must be found between the upper and lower feasible limits. Since stiffness is probably the most critical property in this application, the optimum is evidently closer to the upper limit which provides paper with

decreased density. In other words, the optimum calcium carbonate portion of SuperFill is dependent at least on the paper product to be produced, fines source, and paper machine construction.

4.6 Conclusions

As presented in former sections, SuperFill improves many of the important properties of printing and writing papers and paperboards. Table 5 roughly summarizes the improvement of the most relevant strength properties for the products examined, as estimated for constant light scattering coefficient of paper.

Table 5. Tensile index and Scott bond of papers produced under laboratory- and pilot-scale conditions for SuperFill and commercial PCC (scalenohedral, SSA 6 m²/g) of roughly the same CaCO₃ psd, as estimated for a light scattering coefficient of 60 m²/kg.

Filler	Tensile index, Nm/g	Scott bond, J/m ²
SuperFill (lab.)	47	420
PCC (lab.)	25	130
SuperFill (pilot)	40.5	380
PCC (pilot)	31	195

As can be seen from Table 5, SuperFill provides paper with considerably higher strength compared with commercial PCC at constant light scattering coefficient. SuperFill also provided paper with more optimum pore structure with respect to light scattering coefficient compared with commercial fillers.

The bending stiffness of paper was slightly higher with SuperFill compared with commercial PCC. The increase was probably due to the increased elastic modulus rather than decreased density of paper. Furthermore, the combination of retention and formation was improved with SuperFill compared with commercial PCC. The optimum calcium carbonate portion of SuperFill is dependent on the paper product to be produced, fines source, and paper machine construction.

Although many of the experiments were performed using only 2 filler levels, the results are systematic and consistent, suggesting that the findings are correct. Furthermore, the paper-testing results are the mean values of measurements replicated to improve accuracy. Since the experiments were also performed very carefully, it is reasonably certain that the differences observed are significant.

5 MECHANISM OF FINES-FILLER COMPOSITE IN PAPER

5.1 More uniform spatial distribution of filler particles in paper with reduced agglomeration and improved retention: The combined effect of the pigment itself, interruption of the fiber bonded area, and reduced fines collapse

Conventional fillers must be normally bound to the fibers by retention agents for appropriate filler retention in paper machines for reasons presented in Section 4.1. Retention chemicals typically also cause agglomeration of filler particles, as presented in Section 4.1 as well. However, abundant literature suggests that the ability of agglomerated filler particles to improve paper light scattering compared with dispersed filler particles is lower ^{144, 145, 146, 147, 148}, when we consider particles large enough to scatter light as being single particles. Below this size limit agglomeration may be advantageous. Consequently, this suggests for the commonly used fillers in the paper industry with particle sizes higher than this limit, that spatial filler distribution in the paper should be uniform enough to ensure optimum light scattering. This further suggests that agglomeration of filler particles is usually not desirable with high-quality products.

Various phenomena have been proposed in the literature as explanations for the improved light scattering of paper resulting from reduced filler agglomeration. Bown suggested that losses in optical properties for most pigments through homogeneous aggregation may be a consequence of less interruption of fiber bonded area rather than a significant optical crowding effect ^{119, 149}. He further proposed that for pigments with refractive indices similar to that of cellulose, optical crowding is probably also present but has no relative effect, because the optical environment of pigment particles in

homogeneous aggregates differs little from that in heterogeneous aggregates with fibrils or fiber fines or from that of particles loosely associated with fiber surfaces. It has even been suggested that the increase in opacity of papers containing fillers of low refractive index originates not from light scattering of filler particles but from an increase in scattering resulting from the debonding of fibers ¹⁵⁰.

Alinec and Lepoutre ^{151, 152} performed experiments specifically designed to distinguish between the contribution of pigment itself and the effect of fiber debonding to the total scattering. They suggested that for fillers of low refractive index, such as calcium carbonate, the contribution to opacity of the debonding effect could be larger than that of the filler itself. As a result of the debonding, more of the fiber surface becomes available for scattering ^{153, 154, 155, 156, 157}. However, this usually influences paper in such a way that paper strength is lowered ^{149, 152}, as is well known.

Agglomeration can be decreased by using particular retention aids which unfortunately tend to be the least effective in retention ¹⁵⁸. Pigment incorporated into paper as dispersed particles is also more effective in preventing interfiber bonding and is thus more detrimental to tensile strength ¹⁵⁹. Thus, when using commercially available fillers, controlling the state of pigment dispersion does not permit optimization of the strength-opacity ratio, i.e. aggregated pigments will usually lie on the same line as the individual particles from which they are made ^{145, 146}. However, a particular combination is achieved with lower filler level compared with agglomerated pigments. If the pigment is expensive, savings could be realized. In the case of cheaper pigments such as calcium carbonate one typically wishes to agglomerate the pigments to attain certain combinations of light scattering and tensile strength with higher filler level, resulting in saving through fiber replacement. Thus, a method for incorporating pigments of optimum size as dispersed particles to

increase light scattering without sacrificing paper strength has basically not been shown in the literature. For favorable total light scattering, with given filler particle sizes, maximizing filler-to-air interfaces is desired rather than filler-to-fiber interfaces for pigments whose refractive indices lie in the 1.5-1.6 range ¹⁶⁰. An attempt to attain this goal has been to use rigid clustered filler pigments. However, dispersing of these clusters suffers from the same compromises presented above for unclustered pigments. Pigment blends have proven to be beneficial in coatings ¹⁶¹.

SuperFill behaves differently from typical fillers in that an increase in opacity does not inevitably result in decrease in paper strength when compared with analogous PCC crystals. This may be partly explained by a finding of Bown ¹⁴⁹, that well-beaten pulps generally show greater increases in light scattering coefficient with increasing filler loading than poorly beaten pulps, especially with fine fillers at high levels close to 30%. The filler was assumed to prevent areas of the fines and fibrillation of a beaten pulp from collapsing onto the fibers, resulting in increased light scattering coefficient of the sheet. However, a simple mixture of the fines used to produce SuperFill and a reference PCC basically did not provide paper with increased light scattering coefficient compared with pure PCC of the same psd at the filler levels studied, as described in Section 4.3.1. Furthermore, the same behavior was also seen in experiments to further clarify the impacts of added fines, as described in Section 4.3.1. However, these results can be considered to be in line with the findings of Bown in which increases in light scattering coefficient were negligible at filler levels of 20% and below for fillers that were not very fine, when studied as a function of pulp beating. Thus, there must be some additional phenomena explaining the improved performance of SuperFill.

First, calcium carbonate as precipitated on fines may more effectively prevent fines from collapsing onto the fibers, compared with fillers that are simply

mixed with fines. The noncollapsed fines of SuperFill in paper can be seen in the SEM micrograph presented in Fig. 30.

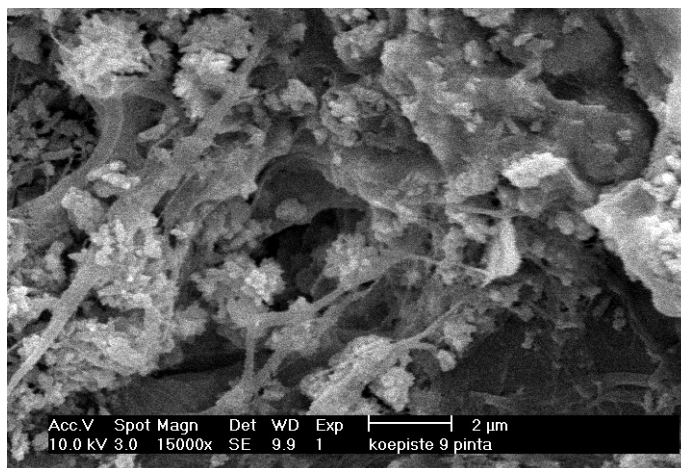


Figure 30. SEM micrograph of a paper sample from a mill-scale trial showing non-collapsed fines of SuperFill.

It is also believed that SuperFill enables reduced agglomeration, together with improved filler retention, because the calcium carbonate particles in SuperFill are tightly precipitated on fines particles, which are effectively retained by paper. Free segments of chemical pulp fines in SuperFill are assumed to further contribute to improved bonding of fibers resulting in increased paper strength, as clarified in more detail in Section 5.2. Agglomeration could perhaps be further decreased through lower dosage of retention polymers as presented in the literature ¹⁶². It also appears from the results that SuperFill itself, apparently due to its fines component, affects paper uniformity positively by filling voids between fibers, thus contributing to more uniform spatial filler distribution and higher light scattering (Fig. 35). The ability of fines to fill voids between fibers has also been mentioned in the literature ¹⁶³. Furthermore, the fines component of SuperFill impacts formation, as presented in Section 4.4, which probably further improves filler distribution

since calcium carbonate is tightly precipitated on fines. Further experimental results clarifying these statements are presented below.

First, the bonds between calcium carbonate and fines are mainly mechanical in nature because precipitation occurs in such a way that fibrils are entrapped by calcium carbonate. The bonding can be clearly seen from the SEM micrographs presented in Figures 31-34.

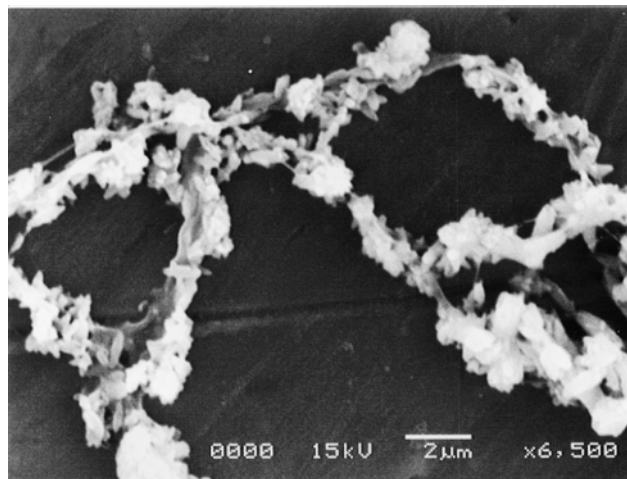


Figure 31. Magnification of a segment of SuperFill produced in a laboratory showing fibrils entrapped by precipitated calcium carbonate.

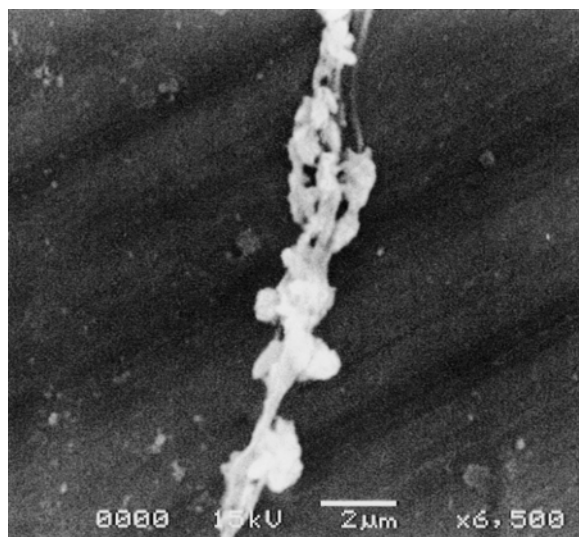


Figure 32. A magnification of a segment of SuperFill produced in a laboratory showing fibril entrapped by precipitated calcium carbonate.

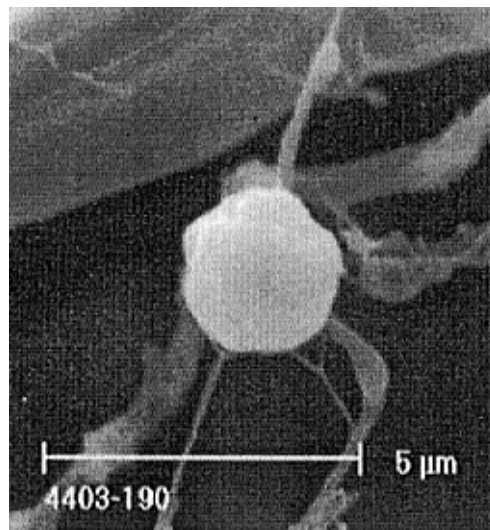


Figure 33. A magnification of a segment of SuperFill produced in a laboratory showing microfibril surrounded by precipitated calcium carbonate.

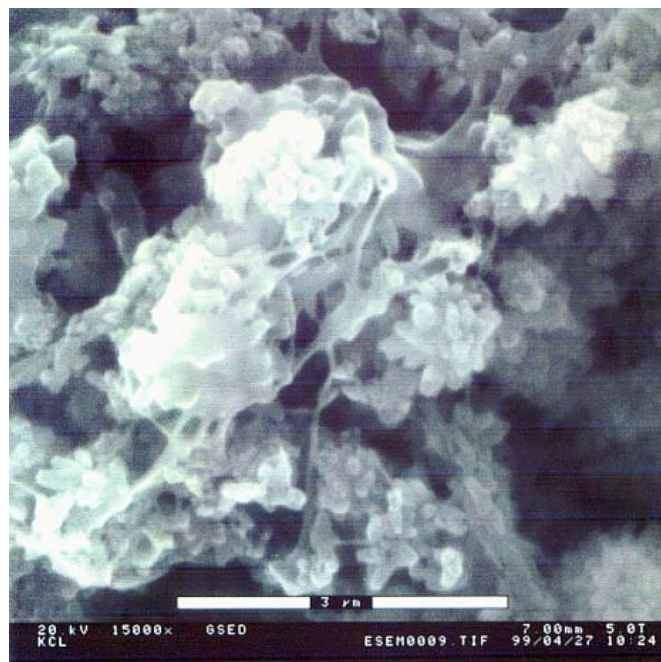
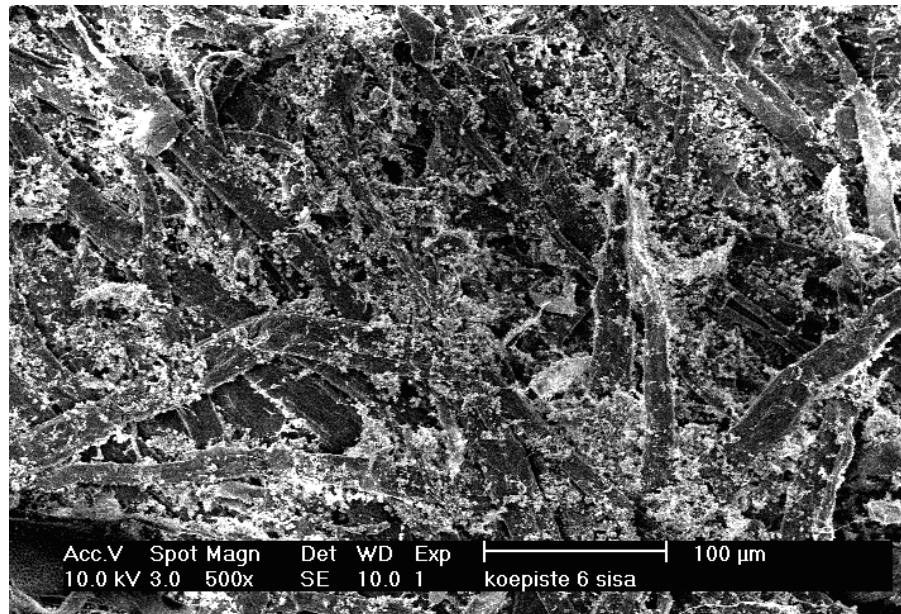


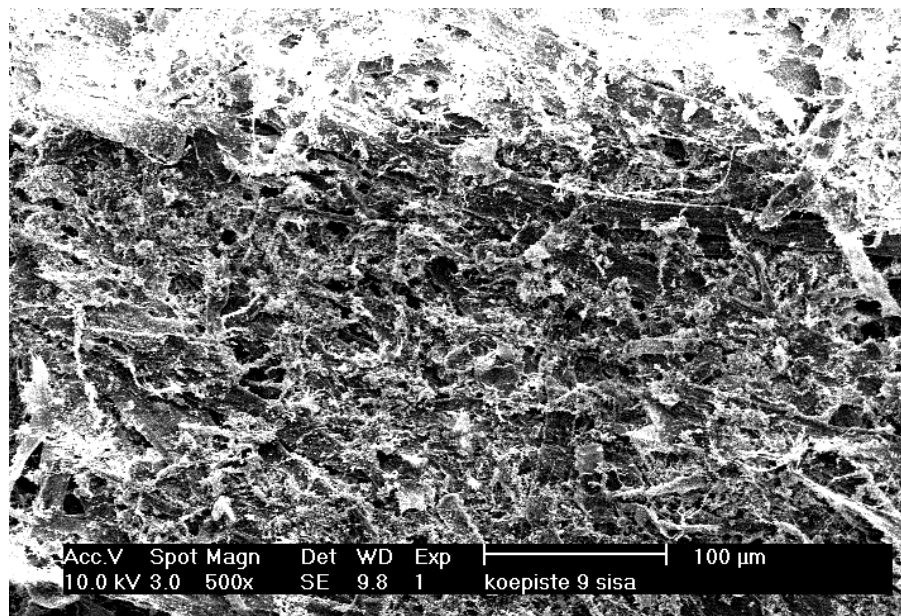
Figure 34. A magnification of a segment of SuperFill produced at mill scale showing fibrils surrounded by precipitated calcium carbonate.

Thus, it can be assumed that calcium carbonate crystals are tightly bound to the fines. Second, the more uniform spatial filler distribution in paper with

SuperFill as filler compared with commercial PCC can be seen from an example presented in Fig. 35.



a) Commercial PCC 18.5% (scalenohedral, SSA 11 m²/g)



b) SuperFill 21.5% (scalenohedral, SSA 9.6 m²/g)

Figure 35. SEM micrographs of split samples from a mill-scale trial showing spatial filler distribution of papers in x,y plane.

Single crystals in the micrographs can be seen as small whiter dots. It can also be seen from Fig. 35 that SuperFill fills voids between fibers in the fiber network, contributing to more uniform spatial filler distribution. Furthermore, the amount of larger agglomerates appears to be lower with SuperFill compared with commercial PCC. Since it is improbable that filler material could be located in paper as a 2-dimensional layer, there is no reason to believe that a 3-dimensional filler distribution would not have been more uniform as well.

Furthermore, since SuperFill can also be located relatively well dispersed in those places not typical for most fillers, i.e. hang in empty spaces between fibers, "optical crowding" may also be decreased with SuperFill, resulting in improved paper light scattering coefficient. This type of SuperFill bridging can be seen in the SEM micrograph presented in Fig. 36.

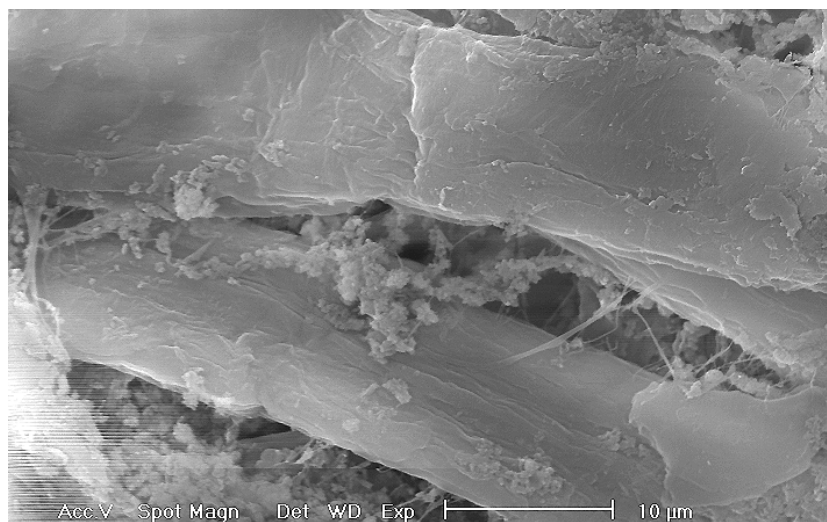


Figure 36. SEM micrograph of a paper sample from a mill-scale trial showing bridging of SuperFill between fibers. The calcium carbonate content of the paper is 21.5%.

A similar location can also be seen in Fig. 38 presented later in Section 5.2. With normal fillers, there may also be filler particles in empty spaces between fibers but accumulating there by a different mechanism, i.e. as part of a larger agglomerate, either homogeneous or heterogeneous, that fills a void or part of it. There is clear evidence that homogeneous filler agglomerates typically exist in conventionally filled papers.

In view of the literature cited earlier in this section, these findings can be considered to be among the reasons contributing to higher paper light scattering coefficient with SuperFill compared with commercial PCC of roughly the same psd, with or without fines addition.

Attempts to quantitatively distinguish between the contributions of the pigment itself, interruption of the fiber bonded area, and reduced collapse of fines to total scattering were outside the scope of this thesis.

5.2 Positive effect of the fines fraction of fines-filler composite on paper strength; the activation model

The second element in the SuperFill mechanism relates to the ability of the fines fraction of SuperFill to alter the fiber network in such a way that improved tensile properties of paper compared with other fillers is achieved. This part of the mechanism is possible in view of the literature cited and the experimental results presented in this thesis.

Retulainen¹⁶⁴ studied the effects of fines addition and fiber beating on fiber network and paper strength. Fines addition and beating appeared to have the same type of effect on the network.

Lobben ^{165, 166} and Giertz ^{167, 168} illustrated the effect of beating on tensile properties as an activation of the fiber network. Lobben postulated that two types of activation occur. First, beating increases the number and size of bonds yielding a decrease in number and length of interbond segments. Second, drying under tension results in improved tensile strength and stiffness of fiber segments, or fibers. Retulainen further suggested ¹⁶⁴ that both these mechanisms are involved, and boosted, when fines are present as explained below.

In activation, which occurs during drying, lateral shrinkage of fibers at bond areas is transmitted to axial shrinkage of intersecting fibers. Furthermore, if shrinkage is restrained, shrinkage at the bonded areas causes free segments to dry under stress, which removes slackness in the segments. When this network is strained both segments and bond areas are ready to bear load; this makes the paper stronger.

Retulainen showed experimentally that the main cause for activation, shrinkage stress, is distinctly increased by the presence of fines ¹⁶⁴. He also concluded from experimental measurements that increase in tensile strength caused by fines addition is mainly due to increase in bonded areas, whereas increase in tensile strength with starch addition is due to increased specific bond strength. It was further concluded that the effect of fines is predominantly structural in nature, whereas starch affects by chemical means. This finding suggests that SuperFill technology and starch-based, or other chemistry-based strength-additive technologies are additive in nature.

Retulainen further postulated the strengthening mechanism of fines and further developed the activation model by Lobben and Giertz. Due to the large surface area of fines, they are able to increase Campbell's forces which are effective during consolidation. Fines can either modify the structure of bond

regions, i.e. interface and peripheral areas with bonds that apparently would have formed anyway, or connect fibers that clearly would have remained apart. The first case is evident with chemical pulp fines. Since Campbell's forces, increased by fines, also keep fibers in contact after wet pressing, the pressing is an essential phase in the presence of fines.

During drying, the network is first compacted prior to fiber shrinkage. During shrinkage, according to Weise and Paulapuro¹⁶⁹, water is first removed from pores between lamellae, causing lamellae aggregation. The next phase is microfibril matrix dehydration. During this phase cross sections of fibers tend to shrink uniformly, which creates stress at the bond areas between fibers.

The model suggested by Retulainen can be demonstrated with two examples, i.e. with and without fines. When fines particles are not present, interaction between fibers is not very strong and the bond area is small. In this case fibers are not strongly collapsed and lateral shrinkage of fibers causes only some axial compression at the bond areas of the neighboring fiber. In the second case, with fines the interaction forces between the fibers in contact are high, causing the internal wall structure to be modified. When sheet shrinkage is prevented these forces result in fiber collapse. Thus, the area of the bonded segment is larger, resulting in enhanced activation. According to the suggested model activation occurs both in bonded and free segments. The activation in the bonded segments evens out the stress concentration at the interface and inside the fiber wall, which enables the fiber wall to bear the load more evenly. Activation in the free segments, when sheet shrinkage is restrained, makes the segment more linear, enabling the sheet to bear the load more evenly. This phenomenon further increases the tensile properties of paper as earlier mentioned.¹⁶⁴

Furthermore, the increase in tensile properties of segments, when stress is applied during drying, was first demonstrated by Jentzen ¹⁷⁰ with individually dried fibers and more recently by Wu *et al.* ¹⁷¹ with 'cut-out' fibers on recycling. Activation starts from enhanced adhesion in the wet sheet and leads, not only to a strong interfiber joint, but to a stronger bonding system with stronger fibers¹⁶⁴.

Since SuperFill contains kraft fines and improves tensile properties of paper compared with conventional fillers in a verifiable way, the present results are in line with the results and deductions of reference regarding the postulated mechanism of enhanced activation in the presence of kraft fines. To further clarify whether activation is really present with SuperFill the values of the elastic modulus for test papers are presented in Fig. 37.

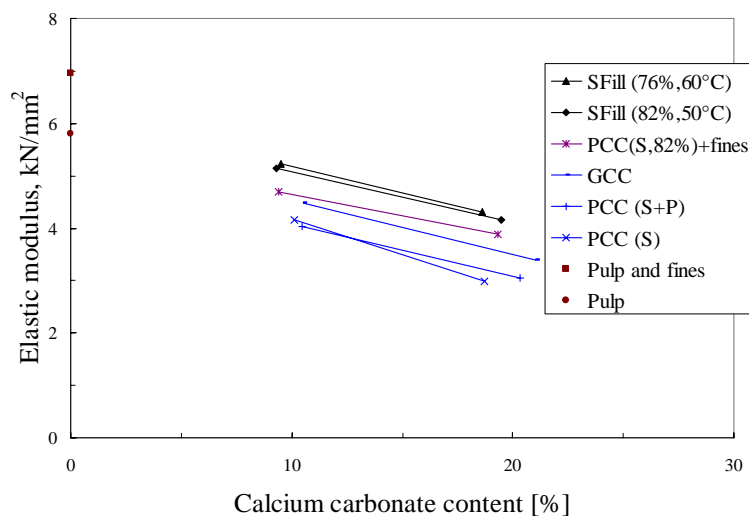


Figure 37. Elastic modulus of handsheets as a function of filler level for the scalenohedral SuperFill obtained under laboratory conditions and for commercial PCCs (S=scalenohedral, SSA 6 m²/g; P=prismatic, SSA 5.5 m²/g; S+P=50/50 mixture) and ground calcium carbonate (GCC=Filler L by Omya). The calcium carbonate portion of SuperFill and initial temperature of precipitation are mentioned in the legend. The psd of the scalenohedral reference PCC was roughly the same as that seen in SuperFill. The furnish consisted of 30% bleached softwood kraft pulp (27 °SR) and 70% bleached birch kraft pulp (22 °SR). Fines were produced from bleached softwood kraft pulp.

It can be seen from Fig. 37 that SuperFill provided papers with considerably higher elastic modulus compared with the reference filler PCC (S) of roughly the same psd. Actually, the elastic modulus with SuperFill was even higher than that with the mixture of fines and PCC (S). This suggests, since paper shrinkage was restrained, that shrinkage at the bonded areas caused free segments to dry under stress, which removed slackness in the segments. When this network was strained both segments and bond areas were ready to bear load, which made the paper stronger. Thus, the increased elastic modulus strongly hints at activation with SuperFill.

To obtain more evidence of activation, fiber bonds and the location of SuperFill in proximity to bond areas were studied with SEM. The micrograph presented in Fig. 38 indicates that there is SuperFill in proximity to bond regions. SuperFill also links fibers together in proximity to bond regions; these features were basically not seen in reference papers with commercial PCC and talc.

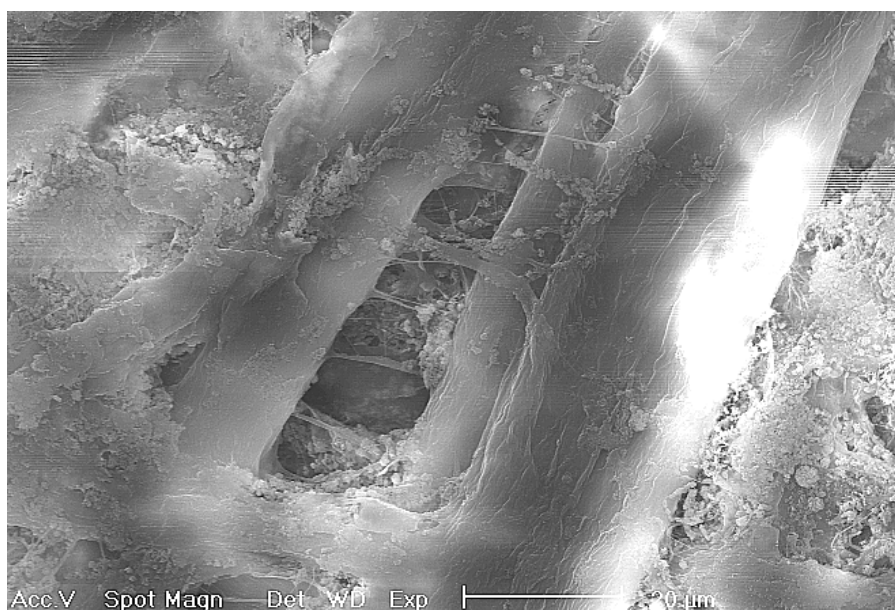


Figure 38. SEM micrograph of a paper sample from a mill-scale trial showing SuperFill bridges between fibers and in proximity to bond regions. The calcium carbonate content of the paper is 21.5%.

It also appears from Fig. 38 that the fibers are somewhat collapsed at the bond areas. All these findings hint at activation.

In view of the above results and findings combined with the results presented earlier in Chapter 4 it is highly probable that enhanced activation is present with SuperFill.

5.3 Improved pore structure with respect to light scattering

An element that contributes to light scattering of paper filled with SuperFill is that SuperFill provides paper with a more optimum pore structure with respect to light scattering. The evidence for this was presented and discussed in detail in Section 4.3.4. The manner by which SuperFill affects the number of optimum structure of pores cannot be concluded for certain in view of the experiments conducted. One explanation may be that SuperFill decreases the number of larger pores by increasing the bond area of fibers. This is in line with the finding that SuperFill usually increases paper density, as kraft fines also do. In addition, another explanation may be related to the improved formation and decreased agglomeration that probably affect positively the pore size distribution. SuperFill was also assumed to fill voids that might have a positive impact on pore size distribution. It is possible that this effect is dependent on the calcium carbonate portion of SuperFill.

5.4 Conclusions

The mechanism of SuperFill in paper can be assumed to consist of three elements, as presented hypothetically in Chapter 3. First, SuperFill provides paper with a more uniform spatial filler distribution with reduced agglomeration, which can be considered an element contributing to the paper light scattering coefficient through the combined effect of the pigment itself, interruption of the fiber bonded area, and reduced fines collapse. Second, the fines fraction of SuperFill most probably contributes to increased activation through enhanced bonding, resulting in increased paper strength. Third, it was shown that SuperFill influences paper in such a way that a more optimum pore structure with respect to light scattering is achieved. Attempts to quantitatively distinguish between the contributions of different elements were outside the scope of this thesis. A unique feature is that the well-

dispersed mineral component of SuperFill may interrupt the fiber bonded area, whereas the fines component simultaneously improves fiber bonding.

SuperFill retention in paper can be assumed to be increasingly mechanical in nature with reduced flocculation, which further provides paper with improved formation. Simultaneous positive elements in the SuperFill mechanism enable simultaneous improvement both in paper strength and light scattering coefficient compared with conventional fillers.

5.5 The role of specific surface area of fines and fibers with respect to the mechanism

When SuperFill is produced, calcium hydroxide and carbon dioxide react mainly on the surfaces of fines particles in water phase to form calcium carbonate. Since the specific surface area (SSA) of fines is high, calcium carbonate tends to precipitate on fines surfaces rather than on larger fiber segments with lower SSA, which are also present to a certain degree. This type of primary heterogeneous nucleation can be concluded by general crystallization theories²³ and the absolute surface area portion of fines. In heterogeneous nucleation a foreign substance makes the free energy barrier lower and the metastable zone narrower,¹⁷² contributing to nucleation. The important role played by heterogeneous nucleation can also be concluded by Figs. 31-34 in Section 5.1, showing that fibrils were entrapped by calcium carbonate. As a clarifying example, the following simple argumentation is made:

According to Luukko's¹⁷³ measurements the average SSA of birch fines is 17.2 m²/g. Furthermore, the amount of the P100 fraction is typically on average of 30% in highly beaten birch pulp material, based on measurements obtained in this thesis. This fraction is considered mainly as fines based on SEM images. According to Luukko, the SSA of the

long-fiber fraction of pine kraft pulp is $2.0 \text{ m}^2/\text{g}$. Since the width of birch kraft fibers suspended in water is not very much different from that of pine kraft fibers regarding Scandinavian pulps¹⁷⁴, the value $2.0 \text{ m}^2/\text{g}$ can also be used, although somewhat erroneously, for birch fibers with sufficient accuracy. The use of this approximation does not make a great difference because the objective is only to clarify the role played by the SSA of fines and fibers in SuperFill technology.

Using these values the net surface area of 1 g of highly beaten birch pulp material is approximately $0.3 \text{ g} \cdot 17.2 \text{ m}^2/\text{g} + 0.7 \text{ g} \cdot 2.0 \text{ m}^2/\text{g} = 6.56 \text{ m}^2$. Furthermore, the portion of the surface area of fines is approximately $0.3 \text{ g} \cdot 17.2 \text{ m}^2/\text{g} / 6.56 \text{ m}^2 \cong 80\%$ of the total surface area of pulp material. This means that approximately 80% of calcium carbonate, which is precipitated on cellulosic material, tends to precipitate on fines.

If we use the value $1.1 \text{ m}^2/\text{g}$ presented by Malton *et al.*¹⁷⁵ instead of the $2.0 \text{ m}^2/\text{g}$ by Luukko for fibers, the conclusion is reached that more than 85% of calcium carbonate tends to precipitate on fines. Furthermore, Szwarcstajn *et al.*¹⁷⁶ presented a SSA for secondary pine kraft fines as high as $140 \text{ m}^2/\text{g}$. If this value for fines is applied together with the $1.1 \text{ m}^2/\text{g}$ for fibers the result is that approximately 98% of calcium carbonate tends to precipitate on fines made of pine kraft pulp.

The previous example includes rough estimates, but indicates the important role played by SSA in the SuperFill technology. Thus, the fines material used in SuperFill technology should contain enough, although not necessarily the total amount, detached fines particles to ensure good performance.

5.6 Paper machine operations with respect to the mechanism

There are certain general issues that should be taken into consideration in paper mills to obtain the most of SuperFill technology. First, additives should generally be dosed prior to SuperFill because the large surface area of the fines fraction tends to dominate the adsorption of additives. For example, starch should be added first to ensure that it is adsorbed by fibers. Under these circumstances the effects of starch and fines are additive in character in terms of tensile properties, as presented earlier in Section 5.2 ¹⁶⁴.

Second, adequate wet pressing is increasingly important because Campbell's forces, increased by the fines fraction of SuperFill, also keep fibers connected after the pressing pressure has ceased. Third, SuperFill functions best in paper machines where drying shrinkage is most effectively prevented. Furthermore, the dewatering capacity of paper machines should be adequate because SuperFill tends to retain water.

There may be additional complicated relationships in certain systems which may affect the optimum dosage points of additives, at least in those applications where other than tensile and light scattering properties are important.

6 ECONOMIC POTENTIAL OF FINES-FILLER COMPOSITE TECHNOLOGY

6.1 Main factors influencing economic potential

The potential of SuperFill technology varies with the paper and board product produced. Within each application parameters such as SuperFill specification can be varied only within a certain range. The added value is in general highest for those products that can be produced with the lowered grammage and increased filler content using SuperFill technology. From the customer's point of view the potential of the technology is highest in those applications with short converting chains where the proportion of paper price in the total price of the end product is high. Furthermore, in certain applications improved quality may enable higher product pricing.

The main requirements for the source of fines are good strength potential and low refining energy input. Both hardwood and softwood chemical pulps can be used. Hardwood pulps usually need less energy to produce a certain amount of fines. Chemical pulps are considered better than mechanical pulps with respect to strength potential of fines and fibrils¹⁶³. Since the source of fines must be easily available, fines should be produced in general from local pulps.

The optimum SuperFill properties are dependent both on paper machine construction and paper product produced, as clarified in Section 4.5. There are also certain prerequisites that must be fulfilled at the mill site prior to implementing SuperFill technology. First, the SuperFill plant location should be as optimum as possible to minimize piping, construction work, electrification costs, etc. Second, an inexpensive high-quality carbon dioxide source should be easily available. Third, lime logistics should be economically arranged.

Since fiber replacement is among the opportunities to achieve savings in raw material costs using SuperFill technology, the economic potential is strongly dependent on pulp price. The higher the pulp price the more savings in raw material costs can be achieved.

6.2 Added value of the technology: a hypothetical paper mill case

The NPV method (net present value) is used in this example ¹⁷⁷. NPV means the added value of investment to shareholders and is defined as the present value of cumulative cash flow of the project. If NPV is positive the technology should be implemented. If NPV is zero the capital investment has a return required by a corporation (added company value, e.g. 15 % return) but added value to the owners does not exist.

The elements of the added value of this sample case within each party are first briefly clarified. First, a papermaker benefits from lower raw material costs per ton of paper due to increased filler content. Second, when grammage is lowered, more printing surface per ton of paper is produced. The profit from this may be shared between a papermaker and its customer. Third, SuperFill technology enables the filler producer to raise the price of calcium carbonate compared with standard PCC fillers. The added value of this is shared between the filler producer and the licensor of the technology. The licensor means the inventor company of the technology and licensee the pigment company.

The assumptions used in this example are:

- data is based on typical local conditions in a paper mill producing 300 000 metric tons of uncoated woodfree paper per year in Europe
- machine speed can be increased with reduced grammage in such a way that capacity will remain unchanged
- average pulp price is same as during the 1990s
- 1/3 of the benefit from decreased grammage can be added to paper price and 2/3 is given to the customer of a papermaker
- calculation period is 10 years
- SuperFill maintains its competitive advantage during the calculation period

The pigment company carries all investment and additional operating costs which thus form part of the SuperFill price. Furthermore, the price of SuperFill is established in such a way that both papermaker and the consortium of the licensor and licensee receive equal shares of the added value beyond the 2/3 of the benefit from decreased grammage given to a customer of a paper company. The setup is also presented schematically in Appendix 12. The total investment of EUR 15 million includes items within corporations using and producing SuperFill as well as research and development costs. The additional operating cost is EUR 18.5/metric ton of calcium carbonate. Depreciation and interest of loan was included in the tax calculation. The amount of loan was estimated to be one half of the investment.

The rough product specification in this example is to increase the filler content of paper from 20% to 28% and to decrease grammage from 80 to 77 g/m². However, a 24% filler content was also used instead of 28%. The proportion of calcium carbonate in SuperFill is 70%. This product specification provides paper with improved opacity, formation, and smoothness with acceptable

bulk and stiffness. Paper brightness and paper machine runnability remain unchanged.

Assuming the presence of long-term mean pulp prices, current market prices for standard PCC and copying paper, 12% interest, and tax rate of 29%, SuperFill results in total added value of EUR 55 million and 40 million for 28% and 24% filler contents from this single paper mill, respectively. For the 28% filler level, according to the setup, the papermaker and consortium both earn EUR 16 million and the papermaker's customer EUR 23 million. Under these conditions the price of SuperFill is slightly less than EUR 240/metric ton of calcium carbonate. When the calculation is repeated for the 24% filler level, the figures are EUR 9 million for the papermaker and the consortium, and EUR 23 million for the papermaker's customer. Under these conditions the price of SuperFill is EUR 210/metric ton of calcium carbonate.

The above figures do not include the paper price premium beyond the benefit from decreased grammage. In practice, when paper quality is improved, an additional price premium can also be added which is not taken into consideration in this example.

This example was performed under constant conditions which in the real paper business vary with the economic situation. The price of pulp follows a cyclical pattern, PCC base price is continuously revised, capital and operating costs vary with the economic situation, etc. By using cyclical pulp prices predicted from the previous cycle the added value does not noticeably change in the long run. However, the annual cash flow varies strongly with pulp price. The result is highly sensitive to the assumptions used in the example.

7 DISCUSSION AND CONCLUSIONS

The present study on diffusion limitations of ionic species inside the fiber wall suggested that fibers without pit apertures cannot be easily fiber wall- or lumen-loaded by a process that utilizes the reaction between calcium hydroxide and carbon dioxide. The measured values of diffusion coefficients indicated that the concentrations of ionic species needed to form calcium carbonate during the precipitation process are much larger on the surface and at close proximity to the surface within the fiber wall as well as in the bulk solution than deeper inside the fiber wall. This finding combined with a general knowledge of crystallization suggests that calcium carbonate tends to precipitate in the bulk solution as well as both on the surfaces and in the first surface layers of fibers rather than deeper inside the fiber walls or in the lumens. This mechanism appears to dominate even at the very start of the precipitation process.

It is also evident that the diffusion coefficient of ions in unfilled fiber walls is about 3 times higher than that in fibers filled with calcium carbonate. This makes sense when we consider the fiber wall as a porous material in which mass transfer occurs between microfibrils and through micropores. Evidently, precipitated calcium carbonate decreases the volume where diffusion can occur and hence obstructs the transfer of ions. The fiber wall loading level attainable is limited, due to these phenomena as well. By considering the facts regarding different wood and pulp fibers that are discussed in Chapter 2, the diffusion coefficients obtained in this study appear to be of the right order of magnitude and in harmony with the information from the literature.

Precipitation on fiber surfaces was assumed to reduce the strength of paper composed of fibers loaded at low consistency. However, paper stiffness appeared to increase with no statistically significant increase in fiber stiffness. This could not be explained by normal paper properties such as bulk and

elastic modulus, unlike the moderate increase in paper stiffness with fibers loaded at medium pulp consistency. A more uniform z-directional filler distribution and complicated interactions between loaded fibers and the other components in the fiber network, which cannot be predicted from the properties of single fibers, were suggested as explanations. Furthermore, the loaded fibers may have behaved differently with respect to the measured and effective thickness of paper.

It was first assumed that satisfactory paper strength using fibers loaded at medium consistency may be due to the lower amount of bulk water present in precipitation, resulting in higher probability of calcium carbonate precipitating within the fiber walls. Since the loading degree was, however, not higher than that achieved at low consistency, the sufficient strength obtained most probably originated from high shear within a medium consistency mixer, which more effectively detached the particles precipitated on the fiber surfaces, resulting in better fiber bonding in papermaking. High shear apparently also further fibrillated the pulp, resulting in higher paper strength in the experiments. Thus, paper stiffness may be slightly increased by using the loaded pulp as a part of the papermaking furnish without sacrificing other paper properties, only when loading is performed at medium pulp consistency. This process also has economic advantages compared with that at low consistency. However, cell wall loading by precipitation either at low- or medium-consistency pulp suspensions appears not to offer any significant quality benefits compared with fillers added normally to the stock. The results are mainly in line with those reported in the literature.

Due to the high tendency for precipitation on surfaces, it was concluded that an effective filler composite may be achieved by precipitating calcium carbonate on cellulosic fines. The result was beneficial in terms of significantly improved paper properties and combination of formation and

retention. The combinations of light scattering coefficient and strength properties especially were significantly improved using this filler innovation, SuperFill. The bending stiffness of paper was also slightly higher with SuperFill compared with commercial PCC. The optimum calcium carbonate portion of SuperFill is dependent on the paper product produced, fines source, and paper machine construction.

The proposed mechanism for SuperFill was assumed to consist of three simultaneous elements. First, SuperFill appears to provide paper with more uniform spatial filler distribution with reduced agglomeration, resulting in higher paper light scattering coefficient and opacity. Second, the fines component of SuperFill most probably contributes to increased activation through enhanced bonding resulting in stronger paper, and third, it was shown that SuperFill provides paper with a more optimum pore structure with respect to light scattering properties. This mechanism is in line with the results concerning critical property combinations of printing and writing papers and paperboards. An advantage is that SuperFill technology and starch-based, or any other chemistry-based, strength aid technologies, are probably additive in nature.

Literature information regarding technologies close to SuperFill is only marginally available. Patents to Cousin *et al.*^{178, 179} describe a method in which calcium carbonate is precipitated on the surface of fibers of expanded surface area having substantial quantity of microfibrils on their surface. Calcium carbonate traps the microfibrils of fibers by mechanical bonding. In contrast to this method, SuperFill is produced by precipitating calcium carbonate on separate detached fines particles which enables the distinctive mechanism of SuperFill, resulting in improved performance.

A patent to Bleakley ¹⁸⁰ relates to a method for recovery and use of particular materials comprising inorganic and organic fines present in an aqueous suspension derived from waste material. Calcium carbonate is precipitated on the fines to be used in papermaking. The method can be used for upgrading waste material to be used mainly in lower-quality paper products in contrast to SuperFill technology which aims at significant quality improvement. The waste material does not contain enough fibrils to function as SuperFill.

A patent to Gavelin ¹⁸¹ relates to a method for producing paper in which filler and pulp containing high proportions of pulp fines are mixed with a retention agent to form flocs that are subjected to a size-controlling shear. The flocs are then fed to a headbox in a paper machine. The method does not comprise precipitation of filler particles. Thus, the bonds between filler particles and fines are chemical compared with the very strong mechanical bonds that exist in SuperFill composites. Due to the presence of weaker bonds flocs more easily break down under conditions of high shear in paper machines, resulting in decreased potential compared with SuperFill. There are also other references such as a patent to Srivatsa et al. ¹⁸² relating to the improvement in brightness of secondary fiber which, however, hint at fiber loading not SuperFill technology.

The added value of SuperFill technology was estimated to be EUR 55 million for a hypothetical paper mill in Europe producing 300 000 tpy uncoated woodfree paper. If the technology is widely implemented the total economic value is multifold. The added value is sensitive to the assumptions used in the example. Thus, the SuperFill technology invented and developed within this thesis seems a promising way for all players in the chain to improve product quality and increase profit.

Further development upgrades of SuperFill may consist of certain chemicals in addition to fines and pigment. An example of this kind of chemical is CMC (carboxy-methyl cellulose) which in preliminary experiments was found to further increase paper strength when sorbed onto SuperFill. Alternatively, the chemical could perhaps serve as a dispersing agent to further improve uniformity of the spatial filler distribution in paper, thus contributing to the light scattering coefficient of paper. This may be possible because retention of SuperFill is effective even though the pigment particles are dispersed. Furthermore, the phenomenon that very small filler pigment particles can be well retained by paper using SuperFill technology could be utilized to further improve paper opacity. Calcium carbonate could also be replaced with other pigment materials or combinations of several materials.

The target of this thesis was achieved and the objectives were appropriately defined. The overall hypotheses regarding SuperFill technology were in general justified and in line with the results. The main theoretical implication of the work probably is that it clearly showed the improvements in the combinations of critical properties and process parameters that can be achieved by engineering raw materials and paper structure. The practical applications can be seen in printing and writing papers as well as in white top paperboards.

8 LIST OF APPENDICES

- Appendix 1 Experimental; fiber loading
- Appendix 2 Paper properties with fibers loaded with calcium carbonate at low consistency compared with commercial PCC; verification experiments
- Appendix 3 Paper properties with fibers loaded with calcium carbonate at medium consistency compared with commercial PCC
- Appendix 4 Experimental; experimental paper machine (XPM) trial
- Appendix 5 Experimental; pilot-scale paper production trials
- Appendix 6 Experimental; mill-scale paper production trial
- Appendix 7 Impact of added fines on light scattering coefficient of paper
- Appendix 8 Pore size distributions of XPM-made papers; mercury porosimetry
- Appendix 9 Pore size distributions of XPM-made papers; mercury porosimetry, the impact of filler content
- Appendix 10 Bulk and stiffness of XPM-made papers
- Appendix 11 White water consistencies in mill-scale trial
- Appendix 12 Setup for the added value estimates

9 REFERENCES

- ¹ GREEN, H.V., FOX, T.J., SCALLAN, A.M., "Lumen-loaded Paper Pulp", *Pulp & Paper Canada* 83 (7):T203-T207 (1982).
- ² MIDDLETON, S.R., SCALLAN, A.M., "Lumen-Loaded Paper Pulp: Mechanism of Filler-to-Fiber Bonding", *Colloids and Surfaces* 16:309-322 (1985).
- ³ ALLAN, G.G., CARROLL, J.P., GINDROZ, K.A., NEGRI, A.R., RITZENHALER, P.M.S., "A new route to alkaline high ash paper by filling the cell wall of pulps with calcium carbonate", The 4th International Conference: New Available Techniques and Current Trends, Bologna, Proceedings:238-248 (1992).
- ⁴ YOSHIDA, T., KANEKO, K., KAZUMORI, K., "Manufacture of Paper in Neutral Condition", Japanese Patent 62-162098 (1987).
- ⁵ ALLAN, G.G., NEGRI, A.R., RITZENTHALER, P., "The microporosity of pulp. The properties of paper made from pulp fibers internally filled with calcium carbonate", *Tappi Journal* (3):239-244 (1992).
- ⁶ JÄRVINEN, S., "Selluloosakuidun ontelotäyttö" - täyteaineen saostus lumeniin", Jyväskylän yliopisto, Kemian laitos, Erikoistyö (1987).
- ⁷ CRAIG, W.L., "Production of pigmented cellulosic pulps", U.S. Patent 2,583,548 (1952).
- ⁸ THOMSEN, A.M., "Method of increasing the opacity of cellulose fibers", U.S. Patent 3,029,181 (1962).
- ⁹ KLUNGNESS, J.H., CAULFIELD, D.F., SACHS, I.B., SYKES, M.S., TAN, F., "Method for fiber loading a chemical compound", U.S. Patent 5,223,090 (1993).
- ¹⁰ TAI, C.Y., CHEN, P.C., "Nucleation, Agglomeration and Crystal Morphology of Calcium Carbonate", *AIChE Journal* 41 (1):68-77 (1995).
- ¹¹ YOSHIDA, T., KANEKO, K., KAZUMORI, K., "Manufacture of Paper in Neutral Condition", Japanese Patent Application 60-297382 (1985).
- ¹² ALLAN, G., "Paper for the 21 st Century", *PaperAge* (1):10-15 (1995).

-
- ¹³ KLUNGNESS, J., CAULFIELD, D., SACHS, I., TAN, F., SYKES, M., SHILTS, R., "Fiber Loading: A Progress Report", TAPPI Recycling Symposium, Proceedings:283-290 (1994).
- ¹⁴ MILLER, M., PALIWAL, D., "The Effects of Lumen-Loading on Strength and Optical Properties of Paper", *Journal of Pulp and Paper Science* 11 (3): J84-J88 (1985).
- ¹⁵ FUJIWARA, K., "Progress of Inorganic Filler Composite Pulp for High Performance Papers. On the Utilization of Fiber Lumen Loading and Micropore Loading", *Kami Pa Gikyoshi* 47 (4):437-448 (1993).
- ¹⁶ ALLAN, G.A., CARROLL, J.P., NEGRI, A.R., RAGHURAMAN, M., RITZENTHALER, P., YAHIAOUI, A., "The microporosity of pulp. The precipitation of inorganic fillers within the micropores of the cell wall", *Tappi Journal* (1):175-178 (1992).
- ¹⁷ MALONEY, T.C., PAULAPURO, H., "The Formation of Pores in the Cell Wall", *Journal of Pulp and Paper Science* 25 (12):430-436 (1999).
- ¹⁸ MALONEY, T.C., "On the Pore Structure and Dewatering Properties of the Pulp Fiber Cell Wall", *Acta Polytechnica Scandinavica, Chemical Technology Series* No. 275 (2000).
- ¹⁹ LINDSTRÖM, T., CARLSSON, G., "The effect of chemical environment on fiber swelling", *Svensk Papperstidning* 85 (3):R14-R20 (1982).
- ²⁰ FREIER, R.K., "Aqueous solutions", Walter de Gruyter, Berlin (1976).
- ²¹ PLUMMER, L.N., BUSENBERG, E., "The solubilities of calcite, aragonite and vaterite in CO₂-H₂O solutions between 0 and 90 °C, and an evaluation of the aqueous model for the system CaCO₃-CO₂-H₂O", *Geochimica et Cosmochimica Acta* 46:1011-1040 (1982).
- ²² MULLIN, J.W., "Crystallization", Butterworths, London (1961).
- ²³ NÝVLT, J., SÖHNEL, O., MATUCHOVÁ, M., BROUL, M., "The Kinetics of Industrial Crystallization", Elsevier, New York (1985).

-
- ²⁴ VANDERHEIDEN D.B., "Spherically Shaped Precipitated Calcium Carbonate, Its Preparation and Use", Canadian patent 1 269 223 (1990).
- ²⁵ JONES, A.G., HOSTOMSKY, J., LI, Z., "On the effect of liquid mixing rate on primary crystal size during the gas-liquid precipitation of calcium carbonate", *Chemical Engineering Science* 47 (13/14):3817-3824 (1992).
- ²⁶ HEDBORG, F., Unpublished report (SCAN-Forsk rapport nr. 408) (1984).
- ²⁷ HIGUCHI, M., MIYAUCHI, D., TAKEUCHI, A., KODAIRA, K., "Hydrothermal growth of calcite single crystals from H₂O-CO₂-CaCO₃ system under controlled CO₂ pressure", *Journal of Crystal Growth* 121:39-43 (1992).
- ²⁸ YAMADA, H., "Control of the morphology of precipitated calcium carbonate", *Jpn. Tappi* 44 (1):62-69 (1990).
- ²⁹ REDDY, M.M., GAILLARD, W.D., "Kinetics of Calcium Carbonate (Calcite)-Seeded Crystallization: Influence of Solid/Solution Ratio on the Reaction Rate Constant", *Journal of Colloid and Interface Science* 80 (1):171-178 (1981).
- ³⁰ VAN ROSMALEN, G.M., WITKAMP, G.J., DE VREUGD, C.H., "Additive and impurity effects in crystallization processes", *Industrial Crystallization 87, Proceedings of the 10th Symposium on Industrial Crystallization 87*, Nývlt, J., Záček, S. (Ed.), Elsevier, Amsterdam, p. 15-20 (1989).
- ³¹ VERDOES, D., LANDSCHOOT, R.C., VAN ROSMALEN, G.M., "The influence of additives on the crystal size distribution of CaCO₃ in batch precipitation experiments", Report of Delft University of Technology:621-626 (1988).
- ³² SUHARA, T., ESUMI, K., MEGURO, K., "Effect of Surfactant on Formation of CaCO₃", *Bull. Chem. Soc. Jpn.* 56 (10):2932-2936 (1983).
- ³³ CANSÉLIER, J.P., "The effects of surfactants on crystallization phenomena", *J. Dispersion Science and Technology* 14 (6):625-644 (1993).
- ³⁴ DALAS, E., "Crystallization of Sparingly Soluble Salts on Functionalized Polymers", *J. Mater. Chem.* 1 (3):473-474 (1991).

-
- ³⁵ WAKITA, H., KINOSHITA, S., "Growth of tiny calcite single crystals in an aqueous solutions", *Journal of Crystal Growth* 71:807-809 (1985).
- ³⁶ PETERS, R.W., STEVENS, J.D., "Effect of iron as a trace impurity on the water softening process", Nucleation, Growth, and impurity effects in crystallization process engineering, Epstein, M.A.F. (Ed.), AIChE symposium series 78:46-67 (1982).
- ³⁷ GIANNIMARAS, E.K., KOUTSOUKOS, P.G., "The Crystallization of Calcite in the Presence of Orthophosphate", *Journal of Colloid and Interface Science* 116 (2):423-430 (1987).
- ³⁸ MUCCI, A., "Growth kinetics and composition of magnesian calcite overgrowths precipitated from seawater: Quantitative influence of orthophosphate ions", *Geochimica et Cosmochimica Acta* 50:2255-2265 (1986).
- ³⁹ XYLA, A.G., KOUTSOUKOS, P.G., "Effect of Diphosphonates on the Precipitation of Calcium Carbonate in Aqueous Solutions", *Journal of the Chemical Society, Faraday Transactions 1* 83, part 5:1477-1484 (1987).
- ⁴⁰ KAVANAGH, A.M., RAYMENT, T., "Inhibitor Effects on Calcite Growth at Low Supersaturations", *J. Chem. Soc. Faraday Trans.* 86(6):965-972 (1990).
- ⁴¹ GIANNIMARAS, E.K., KOUTSOUKOS, P.G., "Precipitation of Calcium Carbonate in Aqueous Solutions in the Presence of Oxalate Anions", *Langmuir* 4 (4):855-861 (1988).
- ⁴² MASON, S.G., "The motion of fibres in flowing liquids", *Pulp and Paper Magazine of Canada* (4):93-100 (1950).
- ⁴³ MASON, S.G., "Fiber Motions and Flocculation", *Tappi* 37 (11):494-501 (1954).
- ⁴⁴ RITALA, R., HUIKU, M., "Scaling, percolation and network theories: new insight into papermaking?", *Fundamentals of Papermaking, Transactions of the Ninth Fundamental Research Symposium Held at Cambridge, Baker, C.F.*

and Punton, V.W. (Ed.), Mechanical Engineering Publications Limited, London, Vol. 1:195-218 (1989).

⁴⁵ ROBERTSON, A.A., MASON, S.G., "The Flow Characteristics of Dilute Fiber Suspensions", *Tappi* 40 (5):326-334 (1957).

⁴⁶ FORGACS, O.L., ROBERTSON, A.A., MASON, S.G., "The Hydrodynamic Behaviour of Paper-Making Fibres", *Pulp and Paper Magazine of Canada* (5):117-128 (1958).

⁴⁷ WAHREN, D., "Fiber Network Structures in Papermaking Operations", IPC Conference on Paper Science and Technology, Proceedings:112-129 (1980).

⁴⁸ PARKER, J.D., "The Sheet Forming Process", TAPPI STAP No. 9 (1972).

⁴⁹ KEREKES, R.J., SCHELL, C.J., "Characterization of Fibre Flocculation Regimes by a Crowding Factor", *Journal of Pulp and Paper Science* 18 (1):J32-J38 (1992).

⁵⁰ JOKINEN, O., EBELING, K., "Flocculation tendency of papermaking fibres", *Paperi ja Puu* 67 (5):317-325 (1985).

⁵¹ KEREKES, R.J., SOSZYNSKI, R.M., TAM DOO, P.A., "The flocculation of pulp fibres", the 8th Fundamental Research Symposium, Papermaking Raw Materials, Proceedings:265-309 (1985).

⁵² STEENBERG, B., JOHANSON B., "Viscous Properties of Pulp Suspension at High Shear-Rates", *Svensk Papperstidning* 61 (18B):696-700 (1958).

⁵³ THALÉN, N., WAHREN, D., "Shear Modulus and Ultimate Shear Strength of Some Paper Pulp Fiber Networks", *Svensk Papperstidning* 67 (7):259-264 (1964).

⁵⁴ WAHREN, D., "On the Visco-Elastic Properties of Fibre Networks", *Svensk Papperstidning* 67 (9):378-381 (1964).

⁵⁵ MEYER, R., WAHREN., D., "On the Elastic Properties of Three-Dimensional Fibre Networks", *Svensk Papperstidning* 67 (10):432-436 (1964).

-
- ⁵⁶ THALEN, N., WAHREN, D., "An Experimental Investigation of the Shear Modulus of Model Fibre Networks", *Svensk Papperstidning* 67 (11):474-480 (1964).
- ⁵⁷ BERGMAN, J., TAKAMURA, N., "The Correlation Between the Shear Modulus of Fibre Networks and the Individual Fibre Stiffness", *Svensk Papperstidning* 68 (20):703-710 (1965).
- ⁵⁸ TURNER, J.C., TITCHENER, A.L., DUFFY, G.G., "The flow characteristics of deaerated wood pulp suspensions", *Appita* 30 (1):41-47 (1976).
- ⁵⁹ LONGDILL, G.R., DUFFY, G.G., "The Shear Behaviour of Medium Concentration Wood Pulp Suspensions", *Appita* 41 (6):456-461 (1988).
- ⁶⁰ BENNINGTON, C.P.J., KEREKES, R.J., GRACE, J.R., "The Yield Stress of Fibre Suspensions", *The Canadian Journal of Chemical Engineering* 68:748-757 (1990).
- ⁶¹ DAMANI, R., POWELL, R.L., HAGEN, N., "Viscoelastic characterization of medium consistency pulp suspensions", AICHE Forest Products Symposium, AICHE Proceedings:135-140 (1991).
- ⁶² SWERIN, A., POWELL, R.L., ÖDBERG, L., "Linear and nonlinear dynamic viscoelasticity of pulp fiber suspensions", *Nordic Pulp and paper Research Journal* (3):126-132 (1992).
- ⁶³ SWERIN, A., ÖDBERG, L., "Flocculation and floc strength in suspensions flocculated by retention aids", *Nordic Pulp and paper Research Journal* (1):141-147 (1993).
- ⁶⁴ ANDERSSON, O., "Some Observations on Fibre Suspensions in Turbulent Motion", *Svensk Papperstidning* 69 (2):23-31 (1966).
- ⁶⁵ MIH. W., PARKER, J., "Velocity Profile Measurements and a Phenomenological Description of Turbulent Fiber Suspension Pipe Flow", *Tappi* 50 (5):237-246 (1967).

-
- ⁶⁶ PERSINGER, W.H., MEYER, H., "Scale of flocculation for fully developed turbulent tube flow of dilute fibre suspensions", *Paperi ja Puu* (9):563-577 (1975).
- ⁶⁷ DUFFY, G.G., TITCHENER, A.L., "The disruptive shear stress of pulp networks", *Svensk Papperstidning* (13):474-479 (1975).
- ⁶⁸ DUFFY, G.G., LEE, P.F.W., "Drag reduction in the turbulent flow of wood pulp suspensions", *Appita* 31 (4):280-286 (1978).
- ⁶⁹ TAKEUCHI, N., SENDA, S., NAMBA K., KUWABARA, G., "Formation and destruction of fibre flocs in a flowing pulp suspension", *Appita* 37 (3):223-230 (1983).
- ⁷⁰ D'INCAU, S., "Characterization of the decay of turbulence in a pulp suspension flow", TAPPI Engineering Conference, Proceedings:583-592 (1983).
- ⁷¹ KEREKES, R.J., "Pulp Flocculation in Decaying Turbulence: A Literature Review", *Journal of Pulp and Paper Science* (July):TR86-TR91 (1983).
- ⁷² WAGLE, D.G., LEE, C.W., BRODKEY, R.S., "Further comments on a visual study of pulp floc dispersion mechanisms", *Tappi Journal* 71 (8):137-141 (1988).
- ⁷³ HOURANI, M.J., "Fiber flocculation in pulp suspension flow. Part 1: Theoretical model", *Tappi Journal* 71 (5):115-118 (1988).
- ⁷⁴ HOURANI, M.J., "Fiber flocculation in pulp suspension flow. Part 2: Experimental results", *Tappi Journal* 71 (6):186-189 (1988).
- ⁷⁵ STEEN M., "A concept for fibre flocculation in turbulent flow", *Fundamentals of Papermaking, Transactions of the Ninth Fundamental Research Symposium Held at Cambridge*, Baker C.F. and Punton V.W. (Ed.), Mechanical Engineering Publications Limited, Vol. 1:251-274 (1989).
- ⁷⁶ STEEN, M., "Modeling fiber flocculation in turbulent flow: a numerical study", *Tappi Journal* 74 (9):175-182 (1991).

-
- ⁷⁷ BENNINGTON, C.P.J., MMBAGA, J.P., "Liquid-phase turbulence in pulp fibre suspensions", *The Science of Papermaking, Transactions of the 12th Fundamental Research Symposium Held at Oxford*, Baker, C.F. (Ed.), The Pulp and Paper Fundamental Research Society, Lancashire, Vol. 1:255-286 (2001).
- ⁷⁸ GULLICHSEN, J., HÄRKÖNEN, E., "Medium consistency technology, I. Fundamental data", *Tappi* 64 (6):69-72 (1981).
- ⁷⁹ BENNINGTON, C.P.J., KEREKES, R.J., GRACE, J.R., "Motion of Pulp Fibre Suspensions in Rotary Devices", *The Canadian Journal of Chemical Engineering* 69:251-258 (1991).
- ⁸⁰ TUOMISAARI, M., Unpublished report (PSC Communications 19) (1991).
- ⁸¹ TUOMISAARI, M., GULLICHSEN J., HIETANIEMI, J., "Floc disruption in medium-consistency fiber suspensions", *International Paper Physics Conference, TAPPI Proceedings*:609-612 (1991).
- ⁸² KE-FU, C., SHU-MEI, C., "The determination of the critical shear stress for fluidization of medium consistency suspensions of straw pulps", *Nordic Pulp and Paper Research Journal* (1):20-42 (1991).
- ⁸³ SETH, R.S., FRANCIS, D.W., BENNINGTON, C.P.J., "The effect of mechanical treatment during medium stock concentration fluidization on pulp properties", *Appita* 46(1):54-60 (1993).
- ⁸⁴ HIETANIEMI, J., GULLICHSEN, G., Unpublished Report (PSC Communications 63) (1994).
- ⁸⁵ SILENIUS, P., LINDSTRÖM, M., "Diffusion controlled kinetics of electrolyte transfer within the pulp fiber wall: Estimation of fiber wall pore structure", *The Fundamentals of Papermaking Materials, Transactions of the 11th Fundamental Research Symposium Held at Cambridge*, Baker, C.F. (Ed.), Pira International, Surrey, Vol. 2:815-836 (1997).
- ⁸⁶ SILENIUS, P., "Preparation of Filler Containing Papermaking Materials by Precipitating Calcium Carbonate in-situ in the Presence of Cellulosic

Materials", Lappeenranta University of Technology, Department of Chemical Technology, Licentiate Thesis (1996).

⁸⁷ MEURONEN, J., "Kalsiumkarbonaatin saostus selluhienoaineeseen ja ominaisuudet paperin täyteaineena", Lappeenrannan teknillinen korkeakoulu, kemiantekniikan osasto, Diplomityö (1997).

⁸⁸ SIVÉN, S., "Kalsiumkarbonaatin kiteyttäminen sellukuituun savukaasumenetelmällä ja sen vaikutukset paperin ominaisuuksiin", Lappeenrannan teknillinen korkeakoulu, Kemiantekniikan osasto, Diplomityö (1994).

⁸⁹ SIVÉN, S., SILENIUS, P., LINDSTRÖM, M., "Precipitation of Calcium Carbonate within Pulp Fiber Walls by Means of Carbon Dioxide Process at Low Pulp Consistency", Lappeenranta University of Technology, Department of Chemical Technology, Publication 64 (1996).

⁹⁰ PETLICKI, J., VAN DE VEN, T.G.M., "Kinetics of Lumen Loading", *Journal of Pulp and Paper Science* 20 (12):J375-J382 (1994).

⁹¹ MIDLETON, S.R., SCALLAN, A.M., "A Kinetic Model for the Adsorption of Fillers by Pulp Fibres", *Journal of Pulp and Paper Science* 17 (4):J127-J133 (1991).

⁹² ALINCE, B., PETLICKI, J., VAN DE VEN, T.G.M., "Kinetics of colloidal particle deposition on pulp fibers. 1. Deposition of clay on fibers of opposite charge", *Colloids and Surfaces* 59:265-277 (1991).

⁹³ KREITUSS, A., DRUZ, N., CHIRKOVA, E., LUSE, I., "Estimation of diffusion and distribution of chemical compounds in wood", International Symposium on Wood & Pulping Chemistry, TAPPI Proceedings:13-19 (1989).

⁹⁴ SKAAR, Ch., SIAU, J.F., "Thermal Diffusion of Bound Water in Wood", *Wood Science and Technology* 15:105-112 (1981).

⁹⁵ HEAZEL, T.E., McDONOUGH, T.J., "Cell wall sulfur distribution in sulfonated southern pine latewood - Part 2: Effects of process variables and

mathematical modeling of intrafiber diffusion with reaction", International Paper Physics Conference, TAPPI Proceedings Book 1: 225-246 (1991).

⁹⁶ BEEN, J., OLOMAN, C.W., "Electrical Conductivity of Pulp Suspensions Using the Donnan Equilibrium Theory", *Journal of Pulp and Paper Science* 21 (3):J80-J85 (1995).

⁹⁷ BEEN, J., " A novel approach to kinetic modeling of the hydrogen peroxide brightening of mechanical pulp", *Tappi Journal* 78 (8):144-152 (1995).

⁹⁸ CARSLAW, H.S., JAEGER, J.C., "Conduction of Heat in Solids", Second Edition, Oxford University Press, London (1959).

⁹⁹ TLUČHOŘ, D., GOSMAN, A., "Kinetics of diffusion in dialysis cells", *Acta Polytechnica Scandinavica*, Ch 178:43-55 (1987).

¹⁰⁰ CHURCHILL, R.V., "Operational Mathematics", Third Edition, McGraw-Hill Kogakusha, Ltd., Tokyo (1972).

¹⁰¹ TUMA, J.J., "Handbook of numerical calculations in engineering", McGraw-Hill, New York (1989).

¹⁰² Kuo, J., Fox, E., Mitchell, D., Tuerke, T., Transform and Curve Fitting Reference, Copyright 1990, 1991, 1992, Jandel Scientific.

¹⁰³ SCALLAN, A.M., "The electrical conductance of pulp suspensions", *Tappi Journal* 72 (11):157-162 (1989).

¹⁰⁴ OSTROWSKA, B., NARĘBSKA, A., "Diffusion of Dyes in Polyester Fibers. II. Diffusion Coefficients from the Radial Distribution Curves", *Journal of Applied Polymer Science* 25:2845-2855 (1980).

¹⁰⁵ BRIGGS, G.E., HOPE, A.B., ROBERTSON, R.N., "Electrolytes and plant cells", Botanical monographs Vol. 1, James W.O. (Ed.), Blackwell Scientific Publications, Oxford (1961).

¹⁰⁶ STAMM, A.J., "An electrical conductivity method for determining the effective capillary dimensions of wood", *Journal of Physical Chemistry* 36:312-325 (1932).

-
- ¹⁰⁷ CADY, L.C., WILLIAMS, J.W., "Molecular diffusion into wood", *The Journal of Physical Chemistry* 39 (1):87-102 (1935).
- ¹⁰⁸ LOBO, V.M.M, QUARESMA, J.L., "Electrolyte solutions. Literature data on thermodynamic and transport properties", Vol 2, Faculdade de Ciências, Universidade de Coimbra, Coimbra (1981).
- ¹⁰⁹ LUNER, P., "The effect of pre-treatments on diffusion through wood", *Pulp and Paper Magazine of Canada* 57 (3):216-223 (1956).
- ¹¹⁰ STEADMAN, R., LUNER, P., "The effect of wet fibre flexibility of sheet apparent density", *Papermaking Raw Materials, Transactions of the Eighth Fundamental Research Symposium Held at Oxford*, Punton, V. (Ed.), Mechanical Engineering Publications Limited, London, Vol. 1:311-337 (1985).
- ¹¹¹ NISKANEN, K., KETTUNEN, H., HILTUNEN, E., Unpublished report (KCL) (2000).
- ¹¹² PALENIUS, I., "Kemiallisen massanvalmistuksen uudet haasteet: KUMOUS-projektin loppuseminaari", *Paperi ja Puu* 83 (3):178-181 (2001).
- ¹¹³ GULLICHSEN, J., PAULAPURO, H. (Series Ed.), "Papermaking Science and Technology", NISKANEN, K. (Book Ed.), "Paper Physics", Book 16, Fapet Oy, Jyväskylä (1998).
- ¹¹⁴ KLUNGNESS, J.H., SYKES, M.S., TAN, F., ABUBAKR, S., EISENWASSER, J.D., "Effect of fiber loading on paper properties", *TAPPI Journal* 79 (3):297-301 (1996).
- ¹¹⁵ GULLICHSEN, J., PAULAPURO, H. (Series Ed.), "Papermaking Science and Technology", NEIMO, L. (Book Ed.), "Papermaking Chemistry", Book 4, Fapet Oy, Jyväskylä (1999).
- ¹¹⁶ WEIGL, J., "Allgemeine Anforderungen an Streichpigmente sowie deren Charakterisierung", *PTS Seminar, Proceedings:Chapter 10* (2001).
- ¹¹⁷ RYTI, N., AALTONEN, P., "Method for evaluation paper pulps for a certain end product", *Paper (World research and development number):42-56* (1976).

-
- ¹¹⁸ LEVLIN, J-E., PAULAPURO H., "Characterization strategies for papermaking pulps", *Paperi ja Puu* (5):410-416 (1987).
- ¹¹⁹ BOWN, R., "A review of the influence of pigments on papermaking and coating", *The Fundamentals of Papermaking Materials, Transactions of the 11th Fundamental Research Symposium Held at Cambridge*, Baker, C.F. (Ed.), Pira International, Surrey, Vol. 1:83-137 (1997).
- ¹²⁰ VAN DE VEN, T.G.M., "Physicochemical and hydrodynamic aspects on fines and filler retention", *Fundamentals of Papermaking, Transactions of the Ninth Fundamental Research Symposium Held at Cambridge*, Baker, C.F. and Punton, V.W. (Ed.), Mechanical Engineering Publications Limited, London, Vol. 1:471-494 (1989).
- ¹²¹ BOWN, R., "Paper Chemistry", Roberts, J.C., (Ed.), Blackie & Son Ltd., Glasgow and London (1991).
- ¹²² MÜLLER, F., BECK, U., "Retentionsmittel, Eigenschaften, Wirkungsweise und Einflußgrößen", *Das Papier* 33:V89-V95 (1979).
- ¹²³ LINDSTRÖM, T., "Some fundamental chemical aspects on paper forming", *Fundamentals of Papermaking, Transactions of the Ninth Fundamental Research Symposium Held at Cambridge*, Baker, C.F. and Punton V.W. (Ed.), Mechanical Engineering Publications Limited, London, Vol. 1:311-412 (1989).
- ¹²⁴ HORN, D., LINHART, F., *Paper Chemistry*, Roberts, J.C., (Ed.), Blackie & Son Ltd., Glasgow and London, p. 44-62 (1996).
- ¹²⁵ GERISCHER, G., MURRAY, L.J., VAN WYK, W.J., "Improved retention of filler clay by means of pre-flocculation and selective dosing", *Paperi ja Puu* 78 (1-2):51-56 (1996).
- ¹²⁶ GAVELIN, G., "The Coflocculation Process", *Nordic Pulp and Paper Research Journal* (Special Issue):31-35 (1988).
- ¹²⁷ BOWN, R., "Review of Methods for Increasing Filler Loadings", *Paper Technology and Industry* 26(6):289-292 (1985).

-
- ¹²⁸ STRUTZ, M.D., SPRINGER, A.M., "A wet-end optimization strategy for total water reuse", *Tappi* 65 (3):139-142 (1982).
- ¹²⁹ KIVIRANTA, A., "Fiber and forming-related mechanisms affecting formation", 1996 Papermakers Conference, Tappi Proceedings:239-245 (1996).
- ¹³⁰ KIVIRANTA, A., DODSON, C.T.J., "Evaluating Fourdrinier Formation Performance", *Journal of Pulp and Paper Science* 21 (11):J379-J383 (1995).
- ¹³¹ DODSON, C.T.J., SCHAFFNIT, C., "Flocculation and orientation effects on paper-formation statistics", *Tappi Journal* 75 (1):167-171 (1992).
- ¹³² EGELHOF, D., BUBIK, A., "Der Einfluss des Maschinenbaus auf die Blattbildung", *Wochenblatt für Papierfabrikation* 122 (4):111-117 (1994).
- ¹³³ CORTE, H., "Über die Verteilung der Massendichte in Papier", *Das Papier* 23 (7):381-393 (1969).
- ¹³⁴ CORTE, H., "Faserstruktur und physikalische Eigenschaften von Papier", *Das Papier* 16 (10A):575-587 (1962).
- ¹³⁵ KERÉKES, R.J., SCHELL, C.J., "Characterization of Fibre Flocculation Regimes by a Crowding Factor", *Journal of Pulp and Paper Science* 18 (1):J32-J38 (1992).
- ¹³⁶ HULTÉN M-L., Unpublished report (M-real, project number 221 000) (January 11, 2001).
- ¹³⁷ HULTÉN M-L., Unpublished report (M-real, project number 187 000) (August 15, 2000).
- ¹³⁸ GILL, R.A., AARNI, E., IMPPOLA, O., LAAKSO, A.-P., "Use of precipitated calcium carbonate (PCC) fillers to improve the brightness and opacity of woodfree and wood containing papers", Pira Conference on Use of minerals in papermaking, Manchester, Proceedings (1997).
- ¹³⁹ MARKSTRÖM, H., "The Elastic Properties of Paper - Test Methods and Measurement Instruments", Lorentzen & Wettre, Stockholm (1991).

-
- ¹⁴⁰ KARTOVAARA, I., "Gradienttikalanterointi: gradienttien syntymisen ja kalanterointituloksen arvostelun perusteet", Helsinki University of Technology, Licentiate thesis (1989).
- ¹⁴¹ JOHANSSON, P-Å., NORMAN, B., "Method for evaluating formation, print unevenness and gloss variations developed at STFI", 1996 Process & Product Quality Conference, Proceedings:139-145 (1996).
- ¹⁴² ZHAO, R.H., KEREKES, R.J., "Pressure distribution between forming fabrics in blade gap formers: Thin blades", 80th Annual Meeting, Technical Section, CPPA, Montreal, Canada, Proceedings A:A31-A38 (1994).
- ¹⁴³ KORPI, T., "Kaksoisviirakoneiden retentioon vaikuttavia tekijöitä puupitoisen painopaperin valmistuksessa", Helsingin yliopisto, lisensiaatintyö (1989).
- ¹⁴⁴ ALINCE, B., "Light-scattering of pigments in papermaking", *Paperi ja Puu - Papper och Trä* (8):545-547 (1986).
- ¹⁴⁵ ALINCE, B., LEPOUTRE, P., "Light-scattering of filled sheets: the effect of pigment dispersion", *Tappi* 64 (11):117-118 (1981).
- ¹⁴⁶ PHIPPS, J., "Choosing Fillers for Optimum Paper Properties: Understanding the Compromises", Conference on Scientific and Technical Advances in Fillers and Pigments in Papermaking, Pira, London, Proceedings (2001).
- ¹⁴⁷ HOWARD, G.J., "The influence of polymers on the light scattering of TiO₂ pigment in paper", *Tappi Journal* 66 (6):87-91 (1983).
- ¹⁴⁸ GREEN, K., LUMME, K., "Comparison of radiative transfer Monte Carlo and volume integral equation methods of studying the clustering of small scatterers", *Applied Optics* 40 (22):3711-3717 (2001).
- ¹⁴⁹ BOWN, R., "The relationship between strength and light scattering coefficient for filled papers", Papermaking Raw Materials, Transactions of the Eighth Fundamental Research Symposium Held at Oxford, Punton, V. (Ed.), Mechanical Engineering Publications Limited, London, Vol. 2:543-576 (1985).

¹⁵⁰ DAVIDSON, R.R., "Experiments on loading paper with low refractive index fillers", *Paper Technology* 6 (2):107-114 (1965).

¹⁵¹ ALINCE, B., LEPOUTRE, P., "Light-scattering of filled sheets: The combined effect of pigment size and fiber debonding", *Tappi* 64 (4):135-136 (1981).

¹⁵² ALINCE, B., LEPOUTRE, P., "Light scattering in filled sheets - separating the contribution of the pigment and of fiber debonding", *Tappi Journal* 68 (4):122-123 (1985).

¹⁵³ PARSON, S.R., "Optical Characteristics of Paper as a Function of Fiber Classification", *Paper Trade Journal* 115:314-322 (1942).

¹⁵⁴ RATLIFF, F.T., "The Possible Correlation Between Hemicelluloses and the Physical Properties of Bleached Kraft Pulps", *Tappi* 32 (8):357-367 (1949).

¹⁵⁵ KEENEY, F.C., "Physical Properties of Slash Pine Semichemical Kraft Pulp and of Its Fully Chlorited Component", *Tappi* 35 (12):555-563 (1952).

¹⁵⁶ LEECH, H.J., "An Investigation of the Reasons for Increase in Paper Strength when Locust Bean Gum Is Used as a Beater Adhesive", *Tappi* 37 (8):343-349 (1954).

¹⁵⁷ HASELTON, W.R., "Gas Adsorption by Wood, Pulp, and Paper, II. The Application of Gas Adsorption Techniques to the Study of the Area and Structure of Pulps and the Unbonded and Bonded Area of Paper", *Tappi* 38 (12):716-723 (1955).

¹⁵⁸ ALINCE, B., "Optimization of pigment performance in paper", *Fundamentals of Papermaking, Transactions of the Ninth Fundamental Research Symposium Held at Cambridge*, Baker, C.F. and Punton, V.W. (Ed.), Mechanical Engineering Publications Limited, London, Vol. 1:495-508 (1989).

¹⁵⁹ ALINCE, B., "Performance of pigments in filled sheets", 1985 Papermakers Conference, TAPPI Proceedings:31-34 (1985).

¹⁶⁰ GILL, R.A., HAGEMeyer, R.W., SCOTT, W.E., "Introduction to the basics of fillers used in papermaking", *Dyes, Fillers & Pigments*, TAPPI Course Notes:1-11 (1990).

¹⁶¹ HAGEMeyer, R.W., "The Effect of Pigment Combination and Solids Concentration on Particle Packing and Coated Paper Characteristics. I. Relationship of Particle Shape to Particle Packing", *Tappi* 43 (3):277-288 (1960).

¹⁶² LI, H.M., SCOTT, W.E., "The Use of Britt Jar Retention-RPM Curves and Microscopic Analysis to Determine the Aggregation State of a Papermaking Furnish", 2000 TAPPI Papermakers Conference and Trade Fair, TAPPI proceedings:733-755 (2000).

¹⁶³ LUUKKO, K., "Characterization and Properties of Mechanical Pulp Fines", *Acta Polytechnica Scandinavica, Chemical Technology Series* No. 267 (1999).

¹⁶⁴ RETULAINEN, E., "The Role of Fibre Bonding in Paper Properties", Helsinki University of Technology, Laboratory of Paper Technology, Reports, Series A7 (1997).

¹⁶⁵ LOBBEN, T.H., "The Tensile Stiffness of Paper. Part 1. A model based on activation", *Norsk Skogindustri* 29 (12):311-315 (1975).

¹⁶⁶ LOBBEN, T.H., "The Tensile Stiffness of Paper. Part 2. Activation Studied by Freeze Drying", *Norsk Skogindustri* 30 (3):43-48 (1976).

¹⁶⁷ GIERTZ, H.W., "The influence of beating on individual fibers and the causal effects on paper properties", IPC International Symposium on Fundamental Concepts of Refining, Preprints:87-92 (1980).

¹⁶⁸ GIERTZ, H.W., "Understanding the role of fines", International Symposium on Fundamental Concepts of Refining, Preprints:324-330 (1980).

¹⁶⁹ WEISE, U., PAULAPURO, H., "Changes of fibre dimensions during drying", 1995 International Paper Physics Conference, Niagara on-the Lake, Ontario, Proceedings:121-124 (September, 1995).

-
- ¹⁷⁰ JENTZEN, C.A., "The Effect of Stress Applied During Drying on Some of the Properties of Individual Pulp Fibers", *Tappi* 47 (7):412-418 (1964).
- ¹⁷¹ WUU, F., MARK, R.E., PERKINS, R.W., "Mechanical properties of "cut-out" fibers in recycling", 1991 International Paper Physics Conference, Kona, TAPPI Proceedings: 663-680 (1991).
- ¹⁷² MYERSON, A. S. (Ed.), "Handbook of Industrial Crystallization", Butterworth-Heinemann, London (1993).
- ¹⁷³ LUUKKO, K., "Kemiallisen massan hienoaineen luonnehtiminen", Teknillinen korkeakoulu, Puunjalostustekniikan laitos, Diplomityö (1994).
- ¹⁷⁴ TARVAINEN, N., Unpublished report (M-real, No. 10596/389:2) (2002).
- ¹⁷⁵ MALTON, S., KUYS, K., PARKER, I., VANDERHOEK, N., "The Influence of Fibre Properties on the Adsorption of Cationic Starch by Eucalypt Pulps", 51st Appita Annual General Conference, Melbourne, Vol. 1: 37-44 (1997).
- ¹⁷⁶ SZWARCSZTAJN, E., PRZYBYSZ, K., "Einige Aspekte der Fraktionierung von Zellstoff und Altpapier", *Papier* 29 (7):295-300 (1975).
- ¹⁷⁷ BREALEY, R.A., MYERS, S.C., Principles of Corporate Finance, 5th Edition (International Edition), McGraw-Hill (1996).
- ¹⁷⁸ COUSIN, L., MORA, F., "Highly loaded fiber-based composite material", U.S. Patent 5,731,080 (1998).
- ¹⁷⁹ COUSIN, L., MORA, F., " Methods of manufacture for highly loaded fiber-based composite material", U.S. Patent 5,824,364 (1998).
- ¹⁸⁰ BLEAKLEY, I.S., "Process for the treatment of waste material suspensions", U.S. Patent 5,830,364 (1998).
- ¹⁸¹ GAVELIN, G., "Method for manufacturing filler-containing paper", U.S. Patent 4,889,594 (1989).
- ¹⁸² SRIVATSA, N.R., PATNAIK, S., HART, P., AMIDON, T.E., RENARD, J.J., "Method for improving brightness and cleanliness of secondary fibers for paper and paperboard manufacture", U.S. Patent 5,665,205 (1997).

APPENDICES

Fiber-loading experiments:

Materials and methods

Precipitation at low pulp consistency

Preliminary experiments

In the preliminary experiments a never-dried bleached birch kraft pulp (31 °SR) was selected for precipitation with calcium hydroxide (Merck, p.a.).

Precipitation was performed in a 4-L stirred tank reactor by leading a mixture of carbon dioxide and nitrogen gas (20 volume % CO₂) to a slurry of calcium hydroxide and chemical birch pulp. Sodium oxalate Na₂C₂O₄ (Riedel-De Haën, p.a.) and diammonium hydrogen phosphate (NH₄)₂HPO₄ (Merck, p.a.) were tested as additives in certain carbonations to study the impacts on the process. The additives were selected based on the literature. The amounts of pulp and calcium hydroxide were 44 g (o.d.) and 34.2 g, respectively, resulting in 1.6% chemical pulp consistency. The mixing rate was kept constant during precipitation (800 rpm). The initial temperature of precipitation was 34 °C. Temperature, pH, and conductivity were measured. The gas inflow was 210 L 20% CO₂ · (kg Ca(OH)₂)⁻¹ min⁻¹. The gas flow was stopped when the pH decreased to below 8.

The loaded samples were first washed with 8 L of water to remove both the crystals loosely attached to the fiber surfaces and crystals in the bulk solution. However, most of the samples used in sheetmaking were additionally washed with 16 L of water.

The particle size and shape of the calcium carbonate crystals obtained were examined with a SEM. The cross sections of the fibers prepared by cutting the fibers with a microtome were evaluated to determine whether there were crystals in the lumens. The crystalline form of calcium carbonate was determined by means of an x-ray diffraction method.

The calcium carbonate content within the fibers was determined with the standard SCAN-P 5:63. Fiber stiffness was measured with the Steadman's methodⁱ.

A number of 80 g/m² paper sheets were prepared for paper testing according to the standards SCAN-C 26:76 and SCAN-M 5:76. The SW in the furnish was beaten to 30 °SR. The HW was the same as that used in fiber loading (31 °SR). The furnish consisted of 55% bleached birch and 45% SW pulps. The amount of fiber-loaded calcium carbonate in the paper was controlled by varying both the amounts of fiber-loaded pulp and loading degree. Commercial PCC (scalenoedral, SSA 11 m²/g) was added to the stock with colloidal silica (1.5 g/kg paper) and cationic starch (6.5 g/kg paper) as retention aids to control the total amount of calcium

Appendix 1, 2(3)

carbonate. Sheets were tested according to the appropriate SCAN and Tappi standards (cf. Appendix 4). However, the bending stiffness was measured using a method developed by KCL based on the free-bending flexure of paper sheetsⁱⁱ.

Verification experiments

Further experiments were conducted to verify and examine in more detail the improved bending stiffness observed with HW fibers loaded with calcium carbonate compared with commercial PCC. The reference PCC fillers used in these verification experiments were prismatic (SSA 7 m²/g) and scalenohedral (SSA 11 m²/g). Neither additives were used in precipitation nor washing of loaded fibers to simplify the experiments. The experimental conditions and methods were mainly comparable to those in preliminary experiments, except for stirring rate (1500 rpm), initial temperature, and gas inflow which were varied. Both the HW and SW bleached chemical pulps used in these experiments were either from North America or Finland.

The American SW for sheetmaking was beaten in a Valley beater for 17 min, while the HW was used unbeaten both in precipitation and handsheet production. In these experiments the furnish was a 75/25 mixture of HW and SW pulps. Finnish kraft pulps were used to further study whether paper strength could be improved by postprecipitation refining, possibly removing particles precipitated on birch fiber surfaces. In these experiments a 75% HW / 25% SW furnish was prepared for a Valley beater and refined 2 min with no load followed by 5 min with 2.268 kg weight. Part of this mixture was further used in fiber loading. After precipitation both samples (loaded and blank) were further refined to 380 CSF (Canadian Standard Freeness). The surfaces of loaded fibers were studied with SEM before and after refining.

Handsheets of 60 g/m² and 75 g/m² were formed on the Formax (Noble & Wood) sheet former both with loaded samples and with reference commercial PCC (scalenohedral, SSA 11 m²/g). The principle of the former is similar to that of SCAN standards. Amounts of 5 ml (0.025%) Percol-175 and 2.5 ml (5 g/300 g) Hercon-75 per sheet were used for retention and sizing. After the handsheets were formed they received 2 pressings between stainless steel rolls at 138 kPa. In the first pressing the sheet was still on the forming wire, sandwiched between pieces of paper machine "wet felt" material. The sheet was then removed from the forming wire, sandwiched between 2 pieces of unsized blotting paper, and pressed again. The handsheets were conditioned and tested under Tappi standard conditions of 23 °C and 50% relative humidity. The sheets were tested according to the appropriate Tappi and ISO standards: T494 om-88 for breaking length, T 543 om-94 for bending stiffness, ISO 2470 for ISO brightness, ISO 2471 for ISO opacity, ISO 5636 for porosity, and T 413 om-93 for ash in paper.

Precipitation at medium pulp consistency

Fiber wall loading was conducted under a carbon dioxide atmosphere in a medium consistency mixer, where a bleached birch kraft pulp (20 °SR) suspension at 10% consistency was periodically mixed under fluidizing conditions. The amounts of calcium hydroxide (Merck, p.a.) and other components are presented in Table 1.

Table 1. Amounts of components in the precipitation experiments conducted in a medium-consistency mixer.

Filler level in loaded pulp, %	m CaCO ₃ , g	m Ca(OH) ₂ , g (stoichiometric)	m CO ₂ , g (stoichiometric)
No. 1: 20	25	18.51	10.99
No. 2: 30	42.86	31.73	18.85

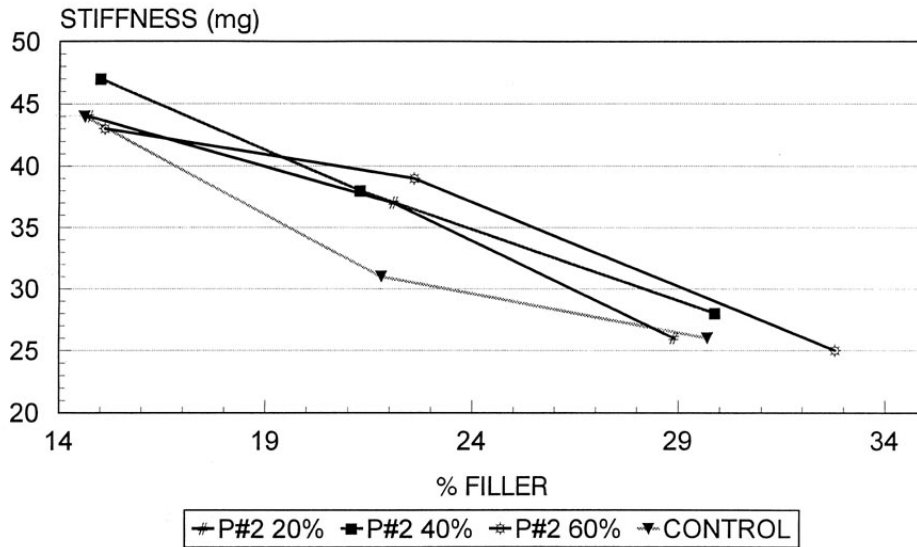
The initial temperature in both experiments was 18 °C. The reaction was followed by measuring the pressure of carbon dioxide which was dosed during 25 s slightly more than stoichiometrically needed. The stirring speed was 3000 rpm. Carbon dioxide was then let to react for 60 s with no stirring followed by a 2-min stirring period with stirring speed of 400 rpm. After a 4-min reaction time the mixture was finally stirred for 20 s with stirring speed of 3000 rpm. The excess CO₂ was removed after 5 min from the start of the reaction. The pH of the mixture was then measured. The loaded samples were washed and analyzed similarly than presented regarding low-consistency precipitation.

A number of 60 g/m² handsheets were made for paper testing using the unwashed sample of the loaded fiber from carbonation No. 2 according to the standards SCAN-C 26:76 and SCAN-M 5:76. 0.8% cationic starch and 0.25% BMA (nanoparticle from EKA Chemicals) of paper were used as retention agents. The amount of loaded calcium carbonate in the sheets was controlled by varying the amount of loaded fiber so that target calcium carbonate levels were 0%, 3.6%, 7.2%, 10.8%, and 14.4%. The pulp in the furnish always consisted of 40% bleached SW kraft pulp (30 °SR) and 60% bleached birch kraft pulp (20 °SR). The reference filler was PCC (prismatic, SSA 7 m²/g). The target filler contents were 9% and 18% with the reference filler. The sheets were tested according to the appropriate SCAN and Tappi standards (cf. Appendix 4). However, the bending stiffness was measured using a method developed by KCL (Finnish Pulp and Paper Research Institute) based on the free-bending flexure of paper sheets ⁱⁱ.

ⁱ STEADMAN, R., LUNER, P., "The Effect of Wet Fibre Flexibility of Sheet Apparent Density", The Eighth Fundamental Research Symposium, Oxford, England, Proceedings:311-337 (1985).

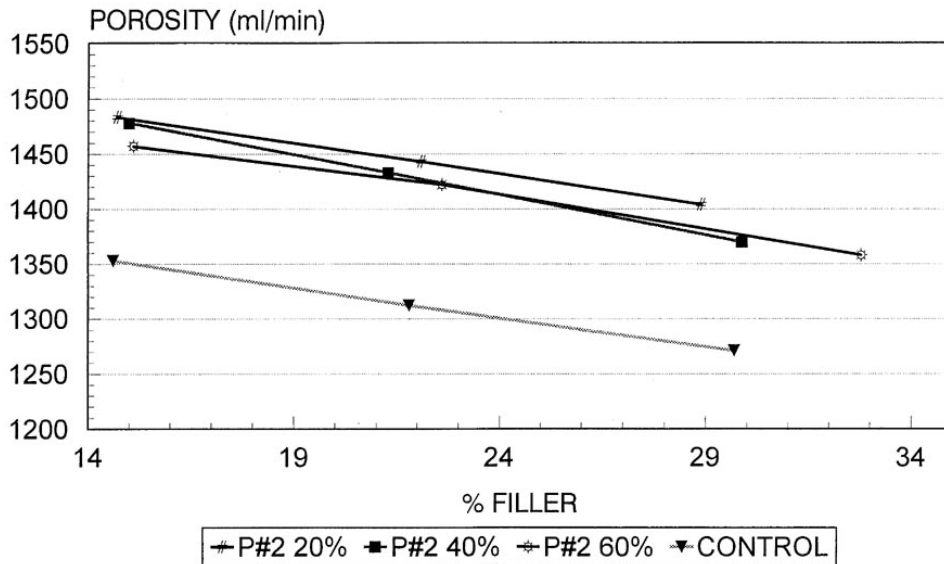
ⁱⁱ KAJANTO, I., "Laite paperin taivutusjäykkyyden mittaamiseksi", Finnish Utility Model 2174 (1995).

Results of loading verification experiments at low consistency



GURLEY STIFFNESS

Figure 1. Stiffness of papers made of fibers loaded at low consistency compared with commercial PCC (prismatic, SSA 7 m²/g). The proportion of loaded pulp in the total HW is presented in the legend.



Porosity

Figure 2. Porosity of papers made of fibers loaded at low consistency compared with commercial PCC (prismatic, SSA 7 m²/g). The proportion of loaded pulp in the total HW is presented in the legend.

Appendix 2, 2(3)

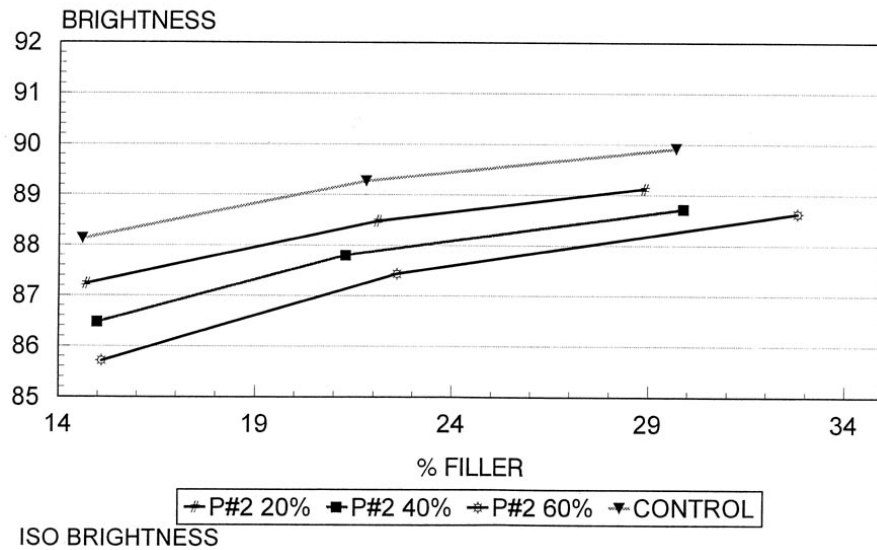


Figure 3. Brightness of papers made of fibers loaded at low consistency compared with commercial PCC (prismatic, SSA 7 m²/g). The proportion of loaded pulp in the total HW is presented in the legend.

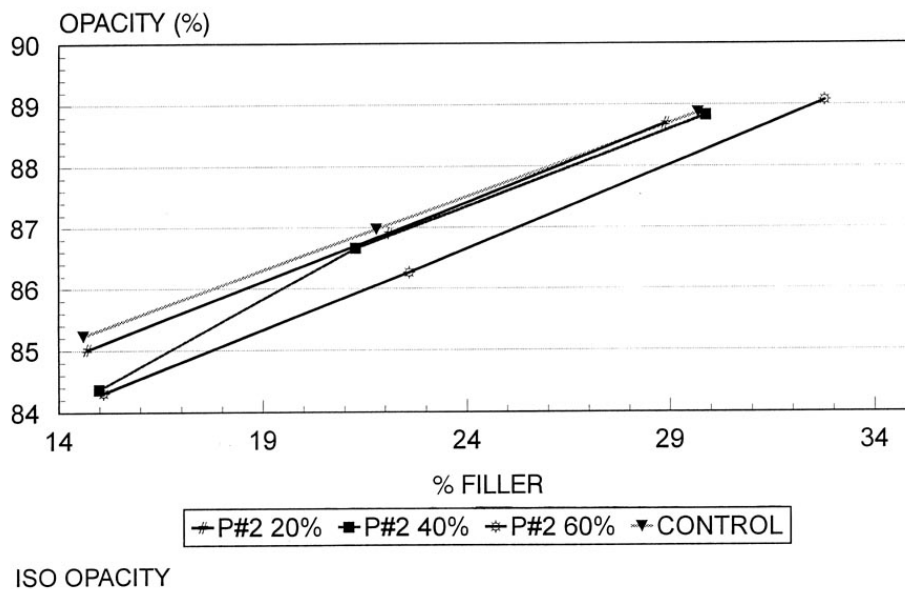
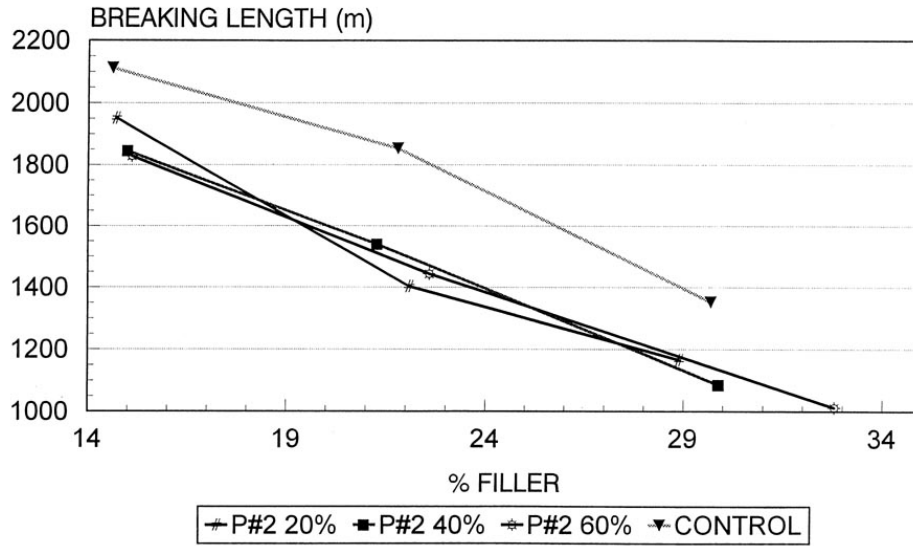


Figure 4. Opacity of papers made of fibers loaded at low consistency compared with commercial PCC (prismatic, SSA 7 m²/g). The proportion of loaded pulp in the total HW is presented in the legend.



BREAKING LENGTH

Figure 5. Breaking length of papers made of fibers loaded at low consistency compared with commercial PCC (prismatic, SSA 7 m²/g). The proportion of loaded pulp in the total HW is presented in the legend.

Results of loading experiments at medium consistency

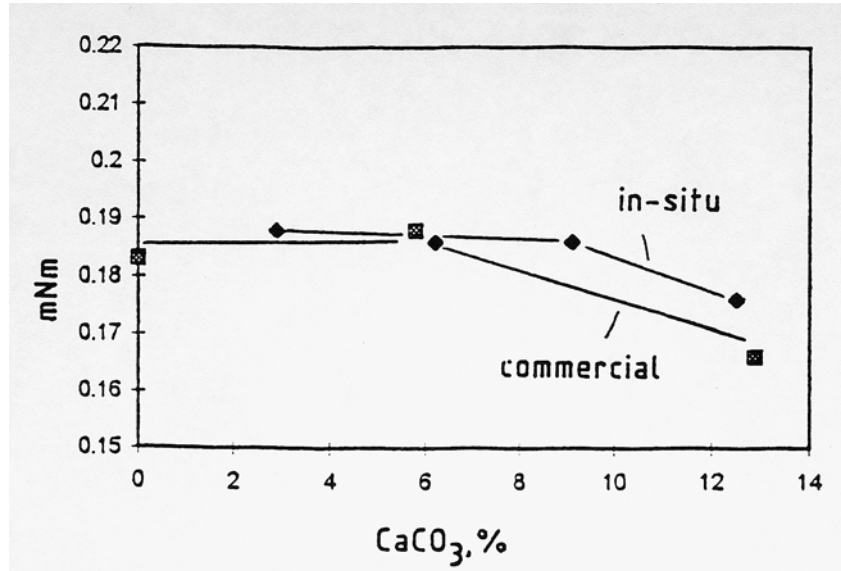


Fig. 1. Bending stiffness of papers made of fibers loaded at medium consistency compared with commercial PCC (prismatic, SSA 7 m²/g).

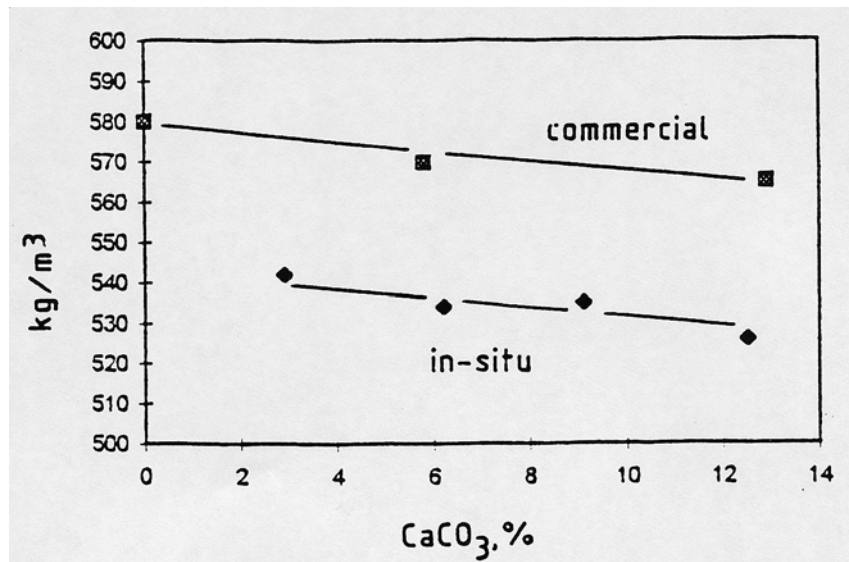


Fig. 2. Density of papers made of fibers loaded at medium consistency compared with commercial PCC (prismatic, SSA 7 m²/g).

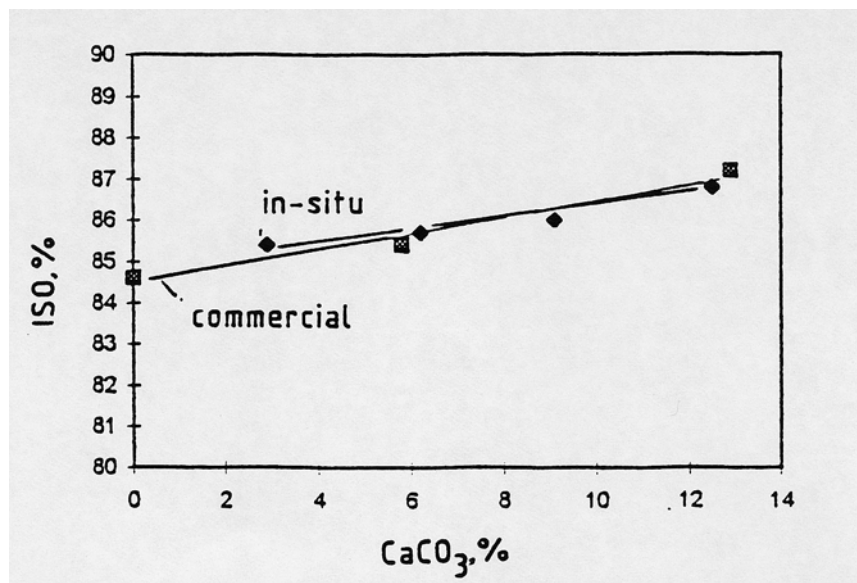


Fig. 3. Brightness of papers made of fibers loaded at medium consistency compared with commercial PCC (prismatic, SSA 7 m²/g).

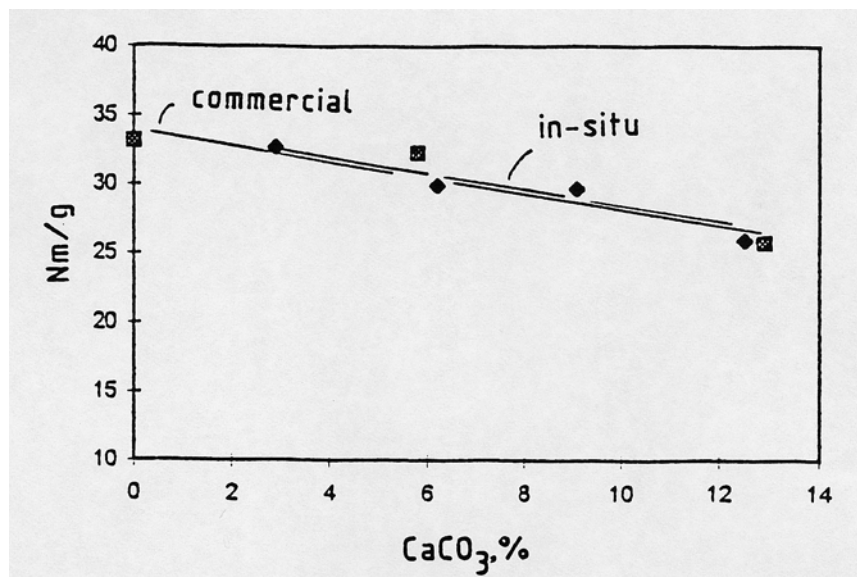


Fig. 4. Tensile strength of papers made of fibers loaded at medium consistency compared with commercial PCC (prismatic, SSA 7 m²/g).

Experimental Paper Machine (XPM) trial: Materials, methods, and conditions

Pulps

The pulp used was a mixture of 70% dried, bleached, mixed hardwood from Alicel and 30% dried, bleached softwood kraft pulp (Modo Kraft, Husum). After disintegration, the pulps were beaten together to 22.7 °SR in an Escher-Wyss conical laboratory refiner at a consistency of 3.0%. The specific edge load was 1.5 Ws/m.

Fines

The following dried bleached pulps were used for fines production:

- Mixed hardwood from Alicel
- Softwood Kraft pulp from Husum
- Botnia Plus Birch TCF (ref), from Kaskinen

During production the pulps were beaten with a Voith Sulzer refiner 90 °SR as a target. The conditions and results are presented in Table 1.

Table 1. Refining conditions and beaten material properties.

	HW Alicel	SW Husum	HW Reference
Disc blade	2/3-1.4-40D	3-1.6-60D	2/3-1.4-40D
Specific edge load [Ws/m]	0.25	0.75	0.25
Net specific energy [kWh/t]	105	340	150
SR [°]	88.0	90.2	91.3
Bauer McNett +28 [%]	19.8	58.2	3.3
Bauer McNett -100 [%]	28.6	21.9	25.9
Fines content DDA [%]	26.6	15.7	16.1

The samples were analyzed with a microscope and were found to have about the same amount of fibrils, except for SuperFill Ref, which had a lower amount of fibrils. The fines were not fractionated.

Fillers

SuperFill

In SuperFill production the target was to attain a CaCO₃/fibrils ratio of 70/30 with 3.25% solids content.

Table 2. Properties of the three SuperFill products (average of three batches).

	Solids [%]	Surface area [m ² /g]	CaCO ₃ titration [%]
HW Alicel	3.3	6.7	70.0
SW Husum	2.9	5.7	70.9
HW Reference	2.9	6.6	73.1

Surface area was analyzed with a special method for SuperFill which detects mainly the surface area of pigment.

PCC

The PCC used was H-60 Syntec produced by OMYA. Based on the specification the BET specific area is 5.5 ± 1 m²/g. The filler dosages are shown in Table 3.

Stock sizing

Alkyl ketene dimer (AKD; Aquapel J 320 from Hercules) was used as the internal sizing agent. AKD was added according to Table 3.

Retention aids

The dosages added were:

- 2.5 kg/t PAC (polyaluminum chloride, Tenfloc)
- 5 kg/t of cationic starch (Lab 2774, Roquette)
- 400 g/t A-PAM (anionic polyacrylamide, Cartarétine) only when PCC was used

Trial conditions

Table 3. Trial conditions in the XPM trial.

Trial number	Filler	Filler content [%]	AKD active dosage [kg/t]	AKD [kg/ton] commercial product	A-PAM [g/t] commercial product
Day 1					
1	SuperFill HW	20	1.5	6.9	0
2	SuperFill HW	20	2.0	9.2	0
3+4	SuperFill HW	20	2.5	11.5	0
5	SuperFill HW	10	2.5	11.5	0
6	SuperFill HW	30	2.5	11.5	0
Day 2					
7	SuperFill SW	20	1.5	6.9	0
8	SuperFill SW	20	2.0	9.2	0
9+10	SuperFill SW	20	2.5	11.5	0
11	SuperFill SW	10	2.5	11.5	0
12	SuperFill SW	30	2.5	11.5	0
13	SuperFill Ref	10	2.5	11.5	0
14	SuperFill Ref	20	2.5	11.5	0
15	SuperFill Ref	30	2.5	11.5	0
Day 3					
16	No	0	1.0	4.6	400
17	Ref PCC	20	1.0	4.6	400
18+19+20	Ref PCC	20	1.5	6.9	400
21	Ref PCC	10	1.5	6.9	400
22	Ref PCC	30	1.5	6.9	400

The dosage positions of fillers and chemicals are shown in the XPM schematic view presented later.

Manufacturing of paper on the XPM

The XPM is a small experimental paper machine. The target grammage was 80 g/m². The XPM was run with white water circulation. The stock was pH-adjusted in the machine chest to 7.5 with H₂SO₄, while 0.28 g/L NaHCO₃ and 0.18 g/L CaCl₂ were also added. The conductivity in the machine chest was 633 μS/cm.

Paper testing

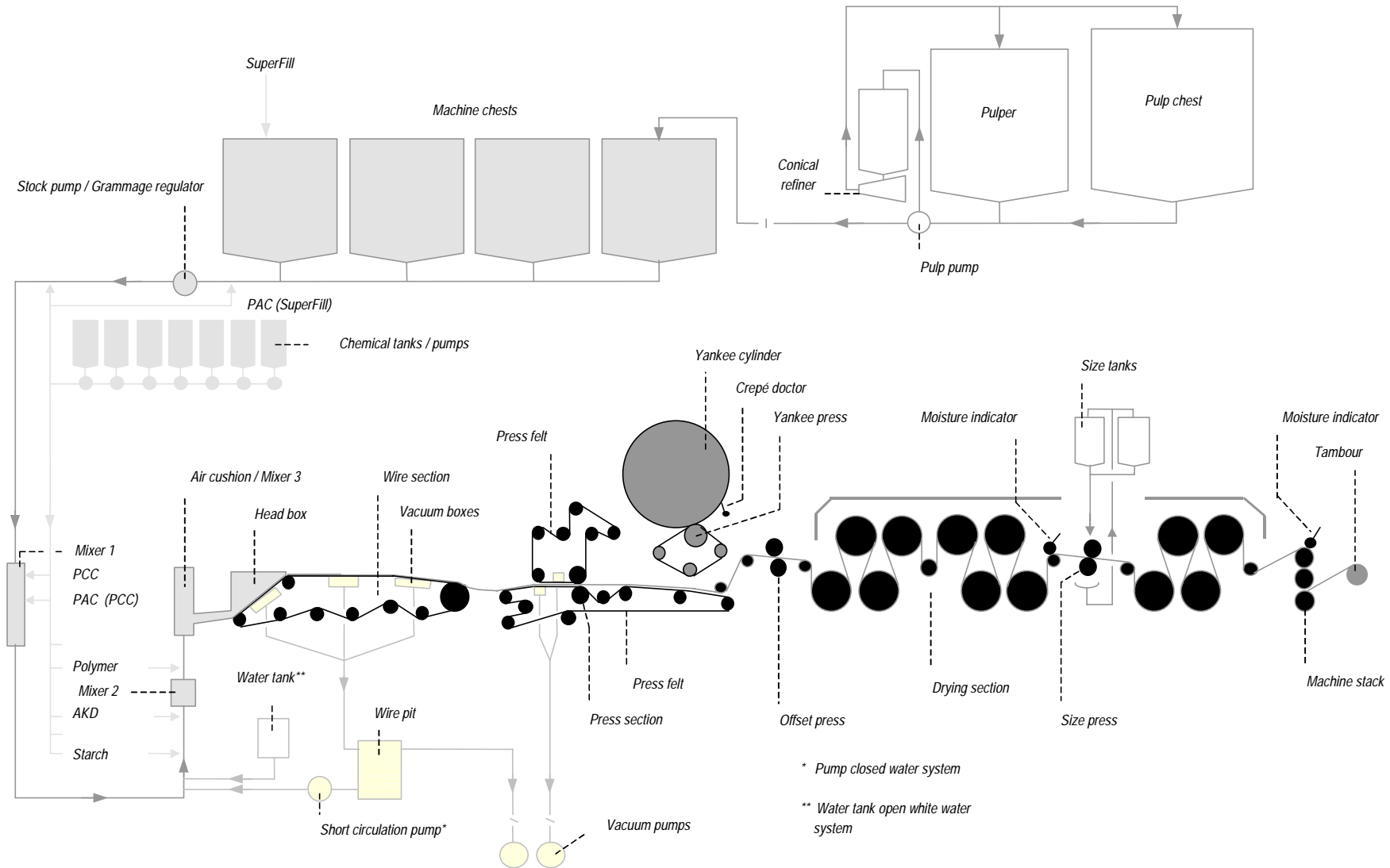
Table 4. Paper analysis summary.

Analysis	Method
Grammage	SCAN-P 6:75
Thickness Density	SCAN-P 7:96
Ash content	At 925 °C according to SCAN-P 5:63
Cobb	SCAN-P 12:64 Stored in standard climate, measured after 1 week
Emtec	Internal method, measured two weeks after production
Optical properties	SCAN-P 8:93 and SCAN-P 66:93 Light scattering, absorption, brightness, whiteness
Tensile testing	SCAN-P 67:73
Tear index	SCAN-P 11:73
Bending stiffness	Resonance, SCAN-P 64:90
Bending resistance*	SCAN-P 29:95
Scott bond	Tappi RC-308
Porosity	Bendtsen, SCAN-P 60:87 Gurley, SCAN-P 19:78
Formation	β -radiation, internal method
Calendering	Lab calender
Surface roughness	Bendtsen, SCAN-P 21:67 PPS, SCAN-P 76:95
Hg porosity	Internal method

* Samples were taken from rolls.

Experimental paper machine XPM

Schematic view



Pilot-scale paper production trials: Materials, methods, and conditions

Pulps

Pulp mixtures consisted of 70% beaten bleached kraft birch pulp (21 and 25 °SR for the 1st and 2nd trial) and 30% beaten bleached kraft softwood pulp (23 and 25 °SR for the 1st and 2nd trial).

The backing layer of the 2-layered product consisted of unbleached kraft pulp (17 °SR) consisting mainly of softwood.

Fines

Bleached birch kraft pulp was beaten at the Metso Mechanical Pulping Technology Center to produce fines for SuperFill. Refining included 6 and 11 passes using a JC-01 refiner with no screening for the 1st and 2nd trial, respectively. The other parameters were: SF fillings, 1000 rpm, refining consistency approximately 4%, specific edge load 0.5 J/m. The energy at each refiner stage was approximately 48 kWh/t and 31.5 kWh/t for the 1st and 2nd trial resulting in total energy consumptions of 286 kWh/t and 347 kWh/t, respectively. The products were not fractionated. The summary of the material characteristics is presented in Table 1.

Table 1. Summary of properties before and after beating.

	Unbeaten		Beaten	
	Trial 1	Trial 2	Trial 1	Trial 2
Fiber length, mm	not measured	0.87	0.56	0.54
SR, °	not measured	17	91	90
BMcNett -100, %	not measured	13.1	not measured	45.2
BMcNett +50, %	not measured	43.6	not measured	18.7

Fillers

SuperFill at approximately 3.25% solids content was produced at PCC on-site plants. SuperFill was thoroughly mixed prior to cleaning with hydrocyclones. The calcium carbonate portions of SuperFill were 63% and 70% for the 1st and 2nd trial, respectively, and SSA values 5.5 m²/g and 8.7 m²/g. PCC (scaleno-hedral, SSA 6 m²/g) was used as reference filler.

Retention aids and stock sizes

In the 1st trial retention chemicals were C-PAM (cationic polyacrylamide, Percol 47) and bentonite from Ciba. The dosages are presented in Table 2. The dosage of C-PAM was lowered with PCC from 300 to 225 kg/t due to poor formation. AKD was used as internal sizing agent. The dosages are presented in Table 2.

In the 2nd trial the retention chemicals were from EKA chemicals (BMA 590 and Hi-Cat EXP M1 starch). The dosages per metric ton of white paper were:

- BMA 500 g/t
- starch 2 kg/t for retention
- stock starch 10 kg/t

Paper machine trial conditions

The following tables summarize the trial settings.

Table 2. Settings of trial 1 (fine paper 80 g/m²).

Filler	Filler content [%]	C-PAM [g/t]	Bentonite [kg/t]	AKD [kg/t]
SuperFill	22.4	300	2	10
PCC	21	300	2	10
PCC	21.7	225	2	10
PCC	18.8	225	2	10
SuperFill	16.4	325	2	14

Table 3. Settings of trial 2.

Product	Filler	Filler content of white paper [%]	Basis weight of white paper at 8% moisture content [g/m ²]	Basis weight of bottom layer at 8% moisture content [g/m ²]
Uncoated wood free paper 75 gsm	PCC	13.7	75	-
	PCC	16.3	75	-
	SuperFill	12.6	75	-
	SuperFill	19.7	75	-
White top linerboard 140 gsm	PCC	16	75	65
	SuperFill	20	75	65
	SuperFill	20	65	75

Fillers and chemicals were used in the top layer of the liner, and filler content is presented as top layer (white paper) filler content. Liner bottom layer was produced with no chemicals. Fillers and retention chemicals were added at headbox consistency after dilution with white water. AKD and stock starch in the 1st and 2nd trial, respectively, were added prior to dilution with white water.

Paper production

White papers were produced using STFI former (combined roll and blade former) and bottom layer of the liner with Fourdrinier former. Machine speed was 800 m/min and 650 m/min for the 1st and 2nd trial, respectively.

Paper testing

Paper testing was performed according to the appropriate SCAN and Tappi standards (cf. Appendix 4).

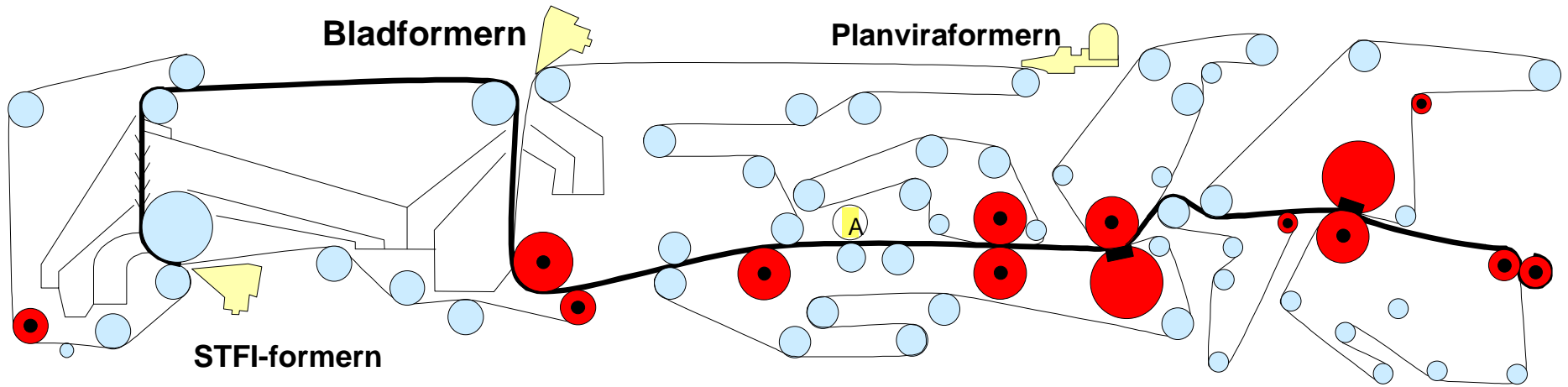
Paper machine

The EuroFEX paper machine contains three forming sections: the STFI former, blade former, and Fourdrinier former, which can be combined for evaluating multilayered products.

The STFI former is a combined roll and blade former in which dewatering in the roll and blade sections are controlled by varying the angle of wrap around the forming roll. In the blade section the intensity can be changed by controlling the contact pressure in the blade unit.

The press section is equipped with a conventional double-felted press followed by two shoe press units. Web reel-up width is 33 cm. Drying is done off-line. The schematic view of the machine is presented in the following figure.

EuroFEX



Mill-scale paper production trial: Materials, methods, and conditions

Pulps

The pulp mixture consisted of 74% beaten bleached birch kraft pulp (22-25 °SR) from Äanekoski and 24% beaten bleached pine kraft pulp (32-34 °SR) from Joutseno.

Fines

The bleached birch kraft pulp was beaten at the Metso Anjalankoski Mechanical Pulping Technology Center to produce fines for SuperFill. Refining included 11 passes using a JC-01 refiner with no screening (SF blades, 1000 rpm, refining consistency 4%, total energy consumption 343 kWh/t, specific edge load 0.5 J/m). The product was not fractionated. A summary of the characteristics is presented in Table 1.

Table 1. Summary of the properties before and after beating.

	Unbeaten	Beaten
Fiber length (length-weighted), mm	0.86	0.58
Fiber length (weight-weighted), mm	1.00	0.77
SR, °	16	86
BMcNett -100, %	8.8	42.0
BMcNett -50, %	35.3	75.1
BMcNett +50, %	64.7	24.9

Fillers

SuperFill was produced in five batches at a PCC on-site plant. The batches were thoroughly mixed prior to cleaning with hydrocyclones. The delivered SuperFill had a 2.22% solids content, and the amount was 248 m³. The CaCO₃ portion of the SuperFill was 69.7% and SSA 9.6 m²/g. Talc (Finntalc F 15 SL; Mondo Minerals) and PCC (scalenohebral, SSA 11 m²/g) were used as reference fillers. The targeted filler levels were 10% and 15% with talc, and 10%, 15%, and 20% with PCC and SuperFill.

Retention aids and stock sizes

The retention chemicals used were from EKA Chemicals (Compozil Plus: EKA NP 780 nanoparticle and EKA PL 1510 C-PAM polymer). The dosages were:

- talc and PCC: nanoparticle 280 g/t, polymer 70 g/t
- SuperFill: nanoparticle 280 g/t, polymer 50 g/t.

The alum dosage was 13 kg/t with talc and 19 kg/t with PCC and SuperFill. The dosage of cationic starch was 8 kg/t and resin size 5.2 kg/t.

Paper machine

The paper machine produces one-side coated paper. The other side is surface-sized. The web reel-up width is 252 cm and machine reel-up speed normally 750 m/min.

The machine is comprised of Valmet's hybrid former (Sym former), Sym-Press II press section, and normal drying section. On-line coating (single blade; BTG's ABC) is done after the 4th drying group which is dried with cylinders (5th drying group). Sizing is done by film transfer on the coater backing roll. The coat weight is between 11 and 13.5 g/m² and sizing weight from 0.5 to 0.8 g/m².

Paper mill trial schedule and conditions

Day 1:

20:00 PM start-up after shutdown. Target level for base paper ash 14% talc. Broke chest at minimum.

Day 2:

05:30 Pulp mixture 74% bleached hardwood kraft pulp and 26% bleached softwood kraft pulp. Broke feed 15% of total pulp flow.

06:30 Adjust base paper ash to 15% (sample point 1). No coating from this point forward.

07:30 Base paper grammage 56 g/m² (sample point 2). Adjust ash level to 10% (sample point 3).

08:00 PCC feeding on.

10:00 PCC, ash level 10% (sample point 4).

11:00 PCC, ash level 15% (sample point 5).

12:00 PCC, ash level 20% (sample point 6). From this point forward PCC switched to SuperFill.

13:30 SuperFill, ash level 10% (sample point 7).

14:30 SuperFill, ash level 15% (sample point 8).

16:30 SuperFill, ash level 20% (sample point 9). From this point forward coating on and coated paper grammage 70 g/m² (sample point 10).

19:50 SuperFill feeding off, return to normal production.

23:00 Sufficient sizing level reached.

Talc, PCC, alum, stock starch, and resin size were dosed prior to dilution with white water, whereas SuperFill was dosed in the dilution stage. Retention polymer was added at headbox consistency after dilution with white water, followed by nanoparticles.

Paper production

The base paper grammage during the trial was 56 g/m². On-line coating and surface sizing were done for the paper samples with talc and SuperFill at 15% levels.

Paper testing

Paper testing both for base papers and coated papers was performed according to the appropriate SCAN and Tappi standards (cf. Appendix 4). Gloss of on-line coated papers was measured according to the Tappi T 480 om-90 standard.

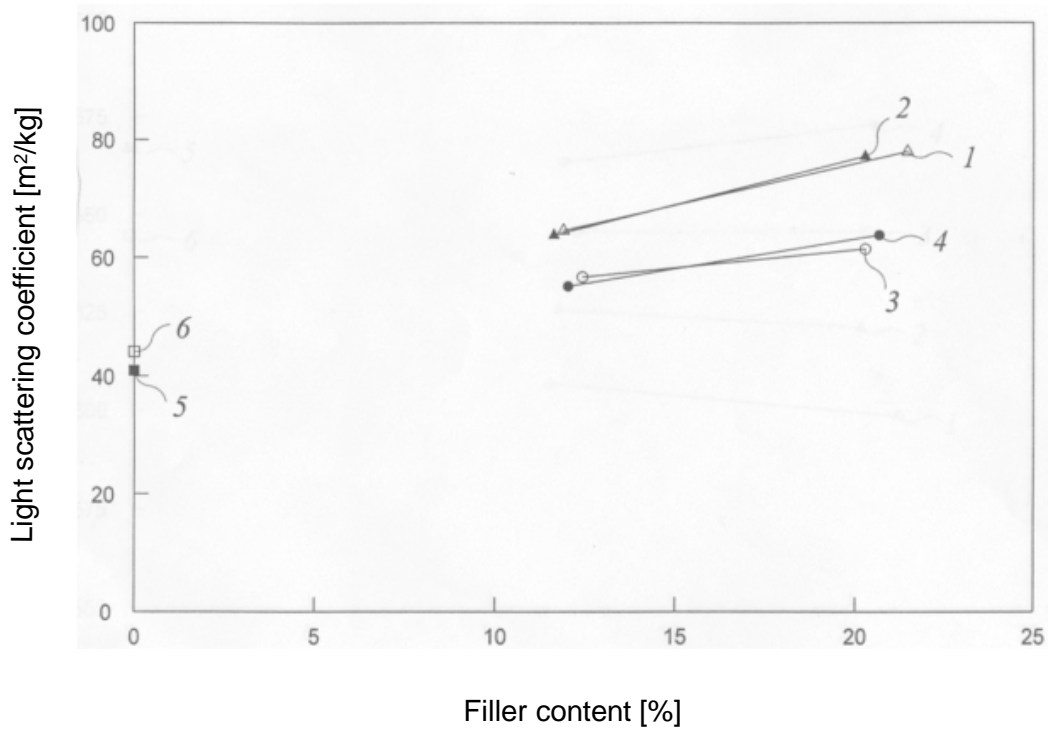


Figure 1. Effect of added fines on light scattering coefficient of 60 g/m² papers containing PCC and GCC as fillers. Different test points are marked with numbers as follows: 1=PCC alone, 2=PCC+fines, 3=GCC alone, 4=GCC+fines, 5=no fillers, 6=no fillers+fines. The amount of added fines in papers was 4.5%. The furnish consisted of 50% bleached SW pulp (CSF 420) and 50% bleached groundwood pulp. The fines were produced from bleached birch kraft pulp by beating for 2.5 hours in a Valley beater according to the standard SCAN-C 25. The product was fractionated with a Bauer McNett apparatus. The fraction that passed through the 200-mesh wire screen (P200) was allowed to settle, whereupon the aqueous phase was separated. The fines and fillers were added simultaneously into the furnish prior to sheetmaking. Levels of 0.65% starch and 0.15% silica of fibers were used for retention. Sheets and paper testing were made according to the respective SCAN and Tappi standards (cf. Appendix 4).

Pore size distributions of XPM-made papers measured by mercury porosimetry

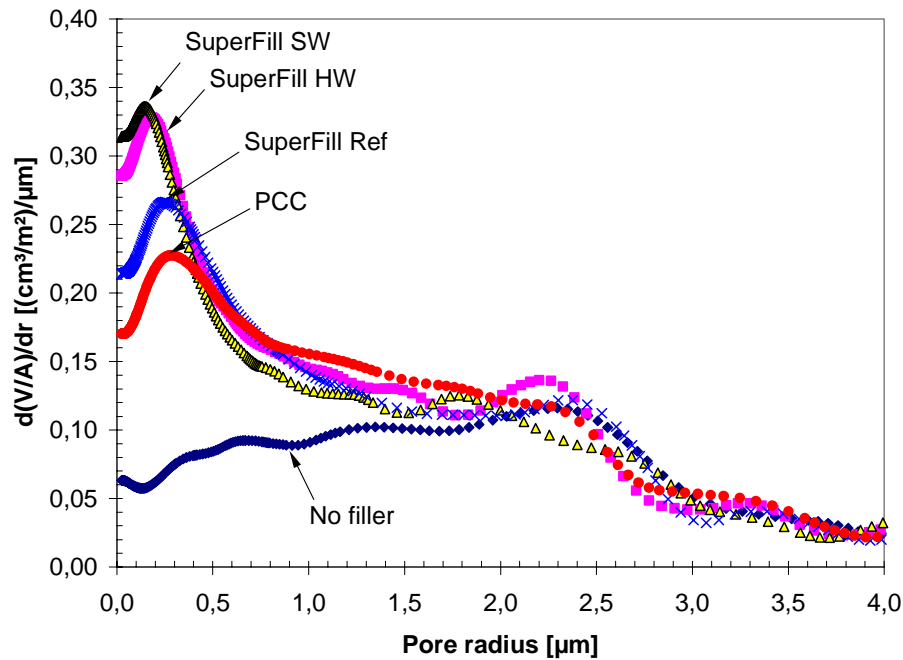


Figure 1. Pore size distributions of XPM-produced papers for scalenohedral SuperFill with three different fines sources and for commercial PCC (H-60 Syntec by Omya) of roughly the same CaCO_3 psd. The calcium carbonate portions of the SuperFill samples were approximately 70% by weight and calcium carbonate content of papers 20%. Fines source for SuperFill is presented in the legend: HW=bleached mixed hardwood kraft pulp, SW=bleached softwood kraft pulp, Ref=bleached birch kraft pulp.

Pore size distributions of XPM-made papers measured by mercury porosimetry

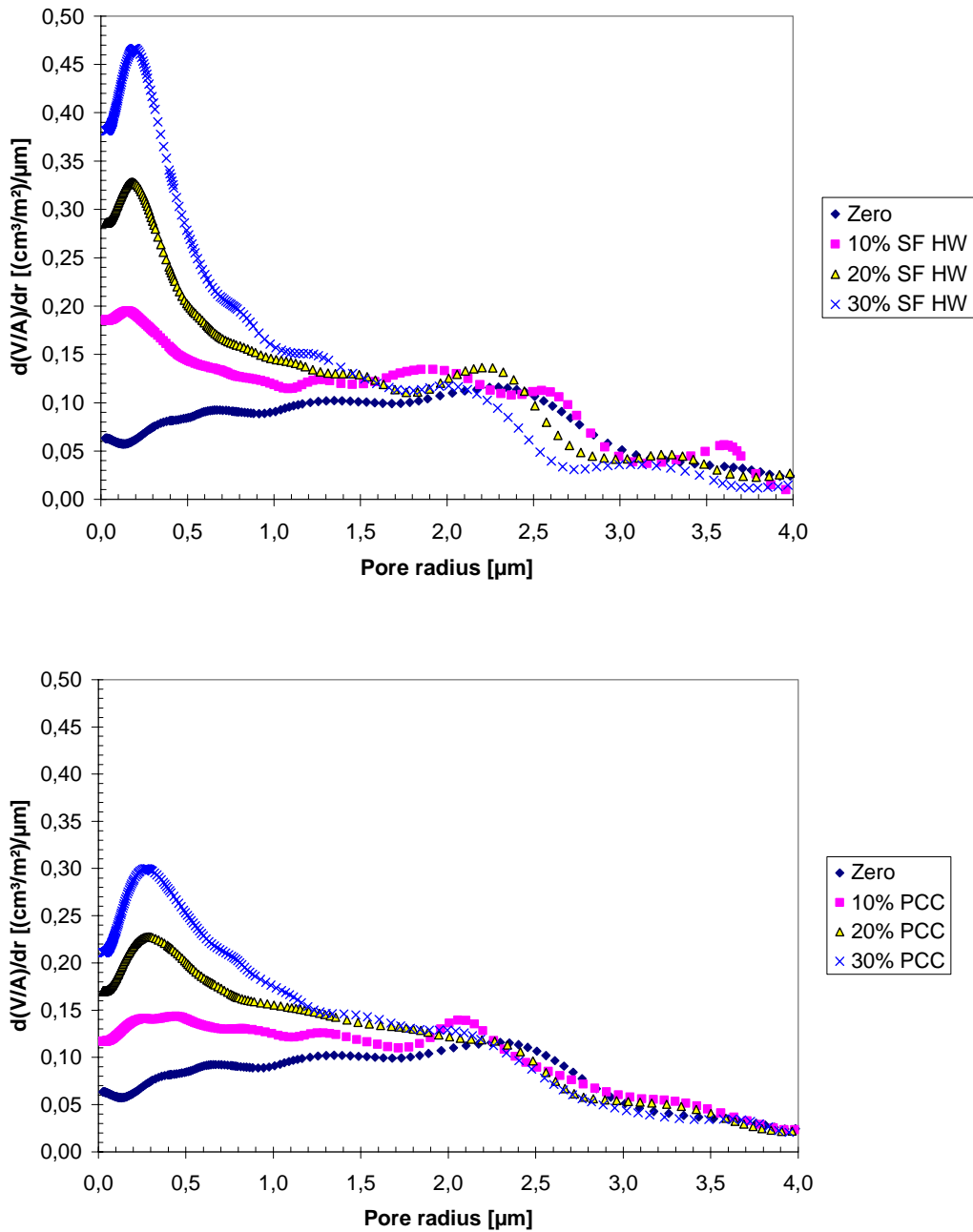


Figure 1. Pore size distributions of XPM-produced papers for sclenohedral SuperFill and for commercial PCC (H-60 Syntec by Omya) of roughly the same CaCO_3 psd. The calcium carbonate portions of the SuperFill samples were approximately 70%. Calcium carbonate contents of papers are presented in the legend. Fines for SuperFill were produced from bleached mixed hardwood kraft pulp.

Bulk and bending stiffness of XPM-produced papers

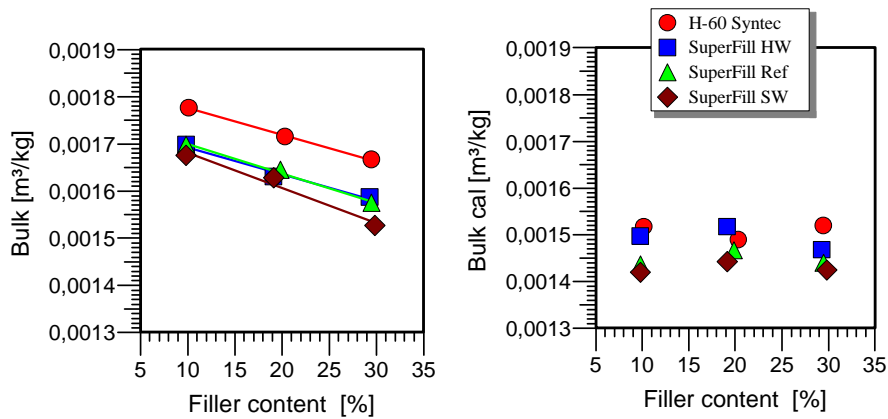


Figure 1. Bulk of XPM-produced papers before and after calendaring for scalenohedral SuperFill with three different fines sources and for commercial PCC (H-60 Syntec by Omya) of roughly the same CaCO_3 psd. The calcium carbonate portions of the SuperFill samples were approximately 70% by weight. Fines source for SuperFill is presented in the legend: HW=bleached mixed hardwood kraft pulp, SW=bleached softwood kraft pulp, Ref=bleached birch kraft pulp.

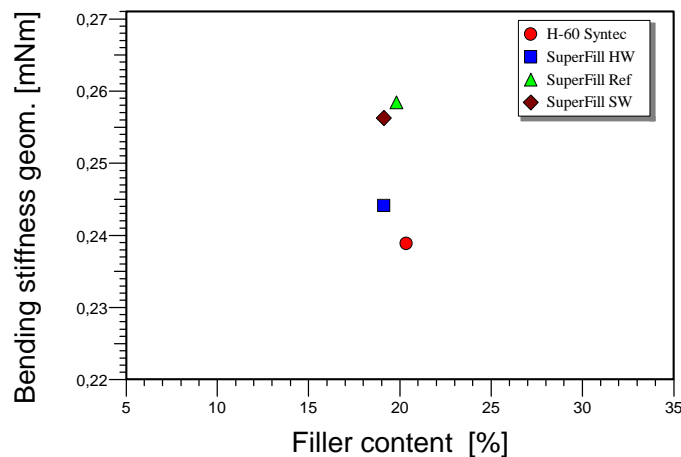


Figure 2. Bending stiffness of XPM-produced papers before calendaring for scalenohedral SuperFill with three different fines sources and for commercial PCC (H-60 Syntec by Omya) of roughly the same CaCO_3 psd. The calcium carbonate portions of the SuperFill samples were approximately 70% by weight. Fines source for SuperFill is presented in the legend: HW=bleached mixed hardwood kraft pulp, SW=bleached softwood kraft pulp, Ref=bleached birch kraft pulp.

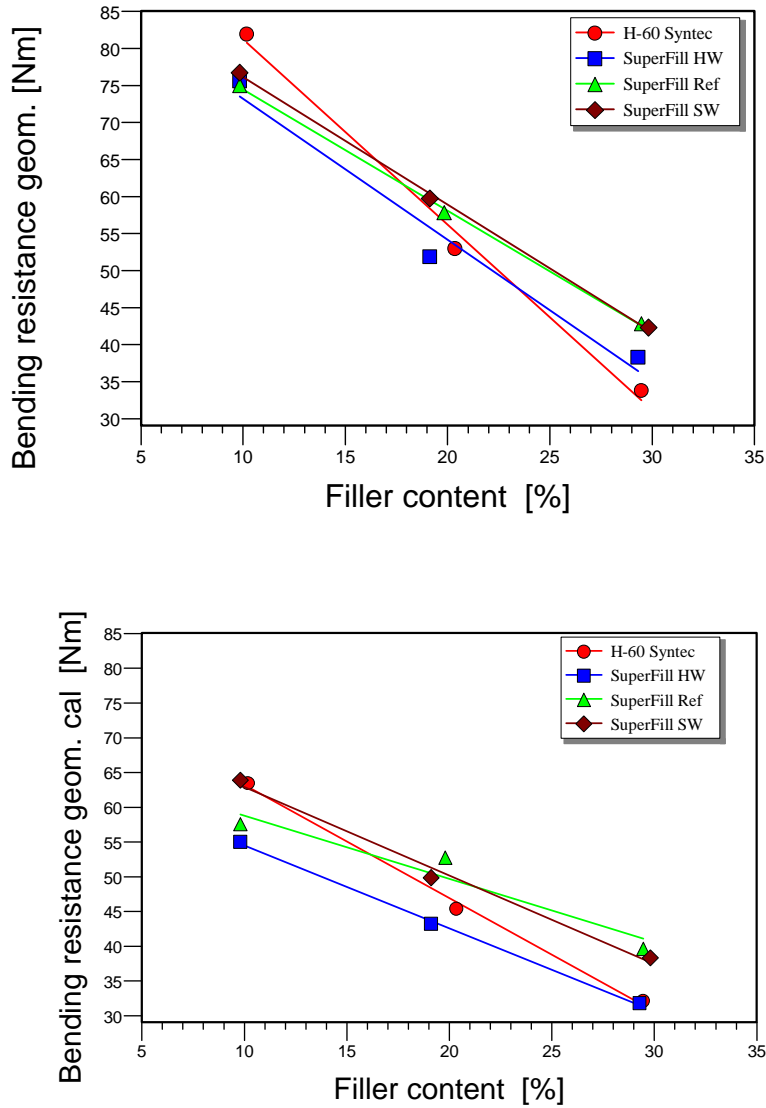


Figure 3. Bending resistance of XPM-produced papers before and after calendaring for scalenohedral SuperFill with three different fines sources and for commercial PCC (H-60 Syntec by Omya) of roughly the same CaCO_3 psd. The calcium carbonate portions of the SuperFill samples were approximately 70% by weight. Fines source for SuperFill is presented in the legend: HW=bleached mixed hardwood kraft pulp, SW=bleached softwood kraft pulp, Ref=bleached birch kraft pulp.

White water consistency in mill scale trial

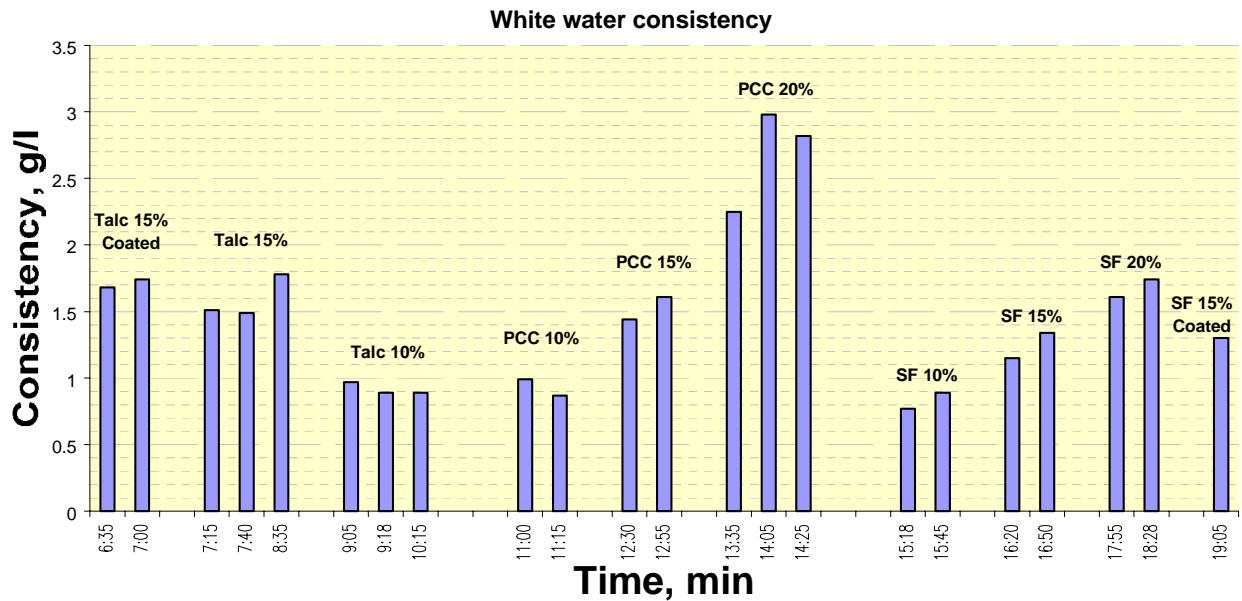


Figure 1. White water consistency in mill scale trial with SuperFill (scaleno-hedral, SSA 9.6 m²/g) and two reference fillers (PCC: scaleno-hedral, SSA 11 m²/g; Talc: Finntalc by Mondo Minerals). The psd of the reference PCC was close to that seen in SuperFill. Filler dosages are marked in the Figure. The furnish consisted of 74% bleached birch kraft pulp (22-25 °SR) and 26% bleached pine kraft pulp (22-25 °SR). SF denotes SuperFill.

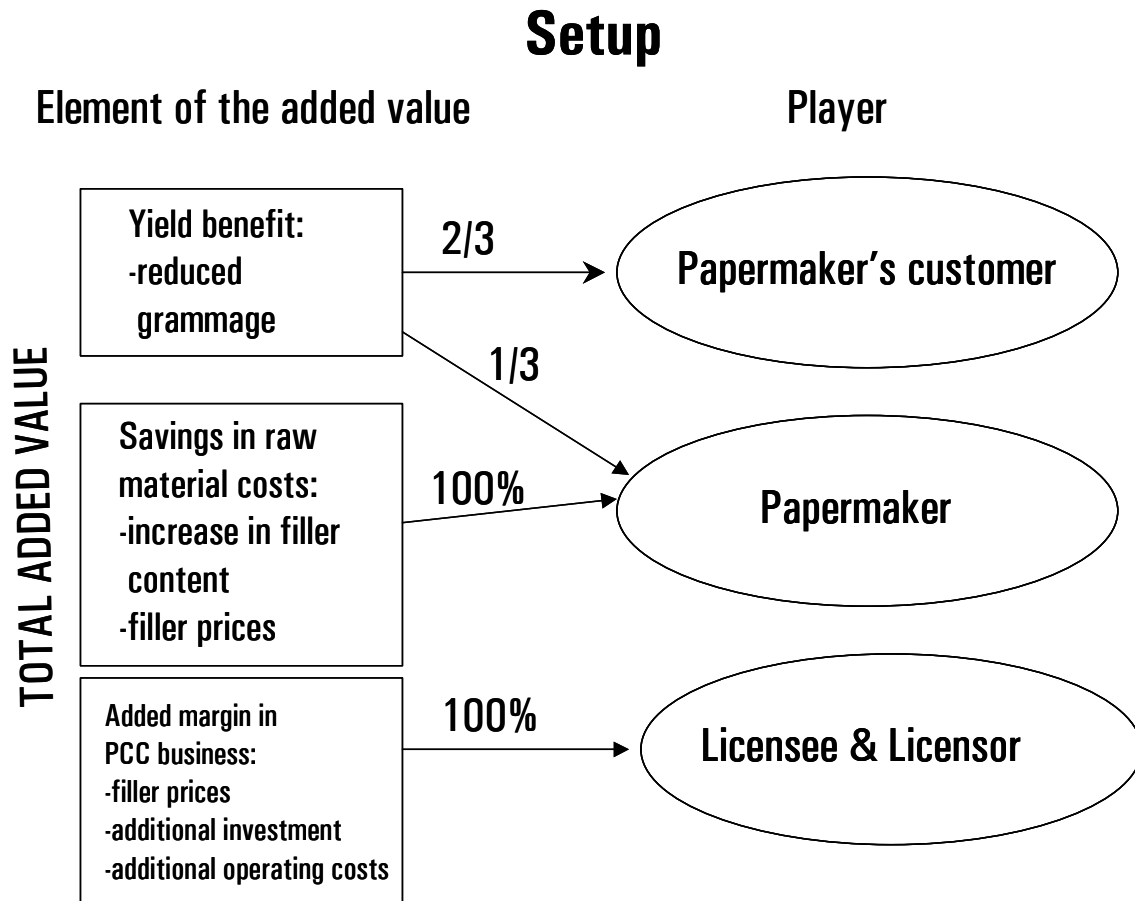


Figure 1. Setup used in the added value estimation of SuperFill technology.