

TAMPERE POLYTECHNIC  
International Pulp and Paper Technology

Engineering thesis

Ville Henttonen

**THE EFFECTS OF CALCIUM FOR RETENTION CHEMICALS**

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TAMPERE POLYTECHIC

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Henttonen, Ville

The Effects of Calcium for Retention Chemicals

Engineering Thesis

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## **ABSTRACT**

A part of gypsum dissolves, which increases the calcium content of paper machine wet end. Uncontrolled dissolving can cause a precipitates, runnability problems and unstable process, which decreases production line profitability and the production rate.

The idea of doing this work was to study how dissolved calcium in process water affects to effectiveness of retention chemicals. The aim was to find out how much dissolved calcium affects to the retention on laboratory circumstances, where mechanical retention is the dominant retention mechanism.

The work was done by making sheets with laboratory sheet former by using birch pulp and kaolin. The calcium level was adjusted by means of gypsum. By measuring the grammage and the ash retention it was possible to study the level of retention.

Mediocre calcium concentration lowered the retention compared to the zero calcium level, if cationic retention chemical was used. Anionic retention chemical did not reacted to changes of calcium concentration. With calcium concentration close to saturation point, dissolution was incomplete and grammages rose considerably. By using anionic retention chemical close to saturation point of calcium, strong electrostatic polymer bridging also increased the grammage. Higher retention chemical dosage raised the retention in every circumstance.

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Kemira Oyj, ohjaaja DI Mikko Mäkinen

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## TIIVISTELMÄ

Osa kipsistä liukenee ja liuennot kalsium nostaa paperikoneen määrään kalsiumpitoisuutta. Kontrollioimaton liukeneminen voi saada aikaan saostumia, ajettavuusongelmia ja epävakaan prosessin, jonka seurauksena linjan tuotannollinen ja taloudellinen kannattavuus kärsii.

Työssä on tutkittu kuinka prosessiveden kalsiumkonsentraatio vaikuttaa retentiokemikaalin toimivuuteen. Työssä päämääränä oli saada selville, kuinka paljon prosessiveden kalsiumpitoisuus vaikuttaa laboratorio-olosuhteissa, jossa mekaaninen retentio on vaikuttavin retentiotyyppi.

Työssä tehtiin laboratoriossa näytearkkeja arkkiformerilla käyttäen koivusellun ja kaoliinin lisäksi retentiokemikaaleja. Prosessiveden kalsiumpitoisuus säädettiin liuenneella kipsillä. Retentiotason vaihtelua tutkittiin mittaamalla arkkien neliömassaa ja tuhkapitoisuutta.

Keskinkertainen prosessiveden kalsiumkonsentraatio alensi retentiota kun käytettiin kationista retentioainetta. Anioninen retentioaine ei reagoanut kalsiumkonsentraation vaihteluille. Kalsiumkonsentraation ollessa lähellä kylläisyyspistettä, liukeneminen oli epätäydellistä ja neliömassat nousivat huomattavasti. Anionisella retentioaineella polymeerin voimakas elektrostaattinen siltautuminen nosti retentiota lähellä kalsiumin kylläisyyspistettä. Suurempi retentioaineannostelu nosti retentiota kaikissa olosuhteissa.

## **FIRST WORDS**

This engineering thesis theoretical part was done during the summer of 2006. Laboratory measurements were done in Tampere Polytechnic Paper Laboratory during the fall of 2006.

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Tampere 13.11.2006

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## THEORETICAL PART

## 1 INTRODUCTION

Stability of paper machine wet end chemistry is usually the priority number one for achieving high level of quality, runnability and cost efficiency. To prevent fluctuations of the critical process parameters, the control and automation system of paper machine has to work flawlessly. The water system has to be clean and raw material flow must be even for avoiding fluctuations. Constant pH and temperature keeps the system stable and clean and prevents appearance of problems such as precipitates, slime and growth of bacteria. Stability of wet end can be defined by measuring the conductivity of white water. It indicates the peaks in content of dissolved salts. Growth of solubility is usually the result from variation in pH or temperature. Growth in solubility changes gradually the cationic demand of wet end. Cationic demand indicates the content of anionic material in the system.

Negatively charged anionic material comes mainly from fibers, fillers and coated broke. A part of gypsum dissolves in every conditions and it is the biggest reason why gypsum is not very popular pigment although gypsum has some advantageous properties compared to other pigments. Dissolving gypsum creates cationic calcium ions  $\text{Ca}^{2+}$ . The result is lower cationic demand, because free calcium ions are attracting anionic material in the process water.

Retention chemicals are used to improve the level of retention. Retention chemical can be cationic or anionic. Also combination system of these two chemical types is used. Retention chemicals are attracting and bonding the opposite charged material. Cationic retention chemical has to compete with calcium ions to attach with anionic material like fibers.

## 2 SOLUBILITY

Dissolving happens when individual molecules or ions are attracted to water molecules. Molecules or ions break away and solid dissolves. Solid can dissolve to



a certain limit. When the solvent has dissolved all the solute it can, some amount of undissolved solute remains. In this point a solution is saturated. Substances molar concentration in a saturated solution is called molar solubility.

Solid continues dissolving after the saturation point is exceeded, but the concentration remains the same in spite of dissolving. Exactly the same rate at which dissolves to the solution returns to the solid form. In this point dissolved and undissolved solutions are in dynamic equilibrium. /7, s. 439./

Water contains molecules which has a dipole nature. It means that molecules one end is positively and the other end negatively charged. The water molecules are able to break down the crystal lattice of ionic compounds. The positively charged end can attach itself to the anion and pull it away from the substance. Similarly negatively charged end can attract away a cation. This means that the substance dissolves. /6, s. 51./ Water is a polar liquid and it is the best solvent for ionic and polar compounds. Compound, which has hydrophilic groups, dissolve to water. Large particles (20-100  $\mu\text{m}$ ) in solutions are called colloids. /7, s. 442, 443./

### 3 ADEQUOUS SOLUTIONS

A solute can be present as ions or as molecules. If solution contains ions, it conducts electricity and it is called electrolyte solution. /6, s.82./ If solute is present entirely as ions, solute is called a strong electrolyte solution. If some molecules survive, solute is called a weak electrolyte solution. When ion moves in solution, it has some amount of water molecules surrounding it. This means that the ions are hydrated. The coating of water molecules keeps ions in solutions and prevents reformation to solid. /6, s.83./

When two electrolyte solutions are mixed, a precipitation reaction occurs. It means that an insoluble solid product is formed during the reaction. /6, s.85./ Precipitate

occurs, when the solubility equilibria of certain salt is exceeded. Variation of temperature or pH changes solubility equilibria and precipitation happens easily. When the crystal is once formed, it grows increasingly. /9./



**Picture 1** Growth of slime in paper machine /9/

By keeping the water system clean and process as stable as possible, undesired appearance of precipitations and slime (picture 1) can be avoided. Understanding the chemistry of paper machine wet end is vital in nowadays complicated water systems.

## 4 IONS

Ion is an electrically charged atom or group of atoms. A positively charged ion is called cation and negatively charged is called anion. /6, s.B13, B5, B2./

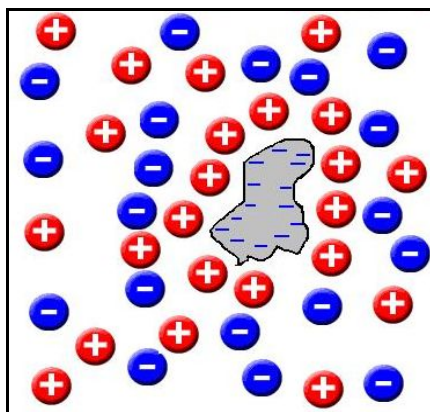
### 4.1 Ionic bonds

The attraction between the opposite charged of anions and cations is called an ionic bond. /7, s.268./ Molecules which contains more than three electrons in the outer shell, tends to be non-ionic. /6, s.52./

Cations are smaller, because the atom loses one or more electrons to form the cation. Reciprocally anions are larger, because they receive electrons to their valence shell. When atoms and ions have the same number of electrons they are called isoelectronic. Ions can have the same electron configuration, but their radii differ because of different nuclear charges. Therefore ions with similar electron configuration can have different intensity in attraction. Smaller radius means that, the nuclear has stronger attraction for its electrons. /6, s.251./

## 4.2 Zeta-potential

In paper making fibers and most of fillers usually receives a negative charge when they are added to water. The charge creates in to the surface of a solid material so called electrical double charge (picture 2). The first layer between the particle and water is called Sterns layer, which is a stable cationic layer. This layer tends to even the charge difference between the particle and the second layer. The second layer is called diffusion layer, which is more anionic and it evens the difference of a charge between the Sterns layer and the water. The potential of this system is called the zeta-potential. Fibers and fillers containing water have usually potential between -10 to -30 mV. /9./



**Picture 2** Illustration of Zeta-potential of a particle


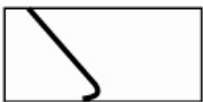

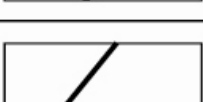
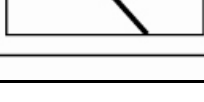
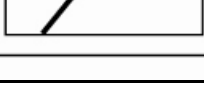
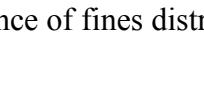
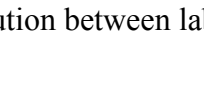
## 5 RETENTION

Retention indicates the amount of furnish, which stays in the wire after it is pumped from headbox. Retention can be calculated from following formula:

$$\text{Total retention} = (\text{headbox consistency} - \text{white water consistency} / \text{headbox consistency}) \times 100\% \quad (1)$$

The same formula (formula 1) can be used when calculating ash retention. Consistency values must be changed with corresponding ash values. Other retentions which can be defined are fiber and size retentions. Maximum retention is not usually the target. More important is to reach a level, where sufficient retention of fines and fillers is achieved without losing a good level of important things such as formation, water removal and retention chemical dosage. / 5, s.149./

In laboratory circumstance filler retention is rather low and the filler distribution differs from paper machine circumstance (picture 3). /8, s.48./

		Fiber orientation increases →	Fines content increases →
Laboratory sheets	Upper side		
	Wire side		
Fourdrinier machine	Upper side		
	Wire side		

**Picture 3** Difference of fines distribution between laboratory sheets and paper machine /8, s. 46/

Picture 3 shows, that fiber orientation with laboratory sheet former is a minor. With conventional Fourdrinier machine wire side has more fiber orientation but fines content on upper side is bigger. Fines content with laboratory sheet former is

opposite compared to Fourdrinier machine. Increasing fines content on the wire side explains why filler retention with sheet former is low. Fillers pass through wire more easily and unequal distribution to fiber mat lowers ash retention.

## 5.1 Retention mechanisms

Retention is divided into two types of retentions: chemical and mechanical retention. Chemical retention is located on the initial water removal process nearby headbox. Small particles such as fines and fillers are bonded to bigger particles by means of retention chemicals. Control of chemical retention is very important, because retention chemicals are very expensive and the disturbances in retention can cause very serious problems in production. / 5, s.149, 150./

Existing literature has established terminology for different retention mechanism.

Usual terms are:

- charge neutralization,
- coagulation,
- patching,
- bridging,
- complex flocculation and
- network flocculation.

Flocculation and aggregation are the most important mechanisms. Remarkable part of furnish components are too small to mechanically retain on the wire. /4, s.43, 45./

## 5.2 Chemical retention

The basis of chemical retention is that small filler particles are bonded to bigger aggregates by means of retention chemical dosage. A chemical retention process is

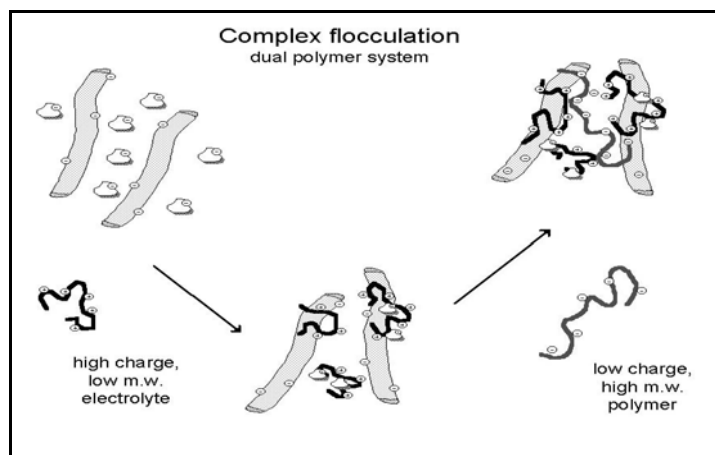
generally described with two basic mechanisms: patching and bridging. In patching process a short chain polymer is adsorbed to the surface of a particle. Particles the electrical double layer changes its charge and the particle create an attraction with the other particle. Bridging is that the long polymer chains are attached to the surface of the particles. By means of bridging is possible to achieve high level of retention in spite of high z-potential. /9./

### 5.3 Complex flocculation

Complex flocculation mechanisms are:

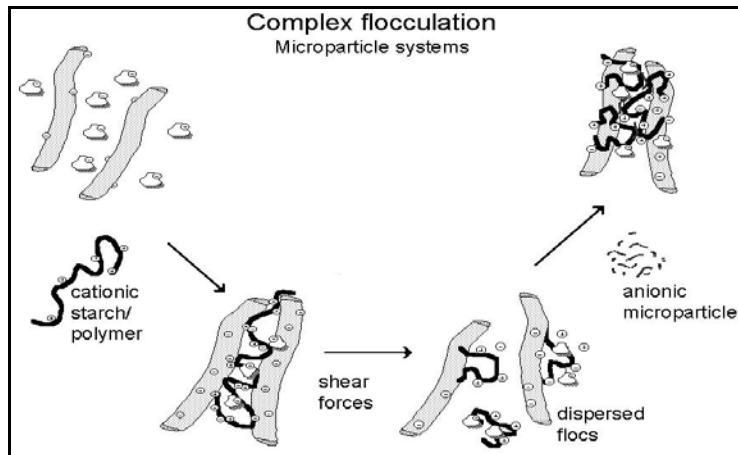
- Dual polymer flocculation
- Nano and micro particle flocculation
- “Network” flocculation
- Site blocking enhanced bridging flocculation.

Dual polymer systems (picture 4) are based to adding an anionic and a cationic polymers. Cationic polymers can be polyethyleneimine, poly-DADMAC or either cationic starch. Anionic polymer is a polyacrylamide. To flocculate anionic fibers and fillers, the cationic polymer is added first. The anionic polymer is added after shear stage to form new flocs by bridging.



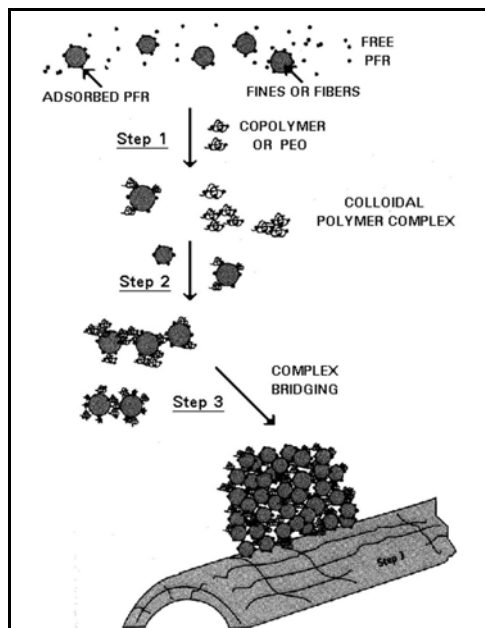
**Picture 4** Illustration of a dual polymer system /4/

In the nano- and microparticle systems (picture 5) a cationic polymer is combined with an anionic particle. In some cases occurs a combination of dual polymer systems and nanoparticle mechanisms.



**Picture 5** The principle of microparticle system /4/

The network flocculation system (complex bridging mechanism) is based on hydrogen bonding (picture 6). Systems, which are based on phenolic resin and polyethyleneoxide or montmorillonite and anionic polyacrylamide, are typical for network flocculation. The latter theory is that the hydrogen bonding combines with an electrostatic bridging, comprising  $\text{Ca}^{2+}$  ions.



**Picture 6** The principle of complex bridging mechanism /4/

To improve bridging more favorable polymer conformation, site blocking agent (SBA) is used in some special cases of complex flocculation. The SBA is usually low molecular weight and highly cationic polymer. /4, s.52, 53, 54, 55./

## 5.4 Mechanical retention

The other retention type is a mechanical retention. It is based on particles attaching to the web. With long fibers mechanical retention is good, but with small fillers it is much worse. Mechanical retention plays bigger role in the end of wire section, where the web is already filtered.

## 5.5 Retention chemicals

In the early days, alum was common retention chemical, which neutralizes the charges of furnish components. Single polymers like PEI were introduced later with patching as the dominant mechanism. The major mechanism – bridging – is attained with single and dual polymer systems. In the early of 1980s micro and nano particle systems were introduced to the markets. Latest development has been organic micro particle systems. Systems are based on network flocculation mechanism with PEO and phenolic resin. /4, s.43./

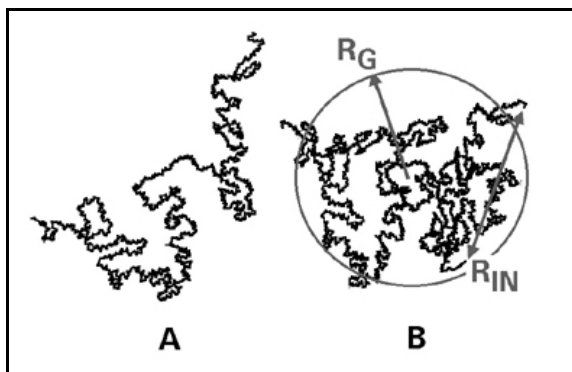
Retention polymers are positively or negatively charged (polyelectrolytes) and they act as:

- flocculants,
- anionic trash catchers,
- wet-strength agents and
- dry-strength additives.

Synthetic polymers are covalently bonded monomers, which are synthesized to homopolymers, block copolymers, or heteropolymers by condensation or free



radical reactions. Polymers can be characterized by the ratio, the weight and number average of the molecular weights. Polymers in liquids are characterized by the average radius of gyration and the average end-to-end distance (picture 7). Under theta conditions can be polymers dissolved in liquids characterized, because there is exact cancellation between steric repulsion and van der Waals' attraction between monomers. /4, s.48./



**Picture 7** Illustration of the gyration of the polymer, where  $R_G$  illustrates the average radius of gyration and  $R_{IN}$  the average end-to-end distance /4, s.48/

Polyelectrolyte will adsorb strongly an opposite charged surface under moderate ionic strengths. Because of extensive contact, polymer can not be removed by rinsing. Instead too high salt concentration decreases electrostatic interactions and affects to the adsorption behavior. Nonelectrostatic interactions affects also to the behavior of polyelectrolyte at a surface. Under electrostatic conditions, there is a maximum adsorption with increasing electrolyte content. /4, s.49./

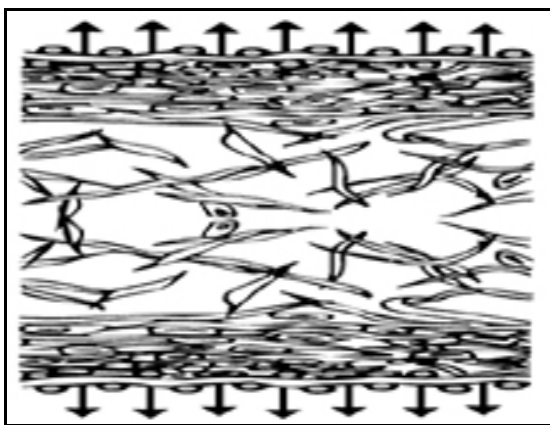
Overdosing of retention chemicals can lead to too positive charge of the system. Too positive charge of the wet end affects problems such as precipitates, holes, poor filtering and formation. Too low dosing can lead to poor functioning of retention system. /5, s.152./

## 5.6 Retention types

There are three types of retention parameters, which are common:

- first-pass retention,
- machine retention and
- system retention. /4, s.69./

First-pass retention (FPR) (picture 8) is a very common retention parameter. Functionality of chemicals is better if first-pass retention is high. Circulating in the wet end makes additives less effective. Better FPR means better runnability, because it prevents deposits and growth of bacteria. Higher FPR means automatically higher degree of efficiency. High first-pass retention is favorable, but too extensive flocculation sets limits for it. Too extensive flocculation can cause inferior formation. /4, s.70./



**Picture 8** An illustration of the first-pass retention with the cap former /9/

First-pass retention affects directly to the machine retention. High FPR decreases work load of internal separation, whereas internal separation such as disc filters and flotation units determines the efficiency of machine retention. Unretained chemicals and fines can be detrimental for the system causing problems such as deposits and unnecessary refining, which are harmful for dewatering. /4, s.71./

System retention means all material leaving the process. Both FPR and machine retention has an influence to system retention. Good degree of system retention is

necessary for achieving optimum raw material use and cost-efficient manufacture process. /4, s.71./

## 5.7 Advantages of a good retention

Higher retention can be achieved for example with higher headbox consistency, lower freeness, slower machine speed and with bigger retention chemical dosage. /5, s.150./ The advantages of a good retention are better quality, better productivity and higher cost-effectiveness. Better retention means better symmetry for fillers in the paper. Because of smaller consumption of additives and cleaner wet end, runnability is better. Cleaner wet end means less washing, so consumption of fresh water and amount of effluent is smaller. Water removal is better and thus the consistency of headbox can be lower. It means better formation and stronger paper. Better water removal means also lower steam consumption in drying section. /5, s.153, 154./

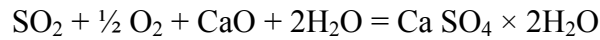
## 6 GYPSUM

Gypsum consists of calcium sulfate, which is a neutral and environmentally safe salt. /2, s.2./ Gypsum is a natural product found in sediments and the estimated resources are approximately 2200 Mt. It is also a by-product of industrial processes. There are three significant industrial production processes:

- phosphoric acid,
- titanium dioxide,
- citric acid and
- hydrofluoric acid.

These altogether produces gypsum annually 150 Mt as a by-product.

Third source of gypsum is flue gas desulphurization. FGD gypsum is a flue gas purification process, where sulfur is bound to calcium: /1, s.153./



/2, s.3./

Annual production is approximately 30 Mt and it keeps growing because of stricter environmental regulations. /1, s.153./

## 6.1 Chemical properties

Calcium sulfate can appear in three different crystal water forms. Every form has its unique physical properties. When calcium sulfate is heated, it undergoes a following conversion process:

- Dihydrate to hemihydrate,  
 $\text{CaSO}_4 \times 2\text{H}_2\text{O} \Rightarrow \text{CaSO}_4 \times \frac{1}{2}\text{H}_2\text{O} + 1 \frac{1}{2} \text{H}_2\text{O}$
- Hemihydrate to anhydrite,  
 $\text{CaSO}_4 \times \frac{1}{2}\text{H}_2\text{O} \Rightarrow \text{CaSO}_4 + \frac{1}{2} \text{H}_2\text{O}$
- Finally, anhydrite decomposes to calcium oxide and sulfur dioxide,  
 $\text{CaSO}_4 \Rightarrow \text{CaO} + \text{SO}_4 + \frac{1}{2} \text{O}_2$

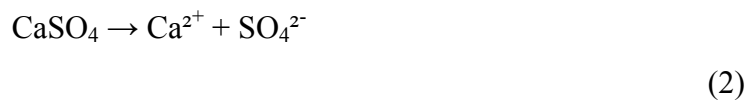
Anhydrite is also known as calcinated gypsum. Crystal water in dihydrate is very easily bounded and it starts to release its crystal water already in 45 °C, if the humidity of ambient air is low. If the heating is still increasing, hemihydrate will go trough conversion to anhydrite. The opposite conversion process from hemihydrate to dihydrate happens also very easily.

The most known utilization of gypsum is based on hardening. First dihydrate is calcinated to hemihydrate and then slurred into water. Hemihydrate binds crystal water and crystallizes into dihydrate.

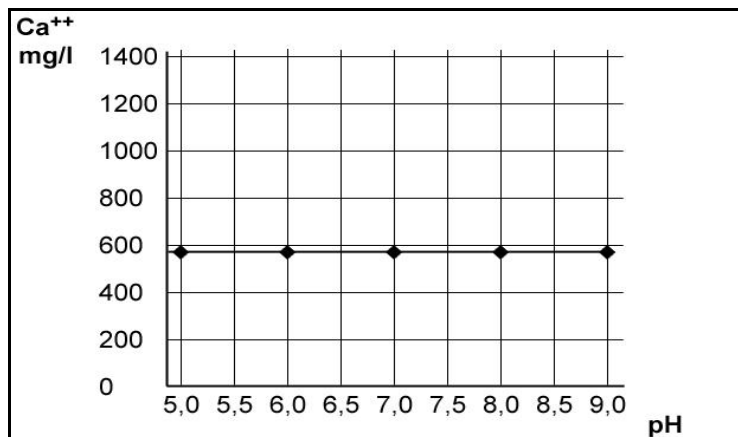
Coating pigments are dihydrate gypsum, because it is stable and its properties are highly suitable for coating. Dihydrate cannot bind any more crystal water and slurries do not harden. /1, s.154./

## 6.2 Solubility of gypsum

Gypsum dissolves in water (formula 2) and forms cationic  $\text{Ca}^{2+}$  ions.

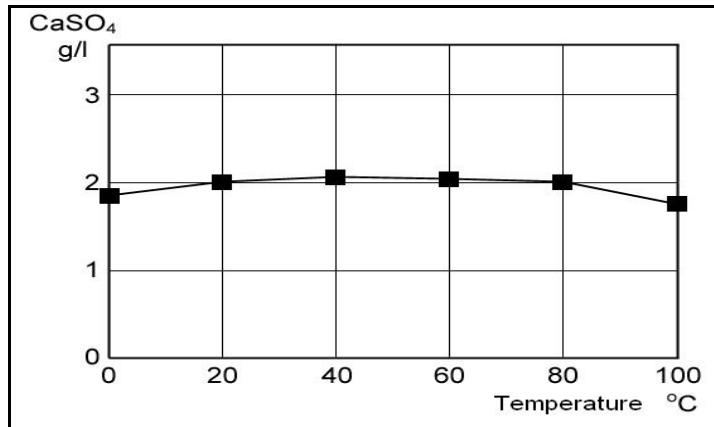


The solubility of gypsum is basically constant regardless of pH operating area (figure 1). Gypsum has almost equal calcium load with calcium carbonate in the area of pseudoneutral pH.



**Figure 1** Solubility of gypsum depending on pH /9/

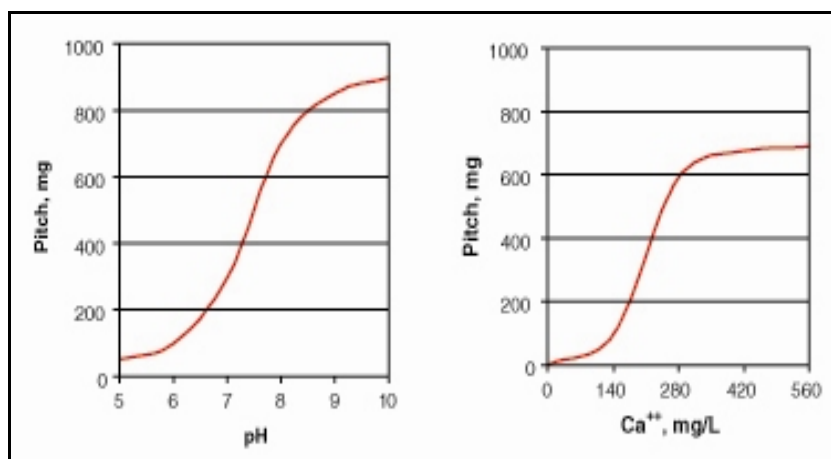
Gypsum does not release gases when decomposed which is great advantage compared to calcium carbonate. Temperature dependency is also rather low (figure 2). Solution of saturated gypsum contains about 2.1 g/L of  $\text{CaSO}_4$  and 580 mg/L as a calcium concentration. Amount of dissolved is larger than with other pigments, which is the biggest reason why gypsum is not very popular paper pigment. /1, s.155; 1./



**Figure 2** Solubility in different temperatures /9/

Calcium concentration of circulation water rises close to the level of 580 mg/L if gypsum used as filler. If gypsum is used as coating pigment, calcium ends to water circulation through broke. In that case concentration is between 200 – 400 mg/L with printing papers. With cardboard it is much less and gypsum does not precipitate. /1, s.163./

Nowadays paper machines are running with higher calcium concentration because of closed circulations. Dissolving gypsum does not influence on pH and the risk of precipitation is bigger with changes of pH than with saturated gypsum solution (figure 3). The process is not susceptible to gypsum broke, if the retention level is good and the flocculating anionic material is bound to paper web. /1, s.164./



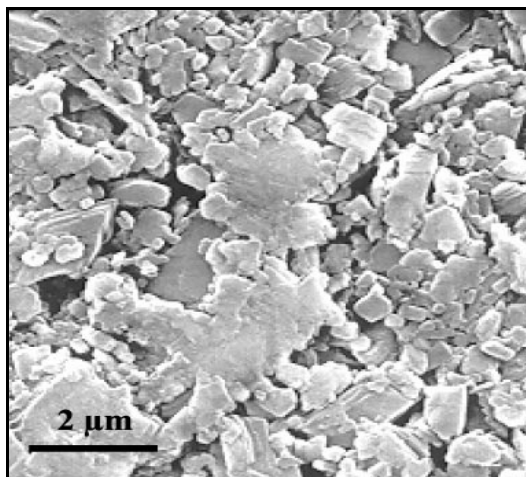
**Figure 3** The effects of pH and calcium for pitch deposits /1, s. 163/

### 6.3 Utilization for paper industry

Gypsum has a high brightness, opacity and printability compared to conventional pigments. A low density makes possible to produce light paper grades and have high filler content. /14./

Industrially produced gypsum contains harmful impurities and therefore utilization is often limited. Natural gypsums (picture 9) brightness is often modest, but those do not contain harmful impurities. Also FGD gypsum is quite gray, but their brightness can be controlled by choosing the most suitable processes and raw materials.

Gypsum produced from sedimentary phosphate rock color is gray or brown. It is a bit radioactive and it contains heavy metals. Instead gypsum produced from magmatic phosphate rock is pure, white and it is very suitable for raw material of pigment gypsum. /1, s.153./



**Picture 9** Microscope picture of a natural gypsum /9/

The most remarkable manufacture countries of gypsum are Spain, Italy, France, England, Germany, Finland and Brazil. Spain has the longest tradition of producing gypsum for paper industry. Spanish gypsum is manufactured from natural gypsum.

By-product gypsum manufacturing countries are for example Italy (titanium gypsum), Brazil and Finland. Brazil and Finland are producing phosphogypsum. /1, s.153; 9./

Finland is the only country, which produce gypsum for paper coating. Kemira production plant in Siilinjärvi has produced phosphogypsum since 1985. Kemira produce phosphoric acid by using apatite. Pigment is very white and its heavy metal content is low. Annual production of coating pigment is about 150 000 tons. /10; 1. s.157./

## **7 WET END CONDITIONS**

### **7.1 Cationic demand**

Cationic demand describes the total amount of available negative charges in furnish or in specific fraction. It indicates the amount of cationic charge, which is required to reach zero electro kinetic charge. It is expressed as mg/L liquid or mg/g solid.

The cationic demand is necessary for the adsorption of the cationic additives. If the polymer fails to compete with the counter-ions of furnish, the cationic demand is strongly reduced. The cationic demand of fibers comes mainly from dissociated carboxylic groups. /4, s.47, 48./ The cationic demand increases along with pH, because carboxylic groups become more dissociated. When the electrokinetic charge goes down to zero, the adsorption of the cationic polymer is reduced. If the addition of cationic polymers is continued after zero level, it will lead to charge reveal and later to imbalances in the wet end. /4, s.47, 48./



## 7.2 Cationic demand in the water phase and in the solid material

Increased cationic demand of the system is the results of dissolved polymers and colloidal anionic material. This “anionic trash” comes from wood (pitch, carbohydrates) and from coating broke. Good knowledge of the cationic demand is very important for controlling the wet end chemistry.

Cationic demand can be divided to two categories: cationic demand in the water phase and cationic demand of solid material. Cationic demand in the water phase has a negative side, because it reduces the adsorption and functionality of cationic polymers. Instead of that, cationic demand in the water phase has also very advantageous side since it enables adding a high amount of cationic compounds such as starch and wet-strength resins. /4, s.56./

## 7.3 Calcium concentration

Calcium ion is a polyvalent ion and its valency number is 2. It has given two electrons away from its third shell, which creates a positive charge. It is strongly attracted by the carboxylic groups of fibers. The cationic polymer has to compete with calcium ions in order to be adsorbed and therefore it is necessary to add the cationic polymers successfully. /4, s.47, 48./

Decomposition of calcium containing substances increases the calcium ion concentration in aqueous phase. Calcium forms precipitates with anions such as oxalate and sulfate. It also forms very tacky soaps with fatty acids. Foam is build up when carbon dioxide is formed. /4, s.209./

## 7.4 Controlling the paper machine water chemistry

Closing the white water system increases the amount of detrimental substances. Fluctuations of pH and temperature in a closed circulation system lead to web breaks and quality problems more easily than in open system. Therefore it is necessary to use high quality controlling and monitoring system to ensure a stable process conditions. /4, s.213./

For controlling effectively the white water system, continuously operating measurements techniques are essential. Collected data from the process must be handled with computer based systems. The process analyzes system converts the data from process into information for operator. /4, s.215./

### 7.4.1 On-line parameters and measuring

Following on-line parameters are essential for successful wet end controlling:

- retention
- pH
- conductivity
- charge
- calcium concentration
- chemical oxygen demand and total organic carbon concentration
- temperature

These on-line parameters are very useful for controlling and observing the behavior of pigment dissolving. Retention control measures white water and head box consistencies. Consistency does not necessarily correlate with the concentration of dissolved colloidal substances. Almost all chemical reactions in the water phase are affected by pH level. The solubility of dissolved and colloidal substances increases

when pH fluctuates. PH is the most important parameter that can be measured continuously and it is logarithmic value of the molar hydrogen ion concentration.

The conductivity measurement is very sensitive for small variations in conductivity. Measuring the conductivity gives rough picture of the total concentration of electrolytes in the aqueous phase. Particle in water has a certain charge and it has a strong influence on its behavior. The most common way to measure a charge is a titration. A sample is titrated with the opposite charged standard polymer. On-line equipments for measuring calcium ion concentration are X-ray, spectrophotometer or titrator. The most common and convenient is the X-ray.

The chemical oxygen demand (COD) and the total organic carbon (TOC) concentration indicate the amount of dissolved organic material in the water phase. The temperature has an effect to many reactions in the water phase. Solubility, dewatering speed and precipitation is the most important ones. /4, s.216, 219./

## EXPERIMENTAL PART

## 8 GENERAL

In the experimental part was focused to study in laboratory how the level of retention varies, when variables are the retention chemical dosage and the calcium concentration. Tests were done by making test sheets with sheet former and defining grammages and ash retentions of sheets. The test conditions were studied and adjusted by measuring the pH and temperature. The pH level was also confirmed from Tampere water plant and it was approximately 7.5. Temperature of used water was adjusted to 22 °C.

Two retention chemicals were used: anionic and cationic. The retention chemical dosage points were the minimum and the maximum dosage points. These dosage points were mentioned in the retention chemicals directions (appendices 3, 4). The calcium concentration points were 0 parts per million (ppm), 200 ppm, 400 ppm and 580 ppm, which is the level of saturation. Calcium concentrations were adjusted with dissolved dihydrate gypsum. The number of made sheets was ten in every calcium concentration level with both anionic and cationic retention chemical in minimum and maximum dosage points. Also ten test samples were made without using calcium slurry or any retention chemical.

After pressing and drying sheets grammages were measured and ash retentions were studied.

## 9 USED MATERIALS

### 9.1 Pulp

The used pulp was dried and bleached sulphate birch cellulose. The fiber length of a birch pulp is between 0.9 – 1.2 mm and the diameter 22 µm. /5, s.31./ Pulp

batches were in refrigerator between the tests to ensure that pulp quality remains the same and deteriorating does not occur. Bleached cellulose pulps can usually be stored for significantly longer times than for example mechanically made unbleached pulps / 8, s.40/. In the tests the maximum storage duration was 3 days.

## 9.2 Kaolin and gypsum

Kaolin in the tests was Intrafill C manufactured by Imerys. Intrafill C is an English filler clay and its particle size distribution is following:

← 1 μm	36%
← 2 μm	55%

/appendix 5/

Kaolin was the most suitable filler pigment for the tests, because it is an insoluble and does not decompose in ash making tests. Used gypsum was Kemiras dihydrate gypsum manufactured in Siilinjärvi. The dry content of the gypsum slurry was 68%.

## 9.3 Retention chemicals

The cationic retention chemical was Fennopol K 7400 R and the anionic retention chemical Fennopol A 3050 R manufactured by Kemira. Both are used to improve paper machines fiber and ash retention.

The chemical structure of both chemicals is polyacrylamide, which is a copolymer of acrylamide and sodiumacrylate. It is used to separate a solid material from liquid material. /12; appendix 3, 4./

States of chemicals were solid and before usage both chemicals had to prepare. First 0.3 % storage solutions were prepared by mixing 3 g of solid chemical to one liter of water. Then the dosing solution was prepared by diluting the storage solution with nine liters of water. All these were done with mixer.

The dosage amounts were mentioned in the chemicals instructions. The minimum dosage is 100 g per ton of paper and the maximum dosage is 500 g per ton. The dosage for one sheet was calculated by making test sheets and measuring grammages. The minimum dosage was 0.56 ml per sheet and the maximum dosage was 2.8 ml. /appendix 6./

## 10 USED METHODS FOR SHEET MAKING

### 10.1 Beating

Before making the sheets, 360 g of dried cellulose pulp was ripped to flakes and wetted over night in 5 liters of water. Before the beating, stock was diluted with 18 liters of water. The beating was done with hollander Valley beating machine manufactured by Ab Lorentzen & Wettre (picture 10).



**Picture 10** Lorentzen & Wettre hollander Valley beater

In the beating process, primary wall of fibers is mainly removed. External and internal fibrillation occurs and also fiber breakage is remarkable with Valley beater. /8, s.43./

Valley beater has a bladed cylinder, which rotates against the counter blades and beats the stock. Pulp was slushed first 20 minutes without any weights and then refined 15 minutes with weights, which gives the needed pressure for the beating blades. Short beating duration ensured that the amount of organic material was as low as possible. Also high Canadian Standard Freeness (CSF) was reasonable to aim for, because it means quick wire passing and therefore low mechanical retention. From the beaten stock 2.4 liters was taken with 1.2 liter measure and every 1.2 liter batch were numbered for the CSF tests. 2.4 liter of beat stock was diluted with 16.4 liters of water to reach a consistency of 2 g/L for sheet making. One batch for sheet making consisted 18.8 liter of stock in consistency of 2 g/L.

## 10.2 Kaolin slurry

The target of ash content was 20% and 100 g of kaolin was slurred to approximately same amount of water. Slurring was done by using fast rotating mixer and the dry content was measured with HG53 Halogen Moisture Analyzer (picture 11). The dry content result was 42%.



**Picture 11** HG53 Halogen moisture analyzer



For measuring CSF one liter of stock was needed and the amount of the stock was 17.8 liters after measuring CSF. The fiber consistency was 2g/L, so one stock portion consisted approximately 35.6 g of fiber. The needed amount for 17.8 liters of stock was 21 g of kaolin slurry to achieve decided 20 % ash content.

### 10.3 Calcium containing water

Whole capacity of sheet former was 20.48 liters and it was divided from the middle with wire. Capacity of the upper part of sheet former, which was filled with calcium containing water, was 9.5 liters. The calcium containing water does not mix much with the lower part water. Gypsum was slurred to the amount of water, which is enough to dissolve whole used amount of gypsum (table 1).

**Table 1** Amount of used gypsum and water to dissolve the gypsum

Material	200 ppm	400 ppm	580 ppm
gypsum, gramme (dc 68%)	10,12	20,24	29,34
water, liters	3,3	6,6	8,7

The needed quantity of slurred gypsum was calculated with 2.1 g/L, which is the solubility of gypsum mentioned in literature. Table 15 shows that slurred gypsum for achieving the calcium content of 580 ppm was 29.34 g and water amount was 8.7 liters. This amount of gypsum does not dissolve completely to 8.7 liters water, but during sheet making 0.8 liter of stock was added to reach 9.5 liters, which is the capacity of sheet former upper part.

Gypsum was slurred with fast rotating mixer and the dissolving times were between 3-5 minutes to ensure complete dissolving.

## 10.4 Sheet making

The sheet former (picture 12) was filled entirely with water when making sheets in calcium concentration of 0 ppm. With calcium concentration of 200, 400 and 580 ppm the sheet former was filled up to the wire level with water and calcium containing water solution was decanted on the top. The amount of stock was 0.8 liter and it was decanted before adding retention chemical with the dropper.



**Picture 12** Conventional Oy Fermeca AB sheet former

To ensure competition between retention chemical and free calcium ions, it was reasonable to add the used components in the mentioned order.

Sheet formers yarn number of wire was  $3 * 26.0 / 27.0$  cm and size of free holes were  $0.15 * 0.21$  mm. The mixing of stock is done by putting air pressure on, which blows air into a stock. After mixing bottom valve is opened and stock filtrate through the wire. Removal of water generates approximately 8.0 kPa pressure difference. The extra water is removed by pressing blotters against fiber mat.

The formation consistency is significantly lower than in paper machine by resulting very good level of formation. The forming process differs also that

orientation does not occur and laboratory sheets are basically isotropic. /8, s.48/

## 10.5 Pressing and drying

Sheets pressing was done with AB Lorentzen & Wettre Sheet Press (picture 13). The machine generates needed pressure with hydraulic cylinder which presses down the metallic plate against pile of fiber mats and blotters.



**Picture 13** L&W Sheet Press machine

Pressing process has two phases. Duration of first pressing phase was 4 minutes and the pressure was 0.5 Mpa. The second phase takes 2 minutes and pressure is the same than in the first stage. Wet fiber mats were put to the pressing machine between blotters.

Final sheet making process was drying with Oy E.Sarlin AB drying drum (picture 14). The drying temperature was 90 °C. Sheets were put against hot drying cylinder between two blotters and drying duration was 4 hours.



**Picture 14** Oy E.Sarlin AB drying cylinder

## **11 USED METHODS FOR PULP AND SHEET MEASURING**

### **11.1 Canadian Standard Freeness**

From refined pulp 2.4 liters were diluted with 16.4 liters of water so that the pulp concentration was 2 g/L. CSF was measured with AB Lorentzen & Wettres Freeness measuring equipment (picture 15). Stock was mixed with fast rotating mixer, so that used 1 liter sample was as homogenous as possible.



**Picture 15** Canadian Standard Freeness measuring equipment

Standard CSF measurement consistency for stock is 3 g/L. /12, s. 44/

Measurements for this thesis work was done in consistency of 2 g/L, which was the consistency of prepared stock for sheet making. More important was to follow that drainability level remained the same during the tests.

## 11.2 Grammage

Grammages were measured by cutting from the sheets 100 cm<sup>2</sup> samples. Sample weight was measured and the results were multiplied with 100 to find out grammages. The precision of the measuring scale was 1 mg.

## 11.3 Ash content

Ash tests differed from the ash making standard for paper and boards SCAN P5:63 by that preheating of crucible and reheating of sample were passed because of large number of samples. In the test two average samples from each 10 sample series were picked up for measuring ash content. If there were remarkable dispersion in weights between samples, the third sample was tested to ensure reliable result. Ash making was done with Heraeus GWB ash furnaces (picture 16). The temperature was close to 1000 °C and burning duration for one sample was 1.5 hours. That ensured that all organic material was dispelled.



**Picture 16** Heraeus GWB ash furnaces

Before ash making weight of used crucible was measured. Precision of scale was 0.1 mg. Then the crucible weight was measured with sample on it. After ash making the crucible weight was measured again and the weight difference before and after burning revealed the amount of inorganic material. Before making another ash test, the furnaces were cooled down for 15 minutes so that the test circumstance was similar with every each sample.

## 12 THE RESULTS AND ANALYSES

### 12.1 Canadian Standard Freeness

Every batch taken from the beater was numbered for controlling stock properties (table 2). First ten sheets without kaolin were made from the first batch. In the other tests two 1.2 litres batches were mixed together, diluted, and before sheet making, CSF measured. Consistencies of the stocks were 2 g/L.

**Table 2** CSF test results

Test batch	CSF, ml
1	610
2+3	590
4+5	610
6+7	590
8+9	590
10+11	590
12+13	605
14+15	605
16+17	595
18+19	590

Measuring results were between 590 – 610 ml. The average CSF was 597.5 ml. Samples standard deviation was 8.9 and it can be calculated with following formula:

$$s = \sqrt{\frac{\sum (x_i - x)^2}{n - 1}} \quad (3)$$

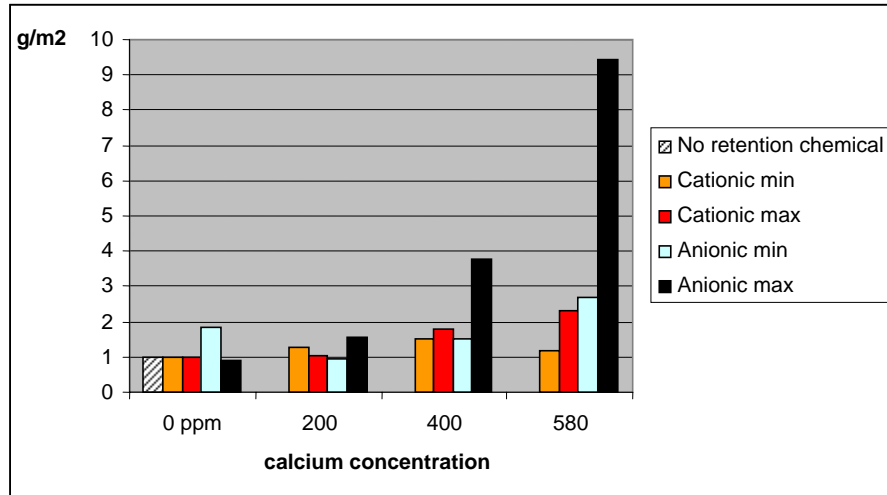
where  $x$  is an average weight and  $n$  is number of the observation value. The standard deviation (formula 3) describes how close the observation values are from the average. /13./

The standard deviation reveals that the dispersion between CSF results is acceptable small to be sure that it does not affect too much to retention.

## 12.2 Grammage measuring results

### Grammage variations

The grammage variation between ten sheets of the same test group was mainly under 2 g/m<sup>2</sup>. It reveals that measurements are reliable and differences between the test groups are not a result from random deviation from tests. Figure 4 indicates how grammages varied between the test groups. Values are from laboratory measuring results (appendix 1) and results are calculated with the formula of standard deviation.



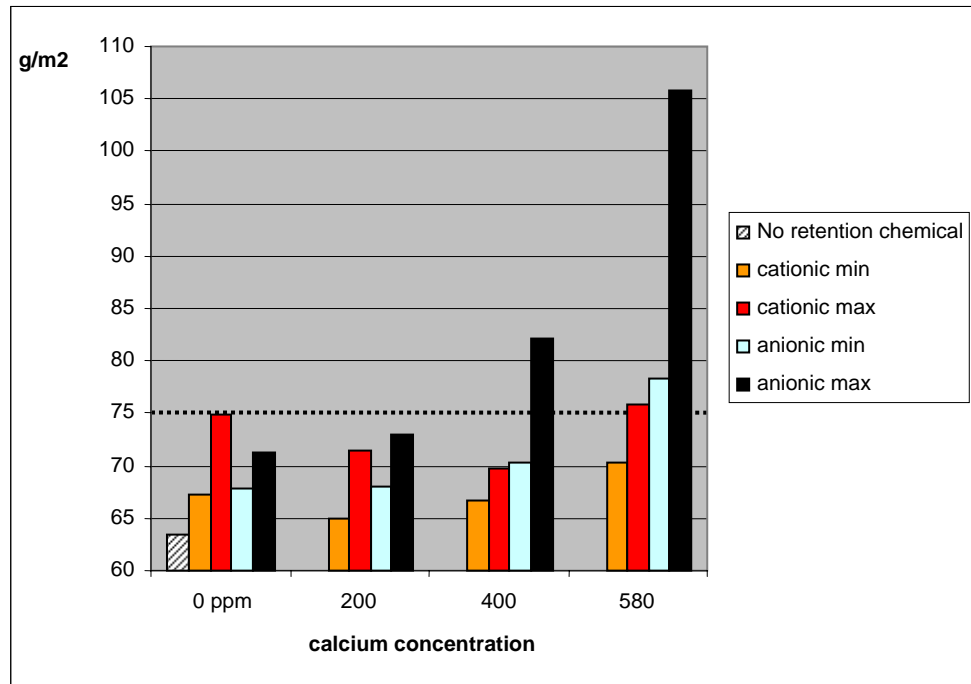
**Figure 4** Grammage variation between ten test sheets with different calcium concentration and retention chemical dosage

Figure 4 shows that with low calcium concentrations the dispersion in results is low. In higher calcium concentrations with anionic retention chemical maximum dosage dispersion grows dramatically. The standard deviation is over 9 g/m<sup>2</sup>.

### Grammages

With anionic retention chemical grammages of paper sheets were in calcium concentration of 200 ppm almost at the same level compared to zero calcium concentration. Free calcium ions had no effect with anionic retention chemical. When calcium concentration was 400 ppm up to saturation level, grammages went up outstandingly. When using maximum dosage of anionic retention chemical, grammages increased almost by 50 percent. Figure 5 illustrates how remarkably grammages went up when using anionic retention chemical.





**Figure 5** Grammage of sheets on different calcium levels with anionic and cationic retention chemical minimum and maximum dosage /appendix 1/

Calculated maximum retention level in the test was approximately  $75 \text{ g/m}^2$  which is marked on the figure 5 with das line. Figure 5 shows that with cationic retention chemical maximum dosage retention was a top level when the calcium content was zero. From the figure 5 can be seen how minimum and maximum dosages follows the same trend when calcium concentration is rising. On calcium concentration 200 ppm the grammage was only approximately  $2 \text{ g/m}^2$  higher with the cationic retention chemical minimum dosage compared when using retention chemical at all on the zero calcium level. On zero calcium concentration the increase of grammage with cationic retention chemical minimum dosage was almost  $4 \text{ g/m}^2$ .

The measured grammages of sample sheets had the desired correlations with the theory from literature (figure 5). With cationic retention chemicals in the calcium concentration levels of 200 and 400 ppm the retention level lowered.

**Table 3** Percentual changes of grammages on different calcium concentrations compared to the calcium concentration level of 0 ppm.

Used chemical	Grammage change %		
	200 ppm	400 ppm	580 ppm
cationic min	-3,35	-0,8	4,61
cationic max	-4,57	-6,87	1,29
anionic min	0,32	3,65	15,5
anionic max	2,27	15,16	48,48

Table 3 (values calculated from appendix 1) reveal how with cationic retention chemicals grammages decreased in calcium concentration 200 ppm approximately 4 percent (table 3). Cationic calcium ions attracted free anionic material from the stock and cationic retention chemical couldn't attract fillers and fibers as much as possible. Percentual decreasing was 1.2 percent higher with maximum dosage compared to minimum dosage.

On calcium concentration of 400 ppm percentual decreasing was only 0.8 percent with minimum dosage and it can be explained by insoluble gypsum particles which increased the grammage. With maximum dosage the retention level decreased more and it was almost 7 percent compared zero calcium concentration. When the calcium concentration level was 580 ppm, grammages raised with both chemicals because of incomplete solubility.

Table 3 shows also very well how anionic retention chemical was a numb to changes of calcium concentration. Grammages did not lowered in any studying points. On calcium level of 580 ppm grammage increasing was almost 50 percent compared to zero calcium level.

With both chemical, the level of retention was much higher compared when not using any retention chemical. Table 4 illustrates how strongly retention chemical affects in spite of laboratory circumstance, where the mechanical retention is the dominant retention type.

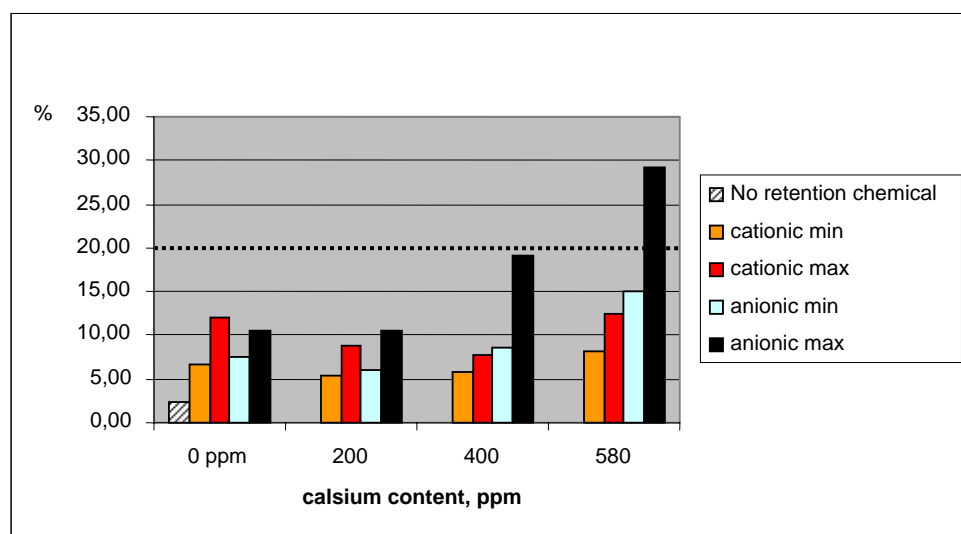
**Table 4** Increase of grammage when using retention chemical in calcium concentration of 0 ppm

Used chemical	The grammage growth g/m <sup>2</sup>
cationic min	6,04
cationic max	18,15
anionic min	6,85
anionic max	12,44

Table 4 (values calculated from appendix 1) results prove that the dosing amount of retention chemical had strong effect on laboratory circumstance. The increase of retention level was approximately same with minimum dosages and with maximum dosage slightly higher with cationic chemical.

### 12.3 Ash content

Ash retention differences between different calcium concentrations had quite similar trend with whole stock retention (figure 6). The ash content lowered with cationic retention chemical on calcium concentration of 200 and 400 ppm. With the maximum chemical dosage ash retention lowered percentually more than with minimum chemical dosage.



**Figure 6** Ash retentions as percent of the whole sheet weight /appendix 2/

From the figure 6 can also see, that with anionic retention chemical ash retention was quite similar on calcium concentrations of 0 and 200 ppm. In the figure 6 is marked theoretical maximum ash retention with das line. On calcium concentration level of 580 ppm the ash retention was almost 30 %.

Very interesting point of view is also that percentually ash retention decreased more with maximum dosage of cationic retention chemical than with minimum dosage. Table 5 shows that with minimum dosage the percentual decreasing of ash retention compared to zero calcium level was only approximately 1 percent with calcium levels of 200 and 400 ppm. Instead with maximum dosage an average decreasing was approximately 4 percent in the same calcium levels.

**Table 5** Changes of ash percent on different calcium concentrations compared to the results on the calcium concentration level of 0 ppm.

Used chemical	Ash % change		
	200 ppm	400 ppm	580 ppm
cationic min	-1,17	-0,81	1,61
cationic max	-3,2	-4,36	0,51
anionic min	-1,53	1,11	7,5
anionic max	-0,08	8,61	18,7

Table 5 shows that on calcium level of 580 ppm by using anionic retention chemical ash retention increased by 18.7 percent compared to 0 ppm with the same dosage and with the same chemical. On calcium concentration 200 ppm by using minimum dosage the percentual ash retention change was similar with cationic and anionic retention chemical.

## 13 CONCLUSIONS

### 13.1 General

The main conclusion in this thesis work was that calcium concentrations have a role with retention chemicals on laboratory circumstance, where the mechanical retention is the dominant retention type. Decreasing of grammages was approximately between 3 to 7 percent with cationic retention chemical on calcium concentrations of 200 and 400 ppm. These are the calcium concentrations when gypsum is used as filler with printing papers (chapter 6.2).

The exceptional grammage increasing with anionic retention chemical was also one of the main things. In chapter 5.3 *Complex flocculation* (page 14) is explained the basic idea of network flocculation. This complex bridging mechanism seemed to occur in this case. On the calcium concentration nearby the saturation point, the content of free calcium ions was so high that it changed the surface charge of anionic material in the system. Anionic polymer flocculated strongly with electrostatic bridging.

Also insoluble gypsum particles increased grammage with anionic polymer. Controlling the solubility nearby the saturation point seems to be very demanding and when gypsum is used as filler, the process runs in this calcium level and some amount of precipitation always occurs.

Remarkable increase of grammage came mainly from higher ash retention. It confirms that the solubility of gypsum was incomplete close to the saturation point. Free calcium precipitated strongly with anionic retention chemical and colloidal material increased the retention level. The actual amount of precipitated gypsum was even higher than the results in ash tests shows because gypsum decomposes to calcium oxide during the ash making process.

With cationic retention chemical the percentual ash retention compared to zero level was 3 percent lower by using maximum dosage than with minimum dosage on calcium concentration of 200 ppm.

Following questions are very interesting to think for and perhaps to further study:

If the aim is to improve the ash retention level, is the increase of retention chemical dosage the most suitable way, when the process water has free calcium ions?

How the results differ in modern paper machine conditions where the retention conditions are quite different?

How the 3 to 7 percent decreasing of the retention affects to the productivity and cost-efficiency of production line?

How the results differ in paper machine conditions where the composition of the process water is much more complicated?

How the results differ if dual polymer retention system is used?

## 13.2 Possible variations

Samples standard deviation was 8.9 in CSF tests. The difference between CSF results was a consequence of inaccuracy working methods. It is not possible to take with a 1.2 liter measure so same amount of a beaten pulp, that the standard deviation would be much smaller than these results.

In the grammage measuring samples results were multiplied by 100 and it increases the small variations, which would be normally compensated by measuring the actual 1 m<sup>2</sup> of paper.

Used gypsum slurry was measured with precision of 0.1 g. On the calcium concentration of 580 ppm it is very challenging to stay under saturation point. Small variation in measured gypsum amount increases the ash content if the saturation point is exceeded.

In the sheet making the stock was added with a 0.8 liter measure. It is natural that some sort of variations occurs when sheets are hand made. The standard deviation was approximately 1.2 g/m<sup>2</sup> when sheets were made without calcium containing water and any retention chemical. This kind of deviation is a result from measuring stock sample by hands and it has no bigger role in results because this deviation occurs in every circumstances.

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## 1 LABORATORY RESULTS OF GRAMMAGE MEASURING

Whole sheet

Sample	Gramme
1	1,696
2	1,694
3	1,712
4	1,722
5	1,645
6	1,659
7	1,664
8	1,667
9	1,626
10	1,707
<b>Average</b>	<b>1,6792</b>

Cellulose + kaolin

Sample	g/m2
1	64,1
2	63,8
3	64,8
4	65,1
5	62,3
6	62,5
7	62,5
8	63,3
9	61,3
10	64,3
<b>Average</b>	<b>63,4</b>

Standard deviation

0,032

1,227

Cationic retention chemical K7400R

Minimum dosage

0 ppm	g/m2
1	66,2
2	67
3	66,7
4	66,9
5	66,5
6	68,2
7	67,8
8	66,9
9	69,5
10	66,6
<b>Average</b>	<b>67,23</b>

200 ppm	g/m2
1	65
2	63,8
3	65,6
4	64,5
5	65,1
6	64,2
7	66,3
8	67,5
9	64,7
10	63,1
<b>Average</b>	<b>64,98</b>

Standard deviation

0,998

1,262

400 ppm	g/m2
1	64,3
2	65,4
3	66,1
4	67,3
5	68,2
6	67,1
7	66,4
8	67,5
9	69,3
10	65,3
<b>Average</b>	<b>66,69</b>

580 ppm	g/m2
1	68,4
2	70,1
3	70,7
4	69,7
5	70,1
6	72,8
7	69,3
8	71
9	70,9
10	70,3
<b>Average</b>	<b>70,33</b>

Standard deviation

1,492

1,169

**Cationic retention chemical K7400R**

**Maximum dosage**

0 ppm	g/m2
1	74,5
2	73,8
3	76
4	73,1
5	75,9
6	74,3
7	75,4
8	74,7
9	75,6
10	75,8
<b>Average</b>	<b>74,91</b>

200 ppm	g/m2
1	70,6
2	69,6
3	70,9
4	71,6
5	72,5
6	70,5
7	72
8	72,4
9	72,5
10	72,3
<b>Average</b>	<b>71,49</b>

Standard deviation

**0,987**

**1,027**

400 ppm	g/m2
1	72,5
2	71,8
3	69,5
4	67,7
5	70,1
6	68
7	71,5
8	69,1
9	70,1
10	67,3
<b>Average</b>	<b>69,76</b>

580 ppm	g/m2
1	73,9
2	73,8
3	77,1
4	74,9
5	80,7
6	77,5
7	77,5
8	75,7
9	73,3
10	74,4
<b>Average</b>	<b>75,88</b>

Standard deviation

**1,790**

**2,311**

**Anionic retention chemical A3050R**

**Minimum dosage**

0 ppm	g/m2
1	65,1
2	65
3	71
4	66,6
5	68,8
6	66,9
7	68,2
8	68,7
9	68,7
10	68,4
<b>Average</b>	<b>67,74</b>

200 ppm	g/m2
1	68,5
2	67,9
3	67
4	66,8
5	68
6	67,5
7	67,9
8	67,3
9	68,7
10	70
<b>Average</b>	<b>67,96</b>

Standard deviation

**1,848**

**0,938**

**Anionic retention chemical A3050R**

**Minimum dosage**

400 ppm	g/m2
1	69,1
2	69
3	69,7
4	70
5	71,7
6	68
7	70,7
8	72
9	72,7
10	69,2
<b>Average</b>	<b>70,21</b>

580 ppm	g/m2
1	76,7
2	80
3	77,6
4	75,9
5	80,2
6	77,8
7	78,9
8	76,8
9	84,4
10	74,1
<b>KA</b>	<b>78,24</b>

Standard deviation

1,519

2,702

**Anionic retention chemical A3050R**

**Maximum dosage**

0 ppm	g/m2
1	71,6
2	70,5
3	71
4	70,9
5	73,3
6	71,5
7	70,5
8	72,1
9	71
10	70,5
<b>Average</b>	<b>71,29</b>

200 ppm	g/m2
1	71,5
2	72,8
3	70,4
4	72,6
5	73,4
6	72
7	72,1
8	74
9	74,4
10	75,9
<b>Average</b>	<b>72,91</b>

Standard deviation

0,884

1,580

400 ppm	g/m2
1	74,8
2	83,9
3	86,8
4	80,1
5	87,1
6	85,1
7	80,3
8	80,9
9	82,7
10	79,3
<b>Average</b>	<b>82,1</b>

580 ppm	g/m2
1	102
2	121,7
3	113,8
4	111,5
5	101,9
6	100,4
7	114,1
8	89,7
9	105,7
10	97,7
<b>Average</b>	<b>105,85</b>

Standard deviation

3,793

9,439

## 2 LABORATORY RESULTS OF ASH TESTS

### No retention chemical added

sheet	crucible	crucible+sample	sample	crucible+ash	ash	ash%
<b>SK 2</b>	29,9411	30,5784	0,6373	29,9566	0,0155	2,43
<b>SK 8</b>	29,9714	30,6048	0,6334	29,986	0,0146	2,31

### Cationic retention chemical K7400R, minimum dosage

<b>K-0 2</b>	30,2918	30,964	0,6722	30,3345	0,0427	6,35
<b>K-0 7</b>	30,0856	30,7656	0,68	30,13167	0,0461	6,78
<b>K-2 3</b>	30,2925	30,9507	0,6582	30,3281	0,0356	5,41
<b>K-2 4</b>	30,0833	30,7284	0,6451	30,118	0,0347	5,38
<b>K-4 4</b>	29,9713	30,6448	0,6735	30,0107	0,0394	5,85
<b>K-4 7</b>	29,9406	30,6062	0,6656	29,9782	0,0376	5,65
<b>K-5 2</b>	30,0759	30,7794	0,7035	30,1331	0,0572	8,13
<b>K-5 10</b>	30,7693	31,4746	0,7053	30,8272	0,0579	8,21

### Cationic retention chemical K7400R, maximum dosage

<b>K+0 1</b>	29,908	30,6556	0,7476	29,9991	0,0911	12,19
<b>K+0 8</b>	30,2941	31,045	0,7509	30,3836	0,0895	11,92
<b>K+2 3</b>	30,2921	31,0063	0,7142	30,3553	0,0632	8,85
<b>K+2 4</b>	30,0836	30,8016	0,718	30,1472	0,0636	8,86
<b>K+4 3</b>	29,9718	30,6698	0,698	30,0342	0,0624	8,94
<b>K+4 9</b>	29,9408	30,6437	0,7029	29,9886	0,0478	6,80
<b>K+4 5</b>	29,9066	30,6034	0,6968	29,9576	0,0510	7,32
<b>K+5 4</b>	30,0759	30,8289	0,753	30,1674	0,0915	12,15
<b>K+5 8</b>	30,7688	31,5293	0,7605	30,8674	0,0986	12,97

### Anionic retention chemical A3050R, minimum dosage

<b>A-0 4</b>	29,9071	30,5782	0,6711	29,9526	0,0455	6,78
<b>A-0 7</b>	30,2938	30,9806	0,6868	30,3487	0,0549	7,99
<b>A-0 6</b>	30,2938	30,961	0,6672	30,3459	0,0521	7,81
<b>A-2 6</b>	30,2921	30,9721	0,68	30,3322	0,0401	5,90
<b>A-2 7</b>	30,0831	30,7664	0,6833	30,1248	0,0417	6,10
<b>A-4 4</b>	29,9715	30,6765	0,705	30,0341	0,0626	8,88
<b>A-4 7</b>	29,9406	30,652	0,7114	30,0004	0,0598	8,41
<b>A-5 3</b>	30,0759	30,8572	0,7813	30,1873	0,1114	14,26
<b>A-5 7</b>	30,7688	31,5608	0,792	30,8954	0,1266	15,98
<b>A-5 6</b>	30,2921	31,0681	0,776	30,4072	0,1151	14,83

**Anionic retention chemical A3050R, maximum dosage**

<b>A+0 3</b>	29,9071	30,6216	0,7145	29,9822	0,0751	10,51
<b>A+0 6</b>	30,2942	31,0122	0,718	30,3696	0,0754	10,50
<b>A+2 2</b>	30,2922	31,0198	0,7276	30,3692	0,0770	10,58
<b>A+2 4</b>	30,0825	30,8087	0,7262	30,1571	0,0746	10,27
<b>A+4 2</b>	29,9711	30,8114	0,8403	30,1402	0,1691	20,12
<b>A+4 9</b>	29,9406	30,7665	0,8259	30,0896	0,1490	18,04
<b>A+4 6</b>	30,0825	30,931	0,8485	30,2454	0,1629	19,20
<b>A+5 1</b>	30,0754	31,0913	1,0159	30,3803	0,3049	30,01
<b>A+5 9</b>	30,7684	31,8185	1,0501	31,0666	0,2982	28,40

### 3 CATIONIC RETENTION CHEMICAL INSTRUCTIONS

**kemira**

## Fennopol K 7400 R

### Retentioaine

Fennopol K 7400 R:ää käytetään paperikoneen kuitu- ja tuhkarention parantamiseen. Kun Fennopol K 7400 R:ää käytetään lisäkemikaalien kuten esiflokkulanttien ja fikseerausaineiden kanssa, on sillä synergistinen vaikutus.

### Käyttö

Fennopol-jauheesta valmistetaan liuotuslaitteella 0,3–0,5 %:nen varastoliuos, joka laimennetaan kymmenkertaisesti ennen annostelua paperikoneelle. Liuotusvedeksi suositellaan 10–40-asteista puhdistettua vettä.

Fennopolit annostellaan yleensä paperikoneen perälaatikon lähestymisputkistoon. Tavallisin annostelumäärä on 100–500 g/t valmista tuotetta. Paras teho saavutetaan annostelemalla Fennopol-liuos painesihntien jälkeen, jolloin flokkeja rikkovia leikkausvoimia on mahdollisimman vähän.

### Toimitukset

Fennopolit toimitetaan asiakkaalle jauheena 20 kg:n säkeissä tai 500 kg:n suursäkeissä sekä 500 kg:n palautettavassa teräskontissa.

### Tuoteturvallisuus

Tuote täyttää FDA:n mukaiset vaatimukset, kun sitä käytetään elintarvikkepaperin ja -kartongin valmistuksessa.

Lattialle joutunut jauhe muodostaa kostuessaan erittäin liukkaita pintoja.

Tutustu ennen käyttöä huolellisesti tuotteen käyttöturvallisuustiedotteeseen.

### Tuoteominaisuudet

#### Spesifikaatiot

Suolaviskositeetti 45–70 mPas  
(0.5 %, 25 °C, 5 % NaCl)

#### Muut ominaisuudet

Olomuoto valkoinen, ygroskooppiainen, hajuton jauhe

Kemiallinen koostumus polyakryyliamidi

Ionisuus kationinen

Liukoisuus liukenee veteen

Raekokojakauma < 0.113 mm enint. 4 %  
> 1.32 mm enint. 5 %

Ominaispaino 0.6 – 0.9 kg/dm<sup>3</sup>

#### Varastointi

Avaamattomina pakkauksia voidaan varastoida kuivassa paikassa useita vuosia. Varastoliuos on käyttökelpoista noin viikon. Käyttöliuos säilyy noin vuorokauden.



## 4 ANIONIC RETENTION CHEMICAL INSTRUCTIONS

**Kemira**

### Fennopol A 3050 R

#### Retentioaine

Fennopol A 3050 R:ää käytetään paperikoneen kuitu- ja tuhkaretention parantamiseen. Kun Fennopol A 3050 R:ää käytetään lisäkemikaalien kuten esiflokkulanttien ja fikseerausaineiden kanssa, on sillä synergistinen vaikutus.

#### Käyttö

Fennopol-jauheesta valmistetaan liuotuslaitteella 0,3–0,5 %:nen varastoliuos, joka laimennetaan kymmenkertaisesti ennen annostelua paperikoneelle. Liuotusvedeksi suositellaan 10–40-asteista puhdistettua vettä.

Fennopolit annostellaan yleensä paperikoneen perälaatikon lähestymisputkistoon. Tavallisin annostelumäärä on 100–500 g/t valmista tuotetta. Paras teho saavutetaan annostelemalla Fennopol-liuos painesihtien jälkeen, jolloin flokkeja rikkovia leikkauvoimia on mahdollisimman vähän.

#### Toimitukset

Fennopolit toimitetaan asiakkaalle jauheena 20 kg:n säkeissä tai 500 kg:n suursäkeissä sekä 500 kg:n palautettavassa teräskontissa.

#### Tuoteturvallisuus

Tuote täyttää FDA:n mukaiset vaatimukset, kun sitä käytetään elintarvikepaperin ja -kartongin valmistuksessa.

Lattialle joutunut jauhe muodostaa kostuessaan erittäin liukkaita pintoja.

Tutustu ennen käyttöä huolellisesti tuotteen käyttöturvallisuustiedotteeseen.

#### Tuoteominaisuudet

##### Spesifikaatiot

Suolaviskositeetti 10-20 mPas  
(0.5 %, 25 °C, 5 % NaCl)

##### Muut ominaisuudet

Olomuoto valkoinen, hajuton  
hygroskooppinen, jauhe

Kemiallinen koostumus polyakryyliamidi

Ionisuus anioninen

Liukoisuus liukenee veteen

Raekokojakauma < 0.113 mm enint. 4 %  
> 1.32 mm enint. 5 %

Ominaispaino 0.6 – 0.9 kg/dm<sup>3</sup>

#### Varastointi

Avaamattomina pakkauksia voidaan varastoida kuivassa paikassa useita vuosia. Varastoliuos on käyttökelpoista noin viikon. Käyttöliuos säilyy noin vuorokauden.

## 5 KAOLIN DESCRIPTION

Product Bulletin PB 157 © IMERYS Minerals Ltd April 2000

# Intrafill™ C

KAOLIN

GCC

PCC

### Product Description

Intrafill C is an English filler clay. It improves quality in a wide range of papers. Benefits include reduced sheet porosity and improved printability whilst maintaining satisfactory optical performance.

### Application

Intrafill C is a good general purpose filler clay for use in a wide range of applications where its combination of brightness and particle size allow good optical and print properties and good retention characteristics.

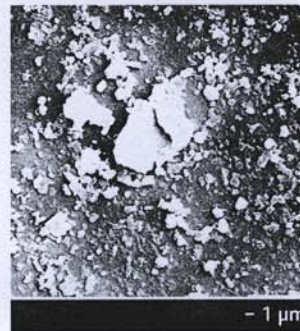
### Shipping

Intrafill C is available in dry bulk and packed.

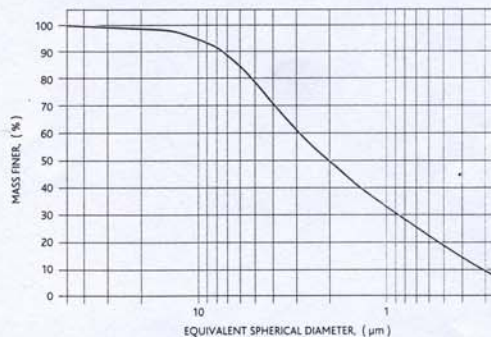
### Typical Product Properties

Property	Unit	Typical Value
Brightness	ISO	81.0
L*		94.1
a*		-0.30
b*		3.95
Particle Size		
< -1µm	%	36
< -2µm	%	55
Residue (ppm, +325 mesh, +45µm)		70
Moisture	%	10

### SEM Product Image



### Particle Size Distribution



KAOLIN PRODUCT BULLETIN

worldwide paper

The data quoted are determined by use of IMERYS Standard Test Methods. The information contained in this document is presented in good faith and believed to be reliable. Many factors affect product application and performance. Each customer must determine for itself, by conducting appropriate tests or other methods, if an IMERYS product is suitable for that customer's needs. The contents of this publication are not intended to constitute or be construed as product specifications.

Intrafill™ is a trademark of IMERYS Minerals Ltd



FM 14752  
BS EN ISO 9002

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## 6 RETENTION CHEMICAL DOSING CALCULATIONS

Dosing amount 100 – 500 g/t

Storage solution 0.3 – 0.5 %

### **Minimum dosage**

1 liter of water = 3 g of a retention chemical

Dosing solution = 10 liters / 0.3 g/L

Dosing amount 100 g/t

Weight of sheet 1.68 g

$0.3 \text{ g} / 1000 * 1.68 \text{ g} = 0.000168 \text{ g} / \text{sheet}$

$0.000168 \text{ g} / 0.3 \text{ g/L} = \underline{\underline{0.56 \text{ milliliter} / \text{sheet}}}$

### **Maximum dosage**

1 liter of water = 3 g of a retention chemical

Dosing solution = 10 liters / 0.3 g/L

Dosing amount 500 g/t

$0.3 \text{ g} / 1000 * 1.68 = 0.00084$

$0.00084 / 0.3 \text{ g} = \underline{\underline{2.8 \text{ milliliter} / \text{sheet}}}$