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**CHARACTERIZATION OF MICROPARTICLE
RETENTION SYSTEMS WITH RETENTION
PROCESS ANALYZER**

Examiners: Professor Jari Käyhkö
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FOREWORD

This master's thesis was made in Kemira Pulp & Paper at Vaasa between the 1.3.2008 – 30.8 2008.

I want to thank Ari Juppo and Kimmo Strengell for an interesting topic. Juha Leino, Tapani Ala-Louvesniemi and Kati Tuppela for their help and support while doing the experiments in Vaasa.

And I really want to thank my family and friends for their support and especially my mother for never stopping to believe that this work would eventually be done and in covers.

ABSTRACT

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Master's Thesis

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Professor Kaj Henricson

Keywords: retention, microparticle, Retention Process Analyzer, RPA,
micropolymer

In the literature survey retention mechanisms, factors effecting retention and microparticles were studied. Also commercial microparticle retention systems and means to measure retention were studied. Optical retention measurement with RPA and Lasentec FBRM was studied.

The experimental part contains study of different cationic polyacrylamides, anionic silica, bentonite and new generation micropolymer. In these studies the dosage, dosing order and dosing history were changing factors.

The experimental work was done with RPA-apparatus with which, the retention process can be followed in real time.

In testing was found that silica yielded better retention, when dosed non-traditionally before the polymer. Also silica was very dependant on the polymer dosage. With bentonite good colloidal retention was achieved with relatively low doses. Unlike silica bentonite was not dependant on polymer dosage. The relation of bentonite and polymer dosage is more defining when high retention is wanted. With 3-component systems using bentonite very high retention was achieved. With silica no improvement in retention was found in 3-component systems compared to dual component systems.

TIIVISTELMÄ

Lappeenrannan teknillinen yliopisto
Kemiantekniikan osasto
Puunjalostustuksen laboratorio

Antti Simola

MIKROPARTIKKELIJÄRJESTELMIEN KARAKTERISOINTI RETENTION PROCESS ANALYZERILLA

Diplomityö

2009

Tarkastajat: professori Jari Käyhkö
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Hakusanat: retentio, mikropartikkeli, RPA, Retention Process Analyzer,
mikropolymeeri

Kirjallisuusosassa perehdyttiin retentiomekanismeihin, tekijöihin jotka vaikuttavat retentioon ja eri mikropartikkeleihin joita käytetään mikropartikkelijärjestelmien komponentteina. Lisäksi käsiteltiin käytössä olevia kaupallisia mikropartikkelijärjestelmiä, sekä laitteita joilla retentiota voidaan mitata laboratorio-olosuhteissa ja retention mittaamista optisesti RPA:lla sekä Lasentecin FBRM-menetelmällä.

Kokeellisessa osassa tutkittiin erilaisia kationisia polyakryyliamideja, anionista silikaa, bentoniittia ja uuden sukupolven mikropolymeeriä. Näillä aineilla tehtiin koesarjoja joissa muuteltiin annoskokoja ja annostelujärjestystä. Lisäksi annosteluhistorian vaikutusta tutkittiin.

Kokeet tehtiin RPA-laitteella, jolla pystytään seuraamaan retentioprosessia reaaliaikaisesti koko prosessin ajan.

Kokeissa todettiin, että annostelemalla silika ennen polymeeriä saatiin korkeampia retentioita. Silika on myös huomattavan riippuvainen polymeeriannoksen suuruudesta. Bentoniitilla saavutettiin hyviä retentioarvoja jo pienillä annoksilla. Toisin kuin silika, bentoniitti ei ole riippuvainen polymeeriannoksesta vaan annostelun suhde on määräävä tekijä retention tehokkuuteen nähden. Kolmikomponenttijärjestelmillä saavutettiin bentoniitin kanssa erittäin korkeita retentioita, kun taas silikalla ei saavutettu lisäystä verrattuna tavalliseen kaksikomponenttijärjestelmään.

Abbreviations

RPA	Retenion Process Analyzer
PAM	Polyacrylamine
C-PAM	Cationic polyacrylamine
Poly-DADMAC	Retention aid
Da	Dalton
1/s	Shear force
PEI	Polyethyleneimine
POSITEK	Microparticle retention system
NALCO 8692	Microparticle retention system
Hydrocol	Microparticle retention system
Telioform	Microparticle retention system
Kemform	Microparticle retention system
PAC	Poly aluminium chloride
Compozil	Microparticle retention system
Hydrozil	Microparticle retention system
Mosaic	Microparticle retention system
DDJ	Dynamic Drainage Jar
DDA	Dynamic Drainage Analyzer
MBF	Moving Belt Former
TPSF	Turbulent Pulse Sheet Former
FBRM	Focused Beam Reflectance Measurement
PDA2000	Photometric Dispersion Analyzer
PCC	Precipitated calcium carbonate
rpm	Revolutions per minute
Fennopol K2400R	Polyacrylamide
Fennopol K3400R	Polyacrylamide
Fennopol K5600R	Polyacrylamide
Fennopol K7400R	Polyacrylamide

Fennosil ES325

Fennosil FS515

Altonit SF

Altonit EF

Micropolymer

Anionic silica

Bentonite

Bentonite

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1 Introduction

Colloidal retention and drainage are expected to limit the papermaking process. An efficient measure to improve the productivity has been the application of retention aid chemicals to the wet-end. Although a wide variety of retention aids is now available commercially, the current papermaking relies particularly on the microparticle retention aid system. Achieving good retention has become very important factor in papermaking. Good retention levels improve runnability of the machine and reduce production costs.

Retention and drainage aid programs have evolved from using single flocculant to include the use of microparticles. Current microparticle retention systems are divided into three categories; bentonite, silica and micropolymer based systems. Microparticle systems yield efficient dewatering, better balance of dewatering, retention and formation than traditional retention systems. Microparticle containing retention aid systems have been increasingly used for fines retention and drainage, especially in the manufacture of fine papers.

In this thesis the different retention mechanisms, microparticles, current commercially used microparticle retention systems and the laboratory equipment used to study retention are studied.

Purpose of experimental study was to characterize different microparticle systems with Retention Process Analyzer. RPA was first created by Erkki Saharinen for his licentiates work in 1994. With RPA the retention process can be followed, so the effects of retention aid are shown continuously. Effects of C-PAM's and different microparticle systems behavior and effectiveness in colloidal retention were studied. Dosing, dosing order and dosing history of retention aids was also studied.

2 Retention

It is generally accepted that the retention on a paper machine is mostly a filtration process, where furnish solids are captured by filtration through the forming fabric and the fiber mat. Good retention is important to the efficiency of the papermaking operation, because it has a large influence on furnish and production costs, as well as on the quality of the product. Low retention can lead to many problems, including:

- Poor runnability
- Increased deposits
- Higher additives costs
- More downtime for wash-ups
- Higher sewer losses

Retention aids can improve the overall runnability of the machine, allow increased speed through better drainage, reduce deposits and sheet breaks caused by high levels of fillers and fines circulating the wet end and reduce furnish costs through better use of fillers and other additives./1/

2.1 Mechanisms

2.1.1 Charge Neutralization

In the early days of papermaking, common retention aids were based on alum, which neutralizes charges on the furnished components. In water suspension all solids have certain negative surface charge. Particles of the same electrostatic charge repel each other but, once this charge is neutralized, the attractive forces dominate and the furnish components flocculate. This happens when Stern-surface adsorbs oppositely charged polymer and diffusion potential reaches zero. This type of mechanism has a narrow maximum in retention versus added

chemicals. By increasing the addition of the flocculant, beyond the point of charge neutralization, the components are redispersed. Retention aids following this mechanism are generally low molecular weight highly cationic compounds, which do not extend beyond the electrical double layer but decrease the net charge to zero. Examples of these are polyvalent cations, polyethyleneimine, poly-DADMAC and polyamines./2/

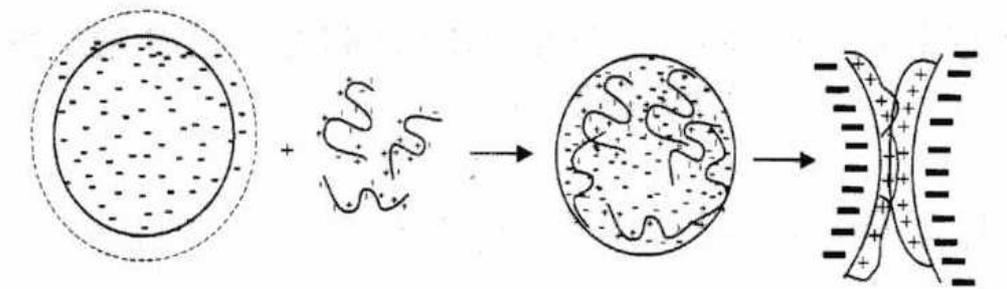


Figure 1 Charge neutralization./2/

2.1.2 Patch Flocculation

Patching occurs when polymer attaches itself in flat patches to the particles surface leaving some of the surface uncovered. Polyelectrolytes of molecular weights in the range of 10^5 to 10^6 Da give a broadening of the flocculation zone, indicating a charge neutralization mechanism whereby complete neutralization is not needed for optimal flocculation. A surface coverage of about 50% or less gives optimum flocculation. In principle, the flocculation occurs through interaction between sites with opposite charges on the different particles which have an uneven charge distribution due to flat adsorption of the charged polymer. Patch flocculation is sensitive to shear, but the particles reflocculate easily. Retention polymers following patch mechanism are polyethyleneimine, polyacrylamide of lower molecular weight and polyamine./2/

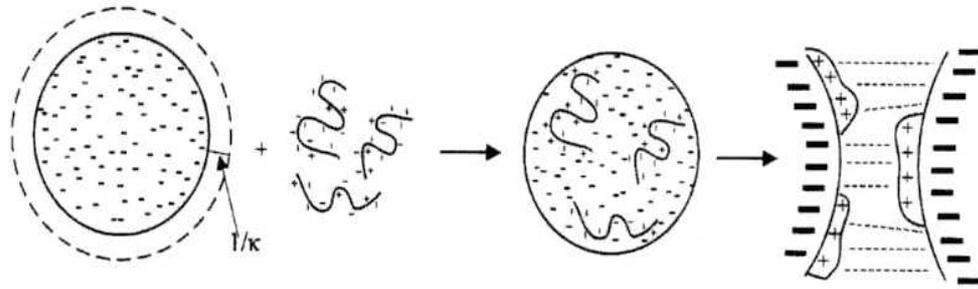


Figure 2 Patch flocculation/2/

2.1.3 Bridging

Polyelectrolytes, such as copolymers of polyacrylamide, of very high molecular weight form relatively strong flocs, in which the polymer adsorbs with loops and tails extending far beyond the electrical double layer. The flocculation region is thus considerably wider for these high molecular weight polymers. The bridging between particles by segments of a high molecular weight polymer contributes to flocculation, already at a concentration corresponding to about ten polymer molecules per particle. Obviously, the conformation of the polymer on the particle surface is very important for bridging flocculation. At low cationicity, only loops and tails are present; as cationicity increases, trains will also be found.

The polymer tails and loops interact with the charged surfaces and form bridges in between the particles. The floc strength is due to the plurality of bonds between each particle. However, if the shear forces are too high, the flocs will break and the polymer will degrade. Reflocculation will not occur through bridging, but rather through the weaker patch mechanism./3/

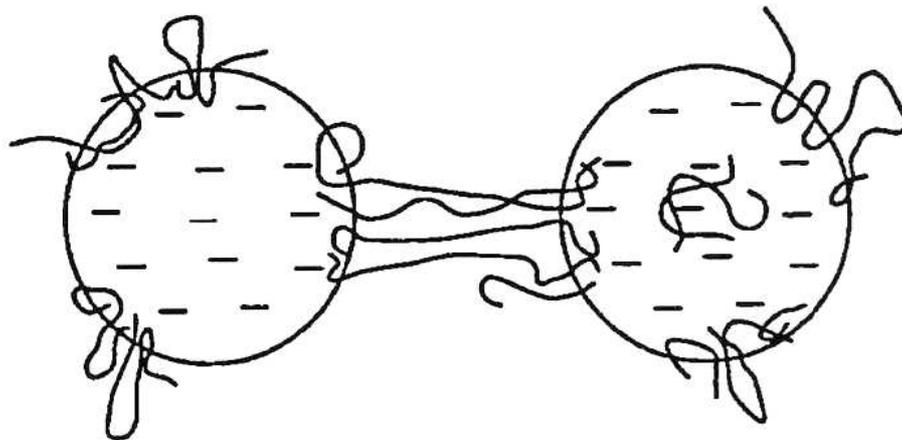


Figure 3 Bridging mechanism/2/

3 Factors affecting retention

3.1 Hydrodynamic effects

First effect of retention chemical is its adsorption to the surface of fiber, filler or fine. In second phase particles form bonds with the aid of polymer. Both of these phases require that the particles are colliding or are in close proximity of each other. When there is no flow the collisions between filler particles and fibers happen by Brownian movement. In flow particles have two transition mechanisms, Brownian movement and turbulent diffusion. With polymers the main transition mechanism is Brownian movement and with particles over $1\ \mu\text{m}$ in size the turbulent diffusion is commanding mechanism.

Research shows that stirring increases the effect of retention chemicals. Stirring increases the movement of particles and therefore increases the collisions between particles compared to the state where collisions are happening just by Brownian movement./4/

3.2 Floc strength

Attachment of filler to fiber is not enough to ensure good retention. Filler must be able to remain attached. Researchers have found that flocs disperse when hydrodynamic forces increase. Dispersing of flocs is affected by the amount of shear, shears angle and direction. Also the floccsize, relative size of particles and bonds have effect on dispersing./5/

Bond strength depends on attractive forces between filler and fiber. Electrolytes and molecules that adsorbs to the particles, such as polymers and polyelectrolytes, affect these forces. Larger fillers and fines could create weaker bonds and dispersing might occur. Retention aids that create bridging between particles and fibers enhance bond strength and prevent dispersing./6/

Research has been conducted to determine the bond strength between particles. It has been noted that larger amount of adsorbed polymer create stronger bonds. Also longer polymer molecules create stronger bonds than shorter polymers. Different retention aids attach filler to fiber with different strengths. In table I is shown few results.

Table I Shear force (1/s) that separates filler from cellulose/5/

Retention aid	particle size 0.1 μm	particle size 0.5 μm
No retention aid pH = 7	84 1/s	6 1/s
No retention aid pH = 3	510 1/s	34 1/s
Cationic starch	990 1/s	75 1/s
PEI	2600 1/s	190 1/s
C-PAM	6700 1/s	150 1/s

As table I illustrates C-PAM creates harder bonding than PEI and cationic starch, which instead create stronger bonding with Van der Waals forces./5/

3.3 Dosing delay

Marton has researched the effect of different dosing places in papermaking and found that there are at least 3 important factors that effect adsorption:

- Consistency of furnish changes from high (> 3 %) to low (< 1 %)
- Effect of shear is higher near headbox's feed pump and after it.
- Contact times are shorter near headbox

Retention aid needs to be mixed evenly out in furnish to ensure efficiency. To ensure mixing flow must be turbulent and chemical additions fast enough. In turbulent flow the reaction speed of retention aids is very fast, even below one second. Adsorbed polymers start to lose effectiveness right after reactions and after ca 20 seconds the effectiveness had dropped considerably. To ensure maximum retention with cationic polyacrylamides, the dosing should be approximately three seconds before headbox./7,8/

3.4 Mixing

Retention chemicals are usually used in diluted solutions to ensure good mixing. Mixing can be enhanced by mixing the retention chemicals from multiple points at the same time or increasing turbulence in furnish.

Mixing can be increased by adding polymer from loop. In loop there are many dosing points for polymer and adequate turbulence is produced throughout the loop./4/

4 Microparticle retention systems

Microparticle systems yields efficient dewatering and better balance of dewatering, retention and formation than with traditional retention systems. Microparticle containing retention aid systems have been increasingly used for fines retention and drainage during papermaking, especially in the manufacture of fine papers. Several types of systems are commercially available. The main difference between the systems is the type of microparticle used, such as anionic silica, anionic aluminium hydroxide and anionic crosslinked acrylate gel particles, bentonite and micropolymers./9/

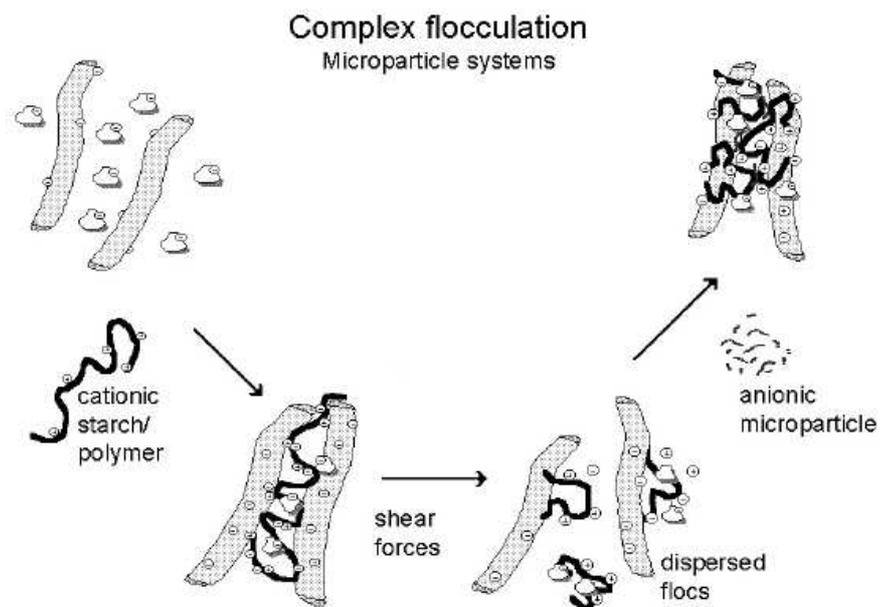


Figure 4 Schematics picture showing the initial adsorption and bridging flocculation of a cationic polymer (high molecular weight starch or synthetic polymer) and, after the shearing stage, the reflocculation by an anionic microparticle./3/

Flocculation in microparticle systems is different than in dual component polymeric systems, but the exact mechanism is not known. It has also been shown that the degree of flocculation on microparticle addition can be high. It is believed

that the difference between microfloculation and conventional flocculation lies in the ability to reflocculate after shear. The size of re-formed floc is small. These microflocs are evenly distributed throughout the sheet, therefore giving better filler distribution./1/

Current microparticle retention systems can be classified into the following categories depending on the type of microparticle used:

- Colloidal silica
- Bentonite
- Micropolymer

These systems can be used in different combinations as shown in table II

Table II Typical combinations of microparticle retention systems/10/

silica	Cationic Starch Cationic polyacrylamide Colloidal silica	Colloidal silica Colloidal silica Cationic polyacrylamide
Bentonite	Cationic polyacrylamide Bentonite Bentonite	Bentonite Cationic polyacrylamide Non-ionic polyacrylamide
Micropolymer	Alum Cationic polyacrylamide + Alum Anionic polyacrylamide + Alum	Micropolymer Micropolymer Micropolymer

The effectiveness of floc forming can be presented with following formulas.

$$E_{\mu\text{part}} = 2\theta\tau(1-\tau)$$

where $E_{\mu\text{part}}$ is floc forming efficiency of microparticles
 τ is coverage between microparticle and high molecular weight polymer

$$E_{\text{bridge}} = 2\theta\tau(1-\tau)(1-\theta)$$

where E_{bridge} is bridge forming efficiency of high molecular weight polymer
 θ is coverage of high molecular weight polymer
 τ is coverage between microparticle and high molecular weight polymer

The flocculation of microparticle system is the sum of $E_{\mu\text{part}}$ and E_{bridge} /11/

4.1 Microparticles

4.1.1 Silica

The sizes of the primary particles in commercially available colloidal silica additives generally lie within the range of 1–5nm. Since these primary particles are non-porous and approximately spherical, the cited dimensions imply surface areas in the range of about 500–3000 m²/g./12/

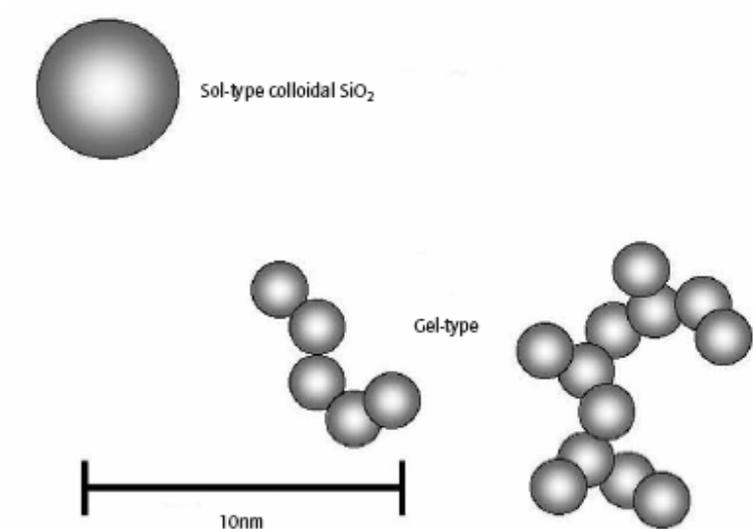


Figure 5 Typical silica particles/12/

The surface of silica can be described as acidic, meaning that protons dissociate from silanol groups, leaving behind a negative charge. Both dissociation and the density of surface charge increase with increasing pH. As well as their high surface area and negative surface charge, the structure of colloidal silica products can also vary. The primary particles may exist as discrete entities, which then may become joined as clusters or chains during their preparation./12/

If colloidal silica is added in dispersed form to slurry of untreated fibers, nothing happens. The fibers are neither flocculated nor dispersed and there is no change in the rate of release of water when the slurry is placed on a screen. The negatively charged particles have little interaction with the negative surfaces of untreated fibers. A high-mass polyelectrolyte, usually of cationic charge, is required before significant benefits in terms of dewatering rates or fine-particle retention is observed./12/

The exact mechanism is not known. The colloidal silicas ability to reflocculate after shear is the major difference between microfloculation and conventional flocculation. When conventional flocs are disrupted, they cannot reform as easily as flocs form by the aid of silica. Colloidal silica aids in the reformation of

bridging. Distribution of microflocs in the sheet is much better, which leads to better filler distribution. Microparticles are usually fed after the screens while retention aid is fed prior to the screens. Microparticles allow greater first pass retention and ash retention without overflocculation./1/

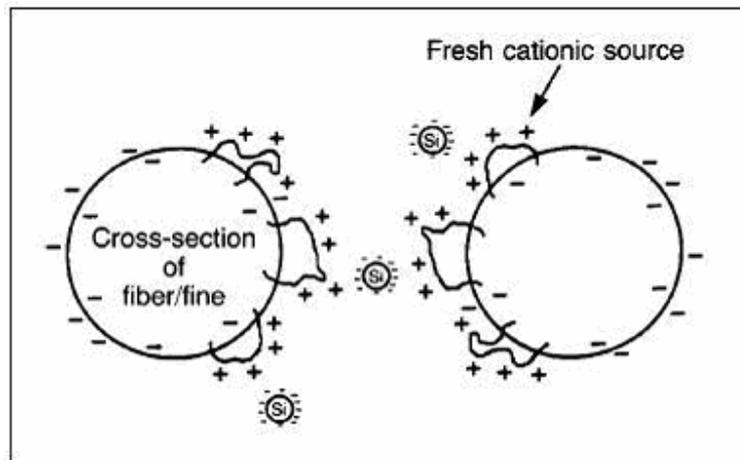


Figure 6 Silica bridging/1/

Traditionally in papermaking silica has been used with cationic starch for dewatering purposes and not with polyelectrolytes.

4.1.2 Bentonite

Bentonite is mainly composed of montmorillonites with traces of silica, quartz and other clay materials. The particular structure of montmorillonites generates a very high surface area and charge when dispersed in water. In the dry state, this aluminosilicate clay consists of stacked dioctahedral layers with a thickness of about 1 nm and a unit formula of $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ in which a fraction of the Al ions are substituted by cations of lower valence, such as Na, Mg, Li, etc. This creates a charge imbalance, which is compensated by the presence of exchangeable cations on the surface of the plates. The theoretical surface area of the montmorillonite is about $800 \text{ m}^2/\text{g}$. The cation exchange capacity depends on the substituting cations, but is generally in the order of 1 meq/g. This leads to a

very high surface charge of approximately 0.2 C m^{-2} , compared to a cellulosic surface charge of about 0.015 C/m^2 ./13/

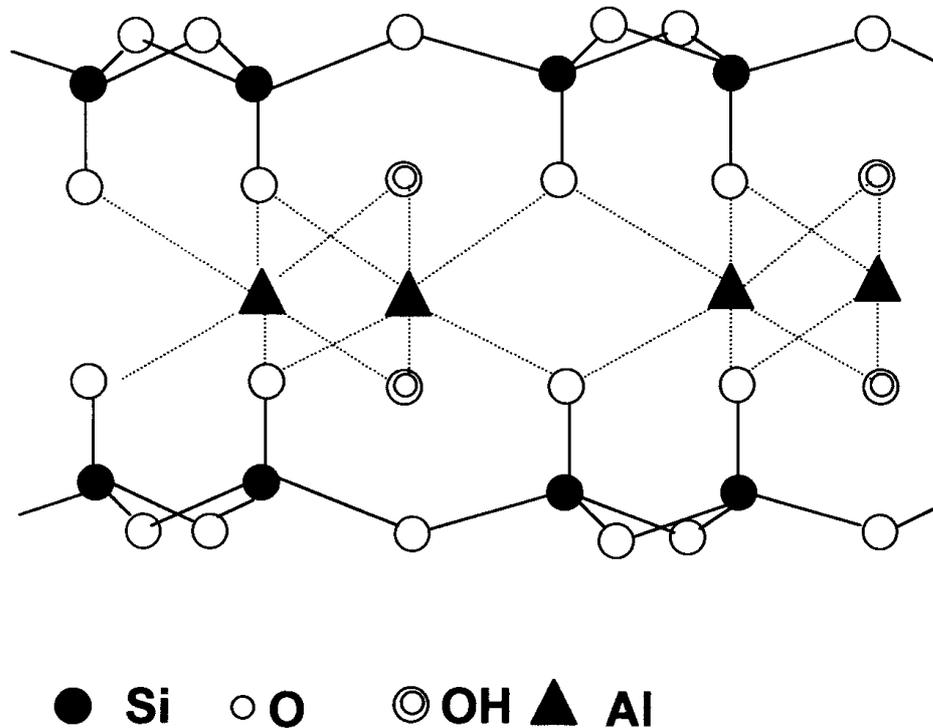


Figure 7 The generic structure of bentonite

The interlayer space, with a thickness of about 0.3 nm, contains both exchangeable cations and intercalated water. Due to charge deficiencies, the edges of the plates are positively charged. When the dry montmorillonite is mixed with water, the water molecules rapidly penetrate in the interlayer space. At low water content, this gives rise to a swelling of the structure that causes an expansion of the interlayer space by several nanometers. However, the plates remain together presumably due to van der Waals attraction. As more water is added, an electrical double layer is created on the plates and electrostatic repulsion of the layers increases. Due to the swelling, the van der Waals attraction decreases and the structure becomes less stable./13/

The degree of swelling depends on salt concentration and cationic charge. There are two types of bentonites, sodium and calcium bentonite. Natural sodium-type bentonite has better swelling properties. The swelling properties of calcium-type bentonite are improved by activation with caustic soda (synthetic sodium bentonite), i.e., by exchanging calcium ions for sodium. In the dry state, the specific surface area is low (about 12 m²/g), but reaches 300-400 m²/g after swelling in water. The shape factor of pure montmorillonite can be as high as 1 000:1. The specific surface area can be as high as 800 m²/g due its large surface area and the high ion exchange capacity./3/

4.1.3 Micropolymers

Long chain polymers with high molecular weight, polyacrylamides (PAM's), are efficient for gross retention. Generally these low charged polymers are linear. Even though some branched or structured versions are used. Linear version still is the most commonly used structure. To obtain sufficient retention of fines and fillers PAM's require the development of a larger floc via bridging. In the presence of filler, PAM's can agglomerate filler particles and therefore effectively increase the average particle size of the mineral which can compromise optical efficiency. With the changes in filler distribution within the sheet and particle size, both opacity and formation can be adversely affected, as well as other physical properties./14/

A new generation of micropolymer technology enables a floc and subsequent sheet structure to be created that maximizes drainage in the former without compromising pressing efficiency. This technology is also very efficient for retention of both calcium carbonates and kaolins. These polymers are synthesized with either cationic or anionic charge./14/

Figure 8 shows how the charge and molar mass of the cationic micropolymers relate to the conventional linear cationic PAM's and short chain high charge coagulants./14/

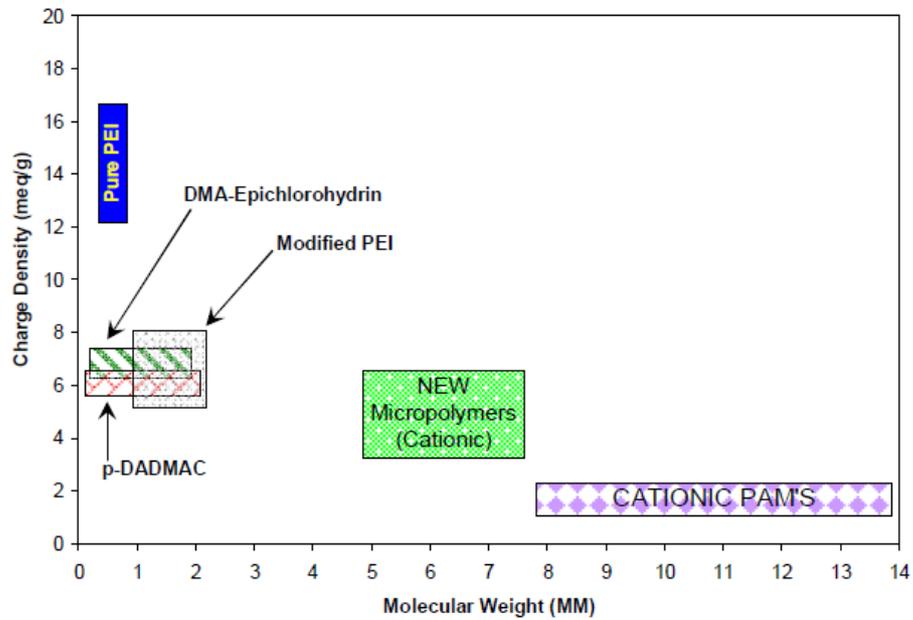


Figure 8 Charge Density versus Molecular Weight for Various Cationic Polymers/14/

Figure 8 shows the unique combination of molecular weight and charge density of the cationic micropolymers, also the structure and composition of these micropolymers differ from conventional. The polymers are synthesized using a controlled molecular weight cationic polyacrylamide polymerized within a coagulant matrix. The end result is a system of high charge density low molar mass polymers and higher molecular weight medium cationic polymers. This system is shown in the following figure 9./14/

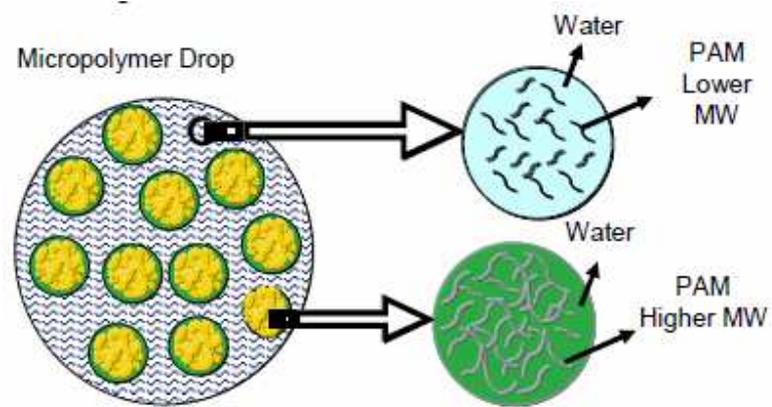


Figure 9 Schematic of New Micropolymer Technology/14/

The micropolymers are highly structured polymers demonstrating very little linearity. This is largely due to the inclusion of hydrophobic associative groups in the synthesis./14/

5 Commercial Microparticle systems

5.1 Nalco Ultra POSITEK

Ultra POSITEK is a product of Nalco, where flocculant can be chosen from variety of products. Microparticles used in this system are known by product name NALCO 8692. The main mechanism in this system is cationic polymer and anionic microparticle./15/

5.2 CIBA Hydrocol

This two component system is comprised of a pre-addition of polyacrylamide followed by a bentonite microparticle. A high molecular weight polymer is added early in the thin stock system and the bridging flocculation is substantially broken down by the action of the fan pump and other shear forces in the approach flow to the headbox. In breaking the flocs, the polymer is distributed more evenly along the fiber and filler particles, giving their surface a controlled cationic charge. Microparticle flocculation is then induced by the addition of modified bentonite clay. This mechanism produces smaller, uniform flocs compared to the normal bridging mechanism./16/

5.3 CIBA Telioform

Ciba Telioform is a combination system of micropolymer and microparticle. It consists of cationic flocculant, bentonite/silica and anionic micropolymer. The system can also contain a 4th component in form of coagulant. The Telioform system has demonstrated in both laboratory evaluations and in machine trials that it is possible to decouple the effect of retention, drainage/dewatering and more importantly, formation/sheet print quality results. It is particularly cost effective when used on high-speed twin wire paper machines where it has at times proved difficult to achieve good ash retention without adversely affecting formation. It has also proved to be valuable on smaller machines with former configurations

that exhibit rapid free drainage and dewatering characteristics that can contribute to poor sheet formation./17/

5.4 KemForm

Kemiras KemForm is a brand new microparticle technique that utilizes new generation micropolymers both cationic and anionic. There are three principle variations that utilize these micropolymers.

- KemForm S
 - Micropolymer (Cationic or Anionic) + Colloidal Silica + Flocculant (Cationic or Anionic PAM or Starch)
- KemForm B
 - Micropolymer (Cationic or Anionic) + Bentonite + Flocculant (Cationic or Anionic PAM or Starch)
- KemForm P
 - Micropolymer (Cationic or Anionic) + Flocculant (Cationic or Anionic PAM or Starch) + Optional inorganic promoter (PAC/ACH/Alum)
 - KemForm P usually utilizes an Anionic Micropolymer

The unique composition and structure of these new generation micropolymers allow them to increase sheet dewatering while increasing retention in both low and high ash environments. Sheets formed with KemForm impart greater strength in both tensile and tear./18/

5.5 Eka Chemicals Compozil

Compozil is a microparticle system that uses cationic starch and anionic silica. The retention mechanism in Compozil is complex. Part of it is traditional bridging and patch flocculation. Silica adsorbs in starch forming a network of very small

flocs after shear. Such network gives good formation and retention. Also dewatering is improved and good starch retention improves tensile properties./15/

Compozil S is modified version of Compozil. Compozil S is designed for closed water systems. Compozil S uses cationic starch and modified colloidal silica. Compozil P is designed for high speed dewatering and better retention, without the loss of formation. Compozil P uses cationic polyacrylamid and structured silica./15/

5.6 Hydrozil

Hydrozil is a microparticle system that is used in alkaline papermaking process. Cationic component is starch and anionic component is precipitated aluminum hydroxide. Anionic colloidal aluminum hydroxide functions as bridging agent between fines and fibers. Cationic starch attaches to fibers and forms cationic spots in which the aluminum hydroxide binds fines. Therefore Hydrozil has good fines retention and good dewatering./15/

5.7 Buckman Mosaic

Buckman Mosaic is retention system that includes 2 – 4 components, which utilizes either Inorganic microparticle and/or organic cationic micropolymer. Optional third and fourth components can be either a PAM and/or cationic polyelectrolyte.

6 Laboratory means to measure retention

6.1 Dynamic Drainage Jar (DDJ)

Perhaps the most known apparatus for retention testing is the Britt Dynamic Drainage Jar, DDJ. It is an excellent device for comparing different chemicals and their effect on retention levels. No sheet is formed and hence no effect of filtration is taken into account, but the influence of shear on colloidal retention can be estimated with good significance. The drainage and the formation potential of furnish however cannot be evaluated satisfactorily. /19/

DDJ-device consists of a cylindrical sample vessel, stirrer and wire. By adjusting the stirring level turbulence is created and also the retention levels are controlled. After a certain stirring time filtrate is collected from the valve and from the filtrate retention etc are measured. /19/

DDJ-device is very simple and easy to use. Therefore many modifications have been made from it./19/



Figure 10 Dynamic Drainage Jar/20/

6.2 Dynamic Drainage Analyzer (DDA)

Dynamic Drainage Analyzer (DDA) is a modification of DDJ. Stock filtrates by vacuum through the wire and retention is measured from the filtrate. Whole process is computer controlled which enables automated chemical dosing, testing and results processing. DDA's advantage over DDJ is that DDA forms a sheet through suction./21/



Figure 11 Dynamic Drainage Analyzer/22/

6.3 Moving Belt Former (MBF)

Moving Belt Former (MBF) was developed for simulating the pulsating high-vacuum dewatering that takes place in the wire section of a paper machine. Main parts of the MBF are a vacuum box connected to a vacuum pump, a moving belt with foils and a commercial paper machine wire. The pulsating drainage created by foils on paper machine is created by the moving belt on the MBF. The pulsating can be controlled by adjusting the speed of the belt, density of the holes in the belt and the size of the holes. The vacuum is also of the same magnitude as on paper machine. Biggest advantage MBF has to the DDJ/DDA is that it form a sheet from which is possible to measure formation and other properties./23/

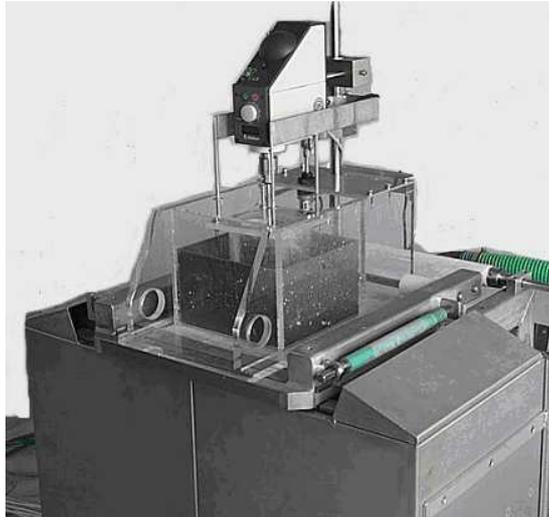


Figure 12 Moving Belt Former./24/

6.4 Turbulent Pulse Sheet Former (TPSF)

Turbulent Pulse Sheet Modifier (TPSF) is a modified Britt jar that incorporates air and vacuum to simulate the dynamics of an industrial paper making machine. Fiber mat filtrates to the wire and the mat is exposed to high pressure and vacuum pulses to scatter the fiber mat. TPSF consists of stirrer, mixing cylinder, wire and pressure pulse control unit./25/



Figure 13 Turbulent Pulse Sheet Former/25/

7 Optical Retention Measurement

7.1 Focused Beam Reflectance Measurement (FBRM)

The Focused beam reflectance measurement (FBRM) probe, a solid-state laser light source provides a continuous beam of monochromatic light that is launched down probe. An intricate set of lenses focuses the laser light to a small spot. This focal spot is carefully calibrated to be positioned at the interface between the probe window and the actual process. The focused beam moves at a fixed speed across particles in suspension and measuring the time duration of the backscattered light from these particles. From that data it is possible to determine a particle size characteristic labeled as chord size. Thousands of chord length measurements are collected per second, producing a histogram in which the number of observed counts is sorted in several chord length bins over the range of used 0.5 – 1000 μm ./26/

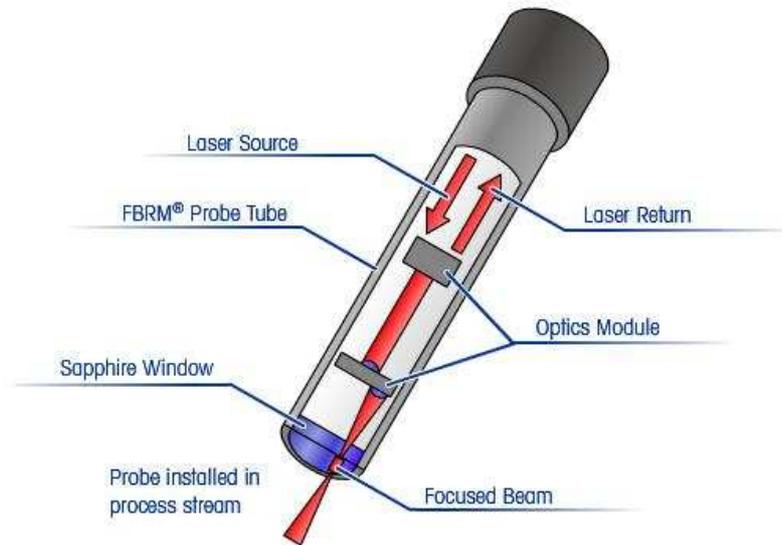


Figure 14 Lasentec FBRM device./27/

Blanco *et al.* were the first to propose that FBRM would be applied in flocculation studies. Since then FBRM has been used to study flocculation mechanisms. Flocculation kinetics have been studied since with different fillers and retention processes.

Gerli *et al.* examined retention aid efficiency with the FBRM. They observed that the results from their laboratory test were observed to correlate with the obtained machine retention values./28/

Markus Patola studied in his master's thesis that could the FBRM method be used to assess the effectiveness of retention aids in terms of flocculation. He found that a change in mean chord length can predict the filler retention. FBRM mean chord length was compared with first pass ash retention of DDJ and correlation between the methods was found. Patola also found no reasons to indicate that FBRM would be unsuitable as an online measuring application for different retention systems./26/

7.2 Retention Process Analyzer (RPA)

Retention Process Analyzer (RPA) was created by Erkki Saharinen, for his licentiate thesis in 1994 in Helsinki. RPA is a modified DDJ. It consists of a DDJ which is connected to a turbidity meter to monitor colloidal retention in real time. In the RPA, the shear force field is evoked by a stirrer. Stirring speed and time can be pre-programmed./4/

Sample flow is circulated through the wire to the turbidity measurement from where the sample circumvents back to the process. Circumvention is kept up by tube pump. Stirring hinders fiber mat from forming to the wire, so testing is carried out without mechanical filtration. As a result the calculated retention refers only to colloidal retention. /4/

The whole process is controlled by a computer that records time, turbidity, torque and stirring speed. Stirring speed and the time of the process is preprogrammed./4/

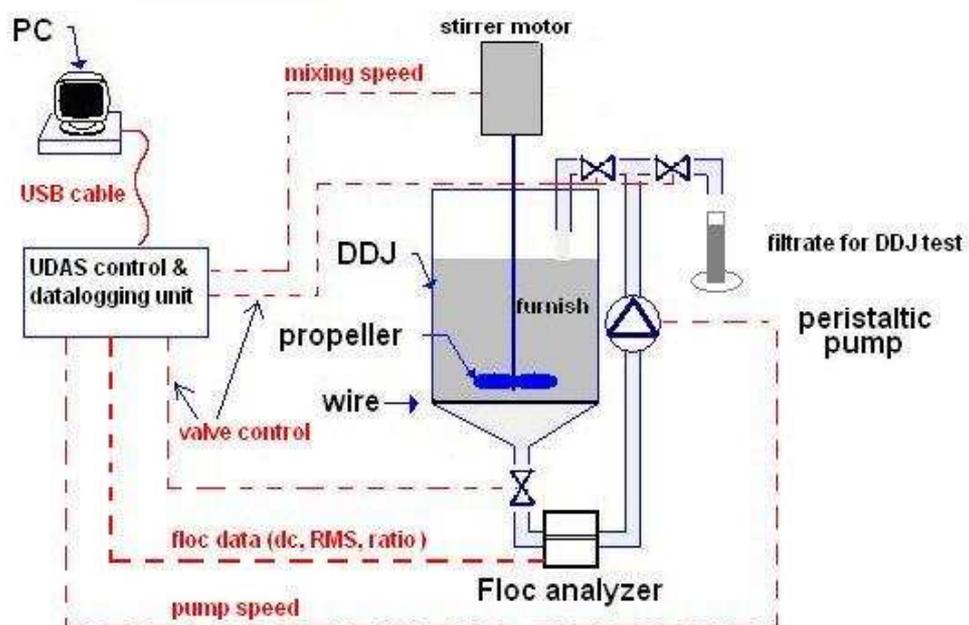


Figure 15 RPA-process/29/



Figure 16 Retention Process Analyzer used by Arsi Rytönen in Savonlinna/30/

Summary

This study dealt with retention, retention mechanisms and the factors that effect retention in papermaking process. Microparticles and retention systems utilizing microparticles were also studied.

The current microparticle systems can be divided into three different categories based on the microparticles used, bentonite, silica and micropolymer based system. All the commercial used microparticle systems in papermaking use these microparticles as components.

Microparticles, usually anionic silica sol or bentonite clay, are used in conjunction with a conventional high molecular weight polymer such as cationic polyacrylamide and cationic starch.

A new generation of micropolymer technology enables a floc and subsequent sheet structure to be created that maximizes drainage in the former without compromising pressing efficiency. Micropolymers are used in conjunction with anionic microparticles and conventional flocculants

Retention systems have been studied in laboratory scale as long as retention chemicals have been used. DDJ, MBF and others give reliable results, but only from one point in the whole retention process. With Retention Process Analyzer and Lasentec FBRM the retention process can be measured throughout the process and also the floc sizes can be measured.

EXPERIMENTAL STUDY

8 Objectives of the Experimental study

In the experimental study the effects of different microparticle retention systems were studied. Five different cationic polyacrylamides, one micropolymer, two different bentonites and one type of silica were used to create the microparticle systems. The effects of different systems to retention were studied with Retention Process Analyzer. With RPA the colloidal retention can be measured throughout the retention process.

9 Materials and methods

9.1 Methods

Retention Process Analyzer (RPA) used in the experiments was made by Juha Leino at Kemira Pulp & Paper R&D laboratory in Vaasa. RPA consists of the following components:

- Dynamic Drainage Jar
- Turbidity meter Photometric Dispersion Analyzer PDA-2000
- Tube pump
- Computer for collecting data

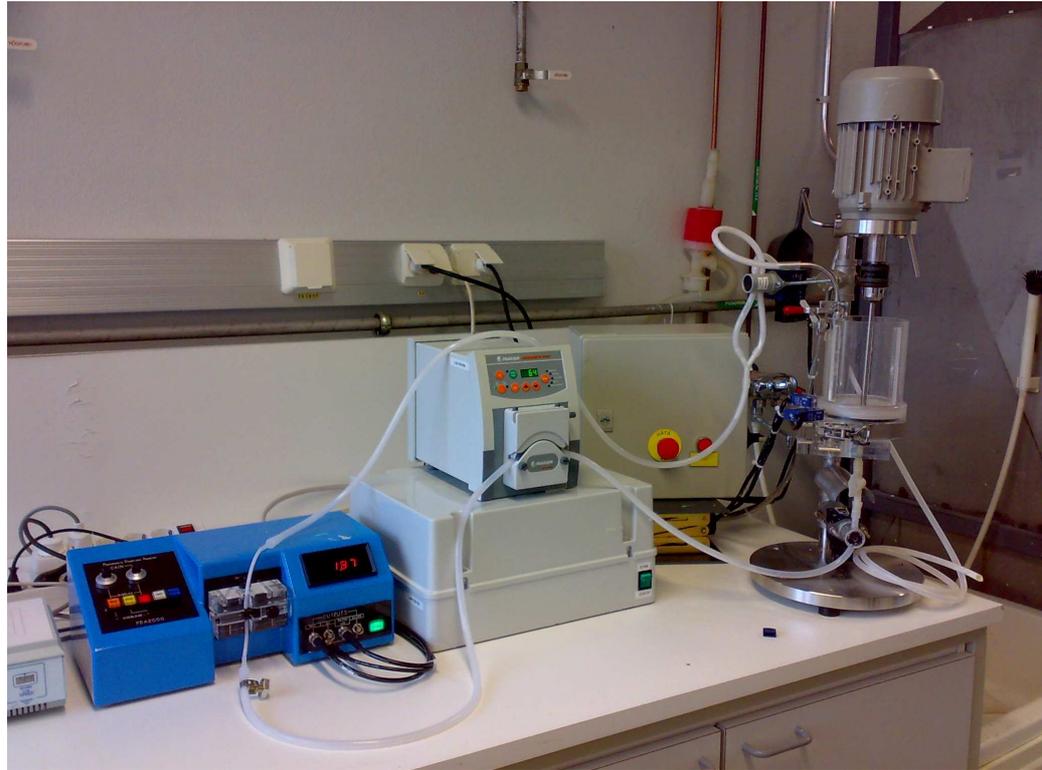


Figure 17 Retention Process Analyzer: DDJ, Turbidity meter and tube pump.

RPA gathers data in 20 Hz frequency:

- DC-signal (direct current). Signal is measured in 850nm wavelength. Turbidity is measured by transmittance, lower the turbidity higher the value in volts.
- RMS (root mean square). Measures the size of the flocks
- Ratio $((RMS/DC)*10)$. Parameter is the ratio of flock size (RMS) to turbidity (DC) times ten.
- Torque

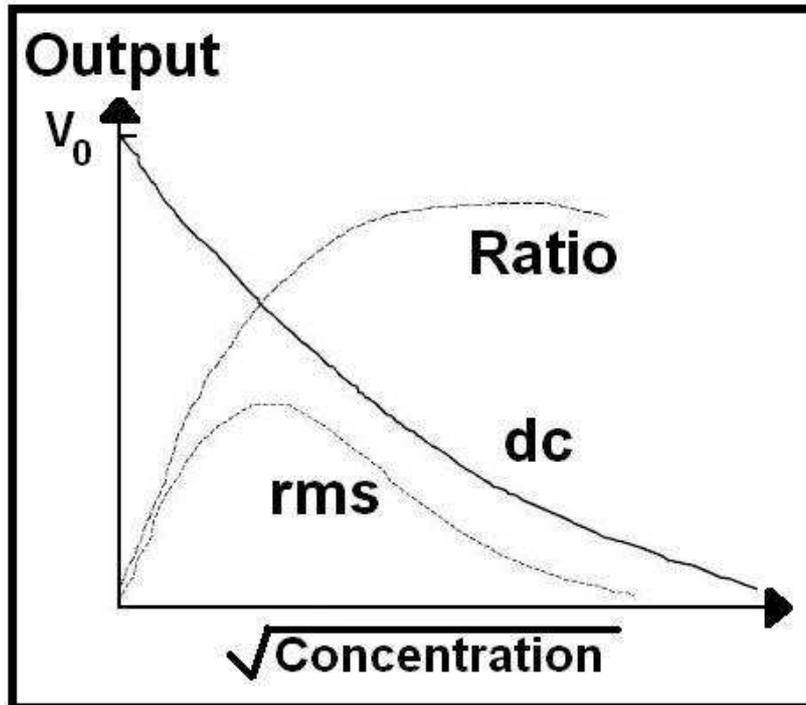


Figure 18 Parameters behavior as particle concentrations function.

At the beginning, when concentration increases also the rms-signal (flocsize) increases. Signals noise increases as more particles pass the optic measurement channel. When particle movement increases even more the rms-signal becomes saturated and starts to act like the dc-signal (turbidity).

Retention is calculated from equations shown in figure 19.

$$\text{Relative Retention \%} = \frac{T_0 - T_t}{T_0} \cdot 100 \%$$

$$\text{Relative Retention (fixed) \%} = \left(1 - \frac{\frac{\text{LN } T_t}{T_{H2O}}}{\frac{\text{LN } T_{H2O}}{T_0}} \right) * 100 \%$$

T_{H2O} = Turbidity of clean water (Volts)
 T_0 = Initial turbidity of the sample (Volts)
 T_t = Turbidity at the moment t (Volts)

Figure 19 Equations to calculate relative retention in RPA

Retention is calculated using relative retention. Fixed relative retention is calculated by taking clean water and initial turbidity of furnish as the starting points. Turbidity of clean water is 100 % and the initial turbidity of furnish 0 %. Calculation is fixed to be nonlinear by using natural logarithm so that the calculations would correlate better with first pass retention (fpr %)

9.2 Furnish, chemicals

Furnish used in tests was of the following content:

- 70 % 50/50 spruce/pine furnish from Stora Enso Kemi PM 3
- 30 % broke from Stora Enso Kemi PM 3
- PCC-filler from Stora Enso Kemi PM 3
- Total ash content of furnish was 45 %
- Dry content of furnish was 0,8 %
- pH 8

3 kg/t of cationic starch was used in every test.

Following polymers and microparticles was used in the experiments:

- Fennopol K2400R (C-PAM)
- Fennopol K3400R (C-PAM)
- Fennopol K5600R (C-PAM)
- Fennopol K5800R (C-PAM)
- Fennopol K7400R (C-PAM)
- Fennosil ES325 (micropolymer)
- Fennosil 515 (anionic silica)
- Altonit SF (bentonite)
- Altonit Weiß EF (bentonite)

9.3 Test procedure with RPA

All the test were done with RPA by adding 500ml of 0.8 % consistency furnish in to the cup then starch was added and furnish was stirred one minute. After the minute test program was started. The stirrer began stirring furnish with the chosen speed. At the same time the white water was circulated at the rate of 700 ml/min. First 30 seconds of the program evened furnish out and removed air from the procedure. Then the first retention aid or first component of the retention system was injected manually into the suspension on desired timing after that every other component was injected in ten second interval. The optimum delay of dosing was researched by Rytönen in his thesis and from those tests the delay of 10 s was decided due to the fact that the highest retention was achieved with short dosing delays. Suspension was measured 15 times per second by PDA2000. After the test was complete RPA was rinsed thoroughly so that the PDA2000's values were equivalent to the zero water value and furnish was removed and the wire was rinsed. Chemical doses were all added manually with Finn-pipettes. Stirring speed in all the tests was 700 rpm, unless otherwise mentioned.

10 Pretesting with RPA

10.1 Cationic Polyacrylamides (C-PAM)

Typical flocculation mechanisms of cationic polyelectrolytes are bridging flocculation and patch flocculation. Mechanism depends greatly on the charge density and molecular weight of polymer. Bridging flocculation is irreversible and patch flocculation is reversible. Retention is a continuously changing process at the beginning, with the retention gradually stabilizing and the level of retention depending on the stirring speed.

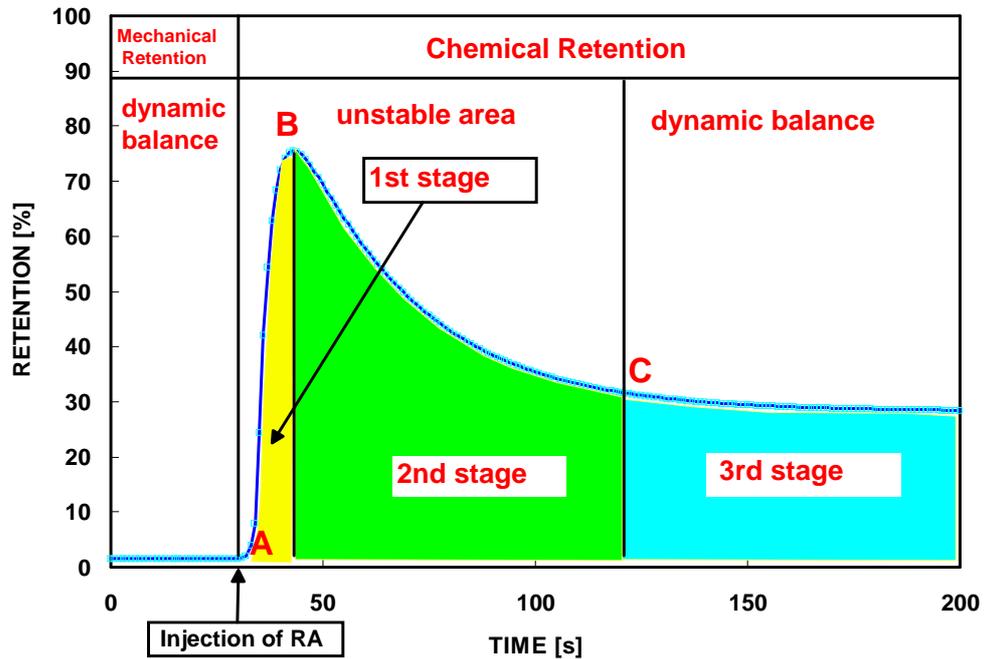


Figure 20 Different stages of retention process/31/

Cationic polyelectrolytes typically flocculate by bridging and patch flocculation. The charge density and polymer weight are the defining factors for which mechanism is in effect. Bridging flocculation is typical for cationic polyacrylamides (C-PAM's). Typical relative retention-time curves are shown in figure 20. At the beginning of the process retention level is approximately 0 %. After injecting the retention aid into furnish retention increases rapidly and in few seconds reaches the maximum. In first stage, retention aid is mixed into the suspension and adsorbed to fibers, fines and filler. A very short intensive mixing pulse increases the retention at the beginning of this stage by enhancing mixing and collisions of particles./31/

Near point B the retention begins to decrease. The cause of this is that almost all initial reactions of the retention aid are completed. Then retention begins to decrease since no new flocs are formed by the bridging mechanism. Shear forces disperse the flocs and deflocculation continues. On particle surfaces there are

cationic sites and therefore the ability to reform flocs is partially retained, with the flocculation mechanism now resembling patch flocculation./31/

At point C the retention reaches a constant level, where the decrease of retention level is almost zero. In this state the forming and deforming of flocs are equal. Retention level is controlled only by shear forces./31/

10.2 Effect of stirring speed on retention

The propeller used in the RPA is 2-blade and reminds the propeller of an airplane. This structure maximizes vertical pressure change that prevents the forming of a fiber blockade to the wire.

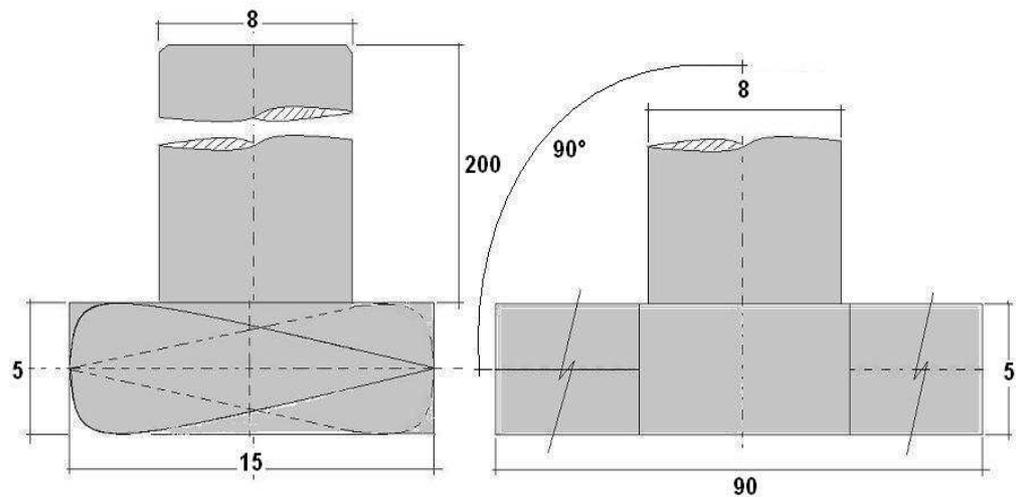


Figure 21 The structure of the propeller used in RPA

In figures 22-24 is shown the effects of stirring speed by using C-PAM as retention aid.

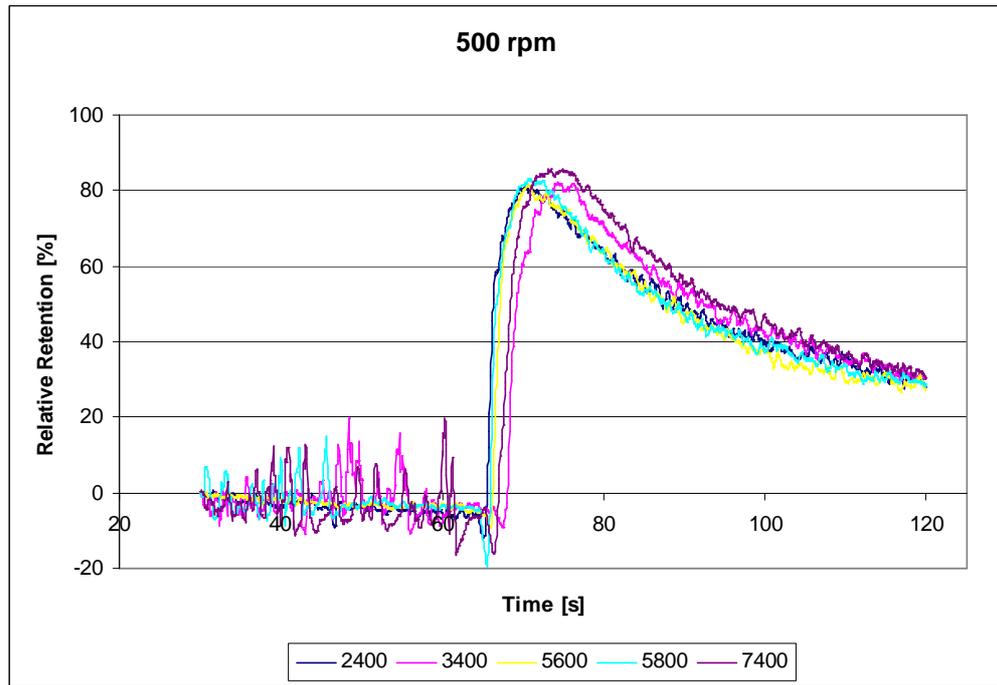


Figure 22 The effects of stirring speed on different C-PAM's, dosage 300 g/t, and stirring speed 500 rpm

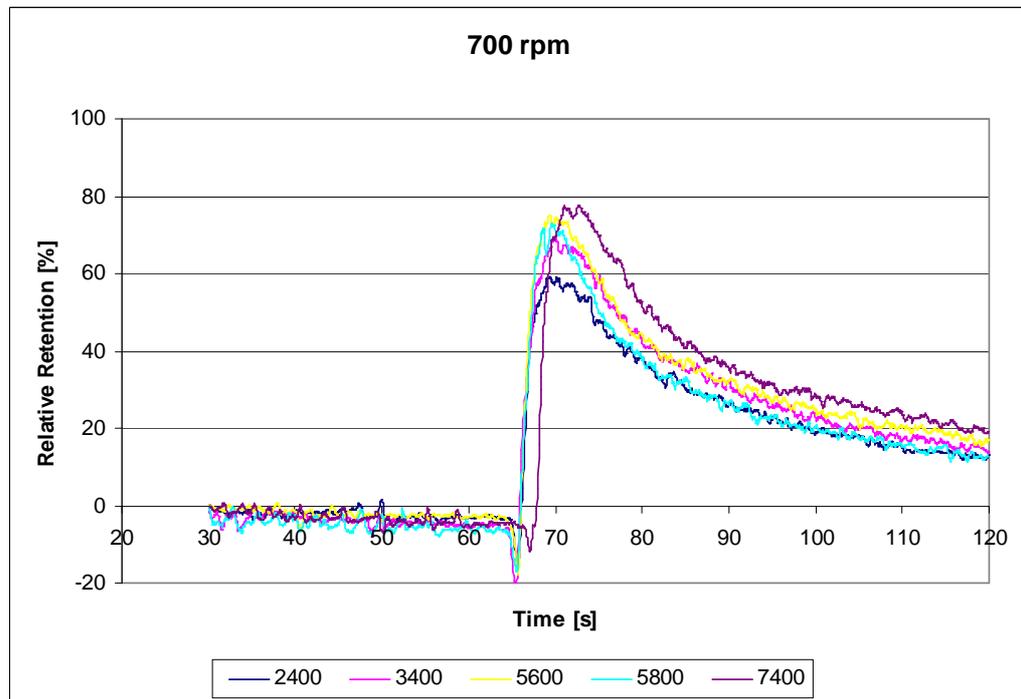


Figure 23 The effects of stirring speed on different C-PAM's, dosage 300 g/t, and stirring speed 700 rpm

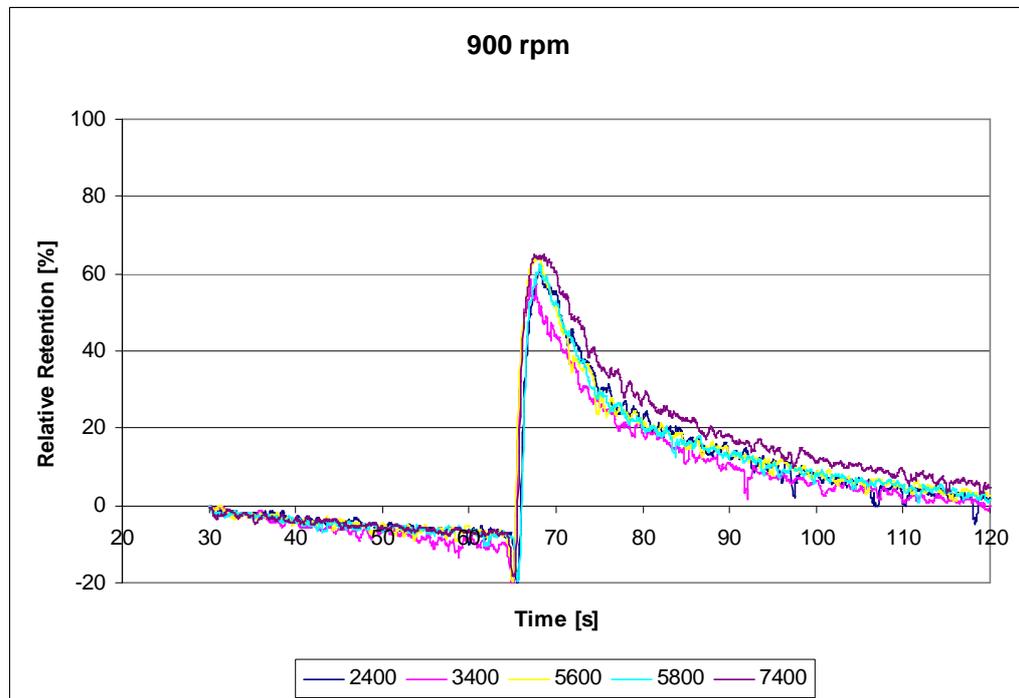


Figure 24 The effects of stirring speed on different C-PAM's, dosage 300 g/t, and stirring speed 900 rpm

The effect of stirring speed can be seen comparing the figures 22-24. 500 rpm yield the highest results because of the lower shear forces than in the 700 and 900 rpm figures. Optimum delay is highest in the 500 rpm and it decreases rapidly when stirring speed is increased. Stirring speeds over 900 rpm resulted splashing of furnish from the cup and therefore are not suitable with this setup.

With higher stirring speeds the retention process also accelerated right after dosing the polymer into the system. This is due to the faster and better mixing and to the higher amount of particle collisions happening in furnish. With stronger mixing the maximum retention is achieved faster with 900 rpm than the lower stirring speeds, but the maximum is considerably lower. Due to higher shear forces the increase of stirring speed has negative effect on retention through out

the process. The disintegration of flocs increased when using 900rpm and yielded worse results when comparing to lower stirring speeds.

10.3 Effects of polymer dosage

Polymer dosage with different C-PAM's was studied by dosing different amounts of same C-PAM. This was tested to determine the dosing for later test with microparticles. In figures 25-27 are shown these results.

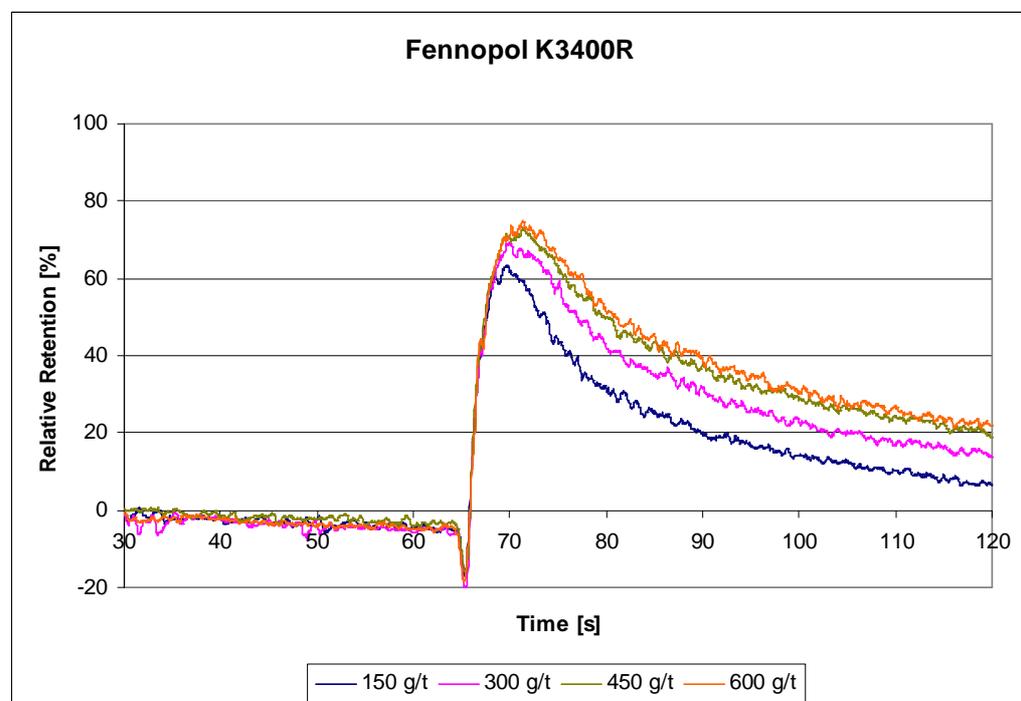


Figure 25 Effect of dosage of cationic polyacrylamide Fennopol K3400R.

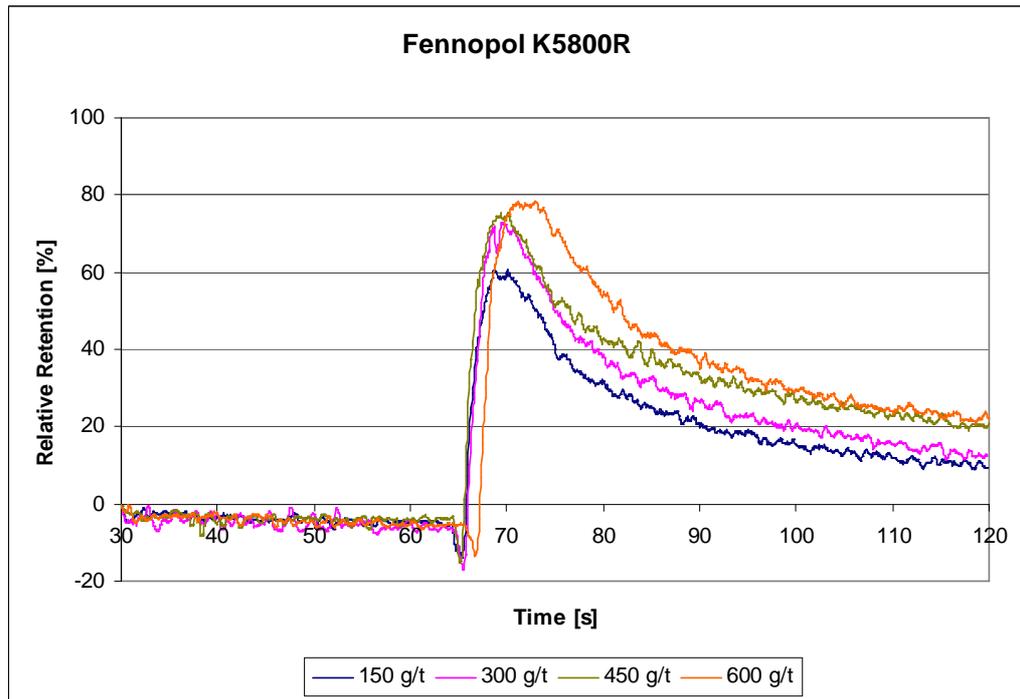


Figure 26 Effect of dosage of cationic polyacrylamide Fennopol K5800R.

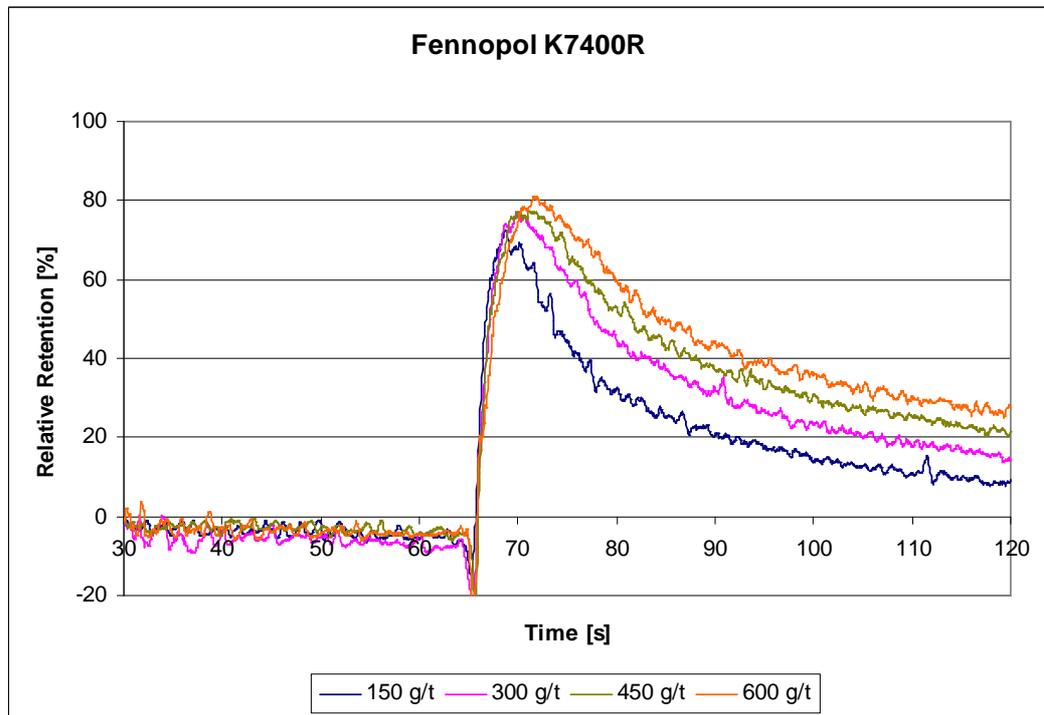


Figure 27 Effect of dosage of cationic polyacrylamide Fennopol K7400R.

Results with different C-PAM vary only by little, with heavier C-PAM's the results are better. All the curves are typical for bridging flocculation that is typical C-PAM's retention mechanism.

10.4 Effects of polymer charge and molecular weight

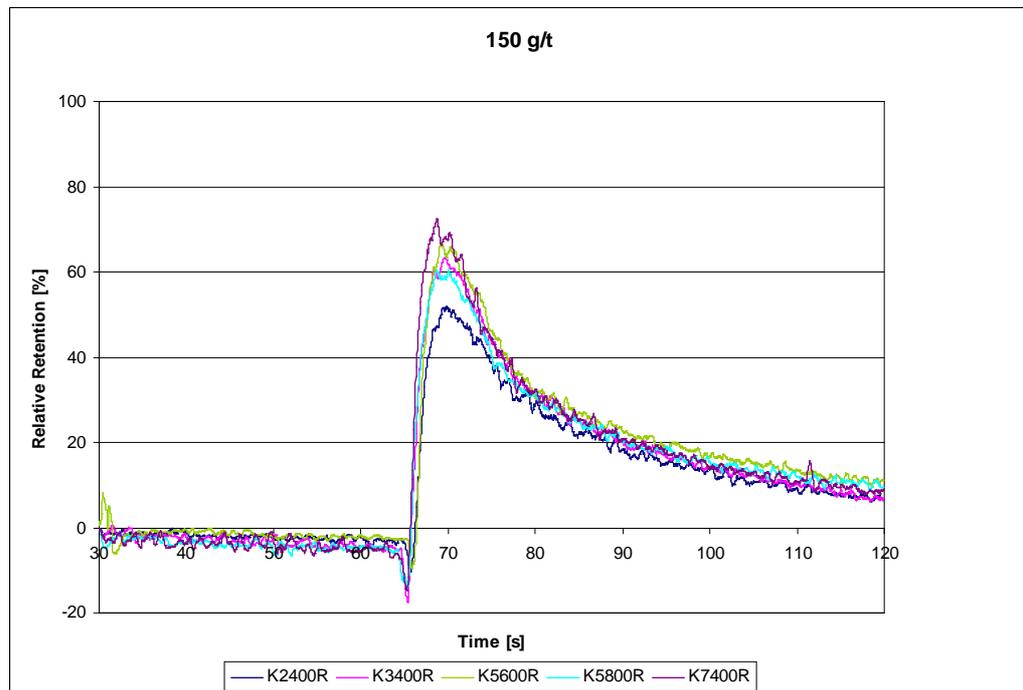


Figure 28 Retention with C-PAM's that have different charges and molecular weights. C-PAM dosage 150 g/t

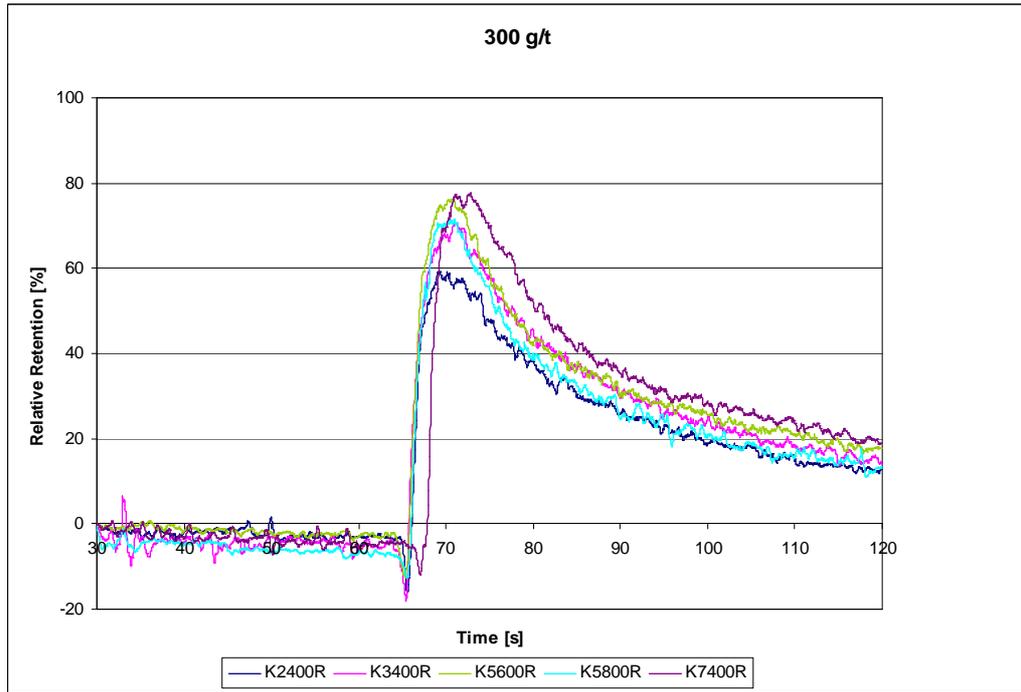


Figure 29 Retention with C-PAM's that have different charges and molecular weights. Dosage of C-PAM 300 g/t

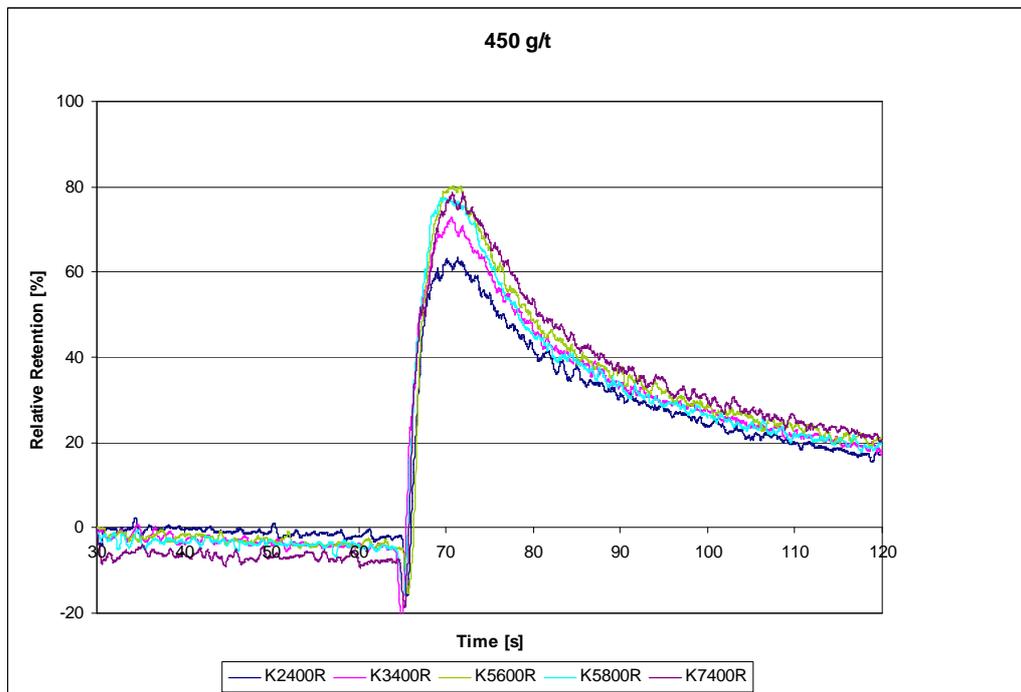


Figure 30 Retention with C-PAM's that have different charges and molecular weights. Dosage of C-PAM 450 g/t

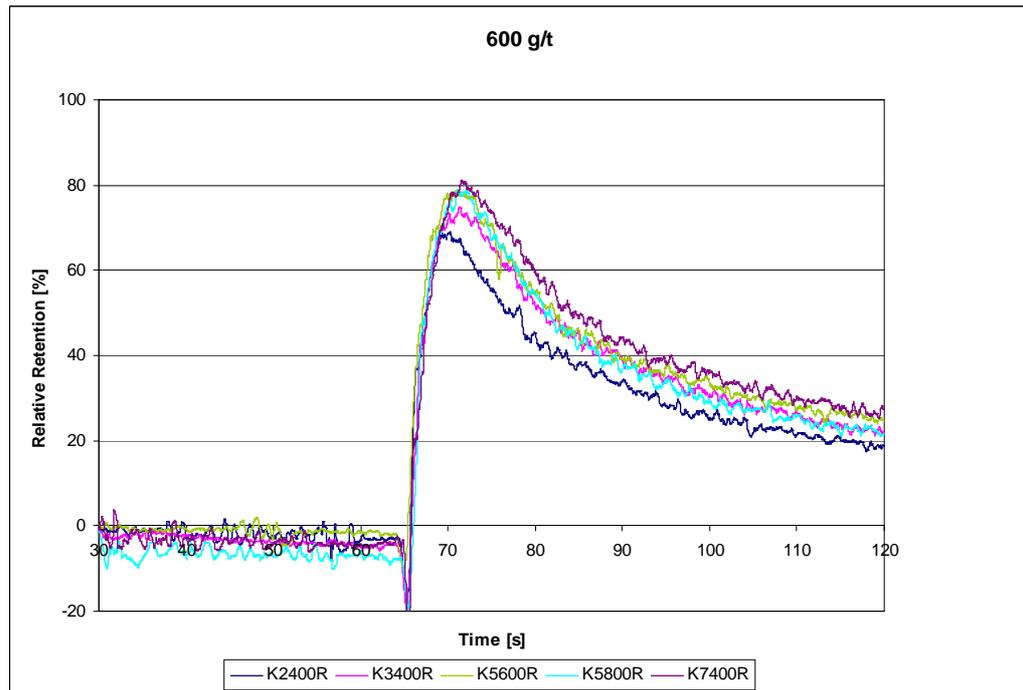


Figure 31 Retention with C-PAM's that have different charges and molecular weights. Dosage of C-PAM 600 g/t

The molecular weight of C-PAM correlates straight into the results, with heavier C-PAM's the better the results. The difference of the Fennopol K2400R and Fennopol K7400R is almost 20 % in relative retention. Otherwise all the C-PAM's use the same retention mechanisms and the curves are almost identical in all the cases. All the constant state values for these chemical are nearly the same, only with the higher dosages the heavier polymers yield constant state values that are higher than 5 %.

There have been experiments by Erkki Saharinen in his licentiate work, where he claims that with the C-PAMs that have higher charge the deflocculation would be faster. It is shown in the figures, that the K5600R and K5800R curves drop faster and time that the effect of C-PAM is half from the maximum is lower. It could be due the facts that flocs formed are harder and not so elastic therefore making these flocs susceptible to shear forces.

11 RPA – DDJ comparison tests

Tests were made by using RPA's DDJ-mode and with normal DDJ-apparatus. With the RPA, retention chemical was added at 50 seconds and at 60 seconds 100 g sample of white water was circulated from the system. That sample was then processed like a normal DJJ-sample to determine the first pass retention.

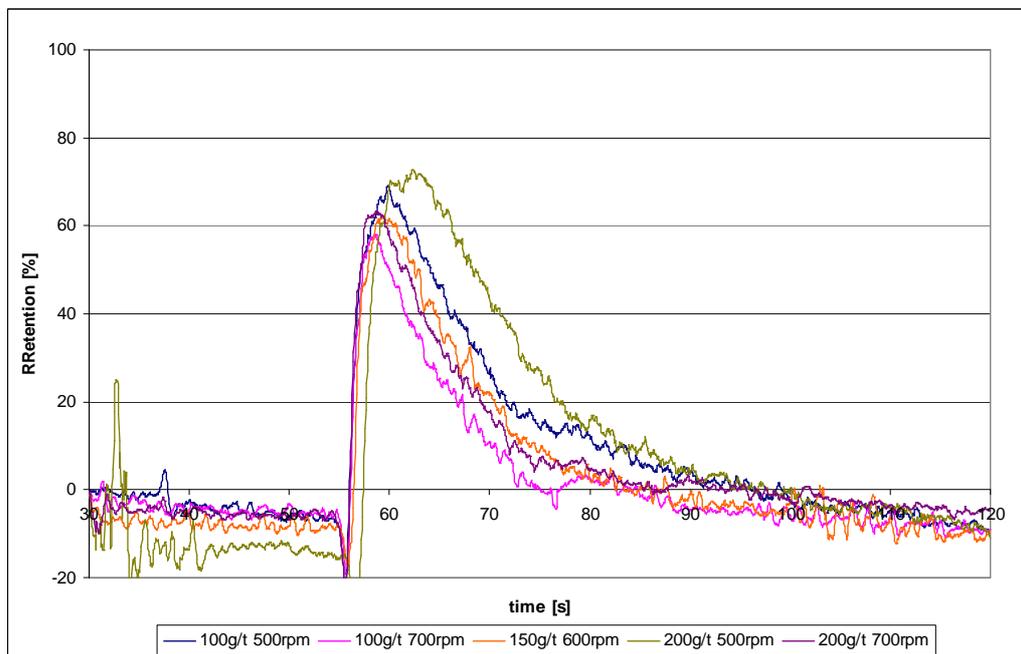


Figure 32 RPA figures using Fennopol K3400R, 100ml for DDJ is removed between 60 and 70 seconds

Figure 32 shows that removing the 100 ml of furnish clearly affects the end result gained from RPA. Retention drops rapidly and goes below zero mainly because the increased shear forces when the mass of furnish drops due removing the DDJ-sample. Also some air may affect the measurement due the smaller mass of furnish. Otherwise the maximum retention is the same as using conventional measurement procedure.



Figure 33 The comparison between retentions obtained from DDJ and RPA, using Fennopol K3400R after processing the 100ml samples.

Test was made using the RPA's DDJ-procedure and the conventional DDJ-test, with the same settings. The samples were dried and ashes were determined by the standard DDJ-process. Results obtained are compared in figure 33. All the results from RPA are approximately 10% higher than the results from DDJ. This could be the result of the different propellers used in the processes, which would indicate that the DDJ's stirring speed settings were inaccurately converted to match RPA's settings. Also the different wires used by the devices may be a factor in the test. The test should be redone with same wires. Still this would indicate that the RPA is comparable to DDJ with the average correlation between the two being 0,92.

12 Dual component retention systems

12.1 Silica based retention systems

Silica is commonly used in combination with starch. In furnish the amount of starch used was small so that the reactions between starch and silica wouldn't affect the retention process. The effect of silica on retention and the effect of dosing order in which silica and C-PAM's are added to furnish are shown in the following figures.

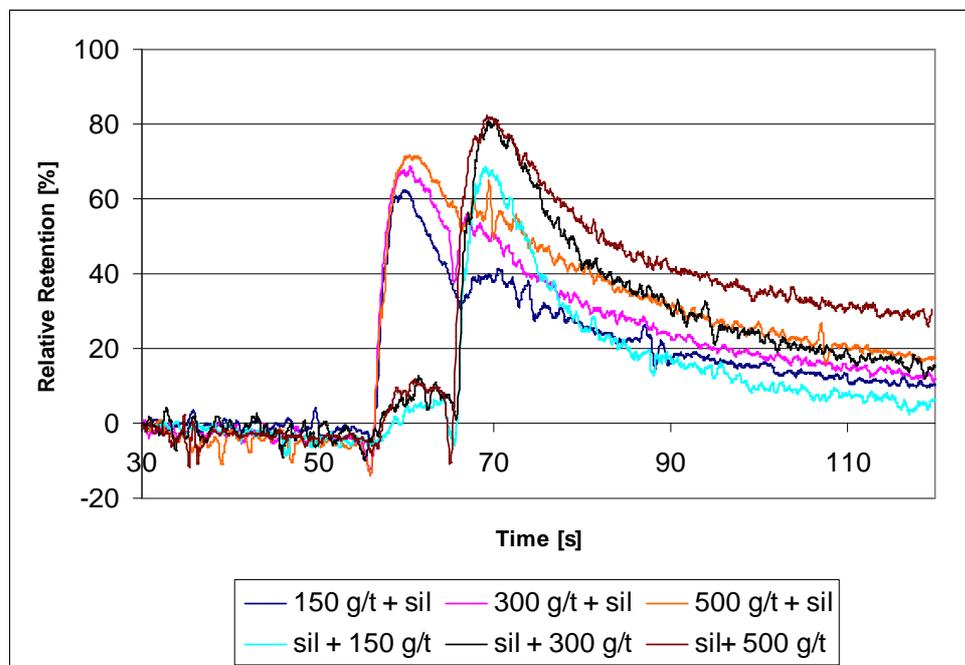


Figure 34 Effect of dosing order and dosage of C-PAM. Silica dose on each was 2000 g/t. C-PAM used was Fennopol K3400R

The figure shows clearly that adding silica before C-PAM yields over 10% higher maximum retention than the conventional method of adding silica after C-PAM. Stabilized retention values at the end of the test are also higher especially when using larger dosages of C-PAM.

Normally silica is added to the papermaking process after the C-PAM. However these results seem to indicate that just by taking retention in to question silica would be more effective when added to furnish before C-PAM.

With silica the formed flocs are much harder and therefore less susceptible to shear forces. This is illustrated in figure 35.

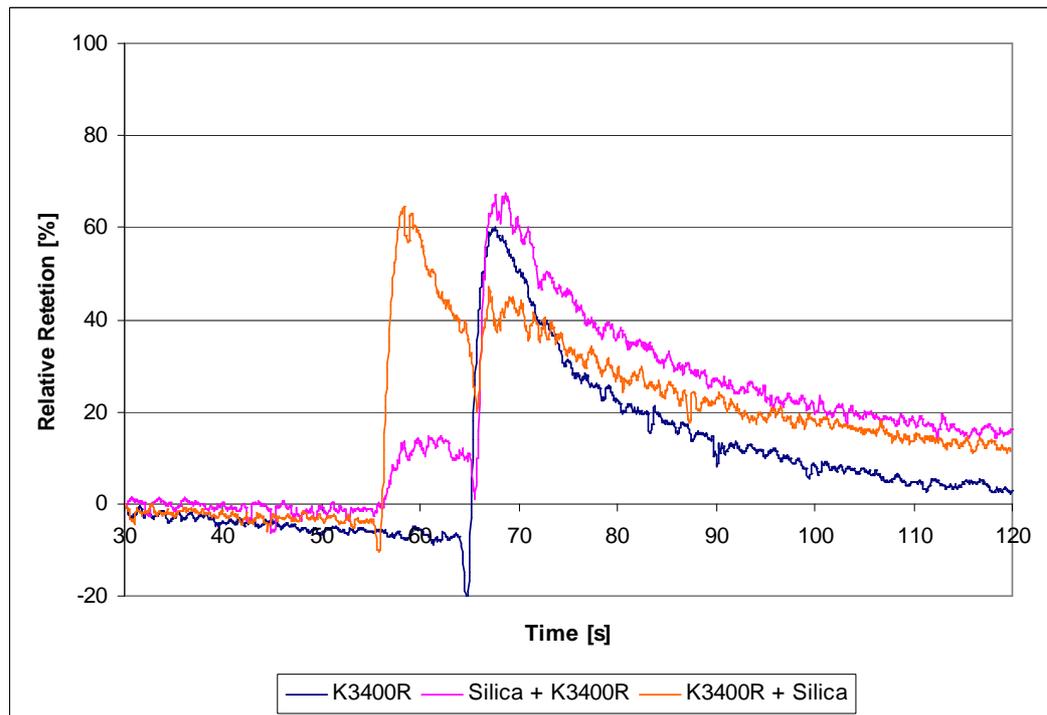


Figure 35 Effects of higher shear forces. Dosage of C-PAM was 300 g/t and silica dosage 2 kg/t

12.2 Bentonite based systems

Purpose of the tests was to determine the effects of bentonite to retention with different dosing order, dosage of bentonite and C-PAM. In figures 36 and 37 show the effect of different C-PAM dosages to retention.

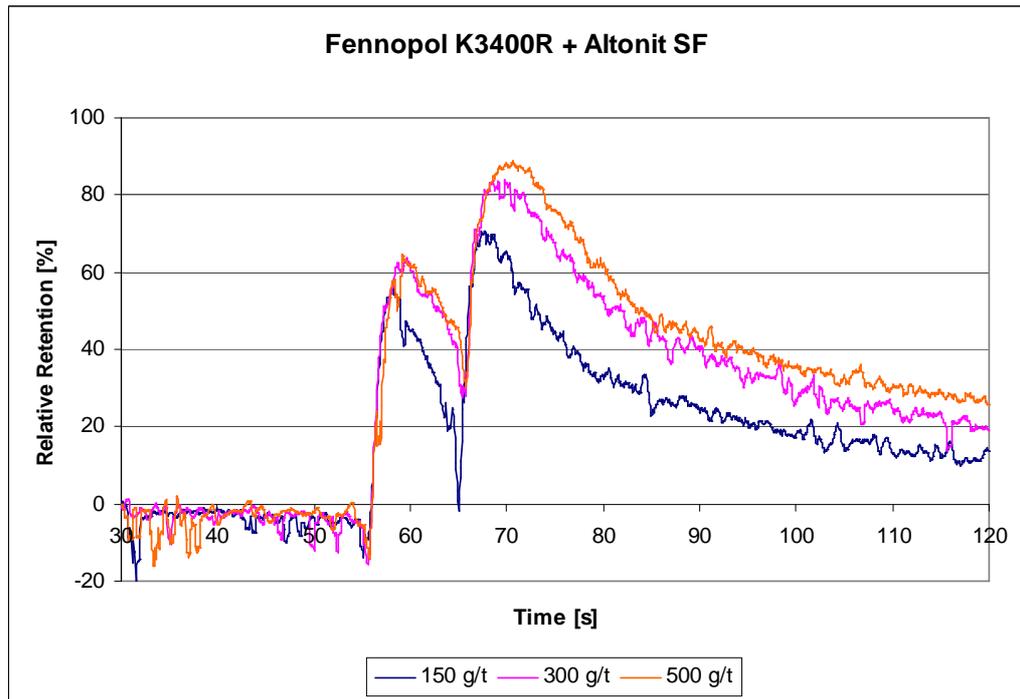


Figure 36 Fennopol K3400R was added at 50 s and Altonit SF added at 60 s. The dosage of Altonit SF was 2 kg/t.

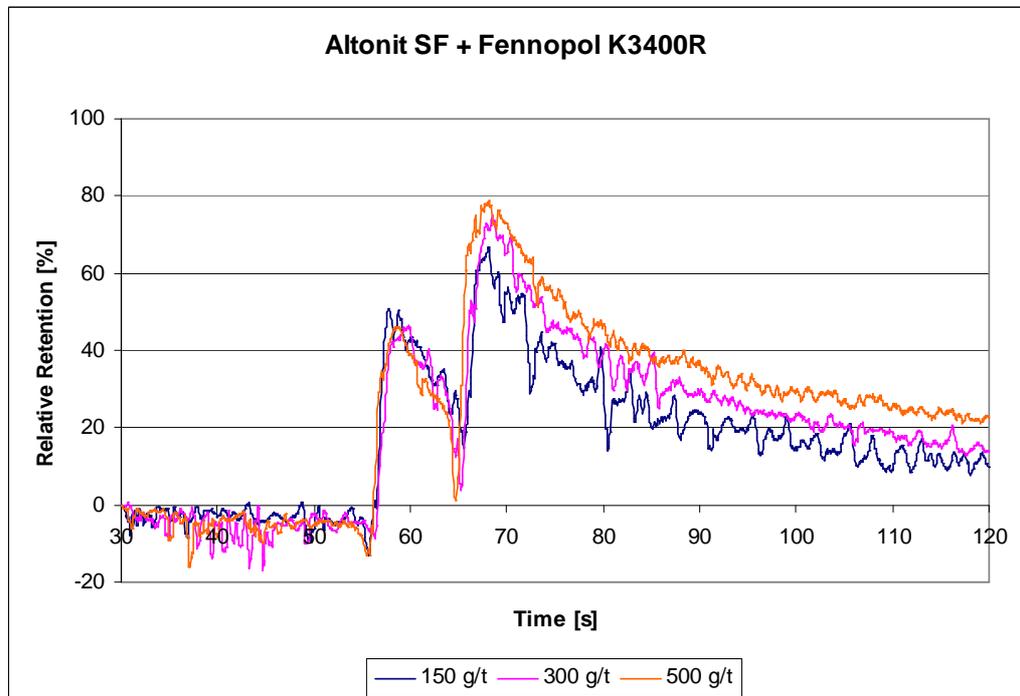


Figure 37 Altonit SF added at 50s and Fennopol K3400R added at 60s. Dosage of Altonit SF was 2 kg/t.

Bentonite alone has a moderate effect on retention. When polymer is added to the system rapid adsorption reaction occurs between bentonite and C-PAM, because of bentonites high surface area and anionic surface charge. By comparing figures 36 and 37 can be concluded that by adding bentonite after the polymer higher retention is gained. Also systems curves have higher surface area in total, therefore having stronger flocs due to the slower disintegration rate and having the end retention rate over 10% higher. It can be seen that if the amount of C-PAM was low, there is no clear advantage of bentonite, but increasing the dose of C-PAM caused a clear big increase in retention level. In figure 38 is shown the effects of different polymers with bentonite.

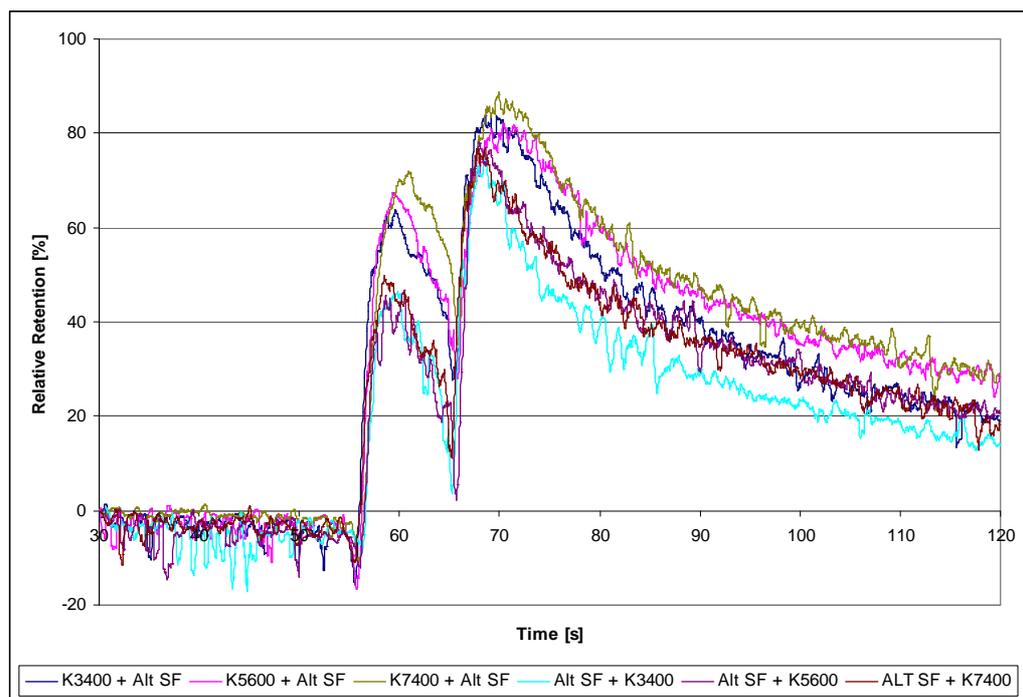


Figure 38 Effects of different C-PAM's with both dosing sequences. Dosage of C-PAM's was 300 g/t and the dosage of Altonit SF was 2 kg/t. First dosage was added at 50 s and second at 60 s.

From the figure 38 can be seen that the heaviest polymer results in best retention due to the better bridging ability. Although the bigger difference comes from the dosing order, when adding bentonite after the C-PAM retention is approximately

10% higher throughout the system. By adding bentonite first the retention level rises to approximately 40 %, which would indicate that bentonite creates some bonds with fines and fillers by the aid of starch. Those bonds however are broken by the addition of C-PAM to the system. This seems to indicate that the C-PAM creates stronger bonds that break the weak bonds between bentonite and filler.

In figures 39 and 40 is shown the effects of different bentonite dosages.

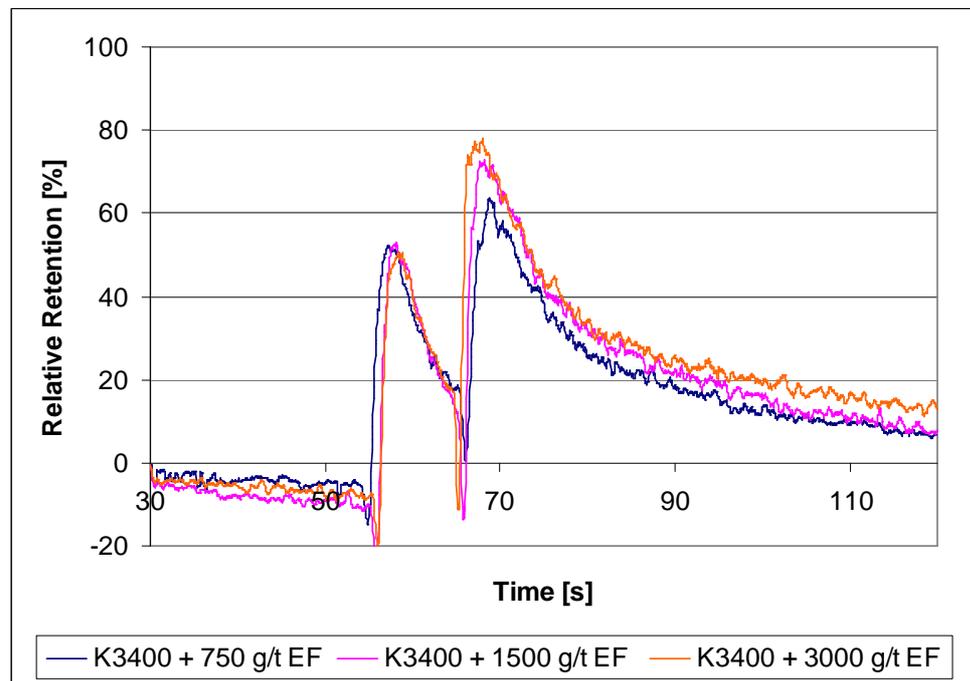


Figure 39 The effect of bentonite dosage in retention. Fennopol K3400R was added at 50s and Altonit EF added at 60s. The dosage of Fennopol K3400R was 150 g/t.

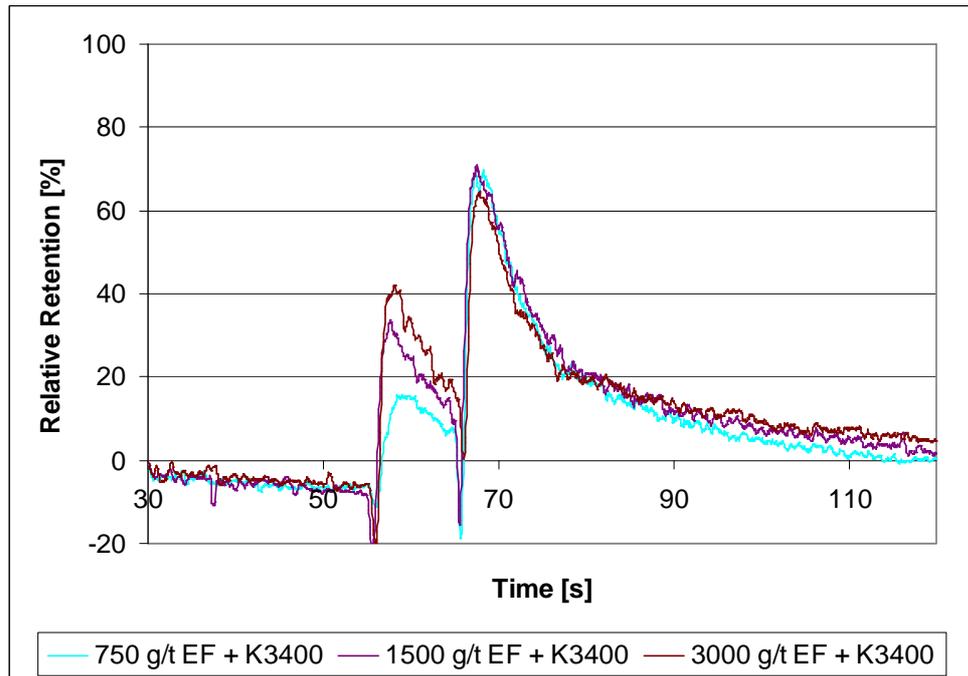


Figure 40 The effect of bentonite dosage in retention. Altonit EF was added at 50s and Fennopol K3400R added at 60s. The dosage of Fennopol K3400R was 150 g/t.

Increasing bentonite dosage improved retention, but the effect was smaller than the increase of dosage in C-PAM. By using a higher amount of C-PAM would have made differences clearer. By adding larger amounts of bentonite the difference in gaining retention is clearly more insignificant than the right dosage of C-PAM. Comparing the results to the figures 39 and 40 it is shown that by increasing the bentonite dosage the overall retention is lower. Therefore the correct relation of C-PAM and bentonite dosages is the key to gaining better retention.

13 Micropolymer based systems

The effects of next generation cationic micropolymer Fennosil ES325 n retention is shown in figure 41.

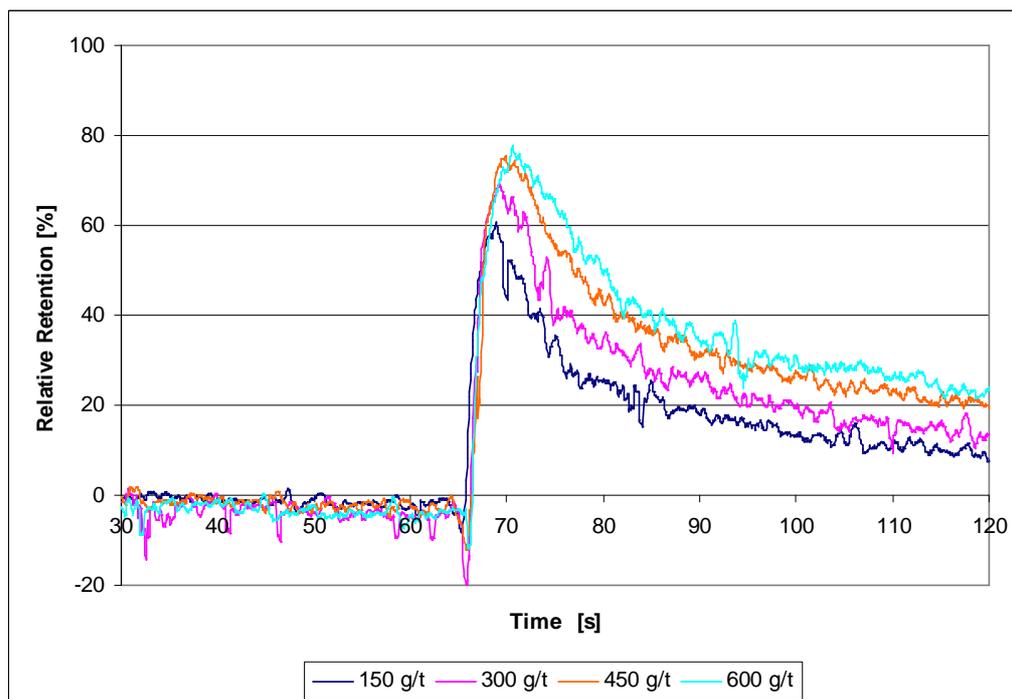


Figure 41 The retention of cationic micropolymer ES325.

The micropolymer ES325 effect on colloidal retention is similar to that of C-PAM. Comparison to a C-PAM Fennopol K3400R is shown on figure 42.

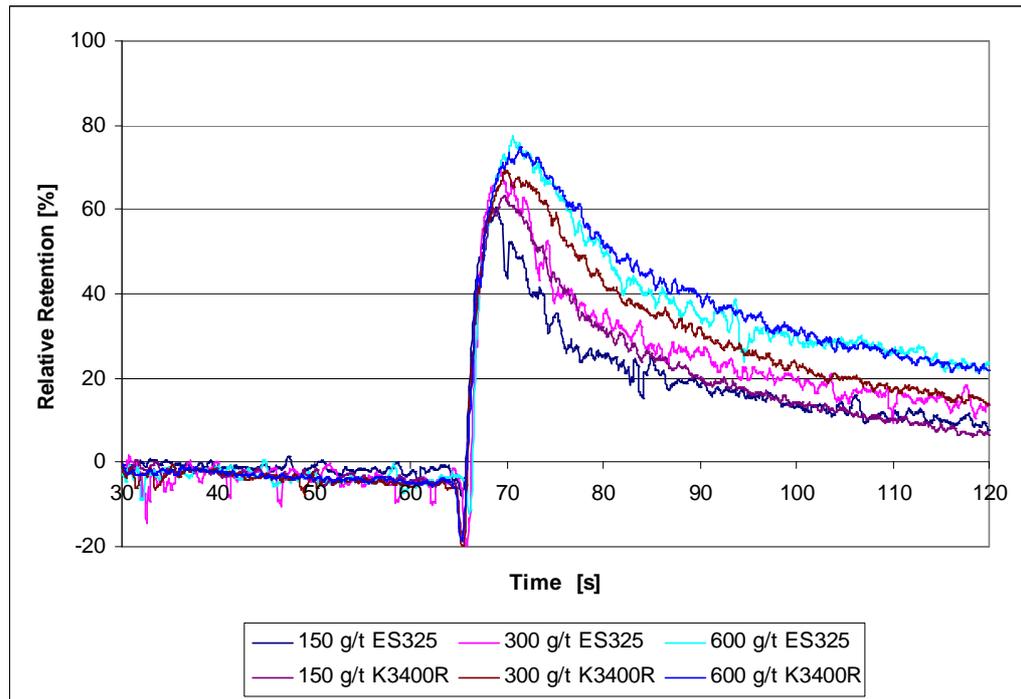


Figure 42 Comparison of C-PAM Fennopol K3400R and micropolymer Fennosil ES325

Figure 42 shows that there was no real difference between the two chemicals in retention. Both the micropolymer and C-PAM seem to use exactly the same retention mechanisms throughout the process. In table III are these results shown.

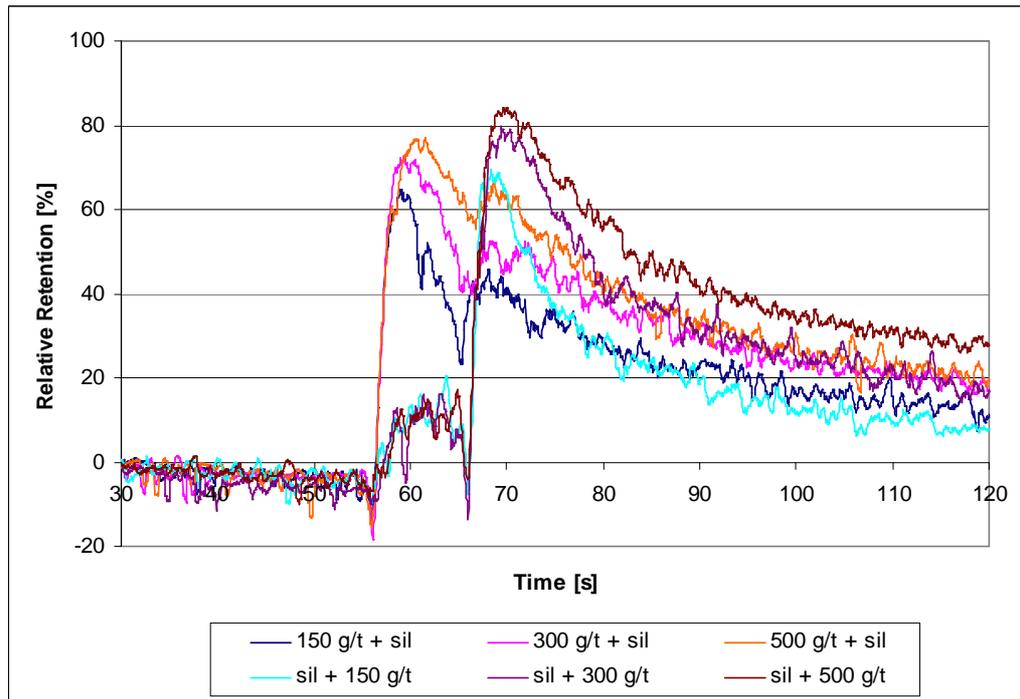


Figure 43 Effect of dosing order and the dosage of micropolymer ES325 with Fennosil 515 silica. Silica dose on each was 2 kg/t. First dose at 50 s and second at 60 s

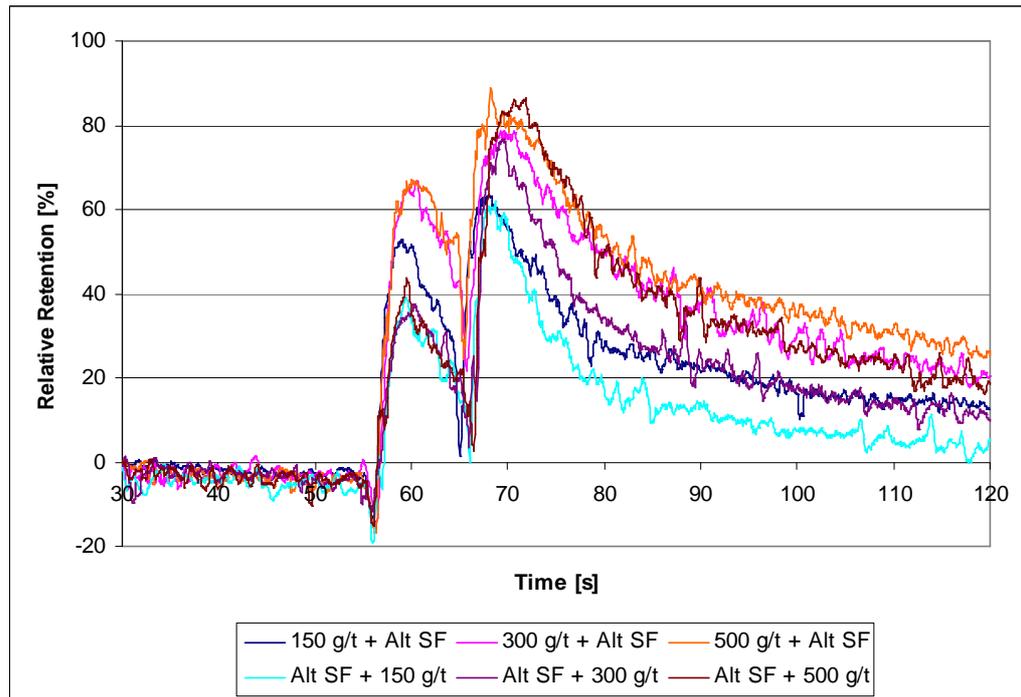


Figure 44 Effect of dosing order and dosage of micropolymer ES325 with bentonite Altonit SF. Bentonite dose on each was 2 kg/t. First dose at 50 s and second at 60 s

When comparing figures 43 and 44 to the results gained with K3400R can be stated that the micropolymer ES325 acts nearly identically. ES325 is nearly as effective bridging agent though it has lower molecular weight and lower charge density. In table III are shown the maximum retentions gained with ES325 and K3400R with silica and bentonite.

Table III Differences in maximum retention between K3400R and ES325 in microparticlesystems, K3400R and ES325 dosages 300 g/t, Altonit SF and Fennosil 515 dosages 2 kg/t

chemical	dosing sequence	max retention
K3400R	C-PAM -> bentonite	84.11
	bentonite -> C-PAM	77.61
	C-PAM -> silica	67.26
	silica -> C-PAM	82.18
ES325	micropolymer -> bentonite	76.16
	bentonite -> micropolymer	74.55
	micropolymer -> silica	72.30
	silica -> micropolymer	78.31

13.1 Reversibility

The Fennosil ES325 is highly structured micropolymer and the charge of the polymer is very accessible, but also a considerable portion of the charge is buried in the network and requires shear to expose it. This charge is referred as ionic regain. The amount of ionic regain in different kind of polymers is illustrated in the figure 45

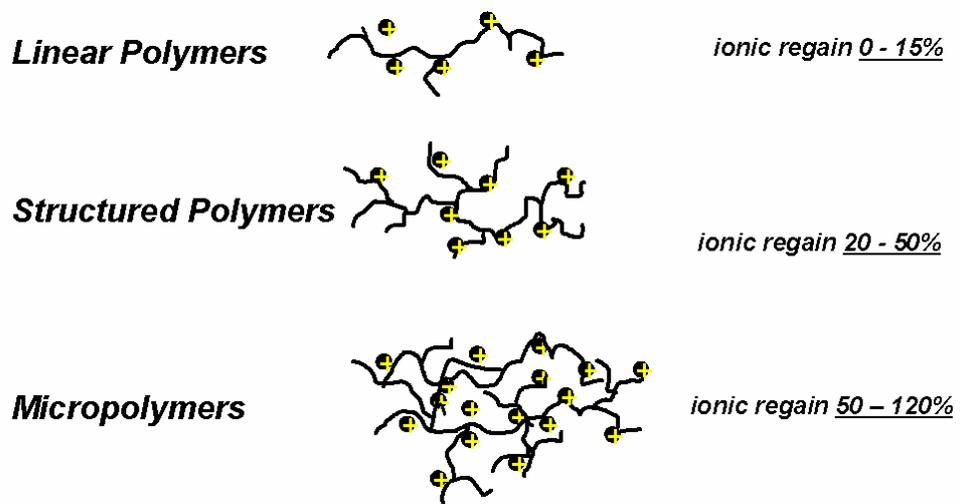


Figure 45 Ionic regain of different polymers/18/

To expose these buried charges following test program was used, from 0 – 70 stirring speed was 700 rpm, from 70 – 110 stirring speed was raised to 900 rpm to expose the ionic regain and from 110 – 180 s the stirring speed was lowered to 700 rpm.

The ionic regain would be seen as a rise in retention levels when the shear forces are lowered in 110 s. These tests were made with both bentonite and silica. The results are shown in figures 46 and 47.

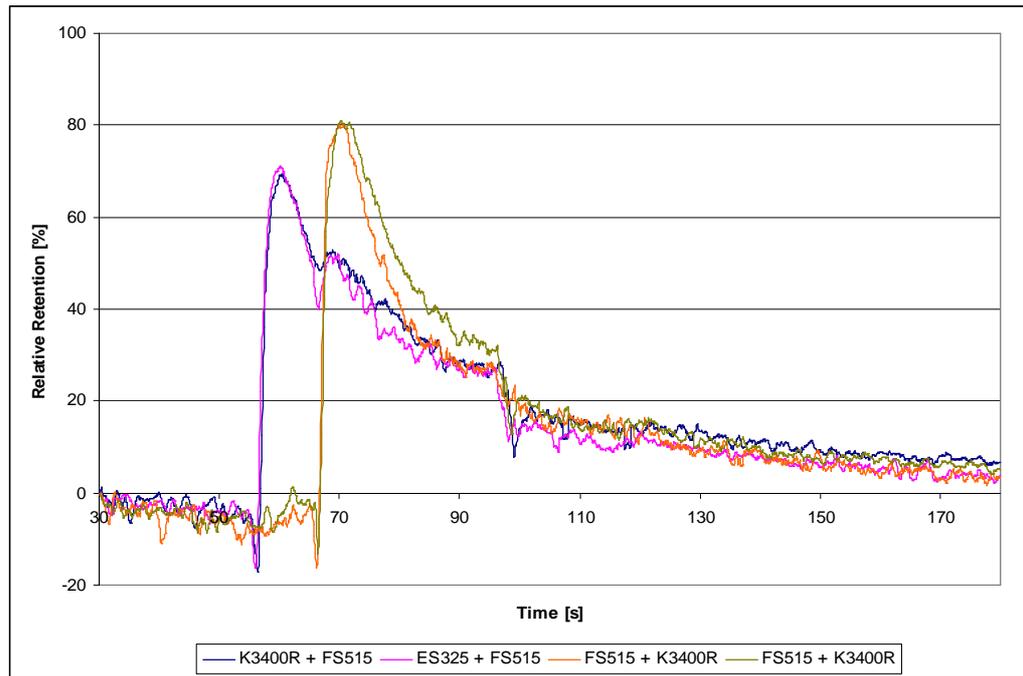


Figure 46 Micropolymer reversibility test with Fennosil ES325, Fennopol K3400R and Fennosil 515. Test program stirring speed from 0 – 90 s 700 rpm, 90 – 110 900 rpm and 110 – 180 s 700 rpm

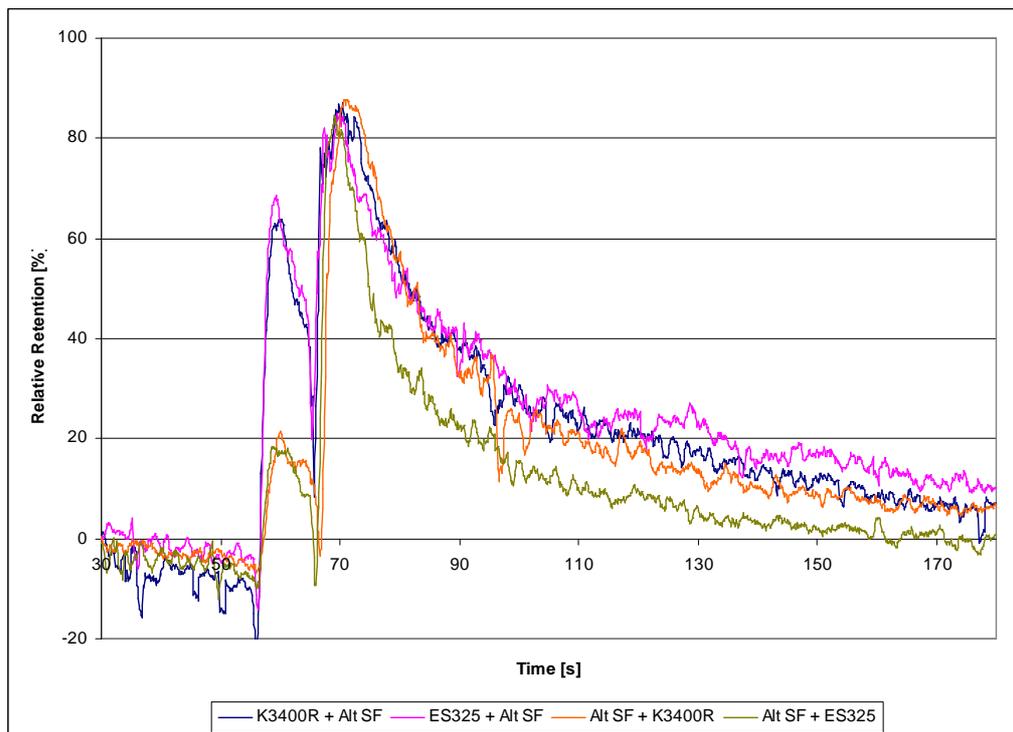


Figure 47 Micropolymer reversibility test with Fennosil ES325, Fennopol K3400R and Altonit SF. Test program stirring speed from 0 – 90 s 700 rpm, 90 – 110 900 rpm and 110 – 180 s 700 rpm

There is no clear difference between the curves obtained from using the C-PAM or micropolymer. In both cases with silica and bentonite the different polymers act similarly. This would indicate that the conventional linear C-PAM and the structured cationic micropolymer have the same properties in ionic regain when studying it from colloidal retentions point of view.

14 Three component microparticle systems

The three component systems tested were:

- C-PAM + micropolymer + silica
- C-PAM + micropolymer + bentonite

Variables were dosing order and the dosage of micropolymer Fennozil ES325. In tables IV and V are shown the maximum and end retention values obtained from the tests.

Table IV Results obtained from tests using silica.

Dosage of ES325	Dosing Sequence	Max Retention	End Retention
100 g/t	K3400R --> ES325 --> FS515	57,16	10,50
	K3400R --> FS515 --> ES325	52,67	5,59
	ES325 --> K3400R --> FS515	47,83	5,26
	ES325 --> FS515 --> K3400R	58,89	4,49
	FS515 --> K3400R --> ES325	54,55	2,61
	FS515 --> ES325 --> K3400R	52,93	4,61
200 g/t	K3400R --> ES325 --> FS515	58,08	14,45
	K3400R --> FS515 --> ES325	70,83	10,86
	ES325 --> K3400R --> FS515	61,68	11,93
	ES325 --> FS515 --> K3400R	58,77	8,31
	FS515 --> K3400R --> ES325	63,17	9,80
	FS515 --> ES325 --> K3400R	70,13	7,95
300 g/t	K3400R --> ES325 --> FS515	60,49	16,47
	K3400R --> FS515 --> ES325	75,64	14,18
	ES325 --> K3400R --> FS515	68,19	14,21
	ES325 --> FS515 --> K3400R	68,35	14,09
	FS515 --> K3400R --> ES325	69,88	14,22
	FS515 --> ES325 --> K3400R	80,32	15,20

Figure 48 shows the retention curves for three component systems using silica.

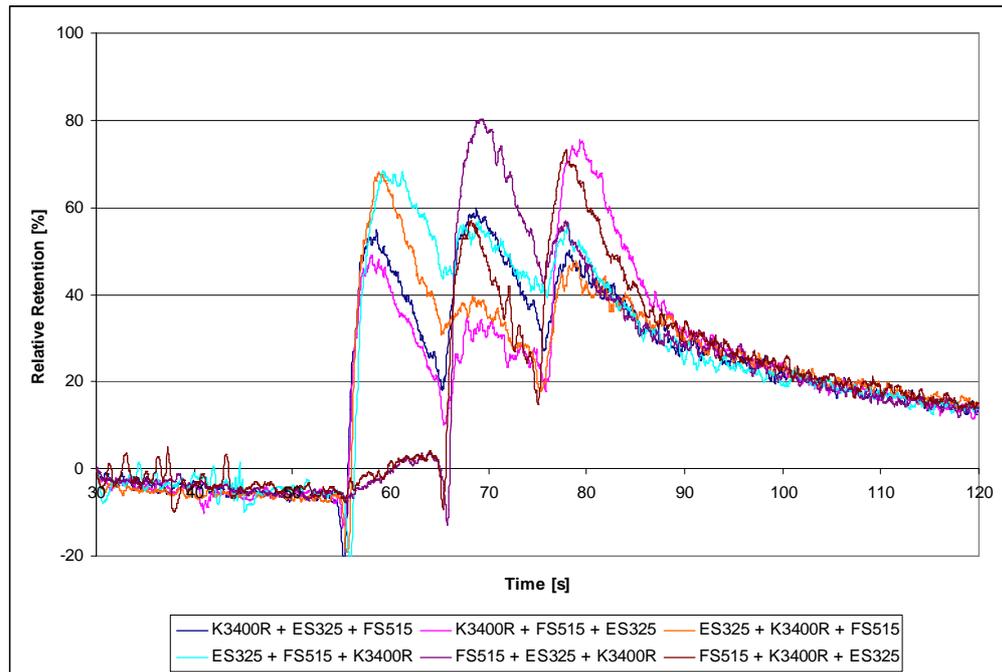


Figure 48 Three component system with Fennopol K3400R (C-PAM), Fennosil ES325 (microparticle) and Fennosil 515(silica). Dosing at 50 s, 60 s and 70 s. Dosage of Fennosil ES325 was 300 g/t, Fennosil 515 2 kg/t and Fennopol K3400R 100 g/t.

The curves in figure 48 and table IV shows that silicas effectiveness is combination of two things, silica is added before polymers and only the highest dosage has a significant effect on retention. The best retention is achieved by adding silica first and then adding 300 g/t of ES325. The dosage of 100 g/t K3400R has no effect on retention when there is larger amount of polymer added. It can be concluded that silica has a large dependency over polymer dosage.

In table V is shown the results obtained from 3-component systems using bentonite.

Table V Results obtained from test using bentonite

Dosage of ES325	Dosing Sequence	Max Retention	End Retention
100 g/t	K3400R --> ES325 --> Alt SF	78,20	19,51
	K3400R --> Alt SF --> ES325	69,96	13,85
	ES325 --> K3400R --> Alt SF	80,84	17,97
	ES325 --> Alt SF --> K3400R	68,14	12,24
	Alt SF --> K3400R --> ES325	67,75	6,32
	Alt SF --> ES325 --> K3400R	67,23	7,88
200 g/t	K3400R --> ES325 --> Alt SF	90,81	26,54
	K3400R --> Alt SF --> ES325	74,99	16,91
	ES325 --> K3400R --> Alt SF	88,75	20,23
	ES325 --> Alt SF --> K3400R	80,27	14,13
	Alt SF --> K3400R --> ES325	70,48	9,93
	Alt SF --> ES325 --> K3400R	73,52	9,20
300 g/t	K3400R --> ES325 --> Alt SF	92,68	30,07
	K3400R --> Alt SF --> ES325	80,10	23,92
	ES325 --> K3400R --> Alt SF	91,80	31,86
	ES325 --> Alt SF --> K3400R	85,54	18,50
	Alt SF --> K3400R --> ES325	78,98	15,30
	Alt SF --> ES325 --> K3400R	83,24	13,09

Figure 49 shows the retention curves using bentonite.

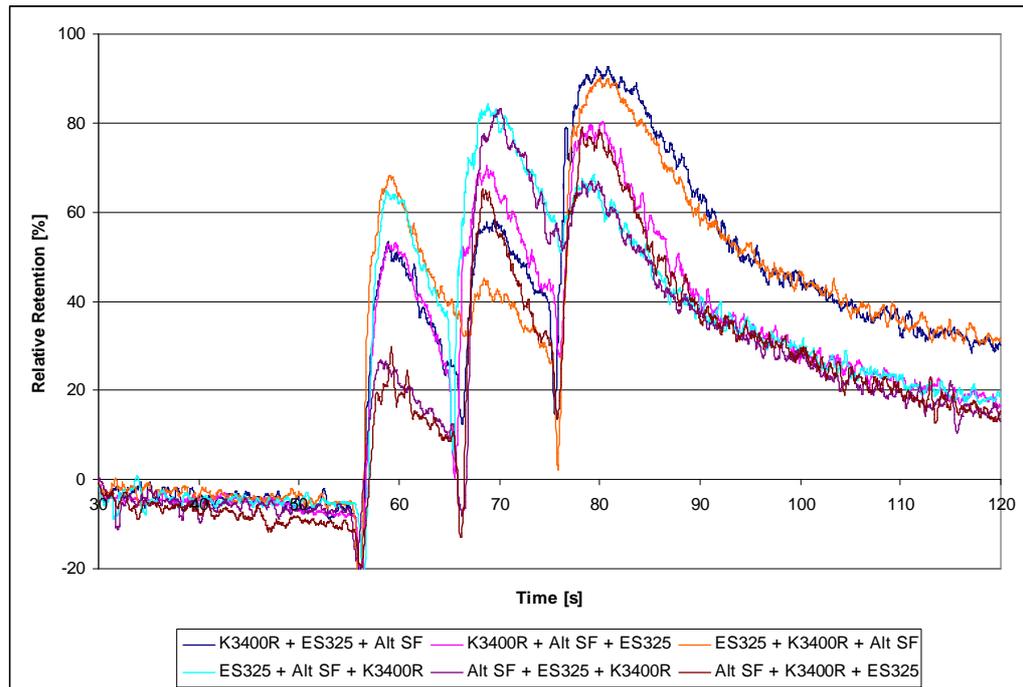


Figure 49 Three component system with Fennopol K3400R (C-PAM), Fennosil ES325 (microparticle) and Altonit SF (bentonite). Dosing at 50 s, 60 s and 70 s. Dosage of Fennosil ES325 was 300 g/t, Altonit SF 2 kg/t and Fennopol K3400R 100 g/t.

Clearly the best results are obtained when bentonite is added last in to furnish. As with dual component systems the best results are gained with bentonite being the last component, but unlike silica bentonite is not that dependant of large polymer dosage.

The constant state values with systems that induced bentonite last have over 10 % higher values. This seems to indicate that the flocs formed with those two systems are different that the rest. This could mean that the two cationic polymers used have some kind of synergy. Another thing that could induce the effect of higher retention is the dosing, by adding the polymer in two dosages could also have effect. This could be easily tested by adding the C-PAM or micropolymer in two dosages into the system. Clearly more testing is needed to determine this.

Table VI Comparison of results the best retention systems, using 3-component system. Dosages of Altonit SF and Fennosil 515 were 2 kg /t, dosage of Fennopol K3400R was 100 g/t

Dosage of ES325	Sequence	Max Retention	End Retention
100 g/t	K3400R --> FS515 --> ES325	52.67	5.59
	FS515 --> ES325 --> K3400R	52.93	4.61
200 g/t	K3400R --> FS515 --> ES325	70.83	10.86
	FS515 --> ES325 --> K3400R	70.13	7.95
300 g/t	K3400R --> FS515 --> ES325	75.64	14.18
	FS515 --> ES325 --> K3400R	80.32	15.20
100 g/t	K3400R --> ES325 --> Alt SF	78.20	19.51
	ES325 --> K3400R --> Alt SF	80.84	17.97
200 g/t	K3400R --> ES325 --> Alt SF	90.81	26.54
	ES325 --> K3400R --> Alt SF	88.75	20.23
300 g/t	K3400R --> ES325 --> Alt SF	92.68	30.07
	ES325 --> K3400R --> Alt SF	91.80	31.86

Table VI clearly shows that the best systems using silica are more dependant of polymer dosage that the systems using bentonite. With the initial dosage of 200 g/t of total polymer only yielded almost 53% in total retention, while with bentonite the maximum retention was 80%. By increasing the dosage of micropolymer in the system the maximum retention with silica was 80% which was obtained with bentonite by using 200 g/t less micropolymer. The overall effectiveness of bentonite in 3-component systems is excelent. With 300 g/t of total polymer dosage the retention reached 90 % which is 10 % higher than the results obtained just by using dual component system with the same polymer dosage. This clearly shows the fact that bentonite benefices greatly from the 3-component system and with silica the same results can be obtained with just a dual component system.

15 Conclusion

In the experimental the colloidal retention efficiency was studied. All the tests were made with Retention Process Analyzer. Microparticles used in the tests were anionic silica, bentonite and a next generation micropolymer.

In the first tests the reliability of RPA was tested by comparing it with DDJ and a good correlation with the two was found, results were comparable. Cationic polyacrylamides were tested to gain knowledge on the basic levels of retention gained only with the bridging C-PAM's. Also it was concluded that with heavier polymer the results were better. The stirring speed of RPA was tested to determine the optimum speed for testing and 700 rpm was found to be the optimal.

With anionic silica was found that the non-traditional dosing of silica, being the first component to be dosed into furnish, yielded considerably higher retentions than the traditional dosing order. Constant state values with silica were also higher than with just using C-PAM. This indicates that the flocs formed with silica are harder than the flocs formed with only C-PAM.

Bentonite based microparticle systems are efficient when using the traditional dosing order, in which bentonite is dosed last into the suspension. Earlier research with bentonite has always concluded that bentonite alone has a very little effect on retention. Here with high filler content furnish bentonite has a moderate effect on retention. This seems to indicate that bentonite creates soft flocks with filler. These flocs are broken with the addition of C-PAM, due to C-PAM's strong bridging ability. With silica the efficiency is dependant of high C-PAM dosage, but with bentonite the correct ratio of polymer and bentonite gives high retention with relative low dosage.

The cationic micropolymer Fennozil ES325 was found to use the same retention mechanism as conventional C-PAM's. Micropolymer has lower molecular weight than conventional C-PAM's still the result were as good as the result obtained with C-PAM. Dual systems with silica and bentonite also yielded similar results. No evidence of the ionic regain was found in colloidal retention with microparticles.

3-component system with silica had no effect in colloidal retention. The behavior of silica was the same as it was with dual component systems. Best results were those when silica was dosed first followed by a large dose of polymer. The obtained maximum retention was the same as the maximum with dual component systems. Also the dosing history had no effect on floc strength since all the tests made had the same constant state value. Bentonite in 3-component system yielded best results by dosing the bentonite last, but unlike silica bentonite clearly benefited from 3-component system. Results were over 10 % higher than results from dual component systems. This would indicate that there is either somekind of synergy between the cationic PAM and the cationic micropolymer or this effect could be induced by the two different dosing points. Either way the results were very good, even with relatively low polymer dosages a high retention was achieved.

16 Need of further studies

In this thesis the retention aids used were limited only to a few, different microparticles and polymers especially anionic polymers were not tested. The presumed synergy of C-PAM and micropolymer has not been proved. So the research of multiple dosing points in retention process would be interesting.

When studying colloidal retention one of the most important things is floc size and that was not included in this thesis. The interpreting of the RMS-signal from RPA would be the next step. Also implementing the Lasentec FBRM device in

RPA would give much needed data of floc dynamics and floc size distribution in the process. High speed imaging would also be beneficial so the flocs could be actually seen.

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