

FIBRE FLOC MORPHOLOGY AND DEWATERABILITY OF A PULP SUSPENSION: ROLE OF FLOCCULATION KINETICS AND CHARACTERISTICS OF FLOCCULATION AGENTS

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The aim of this investigation was to find out how properties of a flocculation agent and flocculation kinetics affect the morphology of fibre flocs and how dewatering of a fibre suspension may be attributed to floc morphology. Fibre flocculation, analysed in terms of floc size, mass fractal dimension, floc strength, and the kinetic constant of flocculation, was measured with a digital image analysis system using cationic polyacrylamides as flocculants and NaCl as a coagulant. The results suggest that the kinetics of fibre flocculation is not a key factor determining floc properties but follows from the high bonding ability of the flocculation agent, which also lies behind the high floc density and size, i.e., the factors that lead to fast flocculation and improved floc properties are partly the same. In addition to interfibre bonding strength, the structure of the bonding layer of polymeric flocculants was found to be a significant factor describing floc morphology. Dewaterability of the fibre suspension was improved by increased floc density, which promotes fast water flow through the large voids around the dense flocs, while large, irregular flocs induced loose floc packing, which further improved dewatering by creating larger voids. Increased floc strength seemed to reduce the sealing of fluid passageways, particularly on the surface of the wire, where fibre squeezing could blind the filter fabric.

Keywords: Flocculation; Floc structure; Floc size; Fractal dimension; Dewatering

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INTRODUCTION

Flocculation agents, i.e., polymeric flocculants and inorganic coagulants, are widely used to improve the dewaterability of suspensions. Flocculation agents promote the attachment of small particles to fibre surfaces in a pulp suspension, but they also induce the aggregation among fibres and the flocculation of small particles, thus forming flocs. Since the influence of fibre flocculation on dewatering is attributed to the morphology of these flocs, the factors affecting it are of particular interest in order to gain a better understanding of the dewatering phenomena in suspensions containing pulp fibres.

The function of polymeric flocculants in fibre flocculation is attributed to their ability to increase the number and strength of the fibre-to-fibre bonds in flocs initially formed through mechanical friction and fibre bending (Wågberg and Lindström 1987a; Swerin 1998; Andersson et al. 1999; Schmid and Klingenberg 2000). This leads to considerable changes in floc size, density, strength, and reversibility (Hubbe 2000;

Schmid and Klingenberg 2000; Saveyn et al. 2005), depending on their molecular weight, charge density and conformation, and on the amount of flocculant adsorbed (Hubbe 1987; Saveyn et al. 2005; Yu et al. 2006). Flocculant agents also affect floc growth and the flocculation kinetics by enhancing the probability of fibre attachment in the collisions that lead to floc formation.

Studies concerning the relationship between floc morphology and suspension dewaterability have focused on mineral particle suspensions and wastewater sludges (Waite 1999; Wu et al. 2003a; Zhao 2003; Turchiuli and Fargues 2004; Zhao 2004; McFarlene et al. 2006; Nasser and James 2007). The effect of pulp fibre floc morphology on dewaterability of fibre suspensions has been demonstrated only in few publications (Antunes et al. 2008; Hubbe et al. 2008). Floc size has been shown to be the most important factor affecting the dewaterability of many suspensions (Wu et al. 2003b, Antunes et al. 2008), which is consistent with the filtration theory of Kozeny (1927) and Carman (1937), despite some conditions under which no direct correlation was established (Zhao 2003). It has also been concluded that increased floc strength will promote dewatering, as it increases the resistance of flocs to deformation under a compressive load (Nasser and James 2006) and reduces pore plugging by the fragments remaining from floc breakage (Boller and Blaser 1998; Wu et al. 2003a). The results with regard to floc density are inconsistent, however, since increased density has been thought to either increase (Sengupta et al. 1997) or reduce (Waite 1999; Antunes et al. 2008) the dewaterability of a suspension. There are also results suggesting that the floc growth rate, i.e. flocculation kinetics, affects floc morphology and dewatering (Amal et al. 1990; McFarlene et al. 2008), but the phenomena lying behind such effects are still largely unclear.

Since only few studies concerning qualitative effects of pulp fibre floc morphology on dewaterability of fibre suspensions have been published (Antunes et al. 2008; Hubbe et al. 2008), the relationship between fibre floc characteristics and the dewaterability of a pulp suspension is still largely unclear. In addition, there is a scarcity of generic knowledge regarding the role of flocculation kinetics in the floc morphology and the dewaterability of particle suspensions. The aim here is to find out how properties of flocculation agents and flocculation kinetics affect the morphology of fibre flocs and how the dewatering of a fibre suspension may be attributed to floc morphology.

Fibre flocculation in a fines-free pulp, analysed in terms of average steady-state floc size, steady-state mass fractal dimension, floc strength, and the kinetic constant of flocculation, was measured with a digital image analysis system using cationic polyacrylamides (CPAMs) as flocculants and NaCl as a coagulant. Fibre network strength was characterised by measuring the torque of the suspension, and the dewaterability of the fibre suspension was analysed with a vacuum filtration apparatus in terms of average specific filtration resistances (SFRs).

EXPERIMENTAL

Materials

Bleached eucalyptus (*E. globulus*) chemical pulp obtained in dry lap form was disintegrated in deionized water, beaten in a PFI mill (3000 revs) according to the EN

ISO 5264-2:2002 standard, and washed with a Bauer McNett classifier in order to remove the fibre fines, i.e., pulp fragments that passed through a 200-mesh (76 μm) screen plate. The fines-free pulp was treated with acid (0.01 M HCl) before the experiments to remove metal ions and then converted to sodium form by treatment with NaHCO_3 (0.001 M) at pH 9.5 (pH adjusted with a 0.1 M NaOH solution). It was then washed with deionized water until its conductivity was less than 5 $\mu\text{S}/\text{cm}$.

The average (length-weighted) length and width of the fibres, as determined with a Metso FiberLab analyser, were 0.81 mm and 16.5 μm , respectively. The total charge as obtained from methylene blue sorption (Fardim et al. 2002) and the zeta potential measured with a Müttek SZP-06 device were -81 $\mu\text{mol}/\text{g}$ and -116 mV, respectively. The Canadian standard freeness (CSF) value of the fibres, describing the dewatering efficiency of the fines-free pulp, was 409 ml as measured according to the TAPPI Method 227 om-99.

Two cationically modified polyacrylamides, one having a low molecular weight and high charge density and other a high molecular weight and low charge density, were obtained from Kemira. CPAM I had a molecular weight of 1.5×10^6 g/mol and charge density of 4 meq/g and CPAM II 7×10^6 g/mol and 1 meq/g, respectively. The stock solutions of polymers, 5 g/dm³, were prepared by mixing polymer granules into deionized water and stirring at 200 rpm for 90 min. The stock solutions were diluted to 50 mg/dm³ before use.

The sodium chloride used as a coagulant was of p.a. grade.

Measurement of Fibre Flocculation with the Image Analysis System

The flocculation of the fibre suspension induced by the polyelectrolytes (CPAM I and II) and salt (NaCl) was studied using a digital image analysis system that consisted of digital camera, sampling beaker with a two-blade stirrer, a light source, and a computer connected to the camera. The experiments were conducted at a pulp consistency of 0.01% using various stirring rates (30-180 rpm) by adding flocculant agent to the stirred beaker and recording the images 90 seconds after the flocculation event. The images stored in the computer were analysed using an image analysis program in order to calculate the size, fractal dimension, and strength of the flocs, and the kinetic constant of flocculation as a function of time.

The maximum floc diameter, d_{max} , calculated from the floc projected area diameter, i.e., the diameter of a circle equal in area to the projected area (Honkanen et al. 2004), was used here to describe the sizes of the flocs. These are expressed as average values obtained between 90 and 120 seconds after the beginning of the experiments, as a steady-state in flocculation was achieved.

Mass fractal dimension, which reflects how the primary particles forming the floc are organised within it and indicates the density of flocs, was used to describe their compactness (Kaji and Monma 1991; Waite 1999). The three-dimensional average mass fractal dimensions of the floc populations were calculated from the two-dimensional fractal dimensions obtained from the floc projected area and maximum dimension using the equation presented by Lee and Kramer (2004).

Floc strength was characterised by means of the floc strength constant, γ , calculated from the steady-state floc sizes measured as a function of stirring rate (30-180 rpm) using the empirical Eq. (1) presented by Jarvis et al. (2006),

$$d_{\max} = c \text{ rpm}^{-\gamma} \quad (1)$$

where c is the characteristic constant and rpm is the stirring rate. We used γ , determined as the slope of the log-log plot of the steady-state floc size versus stirring rate, as a strength indicator instead of the constant c , which also correlates with strength, because it is less sensitive to the characteristic value used for floc size (Jarvis et al. 2005).

The influence of CPAM I, CPAM II, and NaCl on floc growth rate, i.e., the kinetics of fibre flocculation, was described by means of the kinetic constant, k , obtained by a best fit of the exponential Eq. (2) to the diagrams presenting maximum floc diameter as a function of time,

$$d_{\max}(t) = d_{\max}^{st} - (d_{\max}^{st} - d_{\max}^{in})e^{-kt} \quad (2)$$

where d_{\max}^{st} is the maximum steady-state floc diameter, d_{\max}^{in} is the maximum initial floc diameter and t is time.

Measurement of Fibre Network Strength

The network strengths of the flocculated fibre suspensions were evaluated in terms of apparent yield stresses, which describe the stress levels above which the viscoelastic fibre networks break down to their constituent fragments, i.e., flocs (Wikström and Rasmuson 1998). Network strength reflects the strength of individual flocs similar to a floc strength constant, and also the strength of the looser fibre network located within the interfloc space, and the friction between flocs (Swerin and Ödberg 1993).

The fibre network strength was characterised on the basis of torque measurements performed on suspensions at a pulp consistency of 0.8% at room temperature. A similar method has previously been used by Andersson et al. (1999), Jokinen et al. (2006), and Wikström and Rasmuson (1998). In the present case, a Brookfield rotary viscometer DV-1+ with modified blade spindle, as described by Karjalainen (2004), was used and a shear diagram was constructed by measuring ten replicates for suspension torque on the blade at three rotational velocities (0.3 - 1.5 rpm), from which the apparent yield stress was obtained by extrapolating the linear portion of the diagram to a zero shear rate. A detailed description of the method and apparatus used for fibre network strength measurement is given by Karjalainen (2004).

Measurement of Dewaterability of the Flocculated Fibre Suspension

Dewatering of the fibre suspension, characterised in terms of average specific filtration resistance (SFR), was measured with a vacuum filtration apparatus. The filtration apparatus consisted of a 5 dm³ sample container equipped with a changeable wire, a plastic vacuum chamber with filtrate containers, a pressure sensor and a vacuum

pump connected to the chamber via a control valve. The filtrate was split into fractions during filtration in order to take samples and record the cumulative amount of filtrate as a function of time. A schematic illustration of the vacuum filtration system is shown in Liimatainen et al. (2006). The experiments were carried out by filtering the pulp suspensions through a wire (open area 16%; 0.20 mm monofilament) under a constant pressure difference of 18 kPa at room temperature. The fluid drained without fibre mat formation at the beginning of the experiment, but a filter cake started to form on the wire in the course of time, and the thickening of the fibre network evolved into cake filtration. The fibre consistency and total volume of the suspension were 1.0% and 2000 cm³, respectively.

Average specific resistances after 9 seconds of filtration were calculated based on Eq. (3),

$$\frac{1}{A_f} \frac{dV}{dt} = \frac{\Delta p}{\eta \left(\alpha_{av} \frac{W}{A_f} + R \right)} \quad (3)$$

where dV/dt is the volumetric flow rate of the filtrate, A_f is the filtration area, Δp is the pressure difference across the fibrous mat and wire, η is the viscosity of the filtrate, α_{av} is the average specific filtration resistance of the filter cake, W is the mass of solids retained, and R is the filtration resistance of the wire. A detailed method for determining the SFR has been presented by Wakeman and Tarleton (1999), for instance. The effect of particle retention was taken into account in the values presented here.

RESULTS AND DISCUSSION

Measurement of Fibre Flocculation with the Image Analysis System

Steady-state floc size and mass fractal dimension

The influence of the CPAMs and salt on the structure of the fibre flocs was characterised in terms of the average steady-state floc size and mass fractal dimension as determined from the image analysis. The flocs produced by CPAMs and salt differed significantly in size, in that CPAM II resulted in large flocs more than twice the size observed in the case of salt and 1.5 times larger than with CPAM I (Fig. 1). NaCl had a significant effect on floc size here, because the background electrolyte concentration was very low and NaCl was able to screen electrostatic repulsion between fibres. Steady-state floc size showed fast initial growth at low CPAMs doses, but remained almost constant at higher doses. In the case of salt, the floc size increased more slowly as a function of dose and plateau levels of floc size were achieved at high doses.

The mass fractal dimensions, which are shown in Fig. 2 as a function of CPAM and NaCl dosages, followed similar trends to the floc sizes described above, showing fast initial growth at low doses, indicating a powerful increase in floc density before reaching plateau levels. CPAM II resulted in significantly higher floc densities, i.e. higher mass fractal dimensions, than either CPAM I or NaCl, which increased floc density to similar extents. As the stirring rate of suspension was increased, floc density in terms of mass fractal dimension decreased linearly with the CPAM doses, as shown in Fig. 3.

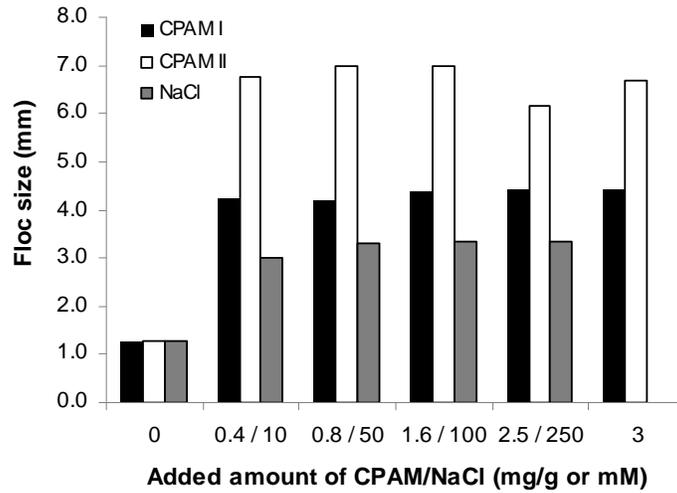


Fig. 1. Average steady-state floc size as a function of CPAM and NaCl dosage.

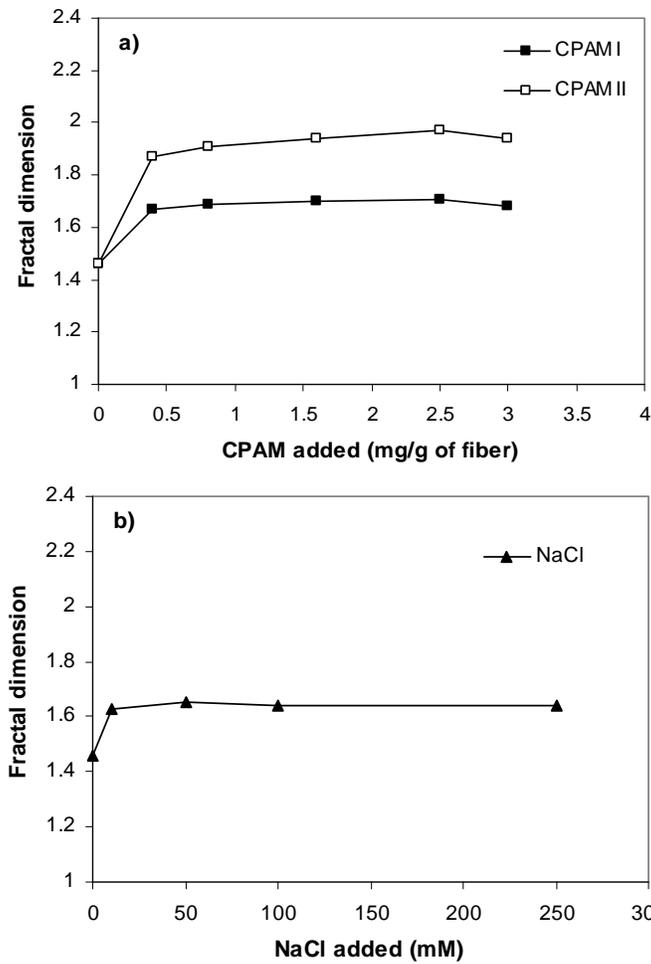


Fig. 2. Steady-state fractal dimension as a function of: (a) CPAM dosages, and (b) NaCl dosage.

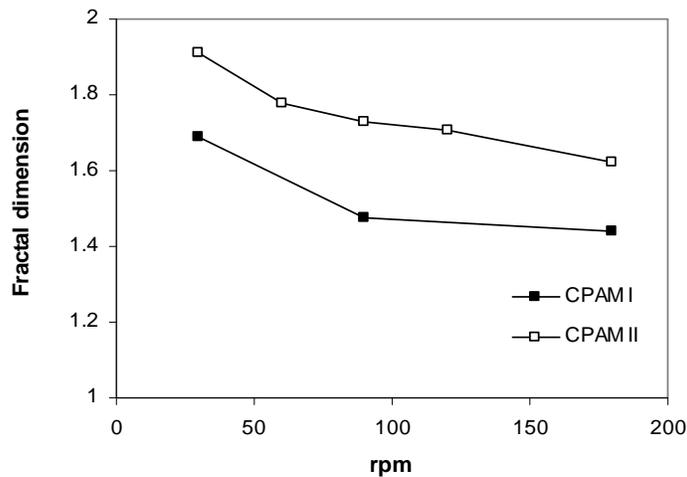


Fig. 3. Steady-state fractal dimension as a function of stirring rate in the presence of CPAMs (0.8 mg/g).

Floc strength

The steady-state floc sizes presented as a function of stirring rate in Fig. 4 show that the flocs produced by CPAM I and salt disintegrated rapidly as the stirring rate was increased and that a constant floc size was achieved beyond 60 rpm, being close to the size of the individual fibres and therefore indicating that practically all the flocs had been ruptured. This is consistent with previous findings that organic flocs will break up when exposed to velocity changes higher than 0.1 m/s, which corresponds to a stirring rate of 65 rpm in our system (Honkanen et al. 2004). The flocs produced by CPAM II, however, appeared to be considerably more resilient to breakage, since moderately large flocs still existed at the highest shear rates. The corresponding values for the floc strength constant (γ) calculated from Eq. (1) are shown in Table 1.

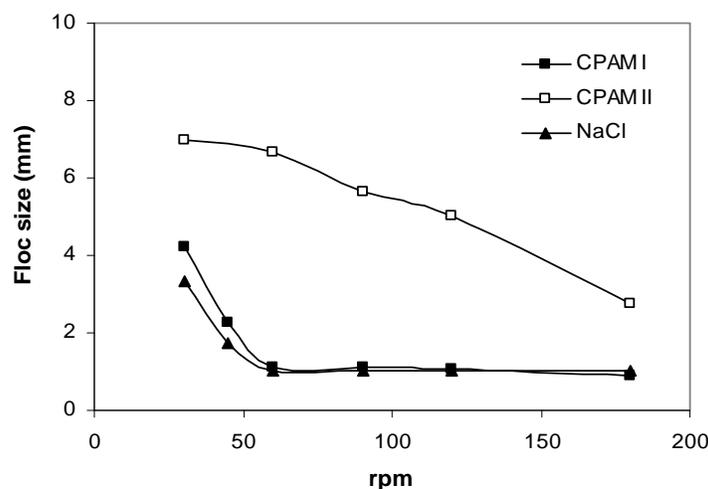


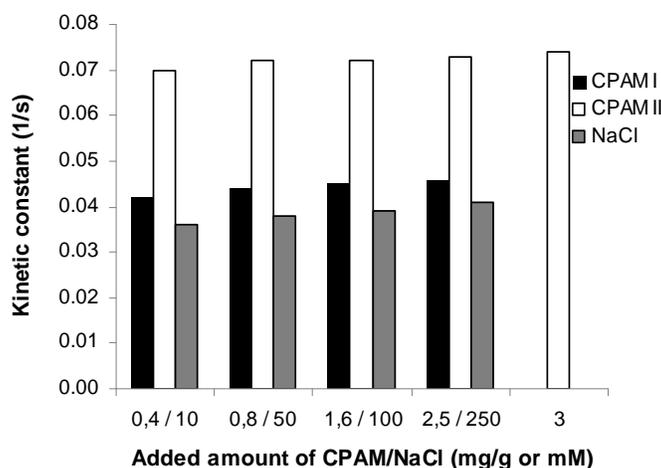
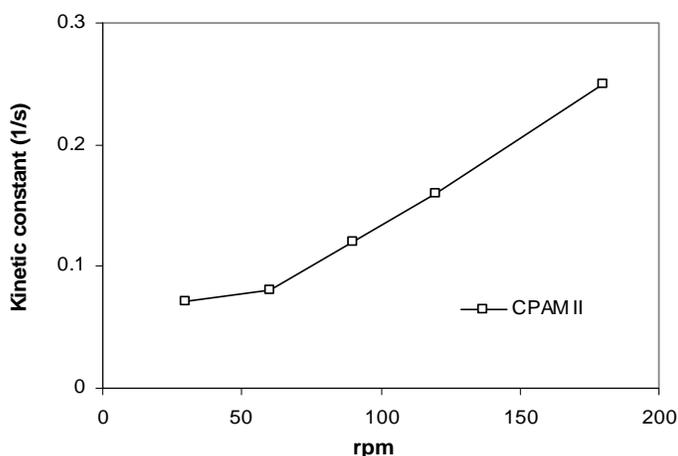
Fig. 4. Steady-state floc size as a function of stirring rate in the presence of CPAMs (0.8 mg/g) and NaCl (100 mM).

Table 1. The Floc Strength Constant γ in the Presence of CPAMs (0.8 mg/g) and NaCl (100 mM)

Chemical	Floc strength constant, γ
CPAM I	1.89
CPAM II	0.83
NaCl	1.72

Kinetics of flocculation

The kinetic constants presented as a function of CPAM and NaCl dosage in Fig. 5 show that CPAM II caused the fastest floc growth, i.e., it had the highest value for the kinetic constant, a finding which was also supported by visual observations. The flocculation induced by CPAM I and NaCl was considerably slower, CPAM I having only slightly higher kinetic constant values than NaCl. The floc growth rate was only slightly affected by the flocculation agent dosage, but the increased shear led to a marked increase in the kinetic constants measured for CPAM II (Fig. 6).

**Fig. 5.** Kinetic constant as a function of CPAM and NaCl dosages.**Fig. 6.** Kinetic constant as a function of stirring rate.

Measurement of Fibre Network Strength

The network strengths, evaluated in terms of apparent yield stresses, are shown in Fig. 7 (presented relative to the value for untreated pulp, i.e., pulp without flocculation agents). Network strength behaved in a similar manner to the floc strength constant, showing that CPAM I and NaCl had a significantly smaller impact on floc strength than CPAM II, which already led to values three times higher than in the reference pulp with the lowest dosage. The network strengths induced by CPAM I and NaCl were almost constant as a function of dosage, whilst those for CPAM II increased linearly up to a dosage of 2.5 mg/g.

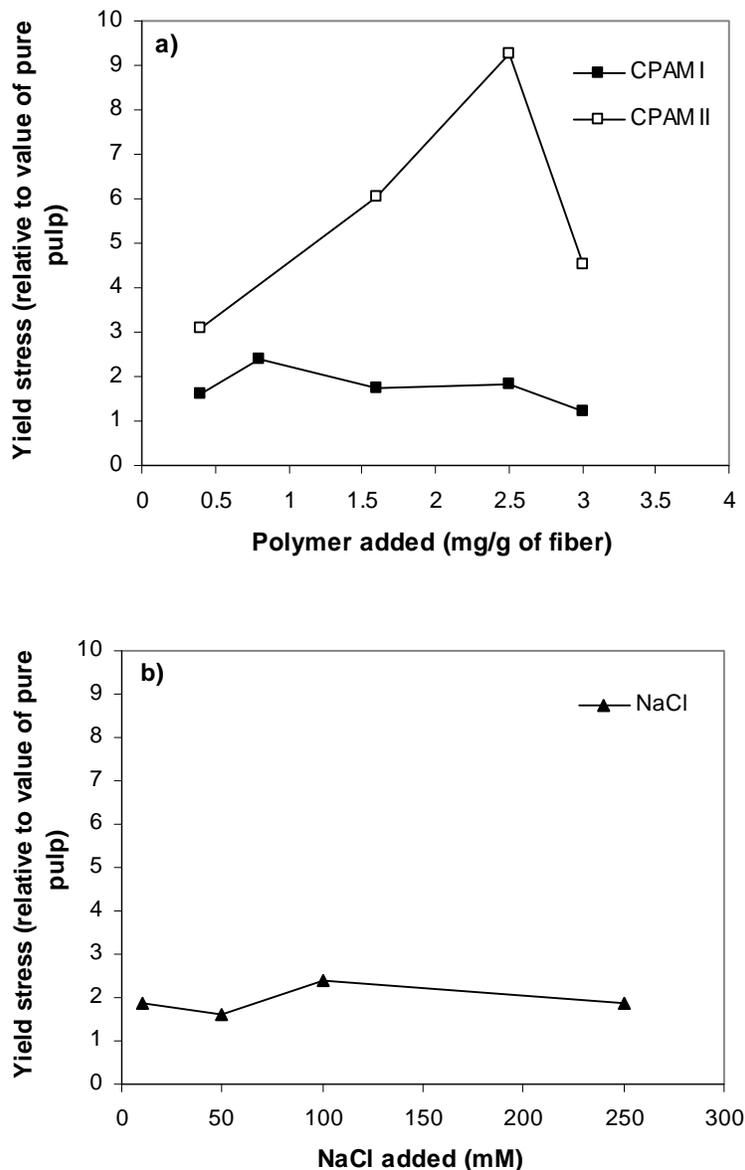


Fig. 7. Yield stress of the fibre suspension as a function of: (a) CPAM dosages, and (b) NaCl dosage.

Measurement of the Dewaterability of Flocculated Fibre Suspensions

The effect of flocculation agents on dewatering, i.e., removal of free water from the pulps, was analysed by measuring the average specific filtration resistance with a vacuum filtration apparatus. CPAM II, which had the highest impact on floc properties and the flocculation kinetics, also led to the lowest SFR values, i.e. it increased dewatering more than did CPAM I or NaCl (Fig. 8). Interestingly, CPAM I promoted more dewatering than NaCl, despite the fact that these chemicals had a similar effect on many floc properties. Filtration resistance was observed to decrease very sharply as a function of flocculant dosage with both CPAM grades up to doses of about 1 mg/g, after which it remained almost constant.

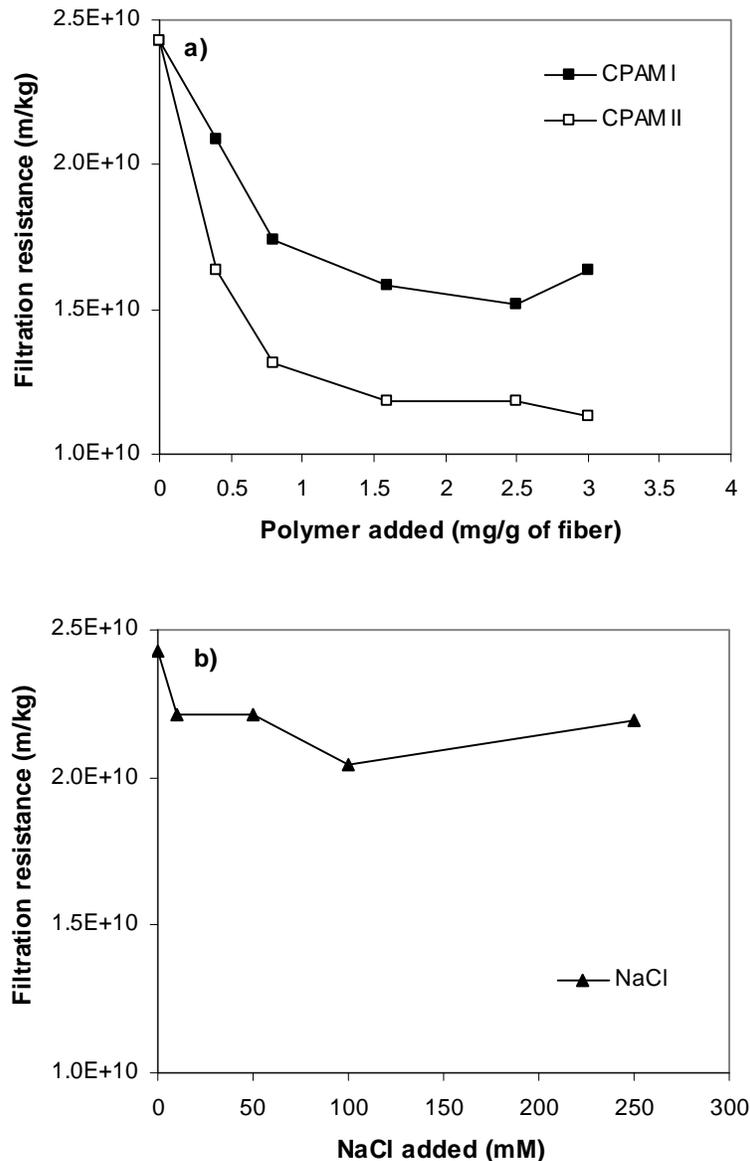


Fig. 8. Filtration resistance of the fibre suspension as a function of: (a) CPAM dosages, and (b) NaCl dosage.

Effect of Polymeric Flocculants and Salt on Floc Morphology

The properties of the fibre flocs were observed to be significantly affected by properties of flocculation agents. The decrease in floc size in rank order of CPAM II > CPAM I > NaCl is consistent with previous results stating that the binding strength of flocculation agents and their influence on floc size decrease in the order: bridging polymers > patching polymers > neutralisation agents (Lindström 1989). In addition, Saveyn et al. (2005) and Swerin and Ödberg (1993) have shown that the degree of flocculation increases with the molecular weight of the CPAM. Steady-state floc size showed fast initial growth at low doses of CPAMs, but remained almost constant at higher doses, as also observed by Zhao (2004) with sludge flocs and Wågberg and Lindström (1987b) with pulp fibres. In the absence of chemical additives, flocculation caused by purely mechanical entanglement between the fibres was weak, because the measured average floc size, 1.26 mm, differed only slightly from the average length of individual fibres, 0.81 mm. Both mass fractal dimension, the values of which were close to those previously reported for sludge flocs by Zhao (2003), and floc strength followed similar trends to the floc sizes. Rasteiro et al. (2008) have previously found, however, that CPAMs with a high charge density (patching polymers) produce denser flocs in calcium carbonate particle suspensions than bridging agents. The values of the strength constants were higher than those reported earlier for sludge and mineral flocs (Jarvis et al. 2005), indicating low strength in the fibre flocs and their sensitivity to rupture by shearing, which may be associated with differences in fibre floc breakage and cohesion mechanism.

The impacts of flocculants on floc properties may be associated with how flocculation agents affect fibre-fibre interactions within the resulting flocs, which is in turn related to the structure of the bonding layers of the flocculants. The polymer layers formed by polyelectrolytes with a high molecular weight and low charge density differ significantly from those produced by ones with a low molecular weight and high charge density. This is due to the fact that the high molecular weight polymers, i.e., bridging polymers, have an extended conformation on the fibre surfaces, with polymer chains protruding a long distance out from the surface, whilst low molecular weight polymers adsorb more readily to a flat conformation and thus form much thinner surface layers (Stenius 2000). The joints produced by bridging polymers can thus be expected to be thicker and more flexible than the bonds formed by low molecular weight polymers (Salmi et al. 2007; Asselman 2000). Salmi et al. (2007) have also reported that the attractive forces caused by bridging agents extend longer distances from the surface than those produced by low molecular weight polymers, being in the range 20-30 nm for a high molecular weight CPAM and about 10 nm for the low charge density polyDADMAC on the surfaces of cellulose spheres. The higher floc and fibre network strength measured here for CPAM II than that for CPAM I suggest that a thick polymer layer has a better ability to elongate, withstand shearing, and store kinetic energy than the thin layer formed by CPAM I, and that as a consequence the fibres were better able to move relative to each other without bond-breakage. The alteration in fractal dimension as a function of shearing also supports this assumption, since a higher reduction in the fractal dimension was obtained with CPAM II than with CPAM I, just as the shear was increased from 30 to 180 rpm, which suggests higher flexibility of interfibre joints

formed by CPAM II. It is also likely that the fibre flocculation caused by CPAM I was mainly based on van der Waals attraction and the thin bonding polymer layer made only a slight additional contribution to it, because the strength of the flocs induced by NaCl was observed to be similar to that achieved with CPAM I.

In addition to the highest strength, the flocs produced by CPAM II were also the largest and had the highest density, as described by the fractal dimension. This suggests that the strength of individual polymer joints in the bonding layer was highest and/or the number of surface connecting joints was most abundant with CPAM II, because strong bonds and a high number of joints will increase floc size due to increased shear resistance and lead to floc compaction due to high floc adhesion. This issue will be considered further in the next section, dealing with the kinetics of flocculation.

Relationship between Flocculation Kinetics and Floc Morphology

Because CPAM II had the highest impact on both floc morphology and the flocculation rate, this raises questions regarding the phenomena that lie behind these effects and the role of the flocculation kinetics in floc properties. Based on previous results dealing with mineral particle flocculation (Amal et al. 1990), our hypothesis was that fast flocculation leads to the formation of weak, loose fibre flocs, due to limited time available for fibres to restructure and come closer to each other. This was not observed here, however, but rather the densest flocs were formed at the highest flocculation rate.

The flocculation kinetics originate from competing processes of fibre flocculation and floc break-down, which are characterised by the flocculation and detachment rate constants, k_f and k_d , respectively. These have in turn been attributed to shear and physicochemical conditions in the suspension (van de Ven 1993), where the shear conditions describe the frequency of collisions between particles and polymers and both affect polymer adsorption to fibre surfaces and collisions that lead to floc formation by the polymer-coated fibres. As the flocs increase in size, they start to break down on account of the shear forces applied to them and dynamic equilibrium comes to exist between floc formation and degradation.

The influence of flocculation agents on the kinetics of floc formation is related to their ability to modify the flocculation efficiency, η , which describes the ratio between the repulsive and attractive forces that exist between particles. The flocculation rate constant of fibres, k_f , is defined as (van de Ven 1993),

$$k_f = \eta k_{fast} \quad (4)$$

where k_{fast} is the fast flocculation rate in the absence of any repulsive colloidal forces. Since the interaction of similarly charged fibres is repulsive, i.e. $\eta < 1$, flocculation agents may reduce this repulsion, causing η to be closer to 1, which would in turn increase the flocculation rate. Actually, η has been found to be close to 1 for cationic polyelectrolytes, because of neutralisation of the negative surface charges and/or the formation of a polymer layer of thickness δ that is greater than the double layer thickness of the charged surfaces, κ^{-1} (Petlicke and van de Ven 1992). The same applies with NaCl if the concentration exceeds the critical coagulation concentration (CCC) of the fibres, as was the case in our experiments. These findings indicate that differences in flocculation rate are more likely to be related to floc break-down phenomena than to floc formation.

The rate of floc break-down under constant shear conditions may be attributed to the interfibre bond strength, E_{ff} (van de Ven 1993),

$$k_d = \omega e^{-E_{ff}/k_B T} \quad (5)$$

where ω describes the shear conditions, k_B is the Boltzmann constant, and T is the temperature. Hence the ability of the flocculation agents to reduce the floc breakage rate depends on their influence on the fibre-to-fibre bond strength, which is in turn associated with the number of polymer joints on the fibre surfaces and with the fibre-to-polymer bond strength, E_{fp} .

What, then, was the reason for the higher flocculation rate achieved with CPAM II than with CPAM I or salt? Earlier results based on the measurement of pull-off forces between CPAM-coated cellulose spheres by atomic force microscopy strongly support the assumption that the E_{fp} of CPAM II will be significantly higher than that of CPAM I. Notably higher pull-off forces have been obtained previously for low-charged, high molecular weight CPAMs than for highly charged, lower molecular weight CPAMs (Salmi et al. 2007), an observation which also supports our floc strength measurements. Besides the higher E_{fp} , the rate of polymer adsorption affecting the surface coverage of the CPAM (number of polymer joints on the surfaces), was presumably also higher with CPAM II, as it had a slightly higher collision rate, k_o , due to its larger size. The collision rate between fibres and the polymer under orthokinetic conditions, based on Schmoluchowski's kinetics, may be described by the formula (Petlicki and van de Ven 1992),

$$k_o = \frac{4}{3}(a_p + a_f)(a_p + b_f)^2 \quad (6)$$

where a_p is the polymer radius ($a_{CPAM I} = 95$ nm and $a_{CPAM II} = 201$ nm (Asselman 1999)), a_f is the fibre half-length and b_f is the radius of the fibre cross-section, which shows that the k_o for CPAM II is about 2.6% higher than that for CPAM I. It is likely, however, that actual surface coverage of CPAM II was higher than this given value, since CPAM I was easily detached due to its low fibre-to-polymer bond strength. Also, the increase in polymer dose promoted floc growth, because it increased the surface coverage of the polymers, i.e., the number of polymer joints on the fibre surfaces. Hence these findings indicate that the high flocculation rate of CPAM II is attributable to its high bonding strength, E_{fp} , which reduces floc breakage, i.e., reduces k_d . This high E_{fp} also has an impact on floc morphology, i.e. floc strength, size, and density.

Thus, the flocculation kinetics of fibres does not appear to be a key factor determining fibre floc properties, but rather it follows from the high bonding ability of the flocculation agent, which also lies behind the high floc density and size. As seen in Fig. 9, which presents the kinetic constant of flocculation as a function of fractal dimension and floc size, good correlations ($R^2 = 0.94$) exist between these variables, supporting the argument that they are interlinked. One implication of these results is that the effect of flocculation agent on floc morphology, and in particular on the flocculation kinetics, which is a crucial factor in many high-speed separation processes such as fibre

suspension filtration during sheet formation, could possibly be evaluated by measuring the particle-polymer bond strength.

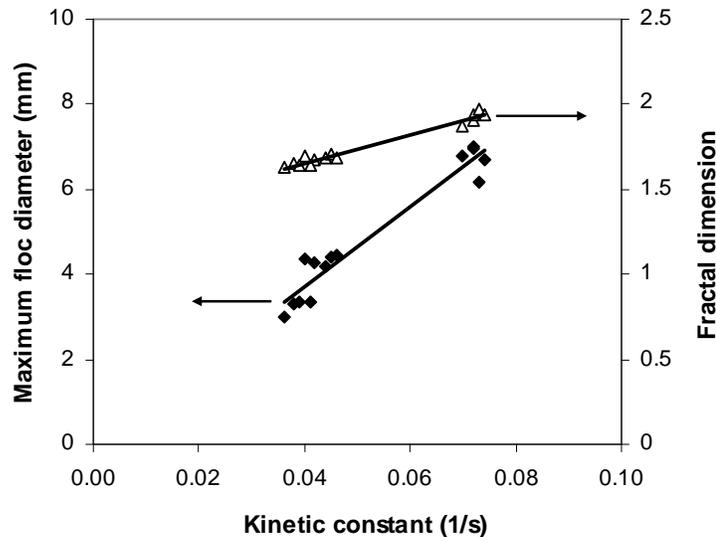


Fig. 9. Floc size and fractal dimension as a function of the kinetic constant.

Influence of Floc Morphology on the Dewaterability of a Fibre Suspension

CPAM II was found to produce the largest flocs, which had higher strength and density in terms of fractal dimension than those resulting from CPAM I or NaCl. It was also found that the suspensions treated with CPAM II had better dewaterability than those treated with CPAM I or salt, which suggests that floc properties are closely related to the dewaterability of a pulp suspension.

The dewaterability of pulp fibre suspension has been attributed to the fibre network porosity and its distribution during filtration, as stated by the Kozeny-Carman equation, which relates the physical properties of a suspension, including its porosity, to the permeability of the filter cake, K (Kozeny 1927; Carman 1937). Flocculation modifies the fibre network porosity by producing local density variations in the continuous network of fibres, resulting in relatively compactly packed fibre flocs with low porosity and a looser interfloc network having large voids. Because the high flow resistance of the small pores inside the flocs hinders water flow, the fluid tends to flow through the larger pores of the interfloc space (Britt and Unbehend 1976; Saveyn et al. 2005; Liimatainen et al. 2009). This “easiest path” mechanism probably promoted fast water flow through the large voids around the dense flocs produced by CPAM II, resulting in a low filtration resistance, because the porosity of the flocs was low. Therefore increased floc density, which follows from the high fibre-to-polymer bond strength, E_{fp} , seems to have a positive effect on dewaterability, despite the formation of loose aggregates has previously suggested to reduce biosolids dewatering (Waite 1999). The correlation between measured floc densities and filtration resistances is illustrated in Fig. 10.

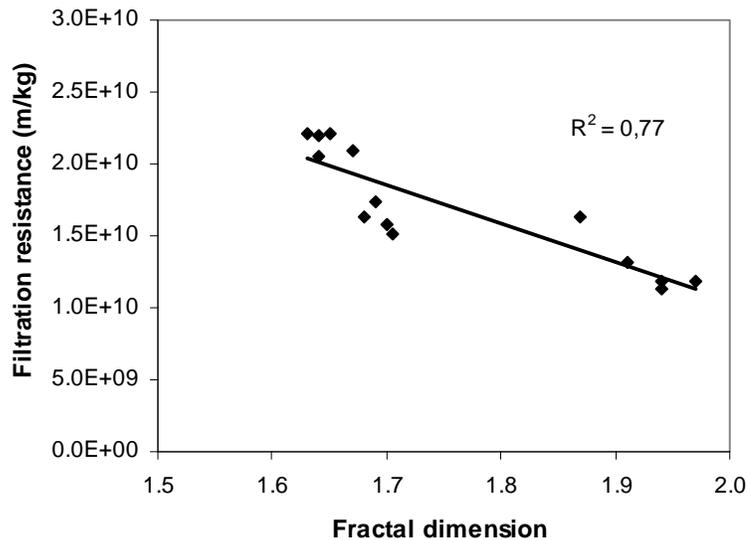


Fig. 10. Filtration resistance of fibre suspension as a function of floc fractal dimension.

While the floc density expressed in terms of fractal dimension reflects the internal porosity of the flocs, the porosity of the interfloc space is described by their packing structure in the cake. Floc packing is in turn related to the size and shape of the flocs, as large and irregular flocs cause the formation of loose structures that have good dewatering properties due to large voids. This is also consistent with our results, since an increase in floc size and density was seen to reduce the filtration resistance of the fibre suspension, i.e., increase the dewaterability of the pulp. The flocs produced by CPAM II were also observed visually to be the most irregular, which might have promoted their loose packing and good dewatering. The high floc and network strength gained with CPAM II presumably increased the ability of filter cake to resist compression and pore collapse, and it will therefore also have reduced the sealing of the fluid passageways, particularly on the surface of the wire, where fibre squeezing could blind the filter fabric (Wildfong et al. 2000; Hubbe and Heitmann 2007).

It is probable that there are also other important factors related to fibre flocculation that affect dewaterability of fibre suspensions, because CPAM I was found to promote more dewatering than NaCl, despite the fact that these chemicals had a similar effect on many floc properties.

CONCLUSIONS

1. The kinetics of fibre flocculation does not appear to be a key factor determining fibre floc morphology, but rather it follows from the high bonding ability of the flocculation agent, which also lies behind the high floc density and size.
2. Properties of flocculation agents have a significant impact on floc morphology, which is related to structure of the bonding layer and the interfibre bonding strength of the flocculant. A high molecular weight, low charge density CPAM, having high fibre-to-

polymer bonding strength, will induce the formation of larger and denser flocs than a low molecular weight, high charge density CPAM or salt, and these flocs will have a greater strength by virtue of the ability of the thick polymer layer to elongate and withstand shearing.

3. Dewaterability in a fibre suspension is promoted by the increased floc density originating from the high bonding strength of the flocculation agent, since this promotes fast water flow through the large voids around the dense flocs. Large, irregular flocs in turn induce the formation of loose floc packing, which further improves dewatering due to the larger voids. Increased floc strength reduces sealing of the fluid passageways, particularly on the surface of the wire, where fibre squeezing could blind the filter fabric.

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REFERENCES CITED

- Amal, R., Raper, J. A., and Waite, T. D. (1990). "Fractal structure of hematite aggregates," *J. Colloid Interface Sci.* 140(1), 158-168.
- Andersson, S. R., Ringnér, J., and Rasmuson, A. (1999). "The network strength of non-flocculated fibre suspensions," *Nord. Pulp Pap. Res. J.* 14(1), 61-70.
- Antunes, E., Garcia F. A. P., Ferreira, P., Blanco, A., Negro, C., and Rasteiro, M. G. (2008). "Use of new branched cationic polyacrylamides to improve retention and drainage in papermaking," *Ind. Eng. Chem. Res.* 47(23), 9370-9375.
- Asselman, T. (1999). *Hetero-flocculation of wood fibres and fines induced by polymers and microparticles*, Doctoral Thesis, McGill University, Canada.
- Asselman, T., and Garnier, G. (2000). "Mechanism of polyelectrolyte transfer during heteroflocculation," *Langmuir* 16(11), 4871-4876.
- Boller, M., and Blaser, S. (1998). "Particles under stress," *Water Sci. Technol.* 37(10), 9-29.
- Britt, K. W., and Unbehend, J. E. (1976). "New methods for monitoring retention," *Tappi* 59(2), 67-70.
- Carman, P. C. (1937). "Fluid flow through granular beds," *Trans. Inst. Chem. Eng.* 15, 150-166.
- Fardim, P., Holmbom, B., Ivaska, A., Karhu, J., Mortha, G., and Laine, J. (2002). "Critical comparison and validation of methods for determination of anionic groups in pulp fibres," *Nord. Pulp Pap. Res. J.* 17(3), 346-351.
- Honkanen, M., Saarenrinne, P., and Reunanen, J. (2004). "Characterization of turbulent flow and floc morphology in a flocculation process: PIV/digital imaging

- experiments,” *3rd International Symposium on Two-Phase Flow Modelling and Experimentation*, 22-24 September, Pisa, Italy, paper cvg11.
- Hubbe, M. A. (1987). “Detachment of colloidal hydrous oxide spheres from flat solids exposed to flow. 3. Forces of adhesion,” *Colloids Surf.* 25(2-4), 311-324.
- Hubbe, M. A. (2000). “Reversibility of polymer-induced fiber flocculation by shear. 1. Experimental methods,” *Nord. Pulp Pap. Res. J.* 15(5), 545-553.
- Hubbe, M. A., and Heitmann, J. A. (2007). “Review of factors affecting the release of water from cellulosic fibers during paper manufacture,” *BioRes.* ([http: www.bioresources.com](http://www.bioresources.com)), 2(3), 500-533.
- Hubbe, M. A., Heitmann J. A., and Cole, C. A. (2008). “Water release from fractionated stock suspensions. Part 2. Effects of consistency, flocculants, shear, and order of mixing,” *Tappi J.* 7(8), 14-19.
- Jarvis, P., Jefferson, B., Gregory, J., and Parsons, S.A. (2005). “A review of floc strength and breakage,” *Water Res.* 39(14), 3121-3137.
- Jarvis, P., Jefferson, B., and Parsons, S.A. (2006). “Floc structural characteristics using conventional coagulation for a high doc, low alkalinity surface water source,” *Water Res.* 40(14), 2727-2737.
- Jokinen, H. M., Niinimäki, J., and Ämmälä, A. (2006). “The effect of anionic polymer additive on fractionation of paper pulp,” *Appita* 59(6), 459-464.
- Kaji, H., and Monma, K. (1991). “Fractal analysis of flocculation in pulp” *Tappi 1991 International Paper Physics Conference*, 22-26 September, Hawaii, 291-297.
- Karjalainen, M. (2004). *Measurement of fibre suspension network strength*, M.Sc. Thesis, University of Oulu, Finland, 106.
- Kozeny, J. (1927). “Über kapillare Leitung der Wasser im Boden,” *Sitzungsber. Akad. Wiss.* 136, 271-306.
- Lee, C., and Kramer, T. (2004). “Prediction of three dimensional fractal dimensions using two-dimensional properties of fractal aggregates,” *Adv. Coll. Int. Sci.* 112(1), 49-57
- Liimatainen, H., Kokko, S., Rousu, P., and Niinimäki, J. (2006). “Effect of PCC filler on dewatering of fiber suspension,” *Tappi J.* 5(11), 11-16.
- Liimatainen, H., Haavisto, S., Haapala, A., and Niinimäki, J. (2009). “Influence of adsorbed and dissolved carboxymethyl cellulose on fibre suspension dispersing, dewaterability, and fines retention,” *BioRes.* ([http: www.bioresources.com](http://www.bioresources.com)), 4(1): 321-340.
- Lindström, T. (1989). “Some fundamental chemical aspects on paper forming,” In: Baker, C.F., and Punton, V.W. *Fundamentals of papermaking*, London, 311-412.
- McFarlane, A., Bremmel, K., and Addai-Mensah, J. (2006). “Improved dewatering behavior of clay minerals dispersions via interfacial chemistry and particle interaction optimization,” *J. Colloid Interface Sci.* 293, 116-127.
- McFarlane, A., Yeap, K. Y., Bremmell, K., and Addai-Mensah, J. (2008). “The influence of flocculant adsorption kinetics on the dewaterability of kaolinite and smectite clay mineral suspensions,” *Colloids Surf. A* 317(1-3), 39-48.
- Nasser, M. S., and James, A. E. (2006). “The effect of polyacrylamide charge density and molecular weight on the flocculation and sedimentation behaviour of kaolinite suspensions,” *Sep. Purif. Technol.* 52(2), 241-252.

- Nasser, M. S., and James A. E. (2007). "Effect of polyacrylamide polymers on floc size and rheological behaviour of kaolinite suspensions," *Colloids Surf. A* 301(1-3), 311-322.
- Petlicki, J., and van de Ven, T. G. M. (1992). "Shear-induced deposition of colloidal particles on spheroids," *J. Colloid Interface Sci.* 148(1), 14-22.
- Rasteiro, M. G., Garcia, F. A. P., Ferreira, P., Blanco, A., Negro, C., and Antunes, E. (2008). "The use of LDS as a tool to evaluate flocculation mechanisms," *Chem. Eng. Process.* 47(8), 1323-1332.
- Salmi, J., Österberg, M., Stenius, P., and Laine, J. (2007). "Surface forces between cellulose surfaces in cationic polyelectrolyte solutions: The effect of polymer molecular weight and charge density," *Nord. Pulp Pap. Res. J.* 22(2), 249-257.
- Saveyn, H., Meersseman, S., Thas, O., and Van der Meeren, P. (2005). "Influence of polyelectrolyte characteristics on pressure-driven activated sludge dewatering," *Colloids Surf. A* 262(1-3), 40-51.
- Schmid, C. F., and Klingenberg, D. J. (2000). "Properties of fiber flocs with frictional and attractive interfiber forces," *J. Colloid Interface Sci.* 236(1), 136-144.
- Sengupta, D. K., Kan, D., Al Taweel, A. M., and Hamza, H. A. (1997). "Dependence of separation properties on flocculation dynamics of kaolinite suspension," *Int. J. Miner. Process.* 49(1), 73-85.
- Stenius, P. (2000). "Macromolecular, surface and colloid chemistry," In: Gullichsen, J., and Paulapuro, H. (ed.) *Forest Products Chemistry*, Fapet Oy, Helsinki, 170-276.
- Swerin, A. (1998). "Rheological properties of cellulosic fibre suspensions flocculated by cationic polyacrylamides," *Colloids Surf. A* 133(3), 279-294.
- Swerin, A., and Ödberg, L. (1993). "Flocculation and floc strength in suspensions flocculated by retention aids," *Nord. Pulp Pap. Res. J.* 8(1), 141-147.
- Turchiuli, C., and Fargues, C. (2004). "Influence of structural properties of alum and ferric flocs on sludge dewaterability," *Chem. Eng. J.* 103(1-3), 123-131.
- van de Ven, T. G. M. (1993). "Particle deposition on pulp fibers –The influence of added chemicals," *Nord. Pulp Pap. Res. J.* 8(1), 130-135.
- Waite, T. D. (1999) "Measurement and implications of floc morphology in water and wastewater treatment," *Colloids Surf. A* 151, 27-41.
- Wakeman, R. J, and Tarleton, E.S. (1999). *Filtration-Equipment Selection Modelling and Process Simulation*, Elsevier Advanced Technology, UK, 55-96.
- Wikström, T., and Rasmuson, A. (1998). "Yield stress of pulp suspensions. The influence of fibre properties and processing conditions," *Nord. Pulp Pap. Res. J.* 13(3), 243-246.
- Wildfong, V. J., Genco, J. M., Shands, J. A., and Bousfield, D. W. (2000). "Filtration mechanics of sheet forming. Part II. Influence of fine material and compression," *J. Pulp Paper Sci.* 26(8), 280-283.
- Wu, C. C., Wu, J. J., and Huang, R. Y. (2003a). "Floc strength and dewatering efficiency of alum sludge," *Adv. Environ. Res.* 7(3), 617-621.
- Wu, C. C., Wu, J. J., and Huang, R. Y. (2003b). "Effect floc strength on sludge dewatering by vacuum filtration," *Colloids Surf. A* 221(1), 141-147.
- Wågberg, L., and Lindström, T. (1987a). "Kinetics of polymer-induced flocculation of cellulosic fibres in turbulent flow," *Colloids Surf.* 27(1-3), 29-42.

- Wågberg, L., and Lindström, T. (1987b). "Flocculation of cellulosic fibers by cationic polyacrylamides with different charge densities," *Nord. Pulp Pap. Res. J.* 2(4), 152-160.
- Yu, J., Wang, D., Ge, X., Yan, M., and Yang, M. (2006). "Flocculation of kaolin particles by two typical polyelectrolytes: A comparative study on the kinetics and floc morphologies," *Colloids Surf. A* 290(1-3), 288-294.
- Zhao, Y.Q. (2003). "Correlations between floc physical properties and optimum polymer dosage in alum sludge conditioning and dewatering," *Chem. Eng. J.* 92(1), 227-235.
- Zhao, Y.Q. (2004). "Settling behaviour of polymer flocculated water-treatment sludge II: effects of floc morphology and floc packing," *Sep. Purif. Technol.* 35(3), 175-183.

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