REVIEW ARTICLE **Lignocellulose**

A Review of Ways to Adjust Papermaking Wet-End Chemistry: Manipulation of Cellulosic Colloidal Behavior

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This article reviews various adjustments in chemical additives and process conditions that can be used in the course of papermaking to manipulate either the efficiency of the process or the attributes of the resulting paper. Published studies show that the effects of certain chemical additives to the fiber suspension can be understood based on the forces of interaction between surfaces, *i.e.* the colloidal forces. There are opportunities to use such concepts to optimize the efficiency of retention of fine particles and the rate of water release during papermaking. It is proposed that – for easier understanding – the papermaking process should be viewed as a series of pairwise interactions, for which the outcomes depend on the ionic charges of surfaces, the hydrophobic or hydrophilic character of those surfaces, the balance of charges of dissolved polyelectrolytes, and conditions of hydrodynamic shear inherent in the unit operations of papermaking.

Keywords: Surface charge; Zeta potential; Cationic demand; Colloidal stability; Coagulation; Flocculation; Adsorption

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INTRODUCTION

Papermaking can be defined as the preparation of a mixture of cellulosic fibers, small particulate materials, and water-soluble chemicals, followed by the removal of water in the course of forming the material into a sheet. Over the course of many years, papermaking practices have evolved in order to achieve efficient retention of the fine particles, a sufficiently rapid rate of release of water from the fibers, and also a sufficiently uniform paper sheet. Substantial benefits in terms of process efficiency and product quality are being achieved every day in paper mills around the world by the addition of well-selected amounts and types of chemical additives in optimized sequences. The way that many of these chemical additives function is by influencing the short-range forces between the surfaces of solids in the suspension. This review article considers various processing conditions, chemical treatments, and strategies that can be used in a systematic manner to make adjustments to these short-range forces.

The term “colloidal behavior” refers to whether the various small particles and fibers in a suspension tend to stick together on contact or whether they tend to remain dispersed (Hiemenz and Rajagopalan1997; Hubbe and Rojas 2008). The term “stable” is used to denote systems in which the particles remain singly dispersed within a time period of interest. The term “unstable” implies that more and more of the particles will tend to stick together over the period of interest. “Coagulation” denotes a process in which suspended particles are destabilized by manipulation of the surface charges. Alternatively, the term "flocculation" means that agglomeration or deposition of the suspended particles is brought about by very-high-mass polyelectrolytes. As will be discussed in the course of this review, at certain points in the papermaking process it is preferred to have a colloidally stable system, favoring good storage conditions, efficient mixing, and avoidance of deposition problems. However, at another point of the processthe same papermakers aim to retain fine particles onto fiber surface by destabilization of the colloidal system (Hubbe and Rojas 2005). Such a transformation can be brought about by manipulation of the system by adjustments to the flows of chemical additives. The goal of this article is to review various studies that have shed light on how adjustments in chemical conditions can be implemented in a strategic way to achieve desired goals in terms of paper machine operating efficiency and product quality.

Control Variables

In theory, there are a wide range of aqueous conditions that could be used by papermakers to make routine, frequent adjustments in colloidal stability. But in fact, only a few of them are in common use in paper machine applications. To simplify later discussion it makes sense to quickly summarize the main parameters that papermakers either use or do not commonly use as means of process control. Also one can point to reasons that papermakers prefer certain control variables in preference to others.

As will become clear from published studies considered in the course of this article, the control variables mainly being used in papermaking operations involve the adjustments to the dosages of various water-soluble additives. In particular, the dosages of the following types of additives are commonly used by papermakers as tools to control colloidal behavior (Table 1):

Table 1. Papermakers' Preferred Control Variables

Type of additive for which the dosage is being actively controlled	**Reasons why the variable is preferred as a control variable by papermakers**	**Some key citations**
Multivalent cations, *e.g.* from $Al_2(SO_4)_3$ ("alum"), poly-aluminum chloride, *etc.*	Relatively inexpensive; capable of decreasing or reversing negative surface charges; induces coagulation and lowers water retention by the fibers	Arnson & Stratton 1983; Strazdins 1989; Alfano *et al.* 1999; Cadotte *et al.* 2007
High-charge cationic polyelectrolytes, *e.g.* polyamines	Very effective for reducing or reversing negative surface charges, even when the pH is too high for aluminum products to work well	Horn & Melzer 1975; Wågberg & Ödberg 1991; Pèlach*et al.* 2001
Very-high-mass linear polyelectrolytes, *e.g.* cationic or anionic acrylamide copolymers	Can induce strong flocculation with moderate resistance to hydrodynamic shear at economical dosages	Gregory 1973; Pelzer 2008; Hubbe *et al.* 2009; Mosse *et al.* 2012
Nano-sized anionic particles such as colloidal silica, montmorillonite, or related products	Provides way to cause contraction of cationic polyelectrolyte coils late in the process, giving rise to gentle flocculation and strong dewatering	Langley & Litchfield 1986; Andersson & Lindgren 1996; Hubbe 2005a

In addition to the reasons shown in Table 1, papermakers may prefer certain classes of ionically charged water-soluble or dispersible materials for reasons of their relatively low cost, ease of handling, lack or toxicity, ready availability, and also based on how familiar they are with certain additives.

Table 2 shows a contrasting list, consisting of variables or additives that certainly would influence the colloidal behavior of suspensions employed by papermakers, but which are seldom used as control variables for routine adjustments of colloidal behavior in paper machine systems.

Table 2. Variables that Papermakers Prefer*not* to Employ as a Means of Controlling Colloidal Behavior

Type of additive *not* used as a control variable	**Reasons why *not* preferred by papermakers for control**	**Some key citations**
pH	The pH of paper machine systems is often constrained by the types of wet-end sizing programs (*e.g.* rosin) and the types of fillers (*e.g.* $CaCO_3$). Also, the systems are often pH-buffered.	Douek *et al.* 2003; Gratton & Pruszynski 2003; Hubbe 2005b
Salt addition	The high dosages of ordinary salts that would be required to induce coagulation would be corrosive and would pollute the water, even after effluent treatment.	Kratohvil *et al.* 1969; Canedo-Arguelles*et al.*2013
Surfactant addition	Surfactants tend to stabilize foam, interfere with inter-fiber bonding, and reverse the effects of hydrophobic sizing agents.	Borchardt 1992; Moyers 1992
Dispersant addition	Dispersants such as phosphates or polyacrylates add negative charge to the system, thus increasing the difficulty or cost of later retaining fine particles during paper forming.	Huang *et al.* 1991b; Sanders 1992; Farrokhpay 2009; Hubbe *et al.* 2012
Temperature	Typically the colloidal stability is only a very weak function of temperature, whereas a high input of energy is required to change the temperature. Abrupt changes in system temperature, sometimes brought about by dilution, can be the cause of deposit formation in the system.	Douek *et al.* 2003

To supplement what is shown in Table 2, it should be noted that many paper machine systems are run under certain preferred ranges of pH. In systems where no calcium carbonate fillers are being used, papermakers have the option of relying on aluminum sulfate (papermaker’s alum), which can be very cost-effective for promoting drainage and hydrophobic sizing (with rosin). Alum systems are highly pH-dependent (Strazdins 1989). Abrupt changes to the pH also have been found to increase the formation of deposits onto papermaking equipment (Gratton and Pruszynski 2003), and this can hurt the operating efficiency and product quality. So, even though it is well known that the density of negative charges at the surface of cellulosic materials is a strong function of pH (Jaycock and Pearson 1975; Herrington and Petzold 1992), there are few papermakers who would consider changing the pH as a main means of actively controlling colloidal behavior on a routine basis.

Though papermakers almost never purposefully add simple salts to the fiber suspension, it is typical for paper machine systems to contain substantial concentration of ions, often in the range of about 0.001 to 0.05 moles/liter, corresponding to electrical conductivity values of about 200 to 6000 µS/cm. These ions are present as a result of such processes as pulping, bleaching, and the addition of various water-soluble additives to the system. Also, although there are various washing operations following pulping, bleaching, and deinking operations, such washing is never 100% effective. Papermakers routinely reuse their process water multiple times, *e.g.* for the dilution of purchased dry fibers, so the highly soluble ions tend to become enriched in the system. Well-meaning researchers occasionally carry out laboratory tests using highly purified fiber suspensions together with deionized or distilled water. The intention of such researchers may be to predict the performance of various additives to be used on paper machines. However, such conditions give rise to exaggerated electrostatic forces between surfaces that are not predictive of what happens in a typical paper machine system. At the other end of the spectrum, in some papermaking facilities the process water is so intensively recycled back to the process that it is possible to reduce the amount of liquid effluent to zero, or close to that goal. In such papermills the electrical conductivities of the water can reach up to about 20,000 µS/cm (Pietschker 1996). Such conditions suppress the electrical charge effects in the system so strongly that conventional papermaking additives such as retention aids and dry-strength additives no longer work efficiently (Beaudoin *et al.* 1995; Malton *et al.* 1998). Because of such issues, in the subsequent discussion it will be assumed that the electrical conductivity of the paper machine systems under consideration is within a more favorable range of about 200 to 5000 µS/cm.

MECHANISMS FOR MANIPULATION OF COLLOIDAL BEHAVIOR

Zeta Potential Manipulation

Most of the strategies that papermakers could potentially use to adjust the state of attraction or repulsion between suspended solids are related to ionic charges at the surfaces. So it makes sense to start the discussion by focusing on those ionic charges that can be attributed to the nature of the cellulosic material itself, originating in the chemical functional groups that are present on cellulosic fibers and fine matter present in a typical papermaking operation. In particular, the hemicellulose and extractives components of cellulosic materials contain significant amounts of carboxylic acid groups. Dissociation of such groups at surfaces of fibers and other materials in an aqueous suspension gives rise to negative ionic charges.

One of the ways to learn how such charged groups are affecting colloidal behavior is by measuring the zeta potential. Figure 1 provides a schematic diagram showing how zeta potential can be measured according to the microelectrophoresis method. Note that the parts of the diagram are not drawn to scale, since the actual capillary usually is about 1 mm in height or diameter. The main idea is that a highly dilute suspension of tiny particles (usually less than 100 µm) is placed in the device and subjected to an electric field. The resulting migratory motion of the particles is evaluated at a strategically selected focal plane where effects related to electro-osmosis are zero (at the so-called stationary level in the capillary cell). Though a high absolute value of zeta potential generally means that the average charge density at the solid surface is high, the relationship between charge density and zeta potential is very complex, and the relationship is not the same for different kinds of materials. But as a practical measure, zeta potential data are quite easy to obtain, quite reproducible, and potentially helpful in optimizing the performance of wet-end chemical additive programs for paper machines.

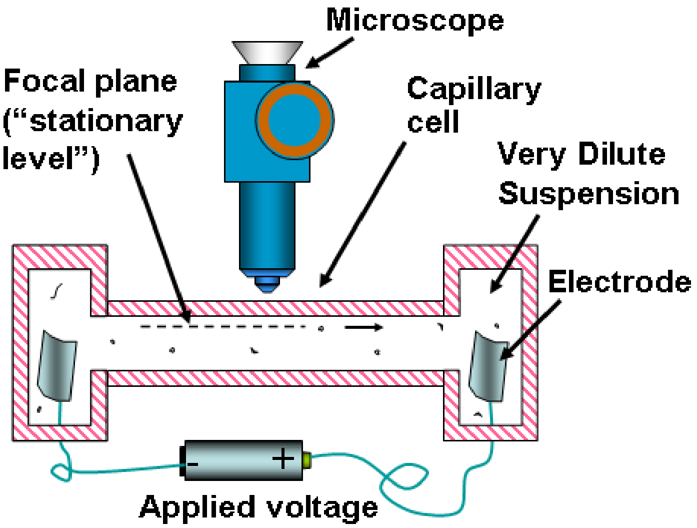

Fig. 1. Schematic illustration of the micro-electrophoresis method for obtaining zeta potential data, based on the velocity of motion of a particle in response to a known electrical field

Levels of carboxylic groups in typical cellulosic fiber pulps fall within a range from about 20 to about 400 µeq/g (Herrington and Petzold 1992; Lloyd and Horne 1992). Though all of the carboxylic acid groups can be classified as weak acid, research has shown that some of them are weaker than others (Stenius and Laine 1994). Those associated with hemicellulose often have pK_a values near to 3.6, which means that they are strong enough that half of such groups remain dissociated down to a pH as low as 3.6. By contrast, the carboxylic groups associated with lignin or extractives tend to be weaker, having pK_avalues near to 5.7 (Stenius and Laine 1994). All of these groups contribute to negative charges of surfaces, especially when the pH value of the mixture is near to or higher than then corresponding pK_a value.

In addition, certain pulping processes result in sulfonation of cellulosic materials (Börås and Gatenholm 1999; Lehto *et al.* 2010). The sulfonic acid groups produced in such operations are strong acids, leading to full dissociation of the protons and giving rise to negative charges. Unlike the carboxylate groups, the sulfonate groups (mainly associated with such pulps as neutral sulfite semichemical pulp or certain chemi-mechanical pulps) are not sensitive to pH within the range in which paper is manufactured.

In addition to the charges of cellulosic matter in a papermaking suspension, it is important to consider also the contribution of mineral filler materials, which often comprise up to 30% of paper products by mass, especially in the case of printing papers. Kaolin clays, which held a dominant position as fillers in paper products in the US until the 1980s (Hubbe 2005b), generally have a negative charge (Sondi *et al.* 1997; van Olphen 1997). This can be attributed to two factors. First, the aluminum silicate structure of kaolin involves isomorphous crystal substitution, which means that certain aluminum atoms occupy sites in the crystal structure that might otherwise be occupied by silicon atoms. Since the two elements have different numbers of valence electrons, the result is that an ionic charge arises when the material is placed into water. The second reason is that clays, as well as other mineral fillers such as ground calcium carbonate, are ground or otherwise prepared and dispersed with the help of dispersants such as phosphates or polyacrylates, which adsorb onto the surfaces (Huang 1991b; Sanders 1992).

Although the amounts of fine materials in paper are usually much less, by mass, compared to the fiber component, the fine materials have a higher specific surface area. In other words, they have more surface area per unit mass. These differences were estimated by Marton (1980) in terms of the relative amounts of cationic starch adsorbed by each component. He found that the ratio of cationic starch taken up by the same mass of fiber, cellulosic fines, and by filler particles was 1 to 5 to 4, respectively. One of the implications of these findings is illustrated in Fig. 2, where one assumes that a given sheet of paper has a composition of 75% long fibers, 7% cellulosic fines, and 18% mineral particles (which are typical values for a sheet of printing paper). Note that when the numbers are converted to a surface area basis, using the factors cited above, the cellulosic fines and filler particles together constitute a majority of the surface area in the system.

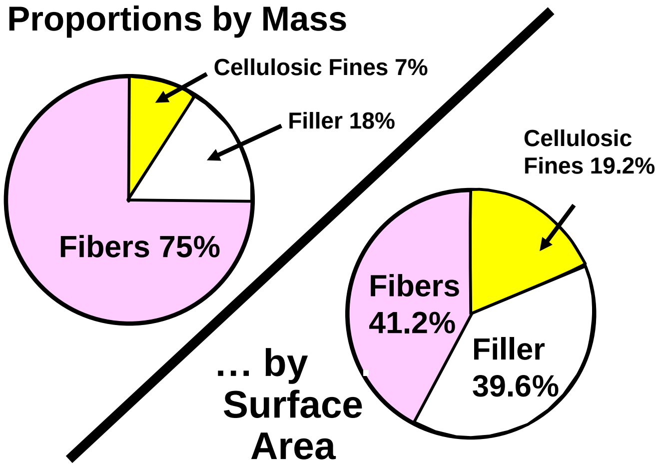

Fig. 2. Relative proportions of solid ingredients in a typical printing paper sheet based on mass (left side of figure), and surface area (right side).

Regardless of the origin of acidic functional groups on the filler or fiber surfaces, the challenge is to somehow figure out a way to make quick adjustments of surface charge as a means of regulating the papermaking process. To help lay the groundwork for some practical approaches, the first option that will be considered is the control of potential-determining ions.

Potential-determining ions

A potential-determining ion can be defined as an ion that interacts very strongly and reversibly with the surface functional groups and directly determines their ionic charge. The concept has been best developed for mineral surfaces (van Olphen 1997; Fernandez-Nieves and Nieves 1998; Alkan *et al.* 2005; Kozin and Boily 2014), so it makes sense to consider kaolin clay as the first example. Studies have shown that the ionic charge of such surfaces, including both the sign of charge and its density, can be controlled by adjustment of $[OH^-]$ and $[H_3O^+]$. In other words, pH has a direct and immediate effect on the charged nature of kaolin, as well as various oxides and hydroxides. In such systems a relatively high concentration of H_3O^+ gives rise to protonation of surface groups. If $[H_3O^+]$ is low (high pH relative to the iso-electric pH), then more of the sites will be in their negatively charged form. In ideal cases the surface potential is related to the pH in a manner described by a modified form of the Nernst equation (Kallay *et al.* 2005),

$$\varphi_o = \frac{RT\, ln10}{F}\left(pH_{pzp} - pH\right) - \frac{RT}{F}\ln\{\frac{\Gamma\left(\Xi OH_2^{+\frac{1}{2}}\right)}{\Gamma\left(\Xi OH_2^{-\frac{1}{2}}\right)}\} \qquad (1)$$

where *R* is the universal gas constant, *T* is the absolute temperature, *F* is the Faraday constant, $pH_{pzp}$is the pH value at the point of zero charge, *pH* is the solution pH, and the last part of the equation describes how the magnitude of the surface potential can be expected to be lower in absolute value than what is predicted by the Nernst equation; the differences can be attributed tovarious chemical equilibrations that take place during pH adjustment. The second term generally makes the surface potential less sensitive to pH than would be predicted based on simple half-cell electrochemical reactions at the interface. Because many of the counter-ions can be expected to be present inside of a hydrodynamic slip plane, the absolute value of the measured zeta potential will be some fractional amount of the surface potential (Hiemenz and Rajagopalan 1997; Bišćan 2007). In spite of such complications, Eq. 1 can provide some guidance concerning how pH can be expected to influence zeta potential.

Calcium carbonate is likewise highly sensitive to certain ions present in the process water of a paper machine system. However, a different combination of potential-determining ions is involved: Ca^{2+} and HCO_3^- or CO_3^{2-} (Huang *et al.* 1991a; Madsen 2002). Thus, the zeta potential of $CaCO_3$ particles in suspension can be controlled by adjusting the ratio $[Ca^{2+}]/[HCO_3^-]$, *etc.*According to Pierre *et al.* (1990), the surface potential of pure calcium carbonate can be estimated from the following equation,

$$\psi = A + 0.028 \log[Ca^{2+}] \qquad (2)$$

where *A* is a constant. Thus, pure $CaCO_3$in typical water suspensions can be expected to have a positive charge.

To make matters somewhat more complicated, however, $CaCO_3$ is seldom employed in its pure form in papermaking operations. The presence of phosphate species or polyacrylate dispersant will often render the $CaCO_3$ particles more negative than would be expected based on tests carried out with pure mineral (Gill and Scott 1987; Huang *et al.*1991b). Nevertheless, it is still possible to make adjustments to colloidal stability by adding either Ca^{2+} or HCO_3^- to the system.

A somewhat different relationship between charge and pH can be expected in the case of surfaces whose charge is mainly controlled by carboxyl groups.This situation is of great importance to papermakers, since carboxyl groups are primarily responsible for the negative charge character of most cellulosic materials. In the absence of other materials, the dependency of negative charge on pH is expected to conform to the following relationship,

$$[RCOO^-] / [RCOOH] = K_a / [H_3O^+] \qquad (3)$$

where $[RCOO^-]$ is the concentration of surface carboxylic acid groups that are in their dissociated (negatively charged) form, [RCOOH] is the concentration of such groups that are in their protonated (neutral charge) form, K_a is the acid dissociation constant, and $[H_3O^+]$ is the concentration of hydronium ions. It is common for values of the acid dissociation constant to be reported as the negative logarithm (base ten), giving the pK_a value, as mentioned earlier. Table 3 gives some key carboxylic acid groups associated with hemicellulose, lignin, and extractives components of cellulosic materials.

The implication of Eq. 3 is that the surface charge of such a surface will be highly sensitive to pH, especially within a range near where the sign of charge is reversed with a change of pH or of the concentration of potential determining ions. Figure 3 (left frame) illustrates how the charged character of some common materials (represented by their zeta potential) is affected by pH (Jaycock *et al.* 1976).

As shown, it is typical for materials to have a more positive or less negative zeta potential at low pH. Higher pH typically leads to deprotonation of acidic groups, leading to increasingly negative zeta potential as the pH is increased to sufficiently high values. However, note that different pure materials exhibit different relationships between zeta potential and pH.

The right-hand frame of Fig. 3 shows one of the consequences of the surface charge of particles and fibers in an aqueous suspension. The “retention” value obtained in the cited work can be regarded as a measure of how efficiently the particles were becoming attached to the surface of cellulosic fibers. It is notable that the best retention was obtained, in each case, when the surfaces were predicted to be opposite in their sign of charge (as shown by the left frame of the figure).

Table 3 lists data for the pure forms of certain materials commonly used by papermakers that tend to follow the kinds of relationship outlined above. Caution should be used when applying such information, however, since it is usual for many mineral products used in papermaking to be stabilized by the adsorption of phosphates or other substances. Such treatment can shift the isoelectric pHs of the materials.

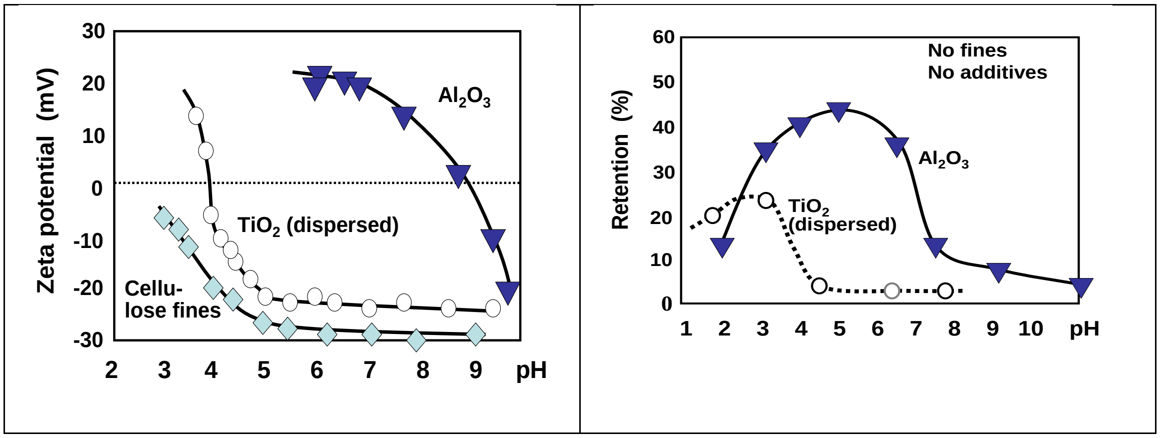

Fig. 3. Left: Effect of pH on the zeta potential of some representative materials suspended in water solution. Right: Effect of pH on the retention of either TiO_2 particles or Al_2O_3 particles onto cellulose under conditions matching those used for the left frame of the figure. Data replotted from Jaycock *et al.* 1976).

Table 3. Potential Determining Ions and Isoelectric Points of Inorganic Materials Often Used in Papermaking (pure compounds in absence of dispersants)

Composition of surface	Potential determining ions	Isoelectric pH or ion concentration	Selected citations
Kaolin clay	H_3O^+, OH^-	2.7-3.2	Appel *et al.* 2003
TiO_2 (if pure)	H_3O^+, OH^-	3.5-6.7	Parks 1965; Kosmulski 2006
$CaCO_3$ (calcite)	Ca^{2+}	Approx. 0.1 mM	Madsen 2002
SiO_2 (colloidal silica)	H_3O^+, OH^-	2.4-3.4	Kosmulski 2002, 2006
Al_2O_3 (if pure)	H_3O^+, OH^-	7.4-8.8	Kosmulski 2006
Cellulosics:		pK_a Values	
Hemicelluloses	H_3O^+, OH^-	3.6	Stenius & Laine 1994
Rosin (abietic acid)	H_3O^+, OH^-	7.4-7.8	Back & Steenberg 1950
Fatty acid (stearic);	H_3O^+, OH^-	7-7.5;	Gomari *et al.* 2006;
(various)	H_3O^+, OH^-	8.3-10.1	Kanicky & Shah 2002
Lignin COOHs	H_3O^+, OH^-	5.7	Stenius & Laine 1994

As was noted already in Table 2, it has been very uncommon for papermakers to consider using pH as a control variable for purposes of adjusting colloidal stability. This is mainly because pH can have such a profound influence on so many aspects of the papermaking process all at the same time. The pH has a major influence on sizing systems such as rosin-alum (Marton 1989; Kitaoka *et al.* 1995, 1997), alkenylsuccinic anhydride (Wasser 1987; Hodgson 1994), or alkylketene dimer (Bottorff and Sullivan 1993; Garnier and Godbout 2000). It affects how swollen the fibers will be with water (Lindström and Carlsson 1982). If the pH is significantly below 7, the rate of dissolution of calcium carbonate filler (if used) becomes unacceptably high (Pierre *et al.* 1990; Madsen 2002). Unstable pH often leads to scale formation or other deposits onto papermaking equipment. Such deposits then can give rise to spots in the product or interruptions in the manufacturing process (Richardson and Hipolit 1990; Froass *et al.*

1997). Finally, if the pH of the process water varies in an erratic manner, the wastewater treatment process can be adversely affected (Lew *et al.* 2009; Hassan and Nelson 2012).

Rather than being a tool for minute-to-minute process control of a papermaking operation, the system pH tends to be a variable that is carefully optimized – either throughout the system or at specific levels at different points. To give one example, papermakers' alum (Al_2SO_4) is highly acidic.In addition to its role of adsorbing onto surfaces and neutralizing negative charges, papermakers often rely on the alum to help keep the system pH at a target value. So when alum is added to the system, the local pH becomes depressed (Strazdins 1989). In cases where papermakers have a strong reason to avoid altering the pH as much, one can substitute the use of poly-aluminum chloride (PAC) in place of alum (Hamzeh *et al.* 2008; Miao *et al.* 2013). And when aluminum chemicals are not needed, for instance when alkylketene dimer (AKD) sizing agent is being used instead of rosin, then papermakers have the option of using cationic polyelectrolytes in place of alum (Horn and Melzer 1975); such an approach makes it possible to make the surfaces less negative or more positive without significant effect on the pH.

Multivalent ions

Since the role of alum already has arisen in the context of pH, it makes sense next to discuss how and why such additives can be used to manipulate the net surface charge of cellulosic materials suspended in water, hence also affecting the degree of electrostatic repulsions (and sometimes attractions) between the surface of suspended materials in a papermaking furnish. Such tendencies of alum, PAC, and related substances can be attributed to a strong tendency of trivalent or higher-valent cations to adsorb onto surfaces bearing a negative charge. In addition, multivalent cations are known to strongly decrease the range of electrostatic forces operating between negatively charged surfaces in aqueous suspension (Hiemenz and Rajagopalan 1997).

The effectiveness of an oppositely charged ion in suppressing or reversing surface charges can increase very strongly with increasing number of valence charges. According to the Shultz-Hardy rule (Hiemenz and Rajagopalan 1997), the concentration of such a counter-ion needed to suppress the range of electrostatic interactions and bring about coagulation is often related to the negative sixth power of the valence. This relationship has particular relevance to the function of the aluminum-based coagulants so often employed by papermakers. Although the trivalent aluminum ion, Al^{3+}, is the dominant cationic species in a pure $AlCl_3$solution at a pH below about 3.5 (Arnson and Stratton 1983), various other species become important at higher pH values. In particular, the species $[AlO_4Al_{12}(OH)_4(H_2O)_{12}]^{7+}$, which forms spontaneously from aluminum chloride solutions at a pH of about 4 to 4.5, has a valence charge of positive 7, rendering it exceptionally effective as a coagulant (Bottéro *et al.* 1980; Jiang and Graham 1997; Exall and vanLoon 2003; Jiang and Graham 1997). Figure 4 provides an illustration of the manner in which twelve aluminums having octahedral coordination structure surround a central aluminum having a tetrahedral coordination (Bi *et al.* 2004).

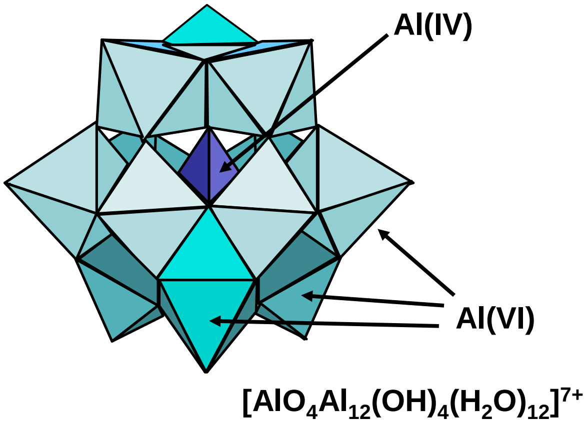

Fig. 4. Illustration of compact structure of stable aluminum oligomer

At higher pH (and also strongly affected by the passage of time), progressive interaction of aluminum species in solution with OH^- ions eventually leads to neutral $Al(OH)_3$, which is the dominant form of aluminum present over a wide range of pH between about 5 and 9 (Arnson and Stratton 1983). At yet higher pH, the negative aluminate ion becomes dominant. So although aluminum chemicals can be very effective coagulants, their use is always highly dependent on pH.

To illustrate how profoundly alum can affect the charged character of a papermaking furnish, Fig. 5 is a replotted version of results originally published by Eklund and Lindström (1991). Note that the addition of alum had a profound effect on zeta potential, but the effect was mainly restricted to the pH range of 5.5 to 8 in the case considered.

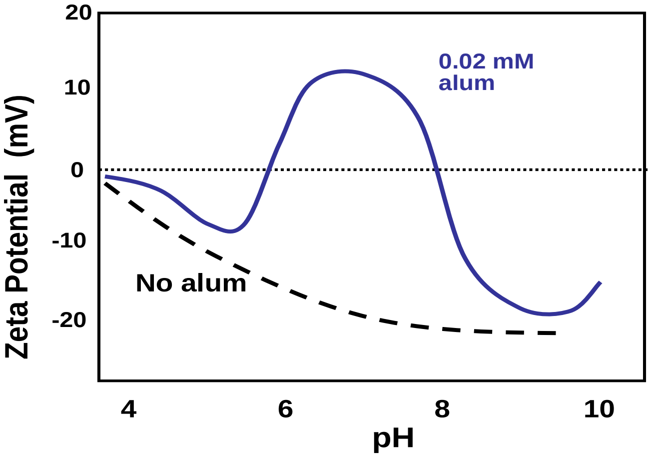

Fig. 5. Effect of pH on the zeta potential of cellulosic fines in the absence (dashed line) and presence (solid line) of aluminum sulfate (freshly added to the suspension just before the measurement). Data replotted from Eklund and Lindström (1991).

As shown by Strazdins (1989), papermakers often can achieve optimum results in use of aluminum-based coagulants such as alum by focusing on the ratio between the aluminum compound and the amount of OH^- equivalents being added to the system.

Such an approach is preferable over the use of pH as a control variable due to the fact that the aluminum species act as a buffer of the pH. Thus, even when using a well-calibrated pH meter, such data do not generally give a reliable means of optimizing the performance of the Al species. Rather, peak performance often is observed when the ratio of Al to OH^- is about 1.5, or at least within the range of 1 to 2.

The presence of sulfate ions in the system can shift various aspects of aluminum ionic behavior (Matijević and Stryker 1966; Akitt *et al.* 1972; Strazdins 1989). In particular, whereas the oligomeric ion,$[AlO_4Al_{12}(OH)_4(H_2O)_{12}]^{7+}$, can readily reverse the charge of a cellulosic surface from negative to positive, aluminum sulfate is more likely to lead to a neutral charge, rather than strongly reversing the charge. This difference is shown in Fig. 6, which was obtained using a suspension of TiO_2 particles in the presence of either alum or aluminum chloride, using the electrokinetic sonic amplitude (ESA) method (Hubbe 1993). Such behavior means that aluminum sulfate is inherently user-friendly, tending to neutralize negative surface charges rather than strongly reversing them. Even if an excessive dosage of alum is employed, the papermaker still can enjoy such benefits as enhanced retention of fine matter, more rapid dewatering, and rosin-based sizing during the preparation of paper.

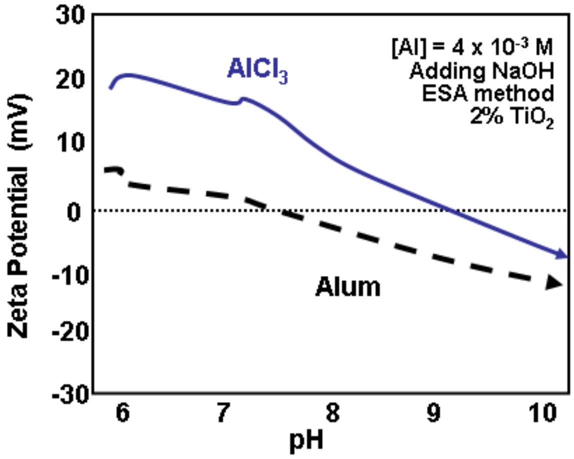

Fig. 6. Dependency of zeta potential of TiO_2particle on the added amounts of aluminum chloride (solid line) and aluminum sulfate (dashed line). Data from Hubbe (1993).

As papermakers have learned from experience, the point of addition and the degree of dilution can greatly influence the effectiveness of aluminum-based coagulants in the papermaking process. The progressive hydrolysis reactions of OH^- with aluminum species require some time to approach equilibrium. In typical situations at pH values of about 4.2 and above it makes sense to add alum relatively late in the papermaking process in order to obtain the greatest impact on drainage and fine-particle retention. Otherwise, a greater proportion of the aluminum is likely to have become converted to neutral $Al(OH)_3$(or maybe also $AlOHSO_4$) before the stock arrives at the headbox. In the course of this transition, a substantial contribution to charge neutralization may have been achieved. In cases where the papermakers are attempting to precipitate pitch-like materials onto talc or fibers at an earlier point in the process (Hubbe *et al.* 2006), an earlier point of addition of Al-based coagulants is often justified. For such purposes the papermakers may prefer to have such precipitation occur relatively early in the process, before the sticky or tacky particles have had much opportunity to agglomerate with each other, leading to large and more visible blemishes in the product.

Regarding the dosage of alum, PAC, and related additives, the general rule of thumb is to attempt to neutralize a majority, but not all of the negatively charged dissolved and colloidal substances present in the papermaking furnish (Spence *et al.* 1997; Hubbe *et al.* 2012). Because alum also plays a role in rosin sizing and control of the pH, the optimum level may be higher than what might be predicted based on the requirements for just coagulation.

Regarding pH control, it is generally recommended to first decide upon an appropriate dosage of the aluminum chemical and then to make any needed pH adjustment with either sulfuric acid (Rao and Maheshwari 1980) or a base such as sodium aluminate (Hechler 1974; Thomas 1979) or an alkali source at an earlier point of addition to the process.

High-charge polyelectrolytes

Given the complexity and pH constraints of the aluminum-based coagulants, as just discussed, papermakers have strong motivation to consider the use of polyamines of various types. Typically such agents are composed of monomers that all bear a positive charge. Molecular masses are often in the range of 10,000 to about 500,000 g/mole. Though the cationic polyelectrolytes are often more expensive than alum, they avoid problems related to abrupt acidification of the process. In addition, polyamines are much more tolerant of higher pH values used in papermaking. In particular, various quaternary amine type coagulants can be reliably used throughout the pH ranges commonly used by papermakers without significant loss of their cationic character. By contrast, polyethylene-imine (PEI) and polyvinylamine (PVAm) products, which have very high charge densities, become substantially less cationic when the pH is raised to alkaline papermaking conditions (pH 7.5 to 9) (Horn 1980). Thus it makes sense to avoid use of such products in systems where the pH is inherently variable or relatively high. Figure 7 shows some examples of commonly used polymeric coagulants.

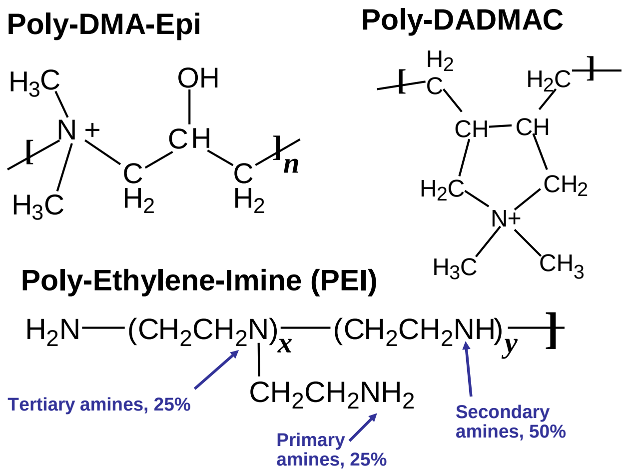

Fig. 7. Examples of commonly used polymeric coagulants

Another reason why high-charge cationic polymers are highly regarded by papermakers for various purposes is that they typically display high-affinity adsorption characteristics (Wågberg 2000). In other words, most of the added polyelectrolyte will remain adsorbed on surfaces even if the residual concentration in solution is extremely low. The reason for this high affinity behavior can be attributed to multi-point interaction. The multiple pairwise interactions between cationic sites on the polymer and anionic sites on a solid particle or anionic polyelectrolyte in the system make it unlikely that all of the connections will be released at once, allowing the polyelectrolyte to diffuse away. In addition, when a cationic polyelectrolyte undergoes adsorption, the counter-ions associated with both the polyelectrolyte and the surface are free to diffuse away from each ion-pair (Wågberg 2000). This mechanism provides positive entropy, which promotes stronger and less easily reversed adsorption. The tendency of high-charge polyelectrolytes to reverse the charge of colloidal systems when they are added in excessive amounts is another consequence of their strong adsorption onto negatively adsorbed surfaces.

Types of Coagulation

When they are asked about the mechanism by which the high-charge cationic agents bring about agglomeration or deposition of finely divided materials suspended in water, the most common response from papermaking technologists tends to be "neutralization of surface charges". It is much less common to hear any reference to patch-wise reversal of charges, leading to localized attractions. The following two subsections will show that although charge neutralization is an important mechanism, the charged patch mechanism is more likely to yield highly advantageous effects in a typical papermaking operation.

Charge neutralization

In principle one can bring about sticking collisions, agglomeration, or deposition of a suspension of charged polymers by either neutralizing or otherwise reducing the effects of ionically charged groups at the surface. In the complete absence of charge interactions, the interactive forces between adjacent surfaces may be dominated by attractive van der Waals – London dispersion forces (Visser 1972).

As was noted in Table 1, one of the simplest ways to minimize electrostatic effects is to add a high concentration of simple salts. Simple ions such as Na^+, Ca^{2+}, Cl^-, and SO_4^{2-} screen the expected electrostatic repulsion between like-charged surfaces in aqueous suspension. The effective range of such repulsions can be estimated from the Debye-Hückel length, κ^{-1},

$$\kappa^{-1} = 1 / [\ \Sigma_i\ (z_i^2 n_i)\ 4\pi e^2 / (\varepsilon kT)]^{1/2} \qquad (4)$$

where $\kappa^{-1}$is a measure of the range of double-layer electrostatic forces, z is the valence of the ion of type "i" being considered, n_i is the solution concentration of that ion, e is the charge of an electron, ε is the dielectric constant, k is the Botzmann constant, and T is the absolute temperature.The summation is made over all of the ions present in the solution. The equation predicts that the range of double-layer forces will decrease with increasing ion concentration in solution, thus leading to increased coagulation. But such an approach would require conversion of fresh water to salty water, which is highly undesirable from an environmental perspective. Alternatively, in the case of cellulosic materials one could achieve charge neutralization by reducing the pH to about 3; such an approach tends to yield highly embrittled and yellowed paper, as well has causing corrosion of various steels used in the equipment. After these various undesirable options are ruled out, most papermakers rely almost completely on certain tried-and-true additives as already mentioned, *i.e.* alum, PAC, and polyamines. These additives meet the requirements of high cationic charge density and a strong adsorption tendency on negatively charged surfaces. But in addition, if one is truly aiming for a charge neutralization effect, then the molecular size ought to be sufficiently small that one achieves a relatively uniform distribution of net charge over the exposed surfaces.

Some of the clearest examples of the charge neutralization mechanism leading to the attachment of fine materials onto cellulosic fibers are those that have been published by Strazdins (1994) and Kratohvil *et al.* (1969). Katohvil *et al.* (1969) showed that purified cellulose particles (microcrystalline cellulose) could be coagulated by adding sufficient amounts of salt ions. Their results are depicted in Fig. 8. As shown, compared to other suspended materials, the colloidal cellulose was less sensitive to the valence of the cations in the electrolytes employed. This difference can be tentatively attributed to a relatively low charge density of the relatively pure cellulosic surfaces that were under study. A relatively low charge density on the cellulose provides less opportunity for multivalent counter-ions to display their ability to form complexes with groups of two or more anionic groups bound to the surface.

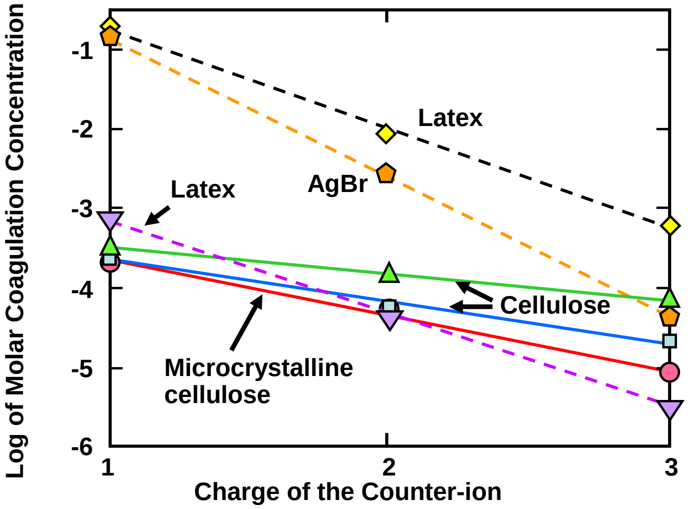

Fig. 8. Examples showing the manner in which cellulosic surfaces were less sensitive to the valence of counter-ions, compared to some types of suspended solids that have been more frequently employed when studying colloidal stability and coagulation. Note that results corresponding to cellulosic particles were plotted with solid lines. Other systems are represented by dashed line. Data are replotted from Kratohvil *et al*. (1969).

Charged patches

Results of certain laboratory studies have raised doubts that the charge neutralization concept, as just outlined, would be able to explain some of the most important effects related to the use of high-charge cationic polyelectrolytes in papermaking. For instance, several studies have shown that such polyelectrolytes having relatively high molecular mass typically out-perform analogous polymeric additives of lower molecular mass (Alince and Robertson 1974; Gruber *et al.* 1996; Tripattharanan *et al.* 2004; Mosse *et al.* 2012). Such advantages can include higher fine-particle retention or faster dewatering at a given dosage, and/or equivalent performance at a lower dosage. Also it has been found that higher-mass highly charged cationic polymers can be much more effective in reducing the water retention value of certain refined cellulosic fiber suspensions (Ström and Kunnas 1991), a finding that is inconsistent with the usual explanations given to explain such effects (Scallan 1983; Swerin *et al.* 1990; Fält and Wågberg 2003). It appears that such reductions in water retention value involve a strong coagulation effect, which is different from the expected charge neutralization explanation often given for the reduced swelling of the treated cellulosic fibers in aqueous suspension.

As noted by Sandell and Luner (1974) and Goossens and Luner (1976), greater effectiveness of higher-mass highly cationic polymers in terms of destabilizing papermaking fiber suspensions can be explained based on a mechanism in which the adsorption of the additive leads to local reversal of ionic charge, leaving at least some of the adjacent areas in their negatively charged condition. The theory had been earlier enunciated by La Mer and Healy (1963) for analytically pure "model" colloidal systems.The concept appears to have been first convincingly demonstrated by Kasper (1971) and by Gregory (1973). According to these researchers the greatest rate of agglomeration can be expected when approximately half of the surface area is covered and the other half remains with its original sign for charge. The dependency of coagulation on the fractional coverage of the surfaces by oppositely charged polyelectrolyte is given by (La Mer and Healy 1963),

$$\mathrm{d}n_\mathrm{o}/\mathrm{d}t = k n_\mathrm{o}^2 \theta (1 - \theta) \qquad (5)$$

wheren_o is the number concentration of individually dispersed particles, k is the rate constant for coagulation, and θ is the fraction of the surface that is covered by oppositely charged polymer.

The reason that larger patches are generally more effective than smaller patches is due to the problems of attempting to fit complex mosaic patterns of charge such that oppositely charged areas face each other. Also, if the charged patches are small relative to the range of the electrostatic forces, then the electrostatic effects would merely become averaged, giving an effect approaching that of simple neutralization of the charges. It is likely that a similar effect of blurring and averaging the charge effects of a colloidal particle results from the random spinning of the particles due to their thermal energy (a form of Brownian motion).The first detailed characterization of the dimensions and shape of charged patches was reported by Horn and coworkers (Pfau *et al.* 1999; Horn 2001), who used atomic force microscopy (AFM) to characterize large adsorbed polyethyleneimine (PEI) molecules on latex particles. Those patches were found to have a “pancake”-type shape, with a width in the range of 23 to 60nm and a thickness or “height” from the surface of about 0.6 to 1.5 nm (Pfau *et al.* 1999).

The effects of highly charged cationic additives on the agglomeration of aqueous suspensions can by very sensitive to the time of equilibration. Figure 9 shows a particularly interesting example of such findings (Goossens and Luner 1976). The cited authors employed a low-mass cationic polymer (only 60,000 g/mole) to coagulate a suspension of microcrystalline cellulose. As shown, when the results were evaluated just 30 seconds after the initial mixing, the maximum reduction in light absorbance (effectively a reduction in turbidity due to settling after coagulation) was observed with a polymer dosage of just 50 µg/L. But the optimum dosage then shifted to the higher values of 130, 250, and 400 µg/L when the system was evaluated after 3, 15, and 60 min, respectively. The results can be attributed to an expected gradual redistribution of the very-low-mass coagulant into the interior pores of the microcrystalline cellulose, which is composed of clusters of much smaller primary crystallites. The results also were consistent with strong decays in the zeta potential from initial positive values toward the negative direction in each case.

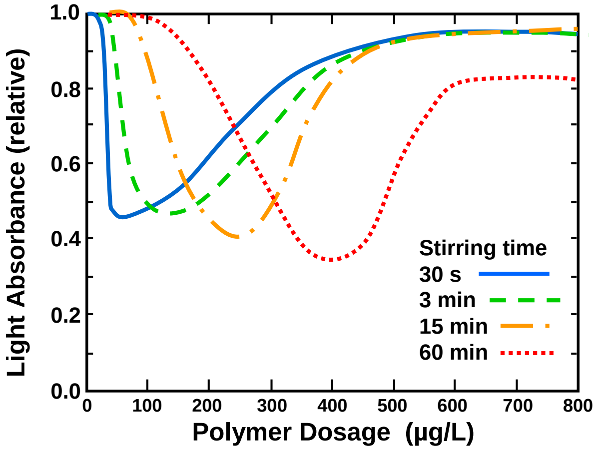

Fig. 9. Effect of time on the optimum dosage of high-charge cationic polymer needed to maximize coagulation of a microcrystalline cellulose suspension. Data replotted from the work of Goossens and Luner (1976).

Flocculation

Relatively strong inter-particle attachments can be created by use of very high mass linear polyelectrolytes, especially if their charge is opposite to that of at least some of the areas on the surfaces of particles in the suspension (Hubbe *et al.* 2009; Jiang and Zhu 2014). The effects of such macromolecules is so important in papermaking applications that the term “retention aid” are often used as a synonym for this kind of additive.

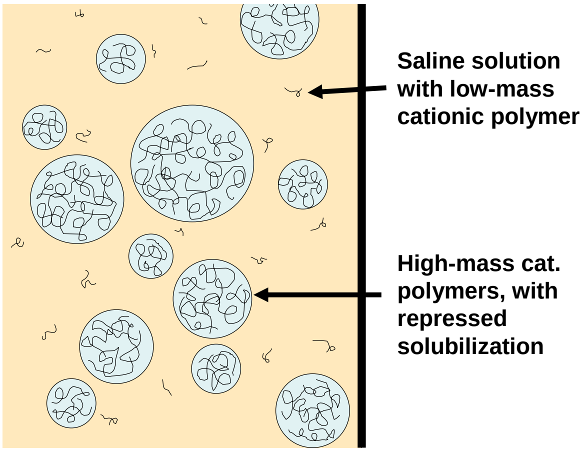

Fig. 10. Illustration of an oil-free aqueous dispersion of water-soluble polyelectrolytes, which is restrained from going into solution by the presence of a sufficient concentration of salt

For various reasons the retention aid molecules need to be highly diluted (*e.g.* lower than 0.1% solids) before addition to the thin stock shortly before the headbox of a paper machine. A higher solids content of the solution imparts an excessively high viscosity and also can result in inefficient mixing of the additive with the fiber suspension. To allow shipping of the material at a very high solids level (to save transportation costs and to be able to pump the mixture easily), retention aid products are often prepared and shipped in an emulsified form (Armanet and Hunkeler 2007; Jiang and Zhu 2014). The conventional approach results in small aqueous droplets of polyelectrolyte dispersed in a paraffin solvent. Another option is to employ a sufficiently high salt concentration to suppress the solubility of the polymerized product in the aqueous phase of the formulation (Pelzer 2008). Such a strategy is illustrated in Fig. 10, which depicts sub-micrometer “gel balls” of acrylamide copolymer dispersed in a saline solution. In any case, such concentrates need to be carefully diluted, with high dilution ratios, to fully invert the emulsion and to allow the macromolecules to uncoil themselves as they dissolve into the aqueous phase.

Bridging interactions

The term bridging goes back to the foundational work by La Mer and Healy (1963) and Gregory (1973). The original idea was that a very long polyelectrolyte chain would be able to span the gap between like-charged particles in a suspension, thus overcoming electrostatic forces tending to hold the surfaces apart from each other. More generally, the term is applied to systems in which the polyelectrolyte is long enough to adsorb onto two facing surfaces simultaneously (Tripattharanan 2004; Hogg 2013). Another piece of evidence in support of a bridging type of flocculation is the fact that in some systems the rate of agglomeration can exceed that which is theoretically possible based on a simple model of sticking collisions between particles; rather, the rate of flocculation seems to be enhanced by the fact that very-high-mass flocculants can extend a relatively long distance outwards from a surface into the suspending medium (Walles 1968).

A further defining characteristic of polymer bridge-type interactions is their irreversibility; once sufficient hydrodynamic forces have been applied to break down such attachments, the system is then unable to achieve the same strength of bonding again if and when the surfaces come into repeated contact. Two phenomena appear to be involved in such irreversibility. First, mechanical detachment can be expected to break covalent bonds in the polyelectrolyte chains (Sikora and Stratton 1981; Ödberg *et al.* 1993; Tanaka *et al.* 1993). Second, the polyelectrolytes can be expected to become increasingly matted down onto the surfaces in the course of time, meaning that there will be fewer tails and loops of polyelectrolytes extending into the solution phase and therefore able to participate in a bridging interaction. The latter mechanism is in agreement with an observed decrease flocculating ability of adsorbed polyelectrolyte with the passage of time (Pelssers *et al.* 1990).

Figure 11 provides an example, showing how the bridging mechanism compares to various other mechanisms of retention of fine particles. The data shown come from a study by Tripattharanan *et al.*(2004). The chemical dosage of each of the systems compared had been optimized to achieve the greatest reduction in filtrate turbidity, which can be viewed as an indication of the effectiveness of the retention aid system. The furnish consisted of 45% bleached kraft fiber, 25% fiber fines, and 30% precipitated calcium carbonate filler. The device employed in the testing was a Positive Pulse Jar (PPJ), which attempts to simulate the effects of hydrofoils on a paper machine. The "preshearing" (see inset to the figure) involved exposure either to moderate impeller stirring or to the lowest setting of a kitchen blender for 30 seconds, just before the start of the retention test. As shown, the control (untreated) system yielded the highest turbidity of the filtrate, indicating the lowest efficiency of fine-particle retention on the fibers. The chemical system providing "charge neutralization" did not provide a statistically significant improvement relative to the control. Substantial decreases in filtrate turbidity were obtained when employing either of the two bridging treatments tested – a single-polymer treatment with cPAM or a dual-polymer treatment consisting of a high-cationic polymer followed by aPAM. Most notably, very effective retention also was exhibited in a system treated just with a high-charge and moderately high mass cationic copolymer of ethylene-imine – giving a charged-patch type of flocculation.

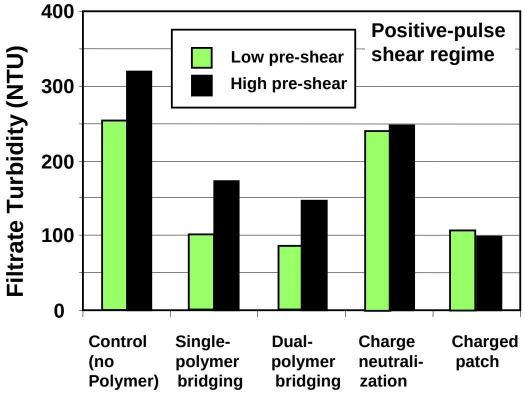

Fig. 11. Comparison of filtrate turbidities, as a measure of the effectiveness of different archetypal retention aid systems, using a Positive-Pulse Jar apparatus with optional exposure of the suspension to shearing in a blender. Data are from Tripattharanan *et al*. 2004.

Hydrodynamic selection

The state of agglomeration of various particles and fibers needs to be optimized with great care so that in the last moments before preparation of a papermaking furnish one achieves an optimum balance between attachment of fine particles onto cellulosic surfaces and avoidance of excessive bridging attachments between adjacent fibers. Such a situation will tend to achieve a relatively good compromise between sufficiently high efficiency of retention of fine particles while avoiding a flocculated appearance of the resulting paper. Given the fact that one of the key goals of adding coagulants and/or flocculants to a paper machine system usually includes holding fine particles onto cellulosic surfaces, the goal of also achieving a high level of dispersion of the fibers in the system can at first seem to be contradictory. However, as shown in earlier work(Sikora and Stratton 1981; Hubbe and Wang 2002), one of keys to achieving the combined goals is to take advantage of high levels of hydrodynamic shear at different points in the unit operations of a typical paper machine. Exposure of the flocculated fibers to shear will tend to separate the fibers from each other, leading to a well-dispersed suspension of fibers and a relatively uniform sheet of paper. Once polymer bridges have been broken, any subsequently formed attachments among the fibers will not be as strong as the first time (Unbehend 1976; Hubbe 2000)

Earlier work has shown that, under matched conditions, larger particles tend to be dislodged from surfaces at lower levels of hydrodynamic shear compared to smaller particles (McKenzie 1968; Stratton 1983; Hubbe 1986; Hubbe and Wang 2002). The relationship and its underlying mechanism were quantified by Hubbe (1985), who studied the shear forces needed to detachdifferent sizes of TiO_2 spheres (very narrow size distributions with radii from 144 to 704nm) from cellulose film or glass surfaces exposed to turbulent shear flow. It was shown both theoretically and experimentally that the shear stress required to bring about detachment was inversely proportional to the 1.5 power of particle diameter.The phenomenon is represented in Fig. 12. Briefly stated, the effect is due to the greater mechanical advantage provided by the larger particles when hydrodynamic forces act on them to impart a rolling motion. Though the circumstances encountered in practical papermaking operations are unlikely to fulfill the details of geometry of the cited work, one can expect that the same general relationship will remain valid. In fact, when two fibers happen to be bound together by polymer bridging at a single point, such an attachment would be expected to be highly vulnerable to disruption by hydrodynamic shear according to the type of analysis used in the cited work (Hubbe 1985, 2007).

Finding a suitable set of coagulant and flocculent products, dosages, and sequential points of addition to a papermaking system can be viewed as an optimization or as a tuning process. In principle one would like to use a set of treatments that is effective enough to bind 100% of filler particles, sizing agent emulsion droplets, *etc.* to cellulosic surfaces, while at the same time any bridges created between cellulosic fibers are to be 100% broken apart by hydrodynamic shear before the formation of the paper sheet. The vulnerability of polymer bridges to irreversible breakage of covalent bonds (Sikora and Stratton 1981; Tanaka *et al.* 1993; Hedborg and Lindström 1996; Hubbe 2007) plays an essential role in such an optimization. In practice it is common for papermakers to run trials on the paper machine, manipulating such variables as the retention aid's dosage, molecular mass, or charge density until arriving at a combination that seems well fitted to the existing papermaking equipment, the grade of paper being made, and such concerns as costs of materials, operating efficiencies, drainage rates, *etc.*

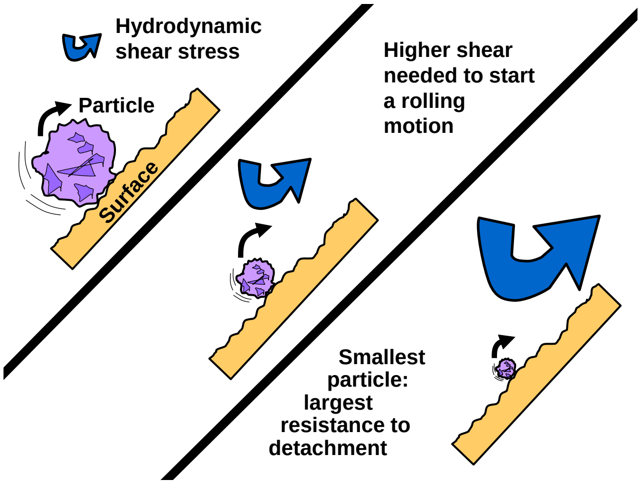

Fig. 12. Schematic illustration of the relationship between the size of an attached particle and the hydrodynamic shear stress required to initiate a rolling motion, as the first step in its detachment. Higher shear is required to detach smaller particles according to this mechanism.

An example of the principle just explained is given by some data presented by Britt and Unbehend (1976). As shown in Fig. 13, these authors evaluated the efficiency of fines retention, employing their "dynamic drainage/retention jar" apparatus. In the series of tests shown, the authors varied the combined amount of polyethylene-imine (PEI) followed by anionic acrylamide copolymer (aPAM). As shown, depending on the dosage selected, it was possible to achieve a wide range of retention targets over a wide range of hydrodynamic shear levels.

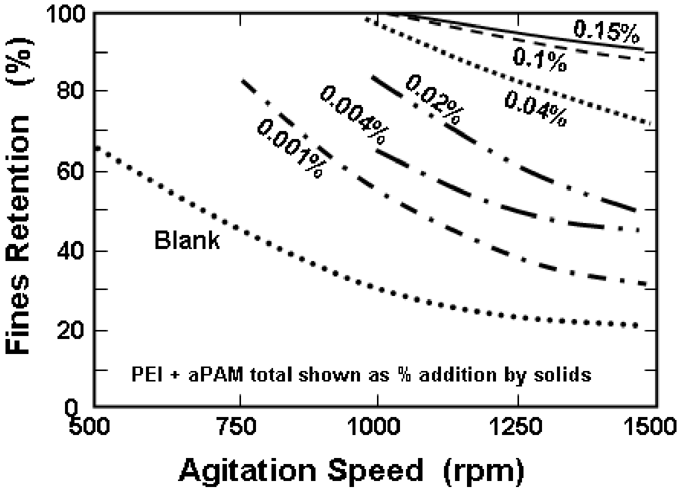

Fig. 13. Replotted data from Britt and Unbehend (1976) showing that by varying the added amounts of retention aid polymers it is possible to tune the system's ability to withstand different levels of hydrodynamic shear, depending on the characteristics of a paper machine system

Microparticle Systems

Starting in the 1980s a major new class of additive began to be widely used on paper machines as a means of manipulating colloidal behavior. The terms "microparticles" and "nanoparticles" have come into common use by papermakers when referring to certain colloidal silica and montmorillonite (bentonite) particles that have been synthesized or selected for use in promoting dewatering and retention on paper machines (Andersson and Lindgren 1996; Wågberg *et al.* 1996; Asselman and Garnier 2001). In addition, certain highly cross-linked acrylate-type polymers, which sometimes have been referred to as "micropolymers", can perform essentially the same function. The products in major use share the characteristics of (a) extremely high surface area, consistent with at least one dimension being in the size range of about 1 to 10 nm, (b) very strong negative charge, and (c) solid-like or gel-like character (Hubbe 2005a). Since all of the major microparticles have the same sign of (negative) charge as untreated cellulosic materials, they have no effect in the absence of a cationic polyelectrolyte. Indeed, their main function always relates to how they undergo a process similar to polyelectrolyte complex formation, except that the negatively charged party to that interaction happens to have a fixed three-dimensional structure. It appears that the strong dewatering effects associated with the use of microparticles are related to a tendency of CPAM or cationic starch molecules to locally wrap themselves around the microparticles. This process causes the polyelectrolyte coils to contract, wringing water from the system (Hubbe 2005a). In support of this concept, Carlson (1990) reported that addition of silica sol particles to a suspension of microcrystalline cellulose that had been flocculated by cationic starch caused an immediatedecrease in the turbidity, consistent with a decrease in aggregate size.

The classical strategy for use of microparticles follows from the earlier discussion of CPAM addition and the selective breakage of polymer bridges between fibers, while attempting to leave other polymer bridges mostly intact. Thus it is common, when using microparticle systems, to move the addition point for a cPAM retention aid to just before the pressure screens (Langley and Litchfield 1986; Hubbe 2005a). Such an addition point ensures that any fiber flocs are broken up as the stock passes through the screen openings (Hubbe and Wang 2002). Then, at an addition point after the pressure screen (often a "ring header"), the microparticle is jetted into the stock stream as a dilute suspension. Such a system is represented in Fig. 14.

Whether the microparticle treatment mainly helps to promote dewatering or whether it also contributes to a higher first-pass retention depends a lot on the shape of the particles. Studies have shown that a pronounced enhancement in dewatering can be achieved by use of single-particle "sol" colloidal silica products together with cationic starch (Sunden *et al.* 1983; Au and Thorn 1995). By contrast, if one wants to achieve enhanced retention of fine particles in addition to enhanced dewatering, then a structured, chain-like colloidal silica particle type is recommended (Andersson and Lindgren 1996; Harms 1998). Alternatively, a combination of both drainage and retention enhancement can be achieved when using montmorillonite products (Langley and Litchfield 1986; Asselman and Garnier 2001). The key appears to be that a high aspect ratio of the microparticle can particulate in a special type of bridging interaction that involves cationic polymer loops or tails extending from adjacent surfaces (Hubbe 2005a).

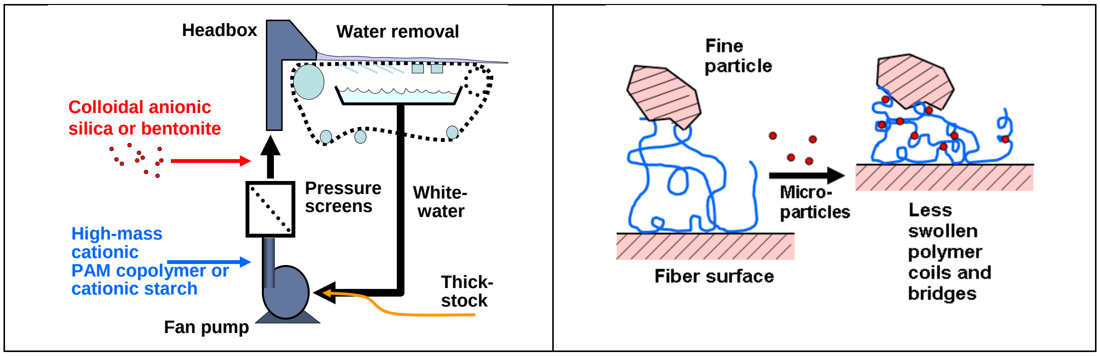

Fig. 14. Left:Simplified diagram of paper machine system employing the most common sequence of addition for a cationic flocculant (pre-screen), followed by a microparticle additive (post-screen), for the purpose of promoting faster dewatering. Right: Conceptual diagram showing how loops of a cationic polyelectrolyte (retention aid or starch) can wrap themselves around negatively charged microparticles, causing contraction at a nano-scale and wringing water from the system.

Figure 15 provides an example showing how a microparticle product having a high aspect ratio can increase the levels of retention that can be achieved with a combination of cPAM and the microparticle. The left-hand frame compares the shapes of typical unstructured (sol-type) colloidal silica *vs.* structured (fused into chains by a partial gelling process) colloidal silica. Unpublished studies have shown much greater increases in the efficiency of fine-particle retention when using the structured silica, rather than sol-type silica, as part of a retention program based on cPAM. As another example, the bentonite (sodium montmorillonite), when added to a system that had been treated with cationic PAM having the right charge density, yielded higher retention efficiency (Miyanishi 1999).

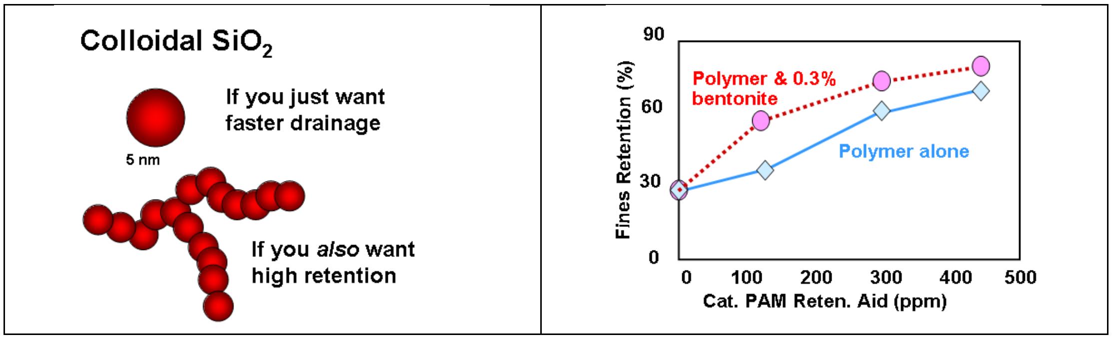

Fig. 15. Left: Schematic comparison of colloidal silica products having different degrees of being fused together as chains, *i.e.* "structure." Individual "sol" $SiO_2$is compared to "structured" gel-type SiO_2. Right: Effect of bentonite (sodium montmorillonite) addition on first-pass retention following treatment of papermaking furnish with cPAM (data from Miyanishi 1999).

During implementation of a microparticle dewatering and retention program one of the most critical aspects is to achieve an optimal and controlled charge balance. Various studies have shown that the greatest benefits in terms of dewatering are achieved when the zeta potential of the final mixture is near to neutral or slightly negative

(Penniman and Makhonin 1993). The importance of achieving a suitable charge balance is demonstrated in Fig. 16, which comes from a study in which cationic starch was added first, followed by colloidal silica (Carlson 1990). Three levels of colloidal silica addition were compared: zero, 0.2% and 0.4% based on solids.

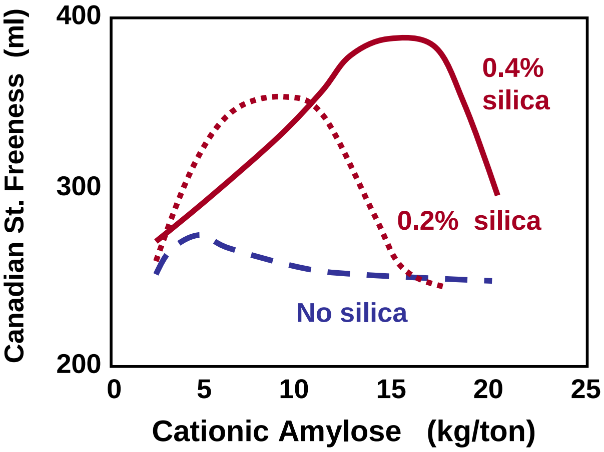

Fig. 16. Effects of cationic starch and colloidal silica addition levels on the freeness of fine paper furnish (data replotted from Carlson 1990)

Notably, only in systems that had been pretreated with cationic starch was there any significant increase in the freeness of the pulp suspension upon addition of the colloidal silica (unstructured, individual sol particles). The other lesson conveyed is that in order to achieve optimum results, the ratio between the cationic polymer and the negatively charged particles must be in a suitable balance.

The presence of excess anionic dissolved and colloidal substances can render a microparticle program ineffective (Wackerberg *et al.* 1994). Such an effect is consistent with premature neutralization of CPAM before it is able to adsorb onto the solids and bring about flocculation. In many cases the best overall treatment sequence actually involves three parts - an initial partial neutralization of the system with a high-charge cationic additive, a subsequent treatment with CPAM, and finally (usually after the stock has passed through a set of screens) addition of the microparticles (Swerin *et al.* 1996). The importance of charge optimization has also been demonstrated by a study looking at the effect of overdosing a system with an excess of micropaticles accompanying cPAM treatment of a surface (Sennerfors *et al.* 2000). The cited work showed that not only was the charge shifted to a net-negative condition, but also that the polyelectrolyte then tended to desorb from the negatively charged surface to which it had been attachedbefore the system was overdosed with negatively charge nanoparticles. The ability of the cationic polymer to form bridges between the macro-surfaces was greatly reduced under such an overdosed situation, and the effect was attributed to an effective reversal of charge of the polyelectrolyte.

Although the sequence of addition just described is representative of common practice, there are many paper mills in which the addition sequence is in the reverse order. In other words, the microparticle is added to the furnish next-to-last (maybe just before the pressure screens) and the cPAM is added last, after the pressure screens. By adding the retention aid very late, such an addition sequence has the potential to achieve a given level of first-pass retention at a lower cost. But a logical problem with such an addition sequence is that one would expect the retention aid to start to interact with the microparticle even before it adsorbs onto fiber surfaces. Such interaction could, in principle, cause the cPAM to contract and to lose its positive charge, rendering it less effective as a retention aid. A likely reason why the reverse order of addition has been found to perform quite acceptably in many instances can be attributed to the extremely rapid convective transport of polyelectrolytes onto fibrillated fibers in the presence of hydrodynamic shear (Alince 1996; Swerin and Ödberg 1997; Hubbe 2007). Such rapid adsorption, resulting from flow-induced wrapping of retention aid chains onto fibrillated fibers, makes it possible for the cPAM to get firmly attached to the cellulosic surfaces before its interaction with the microparticles has proceeded too far.

Van der Waals Force Adjustment

Though the manipulation strategies discussed up to this point are probably the most important tools used by papermakers to control colloidal behavior, there is one more category of manipulation that probably has received insufficient attention. That is, colloidal behavior can in principlebe affected by additives having a hydrophobic component. As will be explained, such approaches are inherently related to the London component of van der Waals forces, as introduced near the beginning of this article.

Hydrophobic effects

A hydrophobic effect can be described as an apparent force of attraction between non-polar entities in a water-based mixture (Meyer *et al.* 2006). A too-easy explanation for such apparent forces is that they arise simply due to London-type forces between the hydrophobic entities. A problem with such an explanation is that London dispersion forces of attraction having approximately the same magnitude are predicted also to act between the water and the non-polar components, and also among the water molecules themselves (Visser 1972, 1995; Bowen and Jenner 1995). The explanation for the apparent attraction between hydrophobic entities lies in the fact that only the water molecules, cellulose, hemicellulose, and other hydrophilic substances are able to interact by hydrogen bonding in addition to the van der Waals forces. By letting the hydrogen bonding substances associate mainly with each other, the overall free energy of the system is more favorable. Thus, the hydrophobic effect can be attributed to the fact that the hydrophilic components of the mixture tend to force the non-polar groups and/or surfaces into association with each other. The effect appears to be highly dependent on the size of the hydrophobic groups; in the case of alkyl groups a longer chain length (within the testing range of 8 to 16) can be expected to provide a much greater tendency to associate (Maibaum *et al.* 2004).

In theory, hydrophobic effects could be used as a possible means to adjust the colloidal behavior of papermaking suspensions. Some aspects of the papermaking process or products that might be influenced by use of different aspects of the hydrophobic effect are listed in Table 4.

Table 4. Challenges to Overcome When Implementing a Hypothetical System to Control Colloidal Behavior by Use of Additives Having Hydrophobic Groups

Problem	Possible solution	Selected citations
Foam	Tuning composition to avoid a critical zone in solubility curve *vs.* temperature	Avery-Edwards *et al.* 1994; Pelton and Flaherty 2003
Deposits	Making sure that any hydrophobic contaminants or emulsified additives become well associated with the cellulosic surfaces by cationic charge and suitable mixing.	Glazer 1991; Hubbe *et al.* 2006
Orientation ofhydrophobic sizing agents at the paper surface	For instance, by the selection of saturated *vs.* unsaturated hydrocarbon chains.	Karademir and Hoyland 2003; Asakura *et al.* 2005; Lindström and Larsson 2008
Thickening of coating color formulations	Associative thickeners can be used to tune the rheology of coating formulations.	Fadat 1993; Kästner 2001; Zhang 2001

An effect of an associative thickener is illustrated in Fig. 17 (Fadat 1993). A coating formulation was prepared with and without a nonionic associative thickener. As shown, both formulations had similar viscosity at a relatively high rate of shear. But at low shear rate the formulation with the associative thickener had a higher viscosity by a factor of about 20. In other words, the coating color became “thickened” at low rates of flow but experienced substantial shear-thinning when agitated.

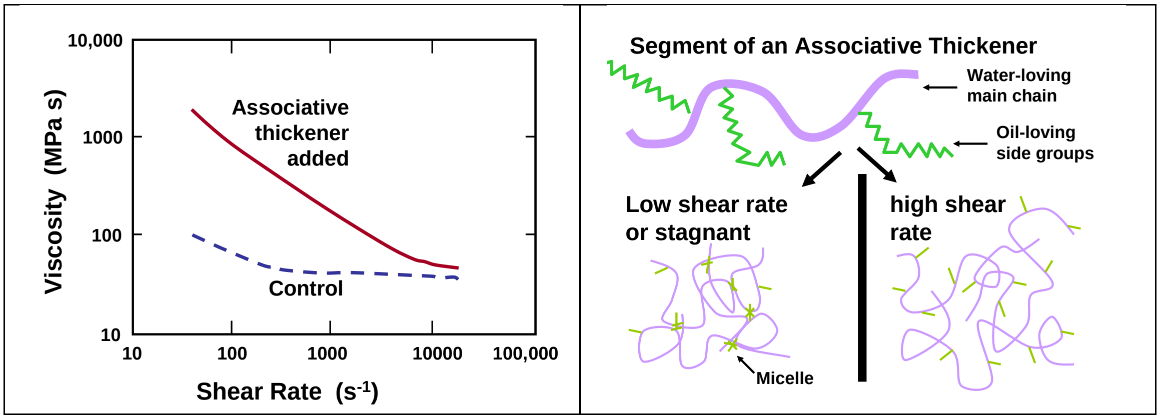

Fig. 17. Left:Effect of adding an associative thickener on the viscosity of a coating color at different rates of shearing (Data replotted from Fadat 1993). Right: Suggested mechanism by which associative thickeners thicken in the absence of rapid flow.

The right-hand frame of Fig. 17 suggests a likely mechanism to explain the effect of an associative thickener. It has been proposed that at low shear rates or in stagnant mixtures the pendant oleophilic groups associate as micelles (Kästner 2001). Such micelles provide a temporary crosslinking of the macromolecular structure throughout the mixture. But when shear is applied, above a critical rate, the oleophilic pendant groups do not have sufficient chance to diffuse and re-associate to a substantial degree, so the crosslinking effect is lost. Such effects can provide opportunities for papermakers to fine-tune such factors as the rates of immobilization of coatings during their application to the paper surface.

A tendency of hydrophobic molecular chains to associate into closely-packed monomolecular films (Swanson and Cordingly 1959; Sakai and Takagi 1994; Kanicky and Shah 2002) is likely an important factor in the hydrophobic sizing of paper. Past studies of the mechanisms of internal sizing general have not considered such an effect. One of the implications of such an association would be a tendency to form coherent patches of hydrophobic character, rather than a random distribution of the molecules of sizing agent on the surface. Strazdins (1985) suggested that only a fraction of such molecules would be required to be anchored to the paper surface. Since insufficient theoretical work has been done on this topic, future research is recommended. Modern surface-sensitive methods, such as spatially-resolved time-of-flight surface-ionization mass spectrometry (TOF-SIMS) might be employed as a way to quantify the tendency of sizing agent molecules to group themselves together at solid surfaces (Gilmore 2013).

Consequences of fibrillation

Forces and energies of interaction among particles or fibers suspended in aqueous solution have been calculated by scientists in isolated cases where the dimensions and shapes were relatively simple and well characterized (Hogg *et al.* 1966; Liang *et al.* 2007; Parsons 2014). But Pelton (1993) has pointed out that such calculations do not properly account for the behavior of cellulosic materials in suspension. In particular, where the cited theories would predict strong van der Waals forces of attachment between particles in such suspensions, which ought to be apparent after neutralization of the ionic charges, no such strong attachments are observed in the absence of bridging polyelectrolytes. The explanation appears to lie in the nano-scale roughness and fibrillation of typical cellulosic surfaces when immersed in water. The tiny water-loving nano-fibrils extending outwards from cellulosic surfaces provide only a very small contribution to van-der-Waals attraction due to their narrowness. At the same time, they get in the way of closer approach of the facing surfaces. The term “superhydrophilic” has sometimes by applied to systems coated with water-loving nanofibrillar or polyelectrolyte materials, leading to stabilization (Nishimoto and Bhushan 2013; Baji *et al.* 2014). Another term that appears to describe this situation is steric stabilization, *i.e.* the coverage of particles with a water-loving material, firmly attached to the surface, that gets in the way of close approach between the surfaces due to its extended conformation and strong association with the water phase (Tadros 1991; Hubbe *et al.* 2006; Opedal *et al.* 2011). The fact that cellulosic materials usually can readily be dispersed by stirring, even when the charges have been fully neutralized or screened by addition of large concentrations of salt, is probably due to such steric stabilization effects or the physical presence of extended nanofibrils at cellulosic surfaces.

Sequential Pair-Wise Interactions

Colloidal interactions in a papermaking system can be complex, especially when one considers the numbers of different additives, the variety of different electrostatic and non-electrostatic types of interactions between them, and various effects of impurities, recirculation loops, and flow regimes. As has been shown by the various studies discussed in this article, colloidal interactions in paper machine systems can involve interactions between charged patches, charge neutralization or screening, polymer bridging, and various hydrophobic effects. If one felt the necessity to consider every pair-wise interaction between all of the components (Gruber *et al.* 1996), then one would have an almost impossible task to consider. However, there is another approach that comes to mind, based on a finding that papermaking systems quite rapidly tend toward an evening-out of the zeta potential of all of the exposed surfaces (Jaycock *et al.* 1976). The reason that the zeta potential of materials in the system tends to become more uniform with the passage of time can be attributed to an exchange of colloidal matter from the bulk of solution back and forth onto such surfaces as fibers, fiber fines, and filler particles. It is proposed, for the sake of simplicity, that one might employ a model in which full equilibration of surface characteristics is assumed to take place between each successive point of addition on the paper machine. Thus, papermakers often rely upon average values, rather than insisting on characterizing the distributions or exact values of zeta potentials or other key indicators of the state of colloidal stability in a papermaking system.

An example illustrating the approach just described in given in Fig. 18, which is based on data distributed by the BTG company (BTG 1999). The figure represents a papermaking process, with the flow direction generally in the direction from left to right. The situation considered involves the addition of coated broke (a highly anionic mixture, due to its content of latex, clay, and dispersant) to a bleached kraft pulp furnish. The coated broke stream was indeed highly anionic, as shown by the initially high negative value of the charge demand titration results (-2.86 mL) and the zeta potential determined by the fiber-pad streaming potential test (-14 mV). As shown by the first downward arrow, a high-charge cationic fixative was added to the suspension of coated broke. Note that both the charge demand and the zeta potential were reduced in magnitude to less negative values as a result of the fixative addition. When the coated broke then was combined with bleached kraft pulp in the blend chest, it is notable that the zeta potential at the fiber surfaces jumped to a quite strongly negative value – intermediate between that of the two streams being combined (fresh kraft pulp and broke that had been treated with fixative). But what is particularly notable is the fact that the cationic demand hardly changed at all upon addition of the fresh bleached kraft pulp, a stream that is generally quite low in colloidal matter. The next additive was cationic starch. The fact that the starch addition decreased the magnitude of zeta potential provides a clue that it was properly being adsorbed onto the fibers. The fact that the cationic starch did *not* decrease the cationic demand of the process water in the system is good news – showing that the fixative had apparently done its job, and the starch was not being wasted by being used as a charge-control agent. In general, cationic starches tend to have rather low levels of cationicity. The response of the cationic demand and zeta potential to the addition of cPAM was quite similar to what happened upon addition of the cationic starch – again tending to confirm that the amount of fixative was suitably optimized, allowing the other additives to perform their intended functions.

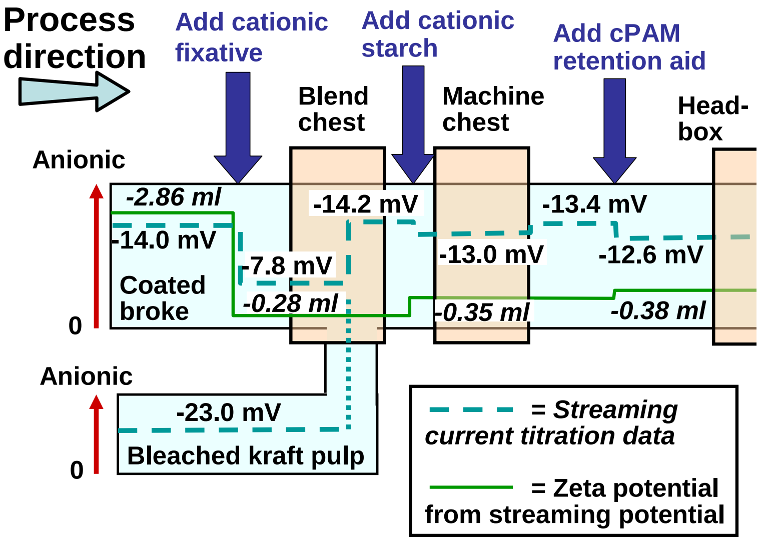

Fig. 18. Example in which average quantities, representing the colloidal condition, were measured after each new additive or stream entering a paper machine system. The solid line and italicized values represent results of streaming current titrations to determine the cationic demand. The dashed lines and non-italic values represent simultaneous results of fiber-pad streaming potential tests to determine the zeta potential.

As has been shown by Sanders and Schaefer (1989, 1991) there can be special situations in paper mills that call for a more detailed analysis. Work by the cited authors showed that in many practical situations there are wide distributions of zeta potentials of particles in samples of process water from papermaking systems. Such information can become important, for instance, when one is trying to resolve hard-to-explain or critical problems, such as persistent deposit problems, high frequencies of web breaks, or an unexpectedly slow rate of dewatering, affecting the production rate.

Whichever approach one elects to follow – an approach based on measuring average values or an approach based on looking at the finer details of colloidal phenomena in paper machine systems, papermakers will continue to be highly dependent on the availability of suitable measurements and data. A future article, in preparation, will therefore deal with the next step beyond the present article – examining some of the experimental approaches for practical analysis of colloidal stability in suspensions of interest to papermakers. Tests to be reviewed in the future article will include turbidity of the process water, particle size analysis, measurement of electrical conductivity, special concerns when attempting to measure pH, various methods related to zeta potential, and various tests to evaluate fine-particle retention and fiber flocculation.

CLOSING REMARKS

The practice of papermaking has been developed in many ways by a multitude of practical people since the invention of the process prior to its first recorded description in the year 105 in China (Hubbe and Bowden 2009). Most ways in which the process was modified might be described as "trial and error," rather than by focusing on the principles laid out in this article. To be realistic, one can expect that trial and error will continue to be a strategy of choice in the future – even in cases where papermaking technologists have the help of tools such as zeta potential measuring devices, tests for cationic demand, and particle size analysis. Approaches based on trial and error are sometimes criticized as being "Edisonian," implying that this is an old-fashioned and inefficient approach. But it is worth bearing in mind that, by using such an approach, Thomas Edison and his team produced important technological breakthroughs at a rate seldom approached by any other individual (Kantha 1992). Thus, when modern papermaking technologists set out to further advance the effectiveness and efficiency of the process, in various ways, it still makes sense to try a great many combinations of chemical additives choices, dosages, sequences, and mixing strategies. The principles outlined in this article hopefully can stimulate the imagination, helping papermakers to envision yet other combinations of chemical and physical treatments that can help them achieve yet better operating efficiency, desired attributes of the paper product, and a lower cost of production. Progress in such areas as particle size analysis (Baosupee *et al.* 2014) and rapid measurements of zeta potential distributions (Uskokovic 2012) can enable progress in understanding wet-end chemistry systems beyond what has been achieved in the past.

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