

The Dispersion Science of Papermaking

Orlando J. Rojas* and Martin A. Hubbe

Department of Wood and Paper Science, North Carolina State University,
Raleigh, North Carolina, USA

ABSTRACT

Paper is one of the most important inventions in the history of civilization, and it is an essential commodity to all people in the world. The fact that we make ubiquitous use of a score of paper products makes it easy to underestimate its value and significance. This review is intended to put into perspective the dispersion science involved in papermaking and to describe how our understanding of key processes has evolve since its conception, approximately 2000 years ago, from art to science. Paper is formed from a slurry of fibers and much smaller particles that are often called “fines” and other chemical additives. Ahead of the paper forming process the slurry is subjected to a series of steps, including treatment with polyionic species and passage through unit operations that impose shear forces on the papermaking suspension. These steps alternately disperse the solids apart or re-gather them back together. The overall process is optimized to achieve a highly uniform product, while at the same time achieving high efficiency in retaining fines in the sheet and allowing water to drain relatively quickly from the wet paper as it is being formed. As we approach the 1900-year anniversary of the first detailed account of the papermaking process, it is the goal of this review to explore the scientific principles that underlie the art of papermaking, emphasizing the state of dispersion of the fibrous slurries during various stages of the manufacturing process. Some concepts that arise out of the experience of papermakers have potential applications in other fields.

Key Words: Papermaking; Dispersion; Flocculation; Aggregation; Coagulation; Bridging; Retention; Fines; Adsorption; Polymers; Polyelectrolytes; Formation; Dewatering.

*Correspondence: Orlando J. Rojas, Department of Wood and Paper Science, North Carolina State University, Campus Box 8005, Raleigh, NC 27695-8005, USA; Tel.: +1-919-513-7494; Fax: +1-919-515-6302; E-mail: orlando_rojas@ncsu.edu.

INTRODUCTION

Worldwide, about 300 million metric tons of paper and paperboard are produced each year in a process that employs paper machines operating at increasingly high speeds. For example, today newsprint paper machines are run at around 120 km/hr in a process that starts with a very dilute fiber suspension (about 0.5–1% total solids concentration) and ends up as a paper web with ca. 20% solids before the pressing and drying stages. The manufacture of paper, which always has involved fascinating aspects of dispersion technology, recently has been subject to important new developments. Science is making inroads into manufacturing practices that historically have been considered in terms of an art or a skill. The purpose of this review is to summarize various aspects of dispersion technology, the understanding of which have the potential to make the paper manufacturing process more efficient and to stimulate the progress of science in allied fields such as water treatment, food processing, and sol–gel technology.

A Brief History of Papermaking

Papermaking is a very old technology, the first detailed account of which was recorded in China in the year 105.^[1] In recognition of the 1900-year anniversary of this event it is appropriate to acknowledge that the most essential features of the papermaking process have not changed. Thus, papermaking still can be described accurately in the following terms: (a) disperse cellulose fibers in water, often using repeated compression and shearing impacts onto the fiber slurry; (b) optionally add hydrosoluble polymers to the mixture; (c) dewater the mixture on a fine screen so that it forms a fairly uniform sheet, usually using hydrodynamic forces in strategic locations to favor dewatering or agitation to achieve a uniform distribution of the fibers; (d) press water from the wet paper; and (e) dry the paper under conditions that favor a flat, relatively defect-free product.

Achieving a sufficiently uniform sheet has been always a key challenge that faces the papermaker. This is because typical cellulosic fibers used in papermaking have length-to-thickness ratios in the range of 50–100, or even larger in the case of many handmade papers^[1–3] and wet-laid nonwoven products.^[4,5] There is a strong tendency for these fibers to become entangled, forming fiber flocs.^[5–7] This is important because the solids content of a fiber's slurry from which paper is formed usually lies within about 0.1–1.5% solids. Within this range it is not possible for one fiber to rotate around

its midpoint without colliding with adjacent fibers. Ancient artisans in China, Korea, and Japan came up with basically two strategies for minimizing the degree of such flocculation in their final product.^[1] One such approach was to strongly agitate, i.e., fluidize, the suspension and thereafter quickly form the sheet by drawing a mesh screen upwards through the suspension. Other papermaking artisans adopted a contrasting strategy in which the fiber slurry is allowed to flow several times parallel to the surface of the mesh screen, gradually building up a series of layers of deposited fibers.^[3]

Another trick known even in ancient times involves addition of mucilaginous gums to the aqueous suspension of fibers.^[2,3,8,9] These additives reduce the tendency of the fibers to form flocs, especially when they are subjected to flow. Strategies involving gums were especially prized when the artisan wanted to prepare strong and attractive papers containing long natural fibers.^[2,3,10] Related approaches have been adopted by modern industry for wet-lay formation of nonwoven fabrics, especially when using chopped tow fibers composed of polyester, glass, carbon, etc.^[4] Gum-like natural polymers,^[11–14] or their synthetic equivalents,^[8,9] appear to reduce interfiber friction,^[15] thus reducing the extent of fiber flocculation. However, in the modern practice of papermaking, employing cellulose fibers, the approach of adding mucilaginous polymer as a dispersant never has become popular. Such “formation aid” treatments can dramatically reduce the rate with which water drains from a paper sheet as it is being formed, an effect that sometimes can decrease the production rate of a paper machine.

Derivatives of natural polymers, e.g., cationic starches and cationic guar gums, have been employed to create just the opposite effect as explained before, i.e., to induce flocculation of fine particles in the fiber suspension. This fact demonstrates that the state of the dispersion can change dramatically by changing the chemical nature of the additive or by adjusting the dosage levels and conditions of addition.^[16,17] In other words, the stock used for paper manufacture is very sensitive to the addition of polymeric additives and there is a need for solid understanding of the involved mechanisms and conditions for optimum performance.

Fast-forward to the year 1807 and we come to another key development in the application of dispersion technology to the field of papermaking. In that year Illig published a method for improving paper's resistance to fluids by precipitating rosin size onto fiber surfaces with aluminum sulfate or “alum.”^[1,18] Alum has become so widely used within the paper industry that it also has become known as “the papermaker's friend.” As papermakers discovered, not only was alum able to interact with rosin to achieve the sizing effect, but it

was also able to coagulate fine materials, increasing the efficiency of their retention by the fiber mat.^[18–22]

When added into water solution, aluminum salts undergo complex hydrolysis reactions and form oligomeric and/or polymeric charged aluminum–hydroxo complexes of various structures, the exact chemical composition and quantity of which depend on the solution pH, total alum concentration, and presence of other chemicals. The effectiveness of alum is attributed to the multi-valent positive charge of some of these ionic species,^[20] allowing alum to function very effectively as a coagulant.^[23,24] The term “friend” also stems from alum’s ability to promote more rapid dewatering of paper, an attribute that became important especially after the 1798 invention of a continuous paper machine.^[1]

Due to its versatility alum may be overused and as a consequence numerous unwanted effects can also be generated. The overdose of alum, for example to prevent the buildup of stickies and deposits, leads to a low pH in the water system which, in turn, can give rise to precipitates or tacky stickies, especially if calcium carbonate is used as filler (see later sections). Hence, a good understanding of the aqueous chemistry of alum is necessary for its proper application.

Another issue is that alum has been no friend of librarians. Much of the paper made between the late 1800s and late 1900s has become brittle, cracking at folds, and this problem has been traced to excessive alum use. The acidity of alum promotes hydrolysis of the cellulose molecules, a process that is accelerated by humid storage conditions.^[25] Fortunately, this situation more recently has been minimized, due largely to the emergence of calcium carbonate as a filler for paper in alkaline systems.^[26] Especially in its synthetic “precipitated” form, calcium carbonate has allowed papermakers to meet brightness and opacity targets at lower cost, compared to more traditional practices relying on clay and titanium dioxide fillers. When using calcium carbonate filler, papermakers usually replace rosin with reactive sizing agents that do not require the use of alum (in the so-called neutral or alkaline systems). As a consequence of these changes most modern books, whether or not they are printed on “archival” paper, experience little embrittlement or acid hydrolysis.

Even before calcium carbonate became the dominant type of filler, already it was clear that alum and related additives could not always achieve sufficiently high retention of fine particles during the forming process. The mechanism by which alum promotes retention usually is explained in terms of a reduction in electrostatic repulsion forces between the solid surfaces in the aqueous suspension of fibers, mineral particles, and other papermaking additives. Early success at achieving yet stronger

flocculation and higher retention was achieved by a combination treatment in which alum addition was followed by a colloidal mixture of animal glue, rosin, alum, and formaldehyde.^[27] The year 1956 saw the first reported application of synthetic polyelectrolytes as retention aids.^[28] The most successful of such additives were prepared by free-radical polymerization of acrylamide, usually employing either cationic or anionic co-monomers in order to achieve a positive or negative charge. The manner of use of these additives, together with their probable mechanism of action, will be discussed later.

Though certain other historical developments also could be mentioned, one of the most surprising and somewhat counter-intuitive advances was achieved in the 1980s with the introduction of “microparticle programs,” which have subsequently become widely used to enhance both retention and dewatering during the production of printing papers. The most important microparticles consist of synthetic colloidal silica,^[29] and an alkali montmorillonite (“bentonite”).^[30] It is ironic that addition of the microparticles alone to untreated papermaking furnish has almost no impact on the state of dispersion of the fiber slurry. However, as will be described in detail in a later section, sequential addition of the microparticles with a high-mass polyelectrolyte flocculant, especially if it is cationic, can produce some striking effects, often allowing the papermaker to achieve a more favorable balance between product uniformity and fine-particle retention, all while increasing the speed of the paper machine.

ADVANCES IN DISPERSION TECHNOLOGY OF PAPERMAKING

Table 1 introduces the main sections to follow in this article and summarizes the most important process stages listed in the order in which they occur in typical paper manufacture. Remarkably, none of the items in this table fundamentally departs from the ancient Chinese recipe for making paper.^[10] Undoubtedly this field of papermaking technology has grown dramatically in sophistication and a comprehensive account of major advances would be impractical. Nevertheless, Table 1 provides a simplified mnemonic for the main innovations in the dispersion technology of papermaking.

LIBERATION OF THE FIBERS

From the viewpoint of a papermaker, trees are an almost ideal source of raw material. The fibers from

Table 1. Main steps in the state of dispersion of fibers in typical papermaking processes before the formation of a sheet. Some keystone developments are also included.

Step	Description of current technology	Key historic development
1. Liberation of the fibers	Dissolution of the phenolic lignin “glue” between cellulose fibers (in an environmentally friendly way), allowing easy dispersion of the fibers	Kraft pulping (1884) ^[31]
2. Refining for fiber surface development	Mechanical dispersion and fibrillation of fibers, using repeated compression and shearing forces applied to a slurry of fibers	Mechanical refining (105 AD)—Cai Lun ^[1]
3. Dispersion of papermaking additives before addition	A variety of dispersing agents are used in the formulation of chemical additives (in the form of solid dispersions, emulsions, etc.)	
4. Chemical coagulation in the fiber suspension and surface-site preparation	In acid systems alum is added to the suspension to “set” rosin size. In alkaline systems other coagulants are added to achieve gains in retention and dewatering	Use of coagulants (with rosin sizing) (1807) ^[18]
5. Flocculation by polyelectrolytes to improve retention	High molecular weight polymers are used to produce polymer bridges between solids in the suspension that help to retain fine particles even under the high hydrodynamic shear of a modern paper machine	Use of very-high mass retention aids (acrylamide type) (1956) ^[28]
6. Selective deflocculation	Incorporation of a “pressure screen” just before the approach flow to a paper machine’s forming section to produce selective deflocculation	Installation of rotary screens (1944) ^[32]
7. Addition of microparticles (optional)	Addition of microparticles to the slurry after the original fiber-to-fiber flocculation (induced by a high-mass retention aid). Floccs are partly broken by hydrodynamic forces and gains in dewatering and formation are achieved	Microparticle systems (1982–1986) ^[30,33]
8. Final deflocculation before forming process	Optimization of the relative fluid velocity to the forming fabric during formation of the sheet (jet-to-wire speed adjustments)	Nagashi-zuki (200–600 AD)—Asian handcraft artisans ^[3]
9. Forming process (web formation) and paper consolidation	Dewatering is assisted by various hydrodynamic and vacuum units. Paper web is consolidated in high-speed, high productivity paper machines. Continuous papermaking was first achieved by Robert. However, Donkin solved key engineering issues, making modern papermaking possible. (1798) ^[1]	Forming the sheet (105 AD)—Cai Lun ^[1]

wood (and also from certain other nonwood sources) tend to be within an ideal size range, quite uniform in size, and having length-to-width ratios in just the right range to produce about 20–50 crossing points with adjacent fibers after formation of the sheet.^[34] Wood also is relatively dense, and it can be harvested year-round, minimizing storage requirements. But the words “almost ideal,” as used above, reflect an important truth: fibers within wood are glued together with an exceedingly insoluble, chemical-resistant phenolic resin, the lignin.^[35]

Technologies used to liberate fibers from wood fall generally within one of two contrasting groups, mechanical vs. chemical pulping. The role of water in these processes is of paramount importance since it swells the wood and decreases the amount of surface energy required to liberate the fibers.^[36]

Due to the strength of the lignin that joins the fibers together; substantial damage to fibers tends to occur when they are “ripped apart” from each other during typical mechanical pulping processes. The resulting

decrease in average fiber length represents an irreversible loss in the potential value of the fibers, relative to their ability to form strong paper. An innovative approach to minimize such damage has involved the pre-steaming of the wood material, usually after it has been converted into chips, and then refining the wood at elevated temperature and pressure. Temperatures of about 120–130°C allow the fibers to be separated more easily, even though somewhat higher values have been reported for the glass transition temperature (T_g) of lignin.^[37,38]

Water appears to function as a plasticizer, lowering the T_g .^[37,38] The resulting thermomechanical pulp (TMP) or pressurized groundwood (PGW) fibers tend to be less damaged than their cousins produced at lower temperature, but they still suffer from two problems that reduce their value from the papermaker's standpoint. Both are related to the fact that almost all of the original lignin from the wood remains with the fibers. Lignin is less hydrophilic, when compared to the polysaccharide components of wood (cellulose and hemicellulose). The adsorption of lignin on cellulose fibers is affected not only by the pH but also by the presence of calcium ions and cationic polyelectrolytes that form complexes with lignin.^[39] Though strong paper still can be formed from fibers with adsorbed lignin, the paper is not as strong as it would have been if the outer surfaces had been rich in the polysaccharide components of wood. Opposite effects have been observed when the lignin adsorbs together with oppositely charged polyelectrolytes.^[39] An issue in terms of the optical properties of paper with high lignin content is that it tends to yellow under storage—and especially when it is exposed to sunlight.

Chemical pulping methods attempt to dissolve the lignin with a minimum of dissolution or degradation of the cellulose and hemicellulose components of the fibers. Historically, the most successful approaches to achieve these goals have employed NaOH (the soda process), SO_3^{2-} (the sulfite process), and alkaline S^{2-} (the kraft process).^[31] Pulp produced by these different processes differ considerably not only in bulk properties but also in surface characteristics. The kraft process, if one excuses the smell, represents a key early advance in green processing, since almost all of the added chemicals are recovered for repeated use, and the whole process is nearly self-sufficient in energy, using steam energy from the combustion of lignin byproducts to run other operations, such as drying the resulting paper.^[31] Modern bleaching methods have permitted the kraft process to dominate the field of printing papers and tissue, in addition to its original applications for paper boxes and bags.

REFINING FOR FIBER SURFACE DEVELOPMENT AND FLEXIBILITY

The main purpose of refining or “beating” of fibers is to make them flexible enough to conform to each others' surfaces in a ribbon-like manner, forming a relatively strong sheet of paper. During a refining process, almost regardless of the kind of equipment employed, each fiber experiences multiple compression and shearing events, usually produced by passage of the pulp suspension between rotating plates that have raised bars on their facing surfaces.^[31] Usually, the bars are spaced far enough apart and the solids content of the suspension is adjusted such that fiber-to-fiber contact is at least equally important, compared to direct contact with the steel bars.

To understand what happens in a refiner, it is worth noting that cellulosic fibers are comprised of a series of layers, each of which tends to be wrapped around the axis of the fiber at a characteristic angle. The outermost (“primary”) layer, which in the wood is joined to adjacent fibers by lignin, is relatively thin and disorganized. Also, it has a relatively high content of lignin (e.g., 70%), which is mostly dissolved away during chemical pulping. As a consequence, most of the primary layer peels away (from for example, kraft fibers) rather early in the refining process. Subsequent layers, in particular the relatively thick “S₂” sublayer of a wood-derived fiber, are partly delaminated by refining, making the fibers more flexible and conformable. Partial peeling of these layers results in a fibrillated surface of fibers. Given the approximately 11-degree wrap angle of the S₂ sublayer, together with the tendency of fibers to become aligned in a certain way as they pass through a refiner,^[40,41] it makes sense to think in terms of a partial “unraveling” of cellulose material lying outermost on the fiber surface.

Though there is no doubt that fibrils at a fiber surface can participate in bonding between fibers in a resulting sheet of paper,^[42] it is important to keep in mind two adverse effects of the refining process. First, the fibrils tend to make it more difficult to remove water from paper as it is being formed, which can limit the rate of production, increase the amount of energy required to evaporate water, or both. Second, the refining process results in the production of fine material (“fines”). The fines content in fiber suspensions varies depending on the raw materials and the processing history. For example, fines concentrations of the order of 10–20% (based on total solids) with specific surface areas of the order of 50–100 m²/g as compared to that of typical fibers (ca. 10 m²/g)^[43] are typically found. This fact implies that the dispersion behaviors for pulp suspensions with

even low fines content is markedly affected by this latter component.

The process stages described so far rely very heavily on surface chemistry phenomena taking place in the fiber suspension and in the paper web itself. It is apparent that the final properties of the paper sheet are strongly dependent on the way the interactions between the fibers are modulated during the process and how other components of the paper stock (including fines, fillers and other naturally-occurring substances and added chemicals) affect the state of dispersion of the colloidal system.

DISPERSING FUNCTIONAL PAPERMAKING COMPONENTS

Besides the need for a homogeneous, deflocculated fiber aqueous suspension, the papermaker may require a wide range of additives, each of which must be delivered to the process as a highly uniform, well-dispersed solution, suspension, or emulsion. Consider for example the list of various possible chemical additives described in a handbook of more than 1000 pages that was published recently.^[44] This large list of chemicals includes process additives that improve the operation of the paper machine (retention and drainage aids, biocides, dispersants, and defoamers); functional additives that improve the properties of the paper product (fillers, sizing agents, colorants and dyes, optical brighteners, and wet-strength and dry-strength additives), and effluent mitigating chemicals (sludge conditioners and wastewater antifoamers/defoamers).

A challenge lies in the fact that a subsequent step in the papermaking process requires at least partial destabilization of the suspended materials, allowing fine particles either to adhere to fiber surfaces or to become sufficiently aggregated so that the agglomerates are large enough to be incorporated into the paper, as it forms, by a filtration mechanism. These seemingly contradictory objectives of papermakers—wanting things to be very well dispersed at first, but then changing their minds midway through the process—means that it is important to avoid excessive usage of dispersants and surface-active agents.

Mineral fillers provide examples of the issue just raised. Paper fillers are natural or synthetic fine, white mineral powders, e.g., clay, talc, calcium carbonate (ground and precipitated), and titanium dioxide. Potential benefits from the use of fillers include brightness, opacity, smoothness, better printability, dimensional stability, gloss, and sometimes reduced overall cost of materials in a sheet of paper. The drawbacks of using

fillers are loss of bonding between fibers, low tensile strength, low stiffness, and sometime two-sidedness.

The surface chemistry of the fillers determines the interactions with fiber, fines, and other additives. When dispersed in aqueous phase the surface of the filler can be subjected to surface hydrolysis and formation of coordinative bonds with metal ions and with ligands. Also, hydrophobic sorption of hydrocarbons and surfactants reduce its surface energy.^[45,46]

Taking advantage of the situation presented before, dispersants such as sodium tripolyphosphate and sodium acrylate are often used, in combination with strong agitation, to disperse the mineral particles in water. Motivations for going “heavy” on the filler dispersant dosage include the need for the product to remain colloidally stable during unpredictable conditions of shipping and storage, the need for more reliable measurement and control of filler addition to the paper suspension, and because optional coating processes (that take place either on the paper machine or on separate equipment) use a large percentage of minerals (especially clays) with little tolerance for agglomerated particles.

Steric effects are also known to play an important role in the dispersion of mineral fillers and other additives by using polyelectrolytes of very low charge density.^[47] In this case, reversal of the surface charge is more difficult to attain (even at very high polyelectrolyte dosage) since adsorption is constrained by steric or volume effects originating from the conformation of the polyelectrolyte molecules initially adsorbed on the surface. This situation offers a better way to stabilize the system by steric forces due to protruding polymer loops and tails. In this case there is less sensitivity to polymer overdose or to changes in pH levels and ionic strength.

An innovative approach, in terms of particle dispersion, has been achieved in many papermaking operations employing precipitated calcium carbonate (PCC). On-site preparation of PCC makes it feasible to minimize both the solids content and the storage times of the mineral suspensions; these factors make it unnecessary to keep a significant presence of dispersing agent in the suspending liquid.

Use of Cationic Polymers in Emulsification of Sizing Agents

In many paper grades it is required that the final product has special wetting abilities. Water penetration in the paper network can be retarded or prevented by the use of hydrophobizing agents that are normally applied in the bulk (to change the surface chemistry of

the fibers) or as a surface treatment (to reduce the surface wettability). The additives employed are the so-called sizing agents and are typically water-insoluble liquid additives, including wood resins and synthetic waxes. These additives can be stabilized with nonionic surfactants.^[48] A more noteworthy strategy has become dominant when it comes to the preparation of hydrophobic sizing agents such as rosin emulsions, alkylketene dimer (AKD), and alkenylsuccinic anhydride (ASA).^[49] It happens that these sizing agents are water-insoluble liquids that undergo gradual hydrolysis. As a result of that process, the surface of any such droplet suspended in near-neutral or alkaline water immediately becomes coated with a layer of negatively charged carboxylate groups. Although, in theory, the charge from such groups could be used as the basis for charge-stabilization of an emulsion, such an emulsion would be vulnerable to the effects of hardness ions, hydrodynamic shear, and time. Instead, it has become common practice to emulsify liquid rosin (above its melting point), ASA, or AKD in the presence of cationic starch, polyamidoamine-epichlorohydrin, or various other water-soluble cationic polymers. Not only do such polymers confer a positively charged layer to the emulsion droplets, thus providing a charge stabilization mechanism, but also they provide steric stabilization to the emulsion droplets. The positive charge also favors efficient retention of the sizing droplets onto the negatively charged surfaces of fibers and other fine materials in a papermaking furnish.

Formation and Control of Inorganic Scales

A phenomenon that frequently occurs in the papermaking aqueous environment and that is related to a different form of aggregation state (in this case with undesirable consequences) is the formation of adherent inorganic aggregates (scale). Inorganic scale can be formed from, e.g., oxalates and carbonates which come mainly as carry-overs from the pulp mill streams.^[50,51] These anionic species have high affinities for metal ions such as Ca^{2+} and Mg^{2+} , and will react to form insoluble precipitates.^[52]

The buildup of the precipitates can lead to scale deposition in the paper machine and the extent of formation is affected by a number of chemical and physical factors, including pH, temperature, total scale-forming species, and the presence of other chemicals.^[53]

Various procedures can be applied to control scale formation and deposition. The most frequently used measure is the use of crystal growth inhibitors such as polyphosphates, hydroxyl ethyl diphosphate (HEDP),

poly(acrylic acids), and relatively low-molecular-weight polymers containing carboxylic, phosphonic, phosphoric, and other functional groups. Trace concentrations of these chemicals act as “poisons” for crystal nucleation and growth, inhibiting the spread of mononuclear steps on the crystal surface by becoming adsorbed on active growth sites such as kinks.^[45,46]

Use of Co-Solvents in Formulation of Dyes

Special strategies also are required in the formulation of dyes for papermaking, many of which lie in an uncomfortable range between full water-solubility and insolubility.^[54] Except in the case of pigment dyes, which are prized for use in certain specialty paper product applications demanding high tolerance towards light-exposure, almost all papermaking dyes are formulated as solutions. Solubility considerations have become even more challenging over the last 25 years as liquid concentrates have gained dominance, displacing powdered dyes and the preparation of more dilute solutions. Though some papermaking dyes are highly water-soluble, many are formulated with co-solvents such as alkylglycols. The use of acidic or basic conditions that maximize dissociation of ionic groups on the dye molecules facilitates their dispersion.

CHEMICAL COAGULATION AND SURFACE-SITE PREPARATION

Though it is possible to rely totally on mechanical filtration to retain fine particles during the formation of paper, such filtration is likely to be ineffective, especially when it comes to retaining substances in the colloidal size range. Also, the mechanism of filtration tends to yield a nonuniform distribution of fine materials as a function of the thickness dimension of the sheet.^[55] Materials in the colloidal size range include elements whose origins can be traced back to naturally-occurring substances from the fiber supply and related treatments (fines, biopolymers, pitch, etc.) and functional or control additives (e.g., mineral fillers, sizing emulsions, dry and wet-strength polymeric additives, etc.). Successful strategies to retain such materials during paper formation almost always entail two steps, the first of which is addition of a high charge cationic additive, or “coagulants.” Some of the coagulants that are most widely used by papermakers include the already-mentioned aluminum sulfate or “alum,” a closely related product called polyaluminum chloride (PAC), polydimethylamine-epichlorohydrin (a polyamine), polyethyleneimine (PEI) and polydiallyldimethylammonium chloride (DADMAC).

As described below, the highly charged additives appear to serve the following three functions: (a) neutralization of excess negative colloidal charges in the suspension; (b) coagulation of assorted colloidal materials so that they become large enough to be filtered by the fiber mat during the formation of the paper; and (c) "site preparation" of the fiber surfaces and other solid surfaces in the suspension, making them more suitable for interaction with retention aids (see next section).

Neutralization of Excess Anionic Charge

Cationic retention aids tend to lose their effectiveness if exposed to high concentrations of anionic dissolved polymeric and colloidal substances (DCS) in the papermaking furnish.^[56–59] Depending on the source of fibers, some of the main components of DCS can include wood extractives (from mechanical pulping), lignin byproducts (from kraft pulping or related processes), oxidized polysaccharides (from bleaching processes), sodium silicate (used in conjunction with certain peroxide bleaching practices), dispersants (from recycled paper that has been coated), and various soaps and surfactants (from de-inking and washing processes).^[45,46]

Of the different pulp types used in papermaking, mechanical pulp brings the largest part of DCS to the water system. For example, in the defibration of mechanical pulps, typically 2–5 kg/ton of materials is dissolved or dispersed into the water phase, depending on the wood species, defibration temperature, shear and turbulence, equipment used, consistency, and degree of water system closure.^[46] Pulp bleaching also has a strong influence on both the amount and composition of DCS.

The amount of DCS brought with chemical pulp depends significantly upon the efficiency of washing. During alkaline delignification in kraft pulping, the lignin decomposes into low-molecular-weight lignin fragments and the hemicellulose decomposes into simple hydroxyl acids. Depending on the efficiency of washing and degree of system closure, these compounds can be found in the water system of the paper machine. The substances released during beating tend to have a higher molecular weight, and these substances have a great ability to form polyelectrolyte complexes with cationic and amphoteric additives. This type of dissolved substances has a more pronounced influence on the interaction of additives with fiber and fillers than low molecular weight fractions originated from the pulping process. It has been shown that the pH and presence of electrolytes have significant effects on the dissolution of wood substance during beating and storage.^[46] High

electrolyte contents will suppress the dissolution of wood substances, and multivalent metal ions are more efficient than monovalent ions. Increasing pH increases the dissolution.

Since the amount of any of the listed quantities is likely to vary over time, especially if there are process interruptions ("breaks") or if the formulation changes (for the production of different paper grades), the papermaker often can achieve smoother, more economical operations by process monitoring, together with online-control of the coagulant dosage. To do this, the papermaker needs a way to measure the cationic demand of the system, i.e., how much DCS is present, in addition to the surface charge of the suspended solids. Titration methods involving streaming current endpoints have become very popular in such applications.^[60,61] Various colloidal mechanisms, as well as some practical limitations related to the streaming current titrations have been studied in recent experimental work.^[62–64]

Coagulation

Collisions among fibers in a flowing slurry of papermaking pulp tend to be dominated by hydrodynamic considerations. By contrast, collisions leading to possible agglomeration of materials in the molecular and colloidal size ranges tend to be more affected by short-range "interparticle" forces, as well as by the random thermal motions (Brownian motion) induced by collisions among adjacent molecules and colloidal particles.^[65] It appears that this is the scale of interaction within which highly charged cationic additives, i.e. "coagulants" play their most critical role. Many readers will be familiar with the electrical double-layer concepts, which predict an especially strong coagulating effect of multivalent ionic species, opposite in charge to the surfaces.^[66] The main idea is that a sufficiently high concentration of counter-ions, especially if they have a high valence, will reduce the range of influence of electrostatic repulsive forces to such an extent that attractive van der Waals dispersion forces between the surfaces cause them to come together and remain agglomerated.

However, with a minor exception, none of the highly charged cationic substances added to the fiber suspension (e.g., coagulants mentioned in foregoing paragraphs) can accurately be described as a "counter-ion" with respect to how they interact with negatively charged surfaces in aqueous suspension. The minor exception involves the relatively rare use of alum at pH conditions significantly lower than 4; these are conditions under which hydrated Al^{3+} appear to be the main positively charged ionic species present in solution. At higher values of pH

the most important aluminum species, with respect to coagulation and other charge effects, appear to be polynuclear ions such as $[\text{AlO}_4\text{Al}_{12}(\text{OH})_4(\text{H}_2\text{O})_{12}]^{7+}$ (the “ Al_{13} ” ion).^[23,24,67] Unlike a well-behaved counter-ion, as assumed in the classical theories of coagulation, it has been shown that polynuclear aluminum species are able to effectively reverse the sign of charge of the surfaces.^[62–64,68] Likewise, highly charged cationic polymers such as polyamines and PEI clearly are able to reverse the charge of surfaces to which they are exposed, depending on the amount added. Except in the case of alum (which, being “papermaker’s friend,” tends to be more tolerant of sloppy dosage practices), an excess amount of these materials can be expected to restabilize the suspension—due to repulsion between the surfaces that have been converted to a net positive charge.

Another limitation of classical theories of coagulation is that they cannot account for the effect of the additive molecular mass on its ability to keep fine particles attached to the (fiber) surfaces. Results of recent studies in our lab suggest that fiber-to-fine-particle contacts brought about by simple neutralization of surface charges are almost completely ineffective relative to the retention of mineral filler during the formation of paper.^[69,70] Much stronger adhesion could be achieved when using a copolymer having sufficiently high mass, e.g. 2 million Da, so that it forms positively charged “patches” that cover a fraction of the surface area of solids in the suspension. Direct evidence of such patch-like adsorption was recently shown by atomic force microscopy in the case of PEI compounds.^[71]

Site Preparation Before Retention Aid Addition

Papermakers have been adopting online charge titration technology, since it gives them a means of keeping the surface charge of fibers in a favorable range, well suited to the addition of a retention aid (see “Flocculation by Polyelectrolytes” section). An excessive dosage of coagulating chemicals can seriously hurt the effectiveness of a cationic retention aid. The reason is that the driving mechanism for adsorption of hydrosoluble cationic macromolecules is mainly electrostatic interactions with the available surface sites.^[72]

Recently, it was shown that the performance of certain retention systems improved when the fiber surfaces were at least partly covered by highly-charged cationic polyelectrolytes.^[72] The proposed mechanism is illustrated in Fig. 1. In the absence of the high-charge cationic materials (left side of the figure), a

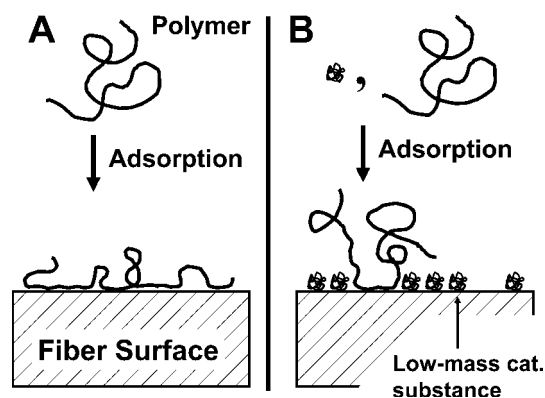


Figure 1. Performance of retention aids such as cationic flocculants of high charge density. (A) Polymer adsorption in the case of a system in the absence of highly-charged cationic materials (left side of the figure). Here a high-molecular-weight, linear cationic chain is expected to initially form loops and trains on the surface and to adopt a flatter conformation over time. (B) The more tight or flat conformation of the adsorbed polymer seen in (A) after some time can be inhibited if the surface already is occupied by low molecular weight, high charge density cationic species.

very-high-mass, linear cationic chain is expected to spread out on an oppositely charged surface, adopting a flatter conformation over time. As indicated on the right-hand side of the figure, such flattening can be inhibited, in principle, if much of the surface already is occupied by high-charge cationic material. The reasons why this state of affairs is thought to be advantageous are discussed later.

FLOCCULATION BY POLYELECTROLYTES

A typical “retention aid” polyelectrolyte molecule, as commonly used within the paper industry, has a molecular mass in the range 4–20 million g/mol, which implies ca. 100,000 monomeric units in each chain. The most common polymers used include random copolymers of acrylamide and derivatized natural polymers (starches and guar gums). Early workers who contemplated the ability of such large molecules to flocculate suspensions of colloidal particles realized that, even when coiled in a semi-random conformation, would be able to extend far beyond the range of the electrostatic double-layer forces that can cause repulsion between surfaces in aqueous suspensions.^[73,74] Such considerations led them to the concept of macromolecular bridges.

Evidence supporting the bridge-like character of attachment resulting from the use of retention aids has

been based on the kinetics of agglomeration in flow,^[73] factors affecting the strength of the resulting attachments,^[75–79] and the irreversible characteristics of flocculation with very-high-mass polyelectrolytes.^[55,80–82] Experimental evidence from surface force measurements has been reported recently in which long-range bridging attraction was measured upon retraction of surfaces covered by adsorbed polyelectrolytes. This effect was detectable when conditions close to charge neutralization and low polymer dosage were used.^[83,84]

It has been shown that in the absence of colloidal contaminants, the strongest resistance to hydrodynamic forces can be achieved with polyelectrolytes having low charge density^[76,77]—a counterintuitive fact if one considers charge effects only. Also, in papermaking systems to which retention aid polymers have been added, the conditions leading to maximum flocculation seldom correspond to charge neutrality of the surfaces.^[85,86]

Tests using hydrodynamic forces have shown that the resistance to detachment of solid particles from surfaces pretreated with very-high-mass cationic acrylamide copolymer can be several orders of magnitude higher than what can be achieved by charge neutralization, or even by adjusting the aqueous conditions so that the interacting surfaces have opposite charges.^[76] However, once such attachments are broken, as in the case of a suspension of papermaking fibers treated with a retention aid, and then sheared in a kitchen blender,^[87] the ability of the macromolecules to reflocculate the fibers is greatly diminished. Rather, the evidence suggests, as shown in Fig. 2, that the process of redispersion causes multiple breakages of polymer chains, rendering them much less effective as flocculants.

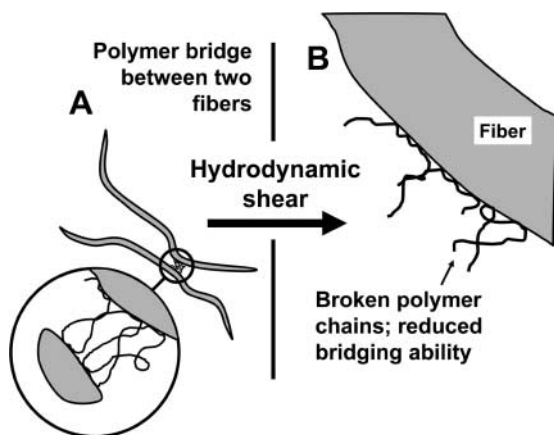


Figure 2. Schematic illustration of the reduction in the effectiveness of a polymeric flocculant subjected to strong hydrodynamic shear.

On the basis of zeta potential measurements, it is demonstrated that the interactions which occur upon addition of cationic polymers to pulp suspensions are driven by electrostatic mechanisms.^[16] The evolution of the zeta potential as a cationic polymer is added to the pulp suspension is rationalized in terms of an initial reaction of the additive with soluble anionics, followed by a progressive neutralization of fines and fibers and a final deflocculation or redispersion of the suspension components.^[86]

Besides differences in adsorption isotherms, the charge density of the polyelectrolyte markedly affects the characteristic electrokinetic and flocculation behaviors. Figure 3 shows a schematic representation of two possible cases for polyelectrolyte-induced flocculation. Figure 3 (left) depicts the scenario for a highly-charged cationic polyelectrolyte that adsorbs rather flat of the cellulosic surfaces, with a large portion of adsorbed trains.^[88,89] In this case little bridging takes place and the existence of patches on the surfaces with negative and positive charge promotes attractive forces between colliding particles (“mosaic” or “patch flocculation”).^[85] In this case adding excess polymer leads to the redispersion of the flocs. The situation depicted in Fig. 3 (right), is typical of a low-charge density polyelectrolyte. In this case, the adsorbed polymer forms loops and tails on the surfaces that are able to bridge two close particles (bridging flocculation). Note that here an excessive polymer dosage is less likely to produce charge reversal or re-dispersion of the flocs.^[85] An important difference relates to the relative resistance to shear. In the patch-type of flocculation shear-induced deflocculation is

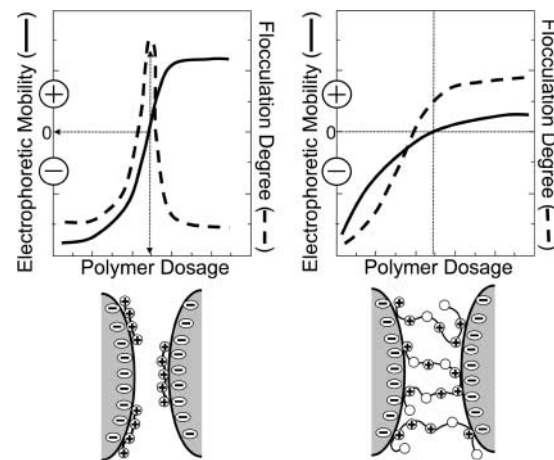


Figure 3. Changes in the electrophoretic mobility and flocculation degree as a high charge density (left) or low charge density (right) cationic polymer is added to the paper stock suspension.

reversible, whereas in the case of bridging flocculation there may be irreversible changes by chain breakage that may prevent reflocculation.^[85]

Results of experiments related to adsorption of neutral polymers suggest that the interactions of polyelectrolytes are not restricted to electrostatic forces^[90] as other intermolecular interactions often play a major part in complex formation such as hydrogen bonding, hydrophobic forces, ion binding, and steric interactions (due to the large hydrodynamic volume of typical polyelectrolyte molecules in solution). As noted before, the long-chain polymer molecules can bridge several cellulose particles, thereby forming large flocs which are easily retained during paper formation.

The addition of most flocculating polymers has an additional effect such as the increment in paper strength. Typical cationic polymers adsorb to the negatively charged fibers and this mediates an increased fiber-fiber bond. The dry strength of the paper increases with decreasing charge density of the polymer, presumably due to increased polymer-polymer interpenetration and due to increased viscoelastic losses that occur during the rupture of the paper sheet under strain.^[91,92] An account has been given of the effects of polymer charge density on the number and strength of electrostatic bridges and entanglement of polymer chains as a cause for strong adhesion in model surfaces.^[93]

Cationic Retention Aid

Because cellulosic fibers, as used by papermakers, generally have a weakly negative surface charge,^[94,95] it is not surprising that cationic copolymers of acrylamide are among the most widely used retention aid in papermaking applications.

The effectiveness of the polymers depends on a subtle balance of factors, most of which have been reviewed extensively.^[88,96,97] The entropy gain upon the release of counterions on the fibers upon polyelectrolyte adsorption is a large contribution to the adsorption energy. Not only is the equilibrium adsorption important, but also the kinetics of the process and the conformation of the adsorbed polymers on the fiber surface (and the change of this conformation with time) are important. The location where the polyelectrolytes are adsorbed (on the external surfaces of the fibers or within the fiber wall) is also a factor to consider. Besides the molecular weight of the polymer, the charge density^[89] and the physicochemical environment, e.g., pH and ionic strength^[47] are crucial for developing any dispersing or, conversely, flocculating effects.

As noted earlier, the effectiveness of cationic polyelectrolytes often can be enhanced by pretreating the system with cationic coagulant,^[72,98] though, as discussed, overdosing must be avoided.

Anionic Retention Aid

Negatively charged copolymers of acrylamide also are popular as retention aids.^[85] Addition of such macromolecules to untreated fiber furnish usually has little effect on either flocculation of the fibers or on attachment of fine materials to the fiber surfaces. Rather, it appears that the anionic macromolecules require positively charged surface sites in order to be effective.^[99,100] In principle there ought to be an ideal density of such sites—formed by adsorption of highly-charged cationic polymers or freshly-added aluminum compounds—to achieve maximum effectiveness of an anionic retention aid, since a high degree of coverage will encourage the flocculant molecule to quickly adopt a flat molecular conformation at the surface, reducing the likelihood of polymer bridging.^[98]

Nonionic Retention Aid

Yet more counter-intuitive is the use of nonionic water-soluble polymers, such as polyethylene oxide (PEO) of very high molecular mass, as retention aids.^[79,101,102] These additives depend, for their effectiveness, on the sequential addition of a “cofactor,” which can be a phenolic resin.^[103] Lignin present in the wood or in the pulping liquors also can play the role of cofactor. The advantage of a PEO-based retention aid systems is that it can be almost immune from problems related to high levels of colloidal charge in the system (DCS) or high salt levels, factors that can hurt the effectiveness of ordinary, charged retention aids. Ideas advanced to explain the effectiveness of nonionic retention aid systems include (a) an entangled nature of PEO chains, greatly increasing the effective molecular mass,^[104] (b) formation of transient networks of polymer chains,^[105] and (c) subtle effects of the cofactor that promote adsorption of macromolecule chain segments onto the solid surfaces.^[102]

SELECTIVE DEFLOCCULATION

One thing that all of the flocculant systems just described have in common is that they can result in strong flocculation of the fibers, tending to form fiber

bunches, reducing the uniformity (formation) of the resulting paper. As noted earlier, such flocs can be redispersed irreversibly if one applies sufficiently intense hydrodynamic shear.^[82,87,106] Conveniently, a typical paper machine system contains a unit process that is almost ideal for achieving that function. That process, involving a device known as a pressure screen,^[32,107] is illustrated in Fig. 4. Though the original goal is to exclude large debris, including incompletely cooked material from knots in the wood, pressure screens are effective in preventing the passage of fiber flocs—at least during the time that such flocs remain together. Slots or small holes in the screens are designed to permit passage only of individual fibers, as well as smaller materials. Various types of rotors, which are used within pressure screens as a means of preventing a build-up of a fiber mat, also tend to disrupt fiber flocs. A study comparing the hydrodynamic shear levels within a typical paper machine system concluded that shear within a pressure screen system is higher than other unit operations that follow it, including the formation of the sheet.^[108]

In view of the description of a pressure screen given above, it would be reasonable to ask, “Why bother adding a retention aid before the screen if the screen operation immediately reverses the effect of the polymer?” The answer lies in the selective nature of the shear forces. Earlier research demonstrated that the intensity of hydrodynamic shear stress required to detach a particle from a surface is inversely related to its size.^[109] Such results suggest that the level of shear forces sufficient to separate two fibers—even in the

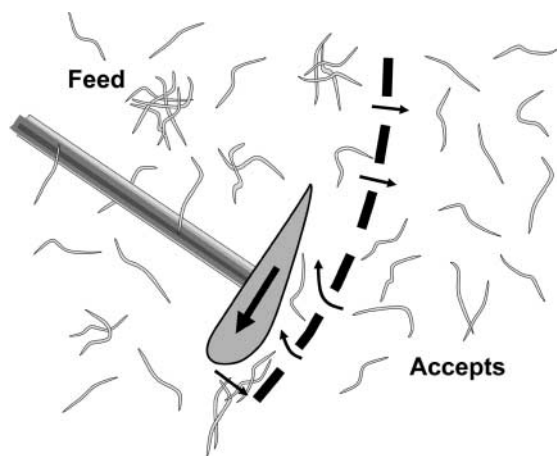


Figure 4. Close view of streamlines in a pressure screen and redispersion of flocs by intense hydrodynamic shear. Though the objective of the pressure screens is to eliminate large debris they are also effective in preventing the passage of fiber flocs.

presence of polymeric bridging by a retention aid—would not necessarily be strong enough to separate a small mineral particle (or other substance) held onto the same surface by a similar mechanism. Ideally the papermaker ought to be able to select a retention aid treatment that is weak enough so that fiber-to-fiber contacts break easily, avoiding a buildup of flocced fibers on the screen surfaces, but also strong enough so that fine materials such as mineral particles and sizing agents are efficiently and uniformly retained in the resulting paper.

Recent confirmation of the “selective deflocculation” theory just mentioned was achieved by using simple bench-scale experiments.^[87] A slurry containing 0.5% cellulosic fibers (typically about 1–3 mm in length, by about 20–30 μm in diameter) and 0.05% calcium carbonate particles (ca. 2 μm in diameter) in aqueous suspension was treated with a very-high-mass cationic acrylamide copolymer. Tests with a modified viscometer probe showed an immediate and persistent increase in signal, consistent with the presence of relatively strong polymer-induced attachments among the fibers.^[87] Vigorous stirring of the suspension caused the viscometer signal to return to the baseline value characteristic of the untreated suspension. However, parallel tests related to the retention of calcium carbonate particles yielded very different results. Increasing dosage of the cationic retention aid caused the turbidity of filtrate collected during sheet formation to fall by as much as 90%, consistent with retention of the particles.^[87] Surprisingly, almost identical turbidity values were obtained in cases where the treated furnish was subjected to subsequent shearing before the sheet was formed. In other words, there was no detectable detachment of fine materials small enough to pass through the fine mesh on which the sheet was formed.

For whatever reasons, the reality of full-scale papermaking does not precisely follow the scenario just given; retention of fine particles does depend on the history of hydrodynamic shear that a fiber suspension experiences between the time of addition of a flocculating polymer and the formation of the paper. Similar effects were observed recently^[69,70] with a new lab-scale device that simulates the washing action of hydrofoils, devices that promote drainage from a wet sheet of paper as it is being formed.^[81] Because of this fact, papermakers interested in improving retention efficiency at the lowest possible cost of chemicals usually add the flocculant after the pressure screen.^[110] By contrast, papermakers who are more concerned about paper uniformity and/or dewatering effects often select the pre-screen strategy of retention aid addition, especially in cases where they also are using a microparticle treatment (see next

section). In summary, not only the point of addition is relevant but also the order and the way in which the polymers and other additives are added are essential to attain the desired goals.

MICROPARTICLE SYSTEMS

One might expect that after having followed the preceding steps as described above, the papermaker would be more than ready to just form the paper and be done with it. After all, the fibers were (1) dispersed, (2) coagulated, (3) flocculated, and (4) selectively deflocculated in a way that is almost ideally suited to achieving good uniformity of the resulting paper, in addition to improved retention of fine particulate matter in the sheet. But papermakers are persistent, and they often employ a fifth step, the addition of microparticles.

Though the motivations favoring the use of microparticles differ, depending on the paper grade, the furnish characteristics, and the type of paper machine, the rate of dewatering usually is a primary consideration.^[80,111,112] To understand why microparticle addition, subsequent to the stage-wise program just described, are so markedly effective for promoting dewatering, it is useful to review some key factors that tend to slow the rate of water removal from paper. One of these factors is the high surface area of a well-refined fiber furnish. The effective surface area of fine materials produced during refining of a kraft pulp tends to be several times higher, per unit mass, compared to the fibers themselves.^[113,114] Idealized "packed bed" experiments and related theory have shown that resistance to flow of liquid through packed media often increases as the square of surface area.^[115-117]

Coagulation as a Means of Reducing Effective Surface Area

In the case of emulsion droplets, it is clear that coalescence results in a net loss of surface area. The situation is more complex in the case of solid particles, but often it is useful to think of a reduction in "effective surface area" accompanying coagulation. Such thinking helps to account for such phenomena as the more rapid settling of colloidal solids after they are caused to come together by the addition of a coagulant. A related effect is believed to occur at the surface of a well-refined fiber. In the absence of chemical additives, the fibrils at a fiber surface usually bear a net negative charge. Electrostatic repulsion causes the fibrils to project outwards from a fiber surface. By either reducing the range of the electrostatic repulsions (based on traditional colloid science),^[66]

or by neutralizing the surface charge (as demonstrated by zeta potential measurements),^[118,119] such repulsion forces are overcome, and the likelihood that the fibrils lie down flat against the fiber surface is increased. Though detailed proof is still lacking, it seems likely that a fiber with its fibrils lying flat against its surface would permit much more streamlined paths for the drainage of water from paper.

The Choke-Point Model

Recent tests have confirmed an additional contributing mechanism leading to slow dewatering of paper. Results were consistent with a mechanism in which unattached fine particles are able to migrate through drainage channels within the wet sheet of paper as it forms, and they tend to get stuck in certain positions ("choke points") where they block those channels.^[120] Attachment of the fine matter to fiber surface by means of a retention aid yielded a large decrease in resistance to dewatering.

The Fiber Friction Model

An often-overlooked factor related to the dewatering of a fiber mat or filter cake is the effect of interparticle friction forces. The best-known experimental work related to these effects comes from studies of the volume occupied by a fixed mass of particulate material after the solids have settled to the bottom of a graduated tube.^[121] Particles that are colloidally stable (having strong repulsive forces between them) tend to produce a relatively dense sediment. The high density has been attributed to an ability of the particles to slide past each other, thus achieving relatively efficient packing.^[121] By contrast, particles whose surfaces tend to stick together on contact tend to form a bulky, porous sediment, through which the suspending medium can flow rather easily. It has been proposed that the somewhat reversible nature of microparticle-induced attachments described in the previous section, in the presence of a cationic retention aid, has a similar effect of raising the effective friction coefficient between fibers, yielding bulkier, more porous paper, compared to a similar furnish without the microparticles.^[57]

De-Swelling of Adsorbed, Water-Loving Polymers

Figure 5 illustrates yet another contributing mechanism that helps to explain the dewatering effect of

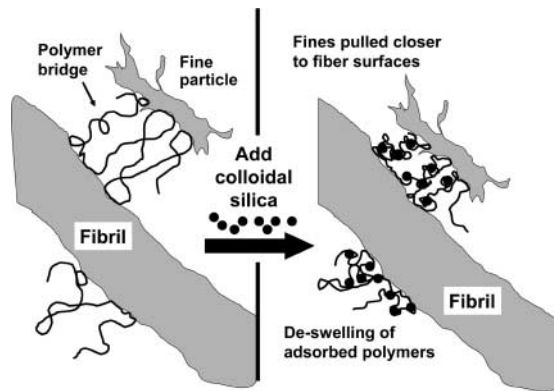


Figure 5. Schematic illustration of the effect of microparticle systems to produce higher dewatering in fiber suspensions due to de-swelling of adsorbed polymers. This effect is most effective when the microparticles are added down-stream of a cationic polymer flocculant.

microparticles, especially when they are added downstream of a cationic polymer flocculant. Let us suppose that the furnish has passed through the previously discussed papermaking steps, and that some of the polymer bridges holding fine particles to the fiber surface have remained intact. Other bridges have been broken, as expected in the case of a polymer bridge that happens to form between two adjacent fibers. A typical colloidal silica microparticle, having a diameter of approximately 5 nm, would be able to diffuse within the coils of these adsorbed polyelectrolytes. Due to strongly opposite charges, the polymer coils then can be expected to wrap themselves around the particles. Not only does such a mechanism result in loss of water from the gelatinous polymeric material, but it also implies that any fine materials connected by polymer bridges will tend to be brought closer to the fiber surface. The latter effect is expected to further enhance the streamlined nature of the fiber surfaces, relative to dewatering. Evidence tending to support the above mechanism includes an ability of microparticles to increase the apparent density of cationic polyelectrolytes, causing them to settle in aqueous solution.^[122,123]

FINAL DEFLOCCULATION JUST BEFORE THE FORMING PROCESS

Because papermaking fibers typically are about 50–100 times longer than they are wide,^[124] shear flow of even a dilute suspension results in countless interfiber collisions. Flow also has the ability to momentarily bend individual fibers, and when the fibers attempt to

straighten themselves out, there is a possibility that they become interlocked with adjacent fibers.^[124] It has been shown that it takes only five flexible fibers, even in the absence of attractive forces between the surfaces, to form a mechanically interlocked floc of fibers.^[6,124–126] Because of these issues, the moments just before formation of a sheet of paper can be very critical in terms of paper's ultimate uniformity. Some of the tricks that papermakers use to tease the fibers into a more uniform layer just before forming the sheet are as follows.

Extensional Flow Within a Hydraulic Headbox

After passing through the pressure screens, and after the final opportunity for chemical addition (often a microparticle), the dilute fiber furnish passes through an approach piping and an intake manifold, arriving at what is called the headbox.^[31] The function of the headbox is to spread the flow into a wide, uniform jet, which leaves the headbox and lands on the surface of a moving fabric screen (see later). On a modern paper machine it is common for the dilute suspension to enter the headbox through a closely spaced bank of parallel tubes. Certain designs involve abrupt expansions in these tubes, resulting in a phenomenon known as extensional flow.^[127,128] Whereas shear flow necessarily causes some degree of flocculation, extensional flow tends to have the opposite effect. One of the unresolved questions related to the strategy just described is whether any potential gain in uniformity is lost due to the unavoidable shear flow when the stock passes through the wide, nozzle-like “slice” of the headbox and emerges into ambient air.

Jet Impingement

A final fluidization can be imparted to the fibers at the moment when the jet lands on the surface of a forming fabric. Two factors are critical, the angle impingement and the relative velocities of the jet and the fabric. A very steep impingement angle sometimes has been used as a cure for excessive flocs, though such an approach suggests a level of desperation—possibly due to defects in headbox design, or over-use of retention aids. A more universal strategy to distribute the fibers into a more uniform mat involves a slight speed difference between the jet and the fabric.^[129] Common practices include both “rushing” and “dragging” of the jet onto the fabric surface, often with a relative speed

difference in the range of 0–10%. Both of rushing and dragging tend to favor a preferential orientation of fibers in the direction of manufacture.^[124,130,131]

PAPER FORMATION AND CONSOLIDATION

The act of forming a sheet of paper can be considered as involving a combination of two idealized descriptions, known as “pure filtration” and “thickening.”^[132] These descriptions are contrasted in Fig. 6. The best practical example of pure filtration is the formation of a test sheet of paper by dewatering of an essentially stagnant fiber suspension through a stationary wire mesh. Such sheets tend to form layer by layer, with the formation of a dense mat adjacent to the mesh. As the sheet continues to be formed, more fibers accumulate at the surface of the densified zone, and fine materials may be trapped by a form of media filtration within the densified zone. In contrast, pure thickening, to the extent that it truly exists, implies a uniform increase in solids content within the mat as water is removed.

Remnants of Vortex Flow

Though the jet opening from a paper machine headbox is essentially rectangular, the interaction of fluid momentum with the jet dimensions give rise to

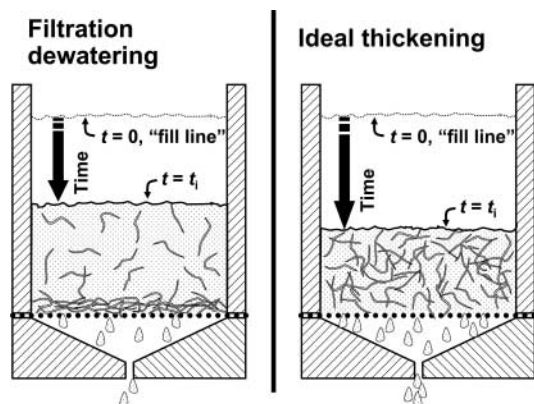


Figure 6. Pure filtration vs. thickening effects in the formation of a sheet of paper by dewatering through a stationary wire mesh. The fibers tend to form a layered structure with a dense mat adjacent to the filtrating surface. As dewatering progresses, more fibers accumulate (the mat densifies even further), and fine materials may be retained. By contrast, pure thickening implies a uniform increase in solids content within the mat as water is removed.

counter-rotating vortices having axes parallel to the direction of production.^[133] These fluid motions persist to some extent in a wave-like manner as the wet web progresses down the forming table of a traditional Fourdrinier-type paper machine. Because the thickness of the paper web decreases due to drainage of water through the fabric, the periodicity of the vortex flow is forced to change. Visible defects sometimes occur if resonant reinforcement of the vortex flow happens to coincide with the location on the forming table where the wet paper loses its fluid character. By careful management of these effects it is possible to minimize subtle streak-like irregularities in typical machine-made paper.

Hydrofoils

If one considers the shape of a typical hydrofoil (see Fig. 7), it is easy to envision the development of a zone of negative pressure over the foil's trailing surface, where the distance between the foil and the forming fabric is increasing. But studies suggest that the leading edge of a typical hydrofoil actually pushes some water in the opposite direction, back up into the wet sheet of paper. The pulsating action, as wet paper passes over a series of hydrofoils appears to play an essential role in speeding up the flow of water from the sheet. In addition, rippling motions known as “action” usually become apparent at the upper surface of the wet paper, especially as the sheet passes over the first several sets of hydrofoil blades. These volcano-like motions, which, when extreme, can result in separation of droplets above the paper, can be tuned by adjusting the type, angular adjustment, and spacing of hydrofoils. Though well-tuned

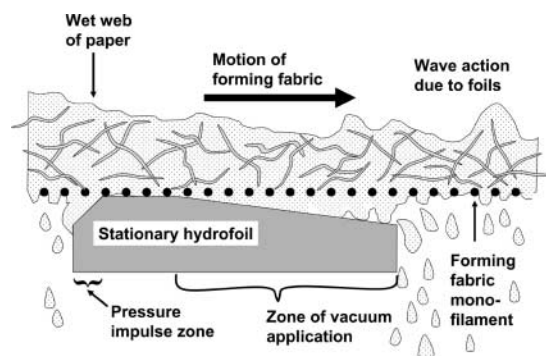


Figure 7. The pulsating action on a wet paper as it passes over a hydrofoil. A zone of negative pressure is developed over the foil's trailing surface, where the distance between the foil and the forming fabric is increasing. The leading of a typical hydrofoil pushes (positive pressure) some water in the opposite direction; back up into the wet sheet of paper.

action tends to even out fiber flocs, making the paper somewhat more uniform, the same hydrodynamic forces also tend to wash fiber fines and filler particles from the side of the sheet facing the forming fabric.^[81,134,135]

CONCLUDING REMARKS

Though further unit operations such as “top formers,” “dandy rolls,” and “wet presses” also can have significant effects on the uniformity of paper, such topics begin to diverge from the present focus on dispersion science. Besides, as shown in this review, the papermaking process as already considered involves a whole series of inter-related steps that affect the state of dispersion of the materials. At first it may appear that papermakers are schizophrenic in their multiple attempts to disperse various solids from each other, usually followed immediately by an attempt to draw some of those same solids back together again. All of these operations provide a truly fascinating area of applied technology, parts of which only recently are becoming understood in a scientific sense.

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