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IMAGING OF MACROMOLECULAR EVENTS OCCURRING DURING THE MANUFACTURE OF PAPER

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ABSTRACT

A novel transmission electron microscopy (TEM) technique, developed to observe the nano-scale interactions of polymeric additives and cellulosic fibrils under idealized laboratory conditions, was applied for the first time in a comprehensive study of the colloidal interactions within a mill producing light-weight coated publication paper. The technique allows the observation of incremental changes in the nano-scale appearance of the papermaking slurry as successive additives are introduced to the system. Such changes include the coagulation of colloidal and dissolved substances present in thermomechanical (TMP) pulp after the addition of a low molecular weight, high charge density polymer, and the subsequent flocculation of the coagulated matter, hydrophobic materials, and fines following the introduction of talc, aluminum sulfate, a high mass cationic polyelectrolyte, and silica nanoparticles. The new results demonstrate that the TEM technique can be applied even in systems as complex as commercial papermaking, leading to a more accurate understanding of what happens on a macromolecular level.

1 INTRODUCTION

Papermakers add polyelectrolytes and other water-soluble materials to the fiber slurry to influence interactions between the fibers, fiber fines, and other components of the papermaking furnish. Wet-end chemistry encompasses the study of how these additives function in papermaking systems. A transmission electron microscopy (TEM) technique has been developed to visualize the adsorption behavior and conformational characteristics of wet-end additives adsorbed on the secondary fines of pulp slurries. This technique has been successfully applied in the case of relatively clean laboratory systems to examine the differences in the adsorption behavior and conformational characteristics of polyacrylamide, starch, and guar derivatives, as well as the effects of varied wet-end conditions [1,2,3,4,5].

The objective of the research presented in this article was to apply the new TEM technique to examine colloidal events in an actual paper mill, to judge whether the macromolecular phenomena observed under laboratory conditions could also be seen under authentic conditions of production. The paper mill selected for this study was producing clay-filled, light-weight coated paper from a blend of thermomechanical (TMP) and bleached kraft pulps. Figure 1 is a generalized schematic diagram of the mill system (pulp streams and additive inlets). Transmission electron microscopy samples were obtained from a series of sampling sites along the TMP stream, focusing on sites where the slurry had undergone significant changes in composition or chemistry. In addition, feeds for talc, alum, BKP, coated broke, and the dilution water from the off machine silo were sampled to facilitate the identification of various components of the papermaking slurry in the micrographs.

2 EXPERIMENTAL

The challenge in this research is to capture the macromolecular wet-end events occurring in a dynamic mill system. To accomplish this, the samples were collected, mounted, fixed, and stained on-site. The prepared samples were then transported to the Institute of Paper Science and Technology for observation by TEM.

2.1 Materials

Chemical and mineral additives employed in the study consisted of conventional industrial materials obtained and used on-site at the paper mill. Sample collection, preparation, and staining equipment and materials were

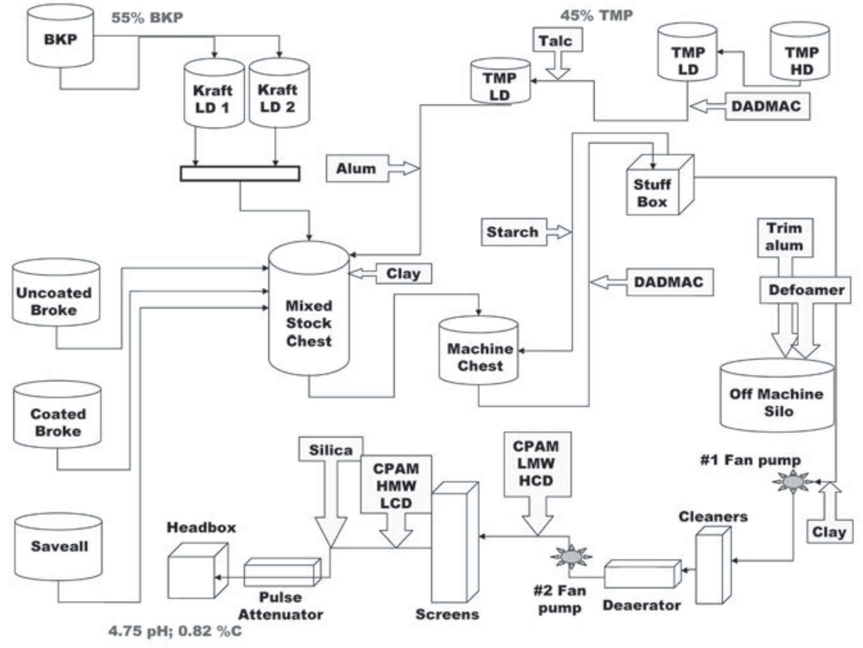

Figure 1 Schematic diagram of the mill system including stock flows and additive inlets.

brought to the mill, along with a large bottle of nanopure water for any necessary dilutions. Collection equipment was limited to several 500 mL wide-mouth, screw-top polyurethane sample jars, and a 7-liter bucket. The sample preparation equipment included a dynamic drainage jar (DDJ) [6], disposable cups for polymer dilutions, and syringes for dosing the slurry. The TEM preparation and staining kit included TEM grids with carbon coated Formvar support membranes, preparation mounts, wire loops, strips of blotter paper, and staining solutions of colloidal gold [7,8] and 2% uranyl acetate [9] in tuberculin syringes.

2.2 Methods

In order to minimize the possibility of artifactual changes from excess contact time, each sample was collected and prepared individually. The samples were collected in 500 mL sample jars. Thick-stock slurry samples were diluted approximately 1:4, and talc and alum samples were diluted 1:200 with nanopure water. Thin-stock samples were not diluted. Slurry samples were shaken in the sample jars to loosen up any large flocs immediately before the TEM grid preparation step, to be described. Again, to minimize the possibility of inadvertent changes during storage, a majority of the microscopy samples were prepared in a laboratory adjacent to the paper machine. Headbox and foil-tray TEM samples were prepared at the paper machine to minimize the interaction time of the drainage and retention additives.

The drainage and retention program employed in the paper mill under investigation can be generally described as a dual cationic polymer system with silica nanoparticles [10,11,12]. As illustrated in Figure 1, the first macromolecular additive, a low to moderate molecular weight, high charge density cationic polyacrylamide, is introduced before the screens. The second polymer, a high molecular weight, low charge density cationic polyacrylamide, is introduced after the screens. Silica microparticles are added immediately after the second polymer. Samples could be obtained from the system prior to the addition of the high molecular weight polyacrylamide and from the headbox. DDJ simulations were performed to prepare samples that could be used to show the interaction of the high molecular weight, low charge density cationic polyacrylamide with the slurry both before and immediately after silica addition. These simulations each used 1 liter of the stock collected from a port situated immediately after the screens. The DDJ was set for 1000 rpm. The polyacrylamide samples were obtained after dosing the slurry and allowing the sample to mix for one second. Mixing was stopped, and samples were prepared for microscopy. The polyacrylamide with silica samples were prepared by dosing the slurry first with CPAM followed a second later by silica. The slurry was allowed to mix for 2 seconds before the DDJ was stopped and samples were prepared.

The procedure for mounting and staining TEM samples is illustrated in Figure 2. Samples suitable for TEM observation were prepared by dipping a wire loop directly into the bulk slurry (sample jar or DDJ). Fibers, fines, filler, and other colloidal materials were suspended in a thin aqueous film spanning the wire loop. The wire loop was passed over the grid, depositing the sample on the supporting membrane. The fluid matrix was removed by holding a piece of absorbent blotter paper up to the edge of the grid. Water was removed very quickly (within half a second), producing a flow of water in the direction of the blotter paper. Secondary currents were created around some fibers and fibrils where that flow was blocked and diverted. Though the sample (fibers, fines, and other hydrophilic materials) itself was wet, there was no thin film of fluid remaining on the grid surface because the carbon coated Formvar membrane surface is hydrophobic. Particles in direct contact with the membrane surface (extending polymer, colloidal particles, fibers, and

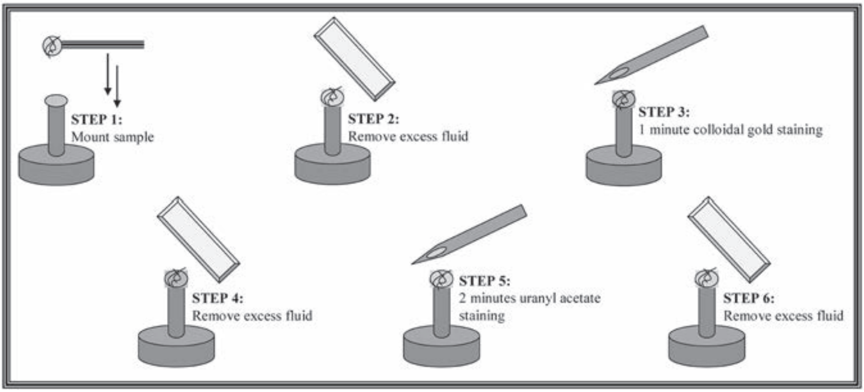

Figure 2 Illustration depicting the steps involved in preparing a sample for transmission electron microscopy observation.

fines) adhere to the membrane and are immobilized. Thus, with the fluid removed, the sample (fibers, fibrils, colloidal matter, and additives) was fixed to the surface of the supporting membrane on the TEM grid (carbon coated Formvar film). The removal of excess fluid with blotter paper limits the time available for polymer reconformation. The elapsed time between stopping the DDJ and removing the fluid from the grid surface was usually less than 1 minute.

The fixed samples are stained on the grid. A droplet of colloidal gold solution was suspended on the grid surface and allowed to stand for 1 minute of contact time with the sample before being removed with blotter paper. Finally, a droplet of 2% uranyl acetate solution was suspended on the grid surface and removed after 2 minutes. The samples were dry within 10 minutes of staining. The dry grids were then placed in a sample holder for transport to the Institute of Paper Science and Technology (Atlanta), where they were observed using a JEOL 100CX transmission electron microscope. Since the samples were taken directly from the mixed slurry and mounted on the grid with the fluid matrix, the authors regard the images obtained as two-dimensional representations of the conditions present in the bulk slurry.

3 RESULTS

The path that thermomechanical pulp takes as it passes through the wet end of the paper machine system has been divided into four sections, separating the areas of major change in the wet-end chemistry of the system. The first section (3.1) deals with thermomechanical pulp and the additions of poly-DADMAC, talc, and alum. The remaining pulps (including the recycle streams) are dealt with as additives to the TMP stream at the mixed stock tank in Section 3.2, along with the introduction of filler clay. Thick stock additions of poly-DADMAC and starch, and the subsequent dilution of the slurry at the off machine silo are covered in Section 3.3. The final section (3.4) encompasses the drainage and retention aid program. Schematics of the pulp stream with general locations of additive inlets and sampling sites are included at the beginning of each section.

3.1 Thermomechanical pulp

Thermomechanical pulps have been noted for their relatively high content of various types of dissolved and colloidal matter, including hydrophobic extractives and anionic trash [13,14,15,16]. The build-up of such materials in the water can be detrimental to certain aspects of paper quality, as well as making it more difficult to reduce the level of fresh water consumption in the manufacturing process [17,18,19]. The schematic shown in Figure 3 illustrates the path of TMP through this section of the wet-end, including additive inlets and the sites from which TEM samples were obtained.

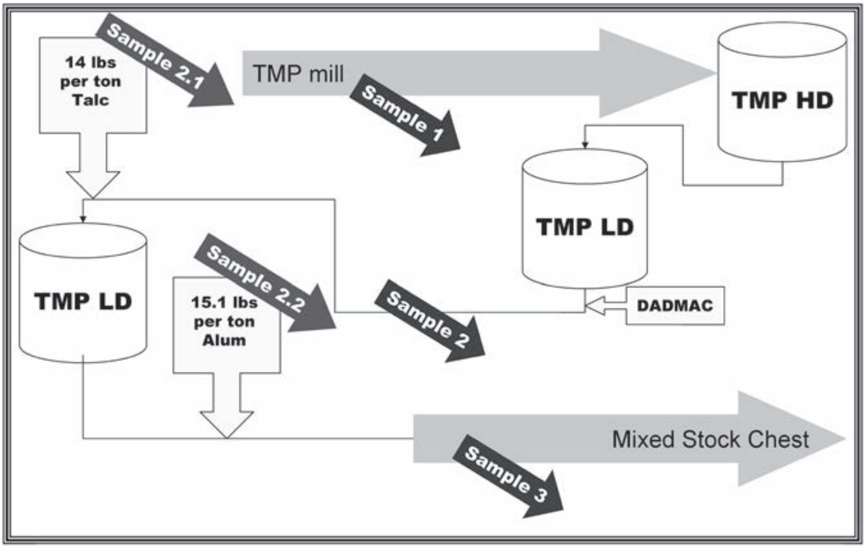

Figure 3 Schematic diagram of the thermomechanical pulp stream from the mill to the mixed stock chest with marked sampling points.

The presence of colloidal matter in the TMP sample is evident in the image obtained from Sample 1 (Figure 4). Hydrophobic materials above their melting points can be expected to form small spheres in the wet-end system of a paper machine in order to minimize the surface area in contact with the water phase. In the micrographs, these materials appear as small circles outlined in gray (small globules) or black (large globules). Colloidal and dissolved materials speckle the image background. Some authors have recommended that such materials be removed from the water matrix and fixed to the fibers and fines of the slurry to reduce the charge demand (cationic additive consumption) as well as the severity of fouling [13,20,21].

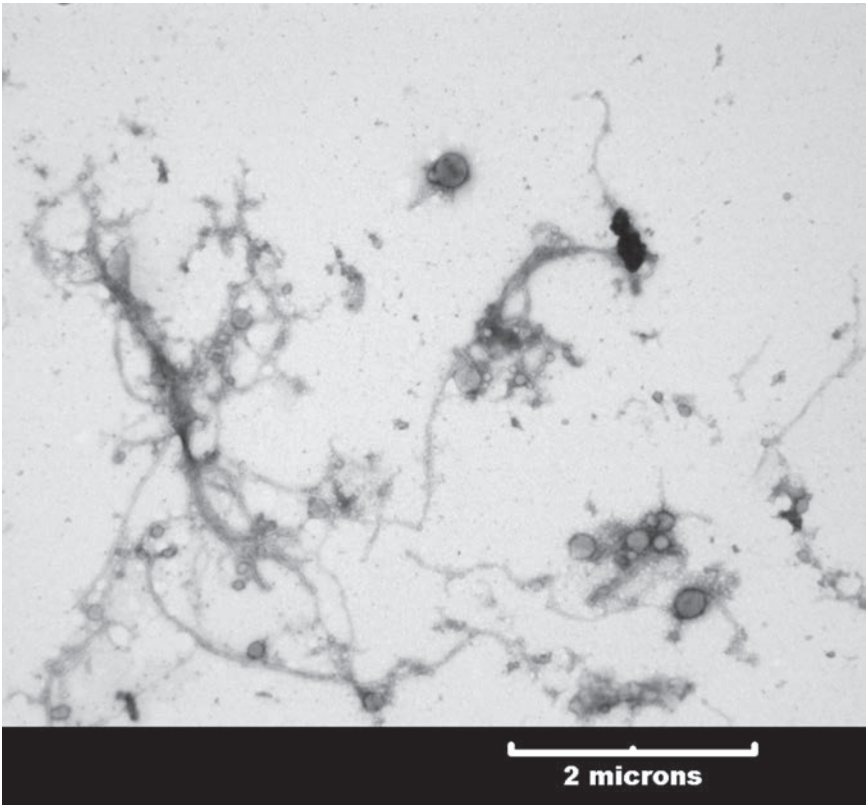

Figure 4 Transmission electron micrograph of the TMP sample collected prior to the introduction of additives showing the dispersed nature of the fibrils and colloidal matter in the system.

Poly-diallyldimethylammonium chloride (poly-DADMAC) is the first additive to enter the pulp stream. Poly-DADMAC is a relatively low molecular weight, high charge density polymer that acts as an anionic trash collector or fixative [22,23]. The micrographs of TMP show the coagulation of some of the colloidal matter in the matrix (porous or branched structures in Figure 5); as well as cationic patches, marked by the anionic colloidal gold nanoparticles, on the surfaces of fibrils are also formed (Figure 6).

Talc and alum are the next additives to be introduced in the wet-end. Talc, shown in Figure 7, is a flat, plate-like mineral, capable of adsorbing both hydrophobic and cationic materials [24]. Particles of alum [25,26] are shown in Figure 8. Alum particles appear as small, branched structures. The cationic

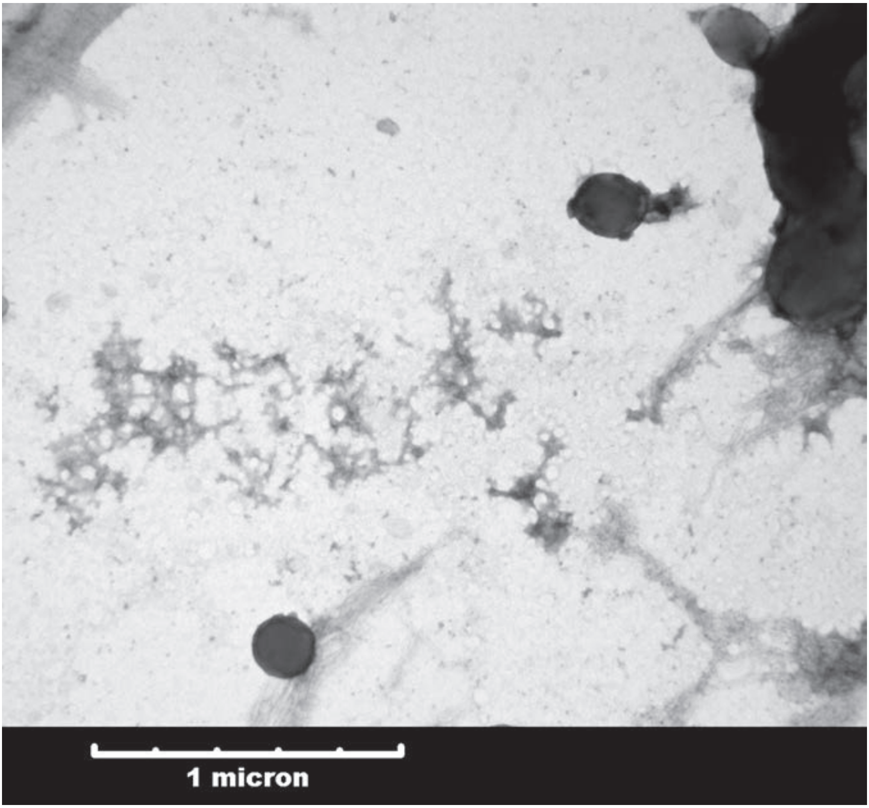

Figure 5 Transmission electron micrograph of the TMP sample collected after the addition of poly-DADMAC showing the coagulation of some colloidal materials in the system. The image background is still speckled with matter.

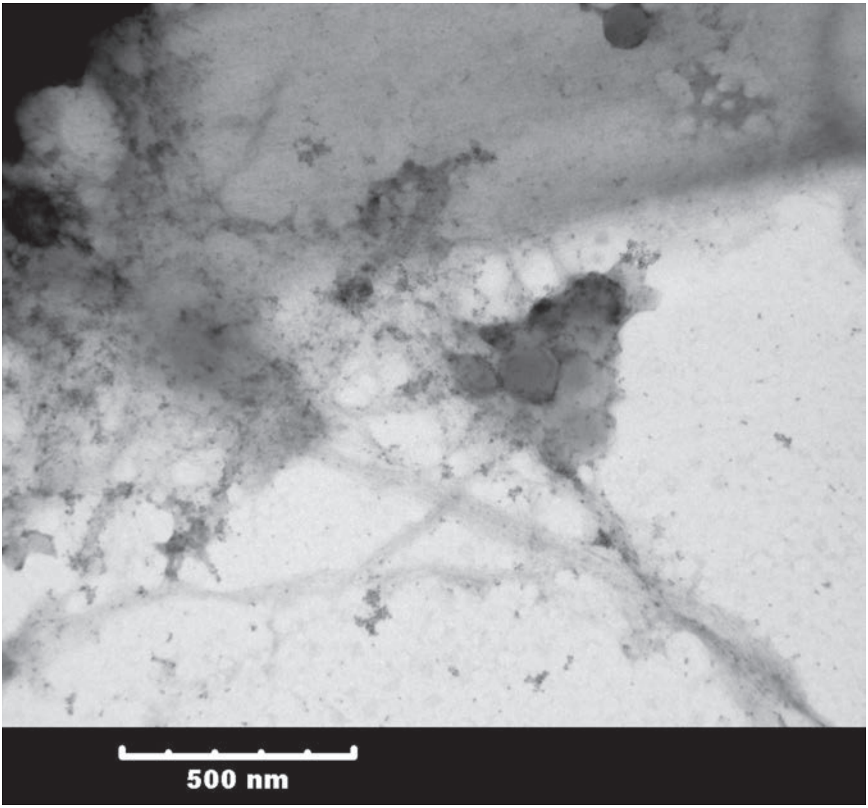

Figure 6 Another micrograph of the TMP sample collected after the addition of poly-DADMAC showing small agglomerations of colloidal gold particles (black spheres measuring 3–7 nm) on and near the fibrils, marking cationic materials (cationic surface patches and small agglomerations).

surface charge of alum is evinced by the adsorption of colloidal gold particles.

The next slurry sample was pulled from the TMP inlet to the mixed stock tank, after the addition of talc and alum to the poly-DADMAC treated pulp. Figure 9 shows porous, branched structures and smaller aggregates, which appear to be fixed on the fibril surfaces. Several talc particles are recognizable in the TEM image by their sharp edges, but the majority of the particles in the agglomerations cannot be identified. Most of the talc particles are probably buried beneath small globules of hydrophobic materials. The image

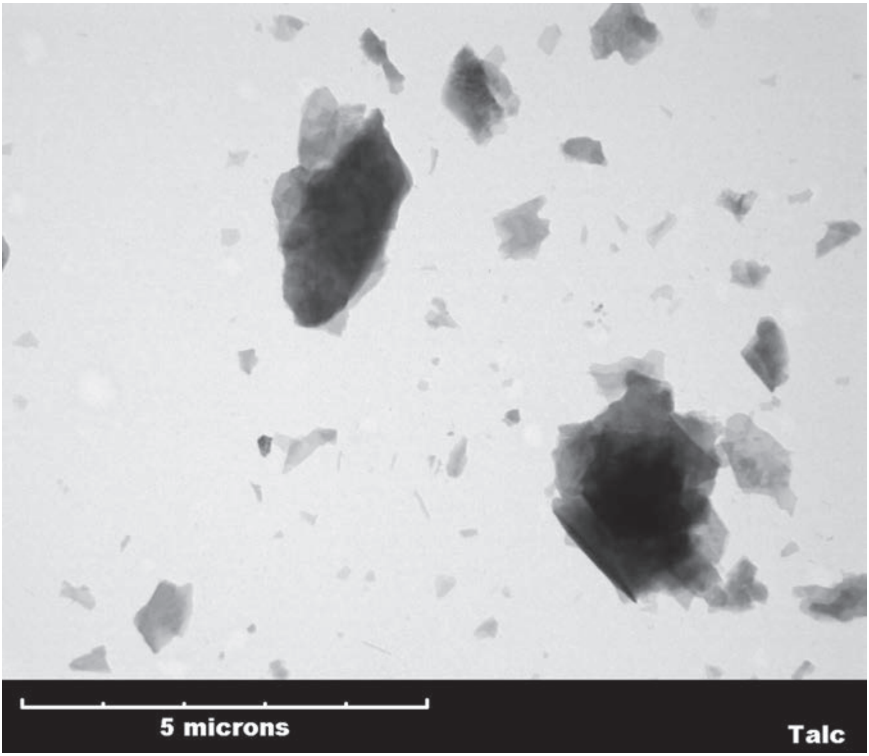

Figure 7 Transmission electron micrograph of talc, a mineral with a flat, plate-like morphology.

background is notably cleaner, indicating that the majority of the colloidal matter has been incorporated into the structures.

Talc and alum thus act as fixatives for the colloidal matter (hydrophobic and anionic materials) brought into the system with the TMP. Anionic colloidal gold particles can be seen in the background, but not notably adsorbed on any of the particle surfaces. The scarcity of anionic colloidal gold particles associated with the solids indicates that few surfaces remained cationic at this stage of the process.

3.2 Mixed stock chest

The mixed stock chest marks the point in the process after which the TMP can no longer be considered as the main component of the pulp slurry. The

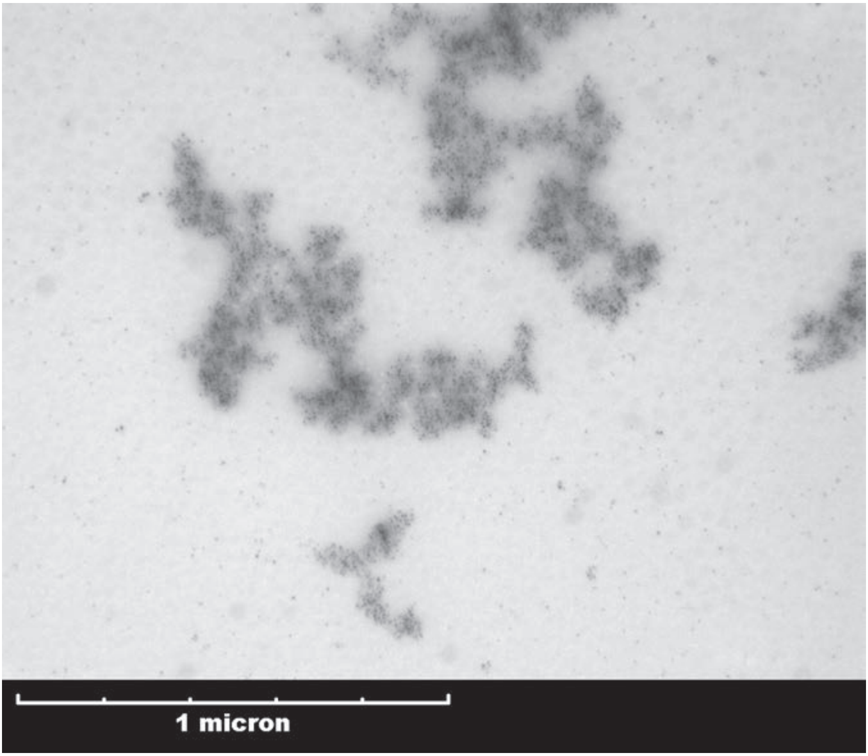

Figure 8 Transmission electron micrograph of aluminum sulfate (alum). Colloidal gold particles adsorb on the alum surfaces through the electrostatic attractive forces of oppositely charged particles.

sampling points are illustrated in the schematic shown in Figure 10. The TMP sample (Sample 3) was discussed in the preceding section. Re-pulped coated broke contains all the materials present in the final paper product, including the materials present in uncoated broke and the saveall, as well as the surface coating (predominantly clay and cornstarch). The sampling around the mixed stock chest was therefore limited to the bleached kraft and coated broke inlets and the mixed stock outlet. The major furnish components can be identified from observations of these four samples, without the need to collect samples from the uncoated broke, saveall, and clay inlets.

The micrographs of bleached kraft pulp reveal the presence of cationic materials in the slurry. Cationic materials are indicated by the presence of

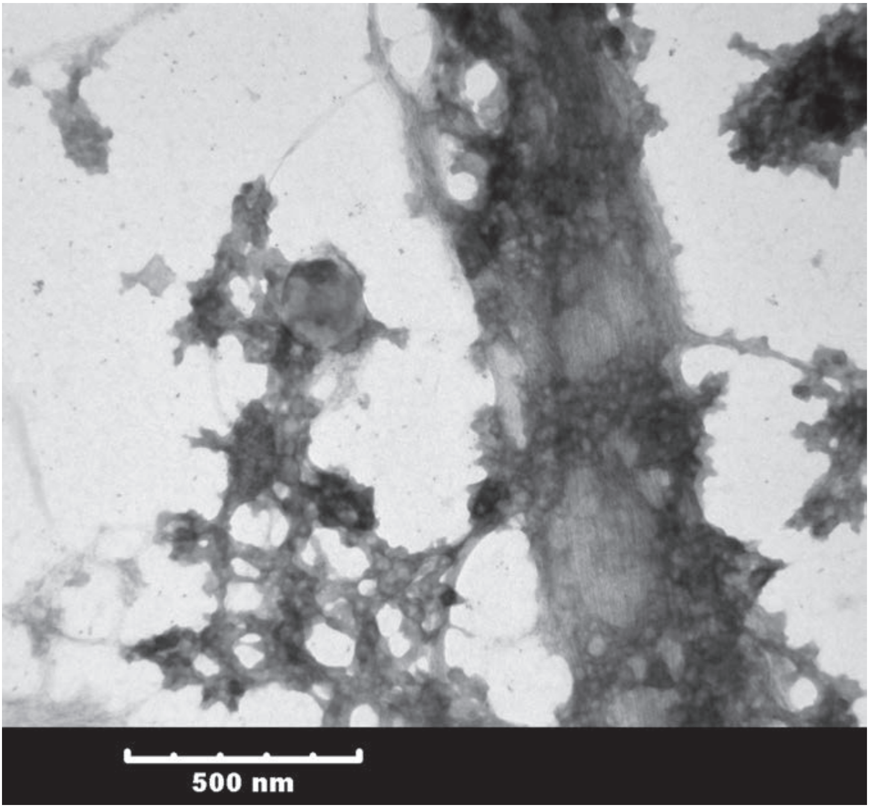

Figure 9 Transmission electron micrograph of the TMP sample collected downstream from the talc and alum additions. Flocculation of coagulated materials and fibrils is evident. Colloidal gold particles are not associated with the flocs, indicating that there is little cationic character to the surfaces.

agglomerated colloidal gold both in the water matrix (Figure 11 background) and on fibril surfaces (Figure 12). The source of these cationic materials is unclear. Cationic material may have been introduced at the point in the process where the pH of the alkaline kraft pulp was reduced. Alternatively, residual cationic materials may have been present in the water used to dilute the BKP for consistency control. Transmission electron microscopy images show a subtle difference between TMP and BKP fines bundles. The striations that mark the orientation of individual cellulose microfibrils in the larger particles of fines are more striking in the images of BKP fines. The kraft pulping and bleaching processes remove many of the materials (notably

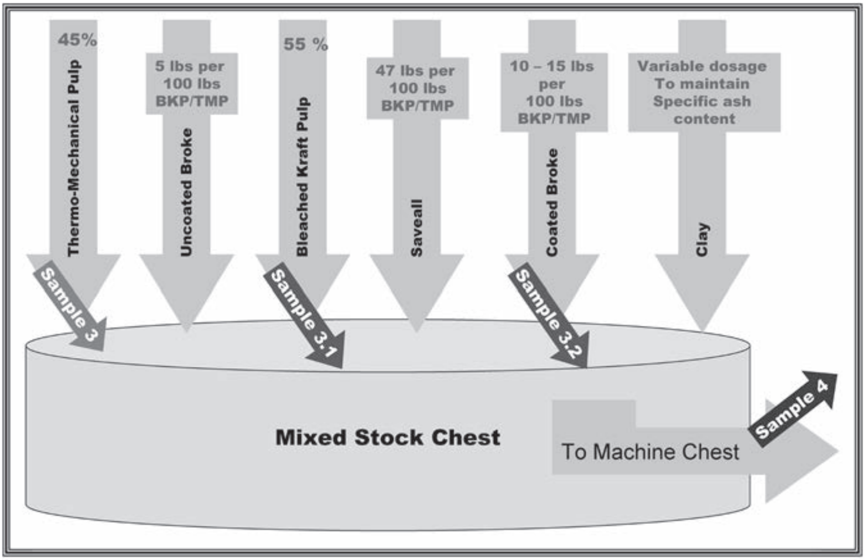

Figure 10 Schematic diagram of the pulp streams surrounding the mixed stock chest with marked sampling points.

lignin) that normally bind the microfibrils into bundles, leaving ridges that can be filled by the uranyl acetate stain [9]. The uranyl acetate has a higher electron density than the materials it replaced, so individual microfibrils are more strongly highlighted in bleached kraft pulp compared to thermo-mechanical pulps.

Coated broke consists of re-pulped coated paper that has been recycled from the dry-line. Thus, it contains all the wet-end additives and fillers from the process, in addition to the surface coating additives. Figure 13 shows clay particles, BKP fibrils, and shadowed areas within the background. The shadowed areas are due to the presence of amorphous coagulated materials. Colloidal gold particles are sparsely adsorbed on one such agglomerate, indicative of the presence of cationic material.

Colloidal and dissolved matter that entered the wet-end system with TMP was dealt with by the additions of poly-DADMAC, talc, and alum. The micrographs showed the incremental cleaning of the water matrix as materials were flocculated and fixed to the surfaces of TMP fines, and the backgrounds of the images became less speckled by free particles. Colloidal materials and loose agglomerations are reintroduced to the system with the bleached kraft and recycle pulp streams. It is also reasonable to expect

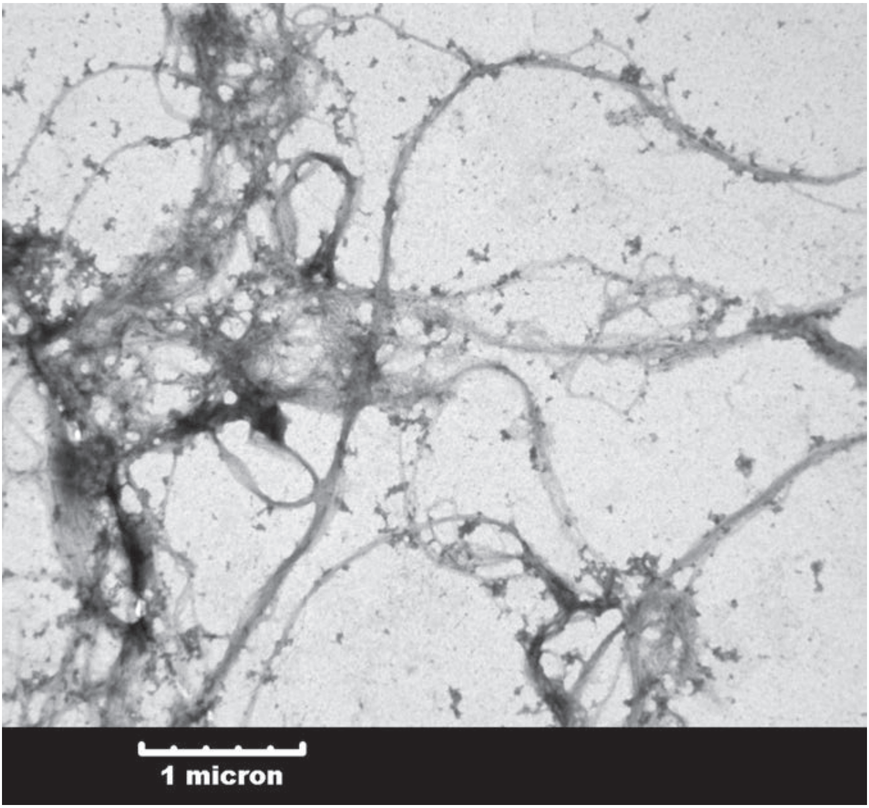

Figure 11 Transmission electron micrograph of the bleached kraft pulp sample collected from the inlet to the mixed stock chest. Colloidal materials are present both in the background and adsorbed on fibril surfaces.

some of the colloidal materials fixed onto the cellulosic surfaces by poly-DADMAC and alum to have become re-entrained, due to continued action of hydrodynamic shear in the process. Thus, the outlet of the mixed stock chest contains all the bulk elements of the papermaking wet-end system: fibers, fillers, and the chemicals added previously, as well as the additives brought in with the save-all and re-pulped coated/uncoated broke streams. Figure 14 contains images of the mixed stock. The top image shows a mass of fibrils and clay particles. The clay can be found as both coagulated masses and free particles. It is not possible to distinguish fresh filler clay from recycled coating clay in the micrographs. The bottom image shows a dense mass associated with BKP fibrils, and colloidal matter lightly

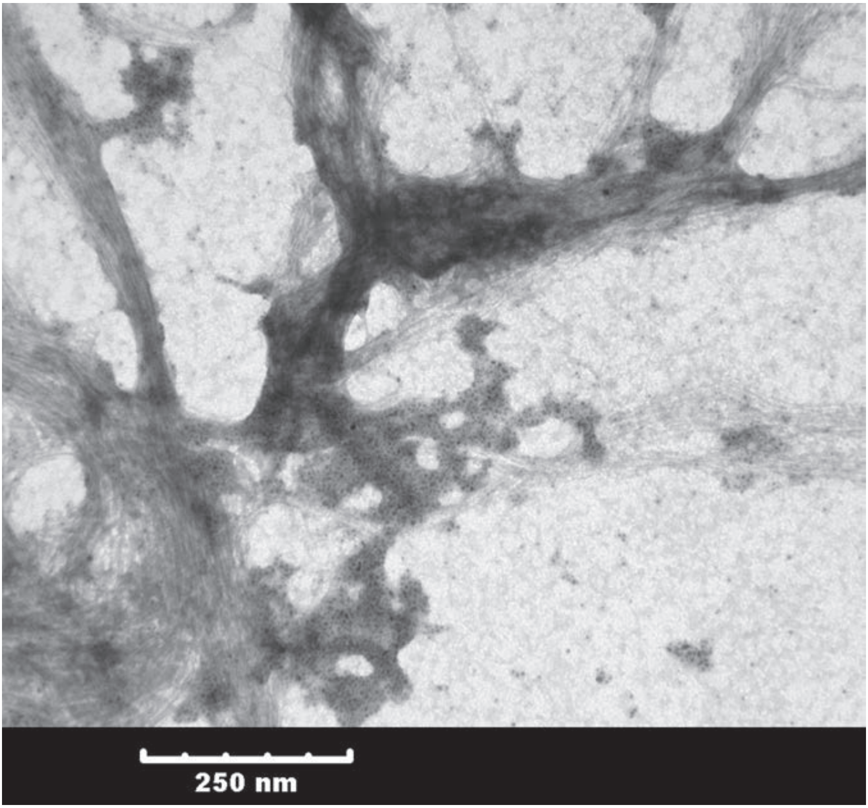

Figure 12 Another micrograph of the bleached kraft pulp sample collected from the inlet to the mixed stock chest, taken at a higher magnification. Colloidal gold particles mark the materials noted at lower magnification, indicating a cationic surface charge on the materials.

speckles the background. The absence of agglomerations of colloidal gold particles is indicative of the absence of active cationic materials in the system.

3.3 Treatment and dilution of mixed stock

After exiting the mixed-stock chest, the slurry undergoes several further wet-end chemical changes before the drainage and retention aid program is applied. A schematic of this section is presented in Figure 15. The mixed stock feeds into the machine chest. There is a pulp recycle stream between the machine chest and the stuff box. The forward stream (from the machine chest

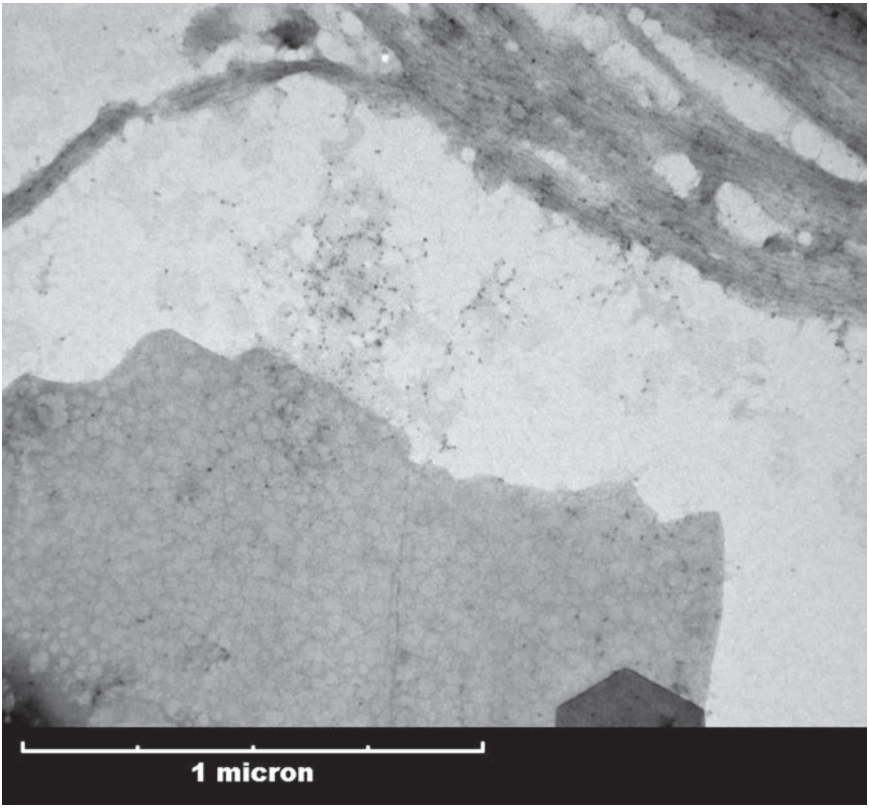

Figure 13 Transmission electron micrograph of the coated broke slurry obtained from the inlet to the mixed stock chest. Colloidal gold is sparsely adsorbed on the fibrils and clay as well as some of the agglomerations, indicating the presence of cationic materials.

to the stuff box) is dosed with poly-DADMAC, and the recycle stream (stuff box overflow) is dosed with a solution of cationic cornstarch before being fed back into the machine chest. Therefore, both poly-DADMAC and starch are present throughout this recycle loop. The thick stock is diluted with recycled whitewater treated with trim alum and defoamer. A second clay feed, situated before the primary fan pump, marks the final alteration in the bulk components of the slurry prior to the introduction of the drainage and retention aid system.

The presence of active cationic polymer in the sample obtained from the stuff box is evident from the presence of adsorbed colloidal gold on surfaces

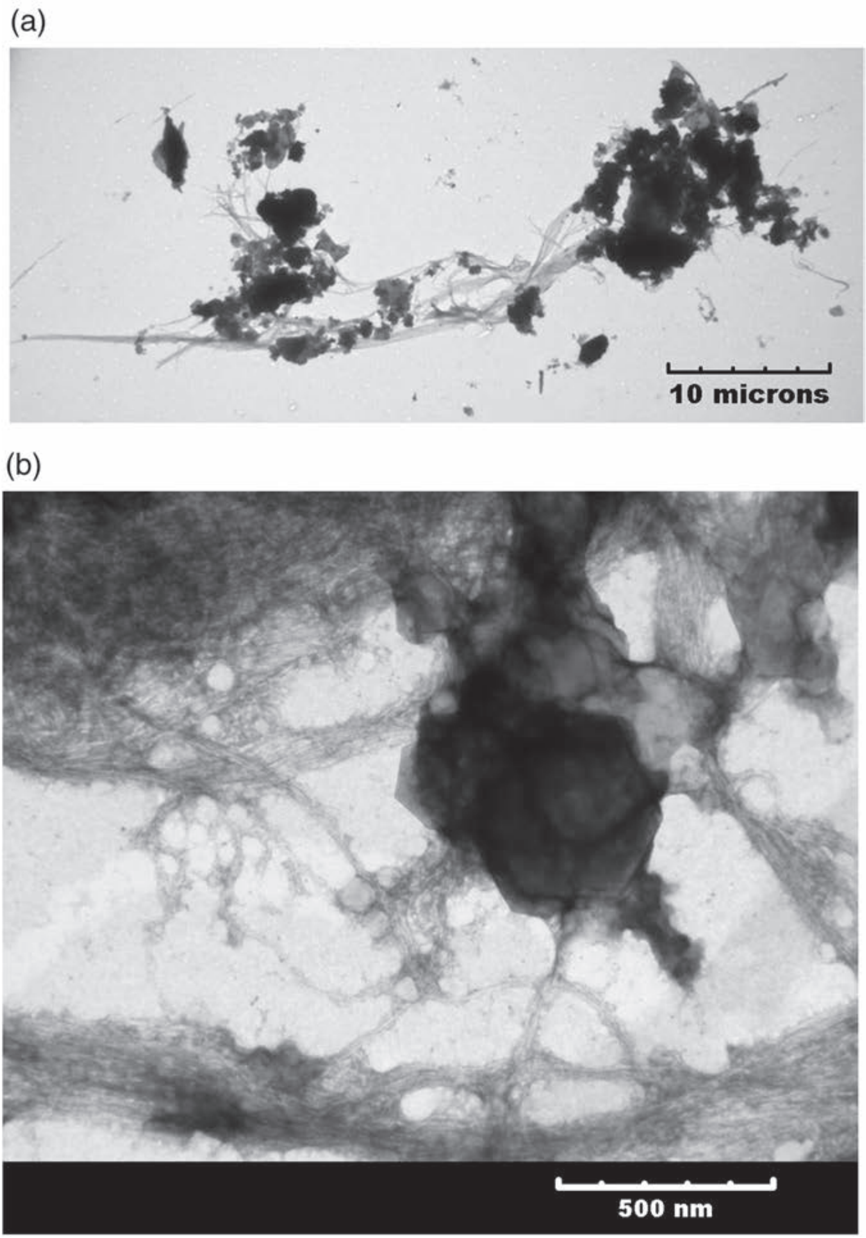

Figure 14 Transmission electron micrographs of the mixed stock. Both flocculated and free particles are present (a). At higher magnification (b), it is evident that the fines, agglomerated materials, and colloidal matter are not heavily marked by colloidal gold, indicating the absence of cationic charge.

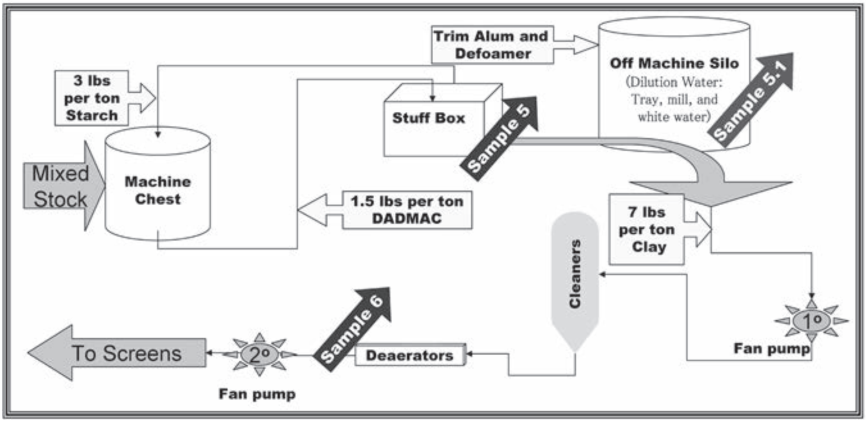

Figure 15 Schematic diagram of the pulp stream from the machine chest to the secondary fan pump with marked sampling points.

of both clay particles and fibrils. Polymers are not uniformly distributed on the surfaces of either fibrils or clay particles. The small cationic patches (less colloidal gold agglomeration), seen in Figure 16, are similar to the cationic patches seen in the TMP sample after poly-DADMAC addition (Figure 6). The larger, bulkier agglomerates (denser colloidal gold agglomerates), seen in Figure 17, are therefore, likely to be patches of adsorbed cationic starch. This interpretation of the images in consistent with the gross molecular structures of the two polymers: poly-DADMAC is a small linear polymer, whereas starch is a composite of amylose (linear) and amylopectin (highly branched). A highly branched polymer is three-dimensional, and it cannot adsorb in a flattened conformation. Linear polymers can assume a two-dimensional structure, allowing them to adsorb in a more flattened conformation.

Judging by the background appearance of the TEM images obtained from stuff-box samples, the water matrix has again been cleaned up by that point in the process. The image backgrounds are relatively free of the colloidal particles and amorphous masses that speckled the backgrounds of the samples obtained from the mixed stock chest inlets and outlets. Another comparison between the treated TMP at the mixed stock chest inlet and the stuff box outlet should be noted. In both cases, the water matrix (image backgrounds) has been cleaned up, but cationic patches, marked by colloidal gold, persist only in the stuff box sample. The poly-DADMAC and alum that had been added to the TMP earlier in the process were probably neutralized by the adsorption of anionic trash in the system.

The off-machine silo provides the dilution water to make the thin stock and

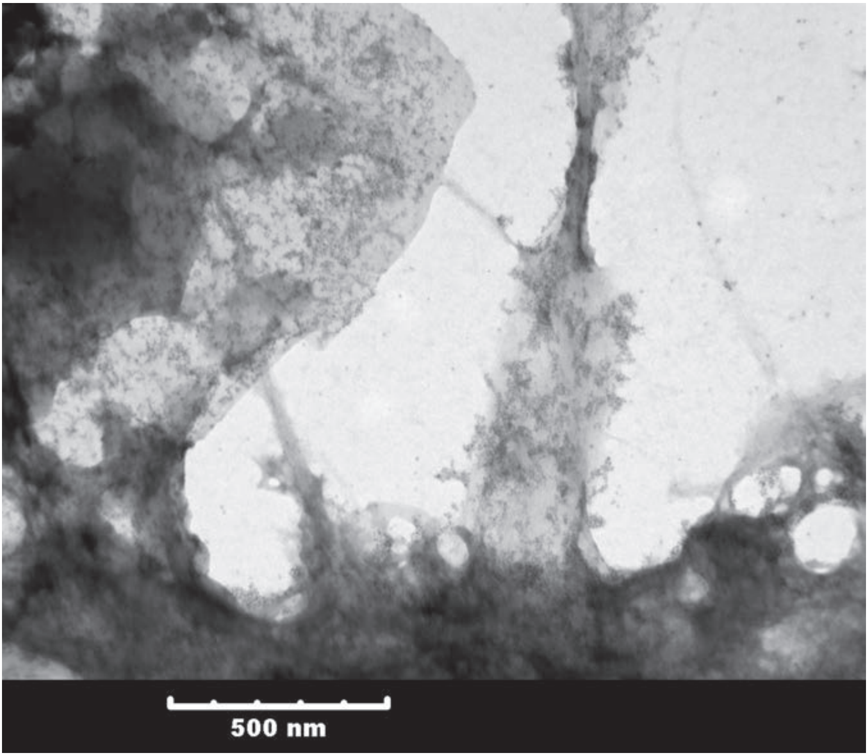

Figure 16 Transmission electron micrograph of the pulp sample collected from the stuff box. Colloidal gold particles are adsorbed on surfaces of fibrils and clay particles (note the large clay particle in the upper left quadrant), indicating the presence of small cationic patches (gold particles are not agglomerated) resulting from the adsorption of cationic polymer. The image background is clear.

includes a recycle loop for the unretained matter from the white water and tray water. This dilution water is treated with trim alum and defoamer. The fines and clay particles are found within dense microflocs in the off-machine silo. Figure 18 and Figure 19 are images of the sample taken from the off-machine silo. The images have relatively clean backgrounds, indicating that the majority of the colloidal and dissolved substances are coagulated and associated with the fibrils. Figure 18 shows positively stained polymer strands and networks extending between fibrils and agglomerated matter. Polymer strands and networks were not evident in any of the previous samples, indicating the presence of recycled retention aid (high molecular weight, linear polymer) in the system that likely originates from the tray water.

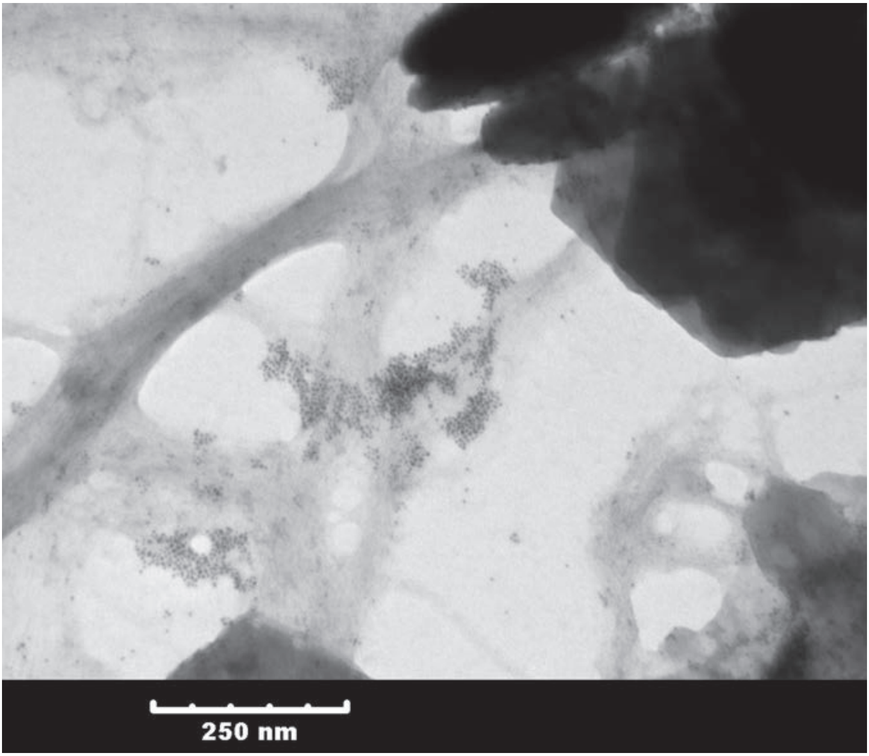

Figure 17 A second micrograph of the stuff box sample showing colloidal gold adsorption in discrete agglomerations, indicating the presence of large cationic patches on the fibril surfaces.

Agglomerates sparsely marked by colloidal gold were rarer (Figure 19). The scarcity of colloidal gold markers indicates a low level of actively cationic materials in the system. It is reasonable to assume that the off-machine silo contains a sufficiently high amount of dissolved anionic substances that, given time, neutralize the residual cationic charge on the materials in the system.

By the time the pulp slurry reaches the secondary fan pump, the system contains all but the drainage and retention aid additives. Fibrils, clay, and cationic patches of adsorbed polymer are readily recognizable in Figure 20. The image background is lightly speckled by the presence of free colloidal matter in the water. The components of the pulp slurry appear well flocculated, but the active (fresh) cationic additives present were all relatively low molecular weight, patch type polymers. These flocs will be unstable under

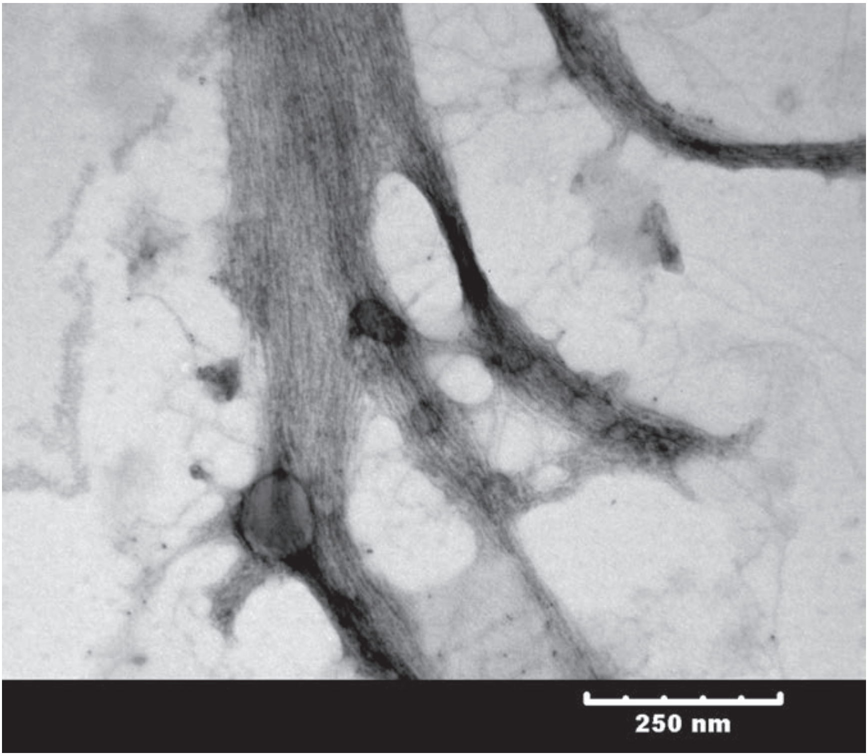

Figure 18 Transmission electron micrograph of a sample of the dilution water obtained from the off-machine silo. Coagulated materials appear bound to the fines by fine strands and networks. Colloidal gold presence is negligible; these materials are not cationic.

shear, and retention of fines and filler on fiber surfaces can be expected to be low.

3.4 The drainage and retention aid system

The final section of the wet-end system, for purposes of this discussion, encompasses the drainage and retention aid system. The stock then proceeds to the headbox and out to the forming fabric. The schematic for this section is presented in Figure 21.

The first component of the drainage and retention program used at the mill is a low to moderate molecular weight, high charge density cationic polyacrylamide that is added just before the screens. Figure 22 reveals cationic

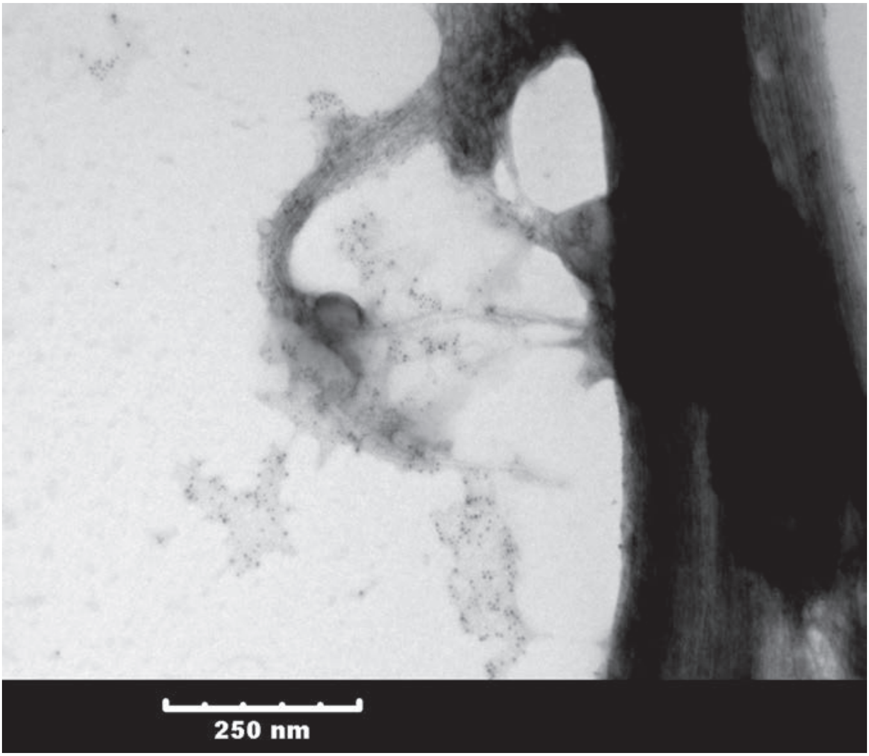

Figure 19 Another micrograph of the off-machine silo sample showing sparse adsorption of colloidal gold on the coagulated materials associated with the fibrils. Some cationic activity has been retained in the system.

materials (colloidal gold presence) both on and near fiber fines. After passing through the screens, the slurry is dosed with a high molecular weight, low charge density cationic polyacrylamide, followed immediately by the introduction of silica nanoparticles. Samples immediately preceding and following silica addition could not be obtained directly from the mill system. Thin stock, sampled from the post-screen site, was dosed in a dynamic drainage jar to obtain microscopy samples for the intermediate conditions.

High molecular weight, low charge density polyacrylamide addition resulted in the formation of long polymer strands and extending networks. Polymer strands were found stretched between particles forming bridges and extending outward into the surrounding medium. Figure 23 shows the bridging strands of high molecular weight polyacrylamide. The polymer strands

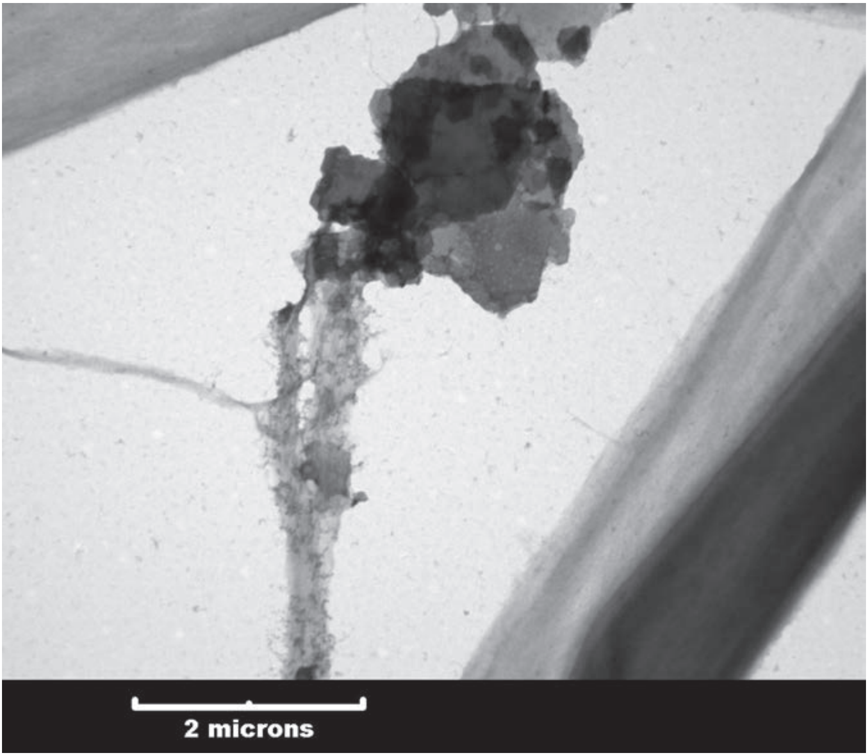

Figure 20 Transmission electron micrograph of a sample of the diluted pulp slurry (obtained before it passed through the secondary fan pump). Cationic patches, marked by colloidal gold particles, are evident only on the small fibrils in the micrograph. The image background is lightly speckled with colloidal materials.

are well marked by colloidal gold particles, indicating active cationic sites along the strands. Linear polymer strands appear to be the most common conformation for the extending segments of anchored, linear, high molecular weight polymers in pulp slurries [1,2,3,4,5]. The cationic character of the high molecular weight polymer was pronounced, compared to the polymer strands found in the microflocs from the off machine silo.

Silica addition in the mill closely follows the polymer addition, without an intervening high-shear point. The slurry then travels through a pulse attenuator, to the headbox, then out to the wire. The next available sampling site is at the headbox. There is ample time for the polymer and silica to interact. To observe intermediate configurations of the polymer/silica interactions, a second simulation was performed to obtain a sample of the slurry immediately

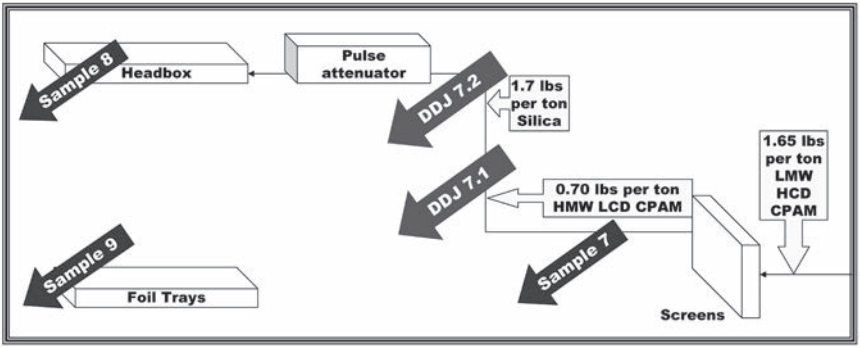

Figure 21 Schematic diagram of the pulp stream as passes from the secondary fan pump to the forming wire with sampling points marked. The dynamic drainage jar (DDJ) was used to simulate the slurry conditions at the sample points designated DDJ 7.1 and DDJ 7.2, using pulp collected from the point labeled Sample 7.

after the addition of silica. The polymer bridges were more entangled after the addition of silica nanoparticles. In areas of low polymer concentration, individual strands can be distinguished in the micrographs (Figure 24). Areas of higher polymer concentration show dense network formations (Figure 25). The polymer bridges and networks are less well marked by colloidal gold than the individual polymer strands found prior to silica addition.

The sample taken from the headbox is shown in Figure 26 and Figure 27. The image backgrounds appear very clean, indicating that dissolved and colloidal materials have been coagulated and are fixed on and within the flocs. Figure 27 shows the flocculation of coagulated materials, fibrils, and clay with colloidal gold lightly marking some of the surfaces within the floc. Polymer strands and networks were less prevalent in the headbox sample than in the previous samples from the DDJ simulations.

Reducing the cationic demand of the system with a coagulant also maximizes the strand formation potential of the high molecular weight, low charge density polyacrylamide (flocculant). Strand formation is important to the mechanisms of nanoparticles. Nanoparticles function by interacting with extended strands of anchored polymer [3]. At this mill, nanoparticles were added within seconds of the flocculant, with no intervening shear point. In such a situation, the bridging mechanism is in progress and floc degradation is negligible if it occurs at all. It follows that the nanoparticles are more likely interacting with long, anchored, polymer bridges and strands as well as free polymer molecules.

The last sample was taken from the tray water. The tray water contains the

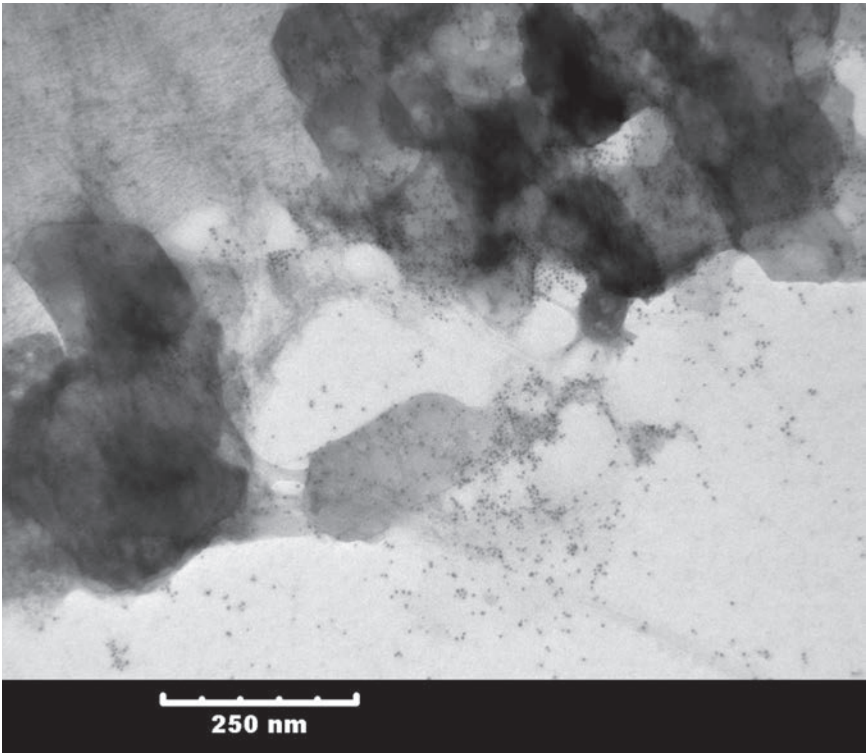

Figure 22 Transmission electron micrograph of pulp sample taken from the screens. Colloidal gold particles are found on clay particles, fibrils, and coagulated materials as well as in the image background, indicative of cationic materials in these areas.

materials not retained in the web. Reflocculation of particles occurs in the tray water. A relatively dense polymer network, sparsely marked by colloidal gold, can be seen extending between clay particles at the edge of a small microfloc in Figure 28. The bridging mechanism of the high molecular weight polymer is observed in Figure 29. The polymer strands are extended between fibrils and clay particles in a loosely entangled network. The image backgrounds are very clean, indicative of a low concentration of free colloidal trash in the system. Only a small fraction of the polymer is marked by colloidal gold. The polymer appears to lose cationic activity as contact time with the system is prolonged. The cationic activity of the polymer may be neutralized by the adsorption of material such as small, polyvalent anions.

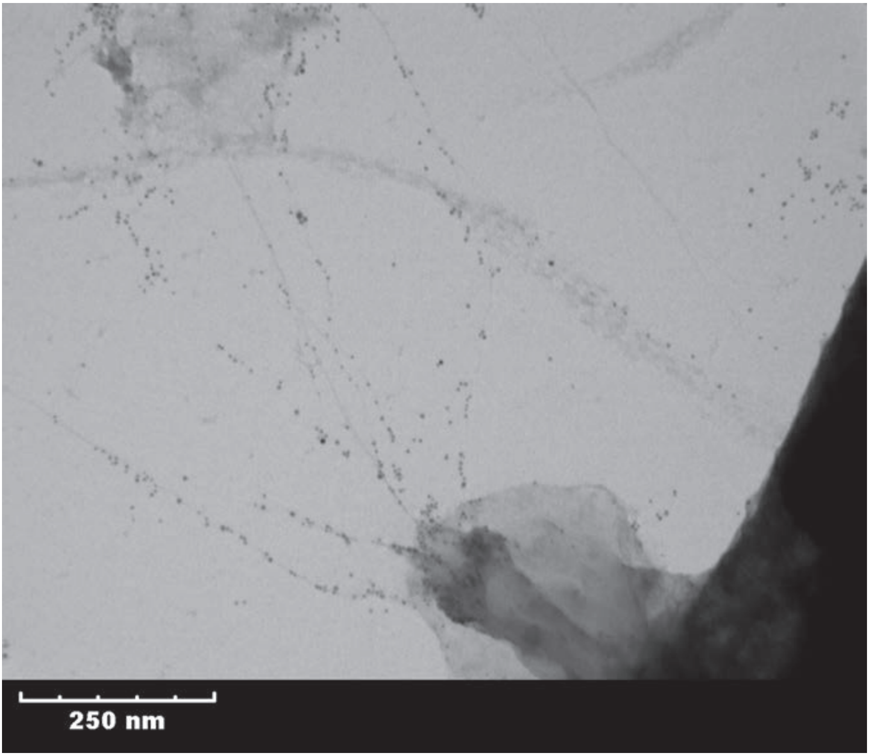

Figure 23 Transmission electron micrograph of the slurry sample immediately after the introduction of a high molecular weight, low charge density cationic polyacrylamide (DDJ 7.1 simulation). Colloidal gold particles are adsorbed on fine strands of polymer extending between discrete particles, forming bridges.

4 DISCUSSION

Though the colloidal phenomena observed in the present study cannot be assumed to be representative of all paper machine systems, especially those involving contrasting fiber furnish or chemical additives [27,28,29,30], it is remarkable how many of the features revealed by the TEM micrographs mirror certain findings of earlier lab studies, as will be discussed. At the same time, it makes sense to discuss aspects of the colloidal events taking place in the paper machine wet end that have been shown for the first time, or more clearly, by means of the present TEM imaging methods.

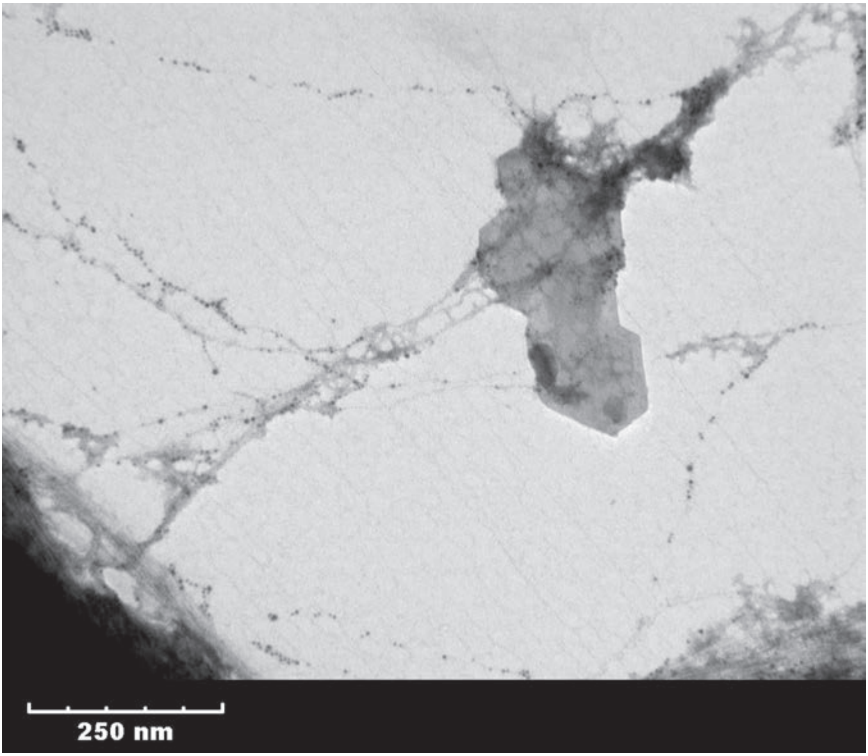

Figure 24 Transmission electron micrograph of the slurry immediately after the addition of silica nanoparticles (DDJ 7.2 simulation). Colloidal gold particles mark the entangled strands of polymer that connect a clay particle to the fibrils around it.

4.1 What we can learn from TEM micrographs

To begin, the following is a summary of the kinds of information that the TEM procedures can provide, not only in the present study, but also in future research or applications in the field:

- Theories of wet-end chemistry in relation to polyelectrolyte adsorption on cellulosic surfaces can be verified by ultra-high resolution images. Such theories may involve retention and drainage aids, nanoparticle systems, sizing agents, and a variety of other wet-end additives.
- The function of polyelectrolyte additives can be understood in relation to the polymer conformation, especially in the case of bonding agents and retention and drainage additives.

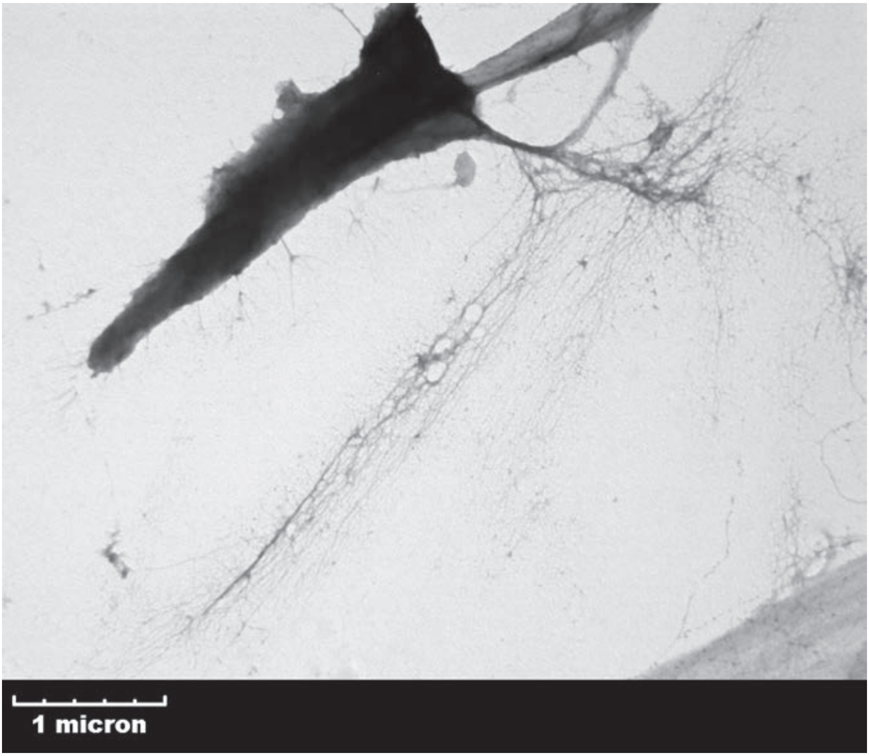

Figure 25 A second micrograph of the slurry immediately after the addition of silica nanoparticles (DDJ 7.2 simulation) showing dense polymer networks and strands extending away from the fibrils of one fines particle and linked to a second mass of fibrils.

- The degree and uniformity of coverage of cellulosic fibril surfaces by a given chemical additive can be visualized in relation to its function, *e.g.* sizing.
- The degree to which charged polymeric additives either retain their charge or become neutralized by interaction with other charged materials in the wet-end system can be explored by a colloidal staining method, as was demonstrated in the present study.
- The dynamics of a paper mill system can be understood in relation to polymer dosage and fluctuations in the concentration of anionic dissolved and colloidal substances. Such information can be valuable from the standpoint of a "particle management" strategy of wet-end chemistry optimization [31,32].

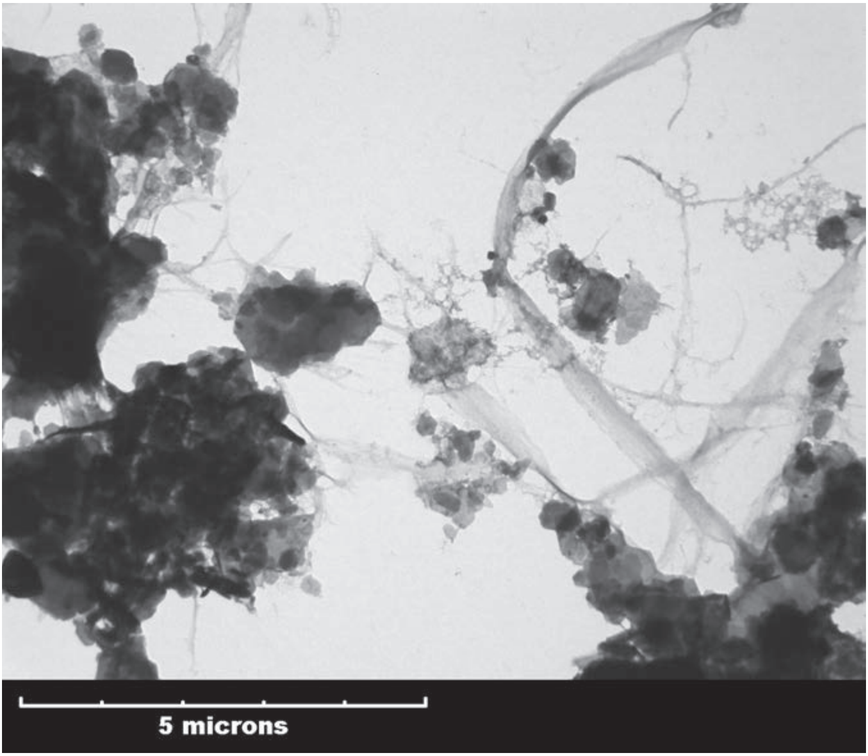

Figure 26 Transmission electron micrograph of the pulp sample obtained from the headbox. The heteroflocculation of fibrils and clay particles is pronounced, and the image background is relatively clear of colloidal matter.

- In-mill diagnosis, trouble-shooting, and process improvement efforts can be carried out [33], in which the TEM method is used, possibly in combination with other well-known procedures.
- The design of new wet-end polymers can benefit from the kind of detailed information about polymer function that the TEM method provides.

4.2 Colloidal matter and its interaction with charged substances

One of the most striking features of the TEM micrographs, when one compares results from the different sample points in the paper machine system, is the contrasting amount of colloidal material that can be observed in the aqueous phase, separate from the cellulosic materials. As noted in a

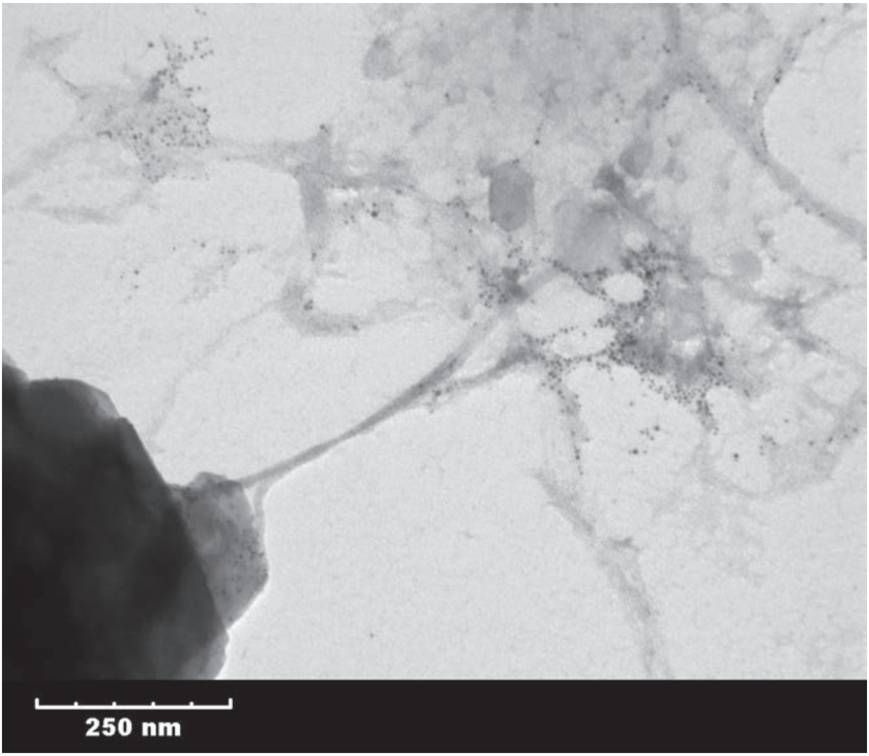

Figure 27 A second transmission electron micrograph of the headbox sample, at higher magnification, showing colloidal gold adsorbed either as discrete particles or in loose agglomerations, indicating the presence of both large and small cationic patches on the flocculated materials.

recent review article [34], the papermaking process can be viewed as a sequence of agglomeration and redispersal steps, and the present results provide a further illustration of this description. The initial well-dispersed state of colloidal materials in papermaking furnish, containing mechanical fibers, such as TMP, can be attributed to a highly negative surface charge. Components that contribute to the charge include anionic wood resins, fatty acids, lignin, and products of peroxide bleaching [14,35,36,37,38,39]. The resulting negative surface charge, and the resulting electrostatic repulsions, may explain the well-dispersed nature of colloidal materials in the system. This was shown in Figure 4, prior to treatment of the furnish with highly charged cationic additives.

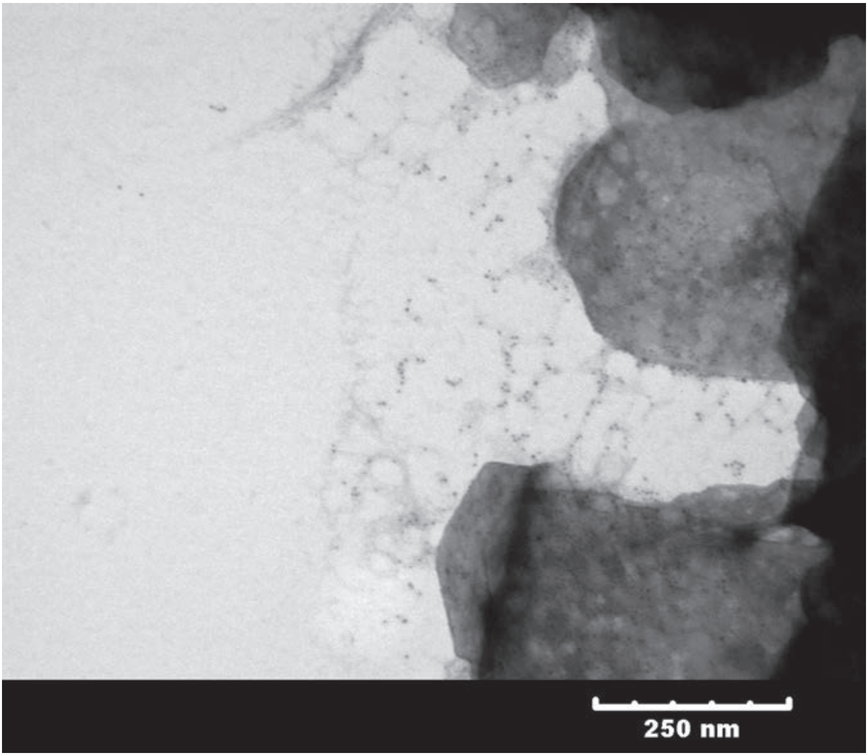

Figure 28 Transmission electron micrograph of the white water sample taken from the foil trays. A network of polymer, lightly marked by colloidal gold particles, extends between clay particles and fibrils. Colloidal gold also marks cationic patches on the surfaces. The background, away from the floc, is clear.

The observation that colloidal materials can be agglomerated together or deposited onto cellulosic fiber surfaces by the addition of cationic materials, such as multivalent inorganic cations and poly-DADMAC, has been shown in earlier fundamental studies [40,41,42], though this is the first time that such events have been captured by a high-resolution imaging method. For example, certain studies have shown that coagulation and the dewatering rate of pulp suspensions could be maximized by adding just enough of a high-charge-density cationic additive to achieve a zeta potential near to zero [43,44,45,46].

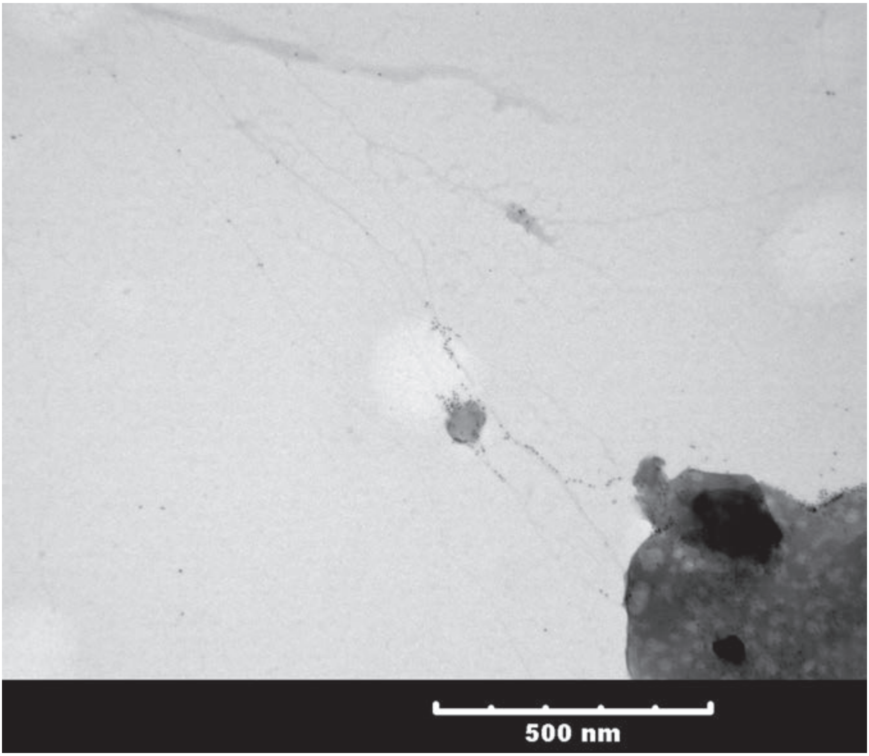

Figure 29 A second micrograph of the tray water sample showing fine polymer strands extending between fibrils, and clay particles. The majority of the polymer in the strands is unmarked by colloidal gold particles, indicating that the polymer lost cationic character.

4.3 Redispersal by hydrodynamic shear

Because of the complex nature of a commercially operating paper machine system, the present results do not provide a conclusive account of whether or not the colloidal materials that were coagulated by alum and poly-DADMAC relatively early in the process remained fixed to fibers, or whether they later become substantially redispersed, due to the continuing action of hydrodynamic shear [34,47,48,49,50]. The subject of flow is doubly significant in the present study, since the polyelectrolytes being sampled experience hydrodynamic shear both while they are in the papermaking process and, to a presumably minor extent, also during their capture onto collodion film, for purposes of TEM imaging. A number of authors have stated, either in principle [47,51,52,53] or by experimental demonstration [49,54], that the intensity of shear stress required to detach very small colloidal particles from fiber surfaces ought to be much greater than the shear stress needed to disperse fibers from each other, assuming that the same types of colloidal forces are acting among all of the solid surfaces. Furthermore, it has been shown that high-mass polyelectrolytes are capable of forming highly shear-resistant attachments [55,56,57], though it is worth noting that polyelectrolyte bridges generally do not form again with the same strength if sufficient shear is applied to break them [58,59,60,61]. For all of these reasons, it seems unlikely that the TEM sampling methods cause significant shear-damage to the deposited colloidal flocs.

The fact that fine materials were observed mainly to collect onto fibrils, rather than adsorbing onto the fibril-free areas of fiber surfaces, agrees with earlier studies, including the early work by Haslam and Steele, observing wet-end chemical events at a very small scale [62]. The mechanistic explanation for colloidal deposition onto fibrils appears to be related to hydrodynamics. Even when the undisturbed streamline paths of two objects immersed in simple shear flow would tend to make them collide, a lubrication effect, related to the difficulty of removing the fluid between them, tends to make them avoid each other when they get close [63]. By comparison, the hydrodynamic resistance to a possible collision with a nano-sized strand of cellulose, attached to a fiber, is expected to be much smaller. Capture efficiency is expected to be more favorable with a fibril, especially in cases where the electrical repulsive forces have been reduced, by suitable addition of cationic additives [64].

4.4 Coexistence of positive and negative surfaces

The observation of strong adsorption of anionic colloidal gold particles onto polymeric materials in some of the samples (see Figures 12,17,23,24) helps to settle a point of apparent conflict between two sets of earlier findings. On the one hand, observations by Jaycock, Pearson, and coworkers [65] suggested that negatively charged colloidal materials tend to cover all exposed surfaces within a slurry of papermaking material, causing all of the surfaces to acquire approximately the same value of zeta potential. It is probably because of such adsorption of colloidal materials, present in the process water, that wet-end addition strategies based on charge alone have achieved only modest levels of success in practice. On the other hand, more recent work by Sanders and Schaeffer has conclusively demonstrated the coexistence of populations of suspended fine particles, in a papermaking furnish, having at least two different modal zeta potentials [66,67,68]. Thus, at least for a short time after addition of a cationic additive, there is precedent for still being able to observe substances having contrasting sign of charge.

The mechanism proposed by Jaycock *et al.* [65], *i.e.* coverage by anionic colloidal materials, is not the only viable explanation for an observed diminishment of the apparent cationic charge of colloidal material, as it is sampled at successively later stages of a papermaking process (compare Figures 6 and 9). Other earlier studies suggest that cationic polymers are able to progressively bury themselves either within dead-end pores in the fiber cell walls [69,70], or within the jungle of fibrillar materials at fiber surfaces [71]. Despite that attractiveness of such explanations, in terms of rationalizing the observed decay of cationic charge [45,72,73,74] or flocculating ability of added cationic polymers [75], it is worth noting the mismatch between the relatively large size of many of the cationic polymers employed in papermaking [27,28,29,30], versus the tiny pore sizes in the cell wall, which generally fall in the range of 1 to 20 nm [76,77,78,79], depending on the type of fiber and the pore-size analysis procedure. Results of streaming potential tests sometimes show cases in which the rates of charge decay are too minor to explain the substantial changes in dewatering characteristics or the state of flocculation which occur following addition of a cationic polymer additive [80]. Yet another way to understand the diminishment of identifiable positively charged entities, as materials pass through a papermaking process, involves the progressive formation of polyelectrolyte complexes [81,82,83,84].

4.5 Effects of sequential cationic polymer additives

The term "dual-cationic-polymer, followed by microparticle" can be used as a shorthand identification for the chemical program being used for retention and dewatering in the paper mill considered in the present study. Leaving the subject of microparticles for later, it is worth considering the synergism between two sequential cationic polymer additives [13,15,21,85,86]. As already pointed out, aluminum sulfate and poly-DADMAC may serve as sacrificial donors of cationic charge, helping to neutralize excess negative colloidal charges in the system [13,36,38,87,88,89]. Then, when a very-high-mass cationic PAM retention aid molecule is added to the system, it does not immediately become neutralized and used up by those anionic colloids [16]. This line of thinking probably is adequate to explain the observed highly effective flocculating ability of the cationic PAM, as illustrated in Figure 23. However, it is also worth considering a second mechanism, which also may contribute to the same ends. That is, the lower-mass, higher-charge cationic additive may act as a site-blocker [85,86]. It has been shown that, even in the absence of anionic colloidal materials, pre-adsorption of a sub-monolayer of highly charged cationic polymer onto the surfaces of suspended solids can greatly enhance bridging flocculation with a cationic PAM retention aid [85,86], as well as enhancing the effectiveness of a microparticle additive added downstream from the cationic PAM [90]. Such effects are consistent with a mechanism in which the first additive covers part of the cellulosic surfaces, forcing the second additive to adsorb with a more extended molecular conformation, leading to more effective polymer bridging interactions.

4.6 Strand formation among PAM molecular chains

In principle, as a precondition for the formation of twisted strands, involving two of more adjacent macromolecular chains of retention aid molecules attached to fiber surfaces, there has to be a high degree of polymer chain extension outwards from the substrate surface. Conditions that favor highly extended conformations of adsorbed macromolecules include relatively short elapsed time after mixing, high molecular mass, and relatively low affinity of the chain segments for the substrate [91,92]. For instance, the net attraction between charged groups on the polyelectrolyte and the substrate can be reduced by addition of an intermediate level of salt [93] or by reducing the charge density of the polyelectrolyte [94]. Under these conditions, state-of-art theories of polyelectrolyte adsorption predict a predominance of macromolecular "tails," rather than "loops" extending outward from the substrate [95].

It is especially notable that the present results, obtained from a commercial papermaking operation, show similar strand-forming behavior of very-high-mass acrylamide-type retention aid polymers, as was shown in earlier lab-based experiments, using the same methodology [1,2,3,4,5]. Although the formation of strands, among adjacent long-chain macromolecules, in no way appears to contradict the main findings of previous fundamental studies, it is interesting that such features are not shown in the cartoon diagrams used by the authors of the best-known descriptions of polymeric bridging phenomena [27,28,30,96,97,98,99,100,101,102,103]. While it is always worth considering that part of the observed formation of strands might be influenced by the presence of flow during the sampling procedure (see Experimental), the shear stress associated with TEM sample preparation is expected to be low in comparison to the unit operations associated with papermaking [48].

Finally it is worth noting the general agreement between published mechanisms and observations immediately following addition of the microparticle additive [10,12,104]. The new observations, based on nano-scale imaging, suggest that one of the main effects of the microparticle addition is to further agglomerate the colloidal materials, possibly forming denser structures than were formed by the polyelectrolytes alone. Similar agglomerating effects also have been observed under idealized laboratory conditions, using a variety of experimental approaches where a cationic acrylamide interacts with negatively charged microparticles or nanoparticles [12,60,105,106]. For example, Burgess and Phipps [106] observed a contraction in the size of PCC flocs, previously flocculated by cationic PAM, upon addition of a microparticle. Swerin [105] observed increases in the yield stress of fiber suspensions, due to an apparent bridging action of the microparticles, when they were added to a system already treated with a cationic retention aid. Various studies have suggested that microparticle-induced flocculation differs in a characteristic way, compared to flocculation by polyelectrolytes alone, giving rise to substantial increases in dewatering rates [12,107], and greater reversibility of fiber flocs, following their disruption by hydrodynamic shear [108,109]. It appears likely that follow-up work, using high-resolution direct imaging methods, such as those used here, can shed more light on such effects in the future.

4.7 Capturing transient events at a nano-scale

Given the very high rates at which certain events can occur at the molecular level, it is reasonable to consider what happens when a small sample of colloidal suspension, taken from a paper machine system, is “captured” on a wire loop and placed on a collodion film (see Experimental). Once the film has been dried, the material deposited on the film is assumed to represent a frozen moment of time. Possible artifacts, if they are significant, would be introduced during the one or more minutes that elapse between removal of the sample from the paper machine system and drying of the collodion film.

The critical nature of the time variable, with respect to wet-end chemical interactions was shown, for instance, in a study by Forsberg and Ström [110]. These authors observed a strong flocculating effect of cationic PAM retention aid when it was freshly added to a flowing suspension; the flocculating ability had essentially disappeared within about 30 seconds. The authors concluded, however, that the loss of retention aid effects was due to flow effects, rather than time alone. A more recent study, concerned with optimization of the addition point for retention aid polymers, led to basically the same conclusion [80]; depending on the nature of the fibers, polyelectrolyte bridges associated with fiber flocculation were found to be stable over a period between 20 minutes and many hours, as long as the flocculated suspensions were unstirred. By contrast, the fiber flocs were quickly broken when such mixtures were agitated, and the fiber slurry became indistinguishable from an untreated control slurry.

Conformational changes of very-high-mass polyelectrolytes, in their adsorbed state, can be expected to take many minutes [92,101]. At the other extreme, the initial adsorption of low-mass cationic polymers can be presumed to take place in a small fraction of a second after addition to the furnish [100]. It has been shown, for instance, that only a few points of attachment are needed in order for a high-mass retention aid molecule to be effectively bound to a fiber surface, [111], and flow-induced collisions are exceedingly rapid [101,112]. Based on the findings just discussed, it is reasonable to assume that TEM images prepared as described in this article mainly show the consequences of polyelectrolyte interactions, including adsorption and complexation, which already have reached a quasi-stable state, although there is no expectation that a true equilibrium state can be achieved.

4.8 The complexity of real paper machine systems

Even in view of the excellent resolution and detail of the TEM images, in addition to the fact that the general observations are mutually supported with other published findings, it is still necessary to admit that the colloidal environment of an operating paper machine is exceedingly complicated. All too frequently, papermakers have had to rely on macroscopic observations, such as flocculation measurements [104], retention effects [113], or drainage effects [114,115], rather than having any direct evidence about the fate of various chemical additives at a colloidal scale of observation. To a large extent, the theories related to the role of polyelectrolytes in flocculation of suspended materials also have been supported by macroscopic observations, rather than by direct imaging. Consequently, some of the conceptual representations of what happens at a colloidal scale in these industrial systems have tended to be oversimplified. It is hoped that the present work, even venturing into the complexity of a real paper mill, will inspire others to develop complementary methods capable of adding to the picture of what is happening at a nano-scale during papermaking, with an ultimate goal of further improving the efficiency and flexibility of these manufacturing processes. For example, methods related to those used in the present study could be developed into a routine system for diagnosis of wet-end additive systems for troubleshooting and process optimization. Complementary methods, including AFM imaging [116], may sense different aspects of what is happening at a molecular level, making it possible to achieve a more multifaceted interpretation.

5 CONCLUSIONS

- The transmission electron microscopy technique is a viable method for examining the macromolecular events occurring in dynamic papermaking systems.
- Theories of polyelectrolyte adsorption on cellulosic surfaces can be both verified and expanded upon using high-resolution imaging methods like the TEM technique described in this paper.
- The mechanisms of additives can be understood in relation to the adsorption, degree of coverage, and extension from the substrate surface, which could aid in the design of new wet-end additives, as well as mill diagnosis and process improvement efforts.

6 ACKNOWLEDGEMENTS

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Transcription of Discussion

IMAGING OF MACROMOLECULAR EVENTS OCCURRING DURING THE MANUFACTURE OF PAPER

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James Watkins Procter & Gamble

Thank you very much Dr Nanko, some great images. My question is: can you push this technique to also see where the cationic material is in the sheet and in bonds?

Hiroki Nanko

It would need to be a different technique, since your paper sample would be in a dry condition. I have some other techniques that can be applied to visualise phenomena existing within a sheet of paper. Basically, whether the cationic activity would be retained after drying is an issue we have recently been exploring. We have repulped and observed various paper and board samples (both MOW and OCC) using the wet technique, and there is definitely cationic activity, in most paper samples, that is recovered through rewetting. So, it may be that the method can be modified for the visualization of cationic materials in the sheet.

Theo van de Ven McGill University

I have a question on how the gold particles affect the conformation of the polyacrylamide itself. Your system behaves more like a microparticulate system where you have small colloidal particles (gold) and a polymer, rather than the polymer itself. The polymer conformation may be very different in the absence of the gold compared to when it is present?

Hiroki Nanko

That is a very good question and everybody wonders how the colloidal gold affects the conformation of the polymer. We were concerned about that, of course, so we experimented by varying both the method and conditions. Based on our findings we concluded that colloidal gold had a minimal effect on the polymer conformation using this technique.

- One reason is related to the method itself: before we apply the colloidal gold to the sample, we mount the sample on the grid and remove the excess fluid (this fluid flow is the source of the stretched, parallel conformation of extending polymer segments). The polymer will adhere to the carbon coated Formvar membrane on the grid surface, and thereafter it cannot change its conformation easily. When we added colloidal gold to pulp suspensions in a vial, we did see changes of the polymer conformation in several cases (most notably after extended staining periods in the vial).
- Colloidal gold particles have specifically adsorbed chloride counterions, rendering the particles anionic. We hypothesize that this translates to a low charge density or weak surface charge on the colloidal gold particles.
- The technique has been applied to microparticle/nanoparticle drainage and retention aid systems in the laboratory. Conformational changes wrought by retention and drainage nanoparticles can be observed using this technique. In the absence of drainage / retention nanoparticles, polyacrylamide strands are found extending from fibril surfaces in a linear, parallel conformation and dotted with colloidal gold markers. The addition of retention / drainage nanoparticles to the slurry converts the linear polymer strands to radiants (parallel strands are converted to radiating strands like the spokes on a bicycle wheel) or networks by the nanoparticles. The polymer networks and radiating strands were dotted with the colloidal gold particles. The conformational characteristics of polyacrylamide are influenced by the retention drainage nanoparticles but not the colloidal gold particles.
- We also applied this technique to an anionic polyacrylamide, Polyflex CP.3. The anionic colloidal gold does not adsorb on the Polyflex, but positive staining of the polymer occurred, and extended strands were visible. Anionic polyacrylamide strands occur without colloidal gold influence,

leading us to believe that the observed strands of cationic polyacrylamide were also formed without the influence of colloidal gold.

- The technique was also applied to polyacrylamides of varying charge densities. Colloidal gold is not densely adsorbed on the polymers, and bare segments with positive staining are easily found on the polymer strands extending from fibril surfaces.

Lars Wågberg KTH

I would like to suggest a control experiment for you and maybe you have already done it. By using ellipsometry to determine the adsorption of your polyelectrolytes on a flat surface it is possible to estimate both adsorbed amount and the thickness of adsorbed layer of the polyelectrolytes. If you then adsorb the gold colloids to that layer it would be possible to detect any changes in the adsorbed layer structure and then you can compare that to the method that you are using. I guess that would strengthen your arguments significantly.

Hiroki Nanko

We have not done any such work with ellipsometry; however, we appreciate that such a study could add significantly to this field of work. There are several challenges that come to mind. Namely, ellipsometry would require the adsorption of a layer of polymer on a flat surface. This is no longer a 'snapshot' of a trapped dynamic papermaking system as we are studying, but more of an ideal equilibrium system. We do not see a layer of polymer coating the fibrils in the dynamic system, but rather patches of adsorbed polymers that extend outward to varying distances. Different areas on the fibril surfaces have flatly adsorbed polymer, polymer strands extending 25 *nm* to 6 *μm* from fibril surfaces, and large areas with no adsorbed polymer at all. Subsequent addition of colloidal gold particles would be expected to make the situation even more complicated, possibly beyond our ability to interpret the results of ellipsometry tests.