Martin A. Hubbe
Associate Professor, North Carolina State University

Water and Papermaking
2. White Water Components

White water can contain many soluble and finely divided components, some of which have the potential to detract from the quality of the paper or add to operating costs. For example, white water composition can sometimes be responsible for:

- *an unexpected decrease in the brightness of paper.*
- *problems related to the water-repellent properties of paper.*
- *unexpected changes in a paper's strength.*
- *slime holes and spots in paper.*
- *the rate of felt-filling and related deposits.*
- *the efficiency of retention aids.*

White water components can come from:
- *Pulpwood; the mechanical and chemical pulping processes and fines.*
- *Recovered paper; recycling can introduce a wide range of materials into white water systems - such as the latex binders and various dispersants from recycled coated grades.*
- *The chemicals that are added during the paper-making process, eg: the fillers in printing grades; wet end additives and sizing agents.*

Many issues related to white water can be addressed via the optimized

The term "white water" can be defined as the aqueous solution that drains from a wet sheet of paper as it is being formed. White water's composition can differ significantly from that of the in-coming fresh water, which was considered in Part 1 of this series. *(See Paper Technology, February 2007).*

Soluble, as well as finely suspended components tend to build up in the white water as it is recirculated multiple times. White water components can come from the wood, from the recycling of paper, and also from chemicals that are intentionally added during the papermaking process.

The composition of white water can affect paper's appearance and strength, as well as the costs associated with achieving efficient fine-particle retention, sizing, and smooth operation of the paper machine.

Papermakers use the term "white water" when referring to the process water present in a paper machine system. The white appearance gives evidence to the presence of various suspended materials, in addition to entrained air. Fine particles, as well as bubbles suspended in white water interact with light, scattering it in all directions.

This review considers some of the main sources and composition of dissolved and suspended materials that are likely to be present in white water. The final sections of this article consider ways in which such components can affect the quality of paper and the efficiency of the papermaking operations.

A paper company can benefit in several ways by carrying out tests related to white water's composition. Such information, collected during periods of smooth operations, can come in handy for overcoming process upsets and quality problems. The information also can be used to track down and deal with causes of variability.

Online sensors, in combination with modern control equipment are making it possible to control some key variables associated with white water composition, including fine-particle retention,[1-2] charge demand,[3] and the content of entrained air.[4] Finally, related measurements can be used as a basis for optimization of chemical dosages, with a goal to maximize paper quality and minimize production costs.

Components of white water can be classed as inorganic, organic, or biological. They also can be classed as dissolved or finely suspended. There are a great many different materials that can be present in white water, and also the possible pair-wise interactions between them are too many to count.

Papermakers face a challenging job when seeking to identify optimum running conditions. Fortunately, as will be reviewed in the next section, a number of simplifying concepts have been published.

Simplifying Concepts – Running Conditions

Enrichment

White water becomes reused multiple times in a modern paper machine system. The primary use is for dilution of the incoming fibres. Each cycle of use provides another opportunity for materials to become dissolved, emulsified, or removed as small particles from the surfaces of fibres or from other additives to the process.

The extent to which such materials can become enriched in the white water depends not only on how many times the same process water is used to dilute the incoming pulp, but also on the degree to which the dissolved or suspended materials become reattached to the fibres and other solid components of the paper furnish.[5-8]

The term "non-substantive" encompasses many materials, such as Na^+ ions, which have little affinity for fibre surfaces. In theory, non-substantive components of the white water can become enriched in concentration by factors as large as 160, if one is comparing the extreme conditions of (a) discarding all of the process water after each pass through the headbox, vs. (b) using so little fresh water that there is no liquid effluent.[6,8]

By contrast, various other components of white water can be described as "substan-

use of process chemicals, by pulp washing and the treatment of the incoming fresh water.

Many of the problems described in this article, can be expected to become more serious as mills minimize the volume of liquid effluent.

Part 3 of this series will consider various types of "kidney" operations that can be considered for the removal of various white water components.

tive." For instance, the divalent cations Ca^{2+} and Mg^{2+} have a greater tendency to remain with the fibres as the paper is being formed. Surface-active materials (such as soaps) and finely suspended materials tend to be much more substantive, in comparison to Na^{2+}.

If one has information about the relative affinity of something for solid surfaces (i.e. the "binding coefficient" or the "partition"), then it is possible to estimate the degree to which that material will tend to build up in a paper machine system.[9-11] In addition, as recently shown,[12] finely divided materials can either become deposited onto the fibres or released from the fibres as the wet web of paper progresses through the forming section of a paper machine.

Though the concepts of enrichment and partition coefficients can help to explain trends in the concentrations of various white water components, there is reason to be cautious when applying these concepts quantitatively.

As was noted in Part 1 of this series,[13] if the concentrations of any pair of positive and negative ions reaches its solubility limit, then one can expect that a precipitate may form, and such precipitates either may be retained during the formation of the paper, or they may form deposits elsewhere in the system. When the precipitate is inorganic in character, and the precipitation occurs at the surface of papermaking equipment, the result is called "scale."[7,14]

In favourable cases, the precipitation occurs in the bulk phase of solution, or, even better, onto solids surfaces in the fibre suspension. The tendency of certain materials to be retained on fibres or fillers is likely to change over time,[15] and there can be competition between two or more species for adsorption sites on the fibres.[16]

Another problem with simple calculations related to enrichment is that it is difficult to keep track of whether or not the surfaces of fibres and other solids materials in the furnish already have become saturated with adsorbable ions, polyelectrolytes, or surface-active materials.

Simple salts such as Na_2SO_4 can have various consequences when they accumulate in white water, and one of the easiest ways to monitor the situation is by measuring the electrical conductivity.[17] As salt levels increase, one can expect a reduction in the strength with which various charged additives interact with oppositely charged materials in the mixture.

Salt also reduces the swelling of fibres, an effect that tends to slow down refining and reduce the strength of the resulting paper. The white water also tends to become more corrosive towards metals with increasing concentration of simple ions.[8,18-21]

Electrical Charge Concepts

Concepts related to electrical charges can help explain a wide variety of issues in paper mills. For instance, inefficient papermaking operations have been attributed to an imbalance of ionic charges at surfaces within the wet-end system.[22-23] In the systems described, the surfaces all tended to be negative in charge due to an excess of anionic polyelectrolytes and colloidal material coming from the wood.

Because "like charges repel," it can be difficult, in such cases, to achieve efficient fine-particle retention. High levels of negatively charged polyelectrolytes and colloidal materials ("anionic trash") can make it difficult and expensive to achieve efficient first-pass retention, sizing, and other production goals.[24-25]

A closely related concept is called "fixation." The idea is that the papermaker can add something relatively inexpensive as a sacrificial additive to tie up the excess anionic charges in the water system.[26] Commonly used fixatives (or "charge scavengers") include :

• aluminum sulphate (alum)
• poly-aluminum chloride (PAC)
• polyamines,
• poly-diallyldimethylammonium chloride (poly-DADMAC), and
• poly-ethyleneimine (PEI).

Studies have shown that the effectiveness of cationic retention aids and strength additives can be improved greatly by such pretreatment.[22,24,27-30]

If too much high-charge cationic material is added, beyond what is needed, then one generally can expect problems. Retention can become less efficient, the system is likely to be foamy, and dewatering is likely to be slow. Studies have shown, in such cases, that the best performance in terms of sizing,[31] strength,[31] and dewatering[32] often coincides with an approximate balance between positively and negatively charged substances (and surfaces) in the white water.

The amount of high-charged cationic additive that is needed to achieve this balanced condition in a paper machine system is called the cationic demand. Test procedures and equipment are available for carrying out charge demand titrations, both in the laboratory[33-34] and in online applications.[3,35]

Like any good rule of thumb, the rule regarding neutralization or "balancing" of charges can be misapplied. For example, a very high level of anionic material may be present in white water if the paper machine is using own-make virgin unbleached kraft or peroxide-bleached thermo-mechanical pulp (TMP).[36-37]

In some cases, it may be uneconomical to add enough high-charge cationic agent to balance the cationic demand. To make matters worse, addition of large amounts of cationic polymer or aluminum-based additives to a highly anionic system can result in precipitation of polyelectrolyte complexes,[38] which can be sticky,[39] and which have the potential to retard drainage.

A recommended approach, when dealing with systems that have excessively high levels of charge demand, is to address the problem at its source. Adequate washing of pulp can yield benefits in terms of lower costs of papermaking chemicals.[40-42] Alternative approaches, based on removing unwanted materials from the process water, will be considered in Part 3 of this series.

Time-Dependent Processes

Because of the relatively large volumes within stock-chests, white-water silos, and save-all systems, a typical paper machine system can be described as "sluggish."[43] White water may need to be recirculated many times in order to approach a steady-state condition.[6] Efforts to simulate or control paper machine operations need to take account of the time required for effects observed at one point in the system to gradually show up elsewhere in the process.

Time-dependent processes also can affect the performance of chemical additives. Sizing agents[44-45] and wet-strength agents[46-47] may decompose or change to less effective chemical forms during the time that they are in contact with white water, making it important to add them rather late in the process and to

retain a high proportion of the additive on the first pass through the forming section.

Retention aid polymers are so large (typically having molecular masses greater that 5 million grams per mole), that they do not have sufficient time to reach an equilibrium conformation at the surfaces of fibres to which they become attached.[48-50] The remarkable ability of retention aids to perform their function, at relatively low dosages, is probably due to the fact that tails and loops of the long-chain molecules remain awkwardly protruding from surfaces long enough to form attachments between fine particles and fibres.

Sources of White Water Components

The chemical composition of white water also can best be understood by considering the materials with which the water has come into contact. As was discussed in Part 1 of this series, the incoming fresh water may contain a variety of materials, depending partly on the mineral nature of the sediments underlying the river or well from which it is taken.[13] As was discussed, the amounts of objectionable materials, including iron, algae, and humic acids, usually can be reduced to minor levels by conventional water treatment.

Some other main sources of white water ingredients, which will be considered next, are the wood, materials associated with recycled fibres, and various items that the papermaker intentionally adds to the system.

Wood as a Source of WWC

A tree in the forest is exposed to countless hours of rainfall without obvious evidence that materials from the wood are becoming dissolved into the water. But once the bark is removed, the wood is reduced to chips, and the chips are separated into fibres, certain characteristic parts of the wood can become either dissolved or finely dispersed. *Figure 1* illustrates examples of important classes of wood-derived material that can end up as part of the white water, either "as-is" or in modified form.

The amounts and proportions of the different chemical constituents of wood that enter the water phase of a paper machine system depend greatly on the pulping method, any procedures used for bleaching, and, most importantly, the manner (or lack thereof) in which the pulp is washed.

Mechanical processes, such as thermomechanical pulping (TMP) or stone groundwood processing[51] can be expected to release extractable materials, i.e. "pitch" components.[36,40] As shown by recent studies,[36,52] these materials are remarkably diverse in their solubility characteristics, as well as their tendencies to deposit onto papermaking equipment under different conditions of pH, ionic concentrations, and temperatures.
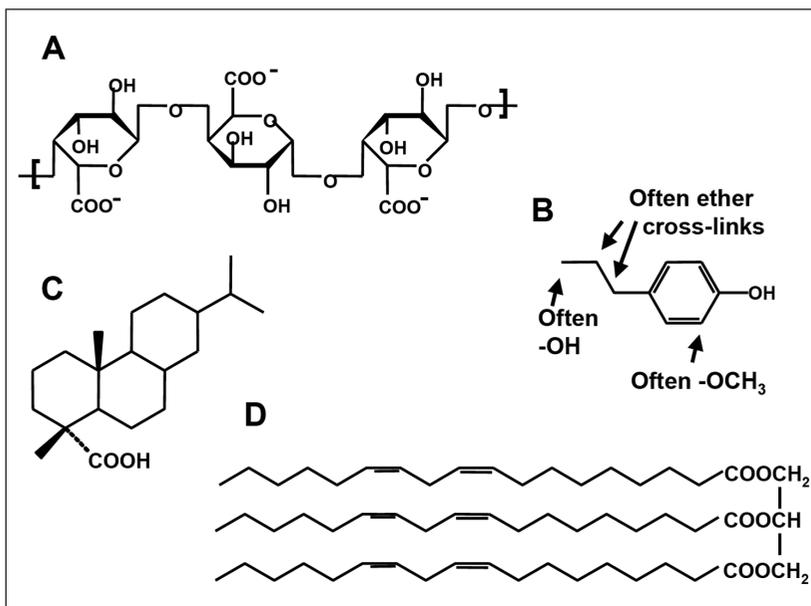

Figure 1 Common wood-derived components of paper machine process water (white water): A = poly-galacturonic acid, a hemicellulose component; B = building block of lignin, often present in sulfonated or oxidized lignin byproducts in white water; C = abietic acid, a component of resin acids present in softwood; D = a triglyceride fat, often present in white water as a mixture with fatty acids of varying saturation

Recent progress has been achieved in understanding the action of certain enzymes for the control of pitch in paper machine systems.[53]

In addition to the pitch-like components, mechanical pulping also releases some of the hemicellulose components of wood into the water phase, especially if the pulp has been exposed to high pH and hydrogen peroxide, a common treatment for the bleaching of such fibres.[36,54-56] The peroxide tends to oxidize the hemicellulosic materials, and the high pH ensures that any additional carboxyl groups created by such oxidation are in their negatively charged, dissociated form.

Galacturonic acid has been found to be a major component of the dissolved material. White water associated with peroxide-bleached mechanical pulp systems tends to have very high cationic demand.[28,57-58] The ability of galacturonic acid to stabilize pitch particles, presumably by a charge-repulsion mechanism, has been confirmed by a study in which its effect was reversed by enzymatic hydrolysis of the hemicellulosic material.[36]

In the case of chemical pulping, the composition of wood-derived material likely to enter the white water system can be quite different. Chemical pulping methods, such as the kraft process, are designed to solubilize and remove lignin, a natural phenolic resin that binds fibres together in wood. For this reason, spent pulping liquors can be expected to contain various highly anionic oxidized or sulfonated byproducts of lignin.

Part of the hemicellulose also tends to become solubilized due to a combination of high pH during pulping, followed by oxidation during subsequent bleaching stages. The pulping liquor initially will contain most of the extractives component of wood (including fatty and resin acid soaps, as well as unsaponifiables, i.e. materials that cannot be converted into soaps).

In addition to soaps, spent kraft liquor also contains a high concentration of salt ions, especially sodium sulphate. Although chemical pulping operations are always followed by washing operations, it is inevitable that a portion of the anionic polymers and colloidal (i.e. extremely finely divided) matter, salt ions, and surface-active materials gets passed along to the paper machine system.

Once in the white water, byproducts of hemicellulose and other anionic "dissolved and colloidal substances" (DCS) tend to interfere with the performance of cationic wet-end additives.[41]

Potential issues related to pulping liquor carry-over into papermaking operations can include pitch deposition, foaminess, difficulties in achieving hydrophobic sizing, and inefficiencies of various positively charged chemical additives to the process. Issues such as pitch can be expected to depend on the season of the year, the length of time during which wood chips have been stored, and the temperature of the papermaking process.[59]

The fines portion of the fibre furnish can have a profound impact on the character of white water.[30,60-61] Mechanical pulping operations tend to fragment the relatively brittle, lignified fibres, producing a broad size range of materials. Shapes of fibre fines derived from mechanical pulping can range from flakes, to highly flexible fibrillar elements.

In the case of chemical pulps, it is useful to differentiate between "primary fines," which are already present before refining, and the "secondary fines," which mainly result from fibrillation and detachment of the P layers and parts of the S_1 and S_2 sublayers of the fibre.[51]

The primary fines, which often amount to several percent of the dry mass of a hardwood pulp, mainly consist of ray cells and other non-fibre components of the wood. In contrast to these, the secondary fines tend to be thinner and more flexible, having a greater contribution to the bonding of paper, but also a more negative effect on dewatering.[62-64] Often it is the smallest fraction of fine material that has the biggest adverse effect on dewatering.[61] In the case of unfilled grades of paper, fibre fines are usually the most prominent solid component of white water.

Paper Recycling as a Source of WWC

Depending on the type of paper being used as a fibre source, recycling operations can introduce a wide range of materials into white water systems. The basic chemical composition of some of these materials is shown in *Figure 2*.
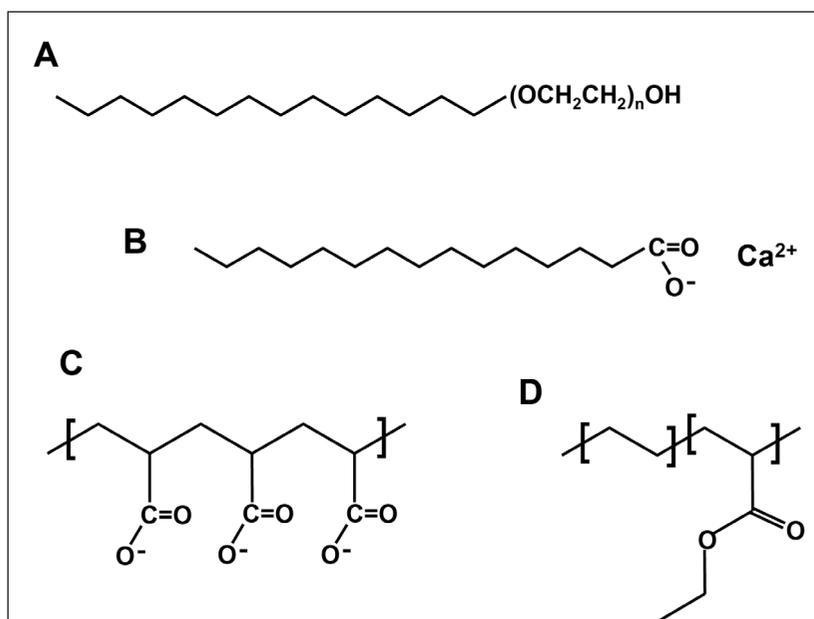

Figure 2 Wastepaper components that often become incorporated into white water: A = example of a nonioinic deinking surfactant (hydrophobic alkyl chain and ethylene-oxide chain); B = calcium salt of stearic acid, also used in deinking; C = polyacrylate, often used as a dispersant; D = ethylenevinylacetate (EVA), a component of pressure-sensitive adhesives that can form "stickies"

Recycled newspaper (ONP), magazine (OMG), and mixed office waste (MOW) processes generally involve de-inking operations.[65] Potential contributions to the associated paper machine white water can include not only ink particles (some of which inevitably escape past the washing operations), but also the surface-active materials that are used in flotation deinking operations.

Deinking operations usually employ either nonionic surfactants or combinations of fatty acid soaps, followed by addition of calcium salts.[65-66] In either case, the efficiency of subsequent washing steps will determine how much of the surface-active material carries over to the white water of the paper machine. Such carry-over can be expected to reduce the surface tension of the white water, increase the level of foam, and make it somewhat more difficult to retain fines and to achieve hydrophobic sizing of the paper.[67]

One of the positive aspects of deinking operations, from the standpoint of white water management, is that the resulting fibres can be, in some respects, cleaner than primary pulps that are produced on site. Much of the fines content, fillers, extractives, and soluble hemicellulose components tend to be separated from the filterable solids and removed during the washing operations associated with deinking.

As a result of a relatively low level of fibre fines, the ease of water removal from various deinked stocks is often high, relative to similarly refined virgin furnish, from which it was originally derived.

Latex and various dispersants can be released into the water phase when coated paper is recycled. The same is true for repulping of coated broke. Certain latex binders of conventional coatings can have a tendency to deposit onto papermaking equipment, similar to wood-pitch.[68-69] Dusting and blemishes in the product can be expected in cases where flakes of coating fail to become completely redispersed in the repulper.

Coating-derived phosphate or acrylate dispersants tend to increase the cationic demand of the system, making it more difficult to achieve the desired levels of first-pass retention, and tending to increase the solids content of white water.

Pressure-sensitive adhesives, such as those used to attach dry stamps and labels to mailing envelopes and magazines, become known as "stickies" when they make it past a deinking operation and enter a paper machine system. Though seldom present as a major component of white water solids, their tendency to self-associate, and their deformable, adhesive nature can be expected to cause bothersome deposits in press felts and other vulnerable parts of the paper machine. Various strategies have been used to control such problems.[70-71]

Chemical Additives as a Source of WWC

In the case of printing grades, fillers often comprise 10 to 25% of the mass of paper. For this reason, one would expect fillers to have a relatively large impact on the properties of white water. Filler particles are generally too small to be efficiently retained by filtration in the web of cellulosic fibres. Thus, depending on the effectiveness of the retention aid programme, there is a good chance that much of the filler will be lost to the white water.

Though the majority is likely to eventually become part of the product, due to multiple passes of white water through the forming section, it is reasonable to expect poorly retained filler to accumulate in the white water.

Even in the case of wet-end additives that have a charge attraction to cellulosic fibres, there is a possibility for significant build-up in the white water if the chemical dosage exceeds the saturation level of fibre surfaces.

An example of this phenomena can be observed at high addition levels of cationic starch.[72] In typical cases, between 1% and 1.5% of cationic starch, based on the dry mass of solids, will become efficiently deposited onto fibres and other surfaces. Depending on the surface area of the furnish (affected by refining, the type and amount of filler, etc.), addition of higher amounts of cationic starch merely results in an increase in the amount that builds up in the white water, contributing to foam and bacterial growth. The biological oxygen demand (BOD)[73] of the water also is increased greatly by unretained starch.

Sizing agents, such as rosin products, alkenylsuccinic anhydride - ASA, *see Figure 3* - and alkylketene dimer (AKD) are tricky,
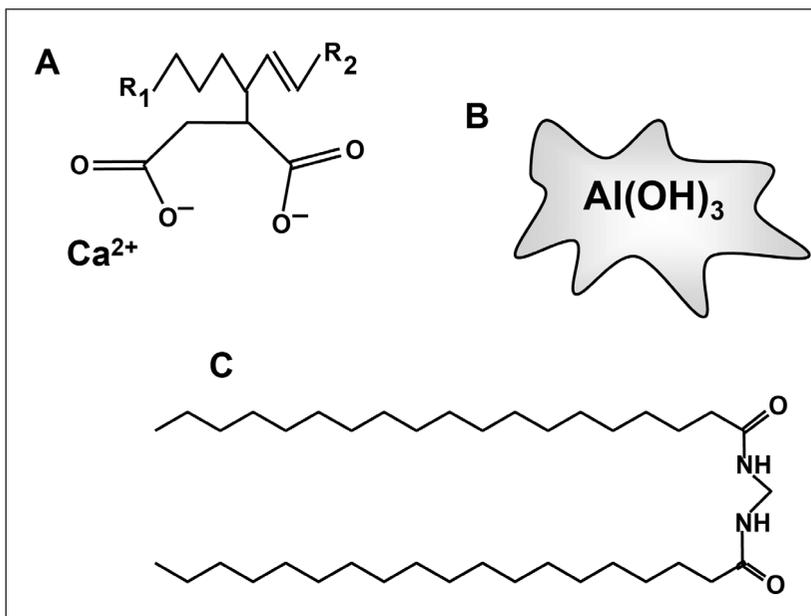

Figure 3 Examples of wet-end additives that can have significant effects when present in white water: A = hydrolyzate (calcium form) of hydrolyzed alkenylsuccinic acid (ASA) sizing agent; B = representation of neutral alum floc; C = ethylene-bis-stearamide (EBS), a component of some defoamers used in kraft pulp mills. EBS is often found in tacky deposits in the wet end.

from the standpoint of white water properties. Ideally, the goal is to adsorb such additives efficiently on the surfaces of fibres and fine particles. In turn, the fine particles (fibre fines, filler particles, etc.) need to be subsequently retained efficiently by retention aids as the paper is formed.

But the water-hating nature of sizing chemicals, which is required in order for them to perform their function in resisting fluid penetration into paper, implies that they can contribute to tacky deposits when present in the white water.[74] Defoamer products share some of the same bad habits, in terms of having a tendency to form deposits on papermaking equipment, due to a hydrophobic and tacky character.

Papermakers generally try to minimize adding surface-active materials to the wet end, due to their concerns about the performance of sizing agents, the generation of foam, and, to some extent, paper's strength properties. However, it is common for some of these materials to "sneak" into the system as part of the stabilizing formulation for such additives as retention aids, biocides, defoamers, and even some sizing agents.

Changes to White Water Resulting from the Papermaking Process

The papermaking process itself can have a substantial effect on the nature of white water components, due to such processes as air entrainment, chemical breakdown, biological growth, and various precipitation and complexation interactions among different materials.

Air is drawn into the white water as it drains from the sheet, with assistance of hydrofoils, vacuum boxes, and related devices. Some, but not all, paper machines include devices for air removal, usually based on application of vacuum or centrifugal acceleration of the white water.[4,75]

Without such removal, a typical furnish stream emerging from a paper machine headbox contains a higher volume of air, in comparison to its volumetric content of solids, leading to decreased rates of dewatering and disruption of the sheet structure on a fine scale.

Some of the air (especially the CO_2 component)[76] tends to enter the dissolved phase, when in the pressurized parts of the flow circuit. However, much of the gas reemerges as small bubbles when the pressure is released at the headbox slice.[4] High levels of CO_2 can result if alkaline furnish, containing $CaCO_3$ filler, comes into contact with acidic conditions.

An important chemical reaction that occurs in white water is the decomposition of alkenylsuccinic anhydride (ASA), a cellulose-reactive sizing agent.[44] The ASA is added to the wet end in the form of tiny droplets of and oily material, usually stabilized by cationic starch. But a reaction with water tends to gradually convert the emulsified ASA to its hydrolyzed form. The ASA hydrolyzate subsequently can interact with calcium and magnesium ions in the solution and become very tacky.[74]

Other chemical changes that occur gradually to the white water components during papermaking include:

(a) precipitation of scale, especially when positive and negative multivalent ions exceed a solubility product in solution,[13,73]

(b) formation of polyelectrolyte complexes, a process that often converts soluble material into fine particulate material,[38] and

(c) the growth of slime bacteria, which can exist either as suspended bacterial cells or as attached films on papermaking equipment.[7-8,42,77-78]

Many papermakers monitor slime by counting the cells in the suspended phase, but the biggest problems usually are due to the surface-bound (i.e. "sessile") bacteria, which often are different in character.[79-80]

White Water can affect Paper Quality

Brightness and Dirt: A list of the ways in which an unexpected decrease in the brightness of paper might possibly be related to a change in the white water[81-83] is presented in *table 1*.

Though the table focuses on issues related to white water, one should not overlook other factors, such as fresh water quality[13] and the brightness of in-coming pulp.

Sizing: Unexpected problems related to the water-repellent properties of paper often can be traced to changes in white water com-

Alum quality	1. Impurities in alum, especially iron
	2. Increased retention of colour bodies due to alum use
pH increase	May cause darkening if high-yield fibres are present
Ink in white water	Due to incomplete ink removal during de-inking
Slime bacteria	1. Due to generalized slime growth
	2. Decay of starch or other additives
Cationic polymers	Increased fixation of chromophoric materials (colour bodies) to the fibres (Lorz *et al* 1994)
Pulp liquor	Due to incomplete washing after pulping or bleaching
Corrosion products	White water composition can affect correction rates

Table 1 Ways that white water sometimes can lower paper's brightness

Surfactants	1. Carry-over of nonionic surfactants or fatty acids, which are commonly used in deinking operations 2. Effects of surfactants used to stabilize defoamer products, biocides, retention aids, etc. 3. Soaps carried over from pulping of wood
ASA breakdown	Loss of efficiency due to excessive storage time of emulsion, too high pH or temperature during storage, or sub-optimal preparation
Rosin aging	1. Agglomeration of rosin emulsion particles 2. Saponification of rosin emulsion particles 3. Aging and agglomeration of aluminum rosinate particles
Poor retention	Inadequate dose or maladjustment of retention chemicals. Fibre fines tend to adsorb a disproportionate amount of sizing agent.[85] Retention of fines and sizing chemicals on the first pass will tend to minimize reaction of the chemicals with water.
Cationic demand	High cationic demand is often a root cause of poor retention of sizing agents. Sizing performance often can be improved by neutralizing the charge with high-charge cationic agents[22,31]
Sheet formation	1. Excessive pin-holes, possibly due to entrained air 2. Very nonuniform paper
Refining	Insufficient refining; sheet too porous

Table 2 Hydrophobic sizing: Likely effects due to changes in white water composition

Wood resins	Precipitation of wood resins (i.e. pitch) onto fibre surfaces can block bonding sites.
Alum, PAC, etc.	1. Reduced swelling and bondability of fibers due to the action of high-charge positive ions 2. Increased retention of non-bonding fine particles (see next two items)
Filler level	An increase in filler content or filler having increased surface area tends to decrease inter-fibre bonding in paper.
Fines from recycled paper	1. In many cases, a high proportion of recycled fine matter consists of filler (previous item). 2. Fibre fines from kraft pulp lose some of their ability to contribute to bonding each time that they are recycled
Surfactants	Surface tension forces, which play an important role in bond development, tend to be reduced by the presence of surfactants.

Table 3 Paper strength effects that may be due to changes in white water

Wood pitch	1. The amount of wood pitch dispersed in the white water may have changed 2. There may have been a seasonal or process-induced change in the nature of pitch, i.e. higher level of triglycerides or increased saponification[59]
Stickies	1. Possibly due to a change in wastepaper quality 2. Possibly due to changes in deinking and pulp processing
Sizing agents	ASA hydrolyzate or other unretained sizing agent byproducts
Low retention	Increased solids in the white water tends to increase the rate of felt-filling.

Table 4 Changes in the rate of felt filling, and possible effects of white water composition

position.[30,84] Some commonly observed effects are listed in *Table 2*.

Strength: As shown in *Table 3*, a variety of white water attributes have the potential to cause unexpected changes in paper's strength.[30,83-84,86-88]

White Water and Papermaking Process

Felt-filling and Deposits: Increased rates at which wet-press felts become filled with solid matter are frequently observed when the amount of fresh water added to a paper mill system is reduced.[60,78,89-90] Some of the ways that white water composition may be related to the rate of felt-filling and related depositis are listed in *Table 4*.

Poor Performance of Retention Aid

As indicated by the items in *Table 5*, white water properties can sometimes (but not in all cases) affect the efficiency of retention aids and related additives.[22,28-29,42,81] Increases in cationic demand may occur for a variety of reasons, including:

- peroxide bleaching - especially if the pulp is not washed
- increases in the content of coated broke
- inefficiencies in kraft pulp washing, and
- high levels of direct dyes (anionic type), as in the production of deeply coloured paper.

Slime Holes and Spots: A list of some ways in which slime problems might be attributed to white water composition is shown in *table 6*. In general terms, problems arise due to the availability of "food" on which slime bacteria can live. Slime problems often become worse as papermakers work to reduce the amount of fresh water that is used.[60]

In the absence of effective biocides, paper machine systems generally provide a welcoming environment for bacteria and fungi, being warm and wet, with plenty of nitrogen and sugar-like materials, e.g. starch and hemicellulose breakdown products. Part 3 of this series will discuss, among other things, progress that has been achieved in removing the food content (i.e. materials contributing to biological oxygen demand) from process water.

Summary

As shown by publications cited in this review, white water can contain many different soluble and finely divided components. Some of these components have the potential to detract from either the quality of the paper or add to the operating cost of the papermaking process.

Many issues related to white water can be addressed the optimized addition of process

chemicals, including high-charge cationic polymers (to balance the charge) and retention aid polymers (to attach fine particles to fibres). An effective retention aid programme can prevent the build-up of fine particulate material in white water, and thereby minimize the rate at which deposits form in the system.

Sometimes the best way to deal with high or variable levels of undesirable components in white water involves washing or treating materials in various entering streams to the paper machine system. Pulp washing is a prime example of an operation that is likely to result in reduced chemical costs and/or higher operation efficiencies during papermaking. Treatment of the incoming fresh water[13] is another example.

Various problems, as mentioned in the final two sections of this article, can be expected to become more serious in cases where efforts are made to minimize the amount of liquid effluent from a papermaking process. In such cases there is a danger that levels of salt ions and highly soluble organic materials, such as the breakdown products of hemicellulose, can become highly enriched.

None of the strategies mentioned in the present article are very effective in retaining low-mass organic compounds or salts. To address such issues, Part 3 of this series will consider various types of "kidney" operations that can be considered for the removal of various white water components.

Literature Cited

1. Rantala, T., Tarhonen, P., and Koivo, H.N., "Control of paper machine wire retention," Tappi J. 77 (12): 125-132 (1994).
2. Artama, M., and Nokelainen, J., "Control of Retention and Ash," Paper Technol. 38 (8): 33-44 (1997).
3. Bley, L., "Latest experiences of on-line charge measurement: A process control concept," Pulp Paper Can. 99 (5): 51-55 (1998).
4. Matula, J., and Kukkamäki, E., "How to deal with difficult passengers," Pulp Paper Europe 1 (10): 12-14 (1997).
5. Pothmann, D. "Accumulation of water-soluble substances in the 'original paper - waste paper - new paper' cycle," Wochenbl. Papierfabr. 121 (7): 241-253 (1993).
6. Alexander, S.D., and Dobbins, R.J., "The buildup of dissolved electrolytes in a closed paper mill system," Tappi J. 60 (12): 117-120 (1999).
7. Pietschker, D.A., "The 100% closed water system - What to expect," Proc. TAPPI 1996 Papermakers Conf., TAPPI Press, Atlanta, 521-528 (1996).
8. Hamm, U., and Göttsching, L., "Wastewater-free papermaking - What consequences to expect?" Wochenbl. Papierfabr. 130 (4): 229-235 (2002).
9. Springer, A., "Considerations in process water reuse in non-integrated paper manufacturing," Paperi Puu 60 (11): 705-716 (1978).
10. Jones, G.L., "Effects of reduced fresh water usage on ion buildup in a typical paper machine water system," IPST Tech. Pap. Ser. 481, 16 pp (1993).
11. Xu, Y., and Deng, Y., "The buildup of dissolved solids in closed white water systems," Tappi J. 3 (8): 17-21 (1993).
12. Donat, V., van de Ven, T.G.M., and Paris, J., "Distribution of dissolved and colloidal substances in the forming and pressing sections of a paper machine," J. Pulp Paper Sci. 29 (9): 294-298 (2003).
13. Hubbe, M.A., "Water and Papermaking. 1. Fresh Water Components," Paper Technol. 48 (2): __-__ (2007).
14. Choi, S.-J., Kim, H.-Y., Kim, Y.-H., Park, H., and Englezos, P., "Gypsum scale formation in white water of a closed-cycled paper mill," Can. J. Chem. Eng. 81 (5): 1083-1086 (2003).
15. Bessonoff, M., Niemi, H., Nguyen, T., Subramanian, R., Laine, J.E., and Paulapuro, H., "The effects of DCS from TMP on paper and fibre surface," Scientific and Technical Advances in Wet End Chemistry, Proceedings, Pira, Leatherhead, Surrey, Paper 12, (2000).
16. Lee, J.-Y., Lee, H.L., and Youn, H.-J., "Effect of white water quality on the adsorption of cationic PAM on fibers," Palpu Chongi Gisul (J. Korea Tech. Assoc. Pulp Paper Ind.) 37 (1): 1-9 (2005).
17. Boegh, K.H., Garver, T.M., Henry, D., Yuan, H., and Hill, G.S., "New methods for on-line analysis of dissolved substances in white water," Pulp Paper Can. 102 (3): 40-45 (2001).
18. Bowers, D.F., "Effect of closed water systems and cleaning procedures on corrosion of papermaking equipment," Proc. TAPPI 1977 Papermakers Conf., TAPPI Press, Atlanta, Paper 1A-1, 1-7 (1977).

Cationic demand	Increased levels of anionic dissolved polyelectrolytes or colloidal substances (DCS) tend to neutralize cationic retention aids, rendering them less effective.
Surface area	An increased surface area of material in the white water, especially filler, can increase the demand for retention aid.
Dispersants	Dispersants used in the formulation of paper coatings can be recirculated to the wet end by way of broke.
Salt content	An increased salt content (often observed as increased electrical conductivity) associated with reductions in fresh water consumption tends to make charged retention aids less effective.

Table 5 Ways in which white water can hurt the performance of retention aids

Biocide program	Usually it is necessary to take a comprehensive approach to slime control, treating many different input streams. Combinations of organic biocides and oxidizing agents (bleaches) are often effective.
Starch overdose	High levels of starch in the white water are sometimes due to addition rates that exceed the "space" available at fiber surfaces for the additive to adsorb (see earlier discussion).
Stagnant areas	Dangers include growth of anaerobic bacteria, toxic gases, corrosion, odors, and discoloration if there are stagnant areas, such as at the bottoms of white water tanks, where sediments build up.
Poor retention	High levels of fine material in the white water make it more likely that deposits will form, creating anaerobic environments

Table 6 Ways in which white water properties can contribute to slime holes

19. Bowers, D.F., "Corrosion in closed white water systems," Tappi J. 61 (3): 57-61 (1978).

20. Collins, J.W., and Dallons, V.J., "Aspects of water reuse in the pulp and paper industry," AIChE Symp. Ser. 75 (190): 263-269 (1979).

21. McCourt, J.E., and Miner, R.E., "Relation of process water quality and its reuse potential in unbleached kraft paper and board mills," Proc. 2nd Water Reuse Symp., Washington, DC, 1, 572-603 (1981).

22. Lorz, R., Mönch, D., and Bohlmann, K., "Improving the effectiveness of process chemicals in recirculation systems loading with interfering substances," Wochenbl. Papierfabr. 122 (22): 888-893 (1994).

23. Holmbom, B., "Molecular interactions in the wet end of papermaking," 1996 International Paper and Coating Chemistry Symp., Proceedings, 97-104, (1996).

24. Bobacka, V., Kreutzman, N., and Eklund, D., "The use of a fixative in combination with cationic starch in peroxide-bleached TMP," J. Pulp Paper Sci. 25 (3): 100-103 (1999).

25. Allen, L., Levesque, B., Polverari, M., and Francis, D., "Effects of system closure on retention and drainage-aid performance in TMP newsprint manufacture," Proc. TAPPI 1998 Coating/Papermakers Conf., New Orleans, May 4, 1998, TAPPI Press, Atlanta, 497-514 (1998).

26. Krüger, E., Göttsching, L., and Mönch, D., "The behavior of fixed interfering systances in the recycling process," Wochenbl. Papierfabr. 125 (20): 986-991 (1997).

27. Glittenberg, D., Hemmes, J.-L., and Bergh, N.-O., "Cationic starches in systems with high levels of anionic trash," Paper Technol. 35 (7): 18-27 (1994).

28. Nurmi, M., and Eklund, D., "Effect of cationic polyacrylamide on colloidal wood resin," Paperi Puu 82 (5): 331-334 (2000).

29. Ryoso, K., and Manner, H., "Purity requirements for the feed water of retention aids," Proc. Tappi Papermakers Conf., TAPPI Press, Atlanta, 2, 775-784 (2002).

30. Lee, H.L., Ham, C.H., and Lee, S.G., "Influence of papermaking system closure on paper properties," Tappi J. 5 (5): 27-31 (2006).

31. Strazdins, E., "Theoretical and practical aspects of alum use in papermaking," Nordic Pulp Paper Res. J. 4 (2): 128-134 (1989).

32. Horn, D., and Melzer, J., "The influence of high molecular mass cationic dewatering aids on the electrical properties of cellulosic fibers," Papier 29 (12): 534-540 (1975).

33. Patton, P.A., and Lee, D.T., "Charge analyses: Powerful tools in wet-end optimization," Tappi J. 76 (8): 107-115 (1993).

34. Gratton, R., and Pruszynski, P., "Cationic demand survey of paper machines: How can we measure and use it?" Pulp Paper Can. 96 (3): T103-T108 (1995).

35. Rantala, T., Nokelainen, J., and Artama, M., "Wet end management by controlling consistencies and charge," TAPPI '99 Proceedings, TAPPI Press, Atlanta, 1999, 1189-1211.

36. Sundberg, K.E., Sundberg, A.C., Thornton, J.W., and Holmbom, B.R., "Pectic acids in the production of wood-containing paper," Tappi J. 81 (7): 131-135 (1998).

37. Nurmi, M., Wallin, S. and Eklund, D. "The effect of molar mass and charge density of cationic polyacrylamide on the flocculation of dissolved and colloidal substances in thermomechanical pulp water," J. Pulp Paper Sci. 32 (1): 43-46 (2006).

38. Linhart, F., Auhorn, W.J., Degen, H.J. and Lorz, R. "Anionic trash: Controlling detrimental substances," Tappi J. 70 (10): 79-85 (1987).

39. Heermann, M.L., Welter, S.R., and Hubbe, M.A., "Effects of high treatment levels in a dry-strength additive program based on deposition of polyelectrolyte complexes: How much glue is too much?" Tappi J. 5 (6): 9-14 (2006).

40. Allen, L.H., and Maine, C.J., "Pitch particle concentrations in pulp and paper mills," Pulp Paper Can. 79 (4): 83-90 (1978).

41. Wegner, T.H., "Effect of kraft black liquor and NSSC spent liquor components on polymeric additive performance," TAPPI 1989 Contaminants Problems and Strategies in Wastepaper Recycling, Seminar Notes, TAPPI Press, Atlanta, 91-96 (1989).

42. Huhtamäki, M., "Closing the water cycles - How far can we go?" Paper Technol. 44 (10): 27-32 (2003).

43. Ahn, H.K., and Lee, H.L., "A study on the accumulation phenomena of oxidized starch in white water of closed fine papermaking process. Part 3. Effect of white water and broke use ratios on the unsteady state papermaking process," Palpu Chongi Gisul (J. Korea Tech. Assoc. Pulp Paper Ind.) 38 (2): 1-8 (2006).

44. Wasser, R.B., "The reactivity of alkenyl succinic anhydride: Its pertinence with respect to alkaline sizing," J. Pulp Paper Sci. 13 (1): J29-J32 (1987).

45. Marton, J., "Mechanistic differences between acid and soap sizing," Nordic Pulp Paper Res. J. 4 (2): 77-80 (1989).

46. Espy, H.H., "Alkaline-curing polymeric amine-epichlorohydrin resins," in L.L. Chan, Ed., Wet-Strength Resins and their Application, TAPPI Press, Atlanta, Ch. 2, 13-44 (1994).

47. Obokata, T., and Isogai, A., "Effects of polyamideamine-epichorohydrin (PAE) resin deterioration on PAE retention and wet strength performance in handsheet making," Appita J. 57 (5): 411-414 (2004).

48. Ödberg, L., Tanaka, H., and Swerin, A., "Kinetic aspects of the adsorption of polymers on cellulosic fibers," Nordic Pulp Paper Res. J. 8 (1): 6-9,47 (1993).

49. Forsberg, S., and Ström, G., "The effect of contact time between cationic polymers and furnish on retention and drainage," J. Pulp Paper Sci. 20 (3): J71-J76 (1994).

50. Alince, B., "Time factor in pigment retention," Tappi J. 79 (3): 291-294 (1996).

51. Smook, G.A., Handbook for Pulp & Paper Technologists, 2nd Ed., Angus Wilde Publ., Vancouver (1992).

52. Ekman, R., and Holmbom, B., "The chemistry of wood resin," in E.L. Back and L.H. Allen, Eds., Pitch Control, Wood Resin and Deresination, TAPPI Press, Atlanta, Ch. 2, 37-76 (2000).

53. Zhang, X., Renaud, S., and Paice, M., "The potential of laccase to remove extractives present in pulp and white water from IMP newsprint mills," J. Pulp Paper Sci. 31 (4): 175-180 (2005).

54. Thornton, J.W., "Enzymatic degradation of poly-galacturonic acids released from mechanical pulp during peroxide bleaching," Tappi J. 77 (3): 161-167 (1994).

55. Jiang, Z-H., van Lierop, B., and Berry, R., "Hex-enuronic acid groups in pulping and bleaching chemistry," Tappi J. 83 (1): 167-175 (2000).

56. Ryösö, K.M., and Manner, H.J., "Reducing fresh water consumption for the feed of retention aids," Appita J. 54 (1): 22-26 (2001).

57. Weigl, J., Grenz, R., and Kastner, M., "Identification of deleterious materials with the streaming current detector and measures for their reduction," Wochenbl. Papierfabr. 118 (3): 109-118 (1990).

58. Grant, J., Li, Z., Court, G., Crosell, M., Mobarak, N., Cole, S., and Sain, M., "Analysis and optimization of used water networks in a TMP mill," Pulp Paper Can. 104 (11): 49-52 (2003).

59. Blazey, M.A., Grimsley, S.A., and Chen., G.C., "Indicators for forecasting 'pitch season'," Tappi J. 1 (10): 28-30 (2002).

60. Barton, A.D., Stuart, R.S., Lagacé, P., and Miner, R., "Experience with water system closure at recycled paperboard mills," Tappi J. 79 (3): 191-197 (1996).

61. Liu, X.A., Whiting, P., Pande, H., and Roy, D.N., "The contribution of different fractions of fines to pulp drainage in mechanical pulps," J. Pulp Paper Sci. 27 (4): 139-143 (2001).

62. Brecht, W., and Klemm, K., "The mixture of structures in a mechanical pulp as a key to the knowledge of its technological properties," Pulp Paper Can. 54 (1): 72-80 (1953).

63. Luukko, K., and Paulapuro, H., "Mechanical pulp fines: Effect of particle size and shape," Tappi J. 82 (2): 95-101 (1999).

64. Hubbe, M.A., "Fines management for increased paper machine productivity," Proc. Sci. Tech. Advan. Wet End Chemistry, Pira Intl., Leather-head, UK (2002).

65. Ferguson, L.D., "Deinking chemistry: Part 1," Tappi J. 75 (7): 75-83 (1992); "Part 2," Tappi J. 75 (8): 49-58 (1992).

66. Weed, D.C., McMellin, T.I., and Downie, A.J., "Advances in fatty acid based deinking chemistry," Wochenbl. Papierfabr. 126 (8): 370-372 (1998).

67. Fernández, C., and Garnier, G., "Retention of fatty acid soaps during recycling. Part 1: A study using packed beds of pulp fibers," J. Pulp Paper Sci. 23 (4): J144-J152 (1997).

68. Feigenbaum, H.N., "The characterization and treatment of white pitch from paper recycling operations," TAPPI 1991 Papermakers Conf., 591-593 (1991).

69. Vähäsalo, L., and Holmbom, B., "Influence of latex properties on the formation of white pitch," Tappi J. 4 (5): 27-31 (2005).

70. Fogarty, T.J., "Cost-effective, common sense approach to stickies control," Tappi J. 76 (3): 161-167 (1993).

71. Venditti, R.A., Chang, H.-M., and Jameel, H., "Overview of stickies research at North Carolina State University," PaperAge 115 (11): 18-20 (1999).

72. Glittenberg, D., Tippett, R.J., and Leonhardt, R., "Wet-end starches - Still up to date for high speed papermaking?" Paper Technol. 45 (6): 27-33 (2004).

73. Boyd, C.E., Water Quality: An Introduction, Kluwer Acad. Publ., Boston, 2000.

74. Scalfarotto, R.E., "Remedies for press picking boost efficiency of ASA synthetic sizing," Pulp Paper 59 (4): 126-129 (1985).

75. Helle, T.-M., Meinander, P.O., Nykänen, R.J., Molander, K.S., and Paulapuro, H., "Air removal mill trials using pomp deaerator," Tappi J. 82 (6): 146-149 (1999).

76. Grist, S.R., and Canty, R.J., "Carbon dioxide in pulp/paper mill stocks: Fix or fizz," Proc. 60th Appita Ann. Conf. Exhib., Melbourne, Apr. 3-5, 2006, Appita, Inc., 13-18 (2006).

77. Brecht, W., and Dalpke, H.L., "Closed water circuits in a paper mill processing waste paper," Wochenbl. Papierfabr. 100 (16): 579-585 (1972).

78. Collins, J.W., and Dallons, V.J., "Aspects of water reuse in the pulp and paper industry," AIChE Symp. Ser. 75 (190): 263-269 (1979).

79. Dickinson, W.H., "Biofouling assessment using an on-line monitor," TAPPI '99 Proc., TAPPI Press, Atlanta, 449-457 (1999).

80. Lie, F., Johnsrud, C., Samuelsson, B., Sjöström, L., and Rudh, M., "A new early warning system for slime formation in paper machines," Paper Technol. 43 (8): 43-46 (2002).

81. Heller, P., Scott, W.E., and Springer, A.M., "Potential operational problems under conditions of complete water reuse. Assessment using a model paper machine," Tappi 62 (12): 79-84 (1979).

82. Geller, A., "Complete water system closure in paper mills - Experience in the Federal Republic of Germany," Proc. Pira Econ. Poll. Control SPB/3, 30 pp. (1982).

83. Zhang, X., Beatson, R.P., Cai, Y.J., and Saddler, J.N., "Accumulation of specific dissolved and colloidal substances during white water recycling affects paper properties," J. Pulp Paper Sci. 25 (6): 206-210 (1999).

84. Moore, G.K., and Guest, D.A., "Closing up water systems. Benefits and effects," Paper Technol. Ind. 23 (2): 65-70 (1982).

85. Marton, J., "Practical aspects of alkaline sizing: Alkyl ketene dimer in mill furnishes," Tappi J. 74 (8): 187-191 (1991).

86. Springer, A.M., Dullforce, J.P., and Wegner, T.H., "Effects of closed white water system contaminants on strength properties of paper produced from secondary fibers," Tappi J. 68 (4): 78-82 (1985).

87. Gilbert, C.D., Hsieh, J.S., Xu, Y., and Deng, Y., "Effects of white-water closure on the physical properties of linerboard," Tappi J. 83 (4): 68 [electronic document] (2000).

88. Francis, D.W., and Ouchi, M.D., "Effect of dissolved and colloidal solids on newsprint properties," J. Pulp Paper Sci. 27 (9): 289-295 (2001).

89. Aldrich, L.C., and Janes, R.L., "White water reuse on a fine paper machine," Tappi 56 (3): 92-96 (1973).

90. Laine, J.E., and Bourgogne, G., "A review of the effects of reduced water consumption on the wet end of the paper machine and the quality of paper," Proc. Scientific and Technical Advances in Wet End Chemistry, Vienna, Austria, May 22-23, 2002, Pira International, Leatherhead, Surrey, UK, Paper 1 (2002).

91. Maltesh, C., and Shing, J.B.W., "Effects of water chemistry on flocculant makedown and subsequent retention and drainage performance," Proc. TAPPI Environ. Conf., TAPPI Press, Atlanta, 1, 227-234 (1998).

92. Allen, L., Polverari, M., Levesque, B., and Francis, W. "Effects of system closure on retention- and drainage-aid performance in TMP newprint manufacture," Tappi J. 82 (4): 188-195 (1999).