Application of Micropaticle Systems in Water Circuit Closure Programs

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ABSTRACT

The consequence of water system closure and reduced water consumption in Paper Mills is increased white-water conductivity associated with increased total dissolved solids. This leads to difficulties managing the wet end chemistry of paper machines, mainly due to stearic hindrance effects on wet end chemical additives. This in turn causes poor productivity and inefficient chemicals usage. The success of a number of projects is reported. The application and development of new multi-component microparticle systems which can further assist in achieving a significant degree of system closure or Zero Effluent is described.

Keywords: *system closure, Zero Effluent, conductivity, retention aid, drainage aid, microparticle, flocculant*

1. Introduction

Water is an essential component in paper-making, which was often ignored in the past due to its ready availability and relatively low cost. It is also the medium in which the complex physical and chemical interactions occur between the fibres, fillers and fines of the stock components and the functional and process additives, which largely determines the properties of the final product and the productivity of the paper machine.

During the last 10 years, many mills succeeded in significantly reducing fresh water requirements with some mills, producing packaging grades from waste paper achiev-ing Zero Effluent.

This has been achieved in a number of ways:
- By installing equipment requiring less fresh water;
- By isolating and reusing uncontaminated, fibre free water;
- By clarifying internal water streams;
- By recycling Primary Clarifier water.

Closure of the mill water system is often regarded as an environmental benefit and some mills are being encouraged to go in this direction by increasingly severe environmental constraints. This is not the full story however. For other mills, the driving force is the potentially significant saving in

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the fresh water costs and treatment, in effluent treatment and in energy conservation, which can result in running with the highest practical level of closure.

Closure of the mill water circuit will result in a build up of dissolved solids and colloidal organic materials within the white water circuit.

Mills have reported escalating problems with loss of drainage, reduced retention, increased addition rates of functional and process additives, deposition problems, and higher corrosion rates as water circuits become progressively more tightly closed.

This presentation deals with how some of the negative effects of system closure can be alleviated by the application of micro-particle flocculation systems.

1.1 Fine paper

In integrated fine paper mills, there is a strong trend where pulp mills are moving to more closed cycles to reduce the environmental impact of mill operations.

Pulp washing and bleaching introduces many soluble ions such as sodium, calcium, sulphate and complex organic species which consist of soluble or colloidal monomers, oligomers, polymers and hydro-colloids.

The term "anionic trash" is generally used to refer to anionic hydrocolloids and wood derived polymers, which have a strong negative effect on the cationic process and functional additives.

Decreased fresh water consumption inevitably leads to a large increase in the level of simple electrolytes and soluble and colloidal organic species in the white water.

As the amount of these substances increases, the reaction mechanisms in the stock will change. Additives such as retention aids, size, and cationic starch are adversely effected by increasing conductivity. The premise

of this paper is that retention and drainage characteristics are the foundation on which paper machine productivity is built. If these characteristics can be maintained, efficient paper machine operation will be achieved.

To demonstrate the effects that increasing conductivity has on paper machine wet end chemistry, laboratory mill data is presented and discussed.

The laboratory study (1) focused on various retention aid systems to determine how sensitive they were to increasing conductivity.

Machine data is also presented to show what happens in a real situation.

A laboratory furnish was prepared having the following properties. See Table 1.

Table 1. A laboratory furnish

Fibre Components	- 50% H.W.K. 50% S.W.K.
Filler	- 25% P.C.C - Scalenohedral
pH	- 8.1
Conductivity	- 700 μs/cm at 25° C
Consistency	- 0.79%

A 50/50 mixture of sodium chloride and sodium sulphate was used to simulate the conductivity increase due to poorly washed pulp.

Four retention systems were used in the evaluation. See Table 2.

Table 2. Four retention system

Retention aid systems
· Single Polymer
· Dual Polymer
· Polymer / Bentonite
· Starch / Colloidal Silica

1.2 Single polymers

High molecular weight cationic polymers are the predominant choice for single reten-

tion programs in the Paper Industry. These products can be regarded as long chain water-soluble organic molecules with a large number of positively charged groups distributed along the polymer chain.

The positive charge is acquired by ionization of the functional groups releasing anions into the solution which are held, together with other ions, in the water phase in a negative atmosphere around the polymer molecule.

Repulsion of the charge groups along the polymer chain generally results in a relatively extended conformation. A build up of ionic strength in the aqueous phase results in a reduction of the intra-polymer charge repulsion, which causes a conformational collapse of the polymer chain. The molecular volume of the polymer chain decreases with increasing ionic strength of the solution.

In bridging flocculation, the polymer acts as a bridge between different particles. One part of the polymer becomes attached to one or several adsorption sites while the other part extends into the bulk solution where the extended "loops" and "tails" can be adsorbed onto other particles and form bridges.

An increasing electrolyte concentration will reduce the extension of the polymer and its ability to form bridges.

The single polymer used in the evaluation is described in Table 3.

Table 3. Single polymer system

· Cationic Polyacrylamide
· Cationic Charge Density 21%
· Molecular Weight 4,000,000

1.3 Dual polymer system

Dual polymer retention systems consist of a primary addition of a short chain, highly cationic poly-electrolyte, preferably branched or structured, followed by a high molecular weight anionic polyacrylamide.

The role of the cationic primary addition is to de-stabilize and coagulate the dispersed system by a combination of an electrostatic patch mechanism and complex formation. On addition of the high molecular weight anionic polymer, the negatively charged groups attach to the cationic sites resulting in bridging flocculation.

Dual polymer systems normally possess a broader "operating window" compared with single neutralizing "anionic trash" and in some cases an excessive amount must be added to provide the cationic sites for adsorption of the anionic polymer. In highly contaminated systems, the products of complex formation with the cationic coagulant can themselves interfere with the adsorption at the fiber surface.

The dual polymers used in this evaluation are described in Table 4.

Table 4. Dual polymer system

1ˢᵗ Component	- A poly DADMAC homopolymer
	- Molecular weight 150,000
2ⁿᵈ Component	- An anionic polyacrylamide
	- Anionic charge density 30%
	- Molecular weight 6,000,000

1.4 Polymer/bentonite system

The polymer/bentonite system is described as a microparticle flocculation system in which the stock is first flocculated using a cationic polyacrylamide.This produces bridging flocculation in the normal way but the key feature of microparticle flocculation is that the resultant floc structure is deliberately broken down by the action of shear forces from the fan pumps, screens, etc. in the stock approach flow to the flow box. Re-flocculation is then brought about by the addition of the microparticle component - in this case a hydrated ben-

tonite with an overall anionic charge and high surface area in the region of 600 m²/g.

This results in a unique extremely regular floc surface.

The polymer/bentonite components used in the evaluation are described in Table 5.

Table 5. Polymer/bentonite system

1ˢᵗ Component	- Cationic polyacrylamide
	- Cationic charge density 21%
	- Molecular weight 4,000,000
2ⁿᵈ Component	- Anionic hydrated bentonite

1.5 Starch/colloidal silica system

The starch/colloidal silica system is described as a microparticle system where the cationic component is a cationic starch.

The microparticle flocculation effect is brought about by the addition of an anionic silica micro-gel with a particle size less than 1 nm.

The starch/silica components used in the evaluation are described in Table 6.

Table 6. starch/colloidal silica system

1ˢᵗ Component	- Cationic potato starch
	- DS - 0.03
2ⁿᵈ Component	- Anionic silica micro-gel
	- Particle size < 1 nm

2. Experimental and Results

2.1 Experimental

The laboratory retention evaluation was carried out using a Britt Dynamic Drainage Jar. The drainage rate under vacuum was measured using a Buchner Funnel Assembly.

2.1.1 Results

Results are described in Figures 1, 2, 3, 4,

5, and 6.

Both graphs show the negative impact of increasing conductivity on First Pass Retention and Vacuum Drainage.

Actual mill data indicates that first pass retention decreases significantly after 2,000 μs/cm.

The filler retention shows an identical trend to first pass total retention which would have a significant effect on quality parameters such as two sidedness.

Not only does high and variable pulp conductivity cause potential quality problems, but the addition of other functional and process chemicals must be adjusted to maintain paper production within specification.

This shows the increase in cationic polyacrylamide with time as the conductivity increases. This machine has closed loop control using a Kajaani consistency measure-
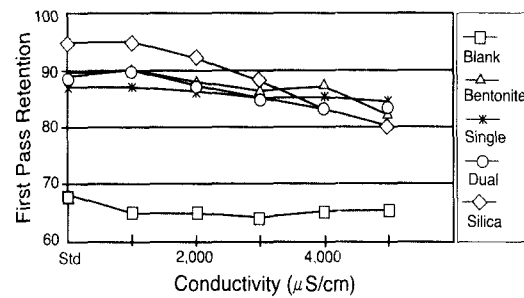

Fig. 1. Effect of conductivity on first pass retention (Laboratory).
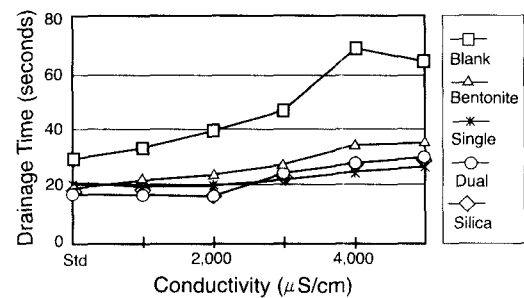

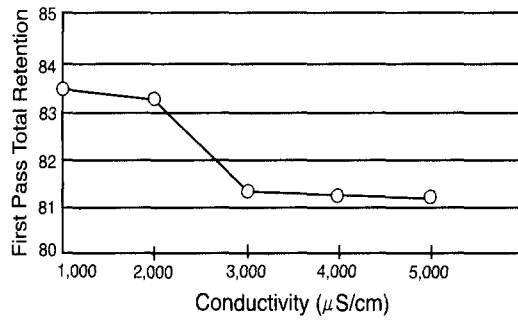**Fig. 2. Effect of conductivity on drainage (Laboratory).**

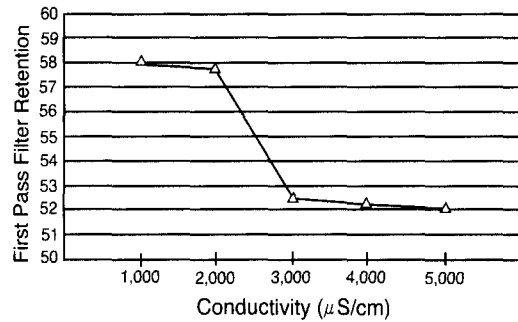Fig. 3. Effect of conductivity on first pass retention (Mill).

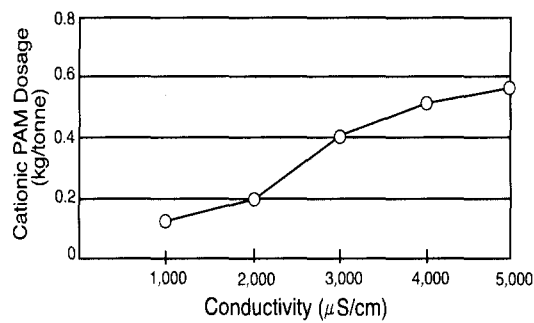Fig. 4. Effect of conductivity on FP pigment retention (Mill).

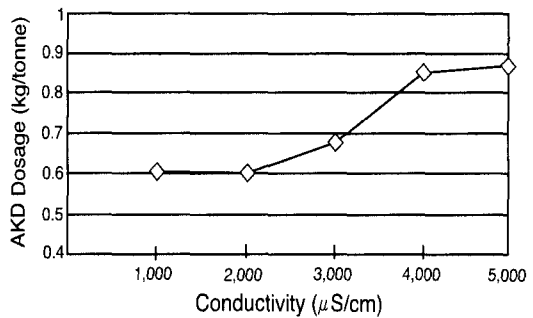Fig. 5. Effect of conductivity on cationic PAM dosage (Mill).

Fig. 6. Effect of conductivity on AKD dosage (Mill).

ment. The cationic polyacrylamide has been automatically increased to maintain a set point white water concentration.

This figure shows the AKD sizing dosage requirements to meet a sizing specification of 100 H.S.T.

A 30% increase in A.K.D addition rate was necessary to maintain in specification paper properties at higher paper machine white water conductivity.

Laboratory studies show that retention and drainage characteristics are adversely affected at higher conductivities.

Conductivities above 2,000 μs/cm will change the efficiency of both functional additives such as size and process additives such as retention aids.

A further laboratory (2) study was carried out to compare the effect of increasing levels

of monovalent and divalent electrolyte on the drainage performance of a single cationic polyacrylamide and a cationic polyacrylamide/bentonite system.

Furnish used was an equal mixture of bleached softwood and bleached hardwood, beaten to 45° SR.

Two retention systems were used. See Table 7.

Table 7. Two retention system

Single Polymer	- Cationic polyacrylamide
	- Cationic charge density 42%
	- Molecular weight 3,000,000
Polymer/Bentonite	Cationic Polyacrylamide
	- Cationic charge density 42%
	- Molecular weight 3,000,000
Bentonite	- Anionic hydrated bentonite

2.2 Experimental

The laboratory drainage evaluation was carried out using a Schopper Riegler Freeness Tester with the rear orifice blocked.

Increasing levels of sodium chloride and calcium chloride were added to the cellulose suspension to give the desired increases in electrolyte concentration.

2.2.1 Results

Results are discussed in Figures 7, 8, 9, and 10.

3. Discussion

It can be seen that in the pure cellulose furnish increasing levels of NaCl and CaCl$_2$

lead to a significant deterioration in the performance of the single cationic polymer. At the very high concentrations used, the drainage effect of the polymer is completely absent.

For the cationic polymer/bentonite system, there is also a reduction in performance, but the drainage results achieved are significantly better compared with single cationic polymers.

There are a number of reasons for this:

When a high molecular weight cationic polyacrylamide is added to the stock, polymer adsorption and bridging flocculation will occur, resulting in a large flocculated structure. When subjected to shear, these flocs will be broken down to smaller units, by cleaving the polymer chains, but the polymer remains attached to its original adsorption sites. The polymer quickly re-
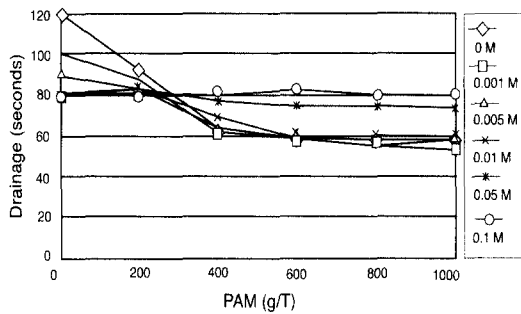

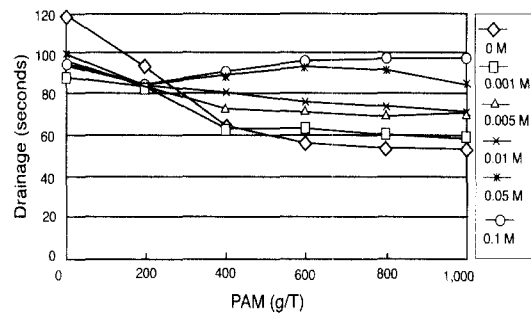Fig. 7. Effect of NaCl on CAT PAM Performance.

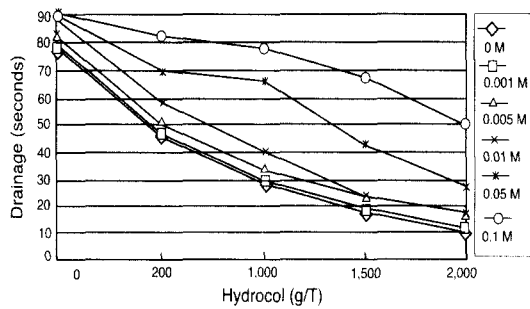Fig. 8. Effect of CaCl$_2$ on CAT PAM performance.

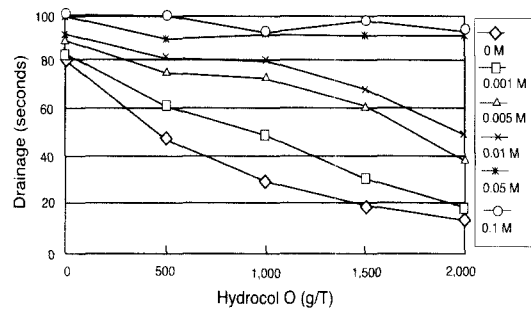Fig. 9. Effect of NaCl on hydrocol system performance CAT PAM 1,000 g/T.

Fig. 10. Effect of CaCl$_2$ on hydrocol system performance CAT PAM 1,000 g/T.

conforms by flattening itself onto the surface to which it is attached and, provided that sufficient polymer is available, this will result in a large proportion of the surface being covered by polymer.

Introducing the anionic microparticle then re-flocculates the system by forming anionic particle/cationic polymer bridge networks.

These particles/polymer bridges are important for the function of microparticle systems, particularly when subject to shear, which will disrupt the flocculated structure. When the shear force is removed or reduced, re-flocculation takes place due to the reformation of particle/polymer bridges. For this reason, microparticle systems are described as reversible systems, which leads to many of the observed advantages.

The microparticle flocculation mechanism is obviously dependent on the adsorption of the cationic polymer so it is clear that the constraints imposed by high electrolyte concentrations are still valid.

Very high levels of electrolyte will eventually deactivates even the most powerful of microparticle systems.

Microparticle systems however are more tolerant of the adverse conditions, which will destroy the performance of totally polymer based systems, and will extend the operating range well beyond that achieved using such systems.

This is attributed to two main factors, the normal addition level of cationic polymer used is significantly higher than that conventionally used in polymer based systems and the mechanism which relies of an anionic particle/cationic polymer bridge rather than a polymer bridging network.

Systems which rely on a polymer bridging mechanism for their performance will be more adversely affected by high electrolyte concentrations in the white water compared with microparticle systems, because they rely on an extended conformation of the polymer, in effect providing the "loops" and "tails" which can be adsorbed on to other particles and form polymer bridges between different particles. It is this effect which is adversely affected by high electrolyte concentrations.

3.1 Packaging grades

A number of paper mills producing packaging grades from waste paper have achieved Zero Effluent Discharge.

One example is St. Laurent Paperboard Inc., Matane, Quebec (3) producing corrugated medium.

From September 1994 to October 1995, St. Laurent Paperboard, Matane successfully undertook and achieved zero process effluent discharge.

The process effluent flow was steadily decreased from 600 m^3/day to zero in October 1995.

Fresh water usage decreased to 550 m^3/day - enough to cover paper machine evaporation losses.

After optimization, the efficiency of the paper machine and the quality of the finished products were unchanged.

At the Zero discharge, the process water total dissolved solids reached equilibrium at about 7,000 mg/1 while the conductivity stabilized at around 2,500 μs/cm.

These figures for dissolved solids are significantly lower than would be expected in a zero effluent mill and are attributed to a high molecular poly DADMAC/hydrated bentonite system which was instigated to give improvements in runnability, retention and drainage.

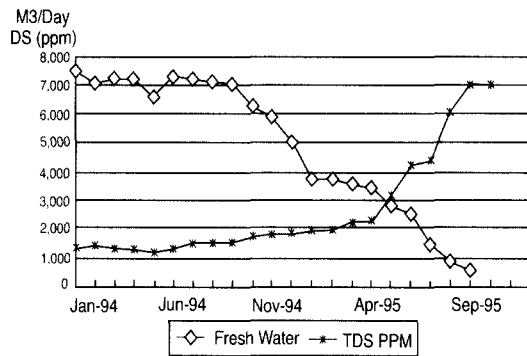Total closure of the water circuit was achieved in three phases. See Figure 11.

Fig. 11. Fresh water make-up to process & TDS build-up.

Phase I

The first phase was strongly focused on reducing fresh water consumption and separating the fresh water used for cooling, called non-contaminated water, from the process effluent. A total of about 2,600 m³/day of fresh water make up to the process water was cut.

Phase II

The fresh water reduction program continued. Many mills use fresh water to the vacuum pumps and consider the sealing water as non-contaminated. Analysis however showed this was contaminated so it was decided to replace fresh water with process water, representing about 800 m³/day of fresh water.

Phase III

The heart of Matane' s zero process discharge system is a high capacity storage tank of consistency pump storage.

The total water balance is the sum of water volumes in the high consistency storage tanks; including the broke tank, and the process water storage tank. All other reservoir capacities in the mill are either negligible or show little variation.

All water volumes that vary are electronically logged every 2 minutes in order to tract

and alarm in the event of a loss of process water into non-contaminated waters or in the case of undesired fresh water make ups into the process.

The mills process water is pumped to the Primary Clarifier with underflow sludge pumped back to the OCC pulper. The over-
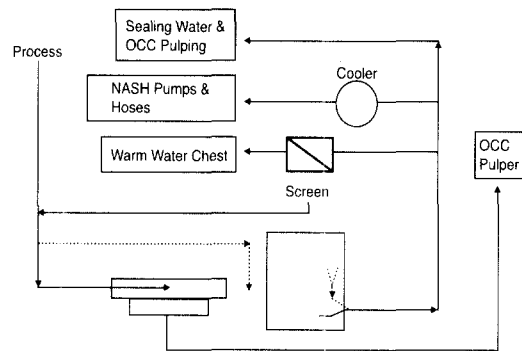

Fig. 12. St-Laurent Paperboard Inc., Matane process water circuit.

flow is transferred to the process water storage tank.

The Matane mill has successfully reduced its process effluent to zero and presently meets all present and "future" environmental regulations.

This has been carried out by a carefully staged program of behavioural and engineering modifications and by the application of the correct retention, drainage and runnability chemical treatment of poly DADMAC/bentonite

4. Conclusions

The benefits of closing mill water circuits are many and varied and the industry will move strongly in this direction in the future. This will present a challenge in terms of finding solutions to the escalating problems which will occur as mills approach or

achieve zero process effluent discharge. Problems such as loss of drainage, reduced retention, increased addition rates of functional and process additives can be addressed by the increased use of microparticle flocculation systems.

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