# Managing anionic detrimental substances in peroxide bleached mechanical pulps – unique benefits of enzymatic treatment.

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## SUMMARY

Brightening processes are the major contributors to variability in wet end chemistry in production of papers based on mechanical pulps. Reductive brightening (hydrosulfite brightening) contributes mainly to increased levels of conductivity, while hydrogen peroxide brightening, due to its initial high pH, generates increased levels of anionic, polymeric materials giving rise to elevated cationic demand values. Both increased conductivity and cationic demand can negatively affect retention, drainage and colloidal stability. Consequently, machine efficiency and product quality are impacted.

This paper reports on continuation of earlier studies dedicated to process water variability in papermaking. Sources and chemical nature of anionic trash generated during hydrogen peroxide brightening are reviewed together with developments in hydrogen peroxide brightening technology. Finally, available anionic trash control strategies, specifically the unique potential of enzymatic treatment are discussed. Results of preliminary laboratory studies and practical applications of pectinase enzymatic technology for two mills are presented.

**KEYWORDS**

Peroxide pulp bleaching, anionic trash, cationic demand, Pectinase, coagulants, fixatives, polyelectrolyte complexes, retention, drainage, mechanical grades, brightness.

Paper machine efficiency is negatively impacted by process instabilities (*1,2*). This impact is especially significant in wood-containing paper production where brightness targets require the use of brightening chemicals, most often sodium hydrosulfite and hydrogen peroxide, and where brightening processes carried out in the pulp mill are highly integrated with paper machine operations (*3-6*). The need to achieve constant brightness targets despite varying wood quality necessitates significant adjustments to the dosage of brightening chemicals in the pulp mill. These circumstances collectively increase the amount and level of contaminant carry-over from the brightening process and are a major source of paper making process instability; since the pulping, brightening and papermaking processes have limited or no separation.

At elevated pH conditions of the hydrogen peroxide brightening process, pectin esters, which are present as a part of the cell wall, undergo rapid general base hydrolysis and are converted to pectic acids (Fig.1, polygalacturonic acids - PGA). PGA are one of the most prevalent and active by-products of hydrogen peroxide brightening. Their negative charge and high molecular weight result in limited thermodynamic stability in the water phase and consequently make them reactive towards cationic wet-end additives (*7-9*). Additionally, usage of other components in the hydrogen peroxide process such as caustic and sodium silicate and a need for post-brightening pH neutralisation, give rise to a significant increase in the ionic strength of the system, generally indicated by elevated conductivity levels.

Both simple electrolytes (increasing conductivity) and polymeric anionic materials (increasing cationic demand) are collectively known as dissolved and colloidal substances (DCS). DCS generated and carried through a peroxide brightening system can complex with cationic additives (cationic demand) (*10-14*), or render conformational changes to flocculants and starches (conductivity) (*15*).

Although the impact of conductivity is important and often underestimated, the focus of this paper remains on the issues related to anionic polymeric materials. These anionic species are quantified by titration with a standardised cationic polymer solution and their concentration is represented in terms of cationic demand, in meq/L or µeq/L. Anionic materials that contribute to the cationic demand form various types of complexes with cationic additives, from soluble species to insoluble precipitates.

Presence of detrimental anionic polymeric materials can significantly reduce the performance of cationic additives. This can lead to increased tray water solids, press felt filling, losses in strength, increases in drying steam demand, and many other negative consequences. Newly formed complexes formed between cationic additives and the DCS may significantly change characteristics of papermaking stock and contribute to retention and dewatering variability, formation of deposits, outbreaks of holes and sheet breaks. For these reasons, a high and varying level of cationic demand has significant, detrimental consequences on machine efficiency and products quality.

Several strategies have been implemented recently to address the amount of anionic materials generated during the peroxide brightening process. Two important examples of these strategies are high consistency peroxide bleaching which utilises a thickening stage and sewering of the pressate, and replacement of sodium hydroxide with magnesium hydroxide as a source of alkalinity (*16,17*). Each of these strategies require compromises or are limited in terms of cost, energy requirements, brightness development, fibre losses and by generation of detrimental substances (*10-12,14*).

The conventional anionic trash control strategy utilises typical coagulants to neu-

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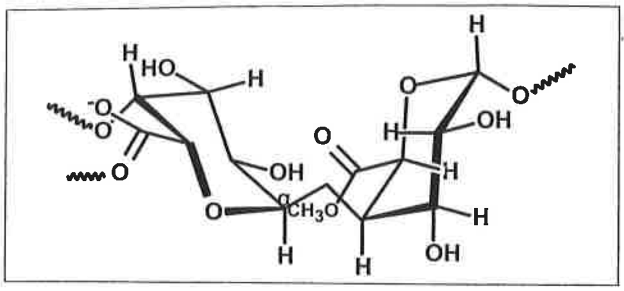

**Fig. 1** **Molecular structure of PGA showing both ester and acid functions.**

tralise the charge of anionic materials generated during peroxide brightening. Thornton established that in the case of hydrogen peroxide brightening process, at least 40% of the measured cationic demand could be attributed to the presence of PGA (*18*) (Fig.1).

The unique molecular structure of PGA, with both ester and acid functionality, provides the opportunity for effective pectinase enzymatic treatment (*8,9,18-23*). Pectinase hydrolytic enzyme catalyses the depolymerisation reaction of polygalacturonic acids, converting them into low molecular weight oligomers. Lower molecular weight materials with 5-6 monomer units, are more soluble in water (increased thermodynamic stability in solution) and consequently display no activity towards cationic polymeric additives (*24*). These lower molecular weight materials are no longer able to form new potentially harmful polyelctrolyte complexes with cationic polymers. Pectinase catalytic activity makes its dosage requirement also very effective when compared to coagulants that require dosages stoichometrically proportional to actual DCS levels.

The active site of Pectinase hydrolytic enzyme contains 3 aspartate residues that participate in the process of water addition to the glycosidic bond (Fig.2) that leads to its cleavage.

It is obvious that the degree of protonation of these aspartic acid carboxylic groups must have a significant impact on Pectinase enzyme activity. Pectinase operates in the slightly acidic environment of fruit and its pH versus activity profile has a maximum around pH 5.0-5.5 with activity falling off sharply above pH 6.

Application of enzymes opens new avenues for cationic demand reduction that until now were cost and runnability prohibited.

In this paper results from machine applications of Pectinase enzyme in two newsprint mills utilizing hydrogen peroxide brightening technology and paper machines operating in acid pH range are discussed. This paper focuses on the benefits of improved efficiency, raw material utilisation and product quality resulting from enzymatic treatment of anionic trash.

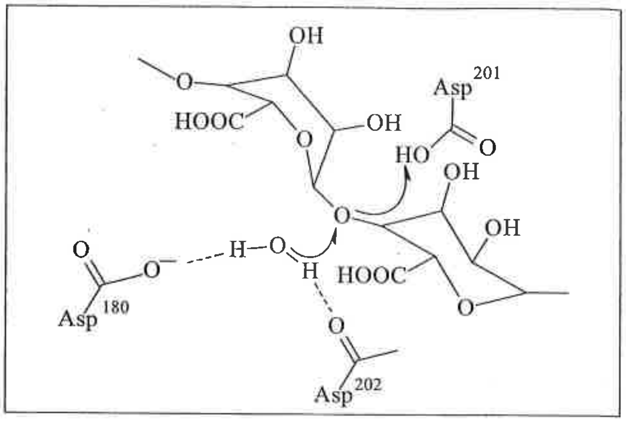

**Fig. 2** **Active site of Pectinase and mechanism of hydrolysis of a-glycosidic bond.**

## RESULT AND DISCUSSION

### Mill Trial 1

This North American mill operates a machine with a Duoformer D forming section and produces a newsprint sheet at 1070 m/min. The pH ranges from 4.7 to 5.1 and the conductivity ranges from 1600 to 2200 µS/cm. Although this machine does not use hydrogen peroxide bleached pulp, it uses filtrate generated in the thickening stage of peroxide bleached TMP, used on another machine, for thick stock pulp dilution. Typical cationic demand levels in this system could reach almost 2000 µeq/L. These high cationic demand values significantly affected the performance of the cationic flocculant causing poor fines retention, poor drainage on the newsprint machine, and as a consequence led to overloading the operation of a DAF unit in the wastewater plant. As a result, the waste water system of the mill required frequent production shutdowns that impacted overall economic results of the mill operation. The charge neutralisation approach of coagulant addition for anionic charge control provided only limited improvements, as could be expected based on earlier discussion. The key mill economical drivers such as on- machine efficiency, raw material utilisation and wastewater treatment plant operations with its impact on environmental compliance, were strongly affected by high cationic demand. The challenge was to overcome these limitations without the negative impact on machine efficiency associated with typical use of coagulants. Considering the high level of the soluble fraction of cationic demand and pH range of paper machine water circuits, Pectinase application offered a potential solution

Initial testing performed on the furnish from the mill showed high effectiveness of the Pectinase in terms of cationic demand reduction, as shown in Figure 3.

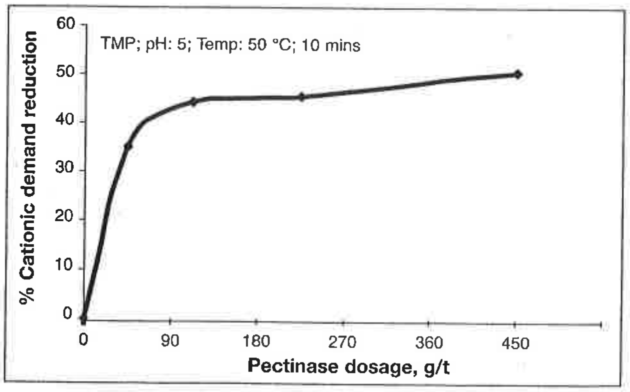

**Fig. 3** **Laboratory evaluation of Pectinase performance using furnish from Mill Trial 1.**

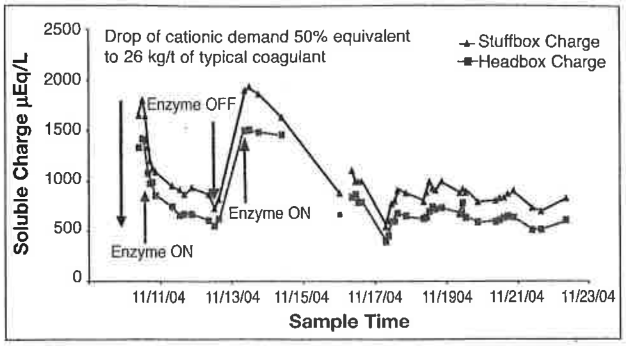

**Fig. 4** Mill trial 1: Impact of Pectinase application on Cationic Demand in the Headbox and Stuff Box samples.

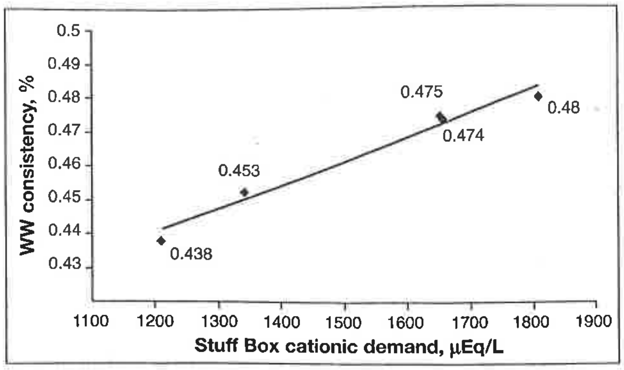

**Fig. 5** Mill Trial 1: Correlation between Cationic Demand in the Stuff Box and White Water Consistency.

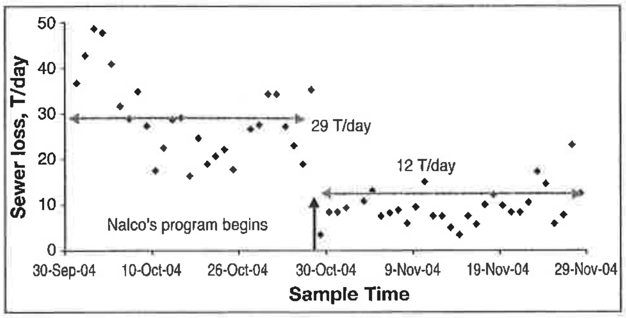

**Fig. 6** Mill Trial 1: Reduction in the sewer losses resulting from Pectinase application.

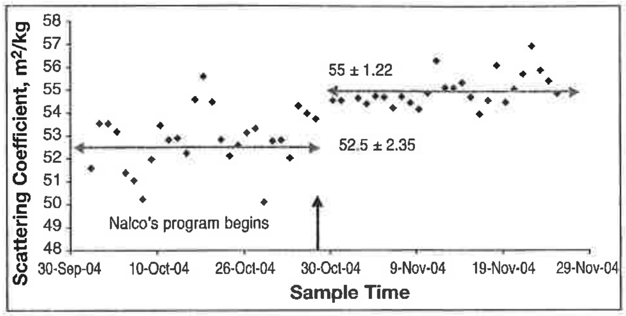

**Fig. 7** Mill Trial 1: Improvement in scattering coefficient at the same filler dosage during Pectinase trial.

Greater than 40% cationic demand reduction was measured at a dose of 0.09 kg/t with reaction conditions of 50 °C, 10 minutes, and a pH of 5.0. On-machine evaluation was therefore proposed to the mill.

The machine application consisted of feeding the pectinase into the contaminated pressate stream from the other machine at the mixing manifold on the inlet to the blend chest. This application point provided excellent mixing, a fundamental requirement for success of any chemical application. From the blend chest, the treated stock progressed through the machine chest, stuff box, cleaners and finally to the approach system with a 20 to 25 minute of total résidence time. The dosage of Pectinase product ranged between 0.05 to 0.10 kg/t.

When the Pectinase was first introduced, the cationic demand of the stuff box and headbox dropped by more than 50%, from 1800 μeq/L and 1500 μeq/L to 700 μeq/L and 550 μeq/L, respectively (Fig. 4). This cationic demand reduction resulted in an increased effectiveness of the retention program.

As Figure 5 indicates, a reduction in the headbox cationic demand correlated with a reduction in the white water consistency, reflecting improved retention program activity.

As the system gradually cleaned up, the sewer losses were reduced on average from 29 t/day to 12 t/day (Fig. 6). The variability in solids loss was also reduced.

Additionally, increasing the fines retention had a positive impact on the final product quality. Figure 7 depicts the scattering coefficient before and during the pectinase trial. An increase of 2.5 units (increased sheet fines content) was noted while the variability in this sheet property was nearly cut in half.

In conclusion, application of the Pectinase resulted in vastly improved machine efficiency, reduction in fibre and filler losses, reduced load on the waste treatment plant and a reduction in paper property variability.

## Mill Trial 2

This European mill produces a high brightness mechanical furnish-based sheet, using hydrogen peroxide bleached pulp on a paper machine equipped with top former and operating at 1100 m/min. As in typical hydrogen peroxide brightening processes, this pulp was acidified after brightening to prevent alkaline darkening, and the wet end of the paper machine operates at a pH range of 4.7-5.1. The furnish blend used in this mill includes TMP, Softwood Kraft (SWK), and calcined clay filler. The mill depends on filler addition for opacity development. This mill operates typically at a very high cationic demand level, reaching 6000 μeq/L. This high level of cationic demand negatively affects filler retention, and consequently, the ability to reach quality specifications of opacity for the product. The required filler content needed to achieve the opacity specification could only be achieved by driving higher filler consistency in the headbox. This led to higher filler losses, which impacted production costs. It also leads to sheet two-sidedness in filler distribution and effectiveness of filler opacifying properties. For the reasons presented during discussion of the case of Mill 1, the classical charge neutralisation approach via coagulant application had only a very limited impact on this situation. Similarly to Mill 1, the key drivers for this mill were on-machine efficiency, filler utilisation and effective wastewater treatment plant operations for environmental compliance. Application of Pectinase presented a real opportunity for significant improvements to mill operations.

Laboratory testing of Pectinase enzyme at a dose of 0.04 kg/t reduced the cationic demand of furnish samples by

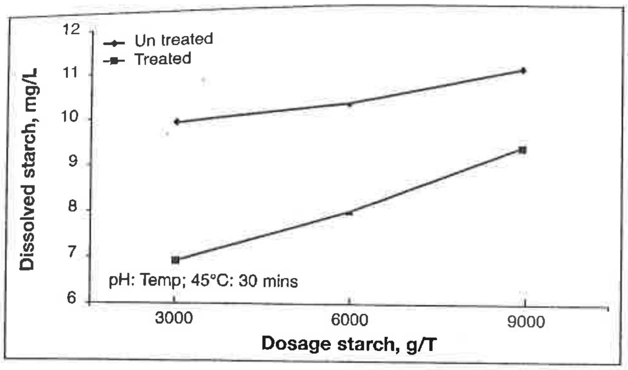

**Fig. 8** Mill Trial 2: Improvement of cationic starch retention following Pectinase pre-treatment of hydrogen peroxide brightened TMP pulp.

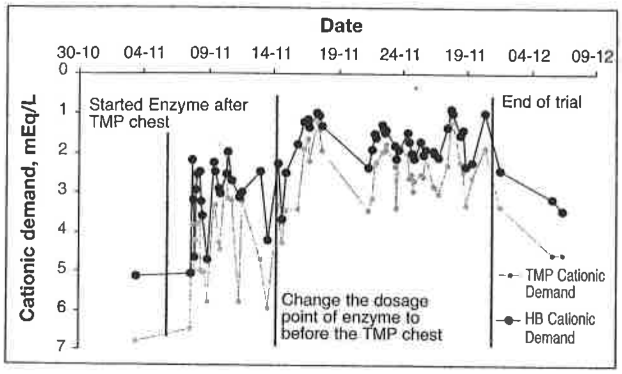

**Fig. 9** Mill Trial 2: Changes in Cationic Demand due to Pectinase application and feed point selection.

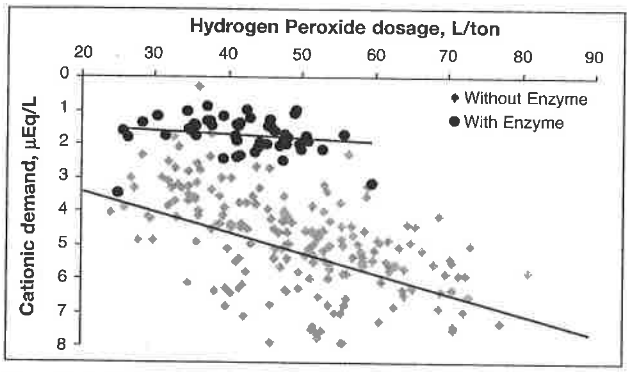

**Fig. 10** Mill Trial 2: Application of Pectinase decouples impact of level of brightening chemicals dosage on resulting Cationic Demand.

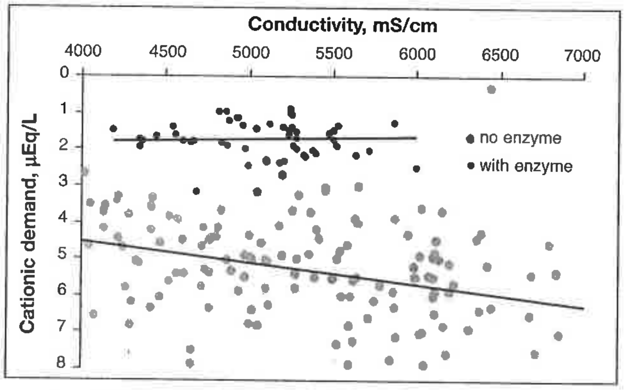

**Fig. 11** Mill Trial 2: Pectinase application decouples Cationic Demand increases from Conductivity changes additionally stabilizing wet end conditions of paper machine.

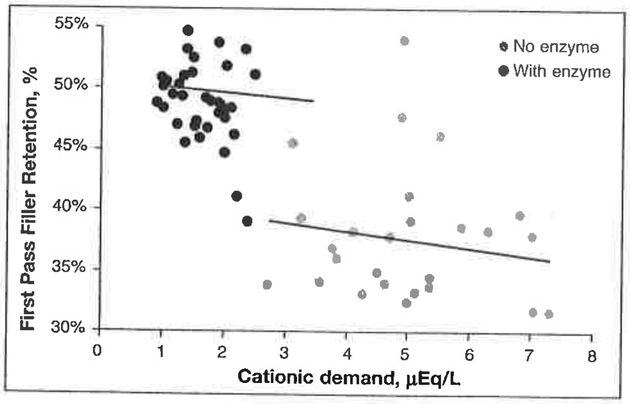

**Fig.12** Mill Trial 2: Impact of Enzyme application on First Pass Filler Retention.

80%. This result was even higher than predicted by Thornton (*3*), suggesting that the component of pectic acids in total cationic demand was higher than the expected 40-50%. A lower contribution from the inorganic fraction of total cationic demand (associated typically with sodium silicate application) is a possible explanation for the occurrence. This result suggested that Mill 2 would significantly benefit from Pectinase treatment. Further laboratory studies indicated that improved flocculant efficiency would permit a 30% reduction of flocculant dosage at the same total retention. In these experiments filler retention was doubled for a given total retention improvement, suggesting certain selectivity in filler retention, resulting from Pectinase application. In addition, drainage benefits from the application of retention program were improved as indicated by a vacuum dewatering time decrease by 15% to 20%.

Starch retention studies were also performed in the laboratory for Mill 2 furnish. The reaction conditions for this study were a pH of 5, a temperature of 45 °C, and a reaction time of 30 minutes. Figure 8 shows that treating furnish with pectinase improves the starch retention (measured indirectly by the lowered concentration of dissolved (unretained) starch in the filtrate.)

These promising laboratory results fully justified recommendation for an on-machine trial. The machine trial began with pectinase applied at an average dose of 0.04 to 0.05 kg/t. The cationic demand dropped 80%, from 6000 to 1000 µeq/L (meq/L in figure), especially after moving the feed point from the exit to the entrance of the TMP high-density chest to achieve increased reaction time. Figure 9 shows cationic demand changes observed during the initial phase of the trial. At the end of the trial, when the Pectinase was

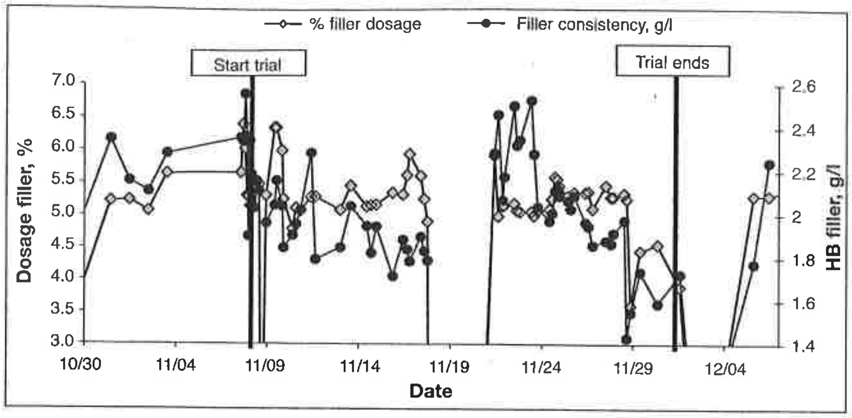

**Fig. 13 Mill Trial 2: Changes in filler dosage and White Water filler consistency required to maintain optical properties of the sheet.**

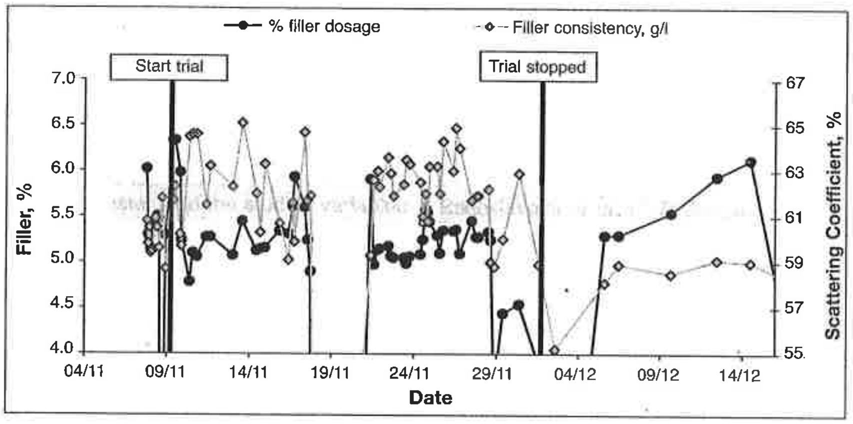

**Fig.14 Mill Trial 2: Increased sheet scattering coefficient at lower filler level as a result of Pectinase application.**

removed from the system, an immediate increase in the cationic demand value was recorded (note the reverse scale of cationic demand on this graph).

Variability observed in cationic demand and conductivity for various brightness targets is a major contributor to process instability. This leads to changes in retention, drainage, centre roll release angle (point) and consequently to reduced on-machine efficiency and lower and variable product quality. The following figures represent the significant benefits of Pectinase application from improved system stability through wet end chemistry (cationic demand and conductivity) when varying levels of hydrogen peroxide dosage were applied to achieve selected brightness targets. The impact of brightening level (via hydrogen peroxide dose) on the cationic demand is presented in Figure 10. Without the Pectinase, as the brightening requirement or peroxide dose increased due to changes in the brightness specifications, the cationic demand increased significantly. When the Pectinase was applied, lower and much more stable levels of cationic demand were observed.

The higher brightening levels resulted in an increase in conductivity as well. Figure 11 illustrates how increases in the conductivity are decoupled from the cationic demand because the pectinase provides a reduction and stabilisation of the cationic demand.

This reduction in the value and variability of cationic demand had a very positive impact on the filler retention as illustrated by Figure 12.

Pectinase application allowed for much more effective performance of the retention program in terms of fines and filler retention. An average increase of First Pass Retention of 10 percentage points was recorded during the trial. The variability in the retention was also reduced. Higher level of filler retention allowed for a reduction of the filler consistency in the headbox needed to reach required ash content in the sheet to meet opacity specifications (Fig. 13).

As a result of the combined benefits of increased filler retention and improved filler distribution, scattering coefficient of the sheet was higher even at lower filler feeding rates, as shown in Figure 14. Machine shutdowns due to clarifier overload were reduced or eliminated and efficiency of the machine improved significantly.

## CONCLUSIONS

Two examples of Pectinase application demonstrate the benefits of enzymatic anionic trash reduction in improving machine efficiencies in peroxide bleached mills. If the requirement of pH < 6 after peroxide bleaching is fulfilled, cationic demand reductions of 40% and higher are possible through the molecular weight reduction of polygalacturonic acid with pectinase. There are no alternative strategies available that match level of performance delivered by Pectinase. Other treatments fall short of this benchmark in terms of effectiveness, cost and their impact on runnability, energy and fibre losses.

Benefits of anionic trash reduction include increased retention, in particular filler retention, drainage, reduction in process and sheet quality variability, reduced downtime improved overall yield of the process and lowered environmental footprint of mill operations.

Laboratory cationic demand reduction results were a good prediction of on-machine performance.

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$u_s$ – Average press speed in m/s

$P_{ref}$ – Blanket reference pressure exerted on ink

$V_{Wall}$ – Penetration velocity into the paper

$U_x$ – Elongation in the $x$ or width direction

$U_y$ – Elongation in the $y$ or width direction

$U_k$ – Elongation at the kth partition of the paper

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