

New Possibilities In Bleaching Wood-Containing Dip: Alternative To Alkaline Peroxide Bleaching

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ABSTRACT

Alkaline conditions are necessary during pulping of recovered papers and during hydrogen peroxide (P) bleaching of deinked pulp. However the alkaline treatment gives rise to a higher solubility of some components, inducing environmental problems and deposits reducing the paper machine efficiency.

Alternatives to P stage were investigated to reduce chemical oxygen demand (COD) in bleaching effluent with the target brightness same as that of the pulp bleached by P.

The substitution of sodium hydroxide (NaOH) by magnesium carbonate ($MgCO_3$), magnesium hydroxide ($Mg(OH)_2$) during P bleaching, allows to reach the brightness target while improving effluent quality (reduction of COD: -20% compared to conventional bleaching).

The use of alkaline silicate ($SiO_2:Na_2O$: 1.75-2.16) instead of standard silicate ($SiO_2:Na_2O$: 3.2-3.7) during P bleaching improves brightness (+1.5pts) of pulp without significant effect on the effluent quality.

KEYWORDS

Alternatives to peroxide, Bleaching, Brightness, COD (Chemical Oxygen Demand), Deinking, Peroxide, Reclaimed fibers.

INTRODUCTION

Conventional bleaching process for wood containing recovered papers usually requires the usage of sodium hydroxide (NaOH) together with sodium silicate (Na_2SiO_3) and hydrogen peroxide (H_2O_2). Hydrogen peroxide bleaching (P) is carried out in alkaline conditions in order to produce the reactive perhydroxyl ion $-OOH$ enabling to destroy some pulp chromophores [1]. Sodium silicate is usually added to reduce hydrogen peroxide decomposition with metal ions and has a buffering effect [2].

However, alkaline peroxide bleaching treatments create a higher solubility of some components [3] which give rise to the following drawbacks:

- a higher dissolved solid concentration in process waters, especially with closed water circuits,
- a higher contamination in the process water sent to the effluent plant,
- a higher carry over of dissolved contaminants towards the paper machine inducing sometimes deposits [4] and reducing the paper machine efficiency.

For all these reasons, the trend is to reduce the alkalinity during the bleaching sequences. However, these changes

induce a brightness loss.

Previous studies have shown that substitution of NaOH by $Mg(OH)_2$ during P bleaching of TMP pulp allows to reduce COD [5] and the use of sodium percarbonate and sodium perborate instead of H_2O_2 allows to obtain similar bleaching efficiency[6]. During this study, NaOH, standard Na_2SiO_3 and H_2O_2 used during P bleaching were substituted by alternative chemicals in order to reduce dissolved and colloidal materials in bleaching effluent, without reduction of brightness gain.

MATERIALS AND METHODS

According to a previous study [7], brightness of unbleached mechanical pulp portion has the major influence on the wood containing DIP brightness fibre mixture. This pulp was determined as the limiting factor. Consequently, unbleached newsprint (100% TMP) was submitted to different alternatives to P bleaching in order to increase their brightness. Bleaching experiments were carried out at 70°C, 10% consistency during 2 hours following conditions listed in . 0.3% DTPA was added to chelate metallic cations to avoid hydrogen peroxide decomposition.

Table I: BLEACHING CONDITIONS

Bleaching	Conditions
Conventional	1% NaOH, 2.5% standard Na_2SiO_3 (SiO_2/Na_2O : 3.3), 3% H_2O_2
Conventional without NaOH	2.5% standard Na_2SiO_3 (SiO_2/Na_2O : 3.3), 3% H_2O_2
Sodium perborate	2.5% standard Na_2SiO_3 (SiO_2/Na_2O :3.3), 8.82% sodium perborate (corresponding to 3% H_2O_2)
Sodium percarbonate	2.5% standard Na_2SiO_3 (SiO_2/Na_2O :3.3), 9.24% sodium percarbonate:corresponding to 3% H_2O_2
$MgCO_3$	2.5% standard Na_2SiO_3 (SiO_2/Na_2O :3.3), 2% $MgCO_3$, 3% H_2O_2
$CaCO_3$	2.5% standard Na_2SiO_3 (SiO_2/Na_2O :3.3), 2% $CaCO_3$, 3% H_2O_2
$Mg(OH)_2$	2.5% standard Na_2SiO_3 (SiO_2/Na_2O :3.3), 1% $Mg(OH)_2$, 3% H_2O_2
PAA	NaOH (to be at pH:7), 0.67% enzyme: catalyse (to neutralise H_2O_2 contained in peracetic acid solution, 6.7% peracetic acid (corresponding to the same amount of active oxygen than 3% H_2O_2))
Alkaline silicate S1	2.5% alkaline S1 (SiO_2/Na_2O :1.75), 3% H_2O_2
Alkaline silicate S2	2.5% alkaline S2 (SiO_2/Na_2O :2), 3% H_2O_2
Alkaline silicate S3	2.5% alkaline S3 (SiO_2/Na_2O :2.16), 3% H_2O_2
Alkaline silicate modified by a binding agent	2.5% alkaline silicate modified by a binding agent (SiO_2/Na_2O :2), 3% H_2O_2

After the alternative P stages, the bleached pulp was separated in two parts. The first part was used for brightness determination and residual H₂O₂ titration and the second part was filtered for effluent characterization such as chemical oxygen demand (COD).

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Immediately after bleaching, 30 g of pulp was washed in a buchner containing a filter (5891) with 5 litres of water in order to eliminate chemicals. Pulp brightness was measured on this pulp and on the hyperwashed pulp (washing of pulp allowed elimination of fin elements and mineral fillers) [8]. Effluent was recovered as follows: bleached pulp was first diluted at 2% consistency and residual hydrogen peroxide was neutralized by sodium sulphite. Pulp was then filtered and centrifuged (1000 G) before analysis.

RESULTS AND DISCUSSION

Figure 1 presents the brightness of the pulp versus COD released in process water after different bleaching sequences. The same trial performed several times allowed to determine the lengths of the error bars. Bleaching with new chemicals were compared to conventional bleaching (P stage) and conventional bleaching without NaOH. The study of conventional bleaching allows to determine the brightness to reach, whereas, conventional bleaching without NaOH indicates the COD measurement in effluent without NaOH.

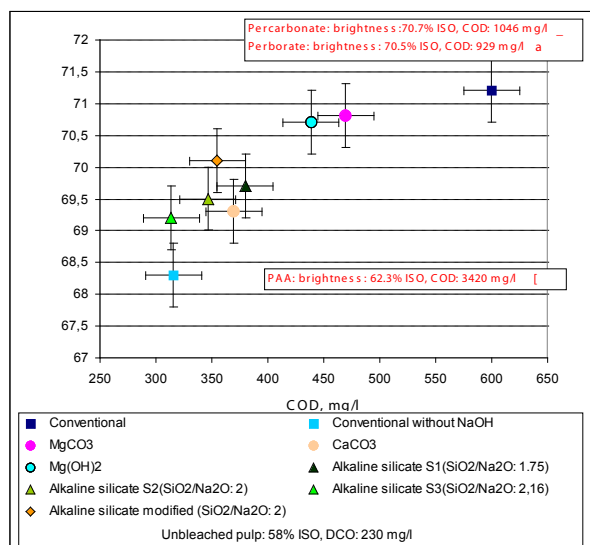


Figure 1 : Brightness and COD compromise of the alternative P bleaching

As shown by Figure 1, the best brightness and COD compromises were obtained after (H₂O₂, MgCO₃) bleaching and (H₂O₂, Mg(OH)₂) bleaching.

The substitution of NaOH by MgCO₃, Mg(OH)₂ during P bleaching allows to reach the brightness target (71% ISO) while improving effluent quality (similar tendencies were obtained on hyperwashed pulp). The COD measured in the effluent of these different alternative bleaching decreased by 20% compared to COD measurement performed in filtrate of conventional bleaching.

H₂O₂ bleaching in presence of MgCO₃, Mg(OH)₂

As shown in **Figure 2**, (H₂O₂, MgCO₃) bleaching and (H₂O₂, Mg(OH)₂) bleaching consume less hydrogen peroxide than conventional bleaching.

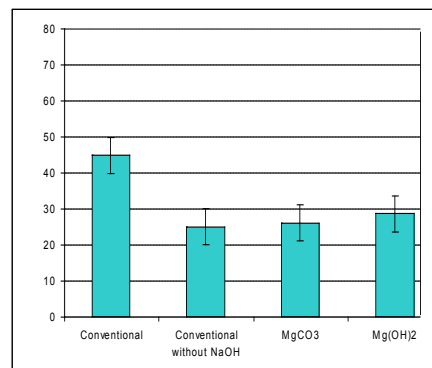


Figure 2 : H₂O₂ consumption during bleaching

In order to understand this phenomenon, the H₂O₂ consumption by MgCO₃ and NaOH was compared versus time during experiment performed without pulp in deionised water with DTPA (**Figure 3**). Results show, that, contrary to NaOH, the presence of MgCO₃ in the bleaching liquor stabilises the H₂O₂.

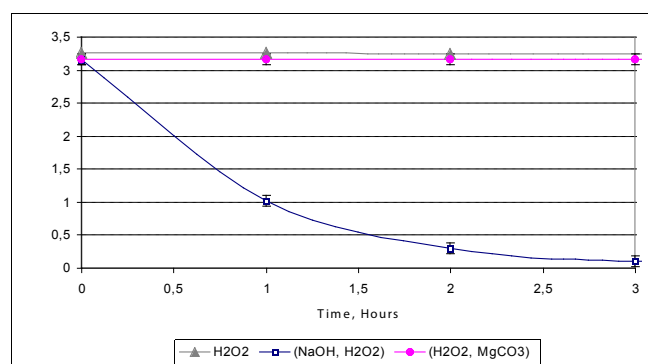
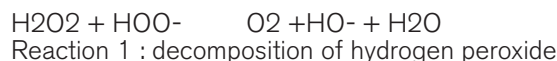


Figure 3 : Variation of H₂O₂ concentration in bleaching liquor versus time

In (H₂O₂, NaOH) liquor, a part of created HOO⁻, decomposes H₂O₂ (Reaction 1) [6].



Mass spectrum of (H₂O₂, MgCO₃) bleaching liquor was determined (Figure 4) and indicates that (Mg(HOO⁻))+ was present in this solution.

The stabilization of H₂O₂ versus time in (H₂O₂, MgCO₃) liquor is attributed to the formation of this (Mg(HOO⁻))+ specie. This component prevents H₂O₂ decomposition in (H₂O₂, MgCO₃) bleaching liquor as less HOO⁻ are present to decompose H₂O₂ according to Reaction 1.

As (H₂O₂, MgCO₃) bleaching is less alkaline than conventional bleaching, it should lead to lower bleaching efficiency. However, less H₂O₂ is decomposed due to i) the formation of (Mg(HOO⁻))+ during (H₂O₂, MgCO₃) bleaching and to ii) the decrease of the rate of H₂O₂ decomposition, compared to conventional bleaching. Consequently, the similar brightness level achieved for both bleaching sequences is partially attributed to the formation of (Mg(HOO⁻))+ avoiding H₂O₂ decomposition during bleaching even if the concentration of the active specie HOO⁻ is lower.

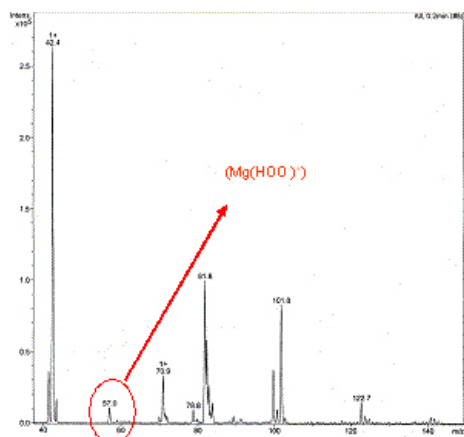


Figure 4 : Mass spectrum analysis

The lowest alkalinity of H₂O₂ bleaching performed with Mg(OH)₂ or MgCO₃ compared to conventional bleaching induces a decrease of COD.

H₂O₂ bleaching in presence of CaCO₃

As shown by Figure 1, the addition of CaCO₃ during conventional bleaching without NaOH is not as effective as addition of sodium hydroxide. Brightness is lower (-2pts), nevertheless COD is reduced (-38%) and a brightness gain is observed compared to conventional bleaching without NaOH(+1 pt).

On Figure 5, (H₂O₂, CaCO₃) bleaching was compared to a conventional bleaching sequence without NaOH, and with or without addition of CaCO₃ at the end of the reaction. Brightness of entire, hyperwashed pulp and the percentage of filler were measured.

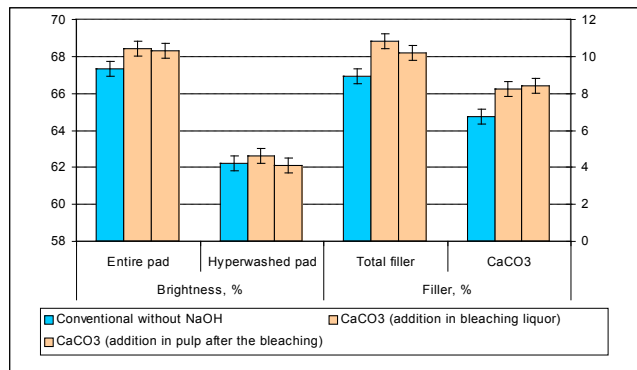


Figure 5 : Influence of addition of CaCO₃ during bleaching

Pulp used to perform this trial was from newspapers (containing fillers: 6.5% CaCO₃). Hyperwashing of pulp eliminates fine elements and fillers, inducing a brightness loss.

The introduction of CaCO₃ in the pulp before or after the bleaching leads to similar results.

Consequently, the brightness gain observed during (H₂O₂, CaCO₃) bleaching is attributed to CaCO₃ filler contribution and it is not due to a reaction between CaCO₃ and H₂O₂. CaCO₃ (used as alkaline source) does not improve H₂O₂ bleaching efficiency.

Use of alkaline silicate instead of standard silicate

The use of alkaline silicate instead of standard silicate improves the brightness (+ 1.5pts) without significant modification of COD (Figure 1).

On Figure 6, conventional bleaching without NaOH with standard silicate or alkaline silicate (SiO₂/Na₂O:1.75) presented in Table I, were compared at same total alkalinity (TA). Calculations were made with the formula given by acid base titration.

$$TA\% = NaOH\% + 0.098 * \text{standard Na}_2\text{SiO}_3\%$$

$$TA\% = NaOH\% + 0.185 * \text{silicate alcalin}\%$$

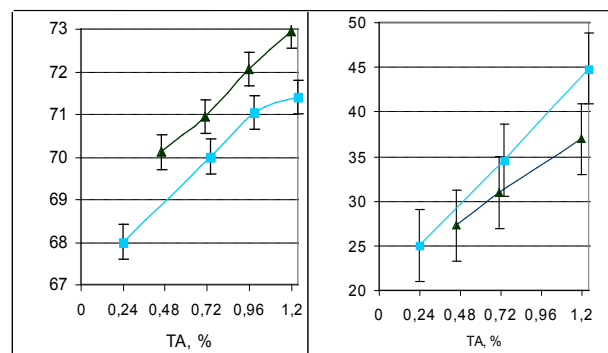


Figure 6 : Comparison between standard silicate and alkaline silicate

The brightness gain observed after H₂O₂ bleaching in the presence of alkaline silicate comes from alkalinity of silicate and it is not a consequence of the increase in liquid phase alkalinity because at same total alkali, substitution of silicate standard by alkaline silicate allows to increase brightness and to reduce H₂O₂ consumption (Figure 6)

Sodium percarbonate, sodium perborate and peracetic acid bleaching

The replacement of H₂O₂ by chemicals generating hydrogen peroxide during their solubilization such as sodium percarbonate or sodium perborate [9] does not result in decrease COD in bleaching effluent (Figure 1).

Sodium percarbonate and sodium perborate are very interesting in term of brightness but generate a higher amount of oxidizable substances (COD: 1046 mg/l for sodium percarbonate bleaching and 928 mg/l for sodium perborate bleaching) in the bleaching effluent compared to conventional bleaching.

The study of H₂O₂ consumption (Figure 7) shows that sodium percarbonate bleaching consumes higher amounts of hydrogen peroxide than conventional bleaching.

During sodium percarbonate bleaching, H₂O₂ is consumed by HOO⁻, as in conventional bleaching, but also by HCO₃⁻ resulting from the reaction between H₂O₂ and Na₂CO₃ (generated during solubilization of sodium percarbonate) [10].

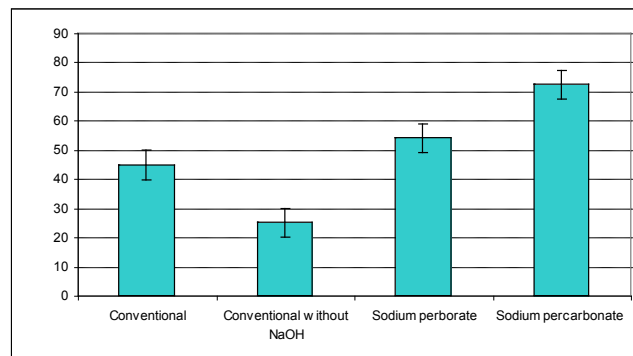


Figure 7 : H₂O₂ consumption during bleaching

On **Figure 8**, the pH of different pulps was measured along the bleaching reaction.

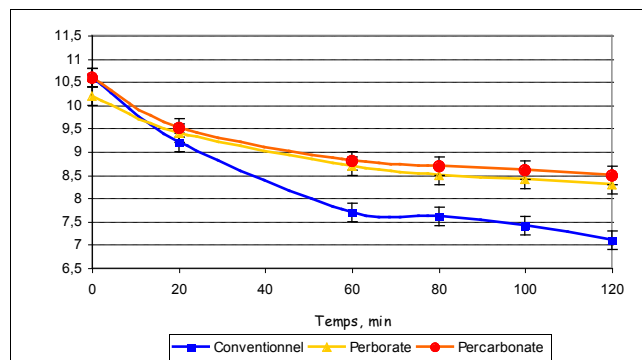


Figure 8 : Variation of pH of pulp during bleaching

At the beginning of bleaching reaction, the amount of hydroxyl anion released by conventional bleaching is similar to sodium percarbonate but higher than sodium perborate bleaching sequences. However, at the end of the reaction, sodium perborate and sodium percarbonate bleaching are more alkaline than conventional bleaching, inducing a higher consumption of H_2O_2 and higher COD measurements in the bleaching filtrate. Nevertheless, these higher alkaline conditions facilitate discoloration of the pulp. Increase of H_2O_2 consumption and efficiency improvement of bleaching could explain similar brightness between conventional, sodium percarbonate and sodium perborate bleaching.

The use of chemical releasing an equivalent amount of active oxygen than H_2O_2 such as peracetic acid (PAA) does not improve the pulp brightness discoloured by conventional bleaching and the effluent quality (Figure 1). PAA bleaching was not performed in optimal conditions. The retention time was too long and the bleaching temperature was too high. Furthermore, a part of COD is coming from acetic acid present in PAA solution.

CONCLUSIONS AND FUTURE PROSPECTS

The substitution of NaOH by $MgCO_3$ or $Mg(OH)_2$ during P bleaching allows to reach the brightness target (71% ISO) while improving effluent quality. The lowest alkalinity of these chemicals reduces COD in bleaching effluent by 20% compared to conventional bleaching. Contrary to NaOH, $MgCO_3$ stabilizes HOO^- due to formation of $(Mg(HOO^-))_+$, avoiding H_2O_2 decomposition and should allow a better efficiency of HOO^- on lignin.

The use of $CaCO_3$ during conventional bleaching without NaOH brings superficial brightness gain, which is attributed to $CaCO_3$ filler contribution.

During conventional bleaching without NaOH, addition of alkaline silicate ($SiO_2:Na_2O$: 1.75-2.16) instead of standard silicate (SiO_2/Na_2O : 3.2-3.7) improves brightness (+1.5pts) of pulp without significant effect on effluent quality. This phenomenon comes from silicate and is not attributed to an increase in liquid phase alkalinity.

The replacement of H_2O_2 during conventional bleaching by sodium percarbonate, sodium perborate or peracetic acid does not reduce the COD of process waters. Alkalinity generated during sodium percarbonate or sodium perborate bleachings or the acetic acid present in peracetic acid solution increased COD.

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Conference Review

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SUMMARY

Recycling related papers presented at the TAPPI EPE (Engineering, Pulping and Environmental) conference held October 2009 in Memphis, Tennessee, are reviewed here. Thirteen (13) papers, listed at the end, are pertinent to this review. There was one round table session to discuss similarities and differences between pitch and stickies. Additionally, there was a Virtual Demonstration of Stickies Measurement Methods Workshop on Sunday afternoon and Fiber Recycling Committee meeting on Wednesday morning. The tour of Buckman USA's Headquarters concluded the conference program.

1.0 INTRODUCTION

The papers covered in this review were part of recycling sessions at the TAPPI EPE conference held in October 2009. These sessions, listed below, were organized by the TAPPI Fiber Recycling Committee except Session 28 that was in cooperation with Alkaline Pulping and Bleaching Committee:

- Session No. 3: Deinking Research,
Chaired by John Cameron
- Session No. 7: Ink Measurement and Additive Influence
Chaired by Garnet Bremner
- Session No. 12: What is New in Recycling
Chaired by Carl Houtman
- Session No. 18: Recycling Trends and Technology
Chaired by Joe Cable
- Session No. 24: Stickies Deposit Control
Chaired by Dan Glover
- Session No. 28: Bleach Plant Deposit Control
Chaired by Joe Wilson
- Session No. 35: Similarities and Differences between
Pitch and Stickies – Panel
Moderator: Mahendra Doshi
Panel members: Philip Hoekstra
Danny Haynes
Sergey Shevchenko

In addition there was a very informative tour of Buckman USA's Headquarters.

Virtual Demonstration of Stickies Measurement Methods Workshop was organized by Mahendra Doshi and Garnet Bremner. Prior to demonstration, Doshi reviewed various methods used for measuring stickies (see PPR, Vol. 18, No. 3, 20-30, 2009). Demonstrated methods and contributors include:

- A. Blue dye method, Carl Houtman
- B. Agglomeration method, Mahendra Doshi and Brent Cowan
- C. TOC method, Danny Haynes
- D. INGEDE methods, Georg Hirsch
- E. Water drop method, Jeff Hsieh

The intent of this feature is to present a synopsis of the significant research results and industry ideas reported at the conference. Due to space constraints, we are not able to cover all of the presented papers (listed at the end) in detail. Readers are encouraged to obtain the original articles from TAPPI for more information.

2.0 TRENDS IN UTILIZATION OF RECOVERED PAPERS

Share of recovered fiber utilization in a country depends on many factors. Hujala et al. (8) developed a model to evaluate the effect of the following parameters on the recovered paper utilization trends:

- Economic factors
- Socio-cultural characteristics
- Environmental factors
- Level of technological development

Available information and data from Global Market Information Database, United Nations Development Programme reports and internet were used to test the model for a period between 1995 and 2007 for 22 leading paper-producing countries.

Utilization rates in 2007 varied from a low of 7% in Finland to a high of 79% in Philippines. Not surprisingly, lowest utilization rates were in countries with enormous forest resources (Finland, Sweden, Norway, Russia, Canada) while highest rates were in Western Europe and Southeast Asian countries (8). For Example, fiber utilization rates increased during 1995 to 2007 from 40% to 65% in China and from 33% to 53% in India. As expected, developed countries increasingly export recovered paper to developing countries.

Some of the important factors affecting recovered fiber utilization rates include country's wealth (as measured by GDP per capita) and environmental awareness (as measured by ISO 14001 certificates per 1000 people). Technological factor (measured by patents and schooling) was not important according to the model. Hujala et al. (8) point out that recovered paper utilization process is relatively standard and known worldwide so that no special technical skills are necessary.

One interesting cultural factor that was considered was masculinity vs. femininity. Hujala et al. (8) suggest that the society with masculine domination corresponds to more assertiveness while femininity refers to caring for others' well being. In other words, one would expect higher recovered fiber utilization in countries with "less masculine cultures." (Authors did not specify how they measured this parameter or indicate specific values for different countries). Surprisingly, model result was exactly opposite – countries with "more masculine cultures" had higher recovered fiber utilization rate. No explanation was offered for the model observation.

Authors hope that results from the model could be useful in planning international and domestic policies to enhance the recovery and utilization of recovered papers (8).

3.0 DEINKING

Several aspects of deinking were considered at this conference. These include, deinking inkjet printed papers (1, 3), low alkali deinking (6), effect of internal and external sizing (2), kaolin clay based deinking agent (7), flotation deinking cell design (9) and ERIC measurement (4, 5).

3.1 Deinking Inkjet Printed Papers

Digital inkjet printed papers are somewhat difficult to deink as ink easily disperses into numerous small particles that are difficult to remove by flotation. In addition dyes used in inks stain the fiber thereby lowering pulp brightness (1). Washing may result in darker filtrate that is difficult to clarify unless expensive processes like membrane filtration are employed. Also, the loss of fillers and fines during washing lowers yield.

Yilgor et al. (1) evaluated the effect of enzyme and surfactant in deinking inkjet printed papers. Papers printed by HP