$Mg(OH)_2$-BASED HYDROGEN PEROXIDE BLEACHING OF CMP PULPS AT HIGH CONSISTENCY

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The objective of this study was to investigate the bleaching performance of a $Mg(OH)_2$-based hydrogen peroxide process at a high consistency. In this work, an industrially produced chemimechanical pulp (CMP) was bleached via $Mg(OH)_2$- or NaOH-based hydrogen peroxide processes at 10% and 25% consistencies. The results showed that the pulp bleached under the conditions of 1.5% $Mg(OH)_2$ and 3% H_2O_2 at 25% consistency had a similar brightness to, a lower yellowness index, and a higher opacity than the pulp produced under the conditions of 2.1% NaOH, 3% Na_2SiO_3, and 3% H_2O_2 at the same consistency. The temperature (70 ºC) and time (150 min) of the bleaching were the same for both processes. Under the conditions stated above, the $Mg(OH)_2$-based process had a higher yield than the NaOH-based process did. The bleaching effluent of the $Mg(OH)_2$-based process had a higher residual H_2O_2, but a lower Chemical Oxygen Demand (COD) load and turbidity, compared with that of the NaOH-based process. However, the strength properties and water retention value (WRV) of the pulp bleached via the $Mg(OH)_2$-based process were lower, while its bulk was higher than those of the pulp bleached via the NaOH-based process.

Key words: CMP; High consistency; H_2O_2, $Mg(OH)_2$; NaOH; Bulk

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INTRODUCTION

The application of chemimechanical pulp (CMP) is readily increasing in various paper grades (Ford and Sharman 1995), due to its good optical properties and relatively low production cost (Zeinaly et al. 2009). As the market demand on pulp brightness is steadily rising, mechanical pulping has become more dependent on hydrogen peroxide bleaching (Wang et al. 2008).

Hydrogen peroxide is an environmentally friendly bleaching chemical that is widely used in the pulping industry (Yesuadian et al. 1997; Wong et al. 2006; Tamper et al. 2007; Dietz et al. 2009; Savoye et al. 2009; Zeinaly et al. 2009). Generally, hydrogen peroxide bleaching is conducted under alkaline condition to achieve a significant brightening effect (Wang et al. 2008). Hydrogen peroxide increases the brightness of pulps by oxidizing choromophoric groups, most of them associated with lignin, so that they do not absorb as much light and possibly by helping to solubilize some of the chomophores so that they can be removed from the pulp. However, the high alkalinity of the NaOH-based process promotes the dissolution of carbohydrates (particularly hemicelluloses) of the fibers, which increases the Chemical Oxygen Demand (COD) load of the bleaching effluent. The high alkalinity also facilitates the formation of anionic trash, which has negative consequences on papermaking operations (Wong et al. 2005; He et al. 2006), such as increased polymer/additive cost, reduced drainage and decreased product quality (Thornton et al. 1993; Suess et al. 2001).

The application of $Mg(OH)_2$ in hydrogen peroxide bleaching has been well established at a low consistency (Nystrom et al. 1993; Ford and Sharman 1995; Suess et al. 2001; Johnson et al. 2002; Harrison et al. 2008) and commercially practiced in the mechanical pulping industry (He et al. 2004a, 2005, 2006; Yu and Ni 2006). However, the incentive for operating pulping and bleaching processes at a high consistency is increasing in recent years. By increasing the consistency of pulp, the amount of water in bleaching processes would decrease, which would affect the energy requirement, and eventually the revenue, of the pulp mill (Anderson and Amini 1996). One objective of this research was to investigate the performance of $Mg(OH)_2$-based hydrogen peroxide bleaching of a mixed hardwood CMP at a high consistency.

Furthermore, $Mg(OH)_2$-based hydrogen peroxide bleaching may suffer a lower brightening performance compared with the NaOH-based hydrogen peroxide bleaching (He and Ni 2008). As is well known, by increasing the consistency of pulp in bleaching processes, the concentration of bleaching chemicals is increased, which may improve the performance of the bleaching chemicals in bleaching processes (Andreson and Amini 1996). The other objective of the current research was to optimize the process conditions of the $Mg(OH)_2$-based hydrogen peroxide bleaching so that the $Mg(OH)_2$-based hydrogen peroxide bleaching could produce a pulp with a brightness that is similar to the brightness of the NaOH-based hydrogen peroxide bleaching for a mixed hardwood CMP at a high consistency.

In this study, an industrially produced CMP pulp was subjected to hydrogen peroxide bleaching at two consistencies (10%, 25%) using either $Mg(OH)_2$ or NaOH as the alkali source. The bleaching performance and effluent characteristics, as well as pulp and paper properties were determined and compared.

EXPERIMENTAL

Materials

The chemimechanical pulp (CMP) sample (60% wt. hornbeam, 20% wt. beech, 20% wt. birch) via a sulfite process was obtained from the secondary refiner of a mill located in northern Iran (Mazandaran Wood and Paper Industries Co.). The Canadian standard freeness (CSF) of the pulp was 410 mL. The other properties of unbleached pulp were described in each section of Results and Discussion.

The pulp was stored in a cold room at 10% consistency prior to use. The analytical grades of diethylenetriaminepentaacetic (DTPA) sodium salt, sulfuric acid, NaOH (1M), and $Mg(OH)_2$ (1 M) were purchased from Merck, Co. Germany, while that of silicate was obtained from Carlo Erba Co. Italy. Sodium silicate is commonly added as a stabilizing and buffering agent in NaOH-based hydrogen peroxide bleaching (Zeinaly et al. 2009).

In this research, five repetitions were conducted for each experiment and the results within 95% confidence interval as well as the standard deviations were reported.

Hydrogen Peroxide Bleaching

Chelation has also been applied as a practical method for removing metal ions prior to peroxide bleaching. There have been different proposals for improving the efficiency of peroxide bleaching in the presence of chelating agents. These include making ring structures with metal ions, thus inhibiting their catalytic effect (Prasakis et al. 1996), buffering action (Fairbank et al. 1989), and interruption of free radical processing through the formation of a stable intermediate (Coldoette et al. 1989). Initially, the DTPA was applied at a charge of 0.2 % to the CMP pulp and the chelation was conducted at a 10% consistency and 70 ºC for 30 min prior to bleaching. Then, peroxide bleaching experiments were conducted on 10 g (od) pulp in plastic bags under conditions of 10% and 25% consistencies at 70 ºC for 150 min while kneading each for 5 min. The DTPA has been regarded as an effective chelation agent in $Mg(OH)_2$-based peroxide bleaching (Lachenal et al. 1979; He et al. 2004a,b, 2006). In one set of experiments, DTPA (0.1%) and $Mg(OH)_2$ were added to the pulp suspensions and then the pulp samples were placed into a water bath at 70 ºC for five min. Subsequently, hydrogen peroxide was added to the pulp sample (He et al. 2004b). However, it was reported that the DTPA chelation was not sufficiently effective in the NaOH-based peroxide bleaching of hardwood CMP (Yesuadian et al. 1997). In another set of experiments, sodium silicate was added to the NaOH-based peroxide bleaching in order to prevent the decomposition of hydrogen peroxide during bleaching (Fairbank et al. 1989). In fact, water, sodium silicate, sodium hydroxide, and hydrogen peroxide were mixed in a beaker and then added to the CMP pulp in NaOH-based peroxide bleaching. The conditions of NaOH-based peroxide bleaching were selected as applied in Mazandaran Wood and Industrial Paper Co. The other conditions of bleaching are listed in Table 1. For bleaching at high consistency (25%), the pulp suspension was thickened to about 25% consistency in a Buchner funnel with a 200-mesh Teflon screen. The filtrate was recycled once to go through the fiber mat to collect the fines. After the bleaching, filtrate was collected via vacuum-filtering of the pulp samples. Afterwards, the pulps were washed thoroughly with deionized distilled water and then pulps were kept in a cold room prior to testing.

Table 1. Chemicals (wt. %) Added to the NaOH- and $Mg(OH)_2$-based Hydrogen Peroxide Chemicals for Bleaching

Chemical, %	NaOH-based		$Mg(OH)_2$-based							
H_2O_2, %	2	3	2	3	2	3	2	3	2	3
NaOH, %	1.6	2.1	-	-	-	-	-	-	-	-
$Mg(OH)_2$, %	-	-	0.25	0.25	0.5	0.5	1	1	1.5	1.5
Na_2SiO_3, %	3	3	-	-	-	-	-	-	-	-
DTPA, %	-	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Pulp Selection

After the bleaching experiments, the CMP pulps that had a similar brightness, but which had been bleached via $Mg(OH)_2$-based and NaOH-based hydrogen peroxide at 25% consistency, were selected for further analysis. The effluent characteristics and papermaking properties of these pulps were determined and compared.

Pulp and Effluent Characterizations

Water Retention Value (WRV) of the selected CMP pulps was determined according to TAPPI UM 256 at 900g for 30 min using a centrifuge, Z206A, HERMLE, Germany. The COD of the bleaching effluent was determined based on the dichromate oxidation method according to the APHA standard method using a PALINTEST 8000 Photometer, PALINTEST, UK. The turbidity of the bleaching effluent was measured using a turbidity meter, IRTB100, EUTECH, Singapore.

Paper Making Properties

The handsheets were prepared from the selected CMP pulps according to TAPPI method T255. The brightness, and opacity were measured according to TAPPI method T452 using an ELREPHO 2000, Data Color, Switzerland. The tensile, tear, and burst indices were determined according to TAPPI methods T495, T414, and T403, respect-tively, using tensile, tear, and burst testers (Lorentzen & Wettre, Kista, Sweden). The bulk was determined according to TAPPI T500.

RESULTS AND DISCUSSION

Impact on Optical Properties

The brightness of unbleached industrially produced mixed hardwood CMP pulp was 52% ISO, which was similar to that (55.5-56.5 %ISO) of white spruce (Kouk et al. 1989), but higher than that (36.5 %ISO) of mixed hardwood (35.5% eucalyptus hybrid, 33% eucalyptus globulus and 30.5% acacia) (Yesuadian et al. 1997). Figure 1 shows the effect of $Mg(OH)_2$ on the brightness of the CMP pulp at 10% and 25% consistencies. The H_2O_2 charge was 2% (wt.) based on pulp in Fig. 1a, whereas it was 3% in Fig. 1b. As can be seen, by increasing the dosage of $Mg(OH)_2$ to 1.5%, the brightness of pulp was increased to 66 %ISO and 71 %ISO at 25% consistency via adding 2% and 3% H_2O_2, respectively.

However, the brightness ceiling of pulp was higher at 25% consistency than at 10% consistency at any dosage of $Mg(OH)_2$ applied, which implies that the impact of $Mg(OH)_2$ on brightness was significantly improved at the higher consistency. It was reported that the performance of bleaching could be improved by increasing the pulp consistency (Andreson and Amini 1996; He and Ni 2008). A higher consistency provides a higher relative concentration of bleaching chemicals in pulp suspensions and a greater direct contact of bleaching chemicals with the pulp (Anderson and Amini 1996; Bajpai 2005).

Included in Fig. 1 are the results of NaOH-based hydrogen peroxide bleaching of the CMP pulp at 10% and 25% consistency. Generally, the medium consistency (10%) $Mg(OH)_2$-based hydrogen peroxide bleaching produced pulp with a lower brightness than the NaOH-based peroxide bleaching. In one study on hardwood TMP, the pulp was bleached under the conditions of 10% consistency, 3% H_2O_2 at 70 ºC for 5 h. The beached TMP pulp had a brightness of 75.45 %ISO or 73.66 %ISO via adding 3% NaOH or $Mg(OH)_2$ to the hydrogen peroxide bleaching processes, respectively (He et al. 2006). The pulp bleached under the conditions of 2% H_2O_2, 25% consistency, and 1.5% $Mg(OH)_2$ had a similar brightness (66% ISO) with that bleached under the conditions of 2% H_2O_2, 10% consistency, and 1.6% NaOH. Furthermore, the pulp bleached under the conditions of 3% H_2O_2 charge, 25% consistency, and 1.5% $Mg(OH)_2$ had slightly higher brightness (71% ISO) than that bleached under the conditions of 3% H_2O_2, 25% consistency, and 2.1% NaOH (70.2 %ISO). This brightness (71% ISO) was higher than that reported (63.3 %ISO) in another study on a different mixed hardwood CMP (35.5% eucalyptus hybrid, 33% eucalyptus globulus and 30.5% acacia), which was conducted under the conditions of 3% H_2O_2, 1.44% NaOH, 1.5 % Na_2SiO_3, 0.03% $MgSO_4$, 20% consistency at 75 ºC for 120 min (Yesuadian et al. 1997).

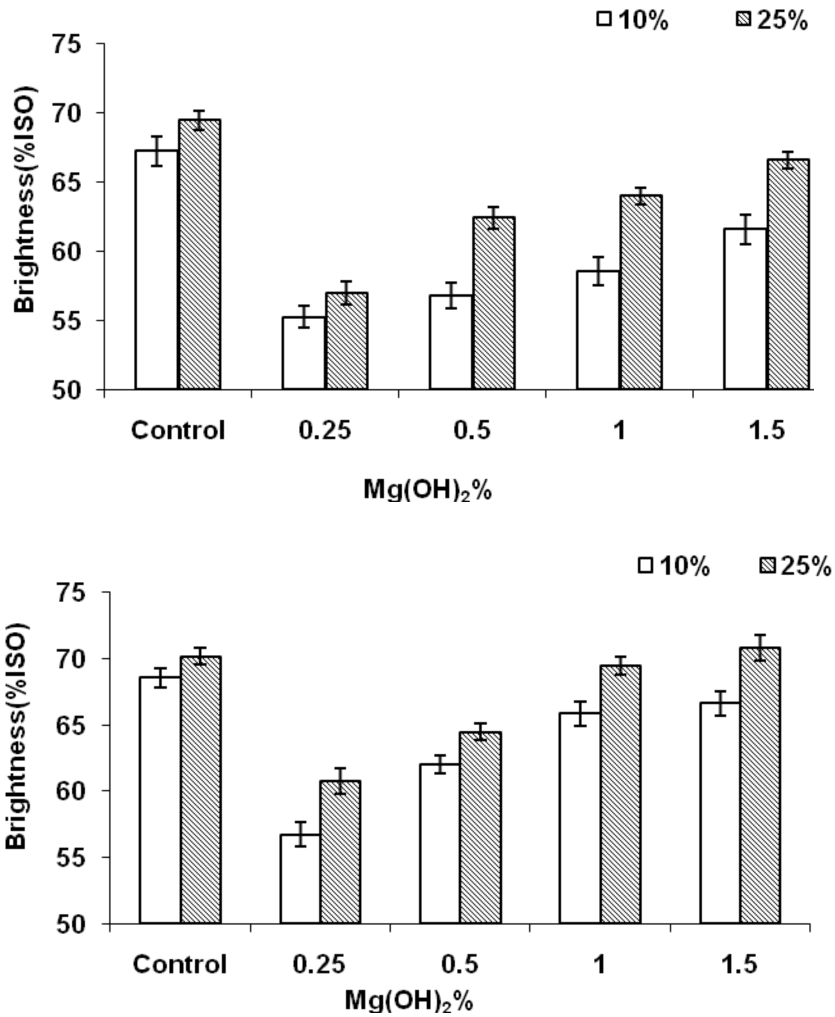


Fig. 1. Brightness of CMP pulp bleached via NaOH-based (control) and $Mg(OH)_2$-based processes at two consistencies (Top 2% H_2O_2, bottom 3% H_2O_2)

Yellowness Index

The yellowness index of pulp is an indication of the presence of chromophoric structures remaining in the pulp. The chromophoric structures could be lignin and/or other lignocellulosic materials of pulp that absorb light. As these materials are not totally removed from the pulp via a CMP process, it is important to evaluate how much the presence of these materials could affect the optical properties. In fact, the yellowness index is an indicator of the changes in these components. The yellowness index of unbleached pulp was 26.2. Figure 2 shows the effect of $Mg(OH)_2$ dosage on the yellowness index of pulp bleached via the $Mg(OH)_2$-based hydrogen peroxide process at 10% and 25% consistencies. Interestingly, by increasing the dosage of $Mg(OH)_2$ to 1.5%, the yellowness index of the pulp was reduced to 12 and 10.5 for 10% and 25% fiber consistencies at 2% H_2O_2 dosage (Fig. 2a), respectively, while it was reduced to 10 and 8.5 for 10% and 25% fiber consistencies at 3% H_2O_2 dosage (Fig. 2b). The decrease in the yellowness index is in agreement with brightness increase (Fig. 1), and implies that lower amounts of chromophoric structures (lignin or other compounds absorbing light) remained in the pulp after the bleaching.

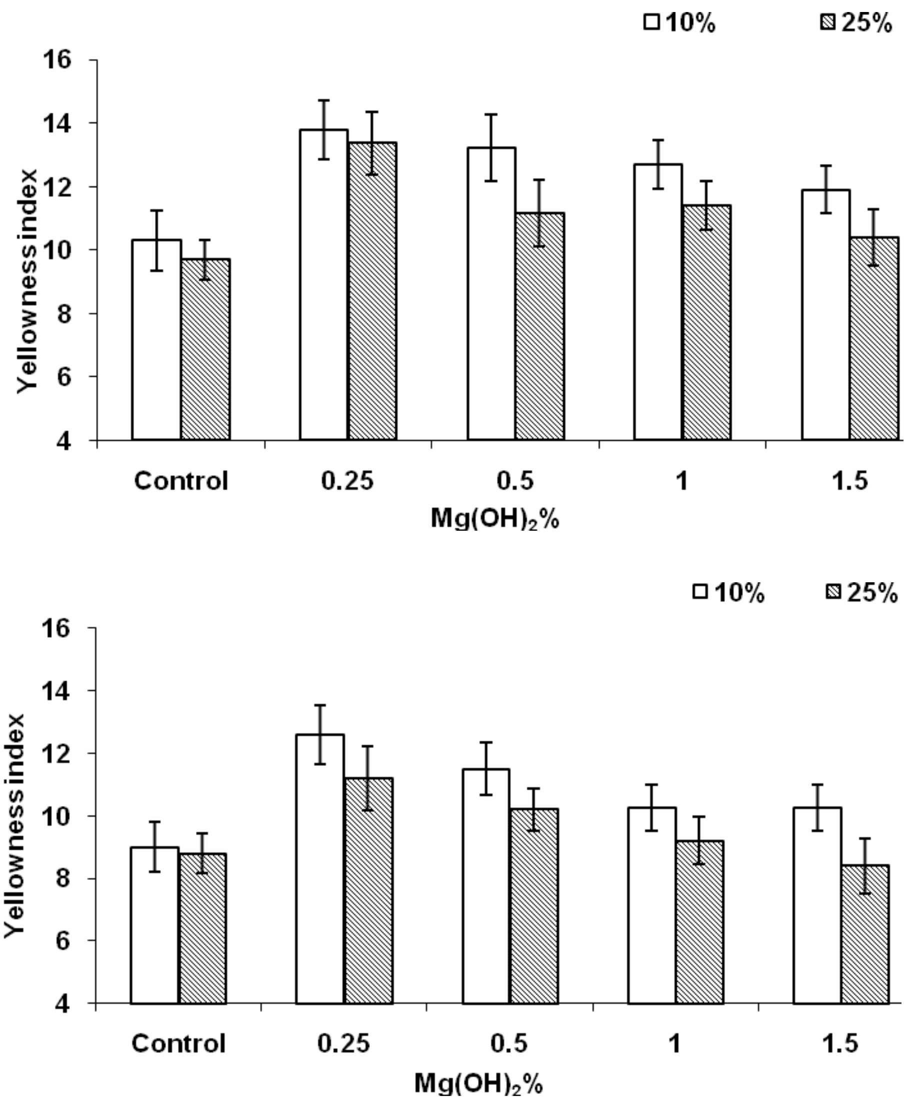
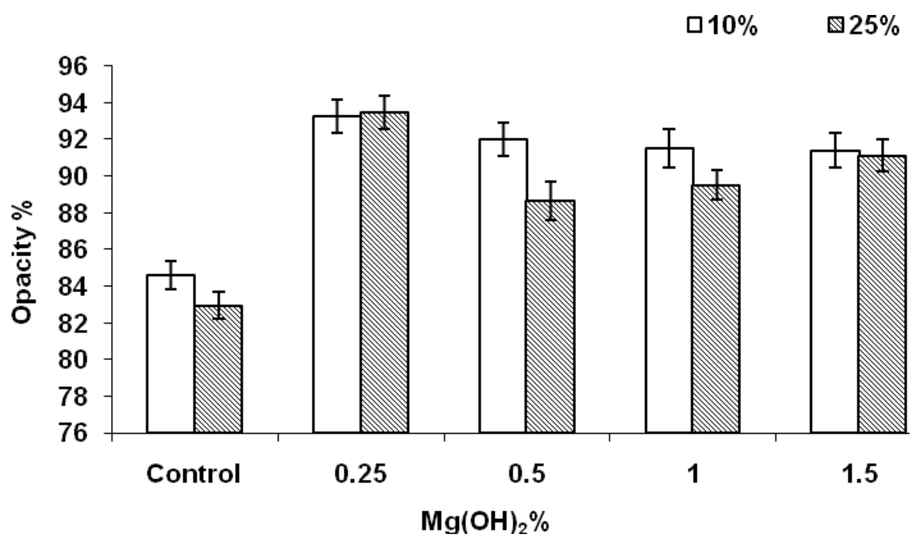


Fig. 2. Yellowness index of CMP pulp bleached via NaOH-based (control) and $Mg(OH)_2$-based processes at two consistencies (Top 2% H_2O_2, bottom 3% H_2O_2)

The yellowness indices of the CMP pulp bleached via the NaOH-based peroxide bleaching at 10% and 25% consistencies are also included in Fig. 2. Evidently, the yellowness indices were between 9 and 10 under different bleaching conditions. Compared with the $Mg(OH)_2$-based peroxide bleaching, the NaOH-based peroxide bleaching has more alkalinity, thus it generates more active anions, which can remove lignin and other chromophoric compounds. Therefore, a lower yellowness index is expected for the pulp produced via the NaOH-based peroxide bleaching. Interestingly, the results in Fig. 2 indicate that, by increasing the dosage of $Mg(OH)_2$ and particularly the fiber consistency in bleaching, the yellowness index of pulp could be reduced to even a lower degree than that of the NaOH-based peroxide bleaching.

The opacity of the papers made of unbleached CMP pulp was 92.5 %. Figure 3 shows the effect of $Mg(OH)_2$ on the opacity of the papers made of the bleached CMP pulp at 10% and 25% consistencies. The H_2O_2 dosage was 2% in Fig. 3a, whereas it was 3% in Fig. 3b. Generally, by increasing the dosage of $Mg(OH)_2$ to 1.5%, the opacity of the papers was decreased, and the decrease was more significant at 3% H_2O_2 addition than at 2%. However, the opacity was insignificantly affected by the consistency of pulp during the hydrogen peroxide bleaching process.



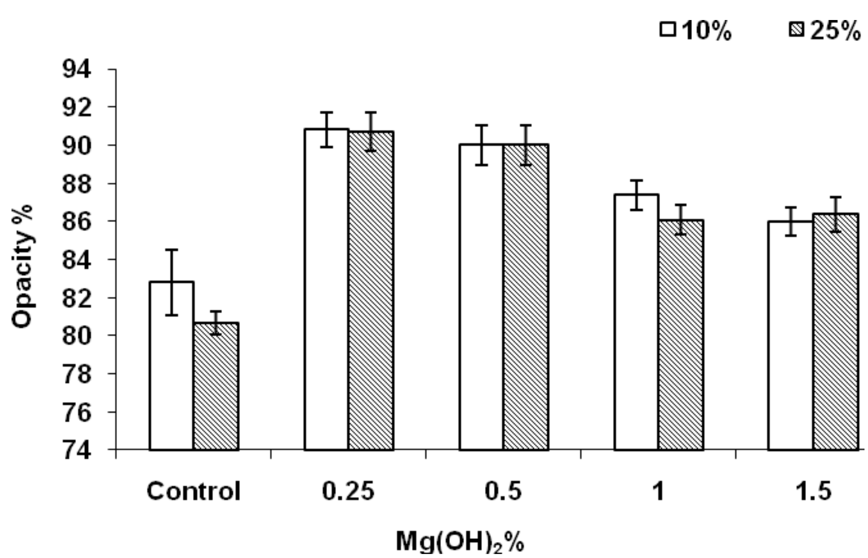


Fig. 3. Opacity of papers made of CMP pulp bleached via the NaOH-based (control) and the $Mg(OH)_2$-based processes at two consistencies. (Top 2% H_2O_2, bottom 3% H_2O_2)

The opacity of papers is affected by several factors including fiber flexibility, fiber morphology, and contact area of fibers in handsheets. As bleaching chemicals influence the fiber properties significantly, it is difficult to determine the reason for the limited changes in the opacity of papers via varying the $Mg(OH)_2$ dosage in the hydrogen peroxide bleaching.

The opacity of the papers made of the CMP pulp bleached via the NaOH-based hydrogen peroxide is also included in Fig. 3. Although the increase in the dosage of the $Mg(OH)_2$ reduced the opacity of papers, it was still higher than that of the NaOH-based peroxide bleaching at the maximum $Mg(OH)_2$ dosage (1.5%) applied, regardless of the fiber consistency. In the literature, a higher opacity was obtained for the papers made of the CMP pulp bleached via the $Mg(OH)_2$-based peroxide process than those made of the CMP pulp bleached via the NaOH-based peroxide bleaching at 10% consistency (He et al. 2006). The results also showed approximately 2% higher opacity at 10% consistency than at 25% consistency for the pulp bleached via the NaOH-based peroxide bleaching, regardless of the peroxide charge (Fig. 3).

As described earlier, the CMP pulp bleached under the conditions of 1.5% $Mg(OH)_2$, 3% H_2O_2 at 25% consistency had a similar brightness to, a lower yellowness index and a higher opacity than, those of the CMP pulp bleached under the conditions of 2.1% NaOH, 3% H_2O_2 at 25% consistency. Therefore, these two CMP pulp were selected for further analysis.

The bleaching yield of the $Mg(OH)_2$-based hydrogen peroxide process was 94.2%, while that of the NaOH-based hydrogen peroxide process was 90%. These results reveal that more lignocelluloses removal occurred during the NaOH-based process than during the $Mg(OH)_2$-based bleaching process (Johnson et al. 2002; He et al. 2004b). However, further analyses are necessary to determine the changes in the characteristics of lignocelluloses in bleaching. In the literature, by adding 2% of NaOH or $Mg(OH)_2$ in the peroxide bleaching of TMP at 11% consistency, a yield of 96.08% or 97.36% was obtained, respectively (He et al. 2004b). The WRV of the CMP pulp bleached via the $Mg(OH)_2$-based process was 2.1 g/g, while that of the CMP pulp bleached via the NaOH-based was 2.6 g/g. These results imply that the CMP pulp was more swollen via adding NaOH than adding $Mg(OH)_2$. In the literature, the adsorption of Mg ions on the fiber in the $Mg(OH)_2$-based peroxide bleaching was claimed as the reason for the decrease in the swelling ability of fibers (He et al. 2006).

Bleaching Effluent Characteristics

The effluent properties of the selected CMP pulp produced via the $Mg(OH)_2$- and NaOH-based hydrogen peroxide bleaching process are listed in Table 2. Evidently, approximately 33% and 20% of hydrogen peroxide was not consumed during the bleaching of $Mg(OH)_2$- and NaOH-based processes, respectively. The pH values were fairly constant during the $Mg(OH)_2$-based process, while initial and final pH were different in the NaOH-based process. The low solubility of $Mg(OH)_2$ allows a constant alkalinity to be maintained during the peroxide bleaching process (Johnson et al. 2002).

It is also evident that the COD and turbidity of the NaOH-based hydrogen peroxide bleaching process were significantly higher than those of the $Mg(OH)_2$-based process. This phenomenon was attributed to the higher alkalinity of NaOH, which probably hydrolyzed the long chain lignocellulosic materials from the fibers (He et al. 2005; Zeinaly et al. 2009).

Consequently, the residual hydrogen peroxide in the bleaching filtrates can be recycled to the system (Johnson et al. 2002). This is particularly interesting for the $Mg(OH)_2$-based process, as it contained a relatively high residual hydrogen peroxide and a low COD and turbidity levels, and constant pH. In other words, if recycled to the fresh bleaching chemicals, the filtrates of the $Mg(OH)_2$ process influences the characteristics of fresh bleaching chemicals to a less extent than those of the NaOH-based process do.

Table 2. Effluent Characteristics of NaOH- and $Mg(OH)_2$-based Bleaching Process for Selected CMP Pulps

Process type	NaOH-based process	$Mg(OH)_2$–based process
Residual H_2O_2 (g/L)*	0.27	0.44
Initial pH	11.6	8.8
Final pH	9.2	8.6
COD, Kg/t	20.1	9.7
Turbidity, NTU	28.1	11.6

* Initial H_2O_2 (g/L): 1.35

Mechanical Properties of Bleached Pulp

The properties of handsheets made of the selected CMP pulps bleached via the $Mg(OH)_2$- and NaOH-based processes are listed in Table 3. It is evident that the tensile, burst, and tear indices of the papers made of the CMP pulp bleached via the NaOH-based process were higher than those of papers made of the CMP pulp bleached via the $Mg(OH)_2$-based process. In the literature, the strength properties of hardwood CMP pulp produced via the NaOH-based hydrogen peroxide was claimed to be generally higher than those of the pulp produced via the $Mg(OH)_2$-based hydrogen peroxide process under various conditions at 10% consistency (He et al. 2006). Our results confirm the fact that the hardwood CMP pulp produced via the NaOH-based process was generally stronger than that produced via the $Mg(OH)_2$-based process, regardless of the consistency of pulp in the hydrogen peroxide bleaching process. The lower strength of bleached pulp via $Mg(OH)_2$-based than NaOH-based peroxide bleaching was due to the less fiber swelling and interfiber bonding of $Mg(OH)_2$-based bleached pulp: 1) As described earlier, more lignocelluloses were removed in the NaOH-based bleaching process than in $Mg(OH)_2$-based bleaching process. Therefore, the NaOH-based pulp bleaching perhaps resulted in more flexible that could develop hydrogen bonding more extensively, 2) as described above, magnesium ions in $Mg(OH)_2$-based bleaching attract and bind with carboxylic groups of fiber surface, thus decrease the fiber swelling and fiber bonding (He et al. 2004a,2006; Zhang et al. 2004).

Interestingly, the bulk of the CMP pulp bleached via the $Mg(OH)_2$-based process was higher than that of the pulp bleached via the Na(OH)-based process. In one study on hardwood TMP, the pulp was bleached under the conditions of 10% consistency, 10% H_2O_2 at 70 ºC for 5 h. The results showed a bulk of 3.5 cm^3/g or 4 cm^3/g via adding 4% NaOH or $Mg(OH)_2$ to the hydrogen peroxide bleaching process, respectively (He et al. 2006). As the bulk is a crucial property of the CMP pulp, the $Mg(OH)_2$-based process showed promising results.

Table 3. Properties of Papers made of the Selected CMP Pulps Bleached via NaOH and $Mg(OH)_2$-based Hydrogen Peroxide Processes

Parameter	NaOH	$Mg(OH)_2$
Tensile index, N.m/g	24.4	18.3
Tear index, $N.m^2/Kg$	2.21	1.74
Burst index, $kPa.m^2/g$	0.7	0.54
Bulk, cm^3/g	2.2	3.0

All in all, $Mg(OH)_2$-based peroxide bleaching at a high consistency provided higher yield and opacity than, a similar brightness to, and a lower strength and load of effluent than the NaOH-based peroxide bleaching under the conditions studied. As the CMP pulp is usually used for contributing bulk and opacity to end-use paper products, the $Mg(OH)_2$-based process produced more promising results than the NaOH-based process did. Furthermore, as explained above, the magnesium ions can be associated with the carboxylic group of fibers in the bleaching, and hence prevent hydrogen bonding development that leads to a lower paper strength. It was suggested that acid washing of the $Mg(OH)_2$-based bleached pulp can help remove the hydrophobic materials and the magnesium ion from the fiber surface and improve the paper strength (Kong et al. 2009).

CONCLUSIONS

- At 10% consistency and 2% or 3% H_2O_2 charge, the $Mg(OH)_2$-based hydrogen peroxide process produced pulp with a lower brightness, and a higher yellowness index and opacity, than the NaOH-based process did.
- At 25% consistency and 3% H_2O_2 charge, the brightness of pulp bleached via the $Mg(OH)_2$- and NaOH-based processes, at 70 ºC for 150 min, were similar. Under these conditions, the yellowness index of pulp bleached via the $Mg(OH)_2$-based process was lower than that of the NaOH-based process.
- At all consistencies and $Mg(OH)_2$ levels, the $Mg(OH)_2$-based process had a greater opacity than the NaOH-based process did.
- Under the selected (optimized) conditions stated above, the residual H_2O_2 in the bleaching effluent of the $Mg(OH)_2$-based process was higher, while the COD load and turbidity of this process were lower, than those of the NaOH-based process. Therefore, there is a greater potential for recycling the effluent of the $Mg(OH)_2$-based process than that of the NaOH-based process.
- Under the optimized conditions, the $Mg(OH)_2$-based process had a higher yield than the NaOH-based process did. However, the strength properties and WRV of the CMP pulp bleached via the $Mg(OH)_2$-based process were lower, while the bulk of this CMP pulp was higher, than those of the CMP pulp bleached via the NaOH-based process.

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