HYDROGEN PEROXIDE BLEACHING OF CMP PULP USING MAGNESIUM HYDROXIDE

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Conventional bleaching of hardwood CMP pulp with magnesium hydroxide ($Mg(OH)_2$) show significant benefits over bleaching with sodium hydroxide (NaOH) under various conditions. Magnesium hydroxide bleaching generate higher optical properties, higher pulp yield and lower effluent COD at the same chemical charge, but the physical properties were found to be similar for both processes. The initial freeness of the bleached pulps and refining value to reach a target freeness (about 350 ml. CSF) were more for the $Mg(OH)_2$-based process. The residual peroxide of filtrate from the $Mg(OH)_2$-based process was very high as compared to conventional bleaching.

Key words: Hardwood; Peroxide Bleaching; Mg(OH)2-based process; Freeness; COD

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INTRODUCTION

Mechanical pulps comprise approximately 25% of the world's wood pulp production. This volume is expected to grow considerably for two reasons: growing global demand for paper and a sharp increase in coated groundwood paper applications (Ionides and Smith 2002). Mechanical pulping is an attractive option for meeting increased fiber demand efficiently with minimal environmental impact (Ford and Sharman 1995). However, the greatest challenge to expanding mechanical pulping is finding ways to dramatically decrease electrical energy consumption, increase strength properties, and reduce color reversion, which are classical disadvantages of mechanical pulp that impact production cost and limit its inclusion in wood-free furnishes (Hoglund 1997).

High yield pulps are bleached using common agents like sodium dithionite in reductive bleaching and hydrogen peroxide in oxidative bleaching. Potentially, $Mg(OH)_2$ could find a place in the mechanical pulping industry. Peroxide bleaching was chosen as the subject of this work because it is performed under alkaline conditions, and is thus compatible with the alkaline nature of magnesium hydroxide. To achieve maximum brightness with hydrogen peroxide in chemi-mechanical pulp bleaching, the following parameters need to be taken into consideration: consistency, temperature and retention time, hydrogen peroxide and alkali concentrations, as well as addition of sodium silicate. The peroxide bleaching with $Mg(OH)_2$ of high yield pulps has recently been developed in the pulp and paper industry (Li et al. 2005). The associated benefits include decreased bleaching cost, decreased chemical oxygen demand COD, less anionic trash, and also

improved optical and physical strength properties of bleached pulps (Li et al. 2005; Maughan et al. 1992; Nystrom et al. 1993; Suess et al. 2001; Vincent et al. 1997).

The milder alkalinity of the $Mg(OH)_2$ system is believed to be the cause of the lower COD formation. The high COD values of NaOH were attributed to its strong alkalinity, with a high pH that hydrolyzes the long chain molecules in the pulp to smaller ones. Another advantage of the Mg alkalis is their low solubility, which result in a lower pH (Nystrom et al. 1993). However, it is not clear how the dissolution of organic substances (carbohydrates, lignin extractives, and low-molecular-weight materials such as acetic acid and methanol) are affected when $Mg(OH)_2$ is used as the alkali source instead of NaOH (He et al. 2004a).

The objective of this study was to investigate the use of $Mg(OH)_2$ as a replacement for NaOH as an alkali source in peroxide bleaching of chemi-mechanical pulp. The work of Vincent et al. (1997) has shown that magnesium oxide (MgO) can be used economically in bleaching chemi-mechanical pulp produced using the cold soda process. It needs to be shown that $Mg(OH)_2$ has the same potential. Hydrogen peroxide bleaching experiments were performed on hardwood chemimechanical pulp (CMP, produced by the sulfite process) using conventional conditions, and then magnesium hydroxide was substituted for caustic in the bleaching process.

EXPERIMENTAL

Pre-refined hardwood mixture CMP pulp (by the sulfite process) was obtained from a mill in the north of Iran (Mazandaran Wood and Paper Industries Co.). The species used in producing the CMP pulp were hornbeam, beech, and birch with mixture percentages of 60, 20, and 20 respectively. The brightness of the brown stock was 37.5% ISO, and the pulp sample had a consistency of 10% and a Canadian standard freeness of 745 ml. All chemicals used for bleaching were purchased from Merck. Chelation of pulp was performed at 3% pulp consistency, pH 6.0, and 70°C for 30 minutes, with 0.3% DTPA (based on oven dry pulp). Then the pulp suspension was thickened to about 25% consistency in a Büchner funnel with a 200-mesh Teflon screen. The filtrate was recycled once to go through the fiber mat to collect the fines.

Peroxide bleaching experiments were conducted in polyethylene bags using the following conditions: 2-4% H_2O_2, 1.5-3.0% NaOH or/and 1.2-2.4% $Mg(OH)_2$, 3% sodium silicate (water glass), 0.2% Epsom salt ($MgSO_4.7H_2O$), 0.1% DTPA, 10% pulp consistency, 70°C, and 120 minutes (Table 1). (The content of all chemicals are expressed based on oven dried pulp).

Table 1. Peroxide Bleaching Conditions

Process type	NaOH-based process			$Mg(OH)_2$-based process		
Treatment code	A	B	C	D	E	F
H_2O_2 (%)	2	3	4	2	3	4
NaOH (%)	1.5	2.25	3		0	
$Mg(OH)_2$ (%)		0		1.2	1.8	2.4

The chemicals were mixed in a beaker in the following order: water, sodium silicate, sodium hydroxide or magnesium hydroxide, Epsom salt, DTPA, and then hydrogen peroxide. The prepared bleach liquor was then added to the pulp, which was heated to the reaction temperature, and good mixing was provided by kneading. The polyethylene bag was sealed and placed into a water bath for the desired retention time at the set temperature. At the completion of the bleaching time, the pulp sample was cooled down with cold running water to room temperature and diluted to 1-2% suspension with deionized water. The well-mixed pulp suspension was then filtered in a Büchner funnel with a 200-mesh Teflon screen. The filtrate was recycled once to go through the fiber mat to collect the fines. The resultant filtrate was further filtered with a Whatman medium-fast filter paper to remove the residual fines, and then used for determining the end pH, conductivity, residual peroxide, and COD according to the PAPTAC standard methods (J.16P and H.3). Bleached pulps were refined to 350 ml. Canadian standard freeness (CSF) using a Labtech PFI machine according to the TAPPI standard methods (T248 sp-00). The freeness (CSF) was determined according to the TAPPI methods (T227 om-99). Handsheets were prepared and optical and physical properties were measured according to the following TAPPI methods: Handsheet making: T205 sp-95 and T220 sp-96, Brightness: T452 om-98, Opacity: T452 om-91, Yellowness: T524 om-94, Tensile strength: T495 om-96, Burst strength: T403 om-97, Tear strength: T414 om-98, Bulk: T500 cm-98.

RESULTS AND DISCUSSION

The alkali is needed to activate hydrogen peroxide by forming the reactive hydroperoxide anion species. On the other hand, too high concentration of the hydroperoxide anions causes decomposition of hydrogen peroxide, especially at elevated temperatures. Therefore it is common practice to add sodium silicate as a stabilizing and buffering agent. As shown in Table 2, the Brightness values of the $Mg(OH)_2$-based process were more than those of the NaOH-based process at the same H_2O_2 charge. This outcome is consistent with results of the previous studies (Johnson et al. 2002; Vincent et al. 1997). The ratios of alkali to peroxide charge for NaOH and $Mg(OH)_2$ were 0.75 and 0.6 respectively. As shown in Table 2, no significant difference in opacity was observed between the two bleaching processes. The yellowness values of bleached pulps by $Mg(OH)_2$-based process were less than those of the NaOH-based process at the same H_2O_2 charge.

Table 2. Optical Properties of Bleached Pulps

Process type	NaOH-based process			$Mg(OH)_2$-based process			LSD*
	A	B	C	D	E	F	
Brightness (%)	72.6^{e}	74.2^{c}	76.0^{b}	73.2^{d}	75.9^{b}	77.8^{a}	0.61
Opacity (%)	88.2^{a}	87.5^{b}	86.7^{c}	88.1^{a}	87.3^{b}	86.5^{c}	0.42
Yellowness index	6.10^{a}	5.79^{b}	5.24^{d}	5.68^{c}	4.71^{e}	4.06^{f}	0.07

* Least Significant Difference

Means with the same letter are not significantly different (P>0.01).

These results can be explained by the milder alkalinity of the $Mg(OH)_2$-based process and thereby decreased alkali darkening (He et al. 2004b). The low solubility of $Mg(OH)_2$ allows it to provide a constant alkalinity at various alkali charges, and also as shown in Fig. 1, pH values were approximately constant during bleaching of the $Mg(OH)_2$-based process, while initial and final pH had a significant difference in NaOH-based process.

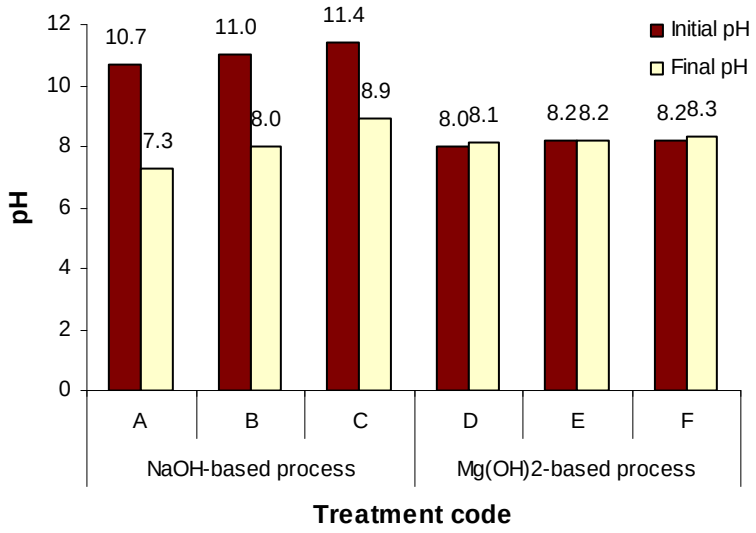

Figure 1. Initial and final pH in the $Mg(OH)_2$ and NaOH processes

From Table 3, both processes had similar mechanical properties. Also, the mechanical properties increased with increasing chemical charges. Similar results have been obtained by others (Johnson et al. 2002; Li et al. 2005).

Table 3. Mechanical Properties of Unrefined Pulps

Process type	NaOH-based process			$Mg(OH)_2$-based process			LSD
	A	B	C	D	E	F	
Tensile index (Nm/g)	31.1^{c}	36.5^{b}	39.5^{a}	30.9^{c}	35.8^{b}	39.2^{a}	0.81
Burst index (kN/g)	2.21^{cd}	2.24^{ab}	2.26^{a}	2.19^{d}	2.22^{cb}	2.26^{a}	0.02
Tear index (mNm^2/g)	6.67^{c}	6.70^{b}	6.72^{ab}	6.66^{c}	6.72^{b}	6.74^{a}	0.02
Bulk (cm^3/g)	2.42^{a}	2.39^{b}	2.35^{c}	2.43^{a}	2.40^{b}	2.36^{c}	0.02

Means with the same letter were not significantly different (P>0.01).

As shown in Table 4, the $Mg(OH)_2$-based and the NaOH-based bleaching process yielded bleached refined pulps that were similar in tensile and burst strength. Tear strengths of the $Mg(OH)_2$-bleached pulps were more than those of NaOH-bleached pulps. Little bleaching damage of the $Mg(OH)_2$-based process and also more beating of $Mg(OH)_2$-bleached pulp lead to increased tear strength (Walker 2006). The mechanical properties increased while the bulk values of handsheets decreased with the chemical charges (Table 4), but these values were similar for both processes, as it was reported earlier (Johnson et al. 2002).

Table 4. Mechanical Properties of Refined Pulps at 350 mL Freeness

Process type	NaOH-based process			$Mg(OH)_2$-based process			LSD
	A	B	C	D	E	F	
Tensile index (Nm/g)	63.2^{d}	64.5^{bc}	67.1^{a}	63.9^{cd}	64.6^{b}	66.8^{a}	0.72
Burst index (kN/g)	4.69^{c}	4.81^{b}	5.02^{a}	4.72^{c}	4.84^{b}	4.98^{a}	0.06
Tear index (mNm^2/g)	7.65^{e}	7.80^{d}	7.78^{d}	7.91^{c}	7.98^{b}	8.02^{a}	0.03
Bulk (cm^3/g)	2.19^{a}	2.11^{b}	2.05^{c}	2.21^{a}	2.11^{b}	2.06^{c}	0.02

Means with the same letter were not significantly different (P>0.01).

Figures 2 and 3 indicate that the initial freeness of bleached pulps and also refining values to reach the target freeness (350 ml.) decreased with increasing chemical charges for both bleaching processes. These results can be explained by the increased removal of hydrophobic compounds such as lignin and formation of hydrophilic functional groups from decreasing DP of macro molecules and also unbraiding the structure of the fiber, at high chemical charges (Nystrom et al. 1993; Pan and Sano 1999).

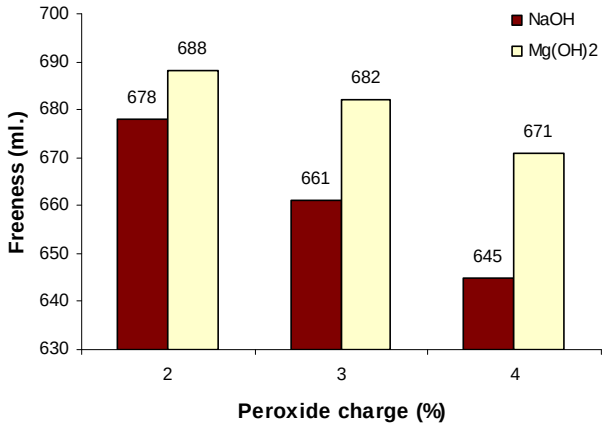

Figure 2. Initial freeness of the bleached pulp from $Mg(OH)_2$ and NaOH processes at the different chemical charges

Conventional bleached pulps had less initial freeness than those of $Mg(OH)_2$-based process also (Fig. 2). Moreover, refining values of conventional bleached pulps to reach the target freeness were lower than those of $Mg(OH)_2$-based process (Fig. 3). These results can be explained by the stronger reaction conditions of the NaOH-based process and so more production of hydrophilic functional groups in this process (Leatham and Myers 1990; Nystrom et al. 1993; Pan and Sano 1999; Copur 2007).

Fig. 4 shows the yield of bleached pulp at various bleaching conditions. Evidently, the bleaching yield from the $Mg(OH)_2$ process was higher than that from the NaOH process. The difference increased significatly as the chemical charges increased, because the bleaching conditions were more severe for the NaOH process. For example, at 4% peroxide charge, the bleaching yield was 97.18% for the $Mg(OH)_2$ process, compared to 95.54% for the NaOH process. The yield gain from the $Mg(OH)_2$ process represents a significant economic benefit to pulp mills that adopt this process. Similar results have been obtained by others (Dietz et al. 2008; He and Ni 2007; He et al., 2004a; Johnson et al. 2002).

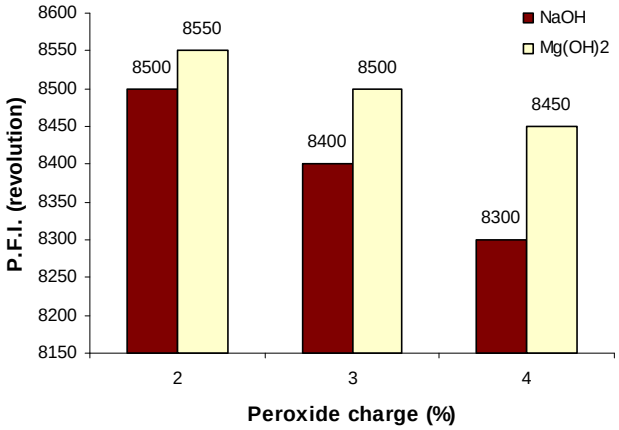

Figure 3. Refining value of the bleached pulp from $Mg(OH)_2$ and NaOH processes at the different chemical charges

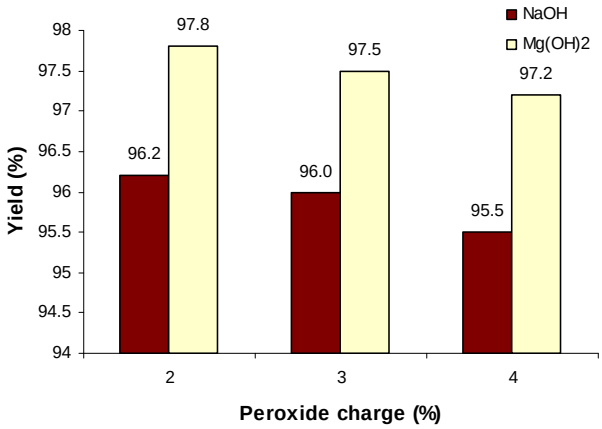

Figure 4. Pulp yield of the $Mg(OH)_2$ and NaOH processes at the different chemical charges

The COD load of the filtrate from $Mg(OH)_2$ bleaching was 37-55% lower than that of the filtrate from the NaOH process, as shown in Table 5. Similar results have been obtained by others (Li et al. 2005; Maughan et al. 1992; Nystrom et al. 1993; Suess et al. 2001; Vincent et al. 1997). COD may come from dissolved carbohydrates, lignin, and other organic substances in the bleaching filtrate (He et al. 2004a). The decrease in COD indicates preservation of pulp yield and lowering of effluent clean-up requirements (Johnson et al. 2002). With the significant decrease in COD formation, the costs associated with effluent treatment would be less significantly in the $Mg(OH)_2$ process.

Table 5. Properties of Bleaching Effluent

Process type	NaOH-based process			$Mg(OH)_2$-based process			LSD
	A	B	C	D	E	F	
Residual H_2O_2 (g/L)*	0.31[e]	0.47[d]	0.60[c]	0.48[d]	0.68[b]	0.88[a]	0.03
COD (kg/t)	43.5[c]	54.3[b]	69.9[a]	27.3[f]	29.6[e]	31.8[d]	1.63
Conductivity (ms/cm)	0.74[c]	0.98[b]	1.51[a]	0.36[e]	0.43[d]	0.47[d]	0.05

*Initial peroxide (g/L): A,D: 2.22; B,E: 3.33; C,F: 4.44

Means with the same letter were not significantly different (P>0.01).

This prediction was confirmed by the results obtained at a paper mill in Eastern Canada, which realized a 25-40% reduction in effluent treatment cost after implementing the $Mg(OH)_2$ peroxide bleaching process (He et al. 2004a). The conductivity values were also much less for the $Mg(OH)_2$ system (Table 5), and remained so at higher levels of $Mg(OH)_2$. Lowering conductivity should lower ionic trash to the paper machines, and reduce the need for retention chemicals. The residual peroxide level in $Mg(OH)_2$-based process is very high as compared to NaOH bleaching. There is the potential to recycle the peroxide in the post-bleaching filtrate back into the bleaching liquor (Johnson et al. 2002), therefore, the total peroxide consumption in the $Mg(OH)_2$-based process is less than that of the NaOH-based process.

CONCLUSIONS

Compared to the NaOH-peroxide bleaching process, the $Mg(OH)_2$-peroxide bleaching process produces bleached CMP pulps with a higher yield, better optical properties, and similar mechanical properties. However, the tear strength of refined pulp samples at 350 ml. freeness, is higher for the $Mg(OH)_2$-based process. The refining value to reach 350 ml. freeness of NaOH-based process pulp samples is lower than $Mg(OH)_2$-based process pulps. Also the initial freeness of NaOH-bleached pulps is less than that of $Mg(OH)_2$-bleached pulps. The greatest advantage of magnesium hydroxide over sodium hydroxide is the much lower chemical oxygen demand, which means higher yield at the same time and, in case of hardwood pulp bleaching, an increased bulk as well.

At the different chemical charges of the $Mg(OH)_2$-based process, the residual peroxide is considerably greater than for the NaOH-based process, indicating that the $Mg(OH)_2$ system has fewer peroxide decomposition reactions. By releasing alkali more slowly due to its low solubility, $Mg(OH)_2$ avoids some of the hydroperoxide ion decomposition reactions.

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Article submitted: June 23, 2009; Peer review completed: July 30, 2009; Revised version received and approved: Sept. 2, 2009; Published: Sept. 6, 2009.