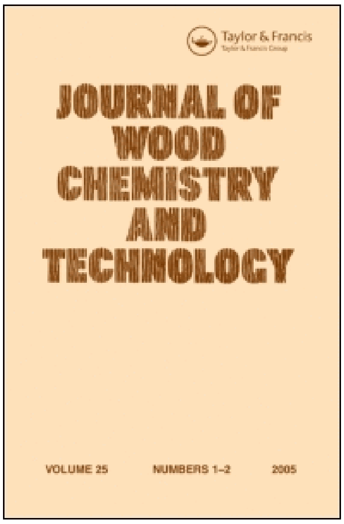

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Fangong Kong[a,b]; Yonghao Ni[a]; Zhibin He[a]
[a] Limerick Pulp and Paper Centre, University of New Brunswick, Fredericton, New Brunswick, Canada
[b] Key Laboratory of Pulp and Paper Engineering of Education Ministry of China, Shandong Institute of Light Industry, Jinan, China

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A Partial Magnesium Hydroxide Substitution for Sodium Hydroxide in Peroxide Bleaching of an Aspen CTMP

Fangong Kong,[1,2] Yonghao Ni,[1] and Zhibin He[1]
[1]Limerick Pulp and Paper Centre, University of New Brunswick, Fredericton, New Brunswick, Canada
[2]Key Laboratory of Pulp and Paper Engineering of Education Ministry of China, Shandong Institute of Light Industry, Jinan, China

Abstract: A partial substitution of sodium hydroxide (NaOH) by magnesium hydroxide ($Mg(OH)_2$) as the alkali source was studied in peroxide bleaching of an aspen chemi-thermomechanical pulp (CTMP). The effects on pulp properties, including pulp strength, optical property and carboxylic groups content, and process characteristics, such as oxalate and anionic trash formation, were studied. The X–ray photoelectron spectroscopy (XPS) technique was used to determine the lignin and extractives concentrations on the fiber surface. With the increased $Mg(OH)_2$ substitution ratio, the peroxide bleaching process gave a higher pulp yield and peroxide bleaching efficiency, produced pulps with higher light scattering coefficient and bulk, while the total oxalate, anionic trash, and chemical oxygen demand load (COD) were less. The total carboxylic groups content and the surface charge of pulp fibers were decreased. The underlying mechanism responsible for the decreased strength properties, when the $Mg(OH)_2$ substitution ratio was increased, is discussed.

Keywords: Anionic trash, aspen CTMP, carboxyl groups, COD, magnesium hydroxide, oxalate, peroxide bleaching, pulp strength, XPS

INTRODUCTION

A number of studies have shown that magnesium hydroxide ($Mg(OH)_2$) is a promising weak alkali to substitute for sodium hydroxide (NaOH).[1–7] The literature results supported the conclusion that a total $Mg(OH)_2$ substitution for NaOH can result in many beneficial effects, such as less anionic trash formation, lower chemical oxygen demand load (COD) in the effluent and

Address correspondence to Yonghao Ni, Limerick Pulp and Paper Centre, University of New Brunswick, Fredericton, New Brunswick E3B 6C2, Canada. E-mail: yonghao@unb.ca

better scattering coefficient and opacity of the bleached pulp and decreased oxalate-related scaling.[1−13] Nyström et al.[5]reported that using $Mg(OH)_2$, instead of NaOH, as the alkali source in peroxide bleaching of spruce SGW gave a lower tensile strength and higher brightness. Zhang et al.[3] found that, for a maple chemi-thermomechanical pulp (CTMP), the $Mg(OH)_2$-based peroxide bleaching gave lower brightness and tensile but higher bulk, compared with the NaOH-based peroxide bleaching. It was shown[14] that there always exists a difference in pulp strength between the $Mg(OH)_2$– and NaOH-based bleaching processes regardless of the wood species, pulp freeness and pulping methods. A partial replacement of NaOH with $Mg(OH)_2$ is effective in decreasing the amount of the precipitated calcium oxalate during peroxide bleaching.[15]

Recently, there is a strong interest from the pulp and paper industry for a partial substitution of NaOH by $Mg(OH)_2$ as the alkali source in peroxide bleaching of mechanical pulps. A systematic study regarding the use of both $Mg(OH)_2$ and NaOH as the alkali source, particularly for aspen CTMP, on the pulp properties and process characteristics, is still lacking. The objective of this study is to determine how the pulp properties, including the fiber surface properties, and process characteristics, such as anionic trash and oxalate formation, were affected for an aspen CTMP when NaOH was partially replaced by $Mg(OH)_2$ as the alkali source in peroxide bleaching under various $Mg(OH)_2$ substitutions.

EXPERIMENTAL

Material

An aspen CTMP was used for the bleaching experiments, and its properties were 450 ml CSF freeness, 54.9% ISO, and 0.75 km tensile. The pulp sample was stored in a cold room until use. Chemicals were reagent grades purchased from Aldrich, St. Louis, MO, USA, except magnesium hydroxide (67% slurry), which was obtained from Martin Marietta Magnesia Specialties, Baltimore, MD, USA.

Chelation

The chelation of pulp was performed at a 3% pulp consistency, pH 5, 70°C, 30min, and 0.2% DTPA. The pulp suspension was thickened to about 25% consistency in a Buchner funnel with a 200-mesh screen. The filtrate was recycled once to go through the fiber mat to collect the fines.

Peroxide Bleaching

The peroxide bleaching experiments were conducted in plastic bags using the following conditions: 5.5% H_2O_2, 4.5% total alkali, 2.5% silicate (water glass), 21% pulp consistency, 78°C and 90 min. The chemicals were mixed in a beaker by the following order: water, sodium silicate, sodium hydroxide or magnesium hydroxide, and then hydrogen peroxide. The prepared bleach liquor was then added to the pulp, which was pre-heated to 78°C, and good mixing was provided by kneading. The plastic bag was sealed and placed into a water bath for the desired retention time.

At the completion of the bleaching time, the pulp sample was immediately cooled to the room temperature by running water. Part of pulp slurry was taken for the total oxalate and anionic trash analyses. The residual pulp slurry was diluted to a 3% pulp suspension with deionized water and then filtered by a Buchner funnel with a 200-mesh screen. The filtrate was recycled once to go through the fiber mat to collect the fines. The resultant filtrate was used for determining end pH, residual peroxide, COD, and dissolved lignin. Another part of well-washed pulp was taken for total carboxylic group and surface charge analyses. Finally, some well-washed pulp cake (about 25% consistency) was dispersed into a 2% pulp suspension with deionized water, and its pH adjusted to 5.0 with sulfuric acid, and then handsheets were prepared according to the TAPPI methods.

Analyses Methods

The total oxalate analysis was carried out according to a procedure established earlier.[16] At the end of peroxide bleaching, pulp slurry (~1 g o.d. pulp) was diluted to a 1% pulp consistency with deionized water and then mixed with 5 g of ion-exchange resin (Amberjet 1200(H+), 60% moisture content, Aldrich. Oakville, ON, Canada) and stirred for 60 min at 60 C.[17] The mixture was then cooled to a room temperature and filtered through a 0.1 um membrane filter. The filtrate was then diluted and analyzed by ion chromatography using the conditions shown in Table 1.

Table 1. Conditions of ion chromatography for total oxalate analysis

System	DIONEX AL-450
Sample loop column	10 ul
Guard column	IonPac AS4A-SC 4 mm Guard column
Analytical column	IonPac AS4A-SC 4 mm analytical column
Eluent	3.0mmol/L Na_2CO_3/2.4 mmol/L $NaHCO_3$
Eluent flow rate	3.0 mL/min
Suppressor	Anion MicroMembrane Suppressor, AMMS-II
Regenerant	12.5 mmol/L H_2SO_4
Regenerant flow rate	4–5 mL/min
Background conductivity	15–20 us

The anionic trash measurement was done using a PCD-02 Müteck particle charge analyzer at two pH levels (i.e., pH 4.5 and pH 7.0). The filtrate sample was adjusted to desired pH and then tested for the cationic demand.[12]

For the lignin determination, the sample (pH adjusted to 6.8 ± 0.1 by using diluted HCl or NaOH solution) was filtered through a 0.22 μm membrane filter and tested for UV absorbance at 280 nm on a Spectronic 1001 Plus spectrophotometer (Milton Roy). The lignin content was calculated using an absorptivity of 20.0 L/g/cm.[18] The residual peroxide and COD were determined according to the Tappi standard methods.

The water retention value (WRV) was measured according to a centrifuge method.[19] The total carboxylic group content was determined using the conductimetric titration method.[20] The surface charge of pulp fibers was measured by following a modified polyelectrolytic titration method.[21,22]

The acetone extraction of bleached pulp was carried out in a Soxhlet extractor with acetone/water (90:10, v/v) for 3 hours. The extracted pulp was washed with deionized water thoroughly before making handsheets.

The XPS analysis of pulp sheet samples was conducted by the Surface Interface Ontario, using a Leybold Max 200 X-ray photoelectron spectrometer with a monochromated A1 Kα X-ray source. The photoelectron collection was at 90 degrees in relation to the sample surface.

RESULTS AND DISCUSSION

Pulp Properties

Table 2 shows the bleaching results. With the increased $Mg(OH)_2$ substitution ratio, the end pH of peroxide bleaching decreased, while the residual H_2O_2

Table 2. Peroxide bleaching results of partial $Mg(OH)_2$ substitution for NaOH as alkali source

Mg $(OH)_2$ Substitution ratio (%)	0	25	40	60	75
End pH	10.18	9.36	9.09	9.00	8.88
H_2O_2 comsumption (%)	4.30	4.24	4.10	3.93	3.81
Res. H_2O_2 (%)	1.20	1.26	1.40	1.57	1.69
Brightness (% ISO)	84.2	84.0	84.1	83.9	83.9
Light-scatt. (m^2/kg)	37.03	44.40	44.63	47.43	47.41
Pulp yield (%)	95.49	95.92	96.23	96.72	97.01
Bulk (cm^3/g)	1.83	2.18	2.28	2.48	2.62
Tensile (km)	3.27	2.28	2.00	1.56	1.45
Tear index (mN · m^2/g)	4.65	3.30	2.96	2.54	2.42
Burst index (kPa · m^2/g)	1.52	0.88	0.72	0.51	0.47

increased from 1.20% to 1.69%. The resultant brightness of bleached pulps at different $Mg(OH)_2$ substitutions were similar, supporting the conclusion that a partial $Mg(OH)_2$ substitution (higher than 25%) in peroxide bleaching can afford a higher bleaching efficiency of hydrogen peroxide. This may be partly explained by the decreased alkaline darkening when $Mg(OH)_2$ is partially used as the alkali source in the peroxide process. It is known that alkaline darkening takes place during peroxide bleaching and it has negative effects on the bleaching efficiency and the brightness ceiling of mechanical pulps.[23–26] Results in the literature[26] have shown that the higher the pH, the more the brightness loss during alkaline darkening. Not all of the newly formed chromophores during alkaline darkening are reactive toward peroxide.[26] As shown in Table 2, when NaOH was partially substituted by $Mg(OH)_2$, the end pH was lower than the control (0% $Mg(OH)_2$ substitution). As a result, the alkaline darkening was decreased, which would be partially responsible for the higher peroxide efficiency.

Table 2 also showed that the light scattering coefficient of the bleached pulp was increased when $Mg(OH)_2$ was partially substituted for NaOH. As the $Mg(OH)_2$ substitution ratio increased from 0% to 25%, the light scattering coefficient increased significantly. In the range of 25–60% $Mg(OH)_2$ substitution, the light scattering coefficient increased further. The substitution of $Mg(OH)_2$ for NaOH can increase the pulp yield and bulk. In fact, both were strongly correlated to the $Mg(OH)_2$ substitution ratio. These results suggest that a partial $Mg(OH)_2$ substitution can offer a greater flexibility to the bleaching process so that pulps with different light scattering coefficient, bulk, can be produced.

The changes of pulp strength properties with the increase of $Mg(OH)_2$ substitution are also included in Table 2. Evidently, the partial $Mg(OH)_2$ substitution for NaOH as alkali source of peroxide bleaching gave a negative effect on the pulp strength. The tensile, tear index, and burst index of bleached pulp decreased with the increase of $Mg(OH)_2$ substitution. The higher the $Mg(OH)_2$ substitution ratio, the lower the pulp strength. When the $Mg(OH)_2$ substitution increased from 0% to 60%, the pulp strength was decreased significantly; when the $Mg(OH)_2$ substitution ratio was more than 60%, the additional loss of pulp strength was small. There are a number of reasons for the loss of pulp strength at a partial $Mg(OH)_2$ substitution: (i) the binding of Mg^{2+} ions to the carboxylic group in fibers, (ii) less total carboxylic group content and surface charge of pulp fibers, and (iii) less removal of hydrophobic materials, such as lignin and extractives.

It was reported that multivalent cations, such as Ca^{2+} and Mg^{2+}, can bind to pulp fibers as the counter ions of fibers' acidic groups, decreasing the fiber swelling and the inter-fiber bonding.[27] As shown in Figure 1, the WRV of the bleached pulp decreased with the increased $Mg(OH)_2$ substitution, indicating a lower degree of swelling when a higher $Mg(OH)_2$ substitution was used. Although the lower WRV can also be explained by the lower carboxylic group content of the pulp bleached from the partial $Mg(OH)_2$ substitution process

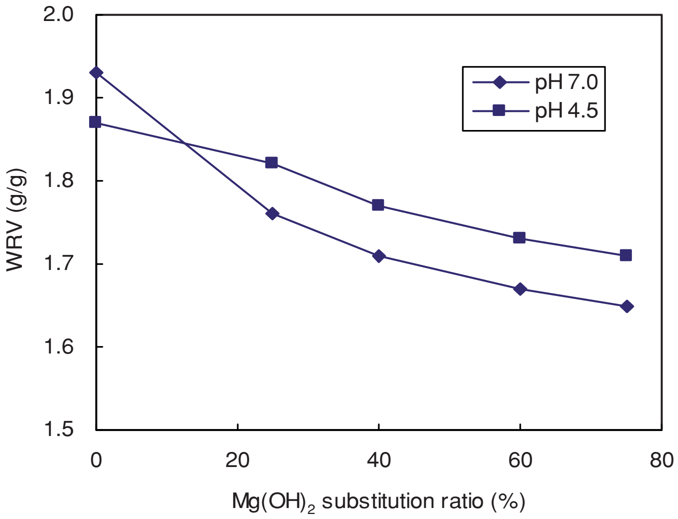


Figure 1. WRV of bleached pulp at different $Mg(OH)_2$ substitution ratios.

(Figure 3, to be discussed later), the presence of Mg^{2+} can lead to a further decrease in WRV. To support this hypothesis, we measured the WRVs at pH 4.5 and 7.0, as shown in Figure 1. At a 0% $Mg(OH)_2$ substitution ratio, the WRV at pH 4.5 was lower than that at pH 7.0, which is in agreement with the results in a previous study.[14]At the $Mg(OH)_2$ substitution ratio of 25–75%, the WRVs at pH 4.5 were higher than those at pH 7.0, which is due to the fact that at pH 7.0 Mg^{2+} ions are bound to carboxylic groups, suppressing the fiber swelling, whereas by replacing the bound Mg^{2+} with proton at pH 4.5, the fiber swelling can then be increased. The effect of an acid washing to remove the bound Mg^{2+} on tensile is shown in Figure 2. The acid washing was carried out at pH 4.0 before the handsheet preparation. One can find that the acid washing had no effect on the tensile strength of the pulp at 0% $Mg(OH)_2$ substitution, while increasing the tensile of pulps obtained at 25–75% $Mg(OH)_2$ substitutions.

It was reported that the content of acidic groups, in particular the fiber surface charge, is an important factor in the development of paper strength due to the fact that ionization of the acidic groups results in increased fiber swelling and their flexibility.[28] We determined both the total carboxylic groups and the surface charge density of bleached pulp fibers (Figure 3). Certainly the decreased surface charge suppressed the fiber swelling and fiber bonding, which correspond to the increase in the bulk and light scattering (Table 2) when the $Mg(OH)_2$ substitution ratio increased.

The decrease in the pulp strength with increase in the $Mg(OH)_2$ substitution ratio can also be caused by the presence of more hydrophobic material, such as extractives and/or lignin on the fiber surface due to the lower end

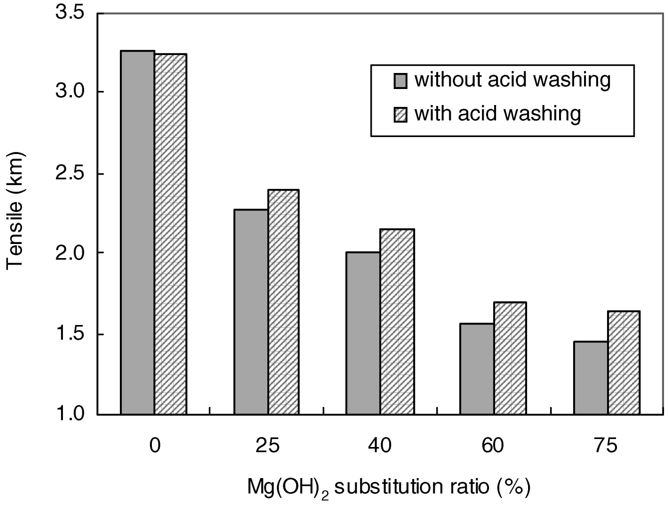


Figure 2. Effect of acid washing on pulp tensile at different $Mg(OH)_2$ substitution ratios.

pH (Table 2). The negative effects of extractives on the strength properties of mechanical pulp have been reported.[14,29,30] In this study, the XPS technique was used to determine the lignin and extractives coverage on the fiber surface.

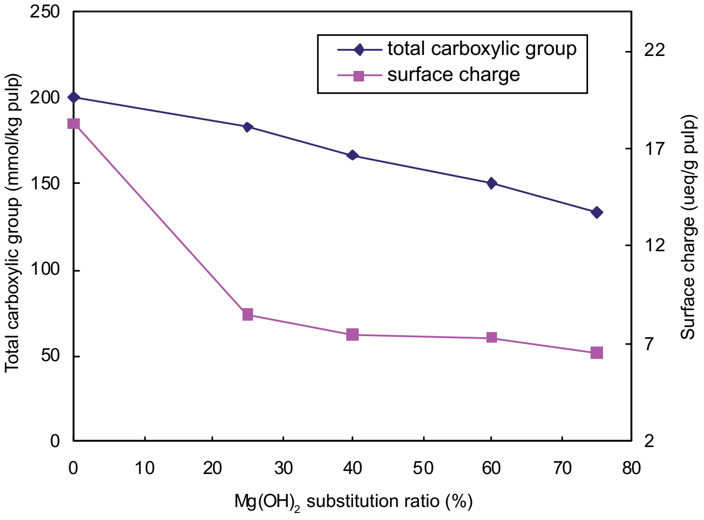


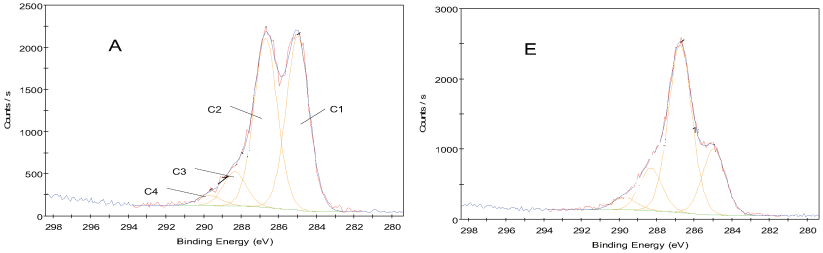
Figure 3. Total carboxylic group and surface charge as a function of the $Mg(OH)_2$ substitution ratio.

Table 3. XPS results of bleached pulp and acetone-extracted bleached pulp

	Bleached pulp		Bleached pulp after acetone extraction	
$Mg(OH)_2$ substitution (%)	O/C	C1/C	O/C	C1/C
Unbleached pulp	0.373	0.445	0.542	0.226
0	0.538	0.246	0.570	0.218
40	0.468	0.347	0.550	0.232
75	0.421	0.379	0.533	0.253

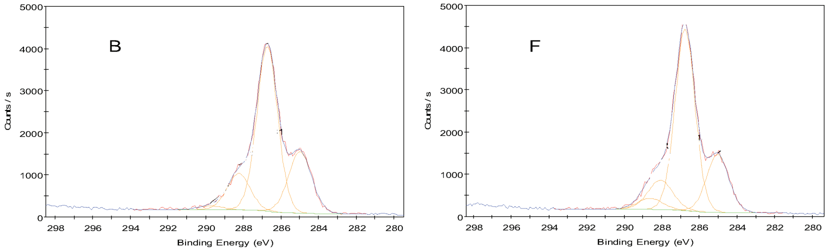
According to the literature,[31]the high-resolution XPS spectrum of the carbon 1s electron can be resolved into four carbon peaks representing C1 (carbon atoms bonded only to a carbon and/or a hydrogen atom, e.g., C-C/C-H), C2 (carbon atoms bonded to a single oxygen atom by a single bond, e.g., C-O-H), C3 (carbon atoms bonded to two noncarbonyl oxygen atoms or to a single carbonyl oxygen atom, e.g., O-C-O and C=O), and C4 (carbon atoms of carboxylic groups, i.e., O-C=O) respectively. Lignin and extractives are rich in the C1 type, while carbohydrates do not have any C1 type. Therefore, the concentration of C1 type can be indirectly related to the concentration of lignin and extractives on the fiber surface. In acetone-extracted pulp samples, lignin is the main contributor for the C1 type.

Figure 4 shows the resolved carbon 1s spectra of the bleached pulp fibers at different $Mg(OH)_2$ substitutions. The changes of oxygen to carbon ratio (O/C) and C1 content (C1/C) were summarized in Table 3. The unbleached pulp had a very high percentage of C1 (Spectrum A) and a low oxygen to carbon ratio (Table 3), supporting the conclusion that there is a high lignin and extractives concentration on the fiber surface. After bleaching, the C1 peak decreased significantly (Spectrum A, B, C, and D) and the O/C ratio increased (Table 3). This can be attributed to the removal of hydrophobic materials (lignin and extractives), particularly from the fiber surface. With the increase of $Mg(OH)_2$ substitution ratio in the bleaching, less hydrophobic materials on the fiber surface were removed as shown by the increase of C1 peak (Spectrum B, C, D) and the decrease of O/C ratio (Table 3), indicating that the higher the $Mg(OH)_2$ substitution ratio, the higher the lignin and extractives concentrations on the fiber surface. As expected, the acetone extraction performed after peroxide bleaching resulted in a significant dissolution of hydrophobic substances on the fiber surface as shown by the decrease of C1 peak (Spectrum A vs. E, B vs. F, C vs. G, and D vs. H) and increased O/C ratio, compared to the bleached pulps without acetone extraction. Based on the changes of C1 peaks in spectrums of extracted pulps (E, F, G, and H) and the results in Table 3, it is evident that when the $Mg(OH)_2$ substitution was 40% or 75%, the C1/C ratio or C1 peak



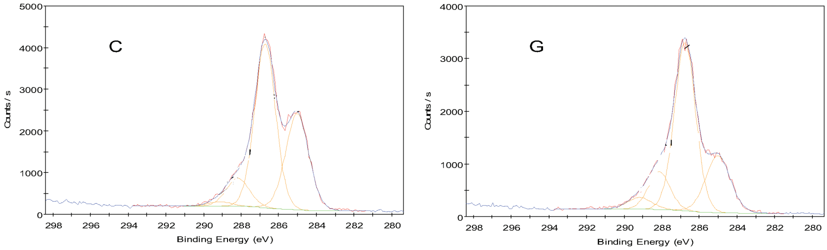
Unbleached pulp

Unbleached pulp, extracted



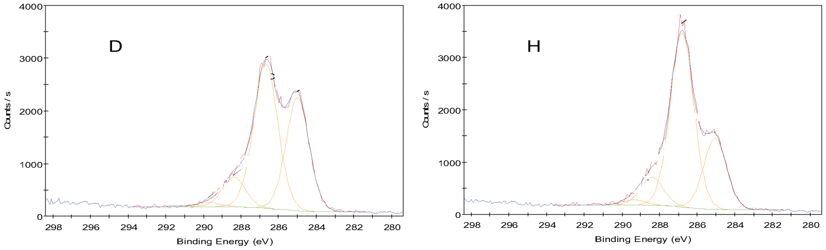
0% $Mg(OH)_2$ substitution

0% $Mg(OH)_2$ substitution, extracted



40% $Mg(OH)_2$ substitution

40% $Mg(OH)_2$ substitution, extracted



75% $Mg(OH)_2$ substitution

75% $Mg(OH)_2$ substitution, extracted

Figure 4. Resolved carbon peaks from high-resolution XPS of aspen CTMP fibers (unbleached, bleached, acetone-extracted).

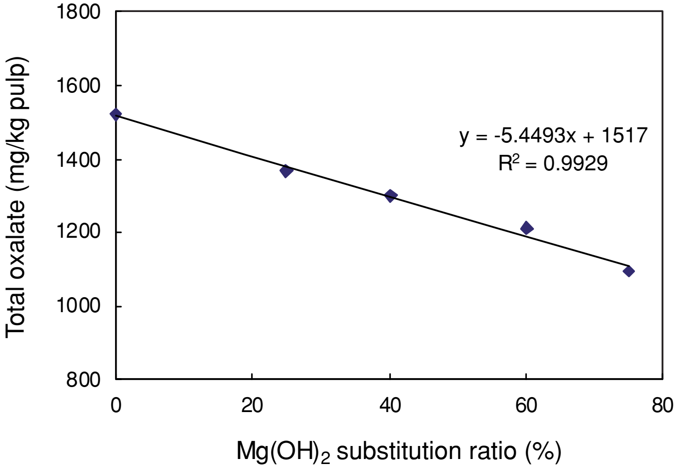


Figure 5. Total oxalate as a function of the $Mg(OH)_2$ substitution ratio.

in spectrum was higher than that of extracted unbleached pulp, supporting the hypothesis that some dissolved hydrophobic substances are redeposited onto the fiber surface. This is more pronounced at a higher $Mg(OH)_2$ substitution due to a lower final pH in the filtrate at the completion of bleaching.

Formation of Oxalate and Anionic Trash

Figure 5 shows the amount of total oxalate formed during the peroxide bleaching as function of the $Mg(OH)_2$ substitution ratio. The decrease in the total oxalate formed during peroxide bleaching was well correlated to the increase of the $Mg(OH)_2$ substitution ratio. We offered the following explanations: (i) the rate of oxalate formation during peroxide bleaching is proportional to the concentration of perhydroxy ion,[32] due to the decreased alkalinity (a lower end pH in Table 2) at a higher $Mg(OH)_2$ substitution ratio, the concentration of perhydroxy ion would be less, as a result, the oxalate formation decreased with the increase in the $Mg(OH)_2$ substitution. (ii) it was shown that less oxalate would be formed if the peroxide consumption was less. As shown in Table 2, the increased $Mg(OH)_2$ substitution led to an increase in the residual H_2O_2, indicating less peroxide consumption, which was partially responsible for the decreased oxalate formation (Figure 5).

The amount of anionic trash was measured as the cationic demand of the dissolved and colloidal substances in the filtrate. Figure 6 shows that a partial $Mg(OH)_2$ substitution significantly decreased the amount of anionic trash and this is true for the results measured at both pH 4.5 and pH 7.0. It was

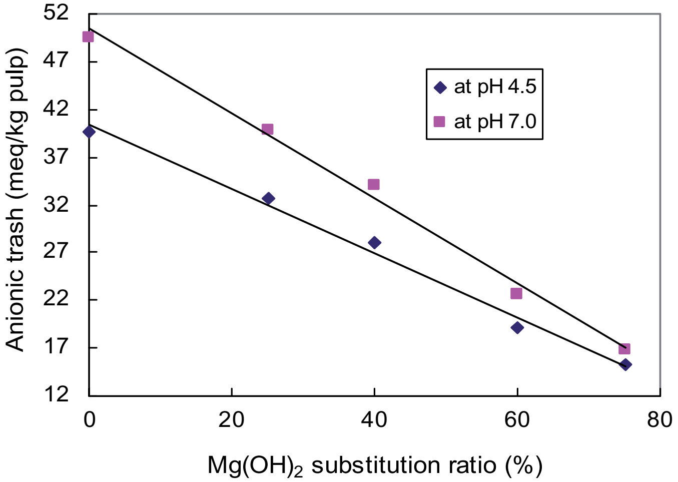


Figure 6. Anionic trash formed as a function of the $Mg(OH)_2$ substitution ratio.

known that the pectic acid/anionic hemicellulose, oxidized lignin, and resin and fatty acid can constitute the total anionic trash. Their relative contribution can be estimated based on the difference of pKa of their carboxylic groups[12]: at pH 4.5, only the uronic type of carboxylic groups of pectic acids/anionic hemicellulose, such as polygalacturonic acids, can be dissociated into anionic groups; at pH 7.0, all of the three types of carboxylic groups (uronic, oxidized lignin, resin and fatty acids) can dissociate into anionic groups,[12,28] therefore, the anionic trash determined at pH 4.5 is mainly due to pectic acids/anionic hemicellulose, while the difference between pH 7.0 and pH 4.5 is attributed to oxidized lignin and resin and fatty acids. The results in Figure 6 show that with the increased $Mg(OH)_2$ substitution ratio, less pectic acids/anionic hemicellulose was dissolved; also, the difference of anionic trash between pH 4.5 and pH 7.0 became smaller when the $Mg(OH)_2$ substitution ratio increased from 0% to 75%, indicating that less oxidized lignin and resin and fatty acids were dissolved. The contribution of resin and fatty acids to anionic trash was relatively small,[13] and the decreased dissolution of polygalacturonic acids and oxidized lignin are mainly responsible for the observed lower anionic trash at higher $Mg(OH)_2$ substitution ratio. The less dissolution of lignin, pectic acids/anionic hemicellulose can also result in less COD load of the filtrate, as shown in Figure 7.

The amount of dissolved lignin was quantified based on the UV absorbance at the wavelength of 280 nm. There was a strong correlation between the $Mg(OH)_2$ substitution ratio and amount of dissolved lignin: much less lignin was dissolved at a higher $Mg(OH)_2$ substitution ratio. The decreased lignin

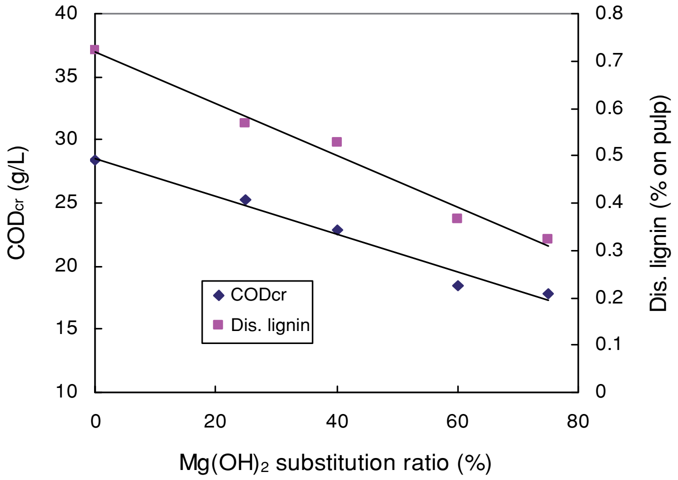


Figure 7. COD and dissolved lignin as a function of the $Mg(OH)_2$ substitution ratio.

dissolution was also partially responsible for the lower COD obtained at a higher $Mg(OH)_2$ substitution ratio.[13]

CONCLUSIONS

A partial substitution of NaOH with $Mg(OH)_2$ as the alkali source in peroxide bleaching of aspen CTMP led to higher peroxide bleaching efficiency, pulp yield, bulk, and light scattering coefficient, all of which increased with the increase of the $Mg(OH)_2$ substitution ratio. Less oxalate and anionic trash were produced in the partial $Mg(OH)_2$ substitution process than the conventional process. A decrease in pulp strength was observed with a partial $Mg(OH)_2$ substitution, which was caused by: (i) the binding of Mg^{2+} ions to the carboxylic group in fibers, (ii) less total carboxylic group content and surface charge of pulp fiber, and (iii) less removal of hydrophobic materials, such as lignin and extractives.

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