



Effect of partially substituting MgO for NaOH on bleaching of pine (*Pinus massoniana*) thermomechanical pulp

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ABSTRACT

Bleached thermomechanical pulp (TMP) has been applied in the production of newsprint and supercalendered (SC) paper or other paper products. Recent studies on the alkaline peroxide bleaching with magnesium-based alkalis indicated that the bulk and optical properties can be improved, and effluent load can be reduced. In this work, MgO was partially used in alkaline peroxide bleaching process of pine (*Pinus massoniana*) TMP to investigate the effect of MgO substitution for NaOH on the pulp properties and effluent characteristics. The present research showed that partial substitution of MgO for NaOH could decrease the dissolution of chemical components in pulp fibers, thus, improving the pulp yield and decreasing the effluent load. When the substitution percentage of MgO for NaOH increased from 0% to 50% at 3.5% alkali charge, the bulk of the bleached pine TMP increased from 3.45 cm³/g to 3.69 cm³/g, while the opacity was improved from 84.7% to 89.1%, the cationic demand and COD_{Cr} of the effluent decreased by 31% and 22%, respectively. However, the MgO substitution had decreased the brightness and tensile index of the bleached TMP.

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1. Introduction

Bleached thermomechanical pulp (TMP), as one of the main high-yield pulps (HYPs), has been applied in the production of newsprint, supercalendered (SC) paper and other paper or paper-board products owing to its excellent bulk, opacity and strength properties. Usually, the proportion of bleached TMP in the SC paper is about 60–80% (Zhang, Guo, & Qiao, 2007).

Recently, studies on the peroxide bleaching of TMP showed that the obtained bleached TMP had a higher bulk and light-scattering coefficient and a lower tensile index from the magnesium-based process than those from the sodium-based process (He, Wekesa, & Ni, 2004; Wong, Schmidt, & Heitner, 2006).

The additional advantages of the magnesium-based peroxide bleaching process included decreased effluent loads, decreased bleaching cost and so on. Magnesium-based alkali (MgO or Mg(OH)₂) has already been used as one bleaching alkali source in pulp and paper industry (Chi & Zhang, 2007; Harrison et al., 2008; He, Ni, & Zhang, 2004; Li et al., 2005; Lu, Yang, & Ni, 2005), leading to a higher bleaching yield, a lower COD and cationic demand, decreased bleaching cost and oxalate scaling. And, the results from a mill in Canada have confirmed that the costs associated with the effluent treatment were reduced by 25–40% after implementing the Mg(OH)₂-based peroxide bleaching process (He, Wekesa,

& Ni, 2004). Meanwhile, the bleached TMP fibers produced from the Mg(OH)₂-based peroxide process had a similar surface charge density, compared to the NaOH-based process.

So far, the studies on the TMP peroxide bleaching have mainly focused on the 100% sodium-based or magnesium-based alkali. In this work, MgO was used in the peroxide bleaching of pine (*Pinus massoniana*) TMP with different substitution percentages at different total alkali charges to investigate the effect of substitution of MgO for NaOH on the opacity, bulk and other pulp properties, as well as the effluent characteristics. It is noted that pine is an important raw material in China for TMP production, in particular, in the southeast region.

2. Experimental

2.1. Materials

The pine (*Pinus massoniana*) TMP (beating degree of 51°SR, initial ISO brightness of 38.1% and bulk of 4.20 cm³/g) was collected from a paper mill in Fujian province, China. The collected pulp was stored in a cold room at 4 °C. All chemicals used in the experiments were analytical-grade products.

2.2. Peroxide bleaching process

The bleaching experiments were conducted in polyethylene bags using a water bath according to the following conditions: the pine TMP of equivalent to 60 g of the oven-dried pulp, 3.5% or 4.0%

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total alkali charge (on NaOH), of which 0%, 25%, 50%, and 75% of NaOH was replaced with MgO (molar ratio), 0.12% diethylenetriaminepentaacetic acid (DTPA), 3.0% Na₂SiO₃, 4.0% H₂O₂, 10% of pulp consistency, 70 °C, and 150 min. All these chemical dosages were based on the weight of the oven-dried pulp.

In the case of peroxide bleaching process, NaOH, MgO, part of deionized water and DTPA were mixed well first with the TMP by kneading the polyethylene bag by hand. The prepared bleaching liquor (i.e., the mixture of remaining deionized water, Na₂SiO₃ and H₂O₂) was then added into the bag. After the pulp and chemicals were mixed well by kneading constantly, the polyethylene bag was sealed and placed into the water bath with a temperature of 70 °C. The bleaching duration time began to count as soon as the temperature of the pulp suspension reached 70 °C. The polyethylene bag was kneaded one time every 10 min in order to make the bleaching reaction uniform. As the bleaching duration time reached 150 min, the bag was taken out of the water bath and put into a cold water bath to make the pulp temperature down to room temperature promptly.

2.3. Collection of the bleaching effluent and preparation of analysis

After finishing bleaching, some bleached pine TMP (equivalent to 5 g of oven-dried pulp) was collected from the polyethylene bag and diluted into 1% pulp consistency with distilled water. Then, the yielded suspension was stirred thoroughly for 30 min at a stirring speed of 500 rpm. Finally, the suspension was filtrated in a Büchner funnel with a 200-mesh screen, and the filtrate was recycled once to retain the fines. After the filtrate was further filtered using medium pore size filter paper, the obtained filtrate was then collected for determination of pH, cationic demand, and COD_{Cr} of the effluent.

The COD_{Cr} was determined according to the USEPA Reactor Digestion Method (Jirka & Carter, 1975) using a DRB 200 COD instrument (HACH Co. Ltd., USA) and a DR 1010 COD instrument (HACH Co. Ltd., USA). The cationic demand was measured using a Müteck PCD-03 charge analyzer (BTG Co. Ltd., Germany). Before determining the cationic demand, 0.10 mol/L of sulfuric acid was prepared for adjusting the pH value of the filtrate to 6.8 ± 0.1 (He, Ni, & Qian, 2005).

2.4. Pulp washing

After completion of taking the bleaching effluent sample from the bleached pine TMP, the sampled pulp and the rest in the polyethylene bag were mixed together in a Büchner funnel with a 200-mesh screen and then washed with distilled water. The filtrate obtained first time was recycled once to collect the fines in the pulp. The bleached pine TMP was washed thoroughly until the filtrate was clear. Finally the washed pulp was collected in a polyethylene bag for later use.

2.5. Determination of bleaching yield and chemical components

The bleaching yield was calculated by the ratio of oven-dried pulp weights after and before bleaching. Some air-dried bleached pine TMP was ground into wood meals using a Wiley mill (Model No. 2, Arthur H., Thomas Co. Ltd., USA). The portion of passing a 40-mesh screen but retaining on a 60-mesh one was collected and used for the analysis of chemical composition according to the method described in the literature (Shi & He, 2009; Xie & Zhan, 2005).

2.6. Determination of water retention value (WRV)

Some wet pulp (equivalent to 1.0 g (oven-dry)) was taken and centrifuged using a centrifugal machine at a speed of 3000 rpm for 30 min, the water retention value (WRV) was calculated according to ISO 23714 (2007).

2.7. Handsheets preparation and testing

Handsheets of 60 ± 2 g/m² (oven-dry) were prepared and formed according to the standard methods of ISO 5263 (1995) and ISO 5269-1 (1998), respectively. In addition, physical properties of the handsheets were determined according to ISO 5270 (1998).

3. Results and discussion

3.1. Effect of substitution of MgO for NaOH on optical properties of handsheets

The effect of substitution of MgO for NaOH on opacity, light-scattering coefficient, and brightness of the handsheets made of the resultant pulps were investigated, as shown in Table 1. The comparison was made between the optical properties at 3.5% and 4.0% alkali charge. Table 1 indicates that the opacity and light-scattering coefficient at 4.0% alkali charge were lower than those at 3.5% alkali charge. However, the brightness at 4.0% alkali charge was somewhat higher than that at 3.5% alkali charge. When the substitution percentage of MgO for NaOH increased from 0% to 50%, the opacity at 3.5% alkali charge increased from 84.7% to 89.1%, 4.4 units gain in opacity. Meanwhile, the ISO brightness decreased by 5.7% but still maintained 59.4% at 3.5% alkali charge.

The alkalinity of the bleaching system would be the main reason for the above changes. Table 1 suggests that the use of MgO in the peroxide bleaching, i.e., a weak alkalinity of the bleaching system, has a negative effect on the brightness and a positive one on the opacity and light-scattering coefficient of the bleached pine TMP.

According to the research (Pi, 2006), ISO brightness of 58–60% would be best suitable for the present newsprint market demand, considering the brightness, opacity and benefit factors comprehensively. Certainly, coating and the use of paper fillers could make up for the loss of brightness and expanded the application of bleached TMP into SC paper and other paper or paperboard products.

Table 1
Optical properties of the resultant pulps.

Substitution percentage of MgO for NaOH	3.5% alkali charge (on NaOH) (wt. on oven-dry pulp)			4.0% alkali charge (on NaOH) (wt. on oven-dry pulp)		
	ISO Brightness (%)	Opacity (%)	Light -scattering coeff. (m ² kg ⁻¹)	ISO Brightness (%)	Opacity (%)	Light - scattering coeff. (m ² kg ⁻¹)
Unbleached pulp	38.1 ± 0.2	98.0 ± 0.2	53.4 ± 0.3	38.1 ± 0.2	98.0 ± 0.2	53.4 ± 0.3
0%	65.1 ± 0.2	84.7 ± 0.2	43.0 ± 0.3	64.7 ± 0.3	85.4 ± 0.2	44.8 ± 0.3
25%	62.7 ± 0.3	86.7 ± 0.2	44.9 ± 0.3	64.1 ± 0.2	85.2 ± 0.1	43.3 ± 0.1
50%	59.4 ± 0.3	89.1 ± 0.4	47.7 ± 0.1	60.4 ± 0.3	88.2 ± 0.4	45.8 ± 0.3
75%	57.5 ± 0.1	91.0 ± 0.3	48.8 ± 0.2	57.9 ± 0.3	90.2 ± 0.2	47.2 ± 0.3

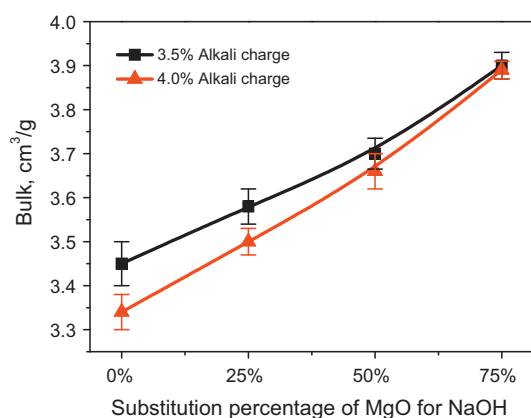


Fig. 1. Effect of substitution of MgO for NaOH on bulk of the handsheets.

3.2. Effect of substitution of MgO for NaOH on bulk and strength properties of the pulp handsheets

The effect of substitution of MgO for NaOH on bulk and some strength properties (e.g., tensile index and tear index) of the pulp handsheets were investigated, as shown in Figs. 1 and 2. It can be found that the tensile index and tear index of pine bleached TMP decrease with increase of the substitution percentage of MgO for NaOH.

Bulk is one important index for mechanical pulps. Adding pulp with a high bulk into the paper stock furnish to make paper or paperboard products means less pulp required to meet the need of the stiffness or thickness of the products. However, pulp with a high bulk has also a negative impact on its strength properties. As shown in Fig. 1, when the substitution percentage of MgO for NaOH increased from 0% to 50%, the bulk of the bleached TMP would increase from 3.45 cm³/g to 3.69 cm³/g at 3.5% alkali charge and from 3.34 cm³/g to 3.66 cm³/g at 4.0% alkali charge, respectively. Correspondingly, the tensile index of the bleached TMP would decrease from 23.3 N/m/g to 18.9 N/m/g at 3.5% alkali charge and from 24.0 N/m/g to 19.3 N/m/g at 4.0% alkali charge, respectively (Fig. 2). Obviously, if the gained bulk is applied to the practical production, the potential economic benefit may be considerable.

Pulp fibers can swell under the alkali condition, so that the fibers become flexible and the strength properties of the pulp fibers can increase. In the present work, the alkalinity of the bleaching system decreased with increase of the substitution percentage of MgO for NaOH. Thus, less hydrophobic materials, such as lignin and benzene alcohol extractives, were removed from pulp fibers (Table 2), resulting in a lower flexibility of the fibers. The stiff fibers would

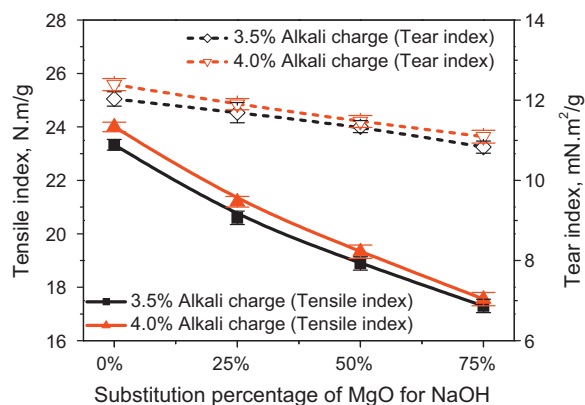


Fig. 2. Effect of substitution of MgO for NaOH on tensile index and tear index of the handsheets.

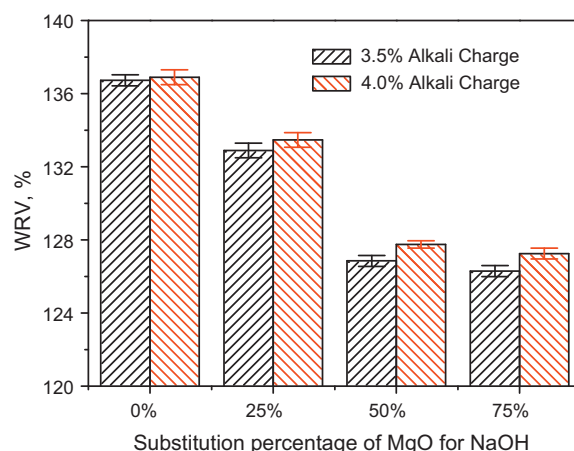


Fig. 3. Effect of substitution of MgO for NaOH on water retention value (WRV).

increase the bulk of pulp and decrease the inter-fiber bonds, leading to an increase in opacity and light-scattering coefficient (Table 1). The MgO addition in the peroxide bleaching process can improve the bulk and optical properties of pine bleached TMP, which can be applied in the production of newsprint and SC paper or other paper and paperboard products.

In addition, according to some previous studies (Katz, Liebergott, & Scallan, 1981; Kong, Ni, & He, 2009; Lossada, Maximino, & Mina, 1998; Maximova, Österberg, Koljonen, & Stenius, 2001; Ni & He, 2010; Scallan & Tigerstrom, 1992; Tchepel, McDonald, & Dixon, 2006), less carboxylic groups were produced and more lignin was retained in pulp due to the weaker alkalinity in the MgO-based alkali peroxide bleaching process. The swelling degree and bonding strength of the bleached TMP fibers became worse than those of the pulp fibers from the NaOH-based process. Moreover, the multivalent cations, such as Mg^{2+} , may also decrease the fiber swelling and internal fiber bonding (Savoye, Petit-Conil, & Meyer, 2011; Scallan & Grignon, 1979). These factors are responsible for the decreased water retention value (WRV) as the substitution percentage of MgO for NaOH increased, as shown in Fig. 3.

3.3. Effect of substitution of MgO for NaOH on bleaching yield and chemical compositions of pulp fibers

During the peroxide bleaching process, some of chemical components of pulp fibers could dissolve into the bleach effluent, causing loss of bleaching yield. In this work, bleaching yield for both NaOH-based and MgO-based processes, and chemical compositions (i.e., holocellulose, Klason lignin and benzene alcohol extractives) at 3.5% and 4.0% alkali charge were all determined, as shown in Table 2. The results demonstrated that the bleaching yield would be higher at higher MgO substitution in the peroxide bleaching process, which was consistent with the fact that more chemical components remained in the bleached pulp fibers. The contents of the lignin, benzene alcohol extractives, and holocellulose in the bleached pulp fibers, as well as the bleaching yield, increased with raise of the substitution percentage of MgO for NaOH. These results can be explained by (1) lower alkalinity caused by substitution of MgO for NaOH; (2) stabilizing H_2O_2 and protecting carbohydrates due to the existence of Mg^{2+} (Xie & Zhan, 2005).

3.4. Effect of substitution of MgO for NaOH on cationic demand and COD_{Cr} of the effluent

Anionic trash is a significant problem in a paper machine operation, especially with the closed recycle enhancement of white water

Table 2
Chemical composition of the resultant pulps.

Substitution percentage of MgO for NaOH	3.5% alkali charge (on NaOH) (wt. on oven-dry unbleached pulp)				4.0% alkali charge (on NaOH) (wt. on oven-dry unbleached pulp)			
	Klason lignin (%)	Benzene alcohol extractives (%)	Holocellulose (%)	Bleaching yield (%)	Klason lignin (%)	Benzene alcohol extractives (%)	Holocellulose (%)	Bleaching yield (%)
Unbleached pulp	28.9 ± 0.2	4.7 ± 0.2	72.2 ± 0.3	100.00	28.9 ± 0.2	4.7 ± 0.2	72.2 ± 0.3	100.00
0%	27.0 ± 0.2	1.9 ± 0.1	71.0 ± 0.2	94.4 ± 0.3	26.5 ± 0.1	1.4 ± 0.1	70.8 ± 0.3	93.3 ± 0.4
25%	27.6 ± 0.1	2.8 ± 0.1	71.1 ± 0.2	96.0 ± 0.3	27.1 ± 0.2	2.4 ± 0.1	71.0 ± 0.1	95.0 ± 0.2
50%	27.9 ± 0.2	3.8 ± 0.2	71.5 ± 0.2	97.5 ± 0.2	27.6 ± 0.2	3.5 ± 0.1	71.4 ± 0.3	96.9 ± 0.4
75%	28.2 ± 0.1	4.0 ± 0.2	71.7 ± 0.3	98.1 ± 0.4	27.7 ± 0.2	3.8 ± 0.2	71.6 ± 0.3	97.7 ± 0.1

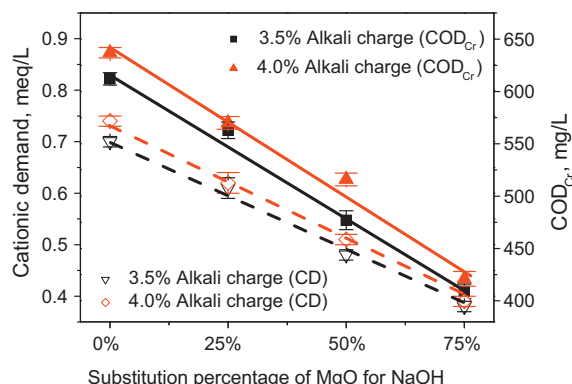


Fig. 4. Effect of substitution of MgO for NaOH on COD_{Cr} and cationic demand of the effluent.

in modern papermaking process. The cationic demand was measured under different substitution percentages of MgO for NaOH. Fig. 4 showed that the cationic demand of the effluent from the peroxide bleaching process decreased greatly with increase of the substitution percentage of MgO for NaOH. The cationic demand of the effluent would decrease by 31% when the substitution percentage of MgO for NaOH increased from 0% to 50% at 3.5% alkali charge. This is mainly due to the lower alkalinity caused by the addition of MgO, leading to a lower dissolution of organics (Table 2), so the cationic demand decreased. In addition, the presence of Mg^{2+} ions in the system can neutralize anionic charges of polygalacturonic acids, oxidized lignin, and resin acids to some extent (Behrooz, Ghasemi, & Asadpour, 2009; Liu et al., 2011).

The weak alkalinity of the bleaching system is further confirmed by the pH value of the effluent. As shown in Fig. 5, pH value of the effluent from the peroxide bleaching decreased with increase of the substitution percentage of MgO for NaOH, which is mainly because

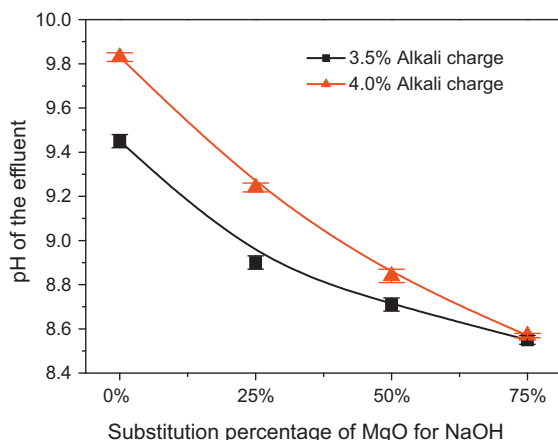


Fig. 5. Effect of substitution of MgO for NaOH on pH of the effluent.

of the lower solubility of MgO (0.086 g/L at 60 °C and 0.062 g/L at 80 °C) than NaOH in water (Hou et al., 2010; Wong, Schmidt, & Heitner, 2006). Johnson et al. (2002) found that $\text{Mg}(\text{OH})_2$ -based process had less peroxide decomposition reactions in the peroxide bleaching of TMP due to its lower alkalinity.

COD is an important indicator of effluent load. The COD_{Cr} decreased notably with increase of the substitution percentage of MgO for NaOH. As shown in Fig. 4, the COD_{Cr} decreased by nearly 22% when the substitution percentage of MgO for NaOH increased from 0% to 50% at 3.5% alkali charge. Consequently, the potential saving in the effluent treatment cost may be also remarkable from partial substitution of MgO for NaOH.

The above inferences can be also verified by the related reports (Johnson et al., 2002; Ni & He, 2010; Petrie, Gibson, & Schmidtchen, 2006), of which using a weak alkali such as magnesium oxide or magnesium hydroxide in other pulps/systems will lead to the decreases in cationic demand and COD of the filtrate.

4. Conclusions

MgO was partially used as one alkali source in the alkaline peroxide bleaching of pine (*Pinus massoniana*) TMP. The opacity and light-scattering coefficient of pine bleached TMP increased with raise of the substitution percentage of MgO for NaOH. When the substitution percentage increased from 0% to 50%, the bulk would increase from 3.45 cm^3/g to 3.69 cm^3/g at 3.5% alkali charge and from 3.34 cm^3/g to 3.66 cm^3/g at 4.0% alkali charge, respectively. Correspondingly, the tensile index would decrease from 23.3 N m/g to 18.9 N m/g at 3.5% alkali charge and from 24.0 N m/g to 19.3 N m/g at 4.0% alkali charge, respectively. The tear index has only a slight decrease. The improvements in bulk and the opacity of pine bleached TMP would be of benefit to the practical production of newsprint and SC paper or other paper and paperboard products.

The cationic demand and COD_{Cr} of the effluent decreased greatly with increase of the substitution percentage of MgO for NaOH. When the substitution percentage of MgO for NaOH increased from 0% to 50% at 3.5% alkali charge, the cationic demand and COD_{Cr} could be decreased by 31% and 22%, respectively. The bleaching yield could be also increased due to less dissolution of the chemical components of the pulp fibers.

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