SUBSTITUTION OF SODIUM HYDROXIDE WITH MAGNESIUM HYDROXIDE AS AN ALKALI SOURCE IN THE PEROXIDE BLEACHING OF SOFTWOOD TMP

HUIREN HU and HONGJIE ZHANG*

Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology, Tianjin, 300457, China
**Key Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou, 510650, China*

Received June 20, 2009

Softwood thermo-mechanical pulp (TMP) was subjected to peroxide bleaching, by substituting sodium hydroxide (NaOH) with magnesium hydroxide ($Mg(OH)_2$) as an alkali source. The optical and physical properties of the bleached pulps were compared, as well as the COD, anionic trash and the organic and inorganic compounds present in the bleaching effluent. The results showed that, at the same hydrogen peroxide charge, the bulk opacity of $Mg(OH)_2$-based bleached pulp increased obviously, while the amount of anionic trash and COD in the bleaching effluent decreased significantly, compared with that observed during NaOH-based bleaching. Furthermore, the consumption of hydrogen peroxide decreased considerably during $Mg(OH)_2$-based TMP bleaching. However, the physical properties and brightness gain resulted from the $Mg(OH)_2$-based process were comparable to or just slightly lower than those obtained by the NaOH-based one.

Keywords: magnesium hydroxide, TMP, peroxide bleaching, anionic trash, conductivity, turbidity

INTRODUCTION

Hydrogen peroxide bleaching is usually carried out under alkaline conditions to achieve a sufficient brightening effect for high yield pulps (HYP), such as SGW, TMP, CTMP and APMP, sodium hydroxide (NaOH) being generally used as an alkali source. However, the high alkalinity of NaOH causes extensive dissolution of the organic substances from pulp fibers during peroxide bleaching, resulting in a low pulp yield of the bleached pulp, high anionic trash production and high COD load of the effluent. Numerous studies[1-16] have shown that magnesium hydroxide ($Mg(OH)_2$) is one of the most promising chemicals, with potential application in the peroxide bleaching of HYP. The literature results supported the conclusion that a total $Mg(OH)_2$ substitution with NaOH may induce several beneficial effects, such as lower anionic trash formation, lower chemical oxygen demand load (COD) in the effluent and a higher scattering coefficient of the bleached pulp. M. Nyström[1] reported that lower tensile strength and higher brightness could be obtained when using $Mg(OH)_2$ instead of NaOH as an alkali source in the peroxide bleaching of spruce SGW. 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.[11] A partial substitution of NaOH with $Mg(OH)_2$ was effective in reducing the amount of calcium oxalate formation during peroxide bleaching.[14,15]

Recently, special interest has been manifested for the substitution of NaOH with $Mg(OH)_2$ as an alkali source in the peroxide bleaching of softwood TMP. However, a systematic study on this issue is still lacking. The objective of the present investigation is to determine how the optical and physical properties of bleached softwood TMP and its process characteristics, such as peroxide consumption, anionic trash, COD and dissolution of organics and inorganics, were influenced when NaOH was partially or completely substituted by $Mg(OH)_2$ as an alkali source in peroxide bleaching.

EXPERIMENTAL

Materials

TMP pulp with 59.1% ISO brightness and 520 mL CSF, made from pine and spruce, supplied by a Canadian pulp mill, was sampled after chelation on an unbleached twin roll press of a TMP line. Most of the bleaching chemicals, such as H_2O_2, NaOH, Na_2SiO_3 and DTPA, were received from Fisher Scientific, and the magnesium hydroxide sample (61% slurry) was obtained from Martin Marietta Magnesia Specialties, Raleigh, NC, USA.

Experiments

Peroxide bleaching experiments were conducted in plastic bags, under the conditions listed in Table 1. The bleaching conditions of the control sample were provided by the pulp mill and an equivalent amount of NaOH was substituted by $Mg(OH)_2$ based one, under mill conditions. The mixture made of bleaching chemicals and water was put in a polyethylene (PE) plastic bag, which was sealed, kneaded by hand for 2 min and placed into a water bath, where bleaching was carried out at predetermined temperature and time.

After bleaching, the pulp was diluted to a pulp consistency of 5%, dispersed evenly with a stirrer, filtered through a Büchner funnel with a 200-mesh screen, then the filtrate was recycled to pass through the pulp mat and collect the fines. The pulp cake (about 25% consistency) was then dispersed into a 2% pulp suspension with deionized water, and handsheets were prepared according to the TAPPI standard methods. The resulting filtrate was used for the determination of residual H_2O_2, according to the J.16P (CPPA) Standard,[16] and for COD measurements, according to the H.3 (CPPA) Standard.[17] As for the anionic trash measurement, the filtrate had to be further filtered through a Whatman medium filter paper to remove the residual fines, then tested for the cationic demand. The anionic trash measurement was done on a PCD-02 Müteck particle charge analyzer. The optical and physical properties were tested according to the TAPPI standard methods.

RESULTS AND DISCUSSION

Effect of NaOH substitution with $Mg(OH)_2$ on the optical properties of bleached pulps

Figure 1 shows the effect of NaOH partial or total substitution with $Mg(OH)_2$ on the optical properties of bleached pulps. With increasing the NaOH substitution by $Mg(OH)_2$, the brightness of the bleached pulp decreased a little, at the same hydrogen peroxide charge (Fig. 1a).

Table 1
Peroxide bleaching conditions for softwood TMP

H_2O_2 charge (%)	4.0	4.0	4.0	4.0	4.0
$Mg(OH)_2$ charge (%)	–	0.73	1.1	1.46	1.46
NaOH charge (%)	2.0	1.0	0.5	–	–
Na_2SiO_3 charge (%)	1.5	1.5	1.5	1.5	1.5
DTPA charge (%)	0.2	0.2	0.2	0.2	0.2
Pulp consistency (%)	30	30	30	30	30
Bleaching temperature (ºC)	70	70	70	70	80
Bleaching time (min)	150	150	150	150	150

When NaOH was totally replaced by $Mg(OH)_2$, about 1 brightness unit was lost. However, the opacity of the bleached pulp improved significantly with increasing the NaOH substitution degree. About 3 units were obtained when 100% $Mg(OH)_2$ was used as an alkali source at the same peroxide charge applied, as shown in Figure 1b, which agrees with the results of previous studies.[4,5,9,10]

Effect of NaOH substitution with $Mg(OH)_2$ on the physical strength properties of bleached pulps

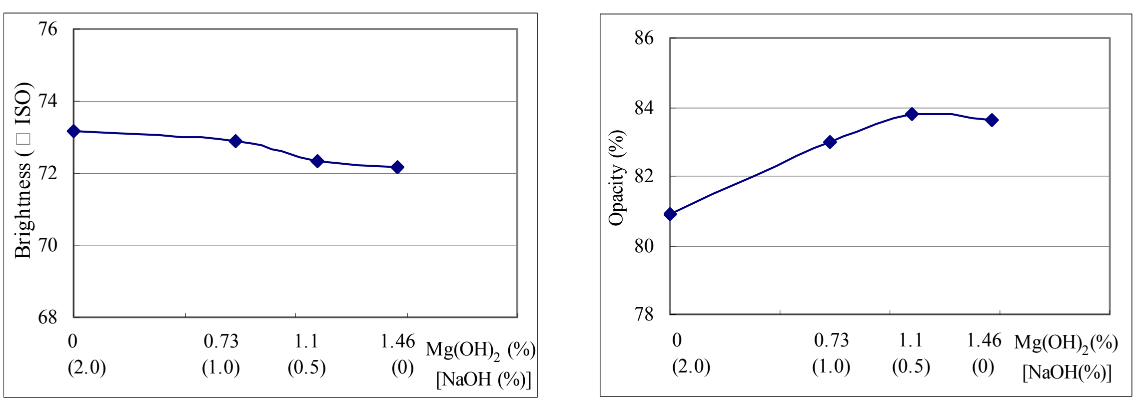
As shown in Figure 2a, the breaking lengths of the bleached pulp, which were of 3.07 km and 2.70 km, respectively, for 100% NaOH-based and 100% $Mg(OH)_2$-based bleaching processes, decreased obviously with increasing the substitution degree of NaOH with $Mg(OH)_2$. Tensile strength decreased almost by 12%, which should be related to the fact that fiber bonding is not well developed during the $Mg(OH)_2$-based process, as due to weak alkali.[11,13] However, the bulk of the pulp resulting from the 100% $Mg(OH)_2$-based process was much higher than that from the 100% NaOH-based one (3.30 *versus* 2.85 cm^3/g), as shown in Fig. 2b. The increment of bulk due to the substitution of 100% NaOH with 100% $Mg(OH)_2$ is of about 16%, which is better for the development of the bulk and stiffness of the finished paper products, also indicating that the mass could be decreased, to save, at least partially, the fiber materials for paper products with the same bulk.

Effect of NaOH substitution with $Mg(OH)_2$ on H_2O_2 consumption

As shown in Figure 3, residual peroxide increased significantly with the increase in the substitution degree of NaOH with $Mg(OH)_2$, indicating that the consumption of hydrogen peroxide decreased obviously for the $Mg(OH)_2$-based bleaching process. This is also due to the weak alkalinity of $Mg(OH)_2$, resulting in a lower peroxide decomposition, since it is well-known[3] that the transition metal-induced peroxide decomposition is much lower at a relatively lower pH.

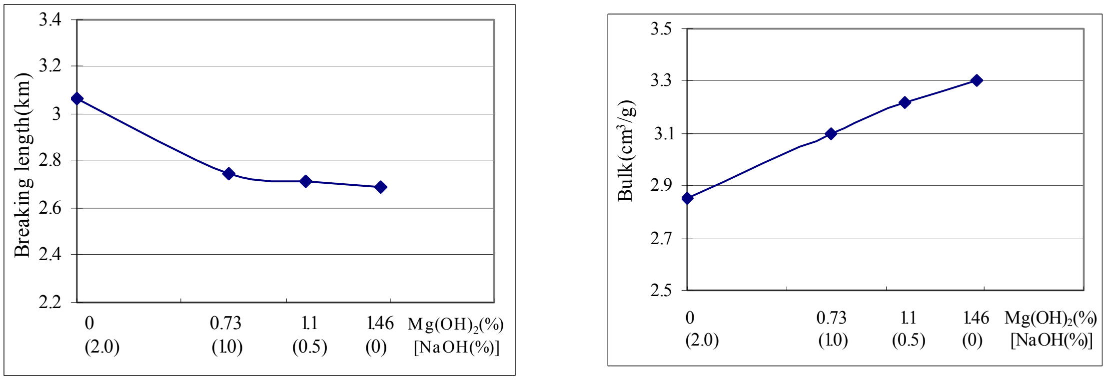
Effect of NaOH substitution with $Mg(OH)_2$ on anionic trash content

The amount of anionic trash is measured as the cationic demand of the dissolved and colloidal substances in the water phase (filtrate). Figure 4 shows that the $Mg(OH)_2$-based bleaching process produced significantly less anionic trash than the NaOH-based one, while a significant decrease of anionic trash, of about 57%, is obtained by replacing NaOH with $Mg(OH)_2$ as an alkali source for peroxide bleaching, which is largely attributed to the weak alkalinity of magnesium hydroxide.



(a) Substitution degree *vs*. brightness (b) Substitution degree *vs*. opacity

Figure 1: Effect of NaOH substitution degree on the brightness and opacity of bleached pulp



(a) Substitution degree *vs*. breaking length (b) Substitution degree *vs*. bulk

Figure 2: Effect of substitution of NaOH on the breaking length and bulk of bleached pulp

Therefore, the charge of cationic additives can be reduced in papermaking wet-end during HYP applications.

Effect of NaOH substitution with $Mg(OH)_2$ on COD_{cr} in bleaching effluent

According to Figure 5, the COD_{cr} in the effluent decreased drastically with increasing the NaOH substitution with $Mg(OH)_2$. When NaOH was totally replaced by $Mg(OH)_2$, the COD_{cr} decreased from 72.2 kg/T to 46.7 kg/T, the reduction being of around 35%, which is mainly due to the formation of less acetic acid, methanol and dissolved lignin.[4]

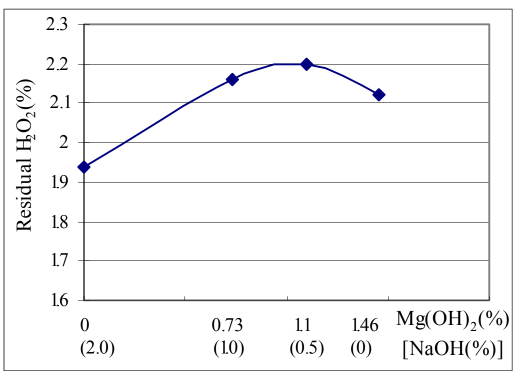


Figure 3: Effect of NaOH substitution on residual H_2O_2

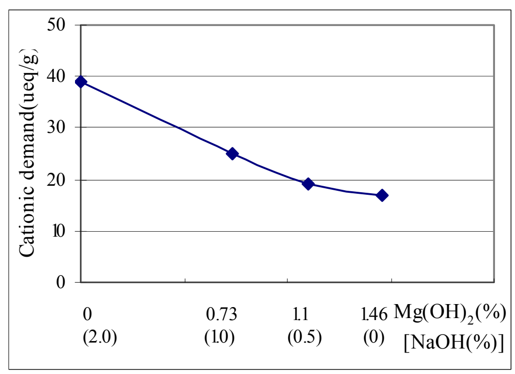


Figure 4: Effect of NaOH substitution on cationic demand

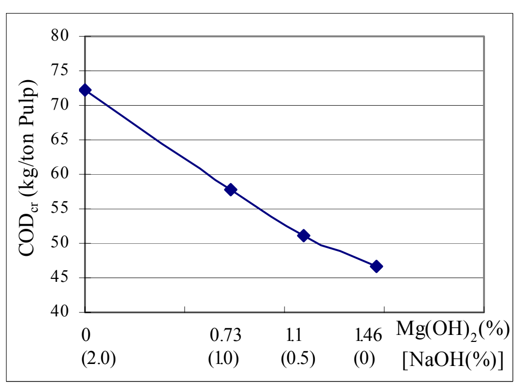
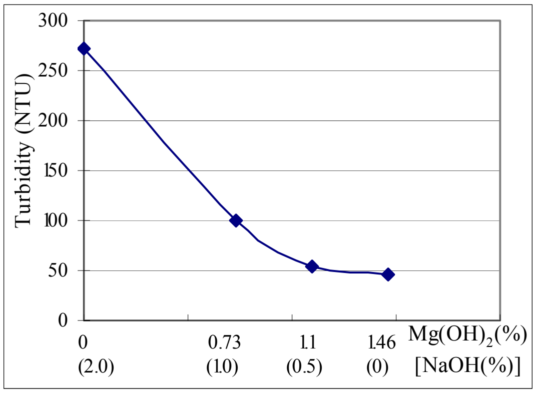
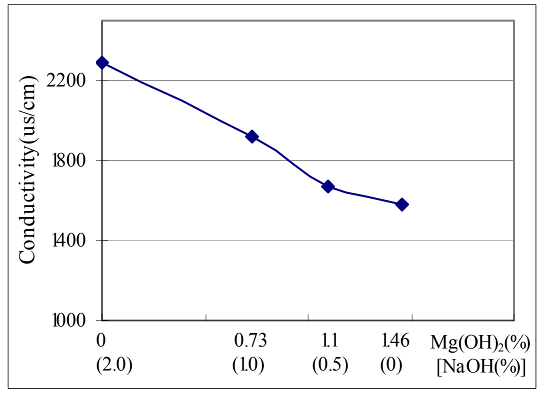


Figure 5 Effect of NaOH substitution degree on COD_{cr}



(a) Turbidity *vs.* substitution degree



(b) Conductivity *vs.* substitution degree

Figure 6: Effect of $Mg(OH)_2$ substitution on turbidity and conductivity

Effect of NaOH substitution with $Mg(OH)_2$ on the dissolution of organics and inorganics

Figure 6a plots the effect of NaOH substitution with $Mg(OH)_2$ on the effluent turbidity. With increasing the NaOH substitution with $Mg(OH)_2$, turbidity decreased dramatically from 273 to 73 NTU, indicating the presence of fewer particles in the filtrate. When NaOH was replaced completely by $Mg(OH)_2$ ($Mg(OH)_2$ charge = 1.46%), turbidity decreased by 83%. Therefore, the pulp yield loss during bleaching is lower when more NaOH is replaced by $Mg(OH)_2$, as an alkali source, in peroxide bleaching. Effluent conductivity, shown in Figure 6b, also decreased significantly (by about 31%) as $Mg(OH)_2$ increased from 0 to 1.46%. Due to the low alkalinity of $Mg(OH)_2$, the amount of organics and inorganics generated in $Mg(OH)_2$-based bleaching is much lower than that in NaOH-based bleaching. Therefore, the required amount of alkali is relatively low.

CONCLUSIONS

When increasing the NaOH substitution with $Mg(OH)_2$ during TMP peroxide bleaching, the brightness and physical strength of the bleached pulp slightly decreased, while opacity and bulk increased significantly. Residual peroxide increases obviously, indicating a considerable decrease in peroxide consumption. Furthermore, the amount of anionic trash and the COD_{cr} are considerably reduced, which is beneficial for both papermaking wet-end and wastewater treatment. The amounts of organics and inorganics decrease significantly due to the low alkalinity of $Mg(OH)_2$. Therefore, both the production cost and the polluting load of the effluent could be reduced and some pulp properties could be improved by the NaOH substitution with $Mg(OH)_2$, as the alkali source in peroxide bleaching of HYP, used in the manufacture of some paper grades with relatively lower requirements of brightness and pulp strength, and higher requirements of bulk and opacity, such as LWC, SC, newsprint, ivory board, munken paper, etc.

ACKNOWLEDGEMENTS: The authors would like to acknowledge the financial support received from the International Scientific and Technological Joint Project of China and Canada (Grant No. 2008DFA91290).

REFERENCES

[1] M. Nyström, J. Pykålåinen and J. Lehto, *Pap. Puu*, **75**, 419 (1993).
[2] Z. He, Y. Ni and E. Zhang, *J. Tianjin University Science Technology*, **21**, 17 (2004).
[3] H. U. Suess, M. Del Grosso, K. Schmidt *et al.*, *Appita J.*, **55**, 419 (2001).
[4] C. Chi, Z. Zhang and G. Huang, *China Pulp Paper*, **25**, 47 (2006).
[5] S. Maughan, E. Beddoe, R. E. Cox *et al.*, in *Procs. 46th APPITA Annual General Conference*,

Launceston, Australia, 1992, pp. 123-131.
[6] M. Mahagaonkar and J. Abbot, *Appita J*., **48**, 40 (1995).
[7] P. Griffiths and J. Abbot, *Appita J*., **47**, 50 (1994).
[8] C. Chi and Z. Zhang, *China Pulp Paper*, **26**, 10 (2007).
[9] D. F. Wong, J. A. Schmidt and C. Heitner, in *Procs. 91st PAPTAC Annual Meeting*, Montreal, Canada, 2005, pp. D723-730.
[10] Z. Li, G. Court, R. Belliveau *et al*., *Pulp Pap. Canada*, **106**, 125 (2005).
[11] Z. He, X. Qian and Y. Ni, *J. Pulp Pap. Sci*., **32**, 47 (2006).
[12] J. X. Zhang, Y. Ni, Y. Zhou and D. Joliette, in *Procs. 90th PAPTAC Annual Meeting*, Montreal, Canada, 2004, pp. B1419-1422.
[13] Z. He, M. Wekesa and Y. Ni, *Tappi J*., **3**, 27 (2004).
[14] L. Yu and Y. Ni, *Appita J*., **58**, 138 (2005).
[15] L. Yu and Y. Ni, *Pulp Pap. Canada*, **108**, 39 (2007).
[16] Standard method for analysis of peroxides, Canadian Pulp Paper Association (CPPA), Standard J. 16P, 2005.
[17] Standard method for chemical oxygen demand, Canadian Pulp Paper Association (CPPA), Standard H.3, 2005.