EFFICIENCY AND EFFLUENT CHARACTERISTICS FROM $Mg(OH)_2$-BASED PEROXIDE BLEACHING OF HIGH-YIELD PULPS AND DEINKED PULP

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Received January 18, 2010

The present research project, devoted to peroxide bleaching, evaluated magnesium hydroxide [$Mg(OH)_2$] as a substitute of sodium hydroxide [NaOH] for different mechanical pulps and deinked pulp. The analysis of the results obtained on both TMP and CTMP showed that the use of $Mg(OH)_2$ as a substitute of NaOH in peroxide bleaching allowed a reduction in both magnesium hydroxide and sodium silicate concentration, and a higher concentration of residual peroxide, which could be recirculated in the process. In deinked pulp, a significant reduction in $Mg(OH)_2$ concentration was also achieved. The yield of the bleaching process was improved by 1 to 2%, yet the final brightness level was slightly lower. Other benefits related to the effluent were observed, such as a significant reduction of the cationic demand and a decrease of some environmental parameters, *e.g.* the biochemical oxygen demand (BOD), the chemical oxygen demand (COD), the dissolved solids (DS) and the total organic carbon (TOC).

Keywords: bleaching, mechanical pulp, deinked pulp, magnesium hydroxide, efficiency, environment

INTRODUCTION

For the production of new value-added paper, the pulp and paper industry requires mechanical pulps with higher brightness levels. The most frequently used bleaching chemical is hydrogen peroxide. However, the efficiency of this oxidizing agent always seems to reach a ceiling when applied to both softwood[1,2] and hardwood[3] mechanical pulps.

Conventional peroxide bleaching uses sodium hydroxide as an alkali source, necessary for producing the bleaching agent, the hydroperoxyl anion. Sodium hydroxide is a strong alkali; in water solution, it is totally dissociated. High alkalinity degrades the organic compounds that are responsible for the cationic demand and chemical oxygen demand effluent load. Magnesium hydroxide is a weaker alkali which, in spite of its low solubility, can be used during peroxide bleaching. In fact, He and Zhang[4,5] reported that the use of an alkali source, such as magnesium hydroxide, can be efficient during bleaching of mechanical pulps. The levels of brightness obtained were similar with those attained in conventional peroxide bleaching. Moreover, a lower alkalinity is beneficial for the bleaching effluent, as it decreases the chemical oxygen demand.

The present research project, dedicated to peroxide bleaching, evaluates magnesium hydroxide as a sodium hydroxide substitute for different commercial pulps, such as thermomechanical softwood pulp (TMP), chemithermomechanical hardwood pulp (CTMP) and deinked pulp. The results obtained will be discussed in terms of bleaching efficiency, chemical characteristics of the bleached pulps and environmental characterization of the bleaching effluents.

MATERIALS AND METHOD

Three pulps from different Canadian mills were selected for bleaching experiments: a TMP pulp (softwood) made from balsam fir and spruce, a CTMP pulp (hardwood) produced from aspen and a deinked pulp composed of 70% old newsprints (ONP) and 30% old magazines

(OMG). The three pulps were screened prior to pre-bleaching sampling, then pretreated with DTPA. Bleaching with peroxide was conducted at 70 °C, for 180 min, at 20% consistency. The procedures for all results are described in literature.[6]

RESULTS AND DISCUSSION

Efficiency of magnesium hydroxide $Mg(OH)_2$-based peroxide bleaching

In the investigations, magnesium hydroxide was used as a 61% commercial aqueous suspension. Table 1 presents the optimization of the chemical concentrations of the bleaching liquors for $Mg(OH)_2$-based peroxide.

Magnesium hydroxide as an alkali source was efficient during peroxide bleaching of TMP, CTMP and deinked pulps, as presented in Figure 1. The brightness levels were slightly lower, by 1.4, 0.9 and 1.7%, respectively for TMP, CTMP and deinked pulps, with the use of magnesium hydroxide. A lower concentration of alkali was necessary with magnesium hydroxide, compared to the use of sodium hydroxide for conventional bleaching. The reduction of alkali concentration during bleaching with magnesium alkali was of 75% for TMP pulp, 50% for CTMP pulp and 90% for deinked pulp. Also, the sodium silicate concentration was reduced for TMP and CTMP pulps. Magnesium alkali protected the yield of pulps by about 1 to 2%, significantly reduced the cationic demand and increased the amount of residual peroxide, as described in Table 2.

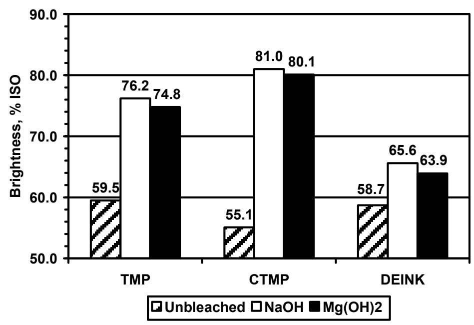

Figure 1: Brightness of different pulps *vs* alkalinity bases (± 0.2% ISO)

Table 1
Composition of bleaching liquors

	TMP		CTMP		DEINK	
Parameter	NaOH	$Mg(OH)_2$	NaOH	$Mg(OH)_2$	NaOH	$Mg(OH)_2$
H_2O_2, %	4.00	4.00	4.00	4.00	3.00	3.00
Na_2SiO_3, %	3.00	2.00	3.00	2.00	3.00	3.00
Alkali, %	3.02	0.76	3.02	1.51	2.36	0.24

Table 2
Yield, cationic demand and residual peroxide for bleached pulps

Parameter	TMP	CTMP	DEINK
Yield, % (± 0.3)			
NaOH	96.0	95.3	98.0
$Mg(OH)_2$	98.2	97.1	99.1
Cationic demand, meq/L (± 1.0)			
NaOH	22.7	14.9	19.3
$Mg(OH)_2$	4.5	6.8	2.3
Residual peroxide, % (± 0.02)			
NaOH	1.09	0.87	0.96
$Mg(OH)_2$	2.24	1.24	2.03

Chemical, optical and physical properties of bleached pulps

Brightness and some chemical properties, such as carboxylic acids (COOH), acetone extractives of the bleached pulps, dissolved lignin, as well as Mg and Na in the bleaching effluent, were evaluated. As to the carboxylic acids content presented in Table 3, the results indicate that, at a similar brightness level, $Mg(OH)_2$ in the peroxide bleaching produces a lower amount of carboxylic acids (average of 24%) than NaOH. The difference regarding the formation of carboxylic acids was more significant for TMP pulp, probably due to the much higher number of functional groups of lignin.[7] The acetone extractive contents were reduced for TMP bleached pulp, yet no differences were recorded as to the use of $Mg(OH)_2$ or NaOH. As for the CTMP pulp and deinked pulp, the extractive contents were almost similar to those of unbleached pulps. Lower contents of dissolved lignin in the bleaching effluent for all bleached pulps were achieved when using $Mg(OH)_2$, compared to the use of NaOH, probably due to the fact that $Mg(OH)_2$ is a weaker base than NaOH, which results in a lower dissolution reaction of the oxidized lignin and lower pH during bleaching.

Electron Spectroscopy for Chemical Analysis (ESCA) has been conducted to better understand the oxidation mechanism. The O/C ratios (± 0.01) for the three pulps are listed in Table 4.

The increase in the O/C ratios suggested the presence of an oxidation mechanism, no difference being recorded between the two alkali bases, except for the pulp deinked with NaOH. The high resolution XPS spectrum of the carbon 1s electron may be divided into four broad classes, for increasing the chemical shifts.[8,9]

C 1sb: Carbon atoms bonded to carbon and/or hydrogen, *e.g.* C–C, C–H

C 1sa: Carbon atoms bonded to a single oxygen, other than a carbonyl oxygen, *e.g.* C–O–H

C 1sc: Carbon atoms bonded to two non-carbonyl oxygens, or to single carbonyl oxygen, *e.g.* O–C–O and C=O

C 1sd: Carbon atoms bonded to carbonyl and non-carbonyl oxygen, *e.g.* O–C=O

Table 3
Brightness and chemical properties of unbleached (UB) and bleached pulps and dissolved lignin in the effluent

	Brightness, % ISO (± 0.2)	COOH, mmol/kg (± 3)	Extractives, % (± 0.1)	Dissolved lignin, % (± 0.01)
TMP				
UB	59.4	134	1.6	–
NaOH	76.2	243	0.9	0.77
$Mg(OH)_2$	75.3	190	1.0	0.34
CTMP				
UB	55.9	93	0.8	–
NaOH	81.0	152	0.5	1.29
$Mg(OH)_2$	79.7	125	0.6	0.65
DEINK				
UB	58.5	105	0.8	–
NaOH	65.2	179	0.6	0.59
$Mg(OH)_2$	63.9	124	0.6	0.15

Table 4
O/C ratios of unbleached and bleached pulps

	TMP	CTMP	DEINK
Unbleached	0.49	0.43	0.52
NaOH	0.53	0.51	0.53
$Mg(OH)_2$	0.54	0.49	0.57

Figures 2 to 4 plot the ESCA spectra of carbon 1s for unbleached TMP pulp, TMP pulp bleached with peroxide-NaOH and TMP pulp bleached with peroxide-$Mg(OH)_2$. For bleached TMP pulp and bleached deinked pulp, the slightly higher reductions – by 5 and 10% – of the C 1sb peak of $Mg(OH)_2$ suggested that there is less lignin at the handsheet surface. However, for bleached CTMP pulp, the result was reversed, as the C 1sb peak of NaOH at the handsheet surface suggested a slightly lower concentration of lignin – by 6%. The slightly lower concentration of lignin at the paper surface with the use of $Mg(OH)_2$ could be beneficial, inducing less brightness reversion and better paper surface properties.

Inductively Coupled Plasma (ICP) was applied to measure the Mg content in bleached pulp and in the effluent, to evaluate the Mg ratio in each phase. For bleached TMP and CTMP pulps, 38% of Mg remained in the pulp and 62% of Mg remained in the effluent, compared to 12 and 88% for Na, respectively. As for the bleached deinked pulp, 79% of Mg remained in the pulp and 21% remained in the effluent, compared to the same results for Na.

The results listed in Table 5 show that, in comparison with NaOH, the use of $Mg(OH)_2$ improved the resulting opacity of bleached TMP pulp and bleached deinked pulp. The use of NaOH was probably responsible for the higher loss of organic compounds and fine fibres, resulting in a lower yield. However, NaOH allowed an increase of the burst index for all pulps and a better breaking length for CTMP pulp and deinked pulp. As for the CTMP pulp, the two alkaline bases were useful for their better tear index. The use of $Mg(OH)_2$ allowed no improvement of the physical properties, which could be explained by the lower formation of carboxylic acids, having a negative impact on fibre swelling, a lower alkalinity level reducing the link between fibres, while the presence of cation Mg^{2+} allowed a decrease in fibre swelling.

Environmental impact of bleaching processes

Environmental characterization and evaluation of the total impact of the bleaching process induced by the bleaching effluent and bleached pulp were performed. Effluent quality was improved by the use of magnesium hydroxide: less organic compounds were found in the effluent, as due to the actual reduction of magnesium alkali – as actually reported in literature for the use of alkali.[7] The results on the use of magnesium hydroxide, compared to the use of sodium hydroxide, presented in Table 6, explain the significant average reductions presented in Table 7. Probably, the use of a weaker base like $Mg(OH)_2$ did allow the reduction of the deacetylation or demethylation reactions, involving the use of NaOH and of fewer organic compounds, such as acetic acid or methanol – produced in a higher yield.

Table 5
Optical and physical properties of unbleached (UB) and bleached pulps

	Opacity, % (± 0.2)	Breaking length, km (± 0.1)	Tear index, $mN*m^2/g$ (± 0.2)	Burst index, $kPa*m^2/g$ (± 0.1)
TMP				
UB	96.7	4.5	7.5	2.3
NaOH	88.4	4.7	7.8	2.7
$Mg(OH)_2$	90.2	4.4	7.7	2.3
CTMP				
UB	94.8	0.9	4.7	0.3
NaOH	83.7	1.6	7.4	0.6
$Mg(OH)_2$	84.2	1.2	6.2	0.4
DEINK				
UB	97.3	3.9	8.2	2.2
NaOH	91.4	5.0	8.2	3.0
$Mg(OH)_2$	95.0	4.1	8.3	2.4

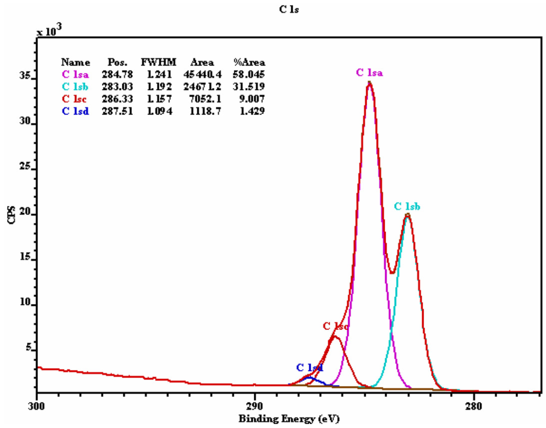

Figure 2: ESCA of carbon for unbleached TMP pulp

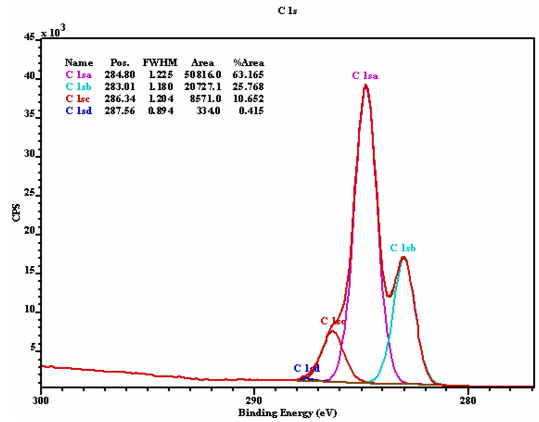

Figure 3: ESCA of carbon for TMP pulp bleached with NaOH

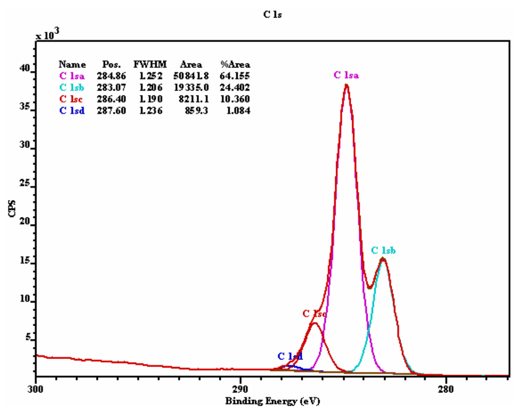

Figure 4: ESCA of carbon for TMP pulp bleached with $Mg(OH)_2$

Table 6
Biochemical oxygen demand, chemical oxygen demand, dissolved solids and total organic carbon for different pulps

Parameter	TMP	CTMP	DEINK
Biochemical oxygen demand, kg/adt (± 0.4)			
NaOH	23.4	42.5	13.9
$Mg(OH)_2$	11.3	25.1	5.8
Chemical oxygen demand, kg/adt (± 0.5)			
NaOH	76.1	84.4	60.0
$Mg(OH)_2$	49.3	59.1	32.3
Dissolved solids, kg/adt (± 0.8)			
NaOH	106.1	93.1	114.5
$Mg(OH)_2$	37.6	57.8	30.6
Total organic carbon, kg/adt (± 0.6)			
NaOH	24.6	26.5	18.0
$Mg(OH)_2$	13.2	18.1	7.0

Table 7
Reduction of effluent charge

Parameter	TMP	CTMP	DEINK
BOD_5, % (± 1)	52	41	58
COD, % (± 1)	35	30	46
DS, % (± 1)	65	38	73
TOC, % (± 1)	46	32	61

CONCLUSIONS

Magnesium hydroxide was efficient during peroxide bleaching. Magnesium alkali concentration was reduced by 75% for TMP pulp, by 50% for CTMP pulp and by 90% for deinked pulp, compared to the sodium alkali concentration. Brightness was slightly lower for the three pulps compared to conventional bleaching: the difference was of 1.4% ISO for TMP pulp, 0.9% ISO for CTMP pulp and 1.7% ISO for deinked pulp. The lower solubility of $Mg(OH)_2$ at reduced and more constant pH levels contributed to a slower kinetic reaction, with a probably lower concentration of the HOO^- ion during the whole bleaching process. This could be useful to the bleaching reaction, because fewer secondary dissolution reactions of organic compounds by the OH^- and HOO^- ions occurred. Magnesium hydroxide significantly protected the yield of the pulps and reduced the cationic demand, resulting in less anionic trash, which could reduce the use of polymers in paper formation. The analysis by ESCA techniques suggested that, for all pulps, the lignin compounds were not located at the same concentration at the handsheet surface and that, apparently, the alkali bases have some influence. Effluent quality was improved with magnesium alkali: BOD_5 and COD were respectively decreased by 50 and 37%, on the average. The alkalinity cost provided by [$Mg(OH)_2$ + Na_2SiO_3] compared to [NaOH + Na_2SiO_3] could be reduced from 50 to 60%, depending on the market price of these commodities.

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