USING Mg(OH)$_2$ IN PEROXIDE BLEACHING OF WHEAT STRAW SODA-AQ PULP

Yanlan Liu, a Kefu Chen, a Keith Luo, b Jun Li, a,* Lihuan Mo, a and Jun Xu a

The peroxide bleaching of high yield pulps from wood with Mg(OH)$_2$ has been developing recently in the pulp and paper industry. However, there is still a lack of data on the application of Mg(OH)$_2$ in peroxide bleaching of non-wood fibres. In this work, our purpose was to study the effect of Mg(OH)$_2$ on peroxide bleaching of wheat straw soda-AQ pulp. The results showed that Mg(OH)$_2$ significantly improved peroxide bleaching efficiency (expressed as the ratio between the brightness gain and the H$_2$O$_2$ consumption) and selectivity (expressed as the ratio between the brightness gain and the viscosity losses) of wheat straw soda-AQ pulp. The brightness, viscosity, and yield of bleached pulp can be significantly enhanced by increasing the replacement ratio of Mg(OH)$_2$. However, at 100% replacement of NaOH with Mg(OH)$_2$, the brightness of bleached pulp was much lower than that of the bleached pulp with NaOH as the sole alkaline source. When 24 to 73% of the NaOH was replaced with Mg(OH)$_2$, the COD of the bleaching filtrate was 11 to 38% lower than that of the NaOH as the sole alkaline source. The lower solubility and alkalinity of Mg(OH)$_2$, as well as the reduction of Cu ion content in bleached pulp were proposed as accounting for the favorable effect of Mg(OH)$_2$ on peroxide bleaching of wheat straw soda-AQ pulp.

Keywords: Mg(OH)$_2$; Wheat straw pulp; Hydrogen peroxide bleaching; Brightness

Contact information: a: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, 510641, Guangzhou, China; b: Forest Products Business Unit, Alberta Innovates Technology Futures, T6N1E4, Edmonton, Alberta, Canada; Corresponding Author: papercctv@yahoo.com.cn

INTRODUCTION

Agricultural residuals such as wheat straw are renewable resources that are easier to regenerate than wood. It has been reported that the world straw production is over 500 million tons per year (Yilmaz 1995). On the other hand, research and practice indicated that wheat straw is a valuable raw material for manufacturing paper (Li et al. 2009; Hedjazi et al. 2009). Hence, in response to increasing cost of manufacturing and shortages of wood fibres, papermakers use wheat straw as a raw material for papermaking, especially in countries having inadequate forest resources, such as China, India, and Spain, etc. Meanwhile, wheat straw pulping is of interest not only in countries lacking wood; research efforts have also been recorded from regions such as North America (Watson et al. 1998). However, the main driving force for using straw for papermaking in North America mainly has stemmed from environmental concerns rather than the immediate shortfall of wood fibre (Law et al. 2001). In the Canadian provinces of Alberta and Saskatchewan, as well as the state of Oregon in the USA, major producers of grain, farmers are confronting disposal difficulties, since burning of straw is damaging...
to the environment. In addition, plowing the straw back into the ground is labor and cost intensive. Hence, wheat straw for pulp and papermaking is not only beneficial for environmental protection, but also promotes the economy of agriculture and society.

Pulp bleaching with hydrogen peroxide has become an attractive process to be used in both elemental chlorine-free (ECF) bleaching technology and totally chlorine free (TCF) bleaching technology. Hydrogen peroxide bleaching of pulp is typically carried out under alkaline conditions. The dissociation of hydrogen peroxide in alkaline media can be expressed as follows: H$_2$O$_2$ + HO$^-$ → HOO$^-$ + H$_2$O. The hydrogen peroxide anion (HOO$^-$) is mainly responsible for the reduction of the chromophores concentration (Mota et al. 2007). The alkali source used in conventional pulp hydrogen peroxide bleaching is sodium hydroxide (NaOH). However, it has been indicated that the use of NaOH as a bleaching auxiliary had undesired side-effects in production practice (Ni 2005). In recognition of the drawbacks associated with the NaOH-based process, peroxide bleaching using magnesium hydroxide (Mg(OH)$_2$) has been receiving much attention recently. In fact, studies done by many researchers on various wood species has shown very interesting results (Zeinaly et al. 2009; He et al. 2008; Li et al. 2004). Mg(OH)$_2$ in a peroxide bleaching process can bring many benefits to pulp and paper mills, including a lower chemical oxygen demand, less formation of anionic trash, lower oxalate scaling, and higher bulk of the bleached pulps. On the other hand, magnesium hydroxide can provide a cost-effective partial replacement of sodium hydroxide and magnesium sulfate for chemical pulp, and the Squamish pulp mill has converted the existing magnesium sulfate system to magnesium hydroxide system in order to benefit from the significant cost savings (Thakore et al. 2005). However, the works described above mainly concerned high yield pulps from wood. There is still a lack of data on application of Mg(OH)$_2$ for peroxide bleaching of non-wood fibres.

For annual plant pulping the soda-AQ process has been employed most often (Hedjazi et al. 2009). The present work seeks to make a contribution to the study of Mg(OH)$_2$ on peroxide bleaching of wheat straw soda-AQ pulp. There are two aspects of this problem to be addressed. The first question involves how the partial substitution of NaOH with Mg(OH)$_2$ may affect the characteristics of the bleached pulp and filtrate. The second problem relates to the effect of Mg(OH)$_2$ on the metal ion profiles in the bleached pulp. Therefore, the results will be discussed in terms of brightness, viscosity, yield, ash, and metal contents of the bleached pulp, also including the residual H$_2$O$_2$ and COD of the bleaching filtrates.

EXPERIMENTAL

Materials

Wheat straw was collected from Alberta, Canada. The stalks were chopped into 3 to 5 cm pieces, then wet-depithed and air-dried for pulping. 50%(W/W) H$_2$O$_2$ solution, 50% (W/W)NaOH solution, diethylene triamine pentaacetic acid sodium salt (DTPA), MgSO$_4$.7H$_2$O, and Mg(OH)$_2$ powder were analytical reagents, supplied by Fischer Scientific, while the 40%(W/W) Na$_2$SiO$_3$ solution was supplied by EMD Chemicals Inc.
All chemical charges used in pulping and bleaching experiments were expressed as percent on pulp oven dry (o.d.) basis.

**Cooking**

Pulping was carried out in the lab of the Forest Products Business Unit, Alberta Innovates Technology Futures. The laboratory digester system consisted of a 45 L reaction tank, a 70 L liquor tank, a 95 liters/min liquor pump, a 1 m² steam heat exchanger, and a computer control and data acquisition software system. The following experimental conditions were applied in the pulping: total alkali charge: 16%; liquor to wood ratio: 1:18; AQ charge: 0.1%; cooking temperature: 160 °C; heating time to cooking temperature: 60 min; cooking time at 160 °C: 60 min. After cooking, the wheat straw pulp was washed, disintegrated in a laboratory disintegrater, and then screened on a 0.15 mm laboratory slot screen. The screened pulp had a kappa number of 8.3, viscosity of 1189 mL.g⁻¹, brightness of 40.1% ISO, and ash of 1.38%.

**Peroxide Bleaching**

The bleach liquors were prepared by adding, in order, the required amounts of sodium silicate, sodium hydroxide, diethylene triamine pentaacetic acid sodium salt (DTPA), magnesium sulfate, and hydrogen peroxide solution to the beaker containing distilled water. Then, the mixed solution was added to the pulp in a polyethylene bag. When Mg(OH)₂ was needed, it was added directly into the pulp before the bleach liquor. Good mixing was achieved with kneading for two minutes. The polyethylene bag was sealed and placed in a water bath for the desired retention time. The conditions for peroxide bleaching stage are listed in Table 1. The Mg(OH)₂ replacement ratio was defined as the weight equivalent of Mg(OH)₂ that replaced NaOH, on a total alkaline charge of 3.00% NaOH, and was reported here as percent replacement. After the required retention time, a liquid sample was taken to determine the final pH, the residual peroxide, and COD. The pulp slurry was washed thoroughly with distilled water.

<table>
<thead>
<tr>
<th>Mg(OH)₂ replacement ratio (%)</th>
<th>0*</th>
<th>24</th>
<th>48</th>
<th>73</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH (%)</td>
<td>3.00</td>
<td>2.27</td>
<td>1.55</td>
<td>0.82</td>
<td>0.00</td>
</tr>
<tr>
<td>Mg(OH)₂ (%)</td>
<td>0.00</td>
<td>0.73</td>
<td>1.45</td>
<td>2.18</td>
<td>3.00</td>
</tr>
<tr>
<td>H₂O₂ (%)</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td>DTPA (%)</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>Silicate (%)</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
</tr>
<tr>
<td>MgSO₄ (%)</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>85</td>
<td>85</td>
<td>85</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>Time (min)</td>
<td>240</td>
<td>240</td>
<td>240</td>
<td>240</td>
<td>240</td>
</tr>
<tr>
<td>Consistency (%)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

0* = Control
Pulp and Filtrate Characterizations

The brightness pads were prepared according to TAPPI T218 and were measured with a Technibrite Micro TB-1C. The viscosity test was performed based on ASTMD1795-96. The contents of the metal ions, i.e., calcium, magnesium, manganese, iron, and copper ions, were measured with an inductively coupled plasma optical emission spectrometer (ICP), according to TAPPI T266.

The residual H$_2$O$_2$ and COD of the filtrate were determined according to PAPTAC J.16 and PAPTAC H.3, respectively. The H$_2$O$_2$ consumption was calculated as follows:

$$\text{H}_2\text{O}_2 \text{ consumption (\%)} = \text{Initial H}_2\text{O}_2 \text{ charge (\%)} - \text{Residual H}_2\text{O}_2 \text{ charge (\%)}$$

RESULTS AND DISCUSSION

**Brightness and H$_2$O$_2$ Consumption**

As can be seen in Fig. 1, the brightness of bleached pulp first increased significantly, then declined with the increase of the Mg(OH)$_2$ replacement ratio. In the range of 24 to 73% replacement ratio of Mg(OH)$_2$, the brightness of bleached pulp was much higher than that of the control (at 0% of Mg(OH)$_2$ replacement ratio). The result was consistent with that of bleaching mechanical pulps (Li et al. 2006).

When the replacement ratio of Mg(OH)$_2$ was 48%, the brightness of bleached pulp was the highest, 6.4% ISO higher than that of the control. However, at a 100% replacement ratio of Mg(OH)$_2$, the brightness of bleached pulp was much lower than that of the control, which was in line with the results for a CTMP hardwood pulp (Zhang et al. 2006).

![Fig. 1. Effect of Mg(OH)$_2$ replacement ratio on the pulp brightness and H$_2$O$_2$ consumption](image-url)
The improved brightness gain may be partly explained by decreased alkaline darkening in the peroxide bleaching process. Alkaline darkening occurs during peroxide bleaching and has negative effects on the brightness of bleached pulps (He et al. 2004). When Mg(OH)$_2$ was partially substituted for NaOH, the pH was lower than that of the control due to the lower solubility and alkalinity of Mg(OH)$_2$, as indicated by Fig. 2. As a result, the decrease of alkaline darkening would be partially responsible for the higher brightness. But at a 100% replacement ratio of Mg(OH)$_2$, the brightness of bleached pulp was much lower than that of the control, supposedly because of the very low initial pH, just 9.2. In hydrogen peroxide bleaching, suitably strong alkaline conditions are needed to activate H$_2$O$_2$ by generating the reactive perhydroxyl anion (HOO$^-$). If the alkalinity is too low to generate HOO$^-$ sufficiently, the brightness gain of bleached pulp would be limited. Therefore, total replacement of NaOH with Mg(OH)$_2$ had an adverse effect on the brightness of bleached pulp. As far as the brightness was concerned, the replacement ratio of NaOH with Mg(OH)$_2$ can reach up to 73% in a certain range of alkalinity.

![Fig. 2. Initial pH and final pH in peroxide bleaching](image)

Meanwhile, the peroxide consumption decreased significantly, from 4.00% to 0.63%, with the increase of Mg(OH)$_2$ replacement ratio, as shown in Fig. 1. For the similar brightness level of bleached pulp at 0% and 73% replacement of NaOH with Mg(OH)$_2$, the peroxide consumption decreased from 4.00% to 1.54%. The residual peroxide level in the filtrate was very high as comparing to that of the control. Consequently, Mg(OH)$_2$ was efficient at reducing the rate of peroxide consumption. Similar results have been obtained by other researchers (Lapierre et al. 2003). The recycle of residual peroxide of the filtrate back into the bleaching liquor has the potential to save chemical costs (Johnson et al. 2002). However, other researchers reported that a higher Mg(OH)$_2$ charge caused more hydrogen peroxide consumption when bleaching mechanical pulp (Li et al. 2006). The reason for this difference may be that the Mg(OH)$_2$...
industrial slurry used by Li et al. may have contained impurities that included transition metals ions. When more Mg(OH)\textsubscript{2} was charged, more transition metal ions were introduced into the system, which hence increased the unintended consumption of hydrogen peroxide. But the Mg(OH)\textsubscript{2} powder used in present study was USP/FCC grade, having higher purity and containing fewer transition metal ions. Therefore, the effect of transition metal ions in Mg(OH)\textsubscript{2} on peroxide consumption was negligible.

Additionally, it was found that the bleaching efficiency (expressed as the ratio between the brightness gain and the H\textsubscript{2}O\textsubscript{2} consumption) consistently increased with the increase of replacement ratio of Mg(OH)\textsubscript{2}, as indicated by Fig. 3. However, the brightness of bleached pulp at 100% replacement ratio of Mg(OH)\textsubscript{2} was much lower than that of the control because of the very low consumption (0.63\%) of H\textsubscript{2}O\textsubscript{2}. For brightness, the bleached pulp achieved the highest brightness at 48% replacement ratio of Mg(OH)\textsubscript{2}.

![Figure 3. Effect of Mg(OH)\textsubscript{2} replacement ratio on bleaching efficiency](image)

**Viscosity and Yield**

Another benefit of Mg(OH)\textsubscript{2} on wheat straw soda-AQ pulp peroxide bleaching was much higher viscosity and yield of the bleached pulp, as shown in Fig. 4. The viscosity and yield of bleached pulp consistently increased with Mg(OH)\textsubscript{2} replacement ratio. When the brightness reached the maximum value at 48% replacement ratio of Mg(OH)\textsubscript{2}, the viscosity and yield of bleached pulp were higher than that of the control by 107 mL.g\textsuperscript{-1} and 7.3\%, respectively. The presence of a strong alkali could facilitate hemicelluloses and cellulose degradation, causing the reduction of yield and viscosity of the bleached pulp. Partial substitution of weakly alkaline Mg(OH)\textsubscript{2} for NaOH promoted peroxide bleaching and protection of the carbohydrates.

The bleaching selectivity (expressed as the ratio between the brightness gain and the viscosity losses) was significantly enhanced at first, then decreased at a 100% replacement ratio of Mg(OH)\textsubscript{2}, as shown in Fig. 5. The reason for this was that at a 100% replacement ratio of Mg(OH)\textsubscript{2} a much lower brightness of bleached pulp caused the
reduction of brightness gain, even though the viscosity losses of bleached pulp decreased continually. But the bleaching selectivity of Mg(OH)₂ peroxide process remained higher than with NaOH as the sole alkaline source, as shown in Fig. 5.

Figure 4. Effect of Mg(OH)₂ replacement ratio on the viscosity and yield

Figure 5. Effect of Mg(OH)₂ replacement ratio on bleaching selectivity
COD

As indicated in Fig. 6, the COD load of bleaching filtrates at 24 to 73% replacement ratio of Mg(OH)₂ were lower than that of the control (11 to 38%). Therefore, the costs associated with effluent treatment would be significantly decreased due to the substantial reduction of COD. The lower solubility and alkalinity of the Mg(OH)₂ were believed to be the cause of the lower COD formation (Zeinaly et al. 2009). The higher COD value of filtrate from the control was attributed to the strong alkalinity of NaOH, resulting in a higher pH (Fig. 2) that decomposed peroxide to produce hydroxyl radicals, which then oxidized the polysaccharides. The oxidized polysaccharides undergo chain cleavage by beta-elimination and subsequent degradation reactions.

![Figure 6. Effect of Mg(OH)₂ replacement ratio on the COD of filtrates](image)

![Figure 7. The relation of COD with viscosity, yield of bleached pulp](image)
Figure 7 shows the relations among the COD, viscosity and yield of bleached pulp. The viscosity of bleached pulp continuously increased as the COD decreased. In addition, the pulp yield increased linearly with the decrease of COD. The lower COD is consistent with a higher yield and viscosity of bleached pulp, since the COD may come from dissolved carbohydrates, lignin, and other organic substances in the bleaching filtrate (He et al. 2004).

**Metal Ions Content**

Previous research suggested that magnesium hydroxide functioned as a cellulose protector by capturing and precipitating transition metal ions as metal hydroxides (Thakore et al. 2005). Metal hydroxides that were less soluble than magnesium hydroxide precipitated out as a result of the reaction between metal ions present in the bleach system and hydroxyl ions derived from magnesium hydroxide. Table 2 lists the solubility products (Ksp) for various metal hydroxides (Lide et al. 2001; Dence et al. 1996).

<table>
<thead>
<tr>
<th>Metal hydroxides</th>
<th>Solubility product constant (Ksp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(OH)\textsubscript{3}</td>
<td>2.8*10\textsuperscript{-39}</td>
</tr>
<tr>
<td>Cu(OH)\textsubscript{2}</td>
<td>2.2*10\textsuperscript{-20}</td>
</tr>
<tr>
<td>Fe(OH)\textsubscript{2}</td>
<td>4.9*10\textsuperscript{-17}</td>
</tr>
<tr>
<td>Mn(OH)\textsubscript{2}</td>
<td>2.0*10\textsuperscript{-13}</td>
</tr>
<tr>
<td>Mg(OH)\textsubscript{2}</td>
<td>5.6*10\textsuperscript{-12}</td>
</tr>
</tbody>
</table>

On the other hand, some authors have concluded that peroxide decomposition during pulp peroxide bleaching stage is largely determined by transition metals associated with the pulp fiber (Lapierre et al. 2003). To study the effect of Mg(OH)\textsubscript{2} on metal ions profile of bleached pulp, the content of metal ions in unbleached pulp and bleached pulp were determined.

<table>
<thead>
<tr>
<th>Mg(OH)\textsubscript{2} replacement ratio (%)</th>
<th>Cu (mg.kg\textsuperscript{-1})</th>
<th>Fe (mg.kg\textsuperscript{-1})</th>
<th>Mn (mg.kg\textsuperscript{-1})</th>
<th>Mg (mg.kg\textsuperscript{-1})</th>
<th>Ca (mg.kg\textsuperscript{-1})</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached pulp</td>
<td>185</td>
<td>55</td>
<td>11</td>
<td>1554</td>
<td>1564</td>
<td>1.38</td>
</tr>
<tr>
<td>0*</td>
<td>84</td>
<td>23</td>
<td>6</td>
<td>982</td>
<td>854</td>
<td>0.78</td>
</tr>
<tr>
<td>24</td>
<td>73</td>
<td>24</td>
<td>6</td>
<td>1428</td>
<td>730</td>
<td>1.13</td>
</tr>
<tr>
<td>48</td>
<td>79</td>
<td>23</td>
<td>6</td>
<td>1466</td>
<td>729</td>
<td>1.17</td>
</tr>
<tr>
<td>73</td>
<td>74</td>
<td>25</td>
<td>6</td>
<td>1925</td>
<td>763</td>
<td>1.33</td>
</tr>
</tbody>
</table>

* = Control

The results presented in Table 3 showed that the Cu ion content of bleached pulp was lower than that of the control and had no appreciable change when the replacement ratio of Mg(OH)\textsubscript{2} increased from 24% to 73%. It can be supposed that part of Cu ion was weakly bonded with fiber and precipitated out, since the Ksp of Cu(OH)\textsubscript{2} is much lower than Mg(OH)\textsubscript{2} (Table 2). The residual Cu ion is much more strongly bonded with the fibre, presumably due to formation of the chemical bonds, and less easily absorbed by
Mg(OH)₂ (Norkus et al. 2006). On the other hand, copper species in the solution phase are known to catalyze the decomposition of hydrogen peroxide in the pH range that would be applicable to bleaching with NaOH only (Colodette et al. 1988). Copper loosely bound to the pulp and in the solution phase was apparently adsorbed by colloidal Mg species and became deactivated (Colodette et al. 1989). Therefore, the use of Mg(OH)₂ lowered both the amount of active Cu species and the pH of the system. Both effects would be expected to improve the stability of hydrogen peroxide. Table 3 also indicated that the content of Mn ion and Fe ion in the bleached pulp maintained the same level with the increase of Mg(OH)₂. Presumably the Mn and Fe ions were more strongly bonded with cellulose than Cu ion in pulp. It was comprehensible that the residual Mg ion in bleached pulp increased gradually along with the replacement ratio of Mg(OH)₂.

CONCLUSIONS

1. Mg(OH)₂ significantly improved the peroxide bleaching efficiency and selectivity of wheat straw soda-AQ pulp. The brightness, yield, and viscosity of bleached pulp significantly increased with the increase of replacement ratio of Mg(OH)₂; meanwhile the consumption of H₂O₂ significantly decreased. However, at a 100% replacement ratio of Mg(OH)₂, the brightness of bleached pulp was much lower than that of pulp bleached with NaOH as the sole alkaline source. At 48% replacement ratio of Mg(OH)₂, the brightness of bleached pulp reached the highest level, 6.4% ISO higher than that of pulp bleached with NaOH as the sole alkaline source, and the viscosity and yield were higher, 107 mL.g⁻¹ and 7.27%, respectively. The lower solubility and alkalinity of Mg(OH)₂ was partly responsible for this favorable effect on peroxide bleaching of wheat straw soda-AQ pulp.

2. The COD load of filtrates from 24 to 73% replacement ratio of Mg(OH)₂ peroxide bleaching process were lower (11% to 38%) than that of the filtrate from the NaOH as the sole alkaline source. In addition, the viscosity and yield of bleached pulp continuously increased with the decrease of COD.

3. The reduction of Cu ion content was another explanation for the improved peroxide bleaching efficiency and selectivity of wheat straw soda-AQ pulp.

REFERENCES CITED


“Alkaline sulfite-anthraquinone (AS/AQ) pulping of wheat straw and totally chlorine free (TCF) bleaching of pulps,” *Industrial Crops and Products* 29, 28-36.


Article submitted: December 13, 2010; Peer review completed: February 21, 2011; Revised version received and accepted: February 25, 2011; Published: February 28, 2011.