**Mg(OH)\(_2\)**-Based Hydrogen Peroxide Bleaching of Deinked Pulp

Na Yun\(^{a,b,*}\) and Beihai He\(^{a,c}\)

Sodium hydroxide (NaOH) has been used as an alkali source in conventional hydrogen peroxide bleaching. In the present work, partial and total replacement of NaOH with magnesium hydroxide (Mg(OH)\(_2\)) as the alkali source for hydrogen peroxide bleaching of deinked pulp was studied. The bleached pulp was studied with respect to brightness, post color (P.C.) number, and mechanical properties (i.e., the tensile, tear, and burst indices). The bleaching effluent was measured for residual peroxide, pH value, and chemical oxygen demand (COD). The main results from this work were that the brightness and mechanical properties of bleached pulp increased while the P.C. number declined when NaOH was partially replaced with Mg(OH)\(_2\). However, the total substitution of NaOH with Mg(OH)\(_2\) resulted in a slight decrease in the brightness and mechanical properties in comparison with NaOH as the sole alkali source. Additionally, the residual peroxide of the bleaching filtrate increased from 3% to 61% and the COD load of the bleaching effluent decreased from 20% to 25% when NaOH was replaced with Mg(OH)\(_2\) at various replacement ratios.

**Keywords:** Deinked pulp; Hydrogen peroxide bleaching; Mg(OH)\(_2\); Brightness; COD

**INTRODUCTION**

Interest in waste paper pulp, a valuable feedstock for the pulp and paper industry, has continued to grow in recent years due to favorable prices and environmental demands, when compared with virgin pulp (Vincent et al. 1997; Kopania et al. 2008). At present, more than half of the raw materials used worldwide by the pulp and paper industry originate from waste paper (Dorris et al. 2011). In 2012, the total amount of waste paper pulp used in China was 59.83 million metric tons, which accounted for about 64% of the total amount of raw materials used in the paper industry (China Paper Association 2013). Some of the waste paper pulp had its origins in the production of brown liner board for box manufacture. However, in recent decades, there has been a drastic increase in the use of waste paper pulp to produce, through deinking, white grades such as higher quality newsprint, tissue, supercalendered (SC) paper, and light weight coated (LWC) paper (Süss et al. 1995; Vincent et al. 1997; Dorris et al. 2011). The use of waste paper pulp for high brightness paper grades has increased the demand for bleaching chemicals that can produce paper products with equivalent brightness to that produced from virgin pulp.

Brightness is one of the most important quality criteria for printing and writing paper grades (Leduc et al. 1998). The high brightness demanded by these grades requires...
hydrogen peroxide bleaching. Hydrogen peroxide has been used commercially as a pulp bleaching agent to brighten mechanical pulp for more than seven decades (Sain et al. 1997) and is now also widely used in waste paper pulp bleaching (Hsieh et al. 2006; Suess 2010). The role of hydrogen peroxide in waste paper pulp bleaching is to improve the brightness by reacting with various colored carbonyl-containing structures in lignin (Hanchett 1994; Behrooz et al. 2012). The advantages of using hydrogen peroxide are the low investment cost and its effectiveness under alkaline conditions. The dissociation of hydrogen peroxide and the formation of the perhydroxyl anion under alkaline conditions can be illustrated as follows: $\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HOO}^- + \text{H}_2\text{O}$.

The alkali source used in conventional hydrogen peroxide bleaching is sodium hydroxide (NaOH). Sodium hydroxide is an efficient and inexpensive alkali, with a drawback of high pH in the initial phase of bleaching, leading to dissolution of organic substances from the pulp that will decrease the pulp yield and increase the effluent load and, in the end, impact the environment (Hu and Zhang 2009). Thus, alkaline conditions are required for hydrogen peroxide bleaching, but conditions that are too alkaline are detrimental. One solution is to replace NaOH with Mg(OH)$_2$ in peroxide bleaching (Zeinaly et al. 2009; He and Ni 2008). Mg(OH)$_2$ has been reported to be an attractive alkali source in peroxide bleaching because it is a solid and can be released slowly into the system, thus acting as a buffer to prevent rapid changes in pH (Johnson et al. 2002). Previous studies have shown the environmental benefits of using magnesium hydroxide on wood mechanical or chemimechanical pulp (e.g., pressurized groundwood, thermomechanical pulp, and chemithermomechanical pulp) in peroxide bleaching (Hietanen et al. 2013; Leduc et al. 2010; Kong et al. 2009) and wood chemical pulp (e.g., kraft pulp) in extraction stages (Gibson and Wajer 2003), as well as non-wood chemical pulp (e.g., wheat straw soda-AQ pulp) in peroxide bleaching (Liu et al. 2010). However, the application of Mg(OH)$_2$ for peroxide bleaching of deinked pulp has not been well-documented in the literature (Leduc et al. 2010; Burnet et al. 2010).

The objective of the present study was to gain systematic knowledge of the effect of replacing NaOH with Mg(OH)$_2$ on the properties of deinked pulp and effluent load. Conventional NaOH-based bleaching agents were gradually replaced with a high-purity Mg(OH)$_2$-based additive. The bleached pulp was then studied in terms of brightness, post color (P.C.) number, and mechanical properties. In addition, the effect of the Mg(OH)$_2$-based additive on the residual peroxide and chemical oxygen demand (COD) of the bleaching filtrates was assessed.

**EXPERIMENTAL**

**Materials**

The deinked pulp (DIP) sample (70% wt. United States waste paper PS#8, 10% wt. European waste paper standard A9, 10% wt. Hong Kong waste paper, 10% wt. Dowling paper) was obtained from a paper mill located in Guangdong Province, China. The brightness of the unbleached pulp sample was 45.7% ISO.

All chemicals used in bleaching and analyses were of analytical grade and supplied by Guangzhou Chemical Reagent Factory, China. Magnesium hydroxide powder was used in this experiment, containing Mg(OH)$_2$ 98%, Fe 31.5 ppm, Mn 1.7 ppm, and Cu less than 1 ppm; the median size (D50) was 10.62 μm and the size
distribution (D10-D90) was from 5.60 μm to 24.59 μm. Chemical dosing of the additives was calculated on an oven dry (o.d.) pulp mass basis.

**Methods**

*Hydrogen peroxide bleaching*

Conventional NaOH-based and Mg(OH)₂-based hydrogen peroxide bleaching experiments were conducted in heat-sealed plastic bags at 10% consistency. To make the bleach liquor for peroxide bleaching, the chemicals were mixed in a beaker in the following order: distilled water, sodium silicate, ethylene diamine tetraacetic acid (EDTA), sodium hydroxide, and hydrogen peroxide. Before the bleach liquor was added, the pulp slurry was heated to 80 °C. When Mg(OH)₂ was needed, it was added directly to the pulp before other chemicals were added. Good mixing was achieved with kneading for 2 min. The plastic bag was then sealed and fully immersed in a pre-heated thermostatically controlled water bath for the desired retention time. The pulp was mixed every 15 min for the duration of the experiment. The experimental conditions for hydrogen peroxide bleaching are listed in Table 1. The Mg(OH)₂ replacement ratio is defined as the mole equivalent of Mg(OH)₂ that replaces NaOH, on a total alkali dosage of 2% NaOH, and is reported here as percent replacement (Yu and Ni 2006). After the required retention time, a liquid sample was taken to determine the final pH, the residual peroxide, and the chemical oxygen demand (COD). The pulp slurry was washed thoroughly with distilled water for further analysis.

**Table 1. Experimental Conditions for Peroxide Bleaching**

<table>
<thead>
<tr>
<th>Experimental Number</th>
<th>Mg(OH)₂ Replacement Ratio</th>
<th>NaOH Dose (% wt.) on Dry Pulp</th>
<th>Mg(OH)₂ Dose (% wt.) on Dry Pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0**</td>
<td>2.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>1.80</td>
<td>0.14</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>1.70</td>
<td>0.22</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>1.60</td>
<td>0.29</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>1.50</td>
<td>0.36</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>1.40</td>
<td>0.44</td>
</tr>
<tr>
<td>7</td>
<td>40</td>
<td>1.20</td>
<td>0.58</td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td>1.00</td>
<td>0.72</td>
</tr>
<tr>
<td>9</td>
<td>75</td>
<td>0.50</td>
<td>1.09</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>0.00</td>
<td>1.45</td>
</tr>
</tbody>
</table>

* The other conditions were H₂O₂ dose 3.00%, EDTA dose 0.50%, Na₂SiO₃ dose 2.00%, temperature 80 °C, reaction time 120 min, and pulp consistency 10%  
** Control

*Pulp and effluent properties analysis*

Handsheets papers were prepared according to TAPPI method T205 in a sheet former (Frank 95854). The brightness was measured according to TAPPI T452 using a brightness apparatus (L&W Elrepho 070). The brightness gain was calculated as follows:

Brightness gain (%ISO) = Brightness of bleached pulp (%ISO) - Brightness of unbleached pulp (%ISO)

The post color (P.C.) number was used to evaluate the brightness reversion; a large number indicates a serious yellowing. The handsheet was put into an automatic
temperature-controlled oven (105±2 °C) for 4 h, then it was taken out and placed in the lab under standard conditions according to TAPPI T402 for 24 h. After that, the brightness of the dried pulp was measured. The formulas for calculating the P.C. number are shown below (McGarry et al. 2002; Fang et al. 2000).

\[
P.C.\ number = [(k/s)_{after} - (k/s)_{before}] \times 100 \tag{1}
\]

\[
k/s = (1 - R_s)^2 / 2R_s \tag{2}
\]

where \( k \) and \( s \) in Eqs. (1) and (2) refer to the absorption and scattering coefficients, respectively, and \( R_s \) is the ISO brightness under R457.

The tensile, tear, and burst indices were determined according to TAPPI methods T495, T414, and T403, respectively, using tensile, tear, and burst testers.

The following measurements were carried out on the filtrate: the amount of residual peroxide by iodometric titration in accordance with the KCL 214:85 method, and the chemical oxygen demand (COD) in accordance with SFS 3020. The \( \text{H}_2\text{O}_2 \) consumption was calculated as follows:

\[
\text{H}_2\text{O}_2 \text{ consumption} \ (\text{g/L}) = \text{initial H}_2\text{O}_2 \ (\text{g/L}) - \text{residual H}_2\text{O}_2 \ (\text{g/L}) \tag{3}
\]

### RESULTS AND DISCUSSION

#### Properties of Bleached Pulp

The brightness of the unbleached industrially produced deinked pulp was 45.7% ISO. Table 2 presents the effect of the \( \text{Mg(OH)}_2 \) replacement ratio on the final brightness of the bleached pulp. In the range of 10% to 75% replacement of \( \text{NaOH} \) with \( \text{Mg(OH)}_2 \), the brightness of the bleached pulp was higher than that of \( \text{NaOH} \)-based peroxide bleached pulp. A relatively higher brightness was achieved when 25% to 50% of \( \text{NaOH} \) was replaced with \( \text{Mg(OH)}_2 \). The improved brightness gain may be partly due to decreased alkaline darkening in the peroxide bleaching process. Alkaline darkening occurs during peroxide bleaching and has negative effects on the brightness of the bleached pulp (Yu and Ni 2006; He et al. 2004a). As previous results have shown (He et al. 2004a), the higher the pH is, the greater the brightness loss during alkaline darkening; moreover, not all the chromophores that form during alkaline darkening are reactive toward hydrogen peroxide. When \( \text{Mg(OH)}_2 \) was substituted for \( \text{NaOH} \), the pH was lower than that of the control (Table 3). Consequently, the decreased alkaline darkening would be partially responsible for the higher brightness. However, at a 100% replacement ratio of \( \text{NaOH} \) with \( \text{Mg(OH)}_2 \), the brightness of the bleached pulp was lower than that of the \( \text{NaOH} \)-based hydrogen bleached pulp, supposedly because of the very low initial pH (Table 3). As in hydrogen peroxide bleaching, sufficiently high alkalinity is needed to activate \( \text{H}_2\text{O}_2 \) by generating the reactive perhydroxyl anion (\( \text{HOO}^\cdot \)). If the alkalinity is too low to generate enough \( \text{HOO}^\cdot \), the brightness gain of bleached pulp would be limited. Hence, the 100% \( \text{Mg(OH)}_2 \) replacement ratio had an adverse effect on the brightness of the bleached pulp.

Additionally, it was found that the bleaching efficiency, which was defined as the ratio between the brightness gain and the peroxide consumption, consistently increased with increasing replacement ratio of \( \text{Mg(OH)}_2 \), as indicated in Fig. 1. However, some
researchers reported that a higher Mg(OH)$_2$ dose may lower the bleaching efficiency when bleaching the mechanical pulp (Yu and Ni 2006). The reason for this difference may be that the industrial-grade Mg(OH)$_2$ was used by Yu and Ni (2006), which may have contained more transition metal ions. When more Mg(OH)$_2$ was added, more transition metal ions were introduced into the bleaching system, which hence increased the invalid decomposition of H$_2$O$_2$; that is, the unintended consumption of H$_2$O$_2$ increased. But the Mg(OH)$_2$ powder used in this study was of a higher purity, containing much fewer transition metal ions. Therefore, the impact of transition metal ions in Mg(OH)$_2$ on H$_2$O$_2$ consumption was trifling.

**Table 2.** The Effect of the Mg(OH)$_2$ Replacement Ratio on the Final Brightness of the Bleached Pulp*

<table>
<thead>
<tr>
<th>Experimental Number</th>
<th>Mg(OH)$_2$ Replacement Ratio</th>
<th>Final Brightness (% ISO)</th>
<th>Brightness Gain (% ISO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>57.0</td>
<td>11.3</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>57.3</td>
<td>11.6</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>57.2</td>
<td>11.5</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>57.5</td>
<td>11.8</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>58.4</td>
<td>12.7</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>58.5</td>
<td>12.8</td>
</tr>
<tr>
<td>7</td>
<td>40</td>
<td>58.4</td>
<td>12.7</td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td>58.2</td>
<td>12.5</td>
</tr>
<tr>
<td>9</td>
<td>75</td>
<td>57.2</td>
<td>11.5</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>56.6</td>
<td>10.9</td>
</tr>
</tbody>
</table>

* Conditions: H$_2$O$_2$ dose 3.00%, EDTA dose 0.50%, Na$_2$SiO$_3$ dose 2.00%, temperature 80 °C, reaction time 120 min, and pulp consistency 10%. Initial brightness 45.7% ISO

![Fig. 1. The effect of the Mg(OH)$_2$ replacement ratio on bleaching efficiency (Error bars: one standard deviation)](image-url)
The post color (P.C.) number of pulp is an indication of the presence of chromophoric structures remaining in the pulp. The chromophoric structures could be lignin or other lignocellulosic materials that absorb light. As these materials are still in the deinked pulp, it is important to evaluate how much the presence of these materials could affect the optical properties. In fact, the P.C. number is an indicator of the changes in these components. The P.C. number of the unbleached pulp was 2.56. Figure 2 shows the effect of the Mg(OH)$_2$ replacement ratio on the P.C. number of bleached pulp. The P.C. number of all the bleached pulps was lower than that of the unbleached pulp; furthermore, the P.C. number of the Mg(OH)$_2$-based peroxide bleached pulp was lower than that of the NaOH-based peroxide bleached pulp. The result implies that lower amounts of chromophoric structures remain in the pulp after the bleaching (Behrooz et al. 2012).

As also shown in Fig. 2, the addition of MgSO$_4$ at a high dosage to a peroxide stage can also decrease the P.C. number, but this approach is not as effective as the partial replacement of NaOH with Mg(OH)$_2$.

### Table 3. The Effect of the Mg(OH)$_2$ Replacement Ratio on the Effluent Characteristics of Bleached Pulp*

<table>
<thead>
<tr>
<th>Experimental Number</th>
<th>Mg(OH)$_2$ Replacement Ratio</th>
<th>Initial pH</th>
<th>Final pH</th>
<th>Residual H$_2$O$_2$ (g/L)</th>
<th>H$_2$O$_2$ Consumption (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>10.6</td>
<td>9.5</td>
<td>0.09</td>
<td>2.91</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>10.5</td>
<td>9.3</td>
<td>0.13</td>
<td>2.87</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>10.3</td>
<td>9.0</td>
<td>0.27</td>
<td>2.73</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>10.1</td>
<td>8.8</td>
<td>0.44</td>
<td>2.56</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>9.4</td>
<td>8.5</td>
<td>0.90</td>
<td>2.10</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>8.9</td>
<td>7.5</td>
<td>1.83</td>
<td>1.17</td>
</tr>
</tbody>
</table>

* Conditions: H$_2$O$_2$ dose 3.00%, EDTA dose 0.50%, Na$_2$SiO$_3$ dose 2.00%, temperature 80 ºC, reaction time 120 min, and pulp consistency 10%. Initial H$_2$O$_2$ 3g/L

The mechanical properties of bleached pulps via replacement of NaOH with Mg(OH)$_2$ processes are listed in Table 4. Evidently, the tensile, burst, and tear indices of the bleached pulp were all higher than for the unbleached pulp. As for fully Mg(OH)$_2$-based peroxide bleached deinked pulp, these strength property values were slightly lower.
than those of the fully NaOH-based bleached pulp. This outcome is consistent with previous results for mechanical pulps (Behrooz et al. 2012; Ghasemi et al. 2010). In the literature, the lower strength of bleached pulp via Mg(OH)₂-based in comparison with NaOH-based peroxide bleaching was explained by the lower alkalinity level and the lower formation of carboxylic acids having a negative impact on fiber swelling (Leduc et al. 2010), while the presence of magnesium ions, which attract and bind with carboxylic groups on fiber surfaces, allowed a decrease in fiber swelling and fiber bonding (He et al. 2006; Zhang et al. 2004). However, in the range of partial replacement of NaOH with Mg(OH)₂ processes, the mechanical pulp properties were slightly higher than in the fully NaOH-based process. This increase may contribute to the high fines content of deinked pulp, which outweighs the impact of the magnesium cation (Hietanen et al. 2013).

### Table 4. The Effect of the Mg(OH)₂ Replacement Ratio on the Mechanical Properties of Bleached Pulp*

<table>
<thead>
<tr>
<th>Experimental Number</th>
<th>Mg(OH)₂ Replacement Ratio</th>
<th>Tensile Index (N·m/g)</th>
<th>Tear Index (mN·m²/g)</th>
<th>Burst Index (kPa·m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached</td>
<td>-</td>
<td>16.8</td>
<td>5.10</td>
<td>0.80</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>19.0</td>
<td>6.13</td>
<td>0.88</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>21.5</td>
<td>6.79</td>
<td>0.96</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>22.0</td>
<td>6.42</td>
<td>1.00</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>22.0</td>
<td>6.91</td>
<td>0.92</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>21.5</td>
<td>7.63</td>
<td>0.94</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>18.6</td>
<td>5.82</td>
<td>0.86</td>
</tr>
</tbody>
</table>

* Conditions: H₂O₂ dose 3.00%, EDTA dose 0.50%, Na₂SiO₃ dose 2.00%, temperature 80 °C, reaction time 120 min, and pulp consistency 10%.

### Bleaching Effluent Properties

The effluent properties of the deinked pulp produced via various replacement ratios of the Mg(OH)₂-based hydrogen peroxide bleaching process are listed in Table 3. Clearly, the Mg(OH)₂ replacement ratio had a significant effect on the amount of residual peroxide in the bleaching effluent. The proportion of residual peroxide increased from 3% to about 61% when the bleaching alkali was changed from fully NaOH-based to fully Mg(OH)₂-based. As seen in this work, and in other work researchers have done with Mg(OH)₂, the residual peroxide level is very high compared with NaOH bleaching (Hietanen et al. 2013; Lapierre et al. 2003; Johnson et al. 2002), indicating fewer side reactions. However, this residual could not be used to increase the brightness response by either increasing reaction time or temperature (Suess et al. 2002). This offers potential savings in bleach chemical costs if the residual peroxide can be recycled. The residual peroxide has been utilized to improve the brightness through a medium consistency pre-bleaching stage by rearrangement of the water circulations in a pulp mill (Tamper 2009) and to prevent harmful slime growth as a biocide in paper mill water circulation loops (Hietanen et al. 2013). In the literature, the bleaching filtrate has been used as a partial charge of peroxide for bleaching fresh pulp; the filtrate from this pulp was then used in the next bleaching, and so on. The filtrate was reused three times, and the brightness and residual results for all the bleach runs were the same, showing that the peroxide residual was still fully active (Johnson et al. 2002).

The COD (chemical oxygen demand) load of the filtrates at 10% to 75% replacement ratios of Mg(OH)₂ was 20% to 25% lower than that of the filtrate from the 100% NaOH process, as shown in Fig. 3. Similar results have been obtained by others (Leduc et
al. 2010; He et al. 2004b). The COD load was believed to come from dissolved lignin, acetic acid, and other organic substances in the bleaching filtrate (He et al. 2004b); the lower solubility and alkalinity of the Mg(OH)$_2$ were considered to be the cause of the lower COD formation (Zeinaly et al. 2009). Therefore, with the significant decrease in COD load, the costs associated with effluent treatment should be substantially less for the Mg(OH)$_2$ process. This prediction was confirmed by the results obtained at a Canadian paper mill, which realized a 25% to 40% reduction in effluent treatment cost after implementing the Mg(OH)$_2$-based peroxide bleaching process (He et al. 2004b; Li et al. 2005).

![Fig. 3. The effect of the Mg(OH)$_2$ replacement ratio on COD](image)

**CONCLUSIONS**

1. At 10% consistency and 3% H$_2$O$_2$ charge, when NaOH was partially replaced with high-purity Mg(OH)$_2$ in peroxide bleaching, the bleached, deinked pulp was produced with a higher brightness, a lower P.C. number, and higher strength properties. However, at a 100% replacement ratio of Mg(OH)$_2$, the brightness and mechanical properties of bleached pulp were lower than those of pulp bleached with NaOH as the sole alkali source.

2. The Mg(OH)$_2$-based peroxide bleaching resulted in a substantial residual peroxide concentration, which offers potential savings in bleach chemical costs if the residual peroxide can be recycled.

3. The COD load of filtrates from 20% to 75% replacement ratios of the Mg(OH)$_2$ peroxide bleaching process was 20% to 25% lower than that of the filtrate from the fully NaOH-based process, which demonstrated that the Mg(OH)$_2$-based bleaching alkali concept had a significant environmental benefit.
ACKNOWLEDGMENTS

The authors are grateful for the support of the Guangdong Industrial Technical College Foundation, Grant No. KY201027.

REFERENCES CITED


Article submitted: June 5, 2013; Peer review completed: July 2, 2013; Revised version received and accepted: July 18, 2013; Published: July 23, 2013.