Decreasing calcium oxalate scaling by partial substitution of $Mg(OH)_2$ for NaOH in the peroxide bleaching of mechanical pulps

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ABSTRACT: Calcium oxalate scaling can be minimized by partially replacing NaOH with $Mg(OH)_2$ as the alkali source in the peroxide bleaching of mechanical pulps. The amount of precipitated oxalate was negligible when 30–50% of the NaOH was replaced with $Mg(OH)_2$ during bleaching. A higher brightness was also achieved compared to the NaOH-based peroxide process. The addition of $MgSO_4$ at a high dosage to a peroxide stage can also decrease the amount of precipitated oxalate, but this approach is not as effective as the partial replacement of NaOH with $Mg(OH)_2$.

Application: By partially replacing NaOH with $Mg(OH)_2$, papermakers may be able to decrease oxalate-related scaling without sacrificing brightness in bleached mechanical pulp.

Scaling can cause operational problems in the production lines of bleached mechanical pulps. In a bleach plant, scaling occurs in the forms of calcium oxalate, calcium carbonate, barium sulfate, and pitch. Apparently, the alkaline peroxide process is primarily responsible for generating oxalate and oxalate-related scaling in these production lines.

Among several approaches proposed for minimizing oxalate-related scaling, the addition of magnesium sulfate ($MgSO_4$) can be used to increase the soluble oxalate, which decreases the deposition of calcium oxalate [1–3]. Oxalates in the system react with magnesium preferentially, rather than with calcium, and magnesium oxalate is much more soluble than calcium oxalate.

In an earlier study on $Mg(OH)_2$-based peroxide bleaching [4], the amount of oxalate formed was found to be similar to that formed in a conventional NaOH-based process for the same brightness target. However, unlike the NaOH-based process, the $Mg(OH)_2$ process resulted in most of the newly formed oxalate being in a soluble state, which solves the scaling problem.

The substitution of NaOH with $Mg(OH)_2$ as the alkaline source in a peroxide bleaching process brings other benefits to pulp and paper mills, including a lower COD load, lower chemical costs, less formation of anionic trash, and higher bulk of the bleached pulps [5–14]. On the other hand, at the same hydrogen peroxide charge, the $Mg(OH)_2$-based peroxide process may produce less brightness gain than the NaOH-based process. For a maple CTMP, for example, the $Mg(OH)_2$ process was reported to produce pulp that was 2 ISO units lower in brightness than the same pulp from the NaOH process at the same H_2O_2 charge [4,6].

In this work, our purpose was to study how the partial substitution of NaOH with $Mg(OH)_2$ affects the formation of oxalate and its partitioning between soluble and precipitated forms during the peroxide bleaching of mechanical pulps. This partial replacement may represent a way to decrease the oxalate-related scaling in the bleach plant without adversely affecting the optical properties of the pulp.

EXPERIMENTAL

A maple CTMP was received by our laboratory from a mill in Quebec and was subjected to chelation for 30 min under the conditions of 0.5% DTPA, pH 6–6.5, 70°C, and 3% pulp consistency. After the chelation stage, the pulp was washed thoroughly. The chelated pulp was found to have a brightness of 39.2% ISO and an oxalate content of 0.19 g per kilogram of pulp. Magnesium hydroxide was an industrial-grade reagent from Martin Marietta, the silicate was industrial grade, and the hydrogen peroxide and sodium hydroxide solutions were from Fisher Scientific.

Peroxide bleaching experiments were conducted in plastic bags. To make the bleach liquor for peroxide bleaching, we mixed the chemicals in a beaker in the following order: water, sodium silicate, sodium hydroxide, and hydrogen peroxide. Before the bleach liquor was added, the pulp slurry was pre-heated to 80°C. When $Mg(OH)_2$ was needed, it was added directly into the pulp slurry before other chemicals were added. Good mixing was achieved with kneading. The plastic bag was sealed and placed in a water bath for the desired retention time.

At the elapsed bleaching time, the pulp sample was cooled to room temperature and filtered through a 200-mesh screen to separate the pulp and the liquid. The pulp and liquid samples were separately mixed with ion exchange resin and water to dissolve precipitated calcium oxalate into oxalate ions [15]. The samples were mixed for two hours on an Innova 2000 platform shaker, were filtered through a 0.45-µm filter, and were subjected to ion chromatography analysis to determine the oxalate concentration. The amount of total oxalates is the sum of the oxalates in both the pulp and liquid samples. Additionally, the liquid sample collected from filtration through the 200-mesh screen was filtered through a 0.45-µm filter before the soluble oxalate was determined.

To determine the oxalate concentration, we used a Dionex DX-300 Ion Chromatographic system, together with a suppressed conductivity detector. Samples were separated in an AS4A-SC 4-mm analytical column and an AG4A-SC 4-mm guard column, with a mixture of 1.8*mM* Na_2CO_3 and 1.7*mM* $NaHCO_3$ as an eluent.

$Mg(OH)_2$ replacement, %	NaOH charge, %	$Mg(OH)_2$ charge, %	H_2O_2 consumed, %	Brightness, % ISO	Initial pH	Final pH
0	4.20	0	4.2	80.2	10.7	8.3
10	3.78	0.31	4.2	80.2	10.5	8.1
15	3.57	0.46	4.1	80.9	10.5	8.2
20	3.36	0.61	4.1	81.2	10.2	8.2
25	3.15	0.77	4.2	81.0	9.9	8.0
30	2.94	0.92	4.3	80.8	10.2	8.0
40	2.52	1.22	4.3	81.2	9.6	8.0
50	2.10	1.53	4.3	80.2	9.7	8.1
75	1.05	2.30	4.8	80.4	9.7	8.1
100	0	3.06	4.8	78.4	8.6	8.0

16% consistency, 80°C, 3 h, 6.2% H_2O_2, 2.6% water glass.

I. Results for partial replacement of NaOH with $Mg(OH)_2$.

$MgSO_4$ charge, % on pulp	$MgSO_4$ replacement*, %	H_2O_2 consumed, %	Brightness, % ISO	Initial pH	Final pH
0	0	4.2	80.2	10.7	8.3
0.13	2.1	4.1	80.3	11.0	8.3
0.5	7.9	4.0	80.8	10.9	8.5
1.0	15.8	3.9	80.8	10.9	8.2
1.26	20	3.7	81.3	10.7	8.1
1.89	30	3.9	81.2	10.6	8.1
3.16	50	3.6	79.9	9.7	8.1

16% consistency, 80°C, 3 h, 6.2% H_2O_2, 4.2% NaOH, 2.6% water glass.
*Equivalent to $Mg(OH)_2$ replacement (% on a total alkali of 4.2% NaOH).

II. Results for bleaching with different $MgSO_4$ charges.

To determine the dissolved calcium and magnesium contents in bleaching filtrate, we followed an Atomic Absorbance Spectrophotometric method. A Perken Elmer A-analyst 100 was used in accordance with TAPPI T 266 om-88. The brightness, pH, and the residual peroxide were determined according to PAPTAC methods.

RESULTS AND DISCUSSION

Partial replacement of NaOH with $Mg(OH)_2$

We first studied the partial replacement of NaOH with $Mg(OH)_2$ as the alkali source for peroxide bleaching of the maple CTMP. **Table I** gives the experimental conditions and bleaching results, and **Fig. 1** shows the total oxalate formation and the partition between the precipitated and soluble oxalates. The $Mg(OH)_2$ replacement ratio is defined as the mole equivalent of $Mg(OH)_2$ that replaces NaOH, on a total alkali of 4.2% NaOH, and is reported here as percent replacement.

The amount of the oxalate formed in the bleaching experiments with 0–50% replacement of NaOH with $Mg(OH)_2$ was found to be at roughly the same level (1.85±0.09 g/kg pulp), as Fig. 1 shows. This result can be explained by the similar peroxide consumption (4.2%±0.1%) reported in Table I. Our earlier results showed a close relationship between the amount of oxalate formed and the peroxide consumed [4]. The magnesium hydroxide slurry used in this study contains impurities that include transition metals. When more $Mg(OH)_2$ was charged, more transition metals were introduced into the system. This change explains the higher peroxide consumption and the higher oxalate formation at 75% and 100% replacement. Other researchers have also reported that a higher $Mg(OH)_2$ charge led to more peroxide consumption [5–6].

Figure 1 further shows that when the $Mg(OH)_2$ replacement increased from 0% to 50%, the precipitated oxalate decreased significantly. In fact, in the range of 30–50% $Mg(OH)_2$, the amount of precipitated oxalate was negligible. Therefore, at a 30–50% replacement of NaOH with $Mg(OH)_2$, the calcium oxalate scaling is essentially inhibited.

These results can be easily explained. Under the conditions of peroxide bleaching, magnesium ions interact with oxalate more quickly than calcium ions interact with oxalate, and the magnesium oxalate formed has a higher solubility than calcium oxalate [6,16,17]. The results are in line with a theoretical calculation based on the stability product constants of magnesium oxalate and calcium oxalate. **Figure 2** shows that the Mg^{2+} concentration increases as the $Mg(OH)_2$ replacement increases.

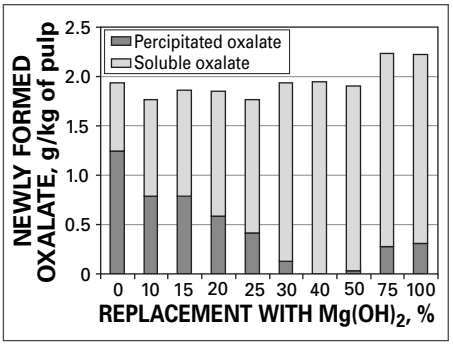
Another benefit of partially substituting $Mg(OH)_2$ for NaOH during peroxide bleaching is a higher brightness gain for the pulp. In the range of 15–75% replacement with $Mg(OH)_2$, the brightness of the bleached pulp was higher than that of the control, as **Fig. 3** shows. This outcome is in agreement with earlier results obtained in a two-stage peroxide process [6].

The improved brightness gain may be partly explained by the decreased alkaline darkening in the peroxide process. Alkaline darkening occurs during peroxide bleaching and has negative effects on the bleaching efficiency and the brightness ceiling of mechanical pulps [18–22]. As results have shown [22], the higher the pH, the greater the brightness loss during alkaline darkening. Also, not all of the chromophores that form during alkaline darkening are reactive towards peroxide [22]. When $Mg(OH)_2$ was partially substituted for NaOH, the pH profile was lower than that of the control (Table I). As a result, the alkaline darkening would be decreased, which would be partially responsible for the higher brightness.

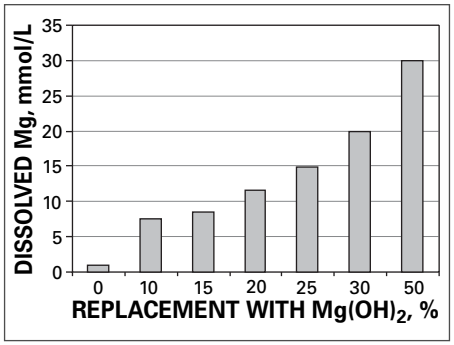
At 100% replacement with $Mg(OH)_2$, the brightness of the resulting pulp was lower than with the control, which is in line with our earlier results for a CTMP hardwood pulp of high brightness [6,22]. On the other hand, for pulp grades of about 70% ISO, the $Mg(OH)_2$-based peroxide process offered a brightness gain similar to that of the NaOH-based peroxide process [7].

Addition of $MgSO_4$

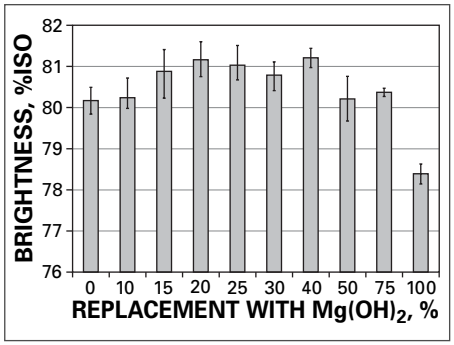
Magnesium sulfate is usually used as one of the stabilizers for peroxide bleaching, and its dosage is normally less than 0.1%. Recently, it was found that magnesium sulfate is also effective in inhibiting calcium oxalate scaling during pulp



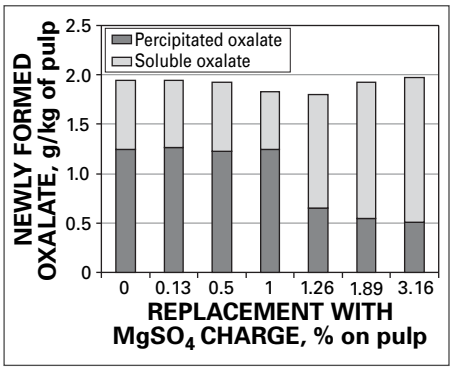
1. Oxalate formation and partition of partial replacement of NaOH with $Mg(OH)_2$.



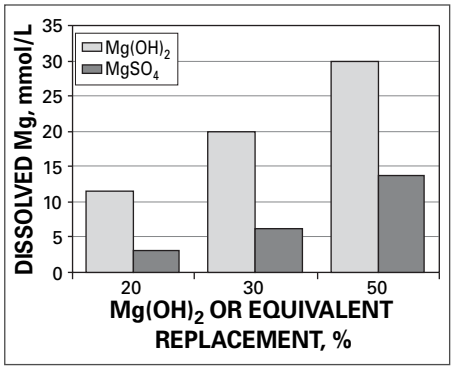
2. Concentrations of dissolved magnesium after bleaching.



3. Brightness levels achieved in a maple CTMP with $Mg(OH)_2$ partially replacing NaOH with $Mg(OH)_2$ at different percentages.



4. Oxalate formation and its partitioning into precipitated and soluble forms during peroxide bleaching with $MgSO_4$ added.



5. Dissolved magnesium in bleaching filtrates after the partial replacement of NaOH with $Mg(OH)_2$ or $MgSO_4$.

bleaching [1,3,23]. **Figure 4** shows the effects that adding $MgSO_4$ to peroxide bleaching has on the formation and partitioning of oxalate for the maple CTMP. **Table II** lists experimental conditions and results.

As Fig. 4 shows, the addition of $MgSO_4$ in a range of 0% to 3.16% (on pulp) did not change the amount of newly formed oxalate. The graph also shows that adding $MgSO_4$ altered the partition between the soluble and precipitated oxalate; a drastic change in the amount of precipitated oxalate is noted at the $MgSO_4$ charge of 1.26%, which is equivalent to an $Mg(OH)_2$ replacement of 20% (based on a total alkali of 4.2% NaOH).

We found that $Mg(OH)_2$ is more effective than $MgSO_4$ in inhibiting the formation of precipitated oxalate (at the same Mg^{2+} mol concentration). For example, at 30% $Mg(OH)_2$ replacement (on 4.2% NaOH), the amount of newly formed precipitated oxalate was 0.13 g/kg of pulp in the case of $Mg(OH)_2$ (Fig. 1). However, the amount was 0.55g/kg of pulp in the case of $MgSO_4$ (Fig. 4).

The reason for this difference is the difference in pH between the two systems: the $Mg(OH)_2$ system has a lower pH than the $MgSO_4$ system. As shown in Tables I and II, at 30% $Mg(OH)_2$, the initial pH values are 10.2 and 10.6, respectively, for the $Mg(OH)_2$ and $MgSO_4$ systems. If the pH is higher, more Mg^{2+} is in the form of $Mg(OH)_2$, and less free Mg^{2+} would be available for the inhibition effect. For this reason, $Mg(OH)_2$ is more effective than $MgSO_4$ under the conditions studied.

To explore this hypothesis further, we determined the amount of dissolved magnesium in bleaching filtrates from the two systems. As the results plotted in **Fig. 5** show, the concentration of dissolved magnesium was always significantly higher in the $Mg(OH)_2$ system than in the $MgSO_4$ system.

Table II also shows the brightness results for bleaching with the $MgSO_4$ addition. These values indicate that bleaching with $MgSO_4$ gave a higher brightness in bleached pulp than the control produced. With 1.26% $MgSO_4$, corresponding to the 20% equivalent replacement with $Mg(OH)_2$, we obtained the highest brightness of 81.3% ISO. The results are comparable to that of 20% $Mg(OH)_2$ replacement, for which the brightness was 81.2% ISO (Fig. 3). However, a further increase in the $MgSO_4$ charge caused a decrease in the final brightness, which is in agreement with other studies and can be explained by the decrease in pH [24–26].

CONCLUSIONS

Partial replacement of NaOH with $Mg(OH)_2$ is effective in decreasing the amount of the precipitated calcium oxalate during the peroxide bleaching of the CTMP maple pulp. At a replacement ratio of 30–50%, the formation of precipitated oxalate is negligible.

In terms of the chemistry, the magnesium ions interact with oxalate more quickly and easily than calcium ions interact with oxalate under these conditions. In addition, the magnesium oxalate formed has a high solubility.

A higher brightness is achieved at a partial substitution with $Mg(OH)_2$. The addition of $MgSO_4$ (higher than 1%) in a peroxide stage can also reduce the precipitated oxalate. However, this approach is not as effective as the partial replacement of NaOH with $Mg(OH)_2$. **TJ**

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INSIGHTS FROM THE AUTHORS

In the manufacturing of high-brightness mechanical pulps, scaling can be a problem. Magnesium sulfate (Epsom salt) is usually used to minimize any scaling that consists of calcium oxalate. We found that a partial substitution of $Mg(OH)_2$ for NaOH as the alkali source for peroxide bleaching is effective in reducing this scaling. A higher brightness is also achieved when $Mg(OH)_2$ is substituted for NaOH as the alkali source.

Our work indicates that the partial replacement of NaOH with $Mg(OH)_2$ could be a practical way to decrease oxalate-related scaling in the production lines of high-brightness mechanical pulps. In the near future, we plan to carry out mill trials to verify the laboratory findings.

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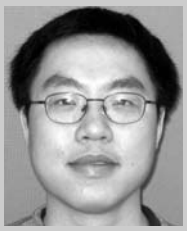

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