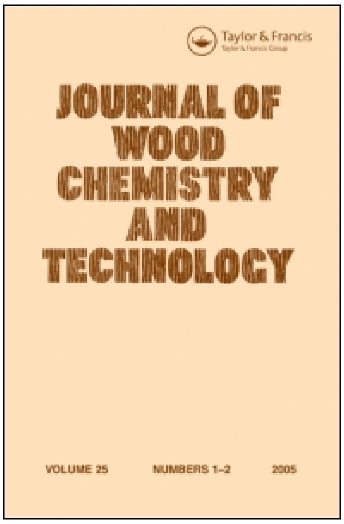

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Formation of Oxalate from the $Mg(OH)_2$-Based Peroxide Bleaching of Mechanical Pulps

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ABSTRACT

Oxalate is a major source of scaling during the manufacturing process of bleached mechanical pulps and the majority is formed during the peroxide bleaching stage. In this paper, we investigated the effect of using $Mg(OH)_2$ as an alkali source during peroxide bleaching on the formation of oxalate and its partition between soluble and precipitated oxalates. We found that at the same brightness target, the total amount of oxalate formed is similar between the $Mg(OH)_2$-based peroxide system and the conventional NaOH-based system, however, almost all of the newly formed oxalate from the former was found in the soluble state, while in the NaOH-based peroxide process, a large fraction is in the precipitate form. Therefore, the oxalate-related scaling is significantly less or even

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negligible during the $Mg(OH)_2$-based peroxide process. The underlying mechanism accounting for the above observation will be discussed.

INTRODUCTION

The $Mg(OH)_2$-based peroxide bleaching process for mechanical pulps has received much attention recently.[1–9] The advantage of such process is that magnesium hydroxide is a weak base acting as a buffer with low alkalinity, which brings multiple benefits to pulp and paper mills, such as lower COD load, less chemical cost, and lower ionic trash in the bleached pulp. As a result, significant economic benefits have been observed in a mill.[9]

Scaling has become a major concern in mills due to the appearance of solid precipitates. These can cause equipment damages, or in extreme cases shutdown of operations. A recent study[10] showed that in a peroxide bleach plant of mechanical pulps, calcium oxalate was the major component of scale. A high oxalate content in the bleached pulp could have the negative impact on papermaking operations, for example, interference with rosin sizing.[11,12]

Therefore, the minimization of oxalate formation and its scaling is of practical importance. Terelius et al.[13] suggested that the addition of $MgSO_4$ could reduce the total amount of oxalate in bleached mechanical pulps. This was explained by the hypothesis that magnesium reacts with oxalate, thereby preventing the formation of porcelain-like deposits of calcium oxalate.

The objective of this research is to determine experimentally the influence of using $Mg(OH)_2$ as the alkali source on the formation of oxalate and its partition between soluble and precipitated form for peroxide bleaching of mechanical pulps. With this information we will be able to determine the calcium oxalate-related scaling during the $Mg(OH)_2$-based peroxide bleaching process.

EXPERIMENTAL

The CTMP maple pulp was received from a mill in Quebec and the spruce TMP from a mill in Eastern Canada. Their initial brightnesses were 45.8% ISO and 63.2% ISO, respectively. The CTMP maple pulp went through lab chelation at 0.5% DTPA, pH 6.5, 70°C, and 3% pulp consistency for

30 min. After the chelation stage, the pulp was washed thoroughly. The TMP was mill-chelated, and therefore no further lab-chelation was carried out. The initial oxalate content was 0.44 g/kg pulp for the TMP pulp and 0.05 g/kg pulp for the CTMP maple pulp. The peroxide bleaching conditions can be found in Tables 1 and 2. Hydrogen peroxide and sodium hydroxide were from Fisher Scientific. Magnesium hydroxide was an industrial-grade from Martin Marietta and silicate was an industrial-grade. The Amberjet^{TM} 1200(H) resin was purchased from Aldrich.

The peroxide bleaching began by pre-heating the pulp in a sealed plastic bag, pre-warmed to the desired temperature. Subsequently, the chemicals were added. Two methods were used: (i) the P process, the chemicals were mixed jointly and (ii) the P_M process,[14] where the peroxide was added 1 min after adding magnesium hydroxide, DTPA, and water to the pulp. The bleaching of the CTMP maple pulp followed the P process. Vigorous mixing was done before the initial pH reading was taken.

At the completion of peroxide bleaching, samples were taken for final pH, pulp brightness, and residual peroxide, which were carried out in accordance with the CPPA standard methods. The oxalate analysis is as follows: for the total oxalates (sum of soluble and precipitated oxalates) both the pulp samples and filtrate were mixed with the resin (Amberjet^{TM} 1200(H)) by following a procedure detailed in Ref.[15]. The oxalate concentration was then determined in an ion chromatographic (IC) system. For the soluble oxalates, the filtrate sample obtained from filtering through a 200-mesh screen was further filtered in a 0.45 μm filter. The filtrate was then analyzed for the oxalate concentration in an IC system. The precipitated oxalates were calculated from the difference between the total and soluble oxalates.

A Dionex DX-300 IC System, together with a suppressed conductivity detector, was used to determine the concentration of oxalate. The conditions

Table 1. Bleaching conditions for the CTMP maple pulp.

	$Mg(OH)_2$-based	NaOH-based
Process	P	P
H_2O_2 (%)	1–6.2	0.2–6.2
NaOH (%)	—	0.1–7.0
$Mg(OH)_2$ (%)	0.7–2.5	—
Silicate (%)	2.6	2.6
$MgSO_4$ (%)	—	0.13

Note: 16% consistency, 80°C, and 3 hr.

Table 2. Bleaching conditions for the TMP pulp.

	$Mg(OH)_2$-based		NaOH-based	
Process	P, P_M	P, P_M	P	P
H_2O_2 (%)	1	2	1	2
NaOH (%)	—	—	1.3	1.8
$Mg(OH)_2$ (%)	1	1.2	—	—
DTPA (%)	0.1	0.1	—	—
Silicate (%)	—	—	2.5	2.5

Note: 10% consistency, 70°C, and 5 hr.

were AS4A-SC analytical column, AG4A-SC guard column, 1.8 mM Na_2CO_3, and 1.7 mM $NaHCO_3$ as the eluant at 2.0 mL/min.

A JEOL JSM6400 Digital SEM system was used to identify calcium oxalate precipitates on the surface of pulp fibers. Pulps from both the $Mg(OH)_2$-based and NaOH-based processes were analyzed after being dried in a vacuum oven at 40°C and −30°C in Hg.

RESULTS

The CTMP maple sample was subjected to a chelation stage with DTPA and then peroxide bleaching using sodium hydroxide (NaOH) or magnesium hydroxide ($Mg(OH)_2$) as the alkali source. In Fig. 1, the two systems were compared in respect to brightness gain vs. oxalate formation. As shown, the amount of oxalate formed was closely correlated to the brightness gain and the relationship followed the same pattern for the $Mg(OH)_2$-based and the NaOH-based peroxide processes. The development of oxalate formation was minimal at a lower brightness gain, however, a drastic increase at a higher brightness gain. The similarity in the oxalate formation between the two processes supports the conclusion that its chemistry is the same regardless of $Mg(OH)_2$ or NaOH as the alkali source.

Oxalate could be in either a soluble or a precipitated state. Figure 2 demonstrates, for the CTMP maple pulp, the partition between the two when using different chemical charges and bases. The results showed that the $Mg(OH)_2$ process has the distinct advantage of having the newly formed oxalate more in the soluble form than the precipitated form. At the most, 18% of the oxalate is in the precipitated form for the $Mg(OH)_2$-based process, while it was 58% for the NaOH-based process.

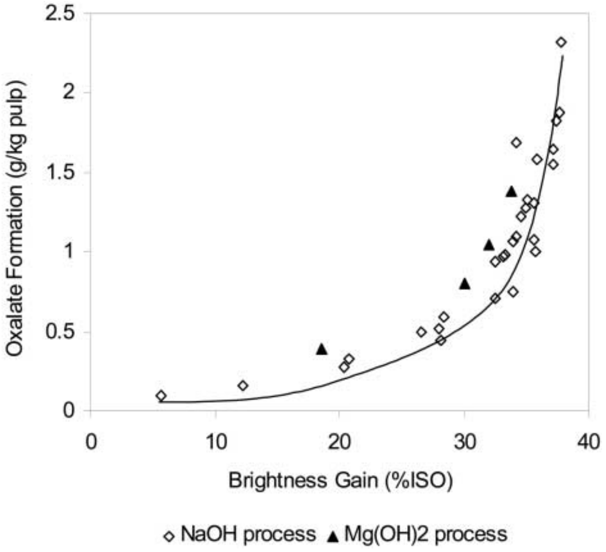


Figure 1. Relationship of oxalate formation and brightness gain during peroxide bleaching of the CTMP maple pulp.

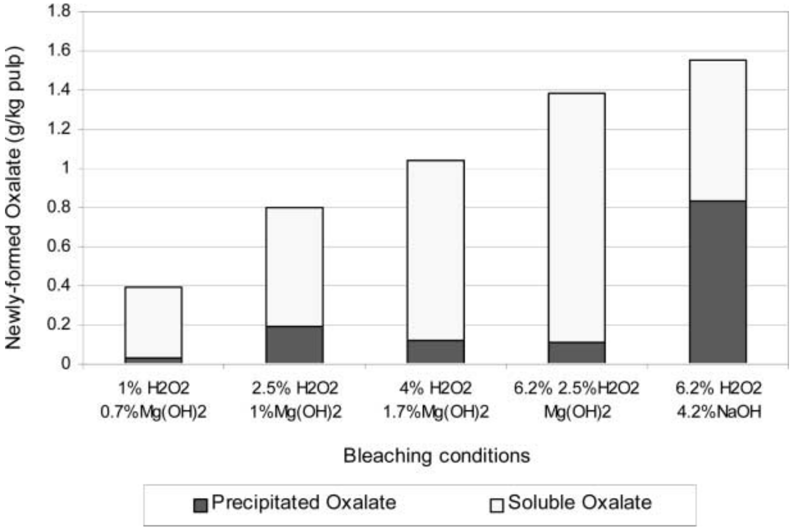
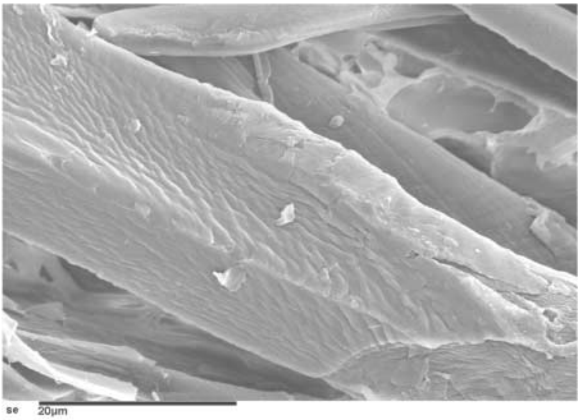
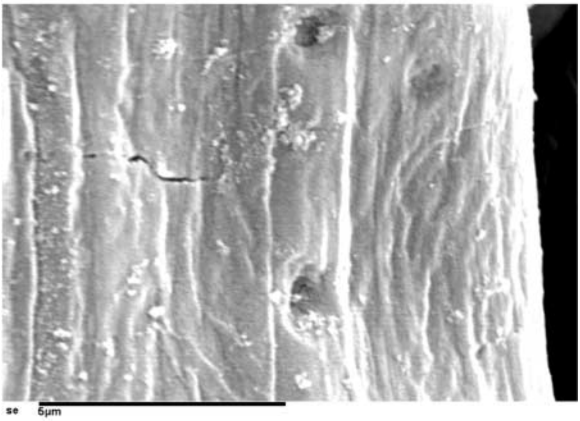


Figure 2. Partition between soluble and precipitated oxalates for the CTMP maple pulp.

We adopted SEM analysis to observe the CaC_2O_4 precipitates. As is shown in Fig. 3(A), the unbleached pulp has a clean surface. The bleached pulp from the NaOH-based process contains many small particles, with the size of hundreds nanometers, as shown in Fig. 3(B), some even in aggregated form [Fig. 3(C)]. On the other hand, in Fig. 3(D), the bleached pulp from the $Mg(OH)_2$-based process is free from these particles, which confirms



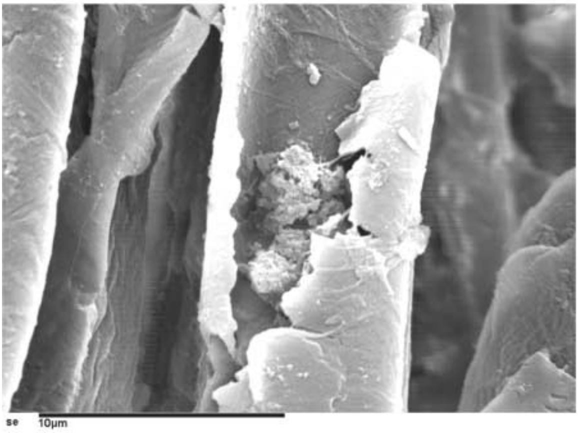
A. Unbleached pulp



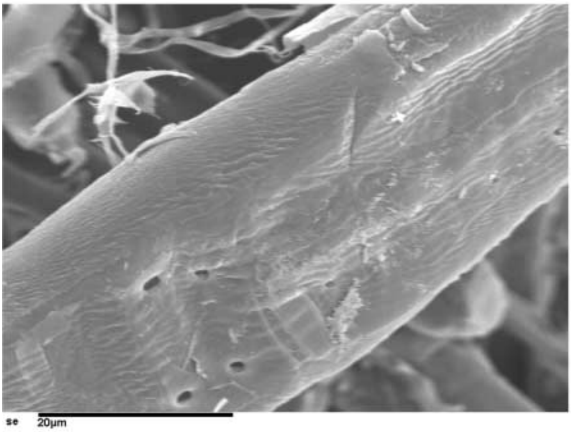
B. Bleached pulp from NaOH process

Figure 3. Comparison of the SEM images from the NaOH-based and $Mg(OH)_2$-based peroxide processes for the CTMP maple pulp.

(*continued*)



C. Bleached pulp from NaOH process



D. Bleached pulp from $Mg(OH)_2$ process

Figure 3. Continued.

the conclusion that negligible amount of newly formed oxalates from the $Mg(OH)_2$-based process is in precipitated form.

To verify the results in Fig. 1, we performed a similar experimental program on an Eastern Canadian TMP. As shown in Fig. 4, we can conclude that the oxalate formation is well correlated to the brightness gain and that there is no difference of this relationship between the $Mg(OH)_2$-based and

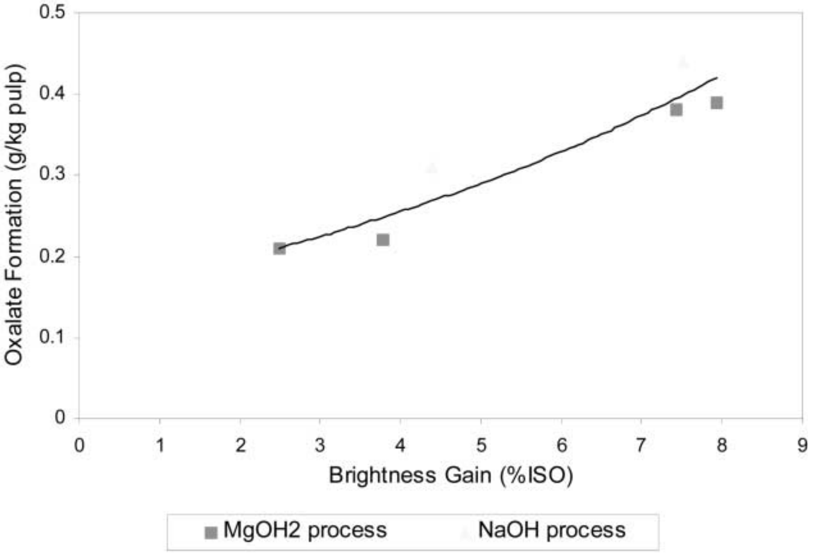


Figure 4. Relationship of oxalate formation and brightness gain during peroxide bleaching of an Eastern Canadian TMP.

the NaOH-based systems. It is noted that the oxalate formation is much less from the TMP, which is made from spruce, than that from the CTMP maple. This is in agreement with the earlier results[16] that a much less oxalate is generated from peroxide bleaching of softwood mechanical pulps than hardwood mechanical pulps.

DISCUSSION

In a previous study,[16] the oxalate formation in the NaOH-based process was been found to be proportional to the alkalinity of the system, and the results were explained with the hypothesis that the kinetics of the oxalate formation is proportional to the perhydroxyl ion concentration, i.e.,

$$r \propto [\mathrm{OOH}^-] \tag{1}$$

where r is the rate of the oxalate formation and $[\mathrm{OOH}^-]$ is the perhydroxyl ion concentration. The above conclusion is further supported by the results in Fig. 5, which shows the oxalate formation as functions of initial pH and final pH for the NaOH-based peroxide process. Due to its low alkalinity of the $Mg(OH)_2$-based processes, the $[\mathrm{OOH}^-]$ would be much lower than that

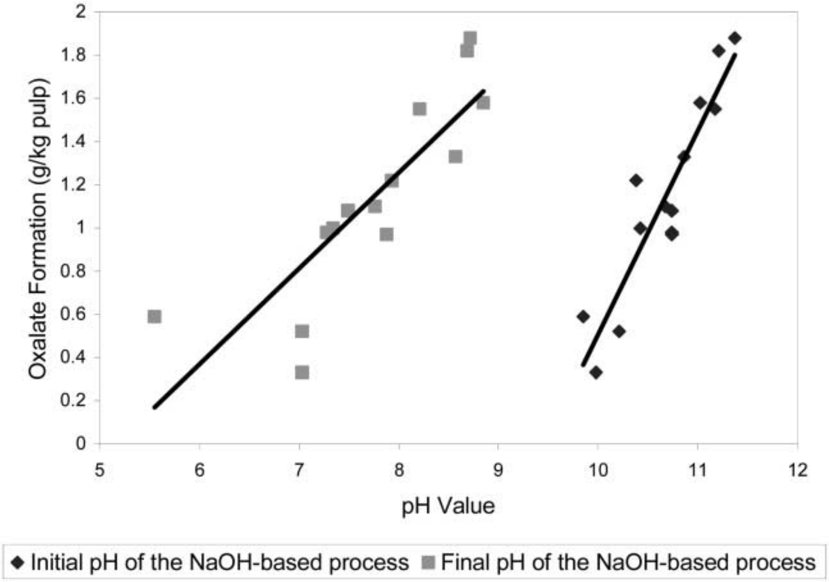


Figure 5. Relationship between initial and final pH in respect to oxalate formation for the CTMP maple pulp.

of the NaOH-based process, as a result, one may expect that the oxalate formation would be less than the NaOH-based process.

However, in the present study, no significant difference in the oxalate formation was observed between the NaOH-based and the $Mg(OH)_2$-based processes (Figs. 1 and 4). We offered the following explanation: the oxalate formation from the $Mg(OH)_2$-based process again follows Eq. (1), i.e., its rate is proportional to the perhydroxyl ion concentration; due to a buffering nature of the $Mg(OH)_2$ system, its pH is relatively stable, which leads to a low but constant concentration of perhydroxyl ion. Therefore, the oxalate formation in the $Mg(OH)_2$-based process is slower, as shown in Fig. 6, than the NaOH-based process. A longer bleaching time is usually allowed to compensate for its lower alkalinity (lower reaction rate), and it is also because of the longer reaction that ultimately generates the same amount of oxalate at the same brightness gain.

Figure 6 shows the kinetics of oxalate formation between the NaOH-based and the $Mg(OH)_2$-based processes. The higher rate of oxalate formation in the NaOH-based system is due to its higher OOH^- concentration, which is a result of its higher alkalinity. Also due to the rapid decrease in pH and $[OOH^-]$, the rate of oxalate formation in the NaOH-based system slows

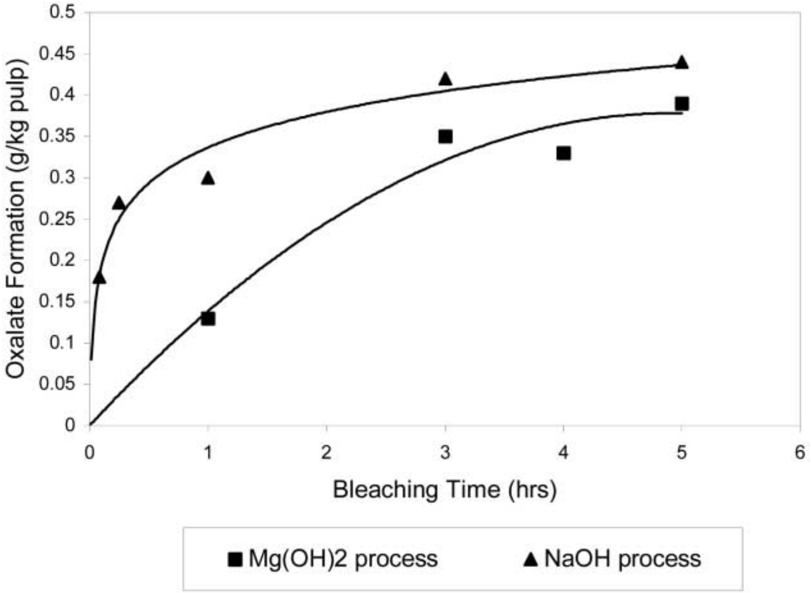


Figure 6. Comparison of the kinetics of the oxalate formation between the NaOH-based and $Mg(OH)_2$-based peroxide processes for the Eastern Canadian TMP.

down dramatically after the completion of the initial phase. The above is in sharp contrast to the kinetics in the $Mg(OH)_2$-based process, whose oxalate formation is much slower, but a rather gradual process. Certainly the difference is due to the lower but constant alkalinity of the $Mg(OH)_2$-based system, resulting in a lower but constant OOH^- concentration, which determines the oxalate formation kinetics.

Based on the discussion so far, one can conclude that both the brightness gain and the oxalate formation are due to the reactions with perhydroxyl ion (OOH^-), which are responsible for the direct correlation between the brightness gain and oxalate formation shown in Figs. 1 and 4. Evidence has been shown[16] that oxalate is formed from the reactions between lignin and hydrogen peroxide. Therefore, it is expected a constant stoichiometric relationship between the oxalate formation and hydrogen peroxide consumption during the course of reaction. This hypothesis is supported by the results in Figs. 7 and 8. It is shown that the same amount of oxalate was formed at the same peroxide consumption, in spite of the different bases used for bleaching. The conclusion that the oxalate formation is proportional to the consumption of bleaching agents and lignin has been well documented in literatures. Elsander et al.[17]

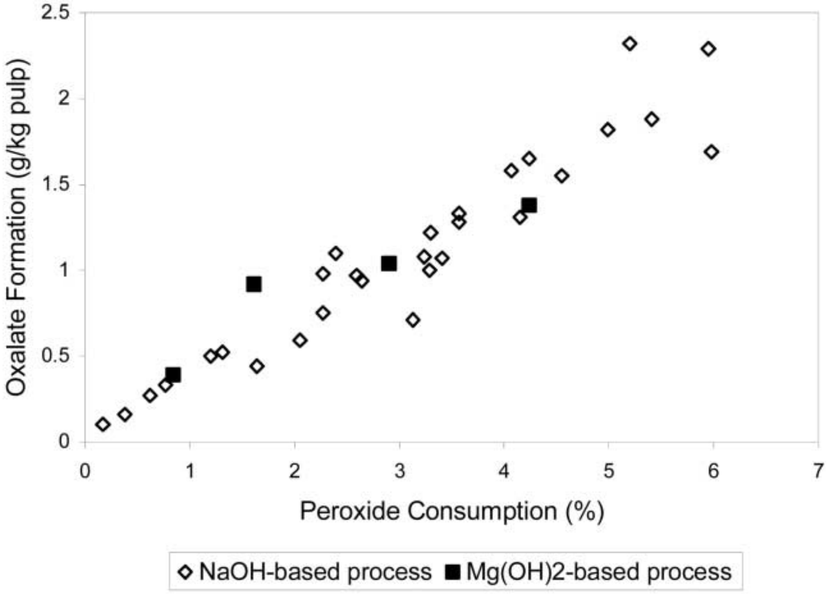


Figure 7. Correlation between oxalate formation and peroxide consumption for the CTMP maple pulp.

found that the oxalate formation increased linearly with the reduction in kappa number and with the consumed oxidation equivalent of bleaching chemicals that are commonly applied during chemical pulp bleaching. Ulmgren and Rådeström[18] reported that the presence of organic substances in the filtrate of a ClO_2 stage led to an increase in the oxalate formation during hot storage.

Figure 2 shows that in comparison with the NaOH-based process, most of newly formed oxalate from the Mg(OH)$_2$-based process was found in the soluble form. The underlying mechanism is that magnesium cations are preferentially interacted with oxalate when compared to calcium.[19] Magnesium oxalate has a much higher solubility, for example, Ulmgren and Rådeström[20] reported that the observed solubility of magnesium oxalate has two or three logarithmic units greater than that of calcium oxalate under the same experimental conditions. Another possibility is that magnesium and calcium can form a co-product with oxalate, for example, $MgCa(C_2O_4)_2$ and its solubility is much higher than that of CaC_2O_4.[21]

The positive effect of magnesium sulfate in decreasing the oxalate-related scaling has been reported in the literature.[11,22,23] STFI in Stockholm Sweden has patented a method to minimize or avoid precipitation of calcium oxalate during bleaching by adding magnesium sulfate to the

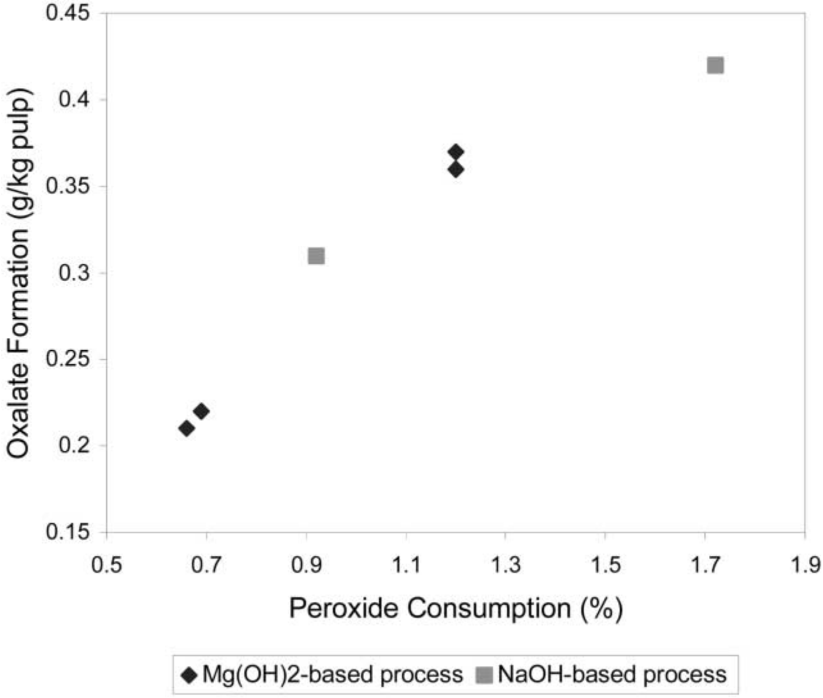


Figure 8. Correlation between oxalate formation and peroxide consumption for the Eastern Canadian TMP pulp.

process.[22] This method has been tested successfully in kraft bleach plants,[23] as well as the refining stage and peroxide stage of the mechanical pulp manufacturing process.[13]

Using magnesium sulfate to decrease the silicate-related scaling in the peroxide bleaching of mechanical pulp manufacturing process has also been implemented in a mill.[19] Its chemistry was suggested as follows: magnesium interacts with silicate as a hydrolyzed cation ($MgOH^+$) throughout the pH range of ~8.2–10.8, which is the typical pH range of peroxide bleaching. The hydrolyzed magnesium cations can then strongly adsorb onto silicate. On the other hand, the concentration of $CaOH^+$ becomes significant only at a pH >10.5. In this way, magnesium preferentially interacts with silicate, minimizing the formation of calcium silicate, which causes the formation of scaling.

It is noted that the dissolved organic substances (measured as COD) of the filtrate can also increase the solubility of calcium oxalate, and thus decrease the oxalate-related scaling.[24,25] The filtrates from the $Mg(OH)_2$-based process contain less COD than that of the NaOH-based process. However, they have more soluble oxalate due to the high magnesium content. The results can be explained by the assumption that the effect of magnesium was greater than the effect of dissolved organic substances.

CONCLUSIONS

When magnesium hydroxide replaces sodium hydroxide as a base for peroxide bleaching of mechanical pulps, the same amount of oxalate is formed at the same brightness target. However, the newly formed oxalate in the $Mg(OH)_2$-based process is almost completely soluble, which is due to the presence of magnesium ions. Therefore, we reached the conclusion that the oxalate-related scaling is significantly less or even negligible during the $Mg(OH)_2$-based peroxide process.

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