Partition of soluble and precipitated oxalate and its implication on decreasing oxalate-related scaling during peroxide bleaching of mechanical pulps

By L. Yu and Y. Ni

Abstract: We determined the effect of various process parameters (hydrogen peroxide charge, caustic soda charge, and bleaching consistency) on the partition between soluble and precipitated oxalate. At a higher peroxide charge or caustic soda charge, more oxalate is in the soluble form. Decreasing the pulp consistency can increase the fraction of soluble oxalate. Also, a partial replacement of NaOH with Mg(OH)₂ as the alkali source during peroxide bleaching can increase the amount of soluble oxalate, thus effectively decreasing oxalate-related scaling.

HE FORMATION OF CALCIUM OXALATE scale continues to be a severe problem in many bleach plants [1,2,3]. During peroxide bleaching of mechanical pulps, particularly for the production of high-brightness bleached mechanical pulps, a significant amount of oxalate is formed, which leads to calcium oxalate-related scaling in mills’ processing equipment [3].

Oxalate in pulp slurry can be present in both soluble and precipitated forms. The precipitated oxalate can (i) be with colloids and/or fines in bleaching filtrate, (ii) deposit onto pulp fibers. The presence of the precipitated oxalate was observed in recent studies on both a bleached aspen mechanical pulp and a bleached CTMP maple pulp [4,5]. The soluble fraction of oxalate contains mainly oxalate ions. It may also contain CaC₂O₄ nuclei and small CaC₂O₄ crystals which are too small to be separated in the 0.45 µm (micrometer) membrane; the latter, however, accounts for a small fraction.

The partition between the soluble and precipitated oxalates is an important issue at pulp mills. Increased soluble oxalate in bleaching filtrate will lead to less CaC₂O₄ related scaling in process equipment, as well as less precipitated oxalate in pulp fibers. While the negative effect of scaling is well known, the presence of the precipitated oxalate in pulp fibers could cause problems in the subsequent operations, such as lower sizing degree [6].

The partition between the soluble and precipitated oxalates is strongly dependent on process conditions, including [7,8]:
* the solubility of CaC₂O₄,
* ion supersaturation,
* the amount of nucleation sites,
* precipitation rate,
* contacting time.

Peroxide bleaching is an ion supersaturated system, with sufficient nucleation sites; its residence time is long enough to have adequate contact time. In addition, the precipitation rate is high in the process [8]. Therefore, one can conclude that the solubility of CaC₂O₄ is a key parameter in the oxalate partition.

The CaC₂O₄ solubility is often affected by temperature, ionic strength, pH, and dissolved organic substances. The change in the solubility of CaC₂O₄ as a function of temperature and ionic strength was found to be rather small, under typical conditions interesting to the pulp and paper industry [8,9]. The concentration of dissolved organic substances and the pH are the key factors affecting the CaC₂O₄ solubility in pulp slurry, and consequently affecting the oxalate partition.

In the present paper, we studied the effects of various factors on the oxalate partition during peroxide bleaching, including hydrogen peroxide charge, caustic soda charge, and bleaching consistency. The underlying mechanism accounting for some observations was investigated by determining the CaC₂O₄ solubility of a model system containing lignin and polygalacturonic acid (PGA). We also examined what effect replacing a portion of the NaOH with Mg(OH)₂ as the alkali source would have on the partition between soluble and precipitated oxalate, and its implication on decreasing oxalate-related scaling.

EXPERIMENTAL

Samples
CTMP maple pulp was received from a mill in Quebec.

Chelation
Prior to peroxide bleaching, a chelation stage with DTPA was carried out at 70°C and 3% pulp consistency for 30 min. The pulp was acidified to pH 6-6.5 by the addition of H₂SO₄ before 0.5% DTPA was charged. After the chelation stage, the pulp was washed thoroughly and its brightness was 42.9% ISO.

Peroxide Bleaching
Hydrogen peroxide bleaching was performed in sealed polyethylene bags at 16% consistency (or other specific consistencies) and 80°C for 3 hours. The bleaching chemicals were composed of H₂O₂ (0.2-6.2%), NaOH (1-7%), silicate (2.6%), and MgSO₄ (0.13%). When Mg(OH)₂ was needed, it was directly added into the pulp slurry before other chemicals. At the completion of peroxide bleaching, samples were taken for final pH, pulp brightness and chemical oxygen

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The Solubility Determination of Model Systems

The solubility of a model solution of bleaching filtrate was studied by observing the spontaneous precipitation from supersaturated solutions [9]. The experiments were carried out at room temperature for 2 hours, according to a procedure established earlier [10]. For the soluble oxalates, the sample was obtained from filtering bleaching filtrate through a 0.45µm filter. The oxalate concentration was analyzed in an IC (Ion Chromatographic) system. The precipitated oxalates were then calculated as the difference between the total and soluble oxalates. A Dionex DX-900 IC System, together with a suppressed conductivity detector, was used to determine the oxalate concentration. The conditions were: AS4A-SC analytical column, AG4A-SC guard column, 1.8 mM Na2CO3 and 1.7 mM NaHCO3 as the eluent at 2.0 ml/min.

RESULTS AND DISCUSSION

Effect of Hydrogen Peroxide Charge on Oxalate Partition

Figure 1 shows the amount of soluble and precipitated oxalate in bleached pulp slurry as a function of hydrogen peroxide charge. Two distinct phases of the oxalate partition in the pulp slurry can be identified: both the soluble and precipitated oxalate increased when the H2O2 charge was raised from 1 to 4%; then they leveled off when the H2O2 charge was further increased from 4 to 6.2%.

The increase in soluble oxalate in the first phase of Fig. 1 indicates an increase in the CaC2O4 solubility in the bleaching filtrate. As mentioned in the introduction above, pH and dissolved organic substance (measured as COD) are the key factors affecting the CaC2O4 solubility. Since the pH of the bleaching filtrate in Fig. 1 was similar, the change in the CaC2O4 solubility is mainly due to the change in COD.

Included in Fig. 1 are also the results for COD of the filtrate as a function of the H2O2 charge. As expected, the COD increases with the H2O2 charge, and the increase in the CaC2O4 solubility in the first phase can be explained by the increase in dissolved organic substance. This is in agreement with the results of Fiskari et al [11] and Ulmgren et al [8,12]. For example, Fiskari et al found that a higher T0C in the bleaching filtrate from a P stage of a hardwood pulp TCF sequence resulted in a higher COD level, a further increase in organic substance had only slight effect on the CaC2O4 solubility. This indicates that the effect of COD has reached a plateau at this high level. A possible explanation would be that the properties of dissolved organic substances had changed at this relatively high COD value. For example, the molecular weight of organic substance might increase with the rise in COD [14]. These organic substances with higher molecular weight would have less anionic sites than those with lower molecular weight. The anionic sites are responsible for crystal distortion.

Solubility of Model Systems

Since the bleaching filtrate contains dissolved organics, we determined the effect of lignin and carbohydrate (polygalacturonic acid as a model) on the CaC2O4 solubility. The observed solubility (Ls) of CaC2O4 of this solution was calculated as:

\[ L_s = \frac{[Ca^{2+}]_{total\ dissolved}[C_2O_4^{2-}]_{total\ dissolved}}{K_{sp}} \]

For a pure water system without any organic substance present, log Ls \( \equiv -7.8 \) (pH 4.5-7.5, 20°C, \( Ca^{2+}/C_2O_4^{2-} = 1.3 \)) was determined. The result was checked against those from the literature: log Ls \( \equiv -7.7 \) (pH 5-10, 30°C, \( Ca^{2+}/C_2O_4^{2-} = 1 \)) by Ulmgren et al [9] and log Ls \( \equiv -7.6 \) (for CaC2O4 monohydrate, at 25-50°C) by Tomazic et al [15]. The observed solubility here is higher than log Ksp of CaC2O4 (~8.5) because of the different ionic strength, I (I = 2.25 \( (10^{-4} \text{ mol/L, versus 0.0266 mol/L for the present system}) \).

The effect of dissolved organics on the CaC2O4 solubility was also confirmed in the model system. In Fig. 2, the observed CaC2O4 solubility was higher when lignin and PGa were present. A higher lignin/PGa concentration resulted in a higher solubility.

As shown in Fig. 2, the solubility is greater with a lower pH in the acidic regime for all systems, mainly due to the formation of oxalic acid. On the other hand, the solubility also increased with increasing pH when the pH was above 6. Ulmgren et al studied the effect of pH on the solubility of CaC2O4 in several bleach plant filtrates (D1, Q, Z) [8]. They found that when pH was raised from 5 to 12, the CaC2O4 solubility remained almost constant, which is different from that in Fig. 2. This difference is due to different experimental conditions. In their case, the ionic strength remained the same at different pH values, while in Fig. 2 the ionic strength increased at a higher pH due to the higher ionic strength, I, (I = 2.25 \( (10^{-4} \text{ mol/L, versus 0.0266 mol/L for the present system}) \).

Effect of Caustic Soda Charge on Oxalate Partition

Figure 3 shows the amount of soluble and precipitated oxalate as a function of the NaOH charge. Included are also the COD results and the pH of filtrates at the end of bleaching (as bracket on the COD curve). An increase in the caustic soda demand (COD), which were carried out in accordance with the PAPTAC standard methods.

The Solubility Determination of Model Systems

The solubility of a model solution of bleaching filtrate was studied by observing the spontaneous precipitation from supersaturated solutions [9]. The experiments were carried out at room temperature for 2 hours, according to a procedure established earlier [10]. For the soluble oxalates, the sample was obtained from filtering bleaching filtrate through a 0.45µm filter. The oxalate concentration was analyzed in an IC (Ion Chromatographic) system. The precipitated oxalates were then calculated as the difference between the total and soluble oxalates. A Dionex DX-900 IC System, together with a suppressed conductivity detector, was used to determine the oxalate concentration. The conditions were: AS4A-SC analytical column, AG4A-SC guard column, 1.8 mM Na2CO3 and 1.7 mM NaHCO3 as the eluent at 2.0 ml/min.
charge results in the increased pH and COD, thus affecting the oxalate partition.

As shown in Fig. 3, the soluble oxalate increased with the increased NaOH charge, while the precipitated oxalate was at its highest level at about 4% NaOH charge (its end pH about 8), and then decreased significantly. According to the study of the model solution, at a pH of higher than 6, the CaC$_2$O$_4$ solubility increased with pH. Thus, the increased solubility at higher than 4% NaOH charge, as seen in Fig. 3, was due to the synergetic effect of a higher pH and more dissolved organic substances.

We further studied the oxalate partition by adjusting the pH of the bleached pulp slurry and the results are shown in Fig. 4. The pH at the completion of bleaching under the specified conditions was 8.7, which was then adjusted to 3.2 or 10.3, respectively. In both cases, the amount of the precipitated oxalate decreased, indicating that some of the precipitated oxalate was dissolved. The practical implication is that the calcium oxalate deposit onto pulp fibers could be largely dissolved by adjusting the system to be more acidic or alkaline. For example, a kraft pulp mill reported a better washing of oxalate from pulp at a higher pH [17].

**Effects of Consistency on Oxalate Partition**

Figure 5 shows the effect of bleaching consistency on the formation and partition of oxalate. The amount of total oxalate formed increased slightly when the consistency was raised from 5 to 16%. This can be explained by the higher reactant concentrations at higher bleaching consistency, resulting in faster kinetics, as well as more total oxalate formation.

As shown in Fig. 5, there is more soluble oxalate in filtrate at a lower pulp consistency than at a higher consistency. Certainly this is because more water is present at the lower consistency.

Usually, the CaC$_2$O$_4$ scaling is difficult to remove. However, our results from Fig. 5 show that it could be readily re-dissolved. Krasowski et al also found that effective washing can reduce oxalate-related scaling [18]. They removed 50% of the total...
oxalate in bleached pulp slurry from C-stage by filtering with deionized water [18]. The difference could be explained by the different crystal structures between newly formed CaC₂O₄ and the oxalate-related scaling. If it is in the form of dihydrate or very fine monohydrate crystals with a disordered lattice, both of which are unstable [12], it can be re-dissolved readily. The dihydrate can be converted to stable monohydrate at equilibrium [13]. The CaC₂O₄ scaling is mostly in the form of monohydrate [3], which is derived from dihydrate when sufficient time is given.

### Partial Replacement of NaOH with Mg(OH)₂

Table I gives the experimental conditions and bleaching results [22], and Fig. 6 shows the oxalate formation and the partition between the precipitated and soluble oxalate. The Mg(OH)₂ replacement ratio is defined as the mole equivalent of Mg(OH)₂ on a total alkali of 4.2% NaOH. The amount of the newly-formed oxalate for bleaching experiments with 0-50% Mg(OH)₂ replacement was found to be at the same level of 1.85±0.09 g/kg pulp, Fig. 6. This can be explained by the similar peroxide consumption (4.2±0.1%), Table I. Our earlier results [19] showed a close relationship between the amount of oxalate formed and the peroxide consumption. The magnesium hydroxide slurry used in the present study contains impurities, including transition metals. When more Mg(OH)₂ was charged, more transition metals were introduced into the system. This explains the higher peroxide consumption and consequently the higher oxalate formation at 75% and 100% replacement. Other researchers also reported that a higher Mg(OH)₂ charge led to increased peroxide consumption [20, 21].

Figure 6 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 replacement, the amount of precipitated oxalate was negligible. Therefore, one can conclude that at a 30-50% replacement of NaOH with Mg(OH)₂, the calcium oxalate scaling is essentially inhibited, which is the basis of our recommendation to the industry to decrease the oxalate-related scaling during the manufacturing of bleached mechanical pulps [22]. The explanation for the above results is as follows: magnesium ions, not calcium, preferentially interact with oxalate under the conditions of peroxide bleaching and magnesium oxalate has a higher solubility [21,23,24]. Figure 6 also shows an increase in the precipitated oxalate at a Mg(OH)₂ substitution of 75% and 100%, which may be due to: i) the increased oxalate formation, or ii) more calcium introduced into the system by the very high charge of Mg(OH)₂.

Another benefit of the partial substitution of Mg(OH)₂ for NaOH during peroxide bleaching of mechanical pulps is a higher brightness gain, as shown in Table I. In a range of 15-40% Mg(OH)₂ replacement ratio, the brightness of the bleached pulp was higher than the control (0% Mg(OH)₂ replacement ratio). This is in agreement with earlier results [21] obtained in a two-stage peroxide process.

The improved brightness gain when part of the NaOH was replaced by Mg(OH)₂ may be partly explained by the decreased alkaline darkening in the peroxide process. It is known that alkaline darkening occurs during peroxide bleaching and has negative effects on the bleaching efficiency and the brightness ceiling of mechanical pulps [25-29]. Results [29] have shown that the higher the pH, the more the brightness loss during alkaline darkening, also not all of the newly-formed chromophores during alkaline darkening are reactive towards peroxide. When Mg(OH)₂ is partially substituted for NaOH, the pH profile was lower than the control, Table I. As a result, the alkaline darkening would be decreased, which would be then partially responsible for the higher brightness.

It is noted that at the 100% Mg(OH)₂ replacement ratio, the brightness of the resulting pulp was lower than the control, which is in agreement with our earlier results for a very high brightness CTMP hardwood pulp [21,29]. On the other hand, for pulp grades of about 70% ISO, the Mg(OH)₂-based peroxide process offered a similar brightness gain to the NaOH-based peroxide process [30].

### CONCLUSIONS

- The formation of oxalate inevitably occurs during peroxide bleaching of mechanical pulp. It was found that the hydrogen peroxide and caustic soda charges can significantly affect the partition between the soluble and precipitated oxalate. These results can be explained by the change in the CaC₂O₄ solubility. The pH and the amount of dissolved organic substance present in the bleaching filtrate are the two main parameters affecting the CaC₂O₄ solubility.
- Lowering the bleaching consistency will lead to more soluble oxalate in the bleaching filtrate.
- A partial replacement of NaOH with Mg(OH)₂ is effective in decreasing the amount of the precipitated calcium oxalate during peroxide bleaching. At a 30-50% replacement ratio, the formation of precipitated oxalate is negligible. The chemistry is that magnesium ions, not calcium, preferentially interact with oxalate under the conditions of peroxide bleaching and the formed magnesium oxalate has high solubility. Also, a higher brightness is achieved at a partial substitution of Mg(OH)₂.

### LITERATURE


### TABLE I. Results for partial replacement of NaOH with Mg(OH)₂

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Keywords: OXALATES, SCALING, PEROXIDE BLEACHING, MECHANICAL PULPS, PRECIPITATES, PROCESS VARIABLES.