The solubility of calcium carbonate in green liquor handling systems

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ABSTRACT: The formation of hard calcite ($CaCO_3$) scale in green liquor handling systems is a persistent problem in many kraft pulp mills. $CaCO_3$ precipitates when its concentration in the green liquor exceeds its solubility. While the solubility of $CaCO_3$ in water is well known, it is not so in the highly alkaline green liquor environment.

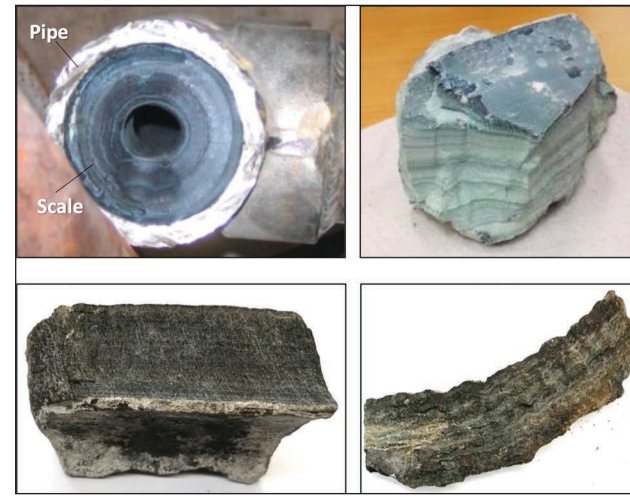
A systematic study was conducted to determine the solubility of $CaCO_3$ in green liquor as a function of temperature, total titratable alkali (TTA), causticity, and sulfidity. The results show that the solubility increases with increased temperature, increased TTA, decreased causticity, and decreased sulfidity. The new solubility data was incorporated into OLI (a thermodynamic simulation program for aqueous salt systems) to generate a series of $CaCO_3$ solubility curves for various green liquor conditions. The results help explain how calcite scale forms in green liquor handling systems.

Application: Understanding how $CaCO_3$ scale is formed helps pulp mills develop viable strategies for mitigating the problem.

Hard scale formation in green liquor handling systems is a persistent problem in kraft pulp mills. Scale has been found throughout the causticizing plant of the chemical recovery process. It occurs virtually everywhere from the dissolving tank walls, floor, and agitators to green liquor filter cloths, pipelines, pumps, and heat exchangers, as well as slaker walls and screws, and causticizer walls and agitators. The severity of scaling varies from mill to mill, and in severe cases, it can lead to unscheduled equipment shutdowns for scale removal, which is both time consuming and costly.

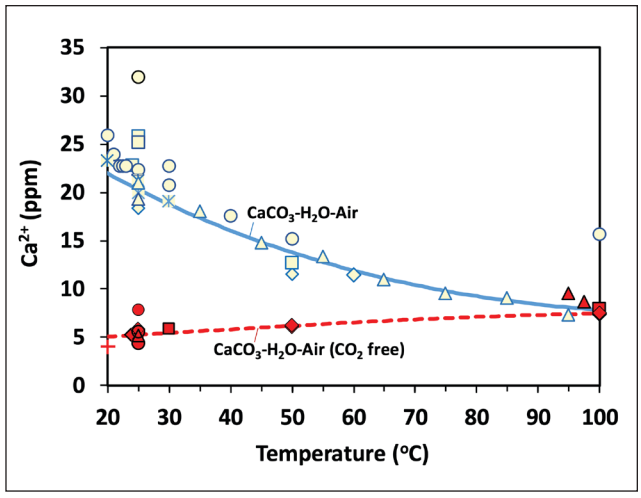
In previous studies [1,2], we have characterized scale samples from the green liquor processing equipment of several kraft mills and studied the formation of pirssonite ($Na_2CO_3 \cdot 2H_2O$), a double salt of sodium and calcium carbonate, in the green liquor handling system. Out of the 12 scale samples that were analyzed from 10 kraft mills, eight samples were calcite, the most stable polymorph of calcium carbonate ($CaCO_3$), and the remaining four samples were pirssonite. Most pirssonite scales were collected from the dissolving tank, and six of the eight $CaCO_3$ scale samples were collected from pipelines following the dissolving tank. $CaCO_3$ scales tend to be harder than pirssonite scales.

In addition to the above, we have analyzed over 30 scale samples from various mills in the past two years. The results show that scales collected from dissolving tanks are mostly pirssonite, whereas scales collected downstream of the dissolving tank are primarily $CaCO_3$ (**Fig. 1**). Similar observations have been made by other researchers [3] who found that that scales collected from the dissolving tank were composed of pirssonite and sodium carbonate monohydrate ($Na_2CO_3 \cdot 2H_2O$), and samples collected from the raw green liquor pipeline were mostly composed of $CaCO_3$.

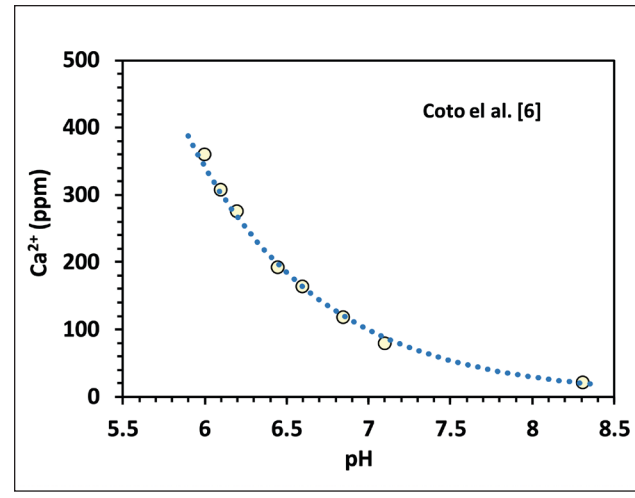


1. Hard calcite ($CaCO_3$) scale formed in green liquor pipelines of various mills.

In order to minimize $CaCO_3$ scale formation in the green liquor system, it is important to understand the solubility of $CaCO_3$ in green liquor and how it is affected by the liquor characteristics; i.e., temperature, total titratable alkali (TTA), and sulfidity. While the solubility of $CaCO_3$ in aqueous systems has been well studied [4-7], there are no published studies of $CaCO_3$ solubility in the strong alkaline green liquor environment. There is therefore a need to develop fundamental experimental data to understand the solubility of $CaCO_3$ in green liquor, and how it is affected by various operating conditions of the causticizing plant.



2. The solubility of $CaCO_3$ in water exposed to air and to a carbon dioxide (CO_2) free environment. Adapted from OLI Systems Inc. [5].



3. Effect of pH on $CaCO_3$ solubility in water exposed to air at 25°C under 1 bar pressure [6].

The objective of this study was to perform laboratory experiments to examine the effect of sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), and sodium sulfide (Na_2S) concentrations on $CaCO_3$ solubility in water, and to use mill experience to explain and minimize scaling problems [8]. The study consisted of two parts. Part 1 investigated the solubility of $CaCO_3$ in green liquor and incorporated the obtained solubility data into OLI (a commercially available advanced thermodynamic simulation program from OLI Systems, Cedar Knolls, NJ, USA) to develop a predictive model for $CaCO_3$ precipitation. OLI has been previously used within our research group to determine the solubility of pirssonite in the green liquor system [2]; the solubilties of sodium chloride (NaCl), potassium chloride (KCl), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), sodium sulfate (Na_2SO_4), and potassium sulfate (K_2SO_4) in ash leaching systems [10]; and the effect of K^+, Cl^- and SO_4^{2-} ions on the causticizing reaction [9]. Part 2 analyzed scaling problems at several kraft pulp mills (i.e., how scales form and how the scaling problem was affected by operating conditions of the causticizing plant).

This paper first discusses the solublity of $CaCO_3$ in water based on data obtained from literature, followed by the results obtained from Part 1 of the study and the practical implications of the results. Part 2 will be discussed in a future paper.

CALCIUM CARBONATE SOLUBILITY IN WATER

The solubility of $CaCO_3$ in water varies depending on the type and concentration of ions present in the water and the temperature of the solution. As shown in **Fig. 2**, the solubility of $CaCO_3$ in water exposed to air is known to decrease with an increase in water temperature (yellow/open symbols and blue/solid curve). This inverse solubility of $CaCO_3$ with temperature is due to the ability of water to absorb carbon dioxide (CO_2), which is present in air at about 300 ppm. As CO_2 is absorbed in water, weak carbonic acid (H_2CO3) is formed (Reaction 1), which dissolves $CaCO_3$, as per Reaction 2 [4].

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad \text{(Reaction 1)}$$

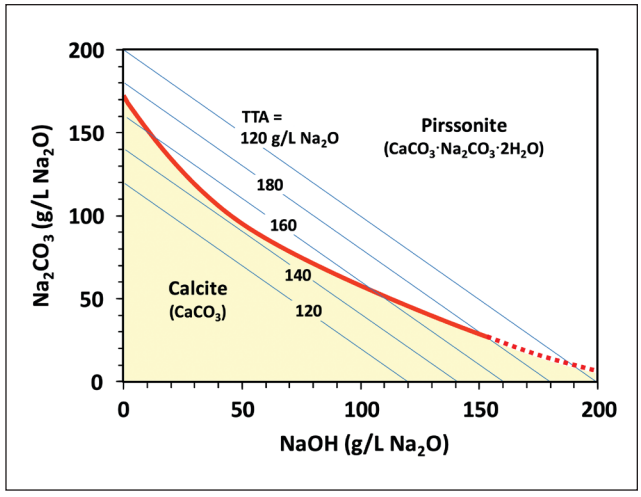
$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \quad \text{(Reaction 2)}$$

As temperature increases, the ability of CO_2 to dissolve in water decreases, making it easier for $CaCO_3$ to precipitate. This, in turn, lowers the calcium ion (Ca^{2+}) concentration in the solution, and hence, the $CaCO_3$ solubility. The decrease in solubility with increased temperature is the main cause of $CaCO_3$ scale formation in kitchen kettles, or on the surface of heat exchanger tubes, which have a higher temperature than the bulk solution.

In a CO_2-free system, the $CaCO_3$ solubility increases with increasing temperature (Fig. 2, red/solid symbols and red-broken curve) due to the hydrolysis of $CaCO_3$ into $CaOH^+$ and HCO_3^-. This figure has been adapted from OLI Systems [5], and the individual data points are a compilation of literature data from 1857 to 2012 in the temperature range between 20°C to 100°C. Because the green liquor is highly alkaline, any acidity induced by dissolved CO_2 will be neutralized and thus prevent Reaction 1 from occurring. The solubility of $CaCO_3$ in green liquor where there is no dissolved CO_2 is likely to increase with temperature, similar to that in the CO_2-free system.

The pH of a $CaCO_3$-H_2O-air system is known to have a significant effect on the solubility of $CaCO_3$. **Figure 3** shows how the $CaCO_3$ solubility is a function of pH, based on the data published by Coto et al. [6]. The $CaCO_3$ solubility decreases as the pH of the solution increases.

Because the pH of green liquor is typically above 12, the solubility of $CaCO_3$ in high alkalinities is of interest. Literature data for $CaCO_3$ solubility does not exist for systems above a pH of 9. However, extrapolation of the trend shown in Fig. 3 suggests that the $CaCO_3$ solubility in green liquor is extremely low. The lack of such data is likely due to the difficulty in obtaining accurate measurements of Ca^{2+} at low concentra-



4. Phase stability of calcite and pirssonite in the Na_2CO_3-NaOH-$CaCO_3$-H_2O system at 95°C [2].

tions and in the presence of large amounts of sodium in the solution. In this work, we have managed to successfully determine the concentration of Ca^{2+} in the green liquor system using inductively coupled plasma optical emission spectrometry (ICP-OES).

CALCIUM CARBONATE STABILTY IN GREEN LIQUOR SYSTEMS

Calcium makes its way into the green liquor system from the lime mud particles in weakwash and from the wood. The major constituents of green liquor are Na_2CO_3 and Na_2S, with small amounts of NaOH, Na_2SO_4, NaCl and potassium salts. A typical green liquor has a TTA (as defined in Eq. 1) between 110–140 g/L sodium oxide (Na_2O), a causticity of 5%–20% (Eq. 2), a sulfidity of 30%–40% on TTA (Eq. 3), and a temperature of 85°C–95°C. This corresponds to NaOH and Na_2S concentrations of 5–20 g/L Na_2O and 30–50 g/L Na_2O, respectively. As mentioned earlier, since the solubility of $CaCO_3$ in the green liquor system is low, green liquor is always saturated or supersaturated with Ca^{2+}, making it easier for $CaCO_3$ to precipitate, particularly during process upsets.

$$TTA = [NaOH] + [Na_2CO_3] + [Na_2S] \quad (1)$$

$$\% \text{ Causticity} = \frac{[NaOH]}{[NaOH]+[Na_2CO_3]} \times 100\% \quad (2)$$

$$\% \text{ Sulfidity} = \frac{[Na_2S]}{[NaOH]+[Na_2CO_3]+[Na_2S]} \times 100\% \quad (3)$$

In the above equations, [NaOH], [Na_2CO_3] and [Na_2S] are concentrations of NaOH, Na_2CO_3, and Na_2S expressed as g/L Na_2O.

Figure 4 shows the phase stability of calcite and pirssonite in the Na_2CO_3-NaOH-$CaCO_3$-H_2O system [2]. $CaCO_3$ is likely present in the liquor with Na_2CO_3 and NaOH concentrations falling below the red line. Liquors with a TTA value greater than 150 g/L Na_2O can expect pirssonite to be present, while liquors with a TTA value below 140 g/L Na_2O can expect $CaCO_3$ to be the main scale component.

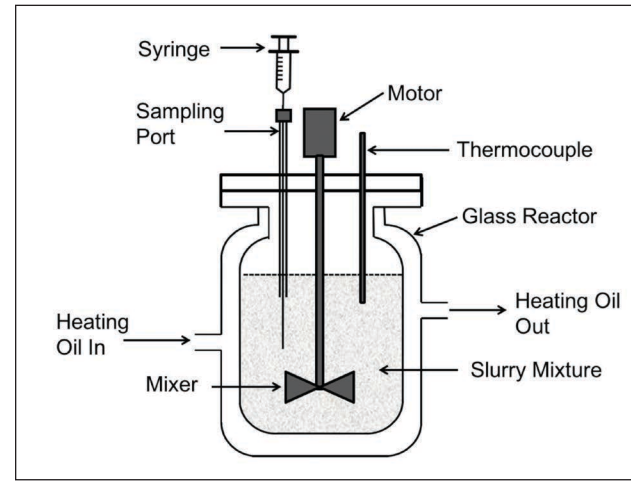
EXPERIMENTAL PROCEDURES

$CaCO_3$ solubility experiments

Two experimental setups were used to determine the solubility of $CaCO_3$. One was for constant temperature experiments and the other for varying temperature experiments. Constant temperature experiments were carried out using a silicone oil bath, which held up to three 100 mL Erlenmeyer flasks. Due to the extremely low solubility of $CaCO_3$ and the difficulty in obtaining precise measurements, this setup was used so that similar experiments at the same temperature could be run concurrently. Varying temperature experiments were carried out in a 1 L jacketed reactor vessel (**Fig. 5**). An automatic stirrer was fastened to the top of the reactor and a circulation bath with silicone oil was used to heat the bath to the desired temperature.

All solutions were prepared using analytical grade chemicals and deionized water. Sodium compounds were added to the reaction vessel, and once dissolved, an excess amount of $CaCO_3$ (approximately 2000 ppm) was added to all solutions to produce a slurry (a mixture of $CaCO_3$ and alkaline solution). Liquid samples were taken from the reaction vessel using a 20-gauge needle attached to a plastic syringe, which were then pre-heated to the reaction temperature. Time zero samples were collected prior to $CaCO_3$ addition, once the sodium solution had reached equilibrium. Samples were acquired by puncturing the rubber stopper of the sampling port to prevent water vapor from escaping the vessel. This was important in order to keep the liquor concentration in the reaction vessel constant.

Immediately following sample acquisition, the liquid was filtered using a 0.22 μm polyethersulfone membrane sterile filter. The filtrate was then diluted with 5% nitric acid (HNO_3),



5. Experimental setup for varying temperature reactions.

or deionized water if the system contained Na_2S, to prevent precipitation. The Ca^{2+} concentration was determined by means of ICP-OES.

Solid samples were collected during solubility experiments by filtering the slurry through a 9-cm filter paper with a particle retention of 25 µm. The solid sample was analyzed using a simultaneous thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) analyzer. The thermal analysis was carried out in nitrogen (N_2) from room temperature to 950°C at a heating rate of 20°C/min. TGA/DSC profiles of the sample were compared against those of pure $CaCO_3$. Selected samples were also analyzed by means of X-ray diffraction (XRD) to confirm that the precipitate was calcite.

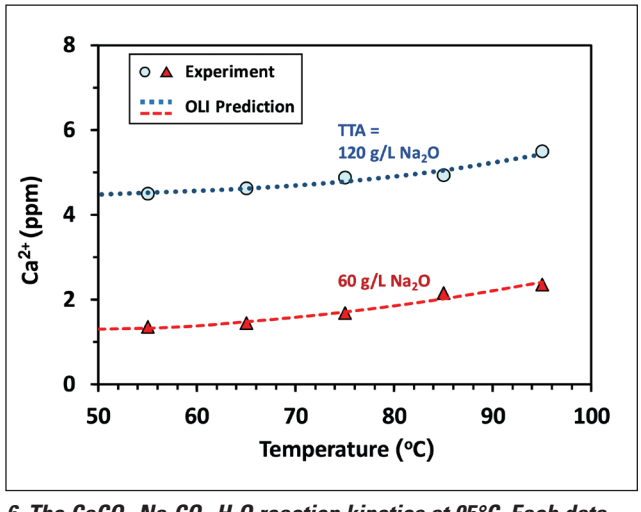
RESULTS AND DISCUSSION

Calcium carbonate solubility

The analysis of $CaCO_3$ solubility in green liquor was broken down into three systems: $CaCO_3$-Na_2CO_3-H_2O, $CaCO_3$-Na_2CO_3-NaOH-H_2O, and $CaCO_3$-Na_2CO_3-Na_2S-H_2O. $CaCO_3$ concentrations have been expressed as parts per million (ppm), which is equivalent to 1 mg/L of green liquor. All other concentrations have been expressed as g/L Na_2O.

Solubility of $CaCO_3$ in a Na_2CO_3 solution

The effect of Na_2CO_3 concentration in the system of $CaCO_3$-Na_2CO_3-H_2O was examined to determine the solubility of $CaCO_3$ at various temperatures. The Na_2CO_3 concentration was varied to produce synthetic liquors with TTA values of 60 and 120 g/L Na_2O. **Figure 6** shows the change in calcium concentration in the solution with time at 95°C. For each data point, several experiments were performed to obtain the average value and standard error. In both TTA cases, the calcium concentration was high at time zero, but decreased over time and approached equilibrium after approximately 4 h. The decrease in $CaCO_3$ solubility is interesting because experiments were performed by dissolving $CaCO_3$ into the system, so one would expect the soluble calcium concentration to increase over time.



6. The $CaCO_3$-Na_2CO_3-H_2O reaction kinetics at 95°C. Each data point is the mean of three trials.

Temperature, °C	Ca^{2+}, ppm	
	Na_2CO_3 = 60 g/L Na_2O	Na_2CO_3 = 120 g/L Na_2O
25	1.23 ± 0.09	4.26 ± 0.14
55	1.36 ± 0.01	4.50 ± 0.96
65	1.44 ± 0.06	4.62 ± 0.55
75	1.67 ± 0.10	4.87 ± 0.31
85	2.15 ± 0.04	4.94 ± 0.20
95	2.35 ± 0.16	5.46 ± 0.40

Ca^{2+} = calcium ion; Na_2CO_3 = sodium carbonate; Na_2O = sodium oxide.

I. Effect of temperature on hard calcite ($CaCO_3$) solubility at Na_2CO_3 (or total titratable alkalki [TTA]) of 60 and 120 g/L Na_2O.

The observed high initial concentration of calcium can be explained as follows: since the analytical grade Na_2CO_3 used contains approximately 0.01% calcium as soluble impurities, when using high concentrations of Na_2CO_3, up to 2000 ppm of calcium may be introduced into the system, resulting in the large initial concentrations as indicated by the time zero sample of Na_2CO_3 in water, prior to $CaCO_3$ addition. When solid $CaCO_3$ particles are added to the reactor, they act as seeding sites for the dissolved calcium to precipitate, decreasing the calcium concentration in the solution until equilibrium is reached.

Table I shows the equilibrium Ca^{2+} concentration at temperatures between 25°C and 95°C for the two synthetic liquors. The equilibrium $CaCO_3$ concentration was found to increase with increasing Na_2CO_3 concentration, or TTA, which follows the trend first published by Felmy et al., who suggested the increase in solubility at high Na_2CO_3 molality (> 0.5 molal, or 31 g/L Na_2O) is due to the formation of the $Ca(CO_3)_2^{2-}$ complex [7]. The increase in $CaCO_3$ solubility with temperature was found to be consistent for both synthetic liquors. A liquor with a Na_2CO_3 concentration of 60 g/L Na_2O had a Ca^{2+} concentration of 1.23 ppm at 25°C, compared to 2.35 ppm at 95°C. At 95°C, the Ca^{2+} concentration in a liquor with a Na_2CO_3 concentration of 120 g/L Na_2O increased to 5.46 ppm. All solid samples collected from the reactor were identified as calcite, as expected.

Solubility of $CaCO_3$ in a Na_2CO_3-NaOH solution

The $CaCO_3$-Na_2CO_3-NaOH-H_2O system was investigated at 95°C for a liquor with a constant TTA of 120 g/L Na_2O to determine the effect of NaOH concentration on $CaCO_3$ solubility. A typical green liquor has a causticity (Eq. 2) of 5%–20%, which corresponds to a NaOH concentration of 6–24 g/L Na_2O when the TTA is equal to 120 g/L Na_2O. For these experiments, the effect of NaOH concentration was studied up to 30 g/L Na_2O. Each experiment took about 4 h to for the system to reach equilibrium. **Table II** shows the equilibrium calcium concentrations at varying NaOH concentrations. Although

NaOH, g/L Na_2O	Ca^{2+}, ppm
0	5.49 ± 0.40
6	5.34 ± 0.29
12	5.17 ± 0.30
18	5.07 ± 0.12
30	4.98 ± 0.36
NaOH = sodium hydroxide; Na_2O = sodium oxide; Ca^{2+} = calcium ion.	

II. Effect of NaOH on $CaCO_3$ solubility at 95°C (TTA = 120 g/L Na_2O).

NaOH, g/L Na_2O	Ca^{2+}, ppm
0	5.49 ± 0.40
12	4.67 ± 0.11
24	3.93 ± 0.01
36	3.49 ± 0.23
48	2.27 ± 0.17
60	1.80 ± 0.06
Na_2O = sodium sulfide; Na_2O = sodium oxide; Ca^{2+} = calcium ion.	

III. Effect of Na_2S on $CaCO_3$ solubility at 95°C (TTA = 120 g/L Na_2O).

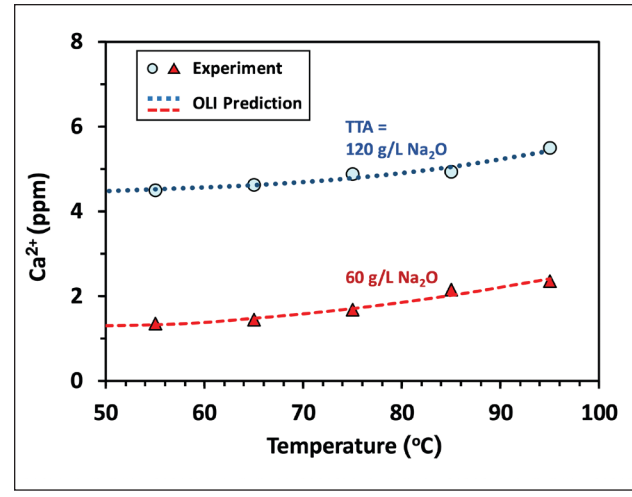
there is a slight decrease in $CaCO_3$ solubility with increasing NaOH concentration, the effect of NaOH is minimal.

Solubility of $CaCO_3$ in a Na_2CO_3-Na_2S solution

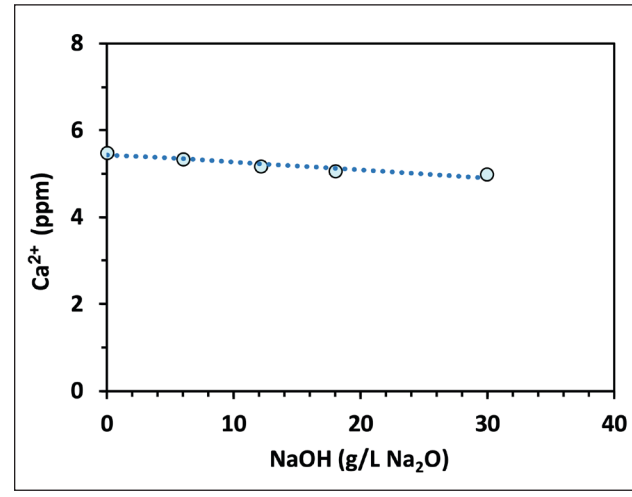
The $CaCO_3$-Na_2CO_3-Na_2S-H_2O system was investigated at 95°C for a liquor with a TTA of 120 g/L Na_2O to determine the effect of Na_2S concentration on $CaCO_3$ solubility. A typical green liquor has a sulfidity (Eq. 3) of 30%–40%. Thus, a liquor with a TTA of 120 g/L Na_2O corresponds to an Na_2S concentration between 24 to 48 g/L Na_2O. For these experiments, the solubility of $CaCO_3$ was investigated in liquors with Na_2S concentrations up to 60 g/L Na_2O. As summarized in **Table III**, the equilibrium calcium concentration decreases with increasing Na_2S concentration. Compared to NaOH, Na_2S has a much larger effect on the solubility of $CaCO_3$, due to the increase in liquor alkalinity, as well as the Na_2S ions.

MODELLING OF $CACO_3$ SOLUBILITY USING OLI

As mentioned previously, OLI has been used widely in our laboratory to examine the solubility of pirssonite [2], and the effects of chloride, potassium, and sulfate ions on the causticizing efficiency [9], as well as the solubility of recovery boiler precipitator ash in water under various ash treatment conditions [10].



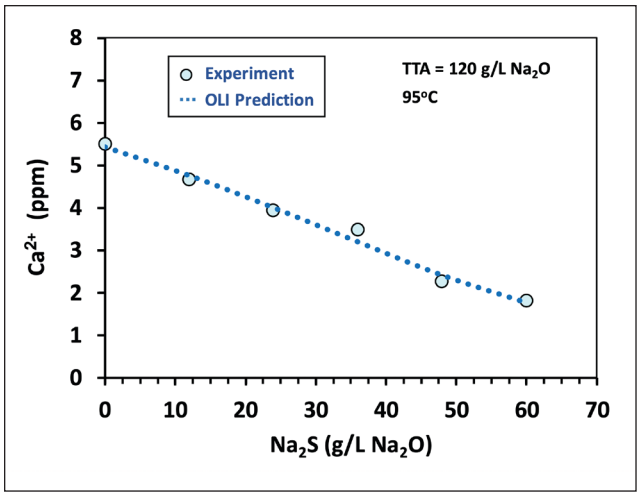
7. Comparison of experimental data and predicted solubility of $CaCO_3$ as a function of temperature at total titratable alkali (TTA) of 60 g/L sodium oxide (Na_2O) and 120 g/L Na_2O in the $CaCO_3$-Na_2CO_3-H_2O system.



8. Comparison of experimental data and predicted model performance for the solubility of $CaCO_3$ as a function of sodium hydroxide (NaOH) concentration in the $CaCO_3$-Na_2CO_3-H_2O system at 95°C.

In order for a thermodynamic program to predict the equilibrium concentration of a certain component in an aqueous system, it requires accurate and reliable thermodynamic properties of all species involved. As discussed previously, since there is no literature data available for $CaCO_3$ solubility in high alkaline solutions, the existing database in OLI cannot be used to predict the $CaCO_3$ solubility in green liquor. In this study, we needed to first produce a new set of thermodynamic data for $CaCO_3$ in high alkaline solutions by regressing the experimental data obtained, and then incorporating them into OLI to calculate the solubility of $CaCO_3$ in green liquor.

Figures 7, **8**, and **9** compare the calculated $CaCO_3$ solubility values and the experimental data for different green liquor temperatures and Na_2S and NaOH contents. In all cases, the agreements were good. The model was subsequently used



9. Comparison of experimental data and predicted model performance for the solubility of $CaCO_3$ as a function of sodium sulfide (Na_2S) concentration in the $CaCO_3$-Na_2CO_3-H_2O system at 95°C.

to investigate effects of green liquor sulfidity, causticity, reduction efficiency, and chloride content on $CaCO_3$ solubility.

Effects of green liquor sulfidity and causticity

For this simulation, the green liquor TTA was set at 120 g/L Na_2O and temperature was at 75°C and 95°C. The green liquor causticity ranged from 0 to 30%, and sulfidity ranged from 0 to 50% on TTA. **Figure 10** shows the effects of green liquor sulfidity and causticity on $CaCO_3$ solubility at 75°C and 95°C. At a given causticity and temperature, the solubility decreases with increasing sulfidity. At a given sulfidity and temperature, the higher the causticity is, the lower the $CaCO_3$ solubility is. The solubility is higher at 95°C (Fig. 10b) compared with that at 75°C (Fig. 10a), consistent with the results shown in Fig. 7. Sulfidity appears to have a greater effect on $CaCO_3$ solubility than causticity, particularly at 95°C.

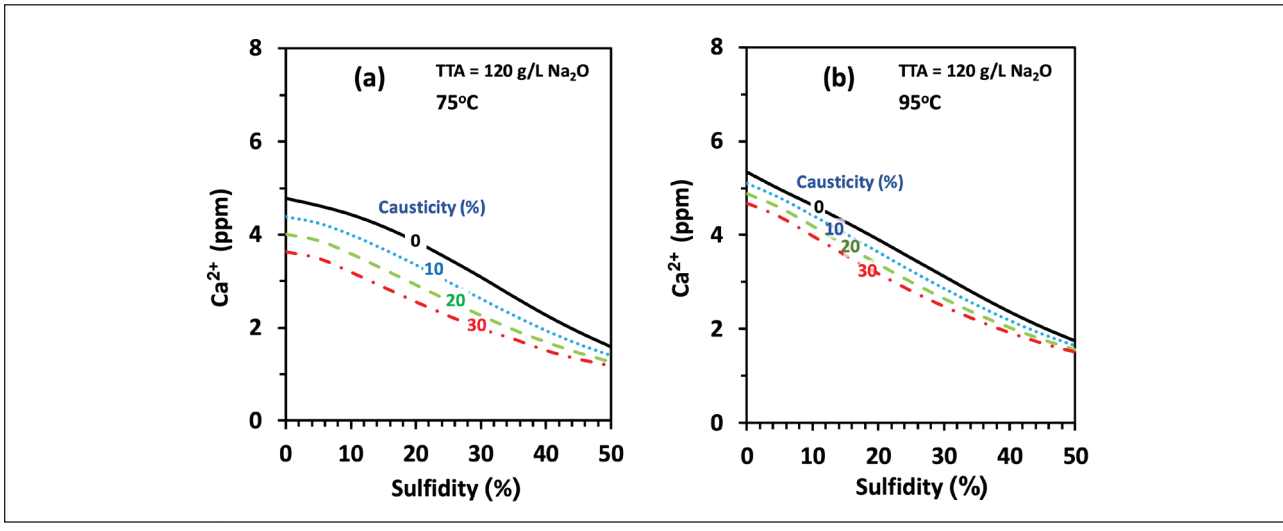
Figure 10 can be used to estimate the amount of calcium that will precipitate from the green liquor solution as a result of temperature change. For example, for a mill with a typical green liquor of 120 g/L Na_2O TTA, 10% causticity, and 30% sulfidity, a decrease in green liquor temperature from 95°C to 75°C will lower the amount of dissolved calcium (Ca^{2+} ions) from 2.8 to 2.6 ppm. This decrease in solubility means that 0.2 ppm of Ca^{2+} will have to precipitate out as $CaCO_3$.

Effects of reduction efficiency and chloride concentration

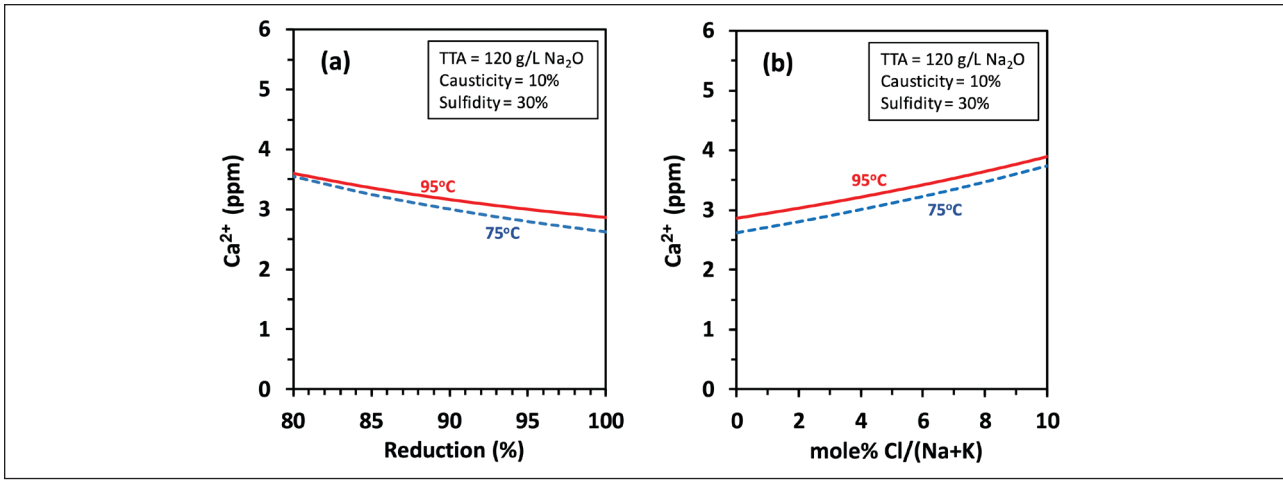
Green liquor reduction efficiency is commonly expressed as percentage of $Na_2S/(Na_2S + Na_2SO_4)$, where Na_2S and Na_2SO_4 are concentrations in g/L Na_2O. It typically varies between 85% and 92%. **Figure 11a** shows the effect of reduction efficiency on $CaCO_3$ solubility. Increasing reduction efficiency causes $CaCO_3$ to dissolve less. This is understandable since a higher reduction efficiency means more Na_2S exists in the liquor, which increases the liquor alkalinity and lowers the $CaCO_3$ solubility (Fig. 9). This also implies that operating at a higher green liquor reduction efficiency will make it easier for calcite scale to form.

Depending on the mill, liquor cycles may have problems with nonprocess element accumulation, most notably chloride (Cl) and potassium (K). Green liquor typically contains 1.5 mole % Cl/(Na+K) for inland mills [11], but can be higher than 10 mole % Cl/(Na+K) in mills where seaborne logs are used. Figure 11b summarizes the effect of Cl in green liquor on $CaCO_3$ solubility at 75°C and 95°C. For simplicity purposes, the potassium concentration in this case is assumed to be zero.

As expected, the 95°C liquor has a higher $CaCO_3$ solubility than the 75°C liquor. Increasing the Cl concentration also increases the $CaCO_3$ solubility. However, because for a given mill, the variation in Cl concentration in the liquor is typically less than +/- 1 mole% Cl/(Na+K), the effect of Cl on $CaCO_3$ scale formation is expected to be insignificant.



10. Predicted $CaCO_3$ solubility curves as a function of sulfidity and causticity for green liquor with 120 g/L Na_2O TTA at (a) 75°C and (b) 95°C.



11. Effects of a) green liquor reduction and b) chloride concentration on $CaCO_3$ solubility at 75°C and 95°C.

SUMMARY AND PRACTICAL IMPLICATIONS

In the caustizing plant of kraft pulp mills, $CaCO_3$ is the major component of scale formed in green liquor handling systems downstream of the dissolving tank. The high alkalinity of green liquor significantly lowers the solubility of $CaCO_3$ in water, making it easier to precipitate. A laboratory study was performed to examine the effects of green liquor properties (temperature, TTA, causticity, and sulfidity) on $CaCO_3$ solubility. The obtained solubility data was used to develop a dedicated database in OLI, a thermodynamic simulation program for electrolyte solutions. The results showed that $CaCO_3$ solubility increases with increasing temperature and TTA, whereas it decreases with increasing causticity and sulfidity.

As the solubility decreases, $CaCO_3$ precipitates. This means that fluctuations within the green liquor system, such as a decrease in temperature or TTA, or an increase in causticity or sulfidity, will result in $CaCO_3$ precipitation. Once the hard scale has already formed, even if these fluctuations are reversed such that the solubility of $CaCO_3$ in the system increases, it is nearly impossible for the already formed $CaCO_3$ scale to re-dissolve. This is because although the solubility of $CaCO_3$ may increase, the surface of the scale is quickly saturated with Ca^{2+} due to its extremely low solubilty. As a result, there is no driving force for dissolution.

From a practical standpoint, the most effective way to prevent $CaCO_3$ scale formation is to minimize temperature, TTA, ating conditions that lead to $CaCO_3$ scale formation. The next step is to assess scale formation conditions at various kraft pulp mills and to see if they are consistent with the laboratory findings.

ABOUT THE AUTHORS

The formation of hard calcite ($CaCO_3$) in the causticizing plant is a persistent problem for many mills. We chose this topic for research in order to understand how scale forms and to devise best strategies for scale formation prevention. The topic complements our previous research, which focused only on pirssonite scale formation.

The most difficult aspect of this study was to accurately measure the extremely low calcium ion (Ca^{2+}) concentrations in green liquor. We addressed the problem using inductively coupled plasma optical emission spectrometry (ICP-OES) and ensuring the machine was accurately calibrated.

As a new graduate student (Giglio), my knowledge of the pulp and paper industry and thermodynamic modeling was limited. This research opened my eyes to both subjects, providing me with a new appreciation for the industry. Our most interesting finding was that the solubility of $CaCO_3$ in green liquor followed the same trends as its solubility in water, with no dissolved CO_2.

Mills might use this information to identify oper-



Giglio



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and sulfidity variations. A simple way to minimize the pipeline temperature fluctuation is to insulate the system. Uninsulated pipelines can produce large temperature gradients, particularly during the winter months. The cooler temperature of the inner pipe surface makes it easier for $CaCO_3$ to precipitate and scale to grow. The low $CaCO_3$ solubility in green liquor also suggests that $CaCO_3$ scale formation is a very slow process. **TJ**

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