MILL EXPERIENCE OF CALCIUM CARBONATE SCALE FORMATION IN GREEN LIQUOR HANDLING SYSTEMS

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ABSTRACT

Calcium carbonate (CaCO₃) often forms hard scale in the green liquor handling equipment in kraft pulp mills. In severe cases, scaling can lead to unscheduled equipment shutdowns for cleaning which can be costly. Scale is formed due to the extremely low solubility of CaCO₃ in the highly alkaline green liquor environment that causes dissolved Ca²⁺ ions in the liquor to precipitate out during a process upset. This paper discusses the scale formation experience at four kraft pulp mills in Canada and Sweden and the results of systematic investigations conducted at these mills. The objective was to determine if there is any correlation between the severity of the scaling problem at each mill, and the design and operating conditions of its causticizing plant. Mill liquors, scale samples and process data (green liquor flow rate, density, TTA, causticity, sulfidity, temperature, suspended solids, etc.) were analyzed to determine the main operating parameters leading to scale formation. The investigation results help identify viable strategies for mills to adopt to minimize scale formation.

INTRODUCTION

In kraft pulp mills, wood is cooked in a digester with white liquor, a hot aqueous solution of sodium hydroxide (NaOH) and sodium sulfide (Na₂S), to make pulp. These cooking chemicals are regenerated by i) concentrating the spent liquor (weak black liquor), ii) burning the concentrated black liquor in a recovery boiler to produce smelt that consists of mostly Na₂CO₃ and Na₂S, iii) dissolving smelt in a dissolving tank to produce green liquor, and iv) causticizing the green liquor with lime (CaO) in the causticizing plant to convert Na₂CO₃ to NaOH. The resulting white liquor is then reused in the pulping process.

One of the major problems in causticizing plant operation is the formation of hard scale in the green liquor handling system. Scale has been found to form virtually everywhere, from the dissolving tank walls, floor and agitators to green liquor filter cloths, pipelines, pumps, heat exchangers, slaker walls and screws, and to causticizer walls and agitators. The severity of scaling varies from mill to mill. Massive scale formed on dissolving tank agitators can throw the agitators off balance causing them to vibrate; hard scale formed on slaker classifier screws makes it difficult to remove grits, while hard scale formed in green liquor pipelines can severely obstruct the liquor flow, resulting ultimately in reduced white liquor production, and hence, low mill productivity. Figure 1 shows examples of scale formation in green liquor pipelines. These scales consisted of over 90% calcium carbonate (CaCO₃). They were hard, stratified and so massive that they almost completely blocked the 8” (20.3 cm) internal diameter pipe.
CaCO₃ has been identified as the main component of the hard scale, particularly at locations downstream of the dissolving tank [1-4]. A systematic study was conducted at the University of Toronto to examine how CaCO₃ forms and what makes the scale hard [5]. The study consisted of two parts. Part 1 investigated the solubility of CaCO₃ in green liquor and incorporated the obtained solubility data into OLI (a commercially available thermodynamic simulation software) to develop a predictive model for CaCO₃ precipitation. The model was then used to predict how operating variables affect the solubility of CaCO₃ and hence scale formation. Part 2 analyzed the scaling experience at several kraft pulp mills, i.e. how scales form, and how the problem was affected by operating conditions of the causticizing plant at each mill.

Solubility experiments carried out in Part 1 of this investigation showed that CaCO₃ solubility increases with increasing temperature and TTA, whereas it decreases with increasing causticity and sulfidity. Based on CaCO₃ solubility curves, it is expected that scaling tendency in the green liquor system increases with low temperature, low TTA, high causticity, and high sulfidity [6].

This paper discusses the results obtained from Part 2 of the study. Four kraft pulp mills, two in Canada (Mill A and Mill B) and two in Sweden (Mill C, Mill D), were visited. The objective was to obtain a better understanding of the scaling problems at each mill. Causticizing plant layouts and operating conditions were compared to determine if the experience at each mill can be explained using the experimental solubility data presented in Part 1 of the study and if there is any correlation between the severity of the scaling problem at each mill, and the design and operating conditions of its causticizing plant.

MILL EXPERIENCE

Mill A, constructed in 1989, is a single production line kraft mill in Canada designed to produce 1100 air dried metric tons/day (admt/d) of bleached hardwood. The mill has been through several major upgrades and is currently running in campaigns of hardwood and softwood with a production target of 1650 admt/d hardwood and 1300 admt/d softwood. The mill has been experiencing severe CaCO₃ scale problems in its raw green liquor pipeline. Anti-scaling chemicals have been used to prevent scale build up with little success. The green liquor lines need to be cleaned every 6 months.

Mill B is an older (1970) single production line kraft mill in Canada, which currently produces 500 admt/d of high performance unleached sack kraft paper with a 50/50 softwood mixture of spruce and pine. Hard scale was often found in pipelines that transport raw green liquor (RGL) from the dissolving tank to the green liquor clarifier. To minimize scaling, the mill adopted the commonly used tactic of line-switching between raw green liquor (RGL) and weakwash (WW), which was mostly successful. In June 2016, the mill stopped practicing the line-switching, and instead added an anti-scaling chemical to the RGL to prevent scale buildup. All pipelines were cleaned prior to this implementation. In October 2017, the mill was forced to shut down due to severe scaling of the lines (Figure 1-Left). Hydroblasting with high pressure (20,000 psi) water for 12 hours was carried out without success. The pipelines were eventually cleaned with hydrochloric acid. The scale formation appeared to be more severe on the inside elbows of
the pipes than the outside, and much of the scaled section was horizontal, although some vertical sections were also affected to some extent. In the spring of 2018 the anti-scaling chemical was removed from the system, and line switching resumed. The mill has not experienced any scale formation since.

Mill C is a 1917 Swedish mill with a current production capacity of 1080 admt/d of bleached/unbleached kraft pulp from softwood. Hard scale is present, but it barely affects the causticizing plant operation.

Mill D is a non-integrated Swedish kraft mill which began its first production in 1895, and has grown to have a current capacity of 1550 admt/d. As with Mill C, scale is always present, but it does not result in unscheduled causticizing plant shutdowns. A summary of each pulp mill can be found in Table 1.

**Table 1. Summary of Investigated Kraft pulp mills.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Mill A</th>
<th>Mill B</th>
<th>Mill C</th>
<th>Mill D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Country</td>
<td>Canada</td>
<td>Canada</td>
<td>Sweden</td>
<td>Sweden</td>
</tr>
<tr>
<td>Year Production Began</td>
<td>1989</td>
<td>1970</td>
<td>1917</td>
<td>1895</td>
</tr>
<tr>
<td>Daily Pulp Production</td>
<td>1,650 (NBHK)</td>
<td>500</td>
<td>1,080</td>
<td>1,550</td>
</tr>
<tr>
<td></td>
<td>1,300 (NBSW)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood Type</td>
<td>56% hardwood</td>
<td>softwood</td>
<td>softwood</td>
<td>2/3 softwood</td>
</tr>
<tr>
<td></td>
<td>46% softwood</td>
<td></td>
<td></td>
<td>1/3 hardwood</td>
</tr>
<tr>
<td>Antiscalants Used</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Pipeline Material</td>
<td>304 SS</td>
<td>304 SS</td>
<td>304 SS</td>
<td>304 SS</td>
</tr>
<tr>
<td>Pipeline Insulation</td>
<td>Partial</td>
<td>Complete</td>
<td>Complete</td>
<td>Complete</td>
</tr>
<tr>
<td>Pipeline ID</td>
<td>20 cm (8&quot;)</td>
<td>15 - 20 cm (6 - 8&quot;)</td>
<td>20 cm (8&quot;)</td>
<td>20 cm (8&quot;)</td>
</tr>
<tr>
<td>Scale Formation Locations</td>
<td>Dissolving tank, green liquor</td>
<td>Raw green liquor</td>
<td>Pressure filters and causticizers</td>
<td>Pressure filters and causticizers</td>
</tr>
<tr>
<td></td>
<td>pipelines</td>
<td>pipelines</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**CAUSTICIZING PLANT DESIGN**

The causticizing plant at Mill A and Mill B (Figure 2) has a much simpler design compared to that at Mill C and D (Figure 3). It consists of a dissolving tank, a green liquor clarifier, a heat exchanger, slaker and a single line of causticizers. There are no green liquor storage tanks. The pipelines between the dissolving tank and clarifier at Mill A are switched between raw green liquor and weak wash every 12 hours to facilitate cleaning of the lines. Mill B did not switch RGL and WW lines between during the period from June 2016 to October 2017, but resumed the line-switching practice after this time. Both mills added antiscalants to their green liquor at the outlet of the dissolving tank.

Mill C and Mill D are equipped with a stabilizing tank after the dissolving tank, and use pressure filters (4 in parallel) and a clarifier to clean the raw green liquor. The pressure filters are cleaned or replaced once a month to remove buildup on filter cloths. The raw green liquor (RGL) and weakwash (WW) lines between the dissolving tank and the stabilizing tank are switched every day at both mills to prevent hard scale from building up in the pipelines. After the green liquor heat exchanger, the system is split into parallel slaking and causticizing lines.
Mills A and B typically experience scale formation in the dissolving tank and raw green liquor lines, while Mills C and D more commonly experience scale buildup downstream in the green liquor pressure filters and causticizers. The design of the causticizing plant at Mills C and D allow for the implementation of scale cleaning procedures that do not impact the daily production of the mill, since the smaller pressure filters at Mill C and D can be taken offline individually to replace or clean the filter. The dual line of causticizers at both mills help keep scale buildup manageable, particularly when cleaning procedures are introduced into the daily operations of the mill. For these reasons, Mills C and D reported less scaling problems compared to Mills A and B.

**OPERATING DATA ANALYSIS**

A site-visit to Mill A was completed in February 2018, and to Mills C and D in June 2018. Four months of operating data (January – April 2018) was gathered for Mill A, while nearly three years of operating data (June 2015 – April 2018) was gathered for Mills B, C and D.

Process data (green liquor TTA, causticity, sulfidity, temperature, and suspended solids) was analyzed to identify any abnormalities in the mill liquor, which could be used to explain the scaling observations in the mills. Plots of the variation in these parameters over the past 3 years are shown in Figure 4-6. Mill A and B have the lowest green liquor TTA, with average values of 114 and 120 g/L Na₂O respectively. Mill D has an average TTA of 126 g/L Na₂O, and Mill C has what is considered a high TTA with average values upwards of 134 g/L Na₂O. Causticity trends are opposite, with Mills A, C, and D having an average causticity of 16.7%, 6.2%, and 4.8% respectively. Causticity is not measured at Mill B. Average sulfidity values are very similar for all mills varying between 27 – 32%.

The temperature drop across the clarified green liquor heat exchanger was plotted for Mills A, C and D as shown in Figure 7. The heat exchanger is typically used to cool the clarified green liquor (CGL) to ensure the temperature in the slaker is between 101-104°C. The average temperature drop across the heat exchanger in Mills A, C and D is 5.7°C, 3.1°C and 2.2°C respectively. The larger temperature variation across the heat exchange could be a cause of the more severe scaling problem at the outlet of the heat exchanger at Mill A compared to Mills C and D.
Figure 3. Green liquor TTA at studied mills (RGL=raw green liquor, CGL=clarified green liquor).

Figure 4. Green liquor causticity for studied mills.
Figure 5. *Green liquor sulfidity for studied mills.*

![Graph showing green liquor sulfidity for studied mills.](image1)

<table>
<thead>
<tr>
<th>Mill</th>
<th>Average Sulfidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mill C RGL</td>
<td>32.3 ± 3.2</td>
</tr>
<tr>
<td>Mill C CGL</td>
<td>32.0 ± 3.2</td>
</tr>
<tr>
<td>Mill D CGL</td>
<td>28.3 ± 2.3</td>
</tr>
<tr>
<td>Mill A RGL</td>
<td>27.2 ± 2.0</td>
</tr>
</tbody>
</table>

*Note: Sulfidity is not recorded at Mill B.*

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Figure 6. *Temperature drop across the green liquor heat exchanger at studied mills.*

![Graph showing temperature drop across the green liquor heat exchanger.](image2)

\[
\Delta T = T_{OUT} - T_{IN}
\]

<table>
<thead>
<tr>
<th>Mill</th>
<th>Average Temperature Drop (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mill A</td>
<td>-5.7</td>
</tr>
<tr>
<td>Mill C</td>
<td>-3.1</td>
</tr>
<tr>
<td>Mill D</td>
<td>-2.2</td>
</tr>
</tbody>
</table>
Figure 8 shows the suspended solids in weak wash, raw green liquor, clarified green liquor, and white liquor at all mills. As expected, the raw green liquor has the highest solids concentration. It is interesting to note that Mills C and D had a very high concentration of suspended solids in the weak wash (200 – 500 mg/L), particularly when compared to Mills A and B which had almost no suspended solids in weakwash. The high concentration of suspended lime mud (CaCO₃) particles in the weak wash may help reduce scale formation in the green liquor system at Mills C and D, as they can act as seeding sites for Ca²⁺ in the green liquor to precipitate in the bulk rather than on equipment walls.

Figure 7. Suspended solid concentration in weak wash (WW), raw green liquor (RGL), clarified green liquor (CGL), and white liquor (WL) for all 4 mills.

ANALYSIS OF SCALE SAMPLES

Four scale samples were collected from Mill A and one was collected from the raw green liquor pipeline blockage at Mill B. Photographs of the scale samples can be seen in Figure 9.

Sample 1 was obtained from the RGL pipeline at the exit of the dissolving tank where the RGL and WW lines were switched every 12 hours. The scale was hard and had a light-grey color. Sample 2 was taken from a blockage in the Mill B raw green liquor pipeline when there was no line switching between the RGL and WW lines. The scale was very hard and dark in colour. Sample 3 was obtained from the RGL “switching tree” where the RGL and WW lines are switched. The scale was black and could break readily with minimal force. Sample 4 was obtained from the CGL outlet of the heat exchanger leading to the slaker. This sample was very hard and took exceptional force to break. Sample 5 was a scale encasing the temperature probe submerged in the dissolving tank. It could be easily crumble with little force, and appears to be porous.

Scale samples were analyzed by means of Thermogravimetric Analyzer/Differential Scanning Calorimeter (TGA/DSC). X-Ray Fluorescence (XRF) spectroscopy was performed to determine the sample composition. Several Scanning Electron Microscope (SEM) images of the samples were also taken.
Figure 9. Scale samples obtained from the causticizing plant of Mill A (samples 1, 3, 4 and 5), and Mill B (sample 2).

TGA/DSC Analysis

Similar characteristics can be seen between the thermal profiles of Samples 4 and 5 (from the CGL and dissolving tank scales), and between the RGL scales (Samples 1, 2, 3). An example of the TGA/DSC profile is shown in Figure 10 for Sample 4. The 41 wt% weight loss between 620°C and 830°C on the TGA curve, accompanied by a strong endothermic peak on the DSC curve is characteristic of the decomposition of CaCO₃ to CaO and CO₂. The weight loss magnitude suggests that the scale sample contains about 93% CaCO₃. Similarly, sample 5 contained about 85% CaCO₃.

Figure 10. TGA/DSC analysis of CGL scale sample 4.
**Figure 11** shows the TGA/DSC profile of Sample 2. It was not clear what caused the 32 wt% weight loss between 395°C and 520°C with no change in heat flow. In the absence of other possible cause, it is speculated that this thermal event was likely due to the antiscalant added to the RGL lines at Mill B. The second weight loss between 620°C and 830°C was due to the decomposition of CaCO₃. If the first weight loss is indeed due to the antiscalant, the amount trapped in the scale sample is about 10 wt% in sample 1, 30 wt% in Sample 2, and 25 wt% in sample 3, while the CaCO₃ content is about 85 wt%, 68 wt%, and 64 wt% in sample 1, 2, and 3 respectively.

Samples 4 and 5 showed no signs of anti-scaling impurities. Sample 4 was taken from the CGL line after the green liquor filtration. It is likely that the anti-scaling chemical was filtered out in the clarifier. Sample 5 was recovered from the temperature probe in the dissolving tank, before the anti-scaling chemical addition to the system.

**XRF Analysis**

Using the results from the XRF and the loss on ignition (LOI) from TGA/DSC results, the compositions of the scale samples, expressed as oxides, are summarized in Table 2.

![TGA/DSC analysis of RGL scale sample 2.](image)
Table 2. XRF Results for Mill A and Mill B scale samples.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td></td>
<td>50.98</td>
<td>50.69</td>
<td>49.84</td>
<td>50.84</td>
<td>51.54</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.42</td>
<td>0.77</td>
<td>0.63</td>
<td>0.63</td>
<td>0.51</td>
<td></td>
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<tr>
<td>MgO</td>
<td>1.76</td>
<td>0.73</td>
<td>2.41</td>
<td>3.21</td>
<td>2.09</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.33</td>
<td>0.22</td>
<td>0.37</td>
<td>0.34</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.56</td>
<td>0.27</td>
<td>0.91</td>
<td>1.24</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.22</td>
<td>0.85</td>
<td>0.86</td>
<td>0.83</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>3.69</td>
<td>2.00</td>
<td>6.76</td>
<td>7.99</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.37</td>
<td>0.49</td>
<td>0.31</td>
<td>0.34</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>0.31</td>
<td>0.24</td>
<td>0.49</td>
<td>0.45</td>
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<tr>
<td>V₂O₅</td>
<td>0.14</td>
<td>0.09</td>
<td>0.11</td>
<td>0.06</td>
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<tr>
<td>MnO</td>
<td>0.32</td>
<td>0.49</td>
<td>1.15</td>
<td>0.57</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.34</td>
<td>0.13</td>
<td>0.58</td>
<td>1.21</td>
<td>0.16</td>
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<tr>
<td>ZnO</td>
<td>0.48</td>
<td>0.15</td>
<td>0.7</td>
<td>0.16</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>BaO</td>
<td>1.62</td>
<td>1.06</td>
<td>1.33</td>
<td>0.77</td>
<td>1.38</td>
<td></td>
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<tr>
<td>LOI*</td>
<td>48</td>
<td>63</td>
<td>57</td>
<td>44</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>110</td>
<td>121</td>
<td>123</td>
<td>112</td>
<td>102</td>
<td></td>
</tr>
</tbody>
</table>

* LOI = loss on ignition (determined from TGA/DSC) including CO₂, H₂O, C, etc.

Scale Growth Rate

Scale sample 4 was used to determine the scale growth rate of the clarified green liquor line of Mill A due to the good quality of the scale and its thickness. An illustration of the scale formation over the cross section of the green liquor pipeline is shown in Figure 12. The scale is 3.5 cm in width and formed in a 20 cm (8 in) inner diameter pipe in 6 months. Assuming the scale thickness is the same around the circumference of the pipe and the scale growth rate is linear with time, the scale growth rate is estimated to be about 0.2 mm/day, covering 43% of the cross section of the pipe in 6 months. The stratified layer shown in the scale, however, suggests that scale formation is an on-and-off process, i.e. it grows rapidly for a short period, stops and grows again.

Figure 12. Scale formed in the clarified green liquor pipeline at Mill A. Scale thickness = 3.5 cm
CaCO$_3$ SCALE FORMATION MECHANISMS

For dissolved Ca$^{2+}$ ions in the liquor to precipitate to form hard CaCO$_3$ scale on a metal substrate, the following three criteria must be met [7]:

1. Supersaturation
2. Nucleation
3. Crystal Growth

Supersaturation is the primary cause of sudden precipitation. As the concentration of a particular solute in a solution exceed its saturated concentration, the solute precipitates out in order to maintain its equilibrium concentration in the solution. Under transient or process upset conditions, however, equilibrium is not sustained, allowing the solute to stay in the solution without precipitation, even after its concentration exceeds its saturated concentration at the same temperature and pressure. Such a solution is said to be supersaturated.

A supersaturated solution is always in a metastable state. This means that when the solubility of CaCO$_3$ exceeds the metastable limit, crystals will start to form, initiating the precipitation process [8]. A saturated solution can be made supersaturated by changing temperature, pressure and pH, or by adding a solid seeding material into the solution, or changing solution flow rates. Supersaturation can be localized. The rate of scale precipitation depends strongly on the degree of supersaturation [7]. The greater the degree of supersaturation, the more abruptly precipitation can occur.

In this study, the degree of supersaturation of the weak wash, raw green liquor and clarified green liquor of Mill A and Mill C was determined by measuring the dissolved soluble Ca$^{2+}$ content using ICP (Inductively Coupled Plasma Spectrometry) and comparing that value to the theoretical equilibrium soluble Ca$^{2+}$ content provided by OLI (a thermodynamic program). The difference between the measured value and the theoretical value is considered to be the degree of supersaturation of the liquor. A plot of this analysis is show in Figure 13. The degree of supersaturation (and hence the driving force for CaCO$_3$ precipitation) is significantly higher in Mill A compared to Mill C particularly in the raw and clarified green liquor lines. This is likely the reason why Mill A experiences more scale formation than Mill C.

![Figure 13. Degree of calcium supersaturation for various liquors at Mill A and Mill C.](image-url)
SCALE PREVENTION STRATEGIES

The results obtained from this study suggest that the formation of hard CaCO₃ scale may be prevented by the following operation strategies:

1. **Reducing Process Fluctuations:** If the solubility of CaCO₃ in green liquor decreases (i.e. when the TTA of the liquor changes from high to low), precipitation occurs, forming a thin scale layer on the pipe inner surface. When the condition is reversed, i.e. from low TTA to high TTA, the CaCO₃ solubility increases. However, it is almost impossible for the formed CaCO₃ to dissolve since the surface of the scale is immediately saturated with Ca²⁺ due to the extremely low solubility of CaCO₃. It is therefore important to reduce process fluctuations (such as temperature and TTA changes) to minimize the precipitation of CaCO₃ in the green liquor system.

2. **Insulating the Green Liquor System:** The simplest way to reduce temperature fluctuations in the green liquor system is to insulate the liquor pipelines. The insulated layer results in a smaller temperature difference between the temperature of the inner wall of the pipe and the bulk liquor temperature, thus reducing the drive for precipitation. Mills with well-insulated pipelines generally experience less scale formation problems than mills with poorly insulated pipelines.

3. **Adding Lime Mud Particles to Weak Wash:** This could help reduce CaCO₃ scale formation in the green liquor lines. Lime mud particles likely act as seed sites for any CaCO₃ to precipitate in the bulk, rather than on the walls of the causticizing plant equipment.

**SUMMARY**

Calcium carbonate (CaCO₃) often forms hard scale in the green liquor handling equipment in kraft pulp mills. In severe cases, scaling can lead to unscheduled equipment shutdowns for cleaning which can be costly. Scale is formed due to the extremely low solubility of CaCO₃ in the highly alkaline green liquor environment that causes dissolved Ca²⁺ ions in the liquor to precipitate out during a process upset.

The scale formation experience at four kraft mills in Canada and Sweden was investigated to determine if there was any correlation between the severity of the scaling problem at each mill and the design and operating conditions of its causticizing plant. Mill liquors, scale samples and process data (green liquor flow rate, density, TTA, causticity, sulfidity, temperature, suspended solids, etc.) were analyzed to determine the main operating parameters leading to scale formation. The results suggest that mills operating at a lower green liquor TTA, higher causticity and a larger temperature drop in the green liquor system will have a greater tendency for hard CaCO₃ scale to form.

Supersaturation of Ca²⁺ ions in the liquor is likely the main cause of scale formation. In order for mills to minimize scale formation, the green handling systems should be operated as steady as possible. This can be accomplished by minimizing variations in green liquor TTA, insulating the green liquor pipelines to reduce temperature gradients, and adding lime mud to weak wash to provide seeds for precipitation to occur on mud particles liquor instead of on metal substrate.

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**REFERENCES**


Mill Experience of Calcium Carbonate Scale Formation in Green Liquor Handling Systems

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\(^4\) Mercer Peace River Pulp, Peace River, AB, CANADA
Introduction

Causticizing Reaction:

\[ \text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3 \rightleftharpoons 2\text{NaOH} + \text{CaCO}_3 \]
**Introduction**

- **Major problem:** hard scale formation in the green liquor handling system

Green liquor composition:
- $\text{Na}_2\text{CO}_3$
- $\text{Na}_2\text{S}$
- $\text{NaOH}$
Scale in Green Liquor Handling Equipment

CaCO₃ has been identified as the main component of scale, particularly at locations downstream of the dissolving tank.
Past Research in Green Liquor Scaling

- Analysed ~ 30 green liquor scale samples
  - Discovered dissolving tank scale can be composed of: pirssonite (Na$_2$CO$_3$•CaCO$_3$•2H$_2$O), monohydrate (Na$_2$CO$_3$•H$_2$O), or calcite (CaCO$_3$)
  - Downstream of the dissolving tank scale is CaCO$_3$

- Little is known about CaCO$_3$ scale formation in green liquor

- A systematic study was conducted at the University of Toronto to examine CaCO$_3$ scale formation:
  2. Part 2 (this presentation): analyses the scaling experience at several kraft pulp mills
CaCO₃ solubility was found to increase with:
- Increasing temperature
- Increasing TTA
- Decreasing causticity
- Decreasing sulfidity
The objective of this research was to obtain a better understanding of the scaling problems at four kraft pulp mills, and determine if the experience at each mill can be explained using the experimental solubility data presented in Part 1 of this study.

Presentation Outline

Part A: CaCO₃ Scale Formation Mill Studies
- Causticizing Plant Design
- Operating Data Analysis
- Scale Sample Analysis

Part B: CaCO₃ Formation Mechanisms and Prevention Strategies
- Scale Formation Mechanism
- Scale Prevention Strategies
Mill Studies Overview

- Mill studies were carried out at 2 mills in Canada (Mills A & B), and 2 mills in Sweden (Mills C & D).
- **Mills A & B reported significant scaling in the causticizing plant resulting in process disruptions**
- **Mills C & D have no process disruptions due to scale formation**

<table>
<thead>
<tr>
<th>Property</th>
<th>Mill A</th>
<th>Mill B</th>
<th>Mill C</th>
<th>Mill D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Canada</td>
<td>Canada</td>
<td>Sweden</td>
<td>Sweden</td>
</tr>
<tr>
<td>Start Up Year</td>
<td>1989</td>
<td>1970</td>
<td>1917</td>
<td>1895</td>
</tr>
<tr>
<td>Daily Production (admt/day)</td>
<td>1,100</td>
<td>500</td>
<td>1,080</td>
<td>1,550</td>
</tr>
<tr>
<td>Wood Type</td>
<td>Softwood &amp; Hardwood campaigns</td>
<td>Softwood</td>
<td>Softwood</td>
<td>2/3 Softwood, 1/3 Hardwood</td>
</tr>
<tr>
<td>Anti Scaling Chemical</td>
<td>Yes</td>
<td>Yes (stop Oct 2017)</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>
Causticizing Plant Design (Mill A & B)

- Mill A has scale build up in dissolving tank, RGL & CGL pipelines
- Mill B has scale build up in RGL pipelines
- Antiscalents are added in both mills to the green liquor at the outlet of the dissolving tank
- Raw green liquor and weak wash lines are switched every 12 hours to facilitate line cleaning (Mill B stopped this process between June 2016 – October 2017 however resumed after scale formation increased)
Causticizing Plant Design (Mill C & D)

- Line switching occurs every 24 hours at both mills
- Scale build up is typically found within the GL pressure filters and causticizers (including causticizer pipelines)
  - Cleaning of the pressure filters is integrated in daily operations
Operating Data Analysis – GL TTA

<table>
<thead>
<tr>
<th>Mill</th>
<th>Average TTA (g/L Na₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mill C RGL</td>
<td>149 ± 8</td>
</tr>
<tr>
<td>Mill C CGL</td>
<td>134 ± 6</td>
</tr>
<tr>
<td>Mill D CGL</td>
<td>126 ± 4</td>
</tr>
<tr>
<td>Mill B RGL</td>
<td>120 ± 4</td>
</tr>
<tr>
<td>Mill A RGL</td>
<td>114 ± 1</td>
</tr>
</tbody>
</table>
Operating Data Analysis – GL Causticity

<table>
<thead>
<tr>
<th>Mill</th>
<th>Average Causticity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mill A RGL</td>
<td>16.7 ± 1.5</td>
</tr>
<tr>
<td>Mill C RGL</td>
<td>6.2 ± 1.3</td>
</tr>
<tr>
<td>Mill C CGL</td>
<td>5.5 ± 1.4</td>
</tr>
<tr>
<td>Mill D CGL</td>
<td>4.8 ± 1.0</td>
</tr>
</tbody>
</table>

*causticity is not recorded at Mill B*
Operating Data Analysis – GL Sulfidity

<table>
<thead>
<tr>
<th>Mill</th>
<th>Average Sulfidity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mill C RGL</td>
<td>32.3 ± 3.2</td>
</tr>
<tr>
<td>Mill C CGL</td>
<td>32.0 ± 3.2</td>
</tr>
<tr>
<td>Mill D CGL</td>
<td>28.3 ± 2.3</td>
</tr>
<tr>
<td>Mill A RGL</td>
<td>27.2 ± 2.0</td>
</tr>
</tbody>
</table>

*sulfidity is not recorded at Mill B*
Operating Data Analysis – GL Heat Exchanger Temperature

- Mill A noticed significant scaling at the heat exchanger outlet
- The heat exchanger is typically cooling the CGL (typical of any mill)
- Larger temperature drops appear to induce scaling

\[ \Delta T = T_{\text{OUT}} - T_{\text{IN}} \]

<table>
<thead>
<tr>
<th>Mill</th>
<th>Average Temperature Drop (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mill A</td>
<td>-5.7</td>
</tr>
<tr>
<td>Mill C</td>
<td>-3.1</td>
</tr>
<tr>
<td>Mill D</td>
<td>-2.2</td>
</tr>
</tbody>
</table>

![Diagram showing temperature drops and scaling](image-url)
Mill C and D have a high concentration of suspended solids in the weak wash, compared to Mill A and B.

This high concentration of suspended solids may help reduce scale formation as they can act as seeding sites for Ca^{2+} in green liquor to precipitate in the bulk rather than on equipment walls.
Operating Data Conclusions

- Mill liquors with:
  - Lower temperature ✓
  - Lower TTA ✓
  - Higher causticity ✓
  - Higher sulfidity ✗
  
  are thought to have more scaling problems (Part 1).

**Mill analysis showed:**

- Mill A and B appears to have more scaling than Mill C and D
  - Lower T at Mill A heat exchanger outlet induced scaling
  - Mill A and B has a lower TTA than Mill C and D (~ 5 – 35 g/L Na₂O lower)
  - Mill A has a higher causticity than Mill C and D (~ 10 – 12% higher)
  - Mill A has a lower sulfidity than Mill C and D (~ 1 – 5% lower)
Analysis of Scale Samples (Mill A and B)
TGA/DSC Analysis – Scale Sample 4

Weight loss 41% indicates 93% CaCO₃

Endothermic peak due to CaCO₃ decomposition
TGA/DSC Analysis – Scale Sample 2

Weight loss (32%) from impurities 350 – 500°C Likely antiscalent

Weight loss (28%) from CaCO₃ decomposition indicating 64% CaCO₃
Scale Growth Rate – Sample D

- Scale formed in the 20 cm (8”) ID pipe in 6 months (180 days)
- This is 43% of the pipe cross sectional area
- If growth rate is linear, approximately 0.2 mm of scale growth is estimated per day
- The stratified layer suggests scale formation is a on off process i.e. grows rapidly for a short period of time
CaCO₃ Scale Formation Mechanisms

- Scale Precipitation Criteria:
  1. Supersaturation
  2. Nucleation
  3. Crystal Growth

- The primary cause of scale formation is a supersaturated solution
  - A supersaturated solution is unstable → can easily precipitate
  - Supersaturation can be localized (i.e. at cooler walls of a pipe)
Supersaturation in Mill Liquors

Degree of supersaturation = \( C - C_{eq} \)

Driving force for precipitation
Scale Prevention Strategies

1. **Reduce Process Fluctuations**
   - i.e. green liquor temperature and concentration changes

2. **Insulate the Green Liquor System**
   - Mills with insulated pipelines generally experience less scale formation

3. **Add Lime Mud Particles to Weak Wash**
   - They could act as seed sites for any CaCO₃ to precipitate in the bulk rather than on the walls of plant equipment

4. **Anti Scaling Polymers**
   - Mill B used an anti-scaling polymer until October 2017 at two addition points
   - The mill found the more polymer they used the harder the scale
   - There has been no line plugging since the mill stopped using the polymer in October 2017
Conclusions

- Mills A & B have more scaling problems than Mills C & D. Most likely due to:
  - Single line causticizing system of Mills A & B compared to dual line of Mills C & D
  - Lower TTA and higher causticity of Mills A & B

- RGL scale samples have large concentrations of impurities which is most likely anti-scaling chemicals. These impurities are not found in CGL scale samples.
  - This may suggest 1) not enough polymer is added to prevent CaCO$_3$ scale formation in the CGL or 2) the polymer is ineffective and gets trapped in the RGL scale or filtered out in the green liquor clarification system

- Scale formation in industry is a very slow process
Conclusions

- CaCO₃ supersaturation is the primary cause of scale formation
  - Temperature and concentration changes can cause supersaturation
- Once scale forms it cannot re-dissolve
- Scale prevention strategies:
  1. Reduce process fluctuations
  2. Insulate green liquor system
  3. Addition of lime mud to weak wash
  4. Stop the use of anti-scaling agents

*more research is needed in these areas*
Acknowledgements
Questions?