A review of green liquor scale formation

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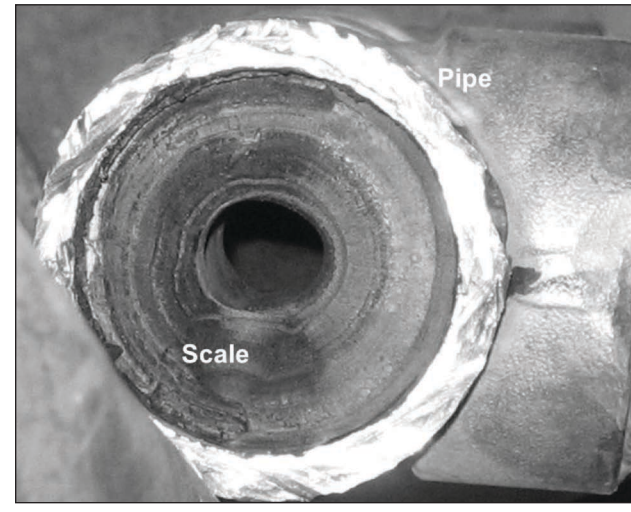
ABSTRACT: Green liquor scale is a recurring problem in most kraft mills. Several types of scale, e.g., pirssonite, calcite, sodium aluminosilicates, etc., have been identified in various green liquor scales. The mechanisms of formation and potential operational methods to control the formation of these scales is reviewed.

Application: For mills, understanding ways to prevent scale formation will benefit the process area.

Green liquor scale is a recurring problem in many pulp and paper mills around the world. A mill in Imatra, Finland, reported scale formation on its dissolving tank impeller blades so large that the amperage rating of the motor was exceeded in less than 3 months of operation. The mill was forced to take unscheduled downtime to remove the scale, ultimately resulting in a recovery boiler shutdown and significant production loss [1]. Scale issues reported from a mill in Springfield, OR, USA, suggested that 6-in. valve openings in raw green liquor lines were scaled to less than an inch of open area after just a few weeks of operation [2]. Significant and rapid green liquor scaling episodes have also been noted at mills in Brazil, Canada, and in various parts of the United States. Taylor and McGuffie found mixed scales containing both pirssonite ($Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$) and calcite ($CaCO_3$) in the green liquor system at the Elk Falls mill in British Columbia, Canada [3]. They found a dissolving tank scale sample was mainly composed of pirssonite, while a scale sample obtained from the green liquor clarifier was mainly calcite. Other researchers analyzed samples of green liquor dregs obtained from a mill in Brazil and reported scale formation from pirssonite, calcite, portlandite ($Ca[OH]_2$), larnite ($CaSiO_4$), and brucite ($Mg[OH]_2$) [4].

Deposits are frequently found on dissolving tank agitator blades, in the dog houses above the dissolving tank, in raw green liquor lines to the clarifiers, and in lines to the slakers [5,6]. Scale has been reported in the slaker screw conveyor as well. Intermittent deposition, characterized by alternating light and dark bands, suggests that scale formation is caused by temperature and/or strength (total titratable alkali [TTA]) variability. Scaling events can be quite difficult to manage under certain conditions. Sometimes, as suggested in the various mill experiences documented earlier, scaling is so severe that lines are plugged, and agitators are broken or damaged, resulting in unscheduled downtime and lost production. **Figure 1** shows a picture of a green liquor transfer line almost completely plugged with green liquor scale [5].



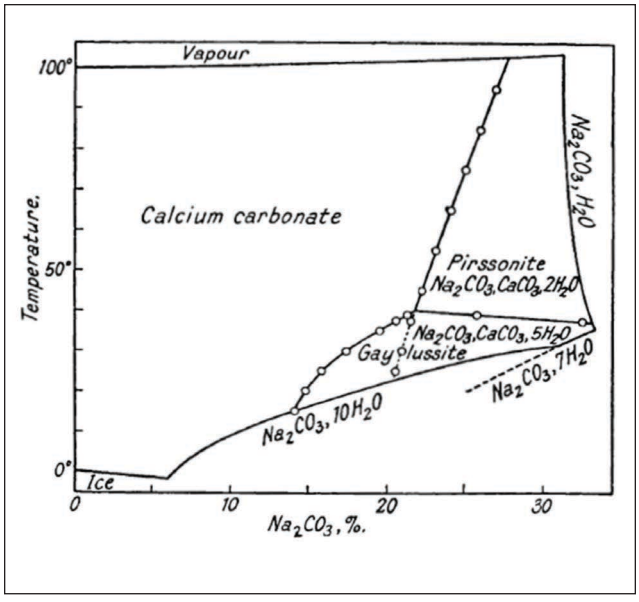
1. Green liquor scale formed inside a process pipeline. Note the reduction on available area for green liquor flow. Photo by Tran [5].

Types of scale formed

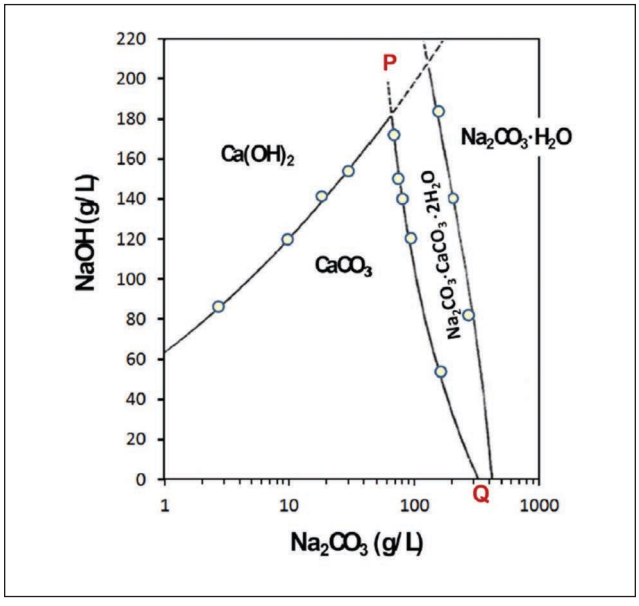
Initial work associated with green liquor scale analysis suggested the main type of scale formed in green liquor is pirssonite, a hydrated double salt of sodium and calcium carbonates ($Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$) [7,8]. More recent work has suggested that calcite, a form of calcium carbonate ($CaCO_3$), co-precipitates within the pirssonite and remains behind as the hard scale on pipe walls and agitators after the pirssonite re-dissolves into the green liquor [9]. To a lesser extent, calcium oxalate (CaC_2O_4) and sodium aluminosilicates ($AlNa_{12}SiO_5$) have also been identified as undesirable scale formations within the green liquor processing system [10].

PIRSSONITE ($NA_2CO_3 \cdot CACO_3 \cdot 2H_2O$)

The sodium carbonate-calcium carbonate-water system was first studied in 1933 by Bury and Redd [7]. Pirssonite was found to form in concentrated sodium carbonate solutions of greater than 20 wt% in strength at temperatures of about



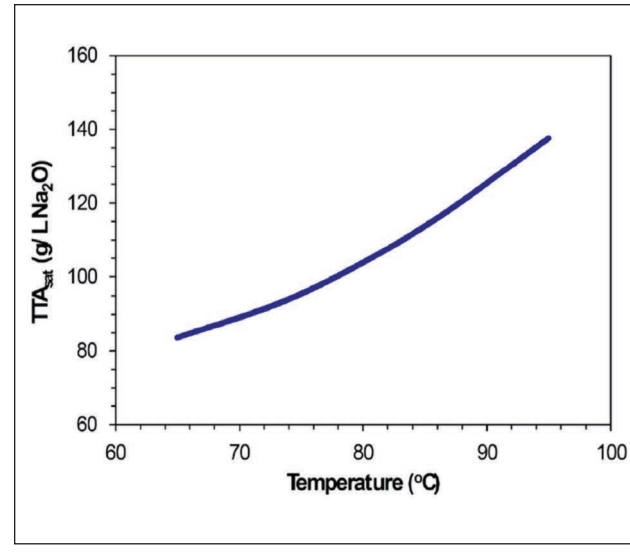
2. Phase diagram for the sodium carbonate-calcium carbonate-water system as developed by Bury and Redd [7].



3. Slaked lime-caustic-sodium carbonate-water system phase diagram at 95°C as developed by Littman and Gaspari [8,9].

40°C. Bury and Red completely investigated the three-component system at 15°C, 25°C, 35°C, 37.5°C, and 45°C. They partially investigated it at 20°C, 30°C, 39°C, 55°C, 65°C, 75°C, 85°C, and 95°C, performing sufficient work at these latter temperatures to fix the compositions of solutions at certain triple points. The phase diagram developed by Bury and Redd is shown in **Fig. 2** [7].

More than 20 years later, Littman and Gaspari studied the system using slaked lime ($Ca[OH]_2$), water and sodium carbonate [8]. As their system contained slaked lime and sodium carbonate, some amount of recaustizing was occurring, resulting in a significant amount of caustic (NaOH) being present in the system as well. They investigated the system at an industrially relevant temperature of 95°C. Their work developed the phase diagram shown in **Fig. 3** [8,9]. Littman and Gaspari's work clearly shows that pirssonite can only exist in a small concentration range of sodium carbonate and caustic in the reaction system solution. If the concentrations change significantly, the pirssonite will change form, likely re-dissolving or partially dissolving into solution.



4. Pirrsonite solubility as a function of temperature for a solution containing 30% sulfidity and 5% causticity [9].

Solubility

Pirssonite is a double salt of sodium and calcium carbonates. It is a semi-soluble scale that forms as deposits from precipitation events that occur when the sodium carbonate concentration exceeds the pirssonite solubility limit. Pirssonite solubility is highly temperature dependent. As green liquor cools, the solubility of pirssonite decreases by about 8 g/L as sodium oxide (Na_2O) for each 10°C decrease in liquor temperature [1]. Work by Frederick et al. determined that not only temperature but the total concentration of all the sodium salts (e.g., sodium sulfide, sodium chloride, sodium hydroxide, etc.) impacts pirssonite solubility. For example, the solubility of pirssonite decreases as the NaOH concentration increases. Therefore, solubility curves should be plotted versus the solution TTA instead of just the sodium carbonate concentration [1]. **Figure 4** shows the impact of temperature upon pirssonite solubility reported as the saturation TTA [9].

Of all the sodium salts contained in green liquor, pirssonite is the least soluble. Sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4), and Burkeite ($2Na_2SO_4 \cdot Na_2CO_3$) are all more soluble than pirssonite under green liquor processing conditions [1]. Work by Frederick et al. suggests that operating the mill TTA below 96% of the TTA saturation level is strongly advised to avoid pirssonite precipitation from occurring in green liquor systems [1].

Proposed formation mechanisms

It has been well demonstrated that pirssonite is formed by precipitation of the bi-salt of sodium carbonate and calcium carbonate in a hydrated form. The question is what is the exact mechanism of formation. As the process occurs in green liquor, the sodium carbonate concentration is always very high. Calcium carbonate has a low solubility in green liquor, and the calcium in the smelt resulting from the wood in the pulping process tends to rapidly form $CaCO_3$ in the dissolving tank. Pirssonite often forms in the dissolving tank where the smelt is dissolved into weak wash because the localized concentration of sodium and calcium carbonates are both quite high. It is possible that pirssonite forms from direct reaction between Na_2CO_3 in the solution and the surface of $CaCO_3$ (lime) particles either present in the weak wash or forming from the calcium obtained from the wood [1,5]. It is also possible that pirssonite forms via continuous dissolution of $CaCO_3$ particles to sustain a level of free Ca^{2+} ions in solution, which subsequently react with both Na+ and CO_3^{2-} ions to form and precipitate pirssonite scale. The continuous dissolution mechanism was first proposed by Bailik et al. [11].

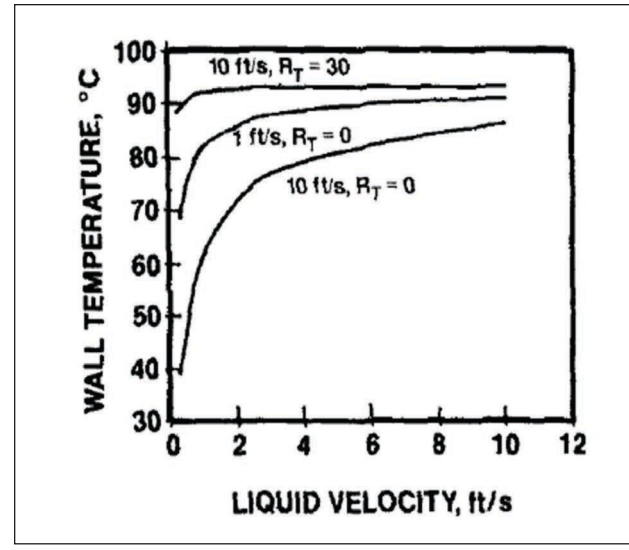
Due to the relatively high operating temperature and the Na_2CO_3 concentration dependence of pirssonite formation in green liquor as shown in the phase diagram in Fig. 4, the sodium phase of pirssonite will dissolve when the sodium carbonate concentration falls below the solubility limit of pirssonite. When this occurs, it is possible for the pirssonite to leave behind a porous skeleton of $CaCO_3$ scale on the pipes and impellors that can build up over time and cause its own scale problems in the form of calcite [5].

Guidelines to minimize pirssonite formation

Several guidelines have been developed to help minimize or prevent pirssonite deposition. These include, but should not be limited to, managing liquor temperature, swapping and cleaning liquor lines, and managing localized concentrations and operation of the green liquor system with a TTA target of 5%–10% below the saturation TTA.

Avoiding the death cycle

Typical saturation TTA for green liquor systems operating at 95°C is around 130 g/L as Na_2O. If a mill experiences significant scaling issues, they may experience unscheduled downtime for line cleaning or removal of scale from agitators. A mill will run a high TTA to ensure that it can supply sufficient green liquor to the slakers, but then the mill lines scale up and limit the green liquor flow because the green liquor TTA is higher than the saturation TTA. Many mills operate in this continual death cycle mode. To ensure they have green liquor to supply the recausticizing area, mills run the TTA as high as possible. This simply increases the rate and likelihood of scale formation, resulting in the mill having to shut down the green liquor system sooner than it normally would for scale removal. After cleaning lines, it is important that the mill lowers the TTA to less than 95% TTA_{sat} in order to break this cycle [12].



5. Wall temperature versus liquor velocity for an 8-in. green liquor line with a bulk fluid temperature of 93°C and an ambient air temperature of 0°C. The air velocity and level of insulation (as reported as thermal resistance, R_T) is indicated for each line [1].

Green liquor scale reduction methods.

Maintaining good mixing is critical to prevent weak wash from short circuiting the smelt dissolving tank and to avoid locally high concentrations of green liquor within the dissolving tank. As noted earlier, localized smelt dissolving concentrations should be maintained below the saturation concentration. Green liquor piping should be cleaned frequently to ensure that the weak wash supply is not limited. Finally, the dissolving tank agitators should be kept operating at all times and should receive a high priority for maintenance. The weak wash should maintain between 150–300 ppm suspended solids. This allows pirssonite to form onto the lime particles instead of on process equipment and piping.

Green liquor line management

All the green liquor lines should be well insulated. As green liquor cools near the pipe walls, the solubility of pirssonite decreases, so scale formation is more prevalent. Maintaining good liquor velocity through well-insulated pipes helps maintain high saturation concentrations. **Figure 5** shows the impact of insulation and liquor velocity on the temperature of liquor at the pipe wall. The conditions used in Fig. 5 are an 8-in. green liquor pipe with a bulk liquid temperature of 93°C and an ambient air temperature of 0°C [1]. Three different temperature lines are shown. One is for an outside air velocity of 10 ft/s, with an insulated line that has a thermal resistance (R_T) of 30 ft²h°F/BTU. The second line is for an uninsulated line with an outside air velocity of 1 ft/s. The third line is for an uninsulated line with an outside air velocity of 10 ft/s.

The results shown in Fig. 5 suggest that slowly moving to near stagnant liquor next to the pipe wall in an uninsulated line is always cool enough to promote pirssonite precipitation.

A reasonably well insulated line will prevent temperature drop-related scale formation if the liquor has some movement [1].

Several mills have installed parallel liquor lines to and from the dissolving tank. One line carries raw green liquor from the dissolving tank to the green liquor clarifier, while the second line carries weak wash from weak wash storage back to the dissolving tank. The mill should regularly switch raw green liquor and weak wash lines to and from the dissolving tank. The weak wash will dissolve sodium carbonate and partially clean the scale that has formed in the pipe. The slight abrasiveness of the suspended lime particles will also remove some of the porous calcium carbonate left behind once the sodium carbonate has dissolved. Hot water should be used to dissolve smelt when weak wash is unavailable. By routinely switching lines, the green liquor line can be cleaned when it is pressed into weak wash (or hot water) service while the other line is carrying green liquor so mill operations will not be interrupted [12]. If the lines are not cleaned enough to ensure an adequate flow of weak wash to the dissolving tank, excessively high levels of TTA are difficult to avoid, resulting in green liquor with extreme scaling tendency.

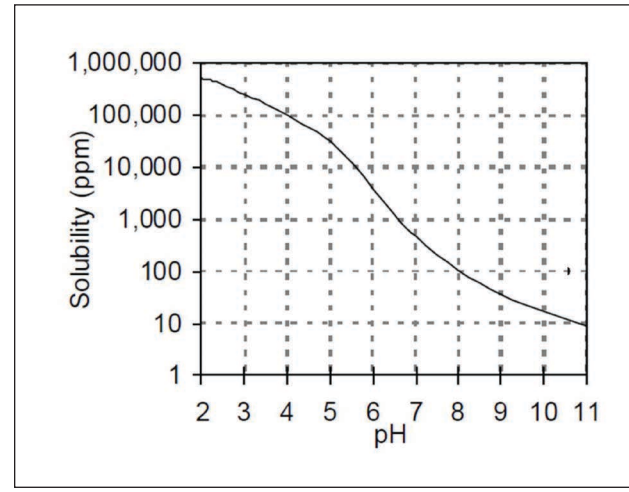
Daily operating practices

Several day-to-day operating practices can help minimize pirssonite formation. Dissolving tank density controllers should not be set on manual control. When the density controllers are on manual control, they are easy to ignore and allow the TTA to swing substantially. Automatic density control helps maintain nearly constant TTA strength in the green liquor system. The acid solution used for TTA titrations should be accurately standardized on a routine basis. Small changes in the titrating solution will result in swings in the actual TTA of the green liquor. When multi-tank systems are employed, tank-to-tank variability should be minimized. Pirssonite scale will form based on localized conditions, not on the average concentration of the multiple tanks.

CALCITE ($CACO_3$)

Besides pirssonite, the other scale commonly found in green liquor systems is calcium carbonate lime scale or calcite [4,5,10]. Calcite tends to be found more often in the green liquor clarifier and in the lines leading from the green liquor clarifier to the slaker. Pirssonite is more commonly found in the dissolving tank and in the lines leading to the green liquor stabilization tank and clarifier. Calcite is not particularly soluble in high pH solutions such as green liquor. As the pH increases, the likelihood of calcite crystallization increases. **Figure 6** shows the solubility of calcite as a function of pH [13].

In addition to pH, temperature and solution strength as measured by TTA also impact calcite solubility in green liquor solutions. Work by Giglio, Tran, and Papangelakis [14] has shown that liquor strength has a significant impact upon calcite solubility, with stronger liquors having significantly higher solubility limits than weaker liquors. At 80°C, Giglio determined the solubility of Ca^{2+} to be approximately 2.5 ppm in a 60 TTA green liquor solution, about 4.9 ppm in a 120 TTA green liquor solution, and about 8.5 ppm in a 180 TTA green liquor solution. The same work also showed that cooler operating temperatures decreased the solubility of calcite [14]. The green liquor causticity and sulfidity were determined to show no effect on calcium solubility.



6. Impact of pH upon calcite solubility [13].

Calcite formation mechanisms

Three hypotheses have been presented for calcite scale formation in green liquor systems. The first involves the formation of pirssonite and the re-dissolution of the sodium carbonate phase when the bulk solution concentration drops below the pirssonite solubility limit, leaving the calcite behind as scale. This hypothesis breaks down due to the prevalence of calcite scales found in lines between the green liquor clarifier and the slaker, where weak wash switching does not occur. As the TTA of the liquor in this line is fairly constant, there would be no driving force to dissolve the sodium carbonate and leave the calcium carbonate behind as scale.

The second hypothesis for calcite formation is related to the temperature solubility of calcite. It has been proposed that temperature gradients within the pipe will cause calcium to precipitate as calcite. The cooler temperatures at the pipe wall result in lower solubility, thus producing calcite scale.

The third hypothesis is that calcium is converted from a more soluble phase in the dissolving tank to a less soluble phase ($CaCO_3$) in the green liquor pipelines, resulting in precipitation as calcite. Work by Giglio et al. did show some kinetic basis for this hypothesis, as keeping raw green liquor at process temperatures for a period of time was found to decrease calcium solubility from about 15 ppm to about 5 ppm in 2.5 hours [14].

Calcite prevention

As green liquor cools or drops in TTA concentration due to various dilution and water infiltration streams, the solution

becomes supersaturated and calcium carbonate nuclei form. Calcite continues to grow in these nuclei until equilibrium conditions with the bulk fluid are obtained. The calcite precipitates onto pipe surfaces, clarifier walls, agitators, etc. Nucleation sites on these surfaces accelerate precipitation, resulting in significant amounts of scale formation that can restrict green liquor flow. Several methods, both physical and chemical, are available to help slow or eliminate calcite formations.

Physical prevention methods

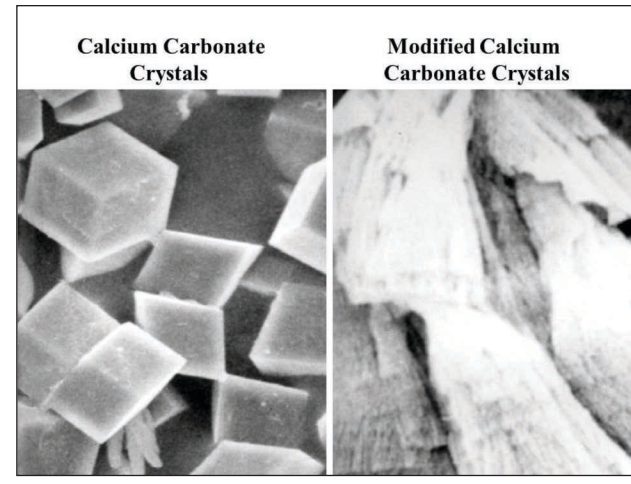
Mills have a limited number of tools available to prevent calcite scale from forming. Two methods are preventative, while the other two methods attempt to modify the crystalline structure of calcite to prevent severe scale build up. The preventative method relies upon TTA measurement and control to maintain the TTA of the green liquor leaving the dissolving tank at a constant and uniform level deemed by the mill to minimize scale formation [15,16]. As scale formation in green liquor lines tends to be episodic, corresponding to changing localized concentration and temperature conditions, maintaining a constant density or TTA out of the dissolving tank will help prevent supersaturation conditions resulting from swings in liquor strength and prevent scaling.

The second preventative method available to mills is to insulate the green liquor lines. As both calcite and pirssonite tend to precipitate at lower temperatures, insulating the green liquor pipes helps maintain the bulk fluid temperature and minimizes temperature gradients within the pipes. Figure 5 shows the impact of insulation and bulk liquor flow rate on the temperature gradients within pipes.

Polymer application

The next two available methods for preventing calcite scale attempt to modify the form or type of crystal growth that occurs. By modifying how the calcite crystal forms and grows, the resulting scale is soft and easily removed through attrition of the fluid and suspended solids moving in the bulk solution. A series of different polymers can be employed to achieve this end. The first way crystals may be modified is through the addition of processing chemicals known as crystal modifiers [13]. These polymers work by attaching themselves to the crystal growth sites, forcing the crystal to become irregular in shape. **Figure 7** shows a pair of high magnification pictures (both at the same magnification level) [13]. The photo on the left is of standard calcite crystals typically found in green liquor. Note the uniform, compact, cubic form of the crystals. The photo on the right is of calcite crystals treated with a polymeric crystal modifier. Note the non-uniform crystalline structure and the far less compact and less dense crystal formation.

Once the crystalline structure is disrupted, the growth rate of the crystal is reduced due to the incapacitation of the crystal growth sites. This effect results in slowing scale formation. Once the crystalline form is altered into non-uniform shapes, the resulting crystals cannot uniformly pack together and form a hard scale. Rather, the modified crystals form a soft scale that is typically removed by the abrasion of green liquor and suspended solids contained within the bulk flowing green liquor solution [17].



7. High magnification of calcite crystals formed with and without the addition of polymeric crystal modifiers [13].

Other polymers are sometimes used to break up the irregular crystals formed via application of the crystal modifiers so the material can be swept away more easily and not form an undesirable sludge at the bottom of the pipe or clarifier. Typically, these sludge conditioning or viscosity modifying materials consist of organic acids, which react with the modified crystal and fragment it into smaller pieces [17].

Finally, dispersion or antiscale polymers are anionic terpolymers that increase the surface charge of microcrystals in solution and prevent them from agglomerating into larger scale forming structures. By increasing the anion surface charge, a barrier is created that prevents further agglomeration [17,18].

External methodologies

Other than polymers, select mills have had some level of success with modification of the microcrystalline structure of calcite in the bulk green liquor through external treatment methods. These systems are typically mounted on the outside of the pipe and apply an external field that modulates rapidly. High frequency electric fields or radio frequencies modify the calcite crystalline structure at the micro level inside the bulk green liquor solution. The new crystalline form does not agglomerate and hence, does not form hard scales on the equipment surfaces [19-21]. Stora installed an electronic descaling system that was reported to have solved a long-term green liquor scaling problem at its mill in Point Tupper, Canada. The device used a frequency modulation technology that formed a pulse wave which changed direction several times a second, creating an induced electric field inside the pipe. The induced field also changed direction several thousand times a second. Crystal growth was thereby promoted, which remained suspended in the liquid and did not deposit onto the pipe walls

[19]. Responding to lower saturation levels, the existing scale deposits were softened, loosened, and reported to be removed in the water flow [19].

Work has continued on the development of these external devices. More recently, an electronic antifouling device has been reported in the literature that not only prevents calcite formation, but also removes existing scale in pipes, at insignificant energy consumption. Induction of a Radio-Frequency Alternating Electric Field (RFAEF) in water at a specific range of frequency and antenna voltage, along with its distinct sinewave waveform, has been reported to change the way minerals precipitate, minimizing hard calcite scale by instead producing a non-adherent mineral powder in the bulk water. Moreover, the unsaturated solution created by the formation of the mineral powder, along with enhanced carbon dioxide production, has been reported to gradually dissolve existing scale within the pipe [20].

Another form of external treatment has been the application of acoustic cavitation-generated erosion technology for the removal of calcite scale as it deposits onto surfaces [21]. As the scale forms, it is exposed to sonotrode-generated acoustic cavitation. The rate of scale removal was determined to be proportional to the pressure amplitude generated by the sonotrode. Descaling can also be intensified by reducing the substrate surface roughness. However, the scale destruction mechanism is largely dependent on the microstructure of the scale deposit, as local inhomogeneity may intensify the erosion rate. Scale deposits can, depending on the hardness of its surface and substrate surface finish, either be eroded layer-by-layer or by breakage of larger areas into chunks of scale [21].

SODIUM ALUMINISILICATES

Sodium aluminosilicates are occasionally found in green liquor scale [10] when there is a buildup of alumina or silica in the recovery cycle. Aluminosilicate scales are extremely hard and glassy in appearance. These scales are sparingly soluble and can precipitate in green, white, and black liquors. Once formed on pipes, tank walls, or agitators, these scales are quite difficult to remove. Aluminosilicates are typically eliminated from the liquor cycle as part of the green liquor dregs because their solubility is lower in green liquor than in white liquor [22-24]. Aluminum and silicon have been identified in dregs from the green liquor clarifier, primarily as the silicate diopside, $CaMgSi_2O_6$; the alummosilicates pargasite, $NaCa_2Mg_3Fe^{2+}Si_6Al_3O_{22}(OH)_2$; and as vermiculite, $Mg_{1.8}Fe^{2+}{}_{0.9}Al_{4.3}SiO_{10}(OH)_2 \cdot 4(H_2O)$ [3].

Aluminosilicates are typically controlled by limiting the amount of aluminum and silica that enters the liquor cycle. Typical sources of these materials include bark and dirt in the wood chips, alum from paper machine white water, lime makeup contamination, and excessive application of silicon-based defoamers. If a mill is having difficulties with aluminosilicate scale formation, efforts should be made to improve debarking of wood and to ensure that papermill white water is not being applied to the brownstock washing system. An analysis of the makeup lime should also be performed.

If aluminosilicate scale continues to be a problem, it is possible to purge these materials through the addition of magnesium sulfate to the green liquor [24]. Work by Ulmgren [24] has shown that treating a side stream of green liquor with sufficient Mg^{2+} to obtain a magnesium-aluminum ratio (Mg:Al) of greater than 3 to 1, and preferably 5 to 1, will result in the formation of $Mg_{1-x}Alx(OH)_2(CO_3)_{x/2} \cdot nH_2O$ with $0.1<x<0.34$. The resulting material will then precipitate out of solution, lowering the aluminum content of the liquor. Other conditions that favor aluminum precipitation are lower hydroxide concentration and lower temperature. Therefore, cooling the bleed stream prior to adding magnesium sulfate ($MgSO_4$) would be desirable to help maximize aluminum removal from the green liquor [10].

METALS REMOVED IN GREEN LIQUOR DREGS

The elemental composition of green liquor dregs samples found in the literature contain significant amounts on sodium and calcium, with the sodium content varying between 9% and 13% and the calcium content varying between 27% and 44%. A small but significant amount of magnesium between 0.5% and 3.2% has also been identified. For predominantly hardwood mills, the magnesium content may be higher. Iron, potassium, and manganese are also present in small amounts in all reported dregs samples. Some dregs samples have also contained lesser amounts of chlorine, zinc, silicon, aluminum, sulfur, and phosphorus. Other elements have been sporadically found in trace amounts [4]. Other studies have reported that sodium, sulfur, potassium, and boron may be found in green liquor dregs, along with aluminum, barium, calcium, cadmium, iron, magnesium, manganese, and zinc [25].

In general, most of the metals that enter the green liquor cycle originate with the wood and other raw materials used in the pulping and pulp washing process [26-28]. These metals come into the liquor cycle through the smelt, which is dissolved in the dissolving tank to make green liquor. When the smelt is dissolved in weak wash to form green liquor, the unburned carbon and several of the metals are only marginally soluble in the highly alkaline fluid. These metals tend to precipitate out of solution and join with the slightly soluble carbon materials to form dregs, which gravity then settles out of solution in the green liquor clarifier. Several mills will add some amount of polymer to the green liquor clarifier to help coagulate the dregs and improve the separation efficiency of the clarifier.

If the dreg settling in the clarifier is upset by thermal gradients, creating undesirable flow patterns or density variations in the clarifier, too high of liquor TTA, or other physical issues, dregs and undesirable metals will carry over into the clarified green liquor lines, slaker, and causticizers. Dregs carryover can result in some more uncommon scale formations, such as magnesium oxide or manganese dioxide. Typi-

cally, carrying a small number of suspended solids (mainly consisting of calcite particles) in the weak wash used for smelt dissolving helps improve dregs settling by providing nucleation sites for metals precipitation and increasing the density of the unburned carbon flocs so they have improved settling. This frequently enhances the performance of the green liquor clarifier and improves dregs removal efficiency. Carrying over too many suspended particles in the weak wash can have an undesirable impact on settling and hurt dregs separation, so it is important to monitor and control the quality of the weak wash being used in smelt dissolving.

SUMMARY

Green liquor scale is mainly composed of pirssonite and calcite. Both materials are formed as precipitation events that are somewhat dependent upon green liquor TTA (concentration) and temperature. Operating the TTA of the dissolving tank at about 95% of the saturation TTA is typically sufficient to prevent or at least significantly reduce pirssonite scaling. Insulating the green liquor transfer lines and clarifiers also reduce the likelihood of precipitation events forming thick scales within the system. Several other operational guidelines have been reviewed that also help mitigate scale formation events.

In addition to precipitation events, scale formation of aluminosilicate scales can result from a buildup of aluminum and silica in the liquor cycle. Typically, these undesirable materials are removed from the liquor cycles as part of the various heavy metals in the dregs. If the concentration of either of these materials gets high enough, they will precipitate onto equipment surfaces and form a very hard, difficult to remove glassy scale. Good debarking, white water segregation away from the liquor cycle, and judicious application of silicon-based defoamers all help maintain low levels of these contaminants and prevent scale formation.

Carryover of dregs from the green liquor clarifier is a source of less common scales, such as magnesium and manganese dioxide. These materials, like aluminum and silica, are only marginally soluble in the highly alkaline green liquor solutions and tend to scale onto equipment and piping when their concentration is increased due to poor dregs removal from the green liquor clarifier. **TJ**

ACKNOWLEDGEMENTS

This manuscript is part of the new *Lime Kiln and Recausticizing* textbook currently being prepared for publication through TAPPI Press.

LITERATURE CITED

1. Frederick, W.J., Jr., Krishnana, R., and Ayers, R.J., *Tappi J.* 73(2): 135(1990).
2. Slamenoja, K. and Kosonen, J., "Solving deposit problems in the smelt dissolving tank," *TAPPI Eng. Conf.*, TAPPI Press, Atlanta, GA, USA, 1996.
3. Taylor, K. and McGuffie, B., *Pulp Pap. Can.* 108(2): 27(2007).
4. Martins, F.M., Martins, J.M., Ferracin, L.C., et al., *J. Hazard. Mater.* 147: 610(2007).
5. Zakir, T., Tran, H., and Papangelakis, V.G., *TAPPI J.* 12(1): 55(2013).
6. Tran, H., "Scale formation in causticizing plants—An overview," *Annual Research Review Meet. Energy & Chemical Recovery*, University of Toronto, Toronto, ON, Canada, 2017.
7. Bury, C.R. and Redd, R., *J. Chem. Soc.* 272: 1160(1933).
8. Littmman, F.E. and Gaspari, H.J., *Ind. Eng. Chem.* 48(3): 408(1956).
9. Zakir, T., Tran, H., and Papangelakis, V.G., *TAPPI J.* 12(7): 33(2013).
10. DeMartini, N. and Frederick, W.J. Jr., "Review of sodium scaling in streams of the chemical recovery cycle of kraft pulp mills," *TAPPI Eng., Pulping, Environ. Conf.*, TAPPI Press, Atlanta, 2008.
11. Biakik, M., Wadsborn, R., Karlholm, I., et al., "Assessment of scaling risk in a pressurized black liquor gasification pilot plant," *Int. Chem. Recovery Conf.*, Vol. 1, TAPPI Press, Atlanta, 2010, p. 279.
12. Hart, P.W., "Green liquor scale – A guide towards minimization or elimination," *Frontline Focus*, TAPPI Press, Atlanta, 4(9): Sept. 2008.
13. Williamson, J., Adedire, A., and Baron, S.J., "Green liquor scale prevention," *TAPPI PEERS Conf.*, TAPPI Press, Atlanta, 2012, p. 2020.

ABOUT THE AUTHORS

This work is part of a text being prepared for the lime kiln and recausticizing areas of the mill. One troubling aspect of this process area is green liquor scale. Putting the current state of green liquor scale formation into one spot can only be of benefit to the industry. This work is a comprehensive review of the current state of the understanding of green liquor scale.

Finding the current work was somewhat difficult. Even though this is a problem area of the mill, there are not a lot of current research efforts in this area. Dr. Honghi Tran's group at the University of Toronto is doing most of the current work in this field. He received an award for detailing pirssonite scale then got an award the next year for determining it was not pirssonite but rather calcium carbonate.

For mills, understanding ways to prevent scale formation will benefit the process area. The next step is application of the technology in practice.

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14. Giglio, A., Tran, H., and Papangelakis, V., "Calcite scale formation in green liquor handling systems," *Univ. Toronto Consortium Meet.*, University of Toronto, Toronto, ON, Canada, 31 October 2017.
15. Pyörälä, K., "Improved causticizing control by digital green liquor TTA measurement," *PAPTAC Annu. Meet., 85th,* Pulp and Paper Technical Association of Canada, Montreal, QC, Canada, Part A, 1999, Vol. B, p. B267.
16. Coyle, I., Russell, S., Rajbhandari, V., et al., "Improving smelt dissolving tank TTA control at Zellstoff-Celgar," PACWEST 2013 Technical Papers, Paper 5, Session 3A – Process Control, Pulp and Paper Technical Association of Canada, Montreal, 2013. Available [Online] http://www.texo-cc.com/images/files/Improving%20Smelt%20Dissolving%20Tank%20TTA%20Control%20at%20Zellstoff-Celgar%20-%20final.pdf.
17. ChemStone, "DSC metals management and scale control: How it works," *ChemStone Paper Training Presentation*, ChemStone Corporation, Greenville, SC, USA.
18. Hamalainen, H., Dutreix, J., and Jakara, J., "Calcium-derived scale control experiences in pulp mills," *Prepr.–PAPTAC Annu. Meet., 90th,* 2004, Vol. B, p. 129.
19. Horvath, R., *PIMA's North American Papermaker* 49(3): 38(1996).
20. Georgiou, D., Bendos, D., Kalis, M., et al., *J. Water Process Eng.* 22: 34(2018).
21. Pečnik, B., Hočevar, M., Širok, B., et al., *Wear* 356-357: 45(2016).
22. Gasteiger, H.A., Frederick, W.J., and Streisel, R.C., *Ind. Eng. Chem. Res.* 31(4): 1183(1992).
23. Wannenenmacher, N., Kimura, S., and Frederick, W.J., *Ind. Eng. Chem. Res.* 44(24): 9316(2005).
24. Ulmgren, P., *Nord. Pulp Pap. Res. J.* 2(1): 4(1987).
25. Golmaei, M., Kinnarinen, T., Jernström, E., et al., *Chem. Eng. J.* 317: 471(2017).
26. Lundqvist, F., Brelid, H., Saltberg, A., et al., *Appita J.* 59(6): 493(2006).
27. Doldán, J., Poukka, O., Salmenoja, K., et al., *O PAPEL* 72(7): 47(2011).
28. Santos, R.B., Gomide, J.L., and Hart, P.W., *BioResources* 10(4): 6538(2015).