Sulfur makeup in an unbleached kraft pulp mill

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ABSTRACT: Sodium sesquisulfate or "sesqui" ($Na_3H(SO_4)_2$) is a by-product of chlorine dioxide production at kraft pulp mills. It is typically used for sodium and sulfur makeup in the liquor loop. Mondi Hinton Inc. (MHI) in Hinton, AB, Canada, was converting from bleached to unbleached kraft pulp production and was thus losing this source of makeup. The only option that was readily available as a substitute was sodium hydrosulfide (NaHS), which was cost prohibitive. Other options such as sodium sulfate (Na_2SO_4), emulsified sulfur, sulfuric acid (H_2SO_4), and sodium bisulfite ($NaHSO_3$) were compared. The mill concluded that pelletized sulfur plus sodium hydroxide or "caustic soda" (NaOH) was the best option.

Laboratory-scale experiments showed that pelletized sulfur dissolved in white liquor (WL). A mill-scale trial revealed that pelletized sulfur added to a causticizer had no adverse impacts on the downstream pressure filters or kiln operation. The sulfur reacted to produce polysulfide upstream of the WL storage tank, giving the liquor an orange hue. This polysulfide appeared to partially degrade into thiosulfate before being fed to the digester. The heavy black liquor (HBL) sulfur:sodium (S:Na) ratio did not change significantly, even though the sulfur/soda addition location was upstream of the original one. In addition, other properties such as liquor heating value and elemental analysis did not significantly change.

Due to polysulfide/thiosulfate concentration in the white liquor, it was determined that the carbon steel equipment was at risk for corrosion. During the annual turnaround that occurred eight months after the addition of sulfur was started, the wash zone of the digester showed no signs of thinning/damage.

The mill has been running exclusively with pelletized sulfur for 22 months (as of August 2024), realizing significant cost savings compared to the use of NaHS or other sulfur/soda addition options.

Application: Kraft pulp mills (unbleached or bleached) require sulfur makeup. This paper reviews chemical makeup options for sulfur makeup and explains the implementation of an unconventional makeup source. This chemical was more inexpensive, abundant, and required a smaller dosing system than other options.

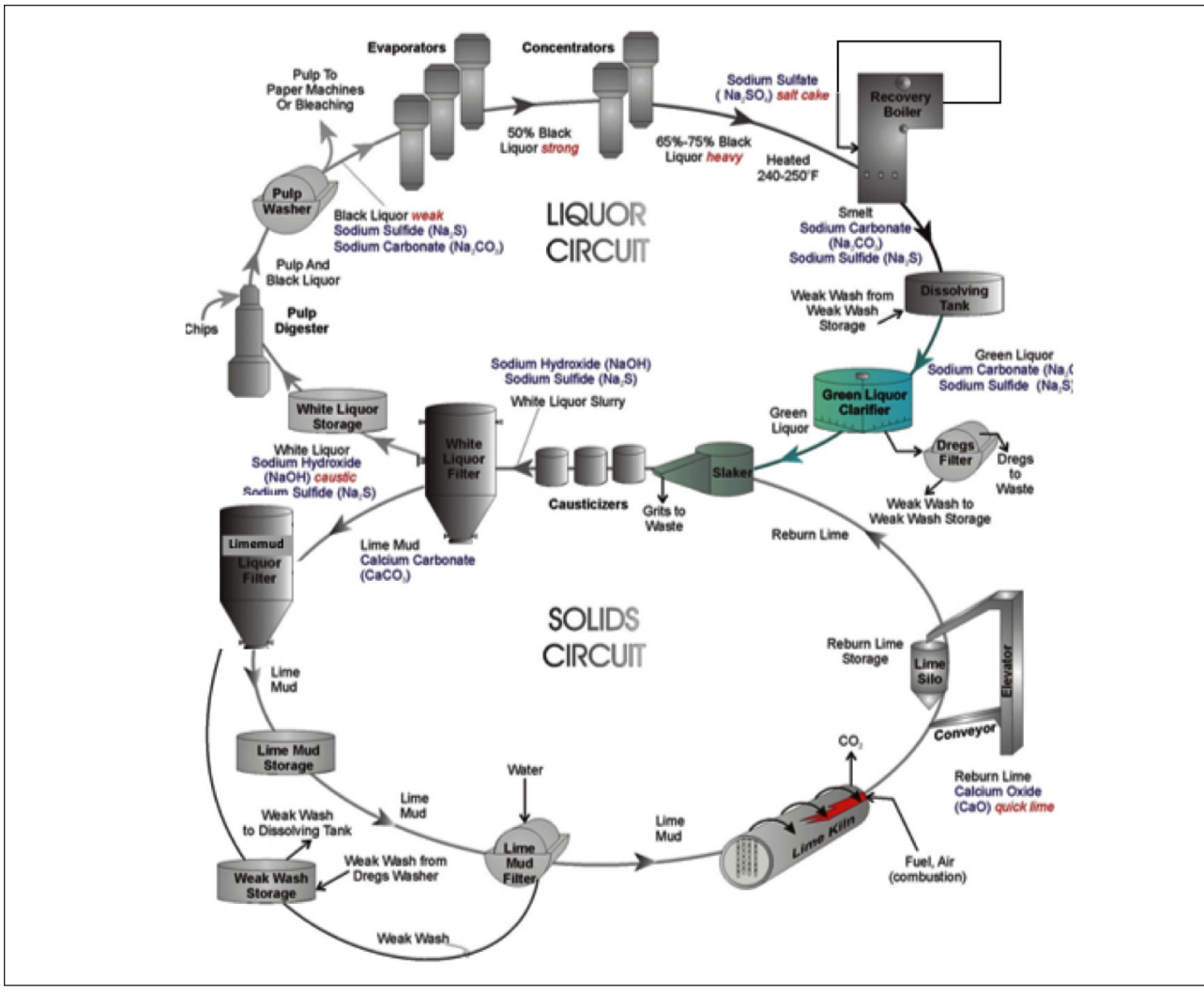
In kraft pulping, wood chips are cooked in a digester vessel at high temperatures and pressures with white liquor (WL). The WL is an aqueous solution comprised mainly of sodium hydroxide (NaOH), sodium sulfide (Na_2S), and lower concentrations of sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4), and other sodium salts. In the digester, hydroxyl ions (OH-) participate in several complex delignification reactions. The sulfide (which hydrolyzes into hydrosulfide ion (HS-) in solution improves the selectivity for the delignification reactions in the digester [1]. Without this species, the reaction would take longer to achieve a lignin content target (kappa number), and there would be more damage to the valuable cellulose fibers in the final pulp [1]. This would negatively impact key final pulp properties such as strength, as well as mill performance parameters such as wood-to-pulp yield. Therefore, sodium (counter cations of anions like hydroxyl that participate in cooking reactions) and sulfide (participates in cooking reactions) are required in the liquor.

The ratio between sodium and sulfur is very important to control and is typically defined by sulfidity. There are numerous definitions of sulfidity; however, for the purpose of this paper, Eq. 1 will be used to define sulfidity in white liquor:

$$Sulfidity\,(\%) = \frac{Na_2S\left(\frac{lb\,Na2O}{ft^3}\right)}{Na_2S\left(\frac{lb\,Na2O}{ft^3}\right) + NaOH\left(\frac{lb\,Na2O}{ft^3}\right) + Na_2CO_3\left(\frac{lb\,Na2O}{ft^3}\right)} \quad (1)$$

Low sulfidity liquor results in poor pulp quality, lower delignification rate and lower pulp yield, all of which significantly impact the mill's profit margin. Furthermore, low sulfidity has adverse impacts on downstream processes and equipment. Namely, the viscosity of the smelt bed in the recovery boiler will increase, leading to thick smelt that "jelly-rolls" and may plug off smelt spouts, creating hazardous conditions [2]. Once a smelt spout is plugged with smelt, inventory builds up behind the spout. When the smelt spout is unplugged, the excess smelt inventory will rush into the dissolving tank with too much volume to be adequately atomized by the steam shatter spray. This can result in a violent reaction that has led to dissolving tank explosions in industry in the past [3].

On the other hand, elevated sulfidity leads to higher total reduced sulfur (TRS) and sulfur dioxide (SO_2) emis-



1. Schematic of kraft recovery process at Mondi Hinton Inc.

sions in the recovery boiler and reduces the melting temperature of the saltcake ash produced in the recovery boiler. This results in a higher deposition rate onto the boiler flue gas path tubes (e.g., boiler bank, superheaters) [4]. Eventually, the flue gas path will plug off and the recovery boiler (and pulp mill) will have to go down for a water wash, which may take days.

Although the liquor loop is closed, there are losses that occur, and the largest source of soda loss is typically with the outgoing pulp from the brownstock washers that are not 100% efficient in recovering/washing liquor back into the liquor loop. Other losses come from spill/leaks, saltcake dumping (to purge non-process elements [NPE] content), boiler emissions (TRS, SO_2), dregs, and grits [5]. Therefore, sodium and sulfur must be made up to maintain liquor inventory and control sulfidity. Typical soda/sulfur makeup in pulp mills comes from purchased saltcake (Na_2SO_4), purchased NaOH, and/or sodium sesquisulfate or "sesqui" ($Na_3H(SO_4)_2$), which is a by-product from the chlorine dioxide (ClO_2) generator.

DESCRIPTION OF PROCESS AT MONDI HINTON INC.

Prior to 2022, Mondi Hinton Inc. (MHI) in Hinton, AB, Canada, was a 2-line northern bleached softwood kraft (NBSK) pulp mill. The mill converted to a 1-line unbleached kraft pulp (UKP) mill in Q4 2022. This conversion posed several process design challenges. One challenge was determining how sulfur and soda loss inherent to the process was going to be made up in the liquor loop with no $Na_3H(SO_4)_2$ available from the discontinued chlorine dioxide production process. The mill's immediate option to make up soda and sulfur was synthetic white liquor (SWL), which uses sodium hydrosulfide (NaHS) and NaOH. This approach was extremely costly and would negate ~2/3 of the cost savings expected by the elimination of the bleaching process. Therefore, there was a need to explore different options.

Figure 1 depicts the general recovery loop process layout at MHI. The pulp mill produces kraft pulp principally from lodgepole pine. Once chips are screened, they are

	Safety & Environmental	Chemical Availability	Chemical Cost	Capital Cost	Maintenance & Operations	Process Effectiveness	Final Score
Molten S	(8) 40	(9) 27	(9) 45	(4) 10	(8) 32	(7) 28	182
Pelletized S	(6) 30	(9) 27	(9) 45	(8) 20	(6) 24	(7) 28	174
H_2SO_4	(5) 25	(7) 21	(7) 35	(6) 15	(7) 28	(4) 16	140
Emulsified S	(8) 40	(3) 9	(7) 35	(4) 10	(8) 32	(8) 32	158
Na_2SO_4	(8) 40	(5) 15	(6) 30	(4) 10	(5) 20	(8) 32	147
NaHS	(3) 15	(3) 9	(1) 5	(10) 25	(3) 12	(5) 20	86

S: sulfur; H_2SO_4: sulfuric acid; Na_2SO_4: sodium sulfate; NaHS: sodium hydrosulfide.

I. Raw rating (in brackets) and scores of chemicals against selection criteria.

steamed and impregnated with white liquor (WL). The impregnated chips are sent to a 1989 Kamyr downflow digester controlled at 135 psig. The effective alkali-to-wood (EA/wood) ratio is typically controlled between 16%–16.25%, and the WL is split 80% to the impregnation vessel (IV) and 20% to the modified cook (MC) zone. Digester targets are 28–32 kappa number and 0.6–0.8 lb sodium oxide (Na_2O)/ft³ wash extraction residual alkali. The mill's sulfidity target is 28%–29%.

Pulp from the digester is sent to a pressure diffusion washer, followed by four stages of displacement and press washing. Equipment decommissioned during the UKP transition includes oxygen (O_2) delignification, bleach plant, and ClO_2 production. A by-product of the ClO_2 production process was $Na_3H(SO_4)_2$, 30%–50% of which was added back to the liquor loop in the weak black liquor (WBL) tank to control sulfidity.

The WBL from digester extraction and brownstock washing at around 15% solids is sent to 5-effect falling-film effects evaporator train followed by a high solids crystallizer set. It thickens the liquor up to 70% solids to produce heavy black liquor (HBL). Soap from the WBL tank is skimmed and removed, as it is no longer fired in the recovery boiler in the 1-line UKP configuration.

After recovering boiler ash from the economizer and precipitator, the HBL liquor is fired in the recovery boiler. This boiler is a 1989 decanting floor Combustion Engineering (CE) unit rated for 443,000 lb/total steam with a three-level air system and one nozzle per wall. The outlet steam spec is 600 psig at 750°F. The boiler flue gas passes through two precipitator chambers (in parallel) to capture saltcake particles.

Smelt runoff is dissolved and sent to the recausticizing plant, which comprises of one slaker, followed by five causticizer tanks in series. The final causticizer feeds a white liquor pressure filter (WLPF) that overflows into the WL storages. The underflow from the WLPF is washed and sent to the lime mud pressure filter (LMPF), which supplies weak wash to dissolve smelt from the recovery boiler. The LMPF underflow is sent to a vacuum drum dryer that dries the mud to ~75% before entering the lime kiln.

2. Prilled elemental sulfur.

PROJECT DEVELOPMENT AND OPTION SELECTION

There are numerous chemicals that can be used for sodium and sulfur makeup in the liquor loop. After surveying various options, NaHS, sulfuric acid (H_2SO_4), emulsified sulfur, sodium sulfate (Na_2SO_4), and elemental sulfur (pelletized and molten) were evaluated. These options were evaluated against several criteria on a 1–10 scale. The rating was then multiplied by a weight on a scale of 1–5 to come to a score for each criterion. Finally, the scores for each criterion were summed to come to an overall final score for the chemical; the higher the rating, the more suitable the option. Since these weights applied depend on the mill priorities, situation, and location, it is likely the weight will be different for other mills. **Table I** breaks down the ratings given for each option.

Selection criteria

Safety and environment (weighting factor of 5)

The most important factor in any project phase is the safety and environmental aspect. Sulfur, in the form of pellets shown in **Fig. 2**, introduced a combustible dust hazard that must be mitigated. However, at the addition rates required at MHI, this hazard was not too concerning if the equipment design and procedures/training for operators were well developed. The combustible dust explosion hazard can be significantly reduced in the equipment design phase. Emulsified sulfur and molten sulfur scored better for safety, as there are no combustible dust hazards. The Na_2SO_4 introduced minimal hazards for process or occupational safety/health. The H_2SO_4 and NaHS posed the highest safety risk due to the extremely corrosive nature of the chemicals.

From an environmental point of view, the main concern with all the chemical options was spills to the ground/loss of containment. Therefore, the liquid chemicals posed the highest risk (likely requiring berms to mitigate spill concerns). The larger the volume required to be on site, the greater the chance for a spill, which highlights the advantage of using pelletized and molten sulfur, as these options would require the least volume to achieve sulfur makeup.

Chemical availability/transportation logistics (weighting factor of 3)

Geography and surrounding industry will impact this category. In the Hinton area, pelletized sulfur and molten sulfur are abundant as a by-product of oil and gas operations. Sulfuric acid, often produced by elemental sulfur, was also readily available to the mill. Emulsified sulfur, NaHS, and Na_2SO_4 were relatively hard to secure, and although each had one viable supplier within reasonable distance, there would be long lead times that could pose an issue in case of emergency orders.

Chemical cost (weighting factor of 5)

The second most important criteria for consideration after safety and environmental impact was cost. In hindsight, the rating of chemical cost should have been 4.5 so that its importance in this evaluation method was not equated to safety and environment. It was found that pelletized sulfur (and caustic soda) was the cheapest option for MHI, with caustic soda contributing 90%–95% of the total makeup cost. Even though Na_2SO_4 (and caustic soda) had the benefit of partially making up the soda requirement along with all the sulfur requirement, this option was 20%–25% more expensive than the pelletized sulfur/caustic soda option. The H_2SO_4 and emulsified sulfur (with caustic soda) were 10%–15% more expensive than the pelletized sulfur/caustic soda option. The NaHS was 95%–100% more expensive than the pelletized sulfur/caustic soda option.

Capital cost/project complexity (weighting factor of 2.5)

Significant resources, time, and money go into projects. In a mill concerned with reliability, this can impact business decisions and allocation of capital. For MHI, the capital cost of a NaHS addition system was zero, as the mill already had a system to make up liquor using NaHS. A system to do so for using H_2SO_4 would be relatively inexpensive, as modifications to an existing system would have been possible. Emulsified sulfur would have required a new surge tank (and berm) equipped with an agitator along with pumps and piping, which was expected to be a capital-intensive solution. Molten sulfur would require similar equipment (and thus capital) as an emulsified sulfur system, with the addition of steam coils and heat traced piping (although no agitator in the tank is required). The Na_2SO_4 and pelletized sulfur would require bulk solids handling systems. Due to layout of plant equipment, an Na_2SO_4 system would require an extensive blowing system to adequately reach an HBL mixing tank. Sulfur cannot be pneumatically blown due to a combustible dust hazard and would have to be conveyed. This, however, was not envisioned to be particularly difficult, since the mill layout favored a small and simple addition system in the recausticizing plant. Furthermore, a bulk handling system for Na_2SO_4 would have to be several times larger than one for elemental sulfur, as the molar mass of Na_2SO_4 is much higher than that of sulfur. Therefore, to achieve a specific sulfur dose, more mass would have to be moved for the saltcake system (by at least a factor of 142/32 = 4.44).

Maintenance and operability (weighting factor of 4)

An emulsified sulfur tank would have to have an agitator to keep the micronized particles in suspension, along with a variable speed pump. This system ranked high (good) for operability and maintenance. Similarly, molten sulfur scored well due to simplicity of the liquid-based system. One concern would be the molten sulfur freezing on loss of power/steam. This is not a major concern, as the melting point of sulfur is ~135°C and thus would not require much energy/time to thaw. The H_2SO_4 also scored well in this category; it may require makedown from 93% to 10%, which already exists. The NaHS must be mixed with caustic soda and water in a batch formula to make "synthetic white liquor" (SWL). This requires operator care and effort, and thus did not score as high from an operability perspective. The Na_2SO_4 and pelletized sulfur would require unloading and conveying bulk solids, and Na_2SO_4 would require unloading of 40 metric ton trucks and use a combination of a silo, baghouse, blower system storage bin, and screw conveyor. Pelletized sulfur would use a bucket elevator/vibrating feeder being fed by 1 metric ton tote bags. The Na_2SO_4 would have more moving parts and would carry the Na_2SO_4 longer distances at larger volumes, therefore increasing the chances for breakdown and replacement of system components. The pelletized sulfur

system would require frequent bag refilling by the operators. Overall, a pelletized sulfur system was rated higher than the Na_2SO_4 and NaHS, but lower than emulsified sulfur and H_2SO_4.

Process control and effectiveness (weighting factor of 4 each)
Pelletized sulfur, emulsified sulfur, molten sulfur, and NaHS could all be fed in the recausticizing plant, thereby providing immediate feedback from the WL sulfidity tests done every 4 h by operators via the ABC titration tests to determine sulfides, effective alkali, and carbonate. For this reason, these chemicals would score the highest for their ability to control and maintain sulfidity. However, sulfur introduces process risks associated with polysulfide and thiosulfate formation that can have an impact on the corrosion of carbon steel equipment. The H_2SO_4 and Na_2SO_4 would be added to BL. Emulsified sulfur could be added to WL or BL. Chemicals, when added in the BL, would have a large time lag between addition point and measurement; therefore, control suffers. Adding these sulfur components to the BL may increase sulfur composition at the recovery boiler. This may increase the potential for higher SO_2 or H_2S emissions. Furthermore, as the sulfur composition increases the ash melting characteristics change (also known as sticky temperature) [4]. This may result in higher deposition rate on the boiler tubes and ultimately furnace pluggage, requiring downtime to water wash the saltcake off the tubes [4]. If there is significant sulfur loss through the recovery boiler flue gases, the WL sulfidity may be lower than desired, as opposed to having the sulfur added where it is typically most important, which is right before the digester in the WL. The H_2SO_4 introduces risks of dropping the WBL pH, resulting in lignin reprecipitation that can foul the evaporators and negatively impact performance; therefore, it had the lowest ranking for process effectiveness.

Chemical selection

Pelletized sulfur and molten sulfur (plus caustic soda) ended up with the highest selection rating. They were the cheapest makeup options, beating out emulsified sulfur, H_2SO_4, Na_2SO_4, and NaHS by 10%, 11%, 23%, and 95%, respectively, which represented significant cost savings and other benefits for the pulp mill. The main concern for the pelletized sulfur option was the potential introduction of an explosion hazard (combustible dust). After visiting a pelletized sulfur plant, it was clear that there are several controls that could be put in place to eliminate/mitigate this hazard. This operation conveyed significantly larger than the mass MHI would have to convey, yet due to good engineering/operational practices, the facility had not experienced any explosions in their operating history. These practices included the following: regular/scheduled cleanup, operator rounds/inspections, good equipment selection, dust-tight design, proper grounding, and installation of deflagration suppression systems. Furthermore, MHI, along with most other pulp mills, already have experience with conveying the higher risk sawdust hog fuel. This fuel is typically moved at much larger volumes/quantity for further distances than the sulfur. Chemical availability was another major advantage of pelletized and molten sulfur, as they were the most abundant forms of sulfur available to the mill. Although molten sulfur was more advantageous than the pelletized sulfur in terms of the cost and safety, the project complexity and capital cost required would have been significant in comparison to a small conveying system for pelletized sulfur. Due to the time constraints on this project, it was therefore decided that a pelletized sulfur system would be implemented as the short-term solution, and in the long-term, a molten sulfur system would be considered.

Table II summarizes the pros and cons of each option.

Chemical	Pros	Cons	Final Score
NaHS	No capital cost, can implement right away	Expensive, unloading safety risks, only one source nearby with long lead time	86
H_2SO_4	Low capital cost, relatively low chemical cost	Risk of lignin reprecipitation/fouling evaporator train	140
Emulsified S	Relatively low chemical cost	High capital cost, only one source nearby with large lead time	158
Na_2SO_4	Relatively low chemical cost, proven makeup source in industry	High capital cost, only one source nearby with long lead time	147
Pelletized S	Cheapest option (chemical), high abundance in Alberta, system size would be small	No references of implementation of such a system (unproven), potential for corrosion, combustible dust hazard	174
Molten S	Cheapest option (chemical), high abundance in Alberta, system size would be small	No references of implementation of such a system (unproven), potential for corrosion, potential for solidification in tank/lines	182

NaHS: sodium hydrosulfide; H_2SO_4: sulfuric acid; S: sulfur; Na_2SO_4: sodium sulfate.

II. Pros and cons of each chemical option at Mondi Hinton Inc. and final rating based on selection criteria.

Sulfur Added, g/L	Temperature, °F	Dissolving Time, min
0	180	0
1	180	12
2	180	12
3	180	12
4	180	12
8	180	12
2	150	23
2	190	11

III. Dissolving rates of prilled sulfur in 500 mL of white liquor at different temperatures.

The main drawback of using pelletized sulfur was the lack of literature or mill references that used pelletized sulfur as their sole source of sulfur makeup. Thus, the mill was concerned that this method of makeup was not proven at scale. The limited literature available on this topic noted that these types of makeup systems have failed in the past, because of their inability to control the sodium-to-sulfur ratio and other issues it may introduce to the kraft liquor loop. For this reason, this project required trials to prove out the process before implementing. The mill's backup solution if the trials failed would have been NaHS and re-evaluation of the other chemical options (Na_2SO_4 was likely the first runner up).

TRIALS

Sulfur reacts with the sodium sulfide in white liquor to create sodium polysulfide as per the reaction below [6]:

$$nS(s) + HS^{-1} + OH^{-1} \longrightarrow SnS^{-2} + H_2O$$

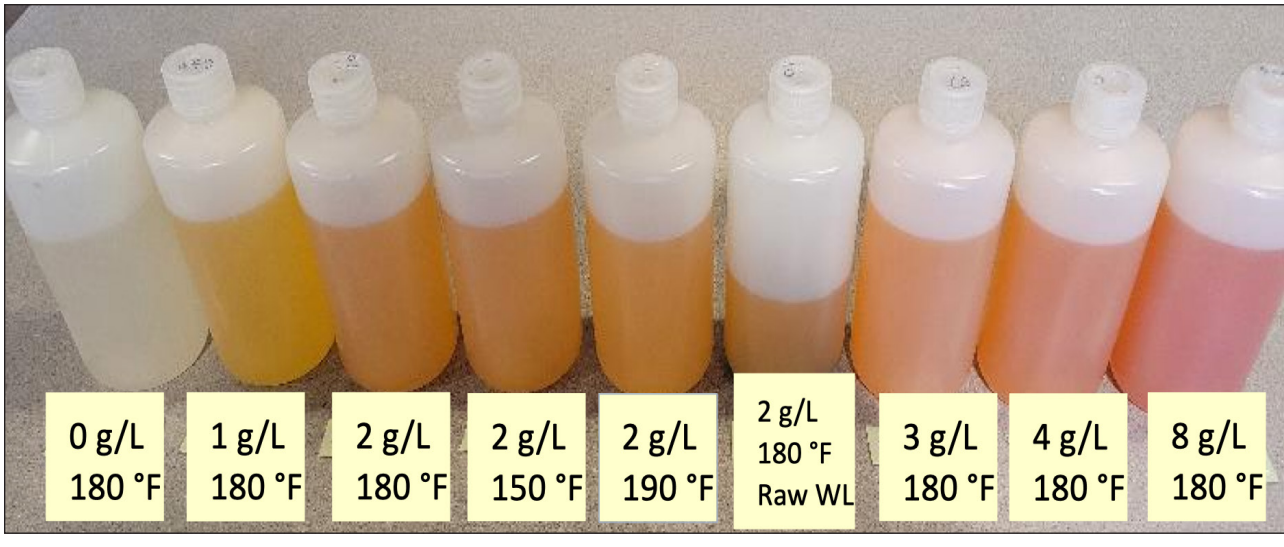
where:
n = average sulfur chain length

The sulfur is soluble in aqueous solution and thus will be dissolved in the liquor. Therefore, the theory was that the sulfur, if given a sufficiently long time, would react with sulfide and hydroxide and dissolve in the liquor to become polysulfide. Trials were performed on a bench scale, then scaled up to the mill scale to demonstrate that:

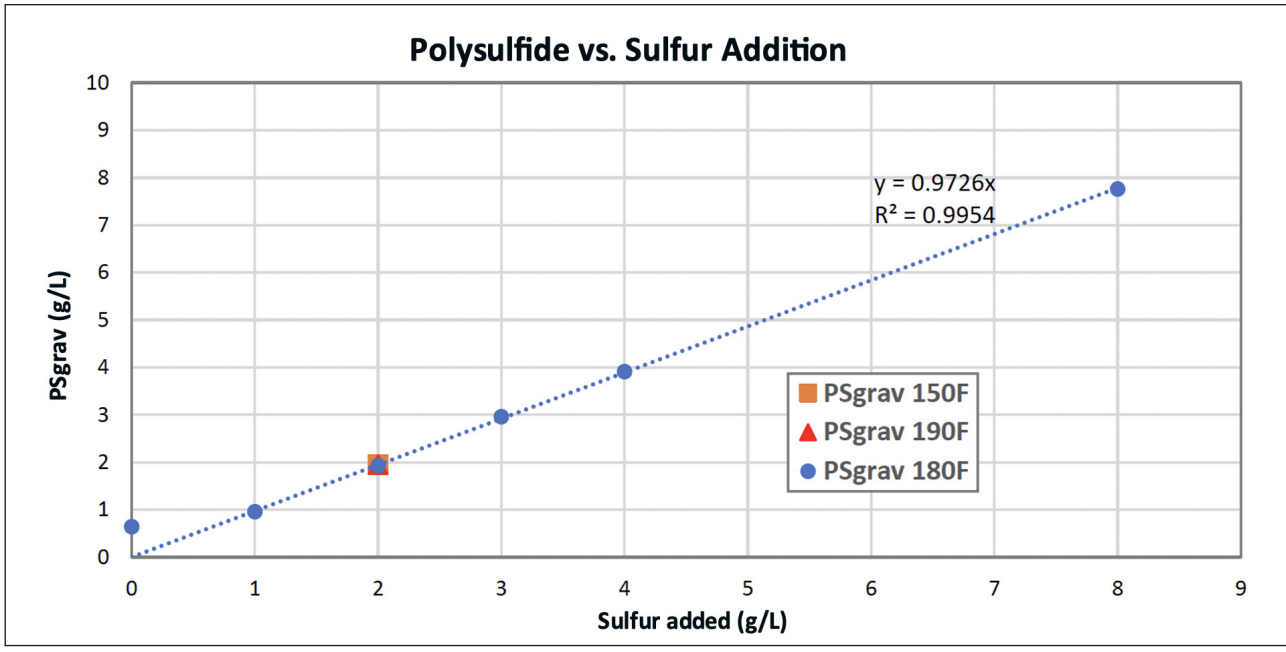
- All the sulfur dissolves into WL.
- Dissolved sulfur produced polysulfide.
- No hydrogen sulfide (H_2S) production is induced.
- No adverse impacts are observed in the liquor cycle.

Laboratory-scale experiments

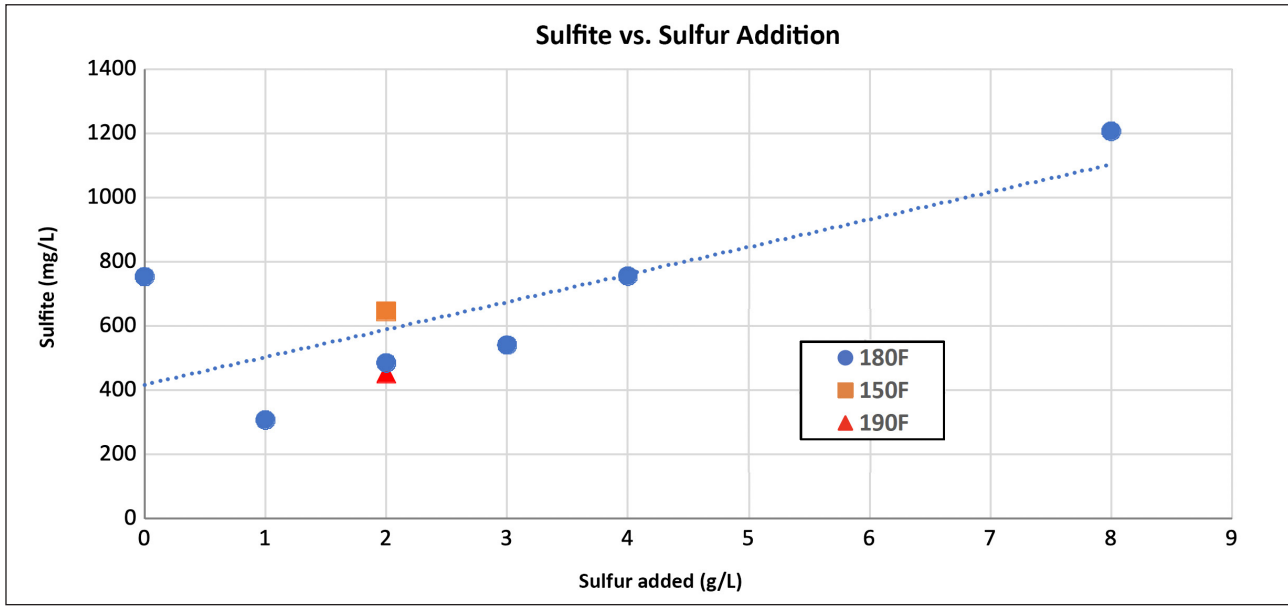
The first step in demonstrating that pelletized sulfur would be a viable solution for makeup sulfur was performing laboratory-scale experiments to determine how the pelletized sulfur reacts with and dissolves into mill white liquor and understanding the impact of factors such as temperature and concentration on dissolving rates. This was done by adding prilled sulfur (0 to 8 g/L) to 500 mL of the mill's raw or clear white liquor to determine dissolving rate at three temperatures (150°F, 180°F, and 190°F). At a given temperature, the dissolving rate was independent of the amount of sulfur added, as it took ~12 min to completely dissolve (determined by visual assessment when no more solid was visible) the added sulfur at 180°F (**Table III**), which is sufficient time to completely dissolve in the causticizer. The temperature, however, did have an effect on dissolving rate, as the dissolving time doubled when the temperature was decreased from 180°F to 150°F. An Industrial Scientific Ventis MX4 gas monitor (Industrial Scientific; Pittsburgh, PA, USA) was used to detect any H_2S emissions while dissolving sulfur in the white liquor, and none was detected. **Figure 3** shows the appearance of the li-



3. Photograph of liquors after completely dissolving different amounts of prilled sulfur.



4. The amount of sulfur added reacts to form polysulfide, almost on 1:1 basis (PSgrav: polysulfide measured gravimetrically).



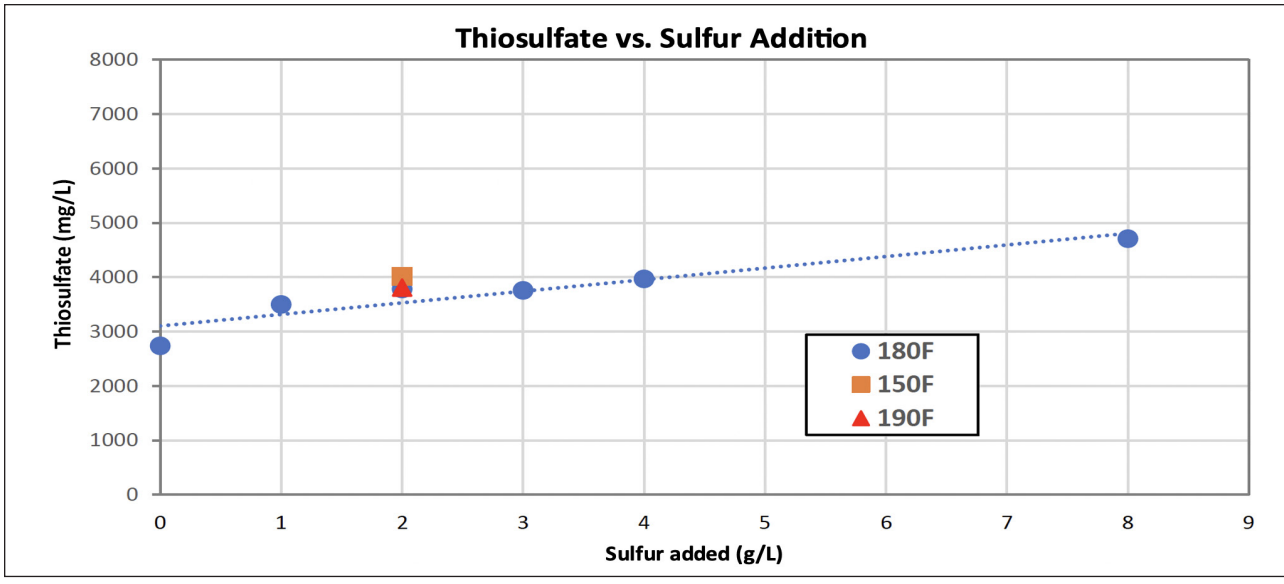
5. The sulfite concentration increased slightly as a result of partial sulfur oxidation.

quors where a distinct color change from light to darker orange occurred, which is typically seen in polysulfide liquors, as the concentration of prilled sulfur increased.

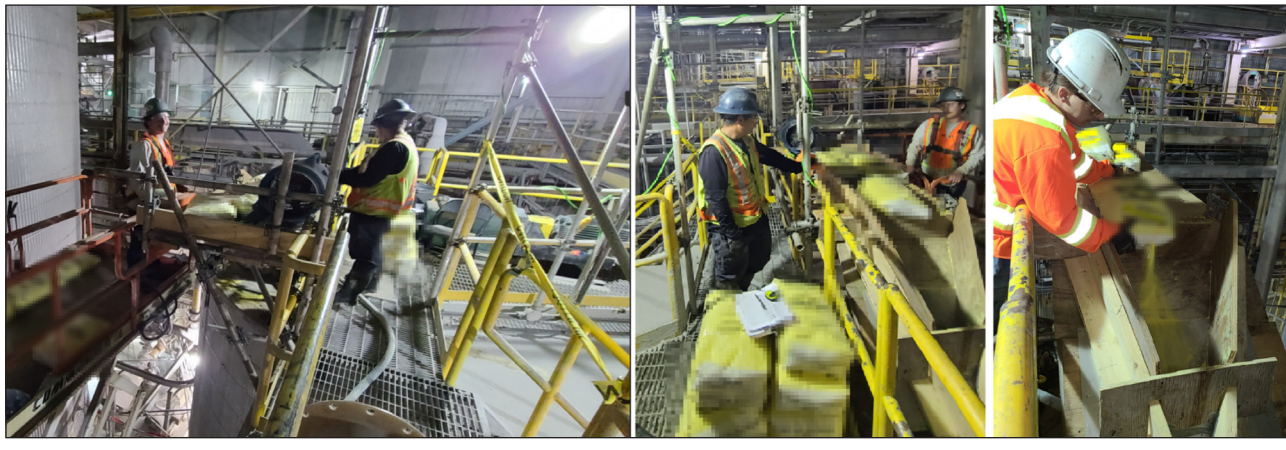
In terms of liquor chemical composition, EA and free sulfides did not change, as measured by a method developed by G.M. Dorris and V.C. Uloth [7]. However, as expected, the bound sulfides and polysulfide measured gravimetrically [8] (denoted as PSgrav) increased. A plot of the PSgrav vs. prilled sulfur added showed a linear relationship (r^2 = 0.995) with a slope of 0.97, indicating that the sulfur added completely reacts to form polysulfide (**Fig. 4**). The levels of deadload sodium salts (e.g., chloride, carbonate, sulfite, sulfate, and thiosulfate, measured by ion chromatography) remained the same, with exception of sulfite and thiosulfate concentrations that increased (**Fig. 5** and **Fig. 6**), especially at high sulfur addition levels.

Mill-scale trial

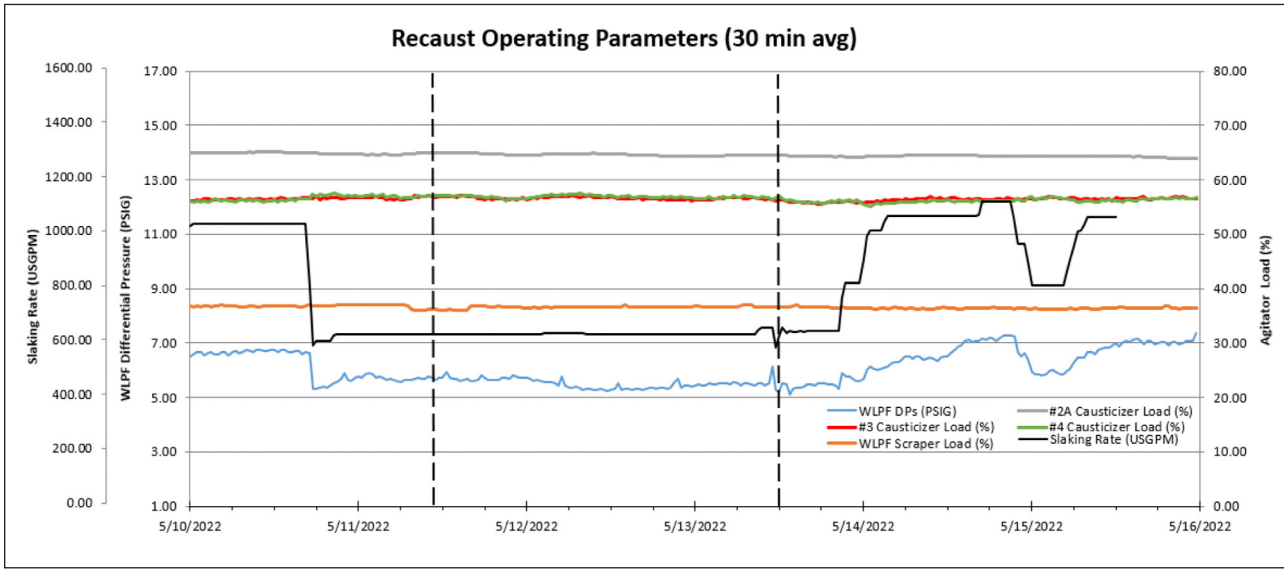
The next step was scaling up the laboratory trial to a mill-scale trial. The purpose of this trial was to confirm that the pelletized sulfur dissolved into the white liquor and did not



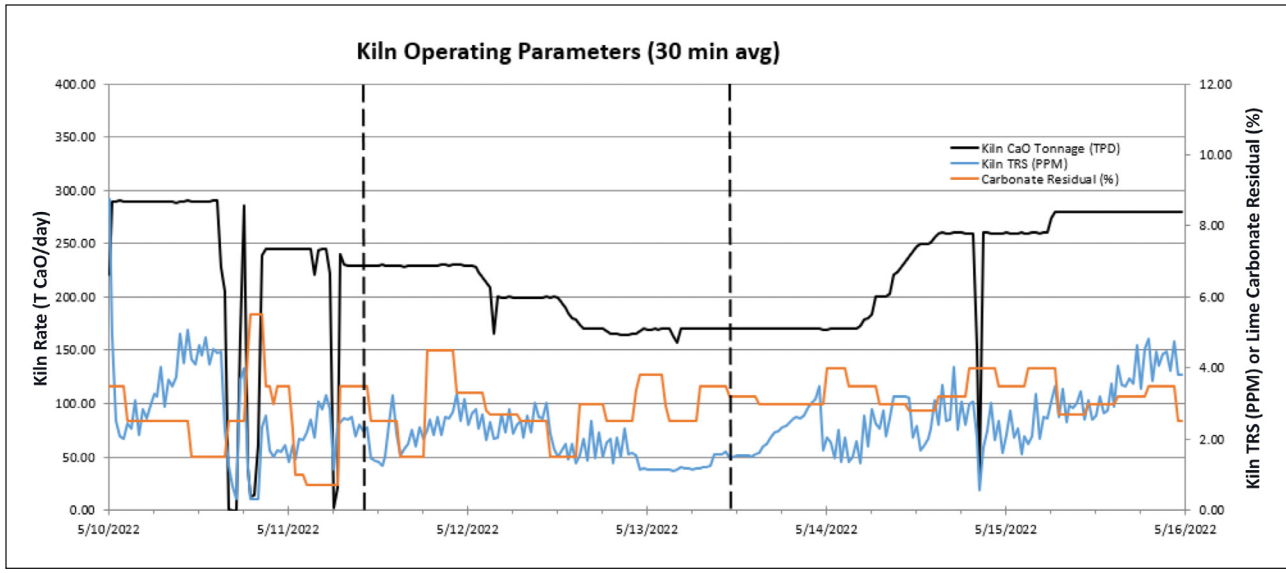
6. The thiosulfate concentration increased slightly as a result of partial sulfur oxidation.



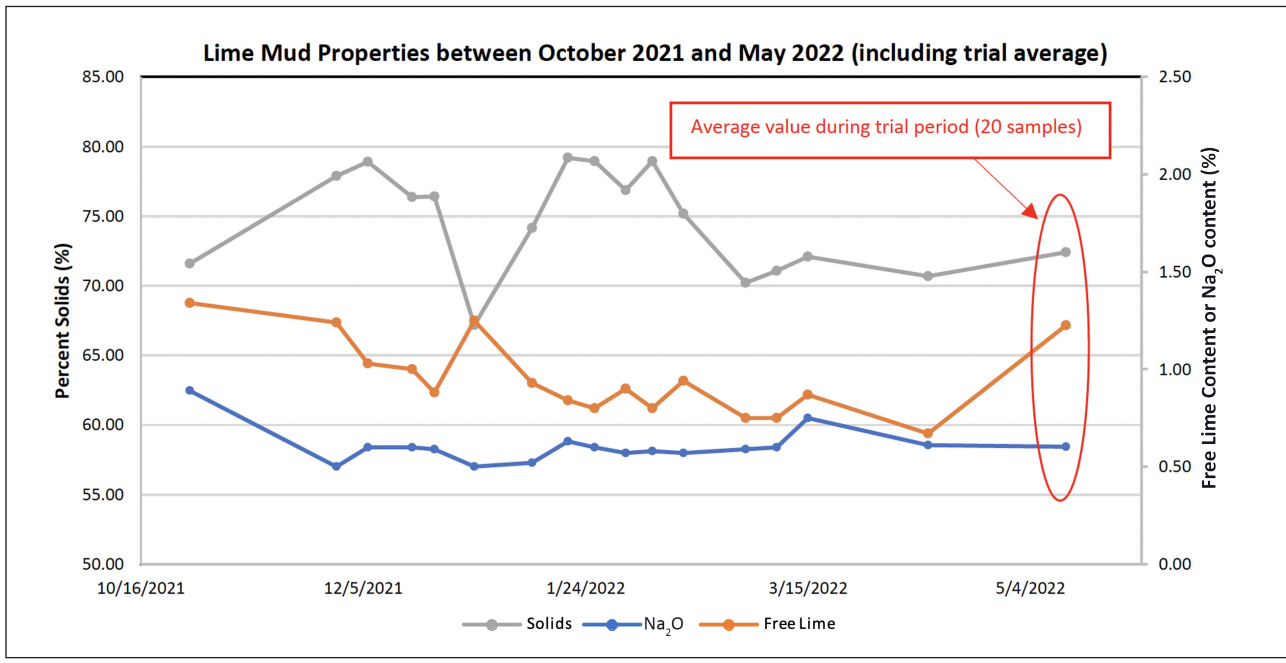
7. Pelletized sulfur mill-scale trial setup.



8. Recaust operating parameters trends before, during, and after mill-scale trial (USGPM: U.S. gal/min; WLPF: white liquor pressure filter; DPs: differential pressures).



9. Kiln operating parameters trends before, during, and after mill-scale trial (T CaO/day: metric tons of calcium oxide per day; TRS: total reduced sulfur).

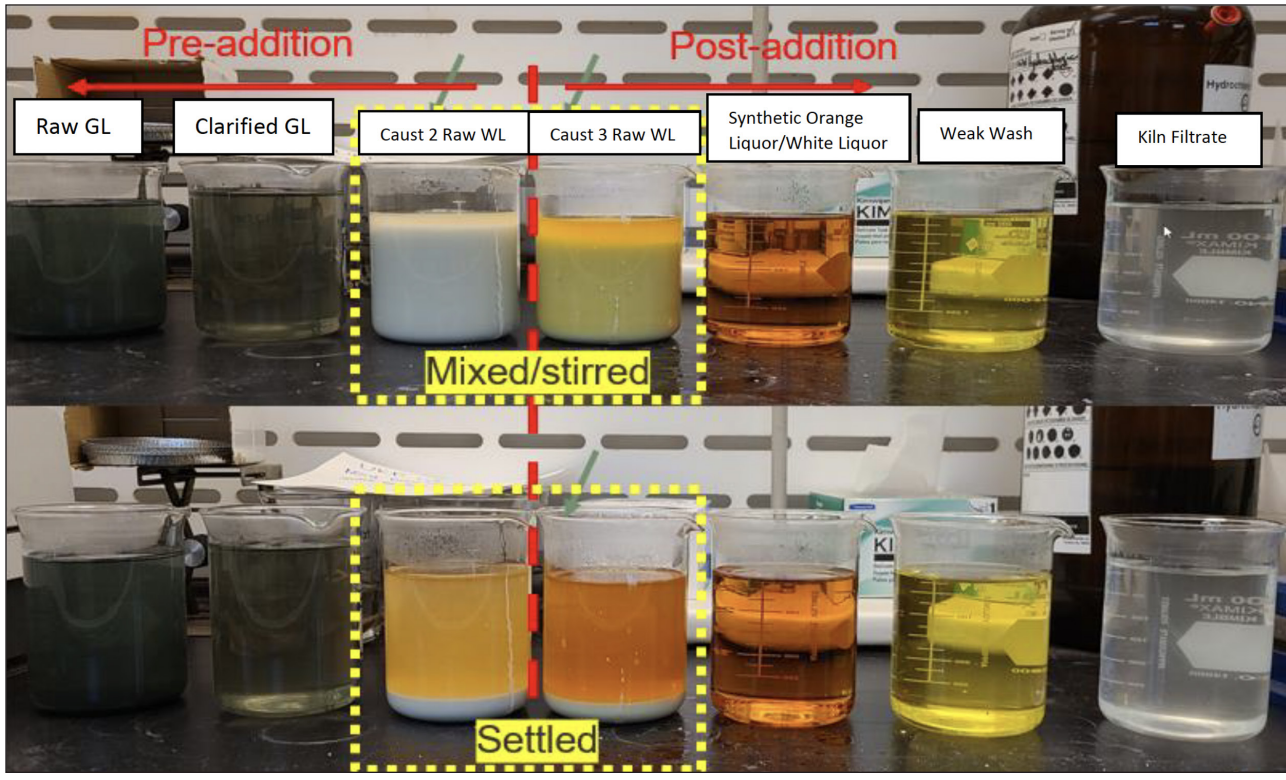


10. Lime mud properties from October 2021 up to trial in May 2022 (Na_2O: sodium oxide).

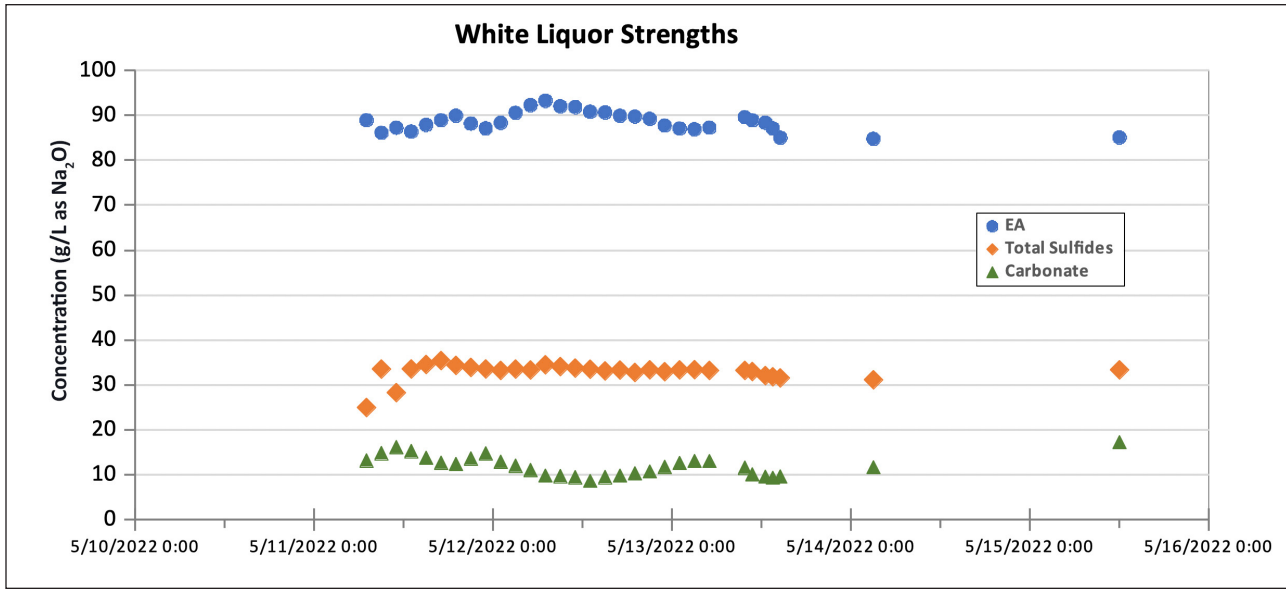
cause any negative impacts to immediate downstream processes, specifically the pressure filters and the kiln.

Sodium sesquisulfate addition was stopped 18 h prior to sulfur addition, and the mill was slowed back to half rate. The mill was slowed back because the transition to unbleached kraft pulp also came with shutting down one of the production lines. Sulfur was purchased in 25 kg bags and dumped into the 3rd causticizer tank (**Fig. 7**) at a predetermined interval to obtain ~ 2 g/L concentration of polysulfide, which was what was calculated to simulate mill sulfur demand in UKP operation.

There was no noticeable impact on recausticizing operations. In particular, the motor loads on the causticizer train agitators (downstream of the addition point) and pressure filter differential pressures (DP) did not change (**Fig. 8**). Furthermore, no impact was seen in lime kiln operation (**Fig. 9**), where there was a concern that TRS emissions would have increased if the sulfur was not dissolving and became re-entrained in the mud. The lime mud percent solids, sodium content, and free lime content averaged 74.7 wt%, 0.61 wt%, and 0.9 wt%, respectively, between October 2021 and May 2022, as shown in **Fig. 10**. During the trial, the average of these values were 72.4%, 0.6%, and 1.23%, respectively, all of which were within 1.2 standard devia-



11. Picture of recausticizing liquor during mill scale trial (GL: green liquor; WL: white liquor).



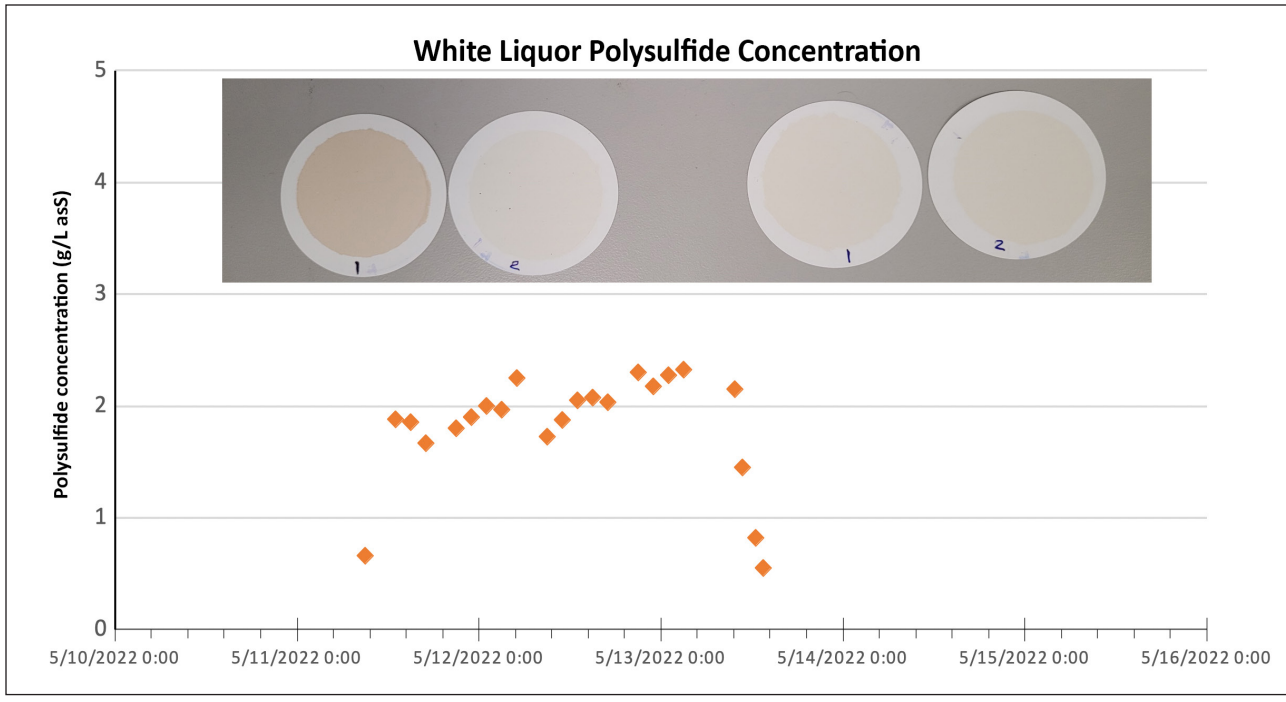
12. Chemical composition of white liquor during sulfur addition mill trial (EA: effective alkali; Na_2O: sodium oxide).

tions of the 1-year sample data, suggesting that there was no significant change in value.

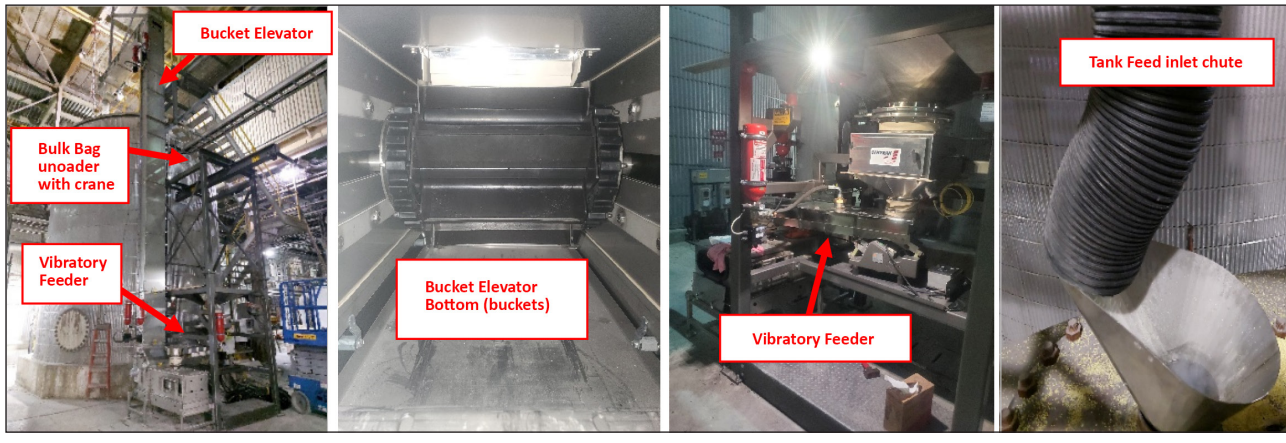
The color of the mud as seen from the precoat cloth also did not change. Lime (CaO) availability (CaO mass percent of lime discharged from kiln) was also unchanged, as the average was 93.0% vs. 93.3% during the trial. The discharged lime maintained regular node size and color.

The cooking liquor, however, changed significantly in color palette. Specifically, after the addition of pelletized sulfur, the white liquor changed from amber to dark orange in color, and the weak wash turned from colorless (similar to the color of kiln filtrate) to yellow due to the presence of polysulfide in these two liquors. The mud itself, however, did not change color, as shown in the picture of the settled mud (**Fig. 11**).

The EA, sulfides, and carbonate content in selected white liquors (**Fig. 12**) did not change during the trial and had normal values (EA 88 g/L; total sulfides 32 g/L; and



13. Polysulfide concentration, as measured gravimetrically, during the pelletized sulfur addition trial.



14. Sulfur addition system.

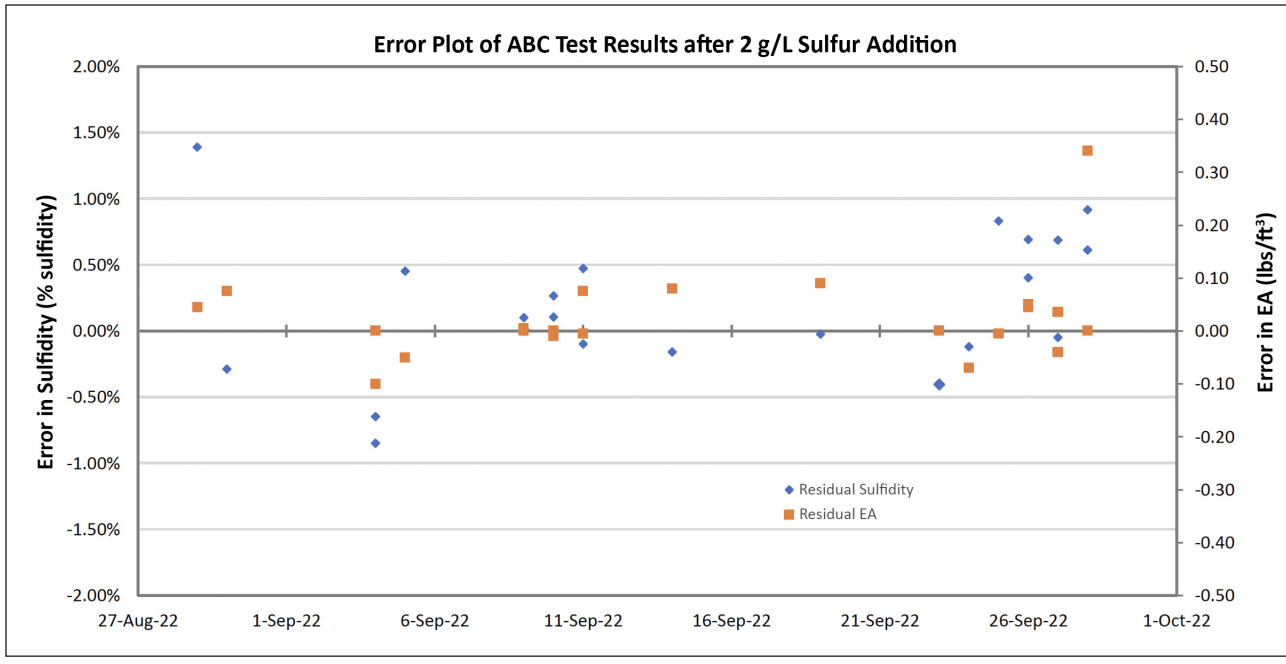
carbonate 13 g/L as Na_2O). Also, the sulfite and thiosulfate contents did not change (or slightly decreased) and had average values of 360 and 2770 ppm, respectively. However, the polysulfide content (**Fig. 13**) measured gravimetrically ranged from 0.2 to 3.1 g/L (average 2.1 g/L during sulfur addition and 0.3 g/L without sulfur addition). Inductively coupled plasma spectroscopy (ICP) was used to determine the composition of the precipitate obtained in the PSgrav analysis, as shown in the Fig. 13 image, and it was composed mainly of 83%–86% sulfur during prilled sulfur addition and 62% sulfur prior to the prilled sulfur addition trial. This suggested that normal mill white liquor (i.e., prior to prilled sulfur addition) contains 0.2–0.3 g/L polysulfide.

IMPLEMENTATION

Once MHI demonstrated the viability of the pelletized sulfur at mill scale, an engineered solution to dose pelletized sulfur was automatically developed.

Mechanical

Mondi Hinton Inc. found that the main driver in selecting equipment for use with solid sulfur was minimizing dust creation. While solid sulfur is not considered flammable, the dust created in handling of the pellets is. Therefore, MHI decided to use prilled sulfur instead of granular sulfur, which is made in a specific and consistent shape that allows easier handling and promotes less degradation/dusting. Sulfur dust has a relatively low ignition point, so the handling equipment must be gentle to prevent the creation of



15. Error plot of the sulfidity values after the addition of 2 g/L of sulfur into WL (EA: effective alkali).

this dust and also operate with low friction to prevent ignition of the dust. This eliminated selecting traditional handling equipment like screw conveyors due to the high friction and shearing zones. The mill decided to use a bucket elevator to feed the pellets into the 3rd causticizer, with the sulfur being metered into the bucket elevator by a vibratory feeder. This setup was in turn fed with sulfur via 1 metric ton bulk bags. Bags are unloaded into the vibratory feeder with a hoist that raises the bag above the feeder, allowing it to drain into the feeder as needed. All the equipment conforms to National Fire Protection Association (NFPA) regulations for explosive dust hazards. Mondi Hinton Inc. worked closely with the manufacturer of the equipment to ensure that regulations were met. The equipment had to be dust contained. Furthermore, valves were added on inlet and outlet to allow for isolation of equipment. Finally, the system was equipped with a fire suppression system to prevent personnel injury or damage to equipment in the event of an explosion. **Figure 14** shows the sulfur addition system installed at MHI.

At the time of this paper, the setup had been running relatively smoothly for approximately 22 months. The only issue MHI has found with operating this system is the metering of the material. It was found that the vibratory feeder is very sensitive to foreign material, especially water. Throughout the winter, the sulfur bulk bags were stored outside, and the snow that accumulated on the bags was melting when brought inside and making its way into the bag, which changed the flow characteristics of the material enough to plug the vibratory feeder. This was mitigated by using bag toppers and wrapping the sulfur bags. In addition, the sensitivity of the vibratory feeder has made it difficult to precisely meter material, and it is believed that a positive displacement feeder like a rotary valve would be a more reliable solution.

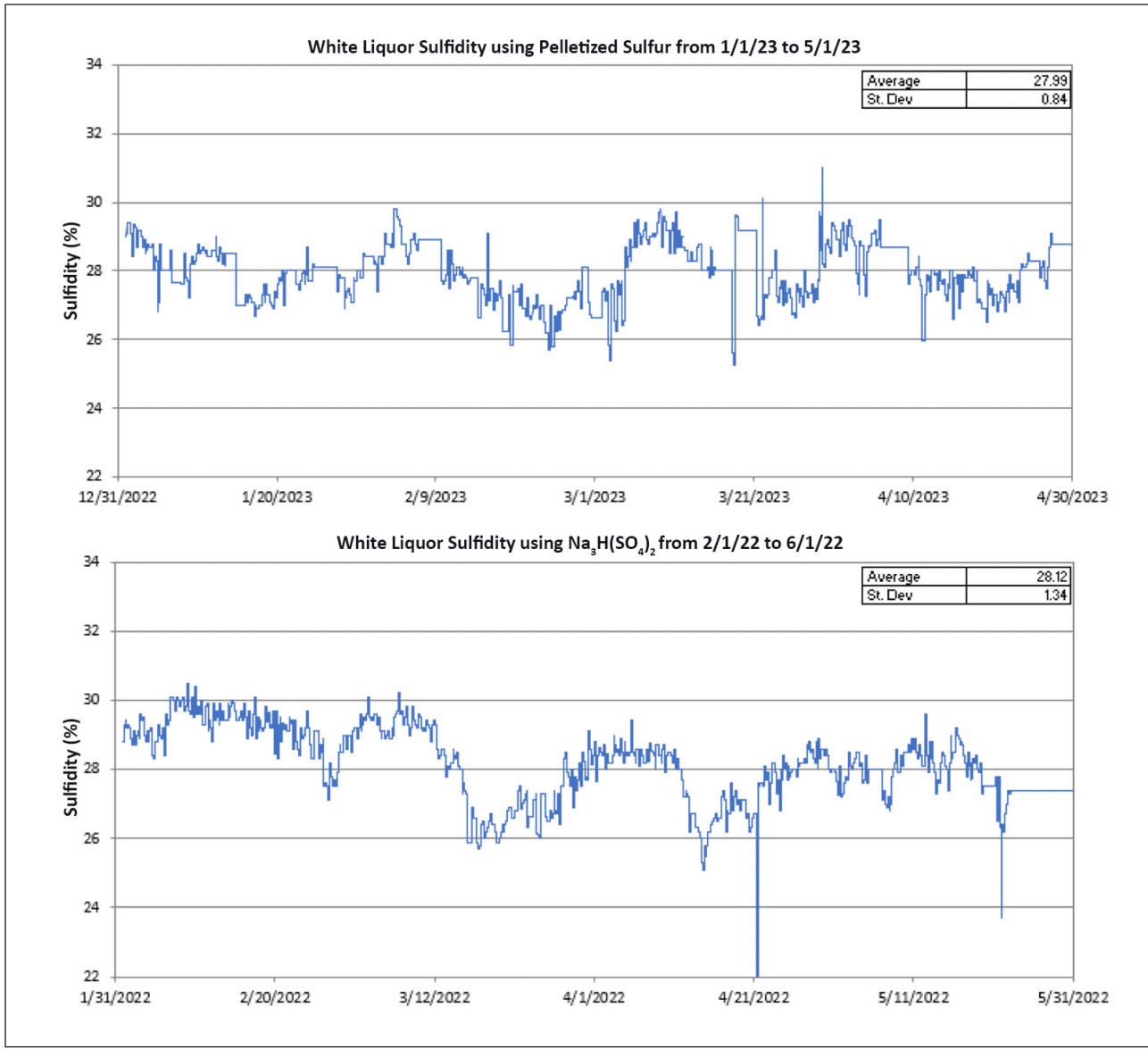
Controls

The overall control strategy at the mill for soda and sulfur makeup is as follows:

1. Dose NaOH for mill liquor inventory control into the WL storage tanks. This is an operational decision made once every day or two.
2. Dose sulfur for sulfidity control using a combination of:
   a. *Feedforward control:* calculating the amount of sulfur required to maintain sulfidity based on the NaOH added in Step 1.
   b. *Feedback bias*: biased up or down by the average sulfidity in the previous 24 h.

Feedforward control

Equation 1 can be used to determine the amount of sulfur required to achieve target sulfidity (care should be taken with unit conversion when performing calculation). However, this amount of calculated sulfur will likely not be enough to control sulfidity. This is because sulfur is not always lost to soda at this ratio, as not all losses in the recovery loop are through loss of liquor to the sewer/landfill [9]. Some losses occur through flue gases, namely from noncondensable gases (NCGs) in the form of TRS/SO_2 losses in the lime kiln and boilers. Since certain sulfur compounds are volatilized at lower temperatures than sodium compounds are, the calculated amount of sulfur required to maintain the target sulfidity will likely require a bias. At MHI, this bias is approximately 0.5 kg sulfur/air-dried metric ton of pulp. The boiler(s)/kiln emissions measurements



16. Sulfidity trend vs. time before and after sulfur addition ($Na_3H(SO_4)_2$: sodium sesquisulfate).

can be used in determining this offset. If electrostatic precipitator (ESP) ash saltcake is sewered from the recovery boiler, this will also have an offset effect. Mondi Hinton Inc. does not have this offset since it does not sewer ESP dust.

Feedback bias

During unsteady state mill operation or coming out of major upset events, it is quite possible that the sulfidity values are not in the desired range, and thus the feedforward control needs to be biased by feeding back the error between the setpoint and the present value of the sulfidity. However, the sulfidity measurement using the ABC titration tests does not have the ability to measure polysulfide content in the WL and potentially throws off the sulfidity result. Furthermore, the hydrosulfide ions generated from the hydrolysis of Na_2S in white liquor would be consumed in the reaction that produces polysulfide, meaning that the sulfidity, even if accurate, will not account for the polysulfide in the liquor.

Data was gathered to determine how much impact/offset might be required (from a sulfidity result that came from an ABC titration test result) to determine a new sulfidity setpoint for maintaining the same Na:S molar ratio in the white liquor. Over a period of 2 months, operators who performed regular ABC tests would occasionally perform a trial test. In this test, the WL would be tested twice using the regular ABC titration test and then repeated twice again after the addition to have an equivalent of 2 g/L concentration. The test results before addition were compared to the test results after the addition. It was found that the average value of EA and sulfidity both increased by 0.03 lb/ft^3 and 0.18%, respectively. This is a discrepancy of less than 2%

Parameter	Units	Pre-UKP Average (8 samples) Aug 22–Sept 22	Post UKP Average (7 samples) Oct 22–Nov 22	% Difference
EA	g/L as Na_2O	83.59	87.67	+4.89%
AA	g/L as Na_2O	100.66	104.94	+4.25%
TTA	g/L as Na_2O	115.88	120.86	+4.30%
Na_2CO_3	g/L as Na_2O	15.18	15.68	+3.29%
NaOH	g/L as Na_2O	66.60	64.24	-3.55%
Na_2S	g/L as Na_2O	32.73	31.69	-3.17%
Na_2SO_4	g/L	6.33	5.63	-11.01%
Na_2SO_3	g/L	1.64	0.11	-93.22%
$Na_2S_2O_3$	g/L	3.58	9.10	+154.01%
PS	g/L as S	0.61	1.16	+90.16%
Total Na	mg/kg	82837	82400	-0.53%
Total S	mg/kg	19.18	19.68	+2.65%

UKP: unbleached kraft pulp; EA: effective alkali; AA: active alkali; TTA: total titratable alkali; Na_2CO_3: sodium carbonate; NaOH: sodium hydroxide; Na_2S: sodium sulfide; Na_2SO_4: sodium sulfate; Na_2SO_3: sodium sulfite; $Na_2S_2O_3$: sodium thiosulfate; PS: polysulfide; Na: sodium; S: sulfur.

IV. White liquor properties before and after sulfur addition started.

each and thus negligible. An error plot (**Fig. 15**) with time showed the distribution of the error was random as a function of time; this plot was done to look for correlation with shift change and thus testing method.

The residual plot showed no correlation. It appeared that the ABC test results were picking up the presence of polysulfide, because if it were not, the sulfidity would have dropped. It is not clear how or why this was occurring; however, the data showed that the sulfidity value was very similar before and after addition. For this reason, the mill decided to continuously use the ABC test results after the implementation of sulfur addition as a measure of Na:S ratio.

FINAL MILL RESULTS

At the time of writing this paper, the mill had been using pelletized sulfur and caustic soda makeup for 11 months. Operating parameters have been monitored to ensure sulfur suitability.

Process control

Using the method explained previously, the mill has achieved its target sulfidity. During a relatively normal operating 5-month window, the average and standard deviation of sulfidity had been 28.0% and 0.84%, respectively, vs. 28.1% and 1.3% under the previous operating regime, as shown in **Fig 16**. The previous regime was when $Na_3H(SO_4)_2$ was used as makeup rather than pelletized sulfur. These are similar values, thereby confirming the validity of this sulfur makeup approach. It is expected that the sulfidity variability will decrease, as MHI is still optimizing the sulfur dosing system and working through issues that were noted in the mechanical implementation section.

Recaustisizing process and WL quality impact

As noted previously, recausticizing and kiln operation were not impacted. Laboratory test results relating to lime mud filter operation after the addition of sulfur show the lime mud solids, %Na_2O, and free lime content (14 samples) were 73.4 %wt, 0.57 %wt, and 1.13 %wt, respectively, compared to 74.7 %wt, 0.61 %wt, and 0.9 %wt for the previous 16 test results. Compared with the same period, it was found that the lime availability went up from 93% to 96% (even though lime mud reclaiming was occurring concurrently). None of these results suggest a change in recausticizing or kiln operation. When the causticizer was opened during the turnaround 8 months after the addition of sulfur started, there was no residual sulfur found. No anomalous scaling was found in the recausticizing plant or digester that could be traced back to sulfur addition.

The WL quality and properties were not much affected by shifting from $Na_3H(SO_4)_2$ to elemental sulfur and sodium hydroxide as the sulfur and sodium makeup chemicals (**Table IV**). However, it appears that polysulfides get partially oxidized to thiosulfate. Furthermore, the sulfite and sulfate content of WL appear to be reduced. Further testing needs to be done to confirm that the thiosulfate concentration is appearing after the addition of sulfur and the creation of polysulfide, and that it is not coming from

Parameter	Units	Pre-UKP (7 samples) Aug 22–Sept 22	Post UKP (10 samples) March 23–April 23	% Difference
Solids	% solids	70.87	71.38	+0.7%
Calorific value	**Btu/lb, o.d. basis**	5819	5766	-0.9%
Sulfur	**% on o.d. basis**	5.33	5.52	+3.5%
Chloride	% on o.d. basis	0.31	0.11	-65.2%
Carbon	% on o.d. basis	33.17	32.44	-2.2%
Hydrogen	% on o.d. basis	3.76	3.32	-11.7%
Nitrogen	% on o.d. basis	0.10	0.10	0.0%
Oxygen	% on o.d. basis	37.11	36.02	-2.9%
Sulfate	% on o.d. basis as Na_2SO_4	8.65	7.66	-11.5%
Carbonate	% on o.d. basis as Na_2CO_3	9.15	9.24	+1.0%
Sulfite	% on o.d. basis as Na_2SO_3	0.13	0.14	+8.9%
Thiosulfate	% on o.d. basis as $Na_2S_2O_3$	2.65	2.74	+3.4%
Organic/inorganic ratio		1.67	1.60	-4.0%
Effective alkali	g/L as Na_2O	5.86	5.79	-1.2%
Active alkali	g/L as Na_2O	8.58	8.91	+3.9%
Potassium, K	mg/kg, o.d. basis	17157	14700	-14.3%
Sodium, Na	**mg/kg, o.d. basis**	**209285**	**207500**	**-0.9%**
Tall oil content	% o.d. basis	1.24	0.68	-45.7%

UKP: unbleached kraft pulp; o.d.: ovendry; Na_2SO_4: sodium sulfate; Na_2CO_3: sodium carbonate; Na_2SO_3: sodium sulfite; Na_2O: sodium oxide.

V. Heavy black liquor properties before and after sulfur addition started.

the upstream green liquor, which would suggest its increase is due the lower reduction efficiencies in the recovery boiler. If the increase in thiosulfate concentration occurs after the addition of sulfur, this may be due to the retention time of WL in storage before it is pumped to the digester. White liquor is usually stored at ~180 °F, and according to Olsson and Samuelson [10], at this temperature and given sufficient time, polysulfide may degrade into thiosulfate, especially in the presence of oxygen.

A possible solution to this problem would be to store the WL under nitrogen blanketing. Sodium thiosulfate contributes significantly to the deadload of chemicals in kraft liquor that must be processed around the liquor loop and the digester, thereby increasing energy consumption. A mill's production capacity may also be impacted if its bottleneck is in the liquor loop. Furthermore, thiosulfate, like polysulfide, may be a concern with respect to digester metallurgy. For MHI, the chemical cost, process simplicity, and chemical supply security outweighed the deadload impact. Also, metallurgy showed no signs of irregular damage in the digester, as discussed in a subsequent section.

Recovery boiler process and HBL quality impact

The HBL was analyzed (**Table V**) to determine if the added sulfur: (a) reduced organic loading to the recovery boiler due to higher polysulfide concentrations in WL, improving the digester yield; and/or (b) reduced the elemental sulfur and sodium content, as the addition point of both soda and sulfur is upstream of the previous location in relation to the recovery boiler. These potential changes may have an impact on the bed conditions of the recovery boiler, which MHI was already struggling with, even though the mill operated at a hearth heat release rate (HHRR) of ~0.9 MMBtu/ft²/h during normal operation, which is lower than typical new recovery boilers at

>1.1 MMBtu/ft²/h. In particular, MHI was concerned that the lower heating value may require air/liquor distribution to be adjusted to manage bed level due to less available heat from the liquor per mass unit. Furthermore, TRS and/or SO_2 emissions may be increased due to lower bed temperature. A reduction in sulfide content of the smelt would increase the viscosity of the bed, which may cause the spouts to plug off more easily and impact bed flowability.

The black liquor heating value did slightly go down; however, the change was hard to ascribe to polysulfide content. This is because in the transition to UKP, pulp yield improvement was expected due to a higher kappa leaving the brownstock area, and thus less organic content would end up in the black liquor. Pulp yield improvement is generally considered good, unless it impacts operability of the recovery boiler. It is especially valued in the case of a recovery limited mill (which MHI is). Furthermore, soap is not fired into the boiler under the new UKP operation, which also reduces the heating value of the HBL. The yield improvement due to polysulfide was expected to be too low in magnitude to measure/realize, as the polysulfide concentration was low at between 1–2 g/L.

The elemental analysis of the liquor showed no significant change in comparison to pre-UKP, including sulfur content. This is surprising, as most of the sulfur loss in a pulp mill is expected to be lost through the brownstock area. Before UKP, the mill added its sulfur downstream of brownstock, and post UKP, the addition was after brownstock.

Overall, it appeared the recovery boiler bed was not impacted by the sulfur addition. No change was noticed in emissions and/or flue gas path pluggage. The heating value of the liquor dropped by 50–100 Btu/lb, which may have caused minor bed management issues, but these were resolved promptly once the liquor spray pattern and air distribution were adjusted. The mill did not take reduction efficiency tests before and after, so this impact has yet to be determined. However, operationally, the consensus is that sulfur addition has had no significant impact on recovery boiler operation.

IMPACT ON CORROSION

High concentrations of polysulfide and thiosulfate in pulp mill liquors can impact corrosion dynamics in vessels made of carbon steel [11]. Mondi Hinton Inc. reviewed the metallurgy of the recausticizing plant and digester area to determine potential locations and vessels that would have a higher risk of corrosion. It was assumed that due to the retention time in the digester and the addition point of the WL in the digester area, the polysulfide would be fully reacted and consumed by the time it was extracted in the wash zone and/or pulp was extracted at the blowline. About 20% of the white liquor is added to the MC zone of the digester, and there are approximately 180 to 240 min before the pulp will be at the wash screens ready to be extracted and 45–60 min before the pulp is out the blowline. The temperature of the MC zone circulated liquor is 280°F–300°F and that of the wash zone extraction liquor is 250°F–270°F, meaning the temperature the liquor and polysulfide see, at minimum for 180 min, is 250°F as they move through the MC zone down to the wash zone. According to experiments carried out by Olsson and Samuelson, at a concentration of 2 g/L of polysulfide, this decomposed within 60 min, even when cooking temperatures were less than 250°F [10]. Taking this into account, the assumption of little-to-no polysulfide leaving the digester was made. Furthermore, although the wash zone of the digester is made of carbon steel and had the lowest residual in the digester, it was theorized that the risk of corrosion was still low for the same reasons. Still, the bottom circulation (BC) zone (carbon steel, high residual) and wash zone (carbon steel, low residual) were the main risk areas for the mill, and thus required more frequent monitoring during annual turnarounds. In recausticizing, all the vessels other than the weak wash polisher were stainless steel; therefore, risk was considered minimal there.

Results from the annual turnaround in June 2023 came back positive, as there was no change in metal thickness in any sections of the digester, including the tested wash zone. Eight months of runtime may not be enough to show a change following addition of sulfur makeup; however, the tests to date suggests that no significant accelerated corrosion occurs.

Further laboratory testing is being performed to compare corrosion dynamics of the wash zone extracted liquor from before and after addition of polysulfides.

CONCLUSION

Mondi Hinton Inc. found that pelletized/molten sulfur was determined to be the best option based on a set of criteria specific to the Hinton mill priorities. Sulfur was the least expensive most abundant chemical that can be used to make up sulfur in the recovery loop in its conversion to UKP. Elemental sulfur also held the advantage of requiring a small system that would require low capital cost and less maintenance in comparison to Na_2SO_4, which is a typical sulfur makeup source in kraft pulp mills. Pelletized sulfur was confirmed to dissolve into white liquor within 12 min at operating temperatures of the causticizers. Almost all the sulfur converted into polysulfide, as confirmed in laboratory- and mill-scale trials. When pelletized sulfur addition was implemented at the pulp mill, it was found that this polysulfide may partially decompose into thiosulfate, which is a chemical that does not participate in cooking. The thiosulfate and polysulfide did not seem to impact corrosion dynamics at MHI in the first 8 months of addition, as the carbon steel sections of the digester BC zone and wash zone showed no change in thickness. During the turnaround, it was also found that no residue or scaling was found in the recausticizing plant or digester that can

be traced back to the sulfur addition. Finally, recausticizing, kiln, and recovery boiler operators have not noticed a noticeable change in operability of equipment.

For the future, MHI would consider using molten sulfur, as it is cheaper than pelletized sulfur and would require virtually no operator intervention. This is because instead of coming in 1 metric ton tote bags that require reloading of bags numerous times per shift, an operator would simply have to unload a truck once every week or two. The feed would be controlled by a pump on a variable frequency drive (VFD), and thus would have minimal components. Also, this would remove any combustible dust hazard. Furthermore, MHI would consider adding the sulfur into the WL storages to minimize any time the polysulfide has to degrade, which may provide a yield benefit and offload the recovery boiler, leading to a higher production rate at the mill. Finally, it is paramount for MHI to continue to strive to close the liquor loop and minimize soda losses. Caustic soda cost for the mill is still significant, and thus a high priority, so perhaps a similar review of different soda makeup options would also be worthwhile.

Many pulp mills face challenges that make it increasingly hard to sustain profit margins. Whether it be aging assets and poor reliability, rising chemical costs, lower pulp prices, or younger/newer workforce, it is increasingly important for pulp mills to look for opportunities to reduce chemical costs and optimize operations. Ultimately, it is recommended for mills to review their soda/sulfur makeup methods and cost per metric ton of pulp, especially coming out of shutdowns. Depending on this cost, consider pelletized sulfur as a makeup method. The cost buying a sulfur makeup chemical or struggling to control the sodium and sulfur balance in their process, they can evaluate pelletized sulfur as an option.

For MHI, the next step is to monitor the process and its impact, especially on corrosion of carbon steel in the digester. We will also optimize the system by improving on equipment used and automation of sulfur addition. Finally, we plan to leverage the process by increasing the production of polysulfide. This can improve yield in the digester and thus production and financial viability of the mill.

ABOUT THIS PAPER

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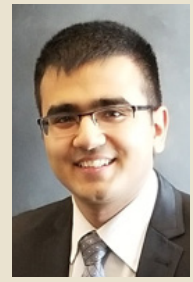
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dynamics will highly depend on the location of the mill and industries in its vicinity. Also, consider that molten and pelletized sulfur are directly or indirectly a feedstock/raw material for most, if not all, the makeup chemicals/compounds that mills typically consider for sulfur makeup. **TJ**

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