

Implementation of an Inexpensive and Effective Alternative Sulphur Makeup Source in an Unbleached Kraft Pulp Mill: Pelletized Sulphur

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ABSTRACT

Sodium sesquisulphate or “sesqui” ($\text{Na}_3\text{H}(\text{SO}_4)_2$) is a by-product of chlorine dioxide production at kraft pulp mills. It is typically used for sodium and sulphur make-up in the liquor loop. Hinton Pulp (HIP) was being converted from bleached to unbleached kraft pulp production and thus was losing this source of make-up. The only option that was readily available as a substitute was sodium hydrosulphide (NaHS), which was cost prohibitive. Other options such as sodium sulphate (Na_2SO_4), emulsified sulphur, sulphuric acid (H_2SO_4) and sodium bisulphite (NaHSO_3) were compared. HIP concluded that pelletized sulphur plus sodium hydroxide or “caustic soda” (NaOH) was the best option.

Lab-scale experiments showed that pelletized sulphur dissolved in white liquor (WL). A mill-scale trial revealed that pelletized sulphur added to a causticizer had no adverse impacts on the downstream pressure filters or kiln operation. The sulphur reacted to produce polysulphide upstream of the WL storage tank giving the liquor an orange hue. This polysulphide appeared to degrade partially into thiosulphate before being fed to the digester. The heavy black liquor (HBL) S:Na ratio did not change significantly even though the sulphur/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 polysulphide/thiosulphate concentration in the white liquor it was determined that the carbon steel equipment were at risk for corrosion. During the annual turnaround 8 months following the addition of sulphur was started the wash zone of the digester showed no signs of thinning/damage.

The mill has been running exclusively with pelletized sulphur for 11 months (as of September 2023), realizing significant cost savings compared to the use of NaHS or other sulphur/soda addition options.

INTRODUCTION

Background

Prior to 2022 Hinton Pulp (HIP) 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 sulphur and soda loss inherent to the process was going to be made up in the liquor loop with no sodium sesquisulphate or “sesqui” ($\text{Na}_3\text{H}(\text{SO}_4)_2$) available from the discontinued chlorine dioxide production process. The mill’s immediate option to makeup soda and sulphur was “synthetic white liquor” (SWL) which uses sodium hydrosulphide (NaHS) and sodium hydroxide (NaOH). This approach was extremely costly and would negate $\sim 2/3$ of the cost savings expected by the elimination of the bleaching process. Therefore, there was a need to explore different options.

Importance of Sodium and Sulphur Makeup

In kraft pulping, wood chips are cooked in a digester vessel at high temperatures and pressures with white liquor. White liquor is an aqueous solution comprised mainly of sodium hydroxide (NaOH), sodium sulphide (Na_2S), and lower concentrations of sodium carbonate (Na_2CO_3), sodium sulphate (Na_2SO_4) and other sodium salts. In the digester hydroxyl ions (OH^-) participate in several complex delignification reactions. The sulphide (which hydrolyzes into hydrosulphide ion (HS^-) in solution improves the selectivity for the delignification reactions in the digester. 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, and mill performance parameters such as wood to pulp yield. Therefore, sodium (counter cations of anions like hydroxyl that participate in cooking reactions) and sulphide (participates in cooking reactions) are required in the liquor. The ratio between sodium and sulphur is very important to control and is defined typically by sulphidity. There are numerous definitions of sulphidity however for this purpose of this paper equation 1 will be used to define sulphidity in white liquor.

$$\text{Sulphidity (\%)} = \frac{\text{Na}_2\text{S} \left(\frac{\text{lb Na}_2\text{O}}{\text{ft}^3} \right)}{\text{Na}_2\text{S} \left(\frac{\text{lb Na}_2\text{O}}{\text{ft}^3} \right) + \text{NaOH} \left(\frac{\text{lb Na}_2\text{O}}{\text{ft}^3} \right) + \text{Na}_2\text{CO}_3 \left(\frac{\text{lb Na}_2\text{O}}{\text{ft}^3} \right)} \quad \text{Equation 1}$$

HIP targets 28-29% sulphidity. Low sulphidity liquor results in poor pulp quality, lower delignification rate, and lower pulp yield, all of which significantly impact the mills profit margin. Furthermore, low sulphidity 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 which “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].

Elevated sulphidity leads to higher total reduced sulphur (TRS) and sulphur dioxide (SO_2) emissions 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 (eg. 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 – 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 sulphur must be made up to maintain liquor inventory and control sulphidity. Typical soda/sulphur makeup in pulp mills comes from purchased saltcake (Na_2SO_4), purchased NaOH and/or sesquisulphate (byproduct from the chlorine dioxide generator).

PROCESS DESCRIPTION

Figure 1 depicts the general recovery loop process layout at Hinton Pulp. The pulp mill is located in Hinton, Alberta, Canada, producing kraft pulp principally from lodgepole pine. Once chips are screened, they are steamed and impregnated with white liquor (WL). The impregnated chips are sent to a 1989 Kamyr down-flow 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 28-32 kappa number and 0.6-0.8 lb Na₂O/ft³ wash extraction residual alkali.

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 (O₂) delignification, bleach plant, and chlorine dioxide (ClO₂) production. A byproduct ClO₂ production process was sodium sesquisulphate 30-50% of which was added back to the liquor loop in the WBL tank to control sulphidity.

Weak Black Liquor (WBL) from digester extraction and brownstock washing at around 15% solids is sent to five-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 one-Line UKP configuration.

After recovering boiler ash from 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 1 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) which 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 which dries the mud to ~75% before entering the lime kiln.

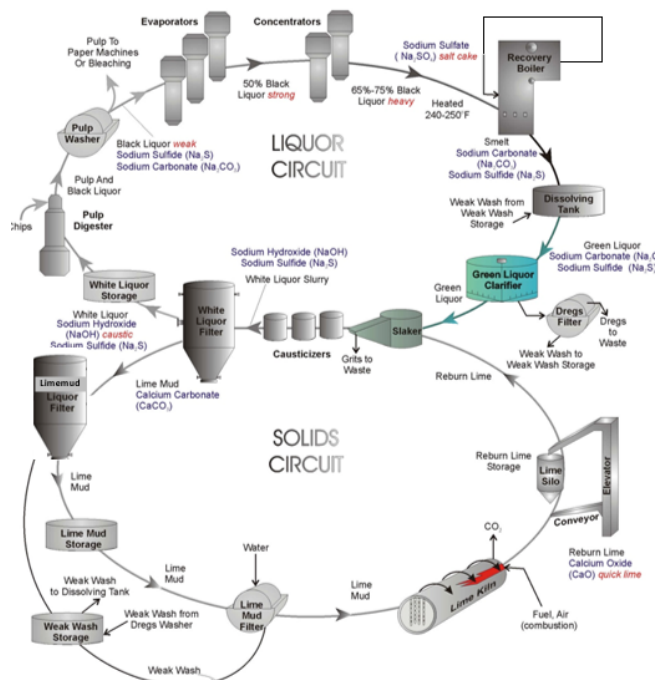


Figure 1 Schematic of kraft recovery process at Hinton Pulp

PROJECT DEVELOPMENT AND OPTION SELECTION

There are numerous chemicals that can be used for sodium and sulphur makeup in the liquor loop. After surveying various options, sodium hydrosulphide (NaHS), sulphuric acid (H_2SO_4), emulsified sulphur, sodium sulphate (Na_2SO_4), and elemental sulphur (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 assigned to determine most suitable option. Table 1 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 aspects. Sulphur in the form of pellets shown in Figure 2, introduced a combustible dust hazard that must be mitigated. However, at the addition rates required at HIP this hazard was not too concerning if the equipment design and procedures/training for operators were developed well. The combustible dust explosion hazard can be significantly reduced in the equipment design phase. Emulsified sulphur and molten sulphur scored better for safety as there is no combustible dust hazards. Na_2SO_4 introduces minimal hazards for process or occupational safety/health. H_2SO_4 and NaHS pose the highest safety risk due to the nature of the chemical being extremely corrosive. From an environmental point of view, the main concern with all the chemicals are spills to the ground/loss of containment. Therefore, the liquid chemicals pose the highest risk (likely requiring berms to mitigate spill concerns). The larger the volume required to be onsite the more chance for spill – which is an advantage of using pelletized and molten sulphur, as it would require the least volume to achieve sulphur makeup.

Chemical availability/transportation logistics (weighting factor of 3) Geography and surrounding industry will impact this category. In the Hinton area, pelletized sulphur and molten sulphur are abundant as a byproduct of oil and gas operations. Sulphuric acid, often produced by elemental sulphur, was also readily available to the mill. Emulsified sulphur, 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 which would be an issue in case of emergency orders.



Figure 2 Prilled elemental sulphur

Chemical cost (weighting factor of 5) The main consideration for this project outside of safety and environmental impact was cost. Pelletized sulphur (and caustic soda) was the cheapest option for Hinton Pulp, 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 sulphur requirement, this option 20-25% more expensive than the pelletized sulphur/caustic soda option. H_2SO_4 and emulsified sulphur (with caustic soda) were 10-15% more expensive than pelletized sulphur/caustic soda option. NaHS was 95-100% more expensive than pelletized sulphur/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 decision and allocation of capital. For HIP, the capital cost of a NaHS addition system was zero as the mill already had a system to makeup liquor using NaHS. A system

to for using H_2SO_4 would be relatively inexpensive, as modifications to an existing system would have been possible. Emulsified sulphur 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 sulphur would require similar equipment and thus capital to an emulsified sulphur system, with the addition of steam coils and heat traced piping (although no agitator in the tank is required). Na_2SO_4 and pelletized sulphur would require bulk solids handling systems. Due to layout of plant equipment, a Na_2SO_4 system would require an extensive blowing system to adequately reach a HBL mixing tank. Sulphur cannot be pneumatically blown due to 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 as one for elemental sulphur as the molar mass of Na_2SO_4 is much higher than that of sulphur therefore to achieve a specific sulphur 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 sulphur 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 sulphur scored well due to simplicity of a liquid-based system. One concern would be the molten sulphur freezing on loss of power/steam. This is not a major concern as the melting point of sulphur is $\sim 135^\circ\text{C}$ and thus would not require much energy/time to thaw. H_2SO_4 also scored well in this category, it may require makedown from 93% to 10% which already exists. 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. Na_2SO_4 and pelletized sulphur would require unloading and conveying bulk solids. Na_2SO_4 would require unloading of 40 tonne trucks, and use a combination of a silo, baghouse, blower system storage bin, and screw conveyor. Pelletized sulphur would use a bucket elevator/vibrating feeder being fed by one-tonne tote bags. 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 sulphur system would require frequent bag refilling by the operators. Overall, a pelletized sulphur system was rated higher than the Na_2SO_4 and NaHS but lower than Emulsified Sulphur and H_2SO_4 .

Process control and effectiveness (weighting factor of 4 each) Pelletized sulphur, emulsified sulphur, molten sulphur and NaHS would all be fed in the recausticizing plant thereby providing immediate feedback from the WL sulphidity tests done every four hours by operators via the ABC titration tests. For this reason, these chemicals would score the highest for their ability to control and maintain sulphidity. However, sulphur introduces process risks associated with polysulphide and thiosulphate formation which can have an impact on the corrosion of carbon steel equipment. H_2SO_4 and Na_2SO_4 would have a time lag between addition point and measurement therefore control suffers. Na_2SO_4 does not introduce too much process risk but does load the sulphur in the liquor loop right at the recovery boiler. If there is significant sulphur loss through the recovery boiler flue gases the WL Sulphidity may be lower than desired as opposed to having the sulphur added where it is typically most important, upstream of the digester. H_2SO_4 introduces risks of dropping the WBL pH resulting in lignin reprecipitation which can foul the evaporators and negatively impact performance, resulting in the lowest ranking for process effectiveness.

Table 1 Rating of chemicals against selection criteria

	Safety & Env.	Chem Avail.	Chem. Cost	Capital Cost	Maint. & Oper.	Process Effectiveness	Final Score
Molten S	40	27	45	10	32	28	182
Pelletized S	30	27	45	20	24	28	174
H_2SO_4	25	21	35	15	28	16	140
Emulsified S	40	9	35	10	32	32	158
Na_2SO_4	40	15	30	10	20	32	147
NaHS	15	9	5	25	12	20	86

Chemical Selection

Pelletized sulphur and molten sulphur (plus caustic soda) ended up with the highest selection rating. They were the cheapest makeup options beating out Emulsified Sulphur, H_2SO_4 and 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 sulphur option introduction of combustible dust explosion hazard, however after visiting a pelletized sulphur 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 HIP would have to convey, yet due to good engineering/operational practices this facility had not experienced any explosions in their operating history. These practices included: regular/scheduled cleanup, operator rounds/inspections, good equipment selection, dust-tight design, proper grounding, and installation of deflagration suppression systems. Furthermore, HIP 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 compared to the sulphur. Chemical availability was another major advantage of pelletized and molten sulphur as they were the most abundant forms of sulphur available to the mill. Although molten sulphur was more advantageous over the pelletized sulphur 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 sulphur. Due to the time constraints on this project, it was therefore decided that a pelletized sulphur system would be implemented as the short-term solution, and in the long-term a molten sulphur system would be considered.

Table 2 summarizes the pros and cons of each option. The main drawback of using pelletized sulphur was the lack of literature or mill references that used pelletized sulphur as their sole source of sulphur 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 sodium to sulphur Na:S ratio and other issues it may introduce to the kraft liquor loop. For this reason, this project required trials to prove out process before implementing. The mills backup solution if the trials failed would have been NaHS, and reevaluation of the other chemical options (Na₂SO₄ was likely the first runner up).

Table 2 Pros and cons of each chemical option and final rating based on selection criteria

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 ₂ SO ₄	Low capital cost, relatively low chemical cost	Risk of lignin reprecipitation/fouling evaps train	140
Emulsified S	Relatively low chemical cost	High capital cost, only one source nearby with large lead time	158
Na ₂ SO 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

TRIALS

Sulphur reacts with the sodium sulphide in white liquor to create sodium polysulphide as per the reaction below [6]:



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

- All the sulphur dissolves into WL
- Dissolved sulphur produced polysulphide
- No hydrogen sulphide (H_2S) production is induced
- No adverse impacts observed in the liquor cycle

Lab Scale Experiments

The first step in demonstrating that pelletized sulphur would be a viable solution for makeup sulphur was performing lab scale experiments to determine how the pelletized sulphur 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 sulphur (0 to 8 g/L) to 500 mL of mill's raw or clear white liquor to determine dissolving rate at three temperatures (150, 180, and 190 °F). At a given temperature, the dissolving rate was independent of the amount of sulfur added – it took ~12 minutes to completely dissolve the added sulphur at 180 °F (Table 3) which is sufficient time to completely dissolve in the causticizer. The temperature, however, did have an effect on dissolving rate – the dissolving time doubled when the temperature was decreased from 180 to 150 °F. A Ventis MX4 Gas Monitor was used to detect any H_2S emissions while dissolving sulphur in the white liquor – none was detected. Figure 3 shows the appearance of the liquors where a distinct color change from light to darker orange occurred, typically seen in polysulphide liquors, as the concentration of prilled sulphur increased.

Table 3 Dissolving rates of prilled sulphur in 500 mL of white liquor at different temperatures

Sulphur 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

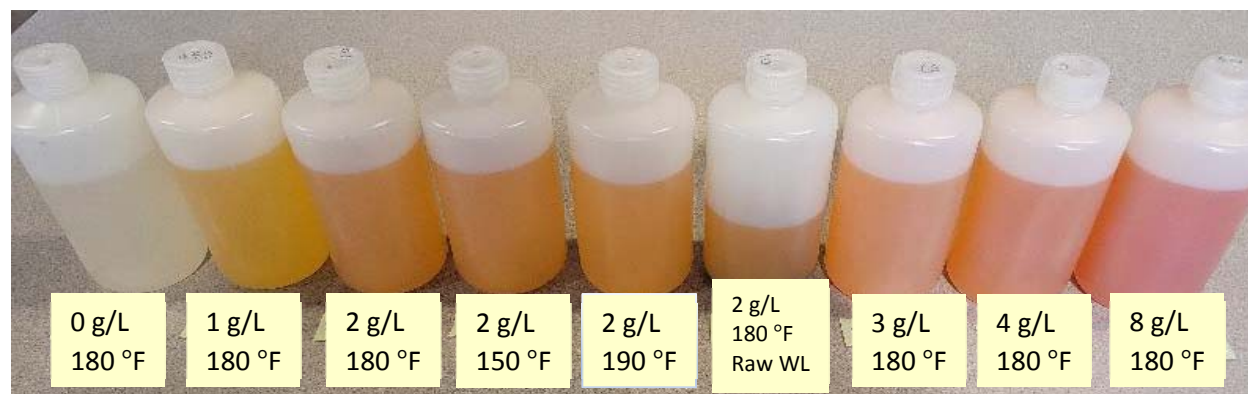


Figure 3 Photograph of liquors after completely dissolving different amounts of prilled sulphur.

In terms of liquor chemical composition, effective alkali and free sulphides (measured by a method developed by J.M. Dorris and V.C. Uloth [7]) did not change however, as expected, the bound sulphides and polysulphide measured gravimetrically [8] (denoted as PSgrav) increased. A plot of PSgrav vs prilled sulphur added showed a linear relationship ($r^2 = 0.995$) with a slope of 0.97 indicating that the sulphur added completely reacts to form polysulphide (Figure 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 sulphite and thiosulphate concentrations that increased (Figure 5 and 6), especially at high sulphur addition levels.

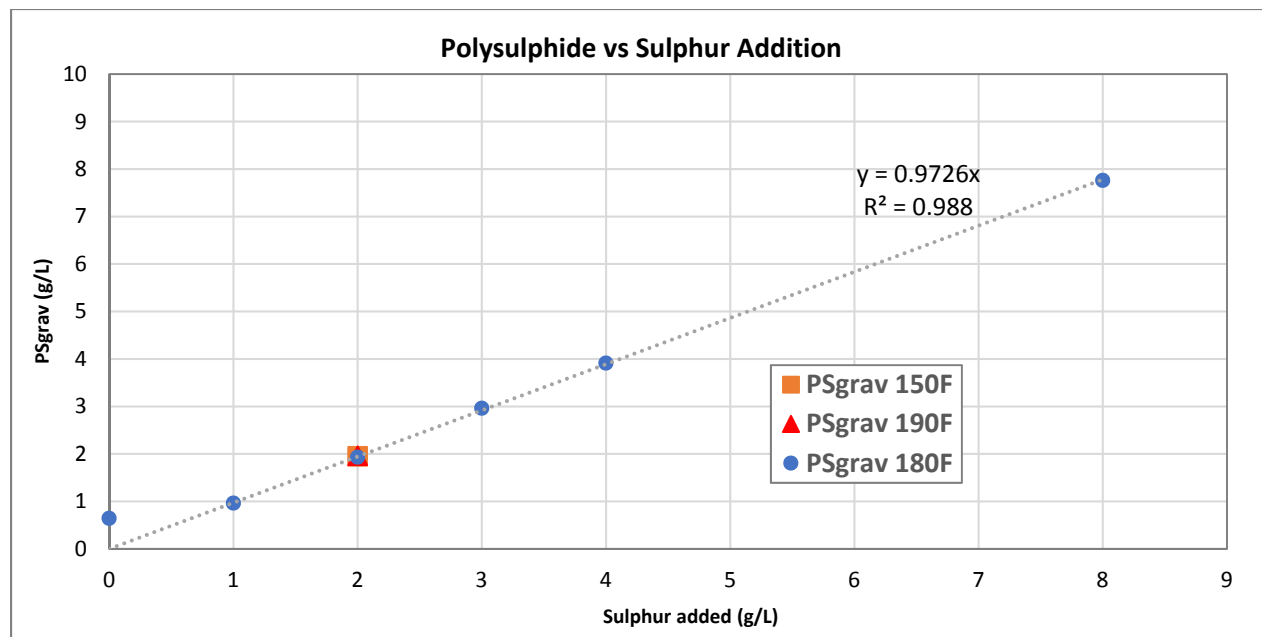


Figure 4 The amount of sulphur added reacts to form polysulphide (almost on 1:1 basis)

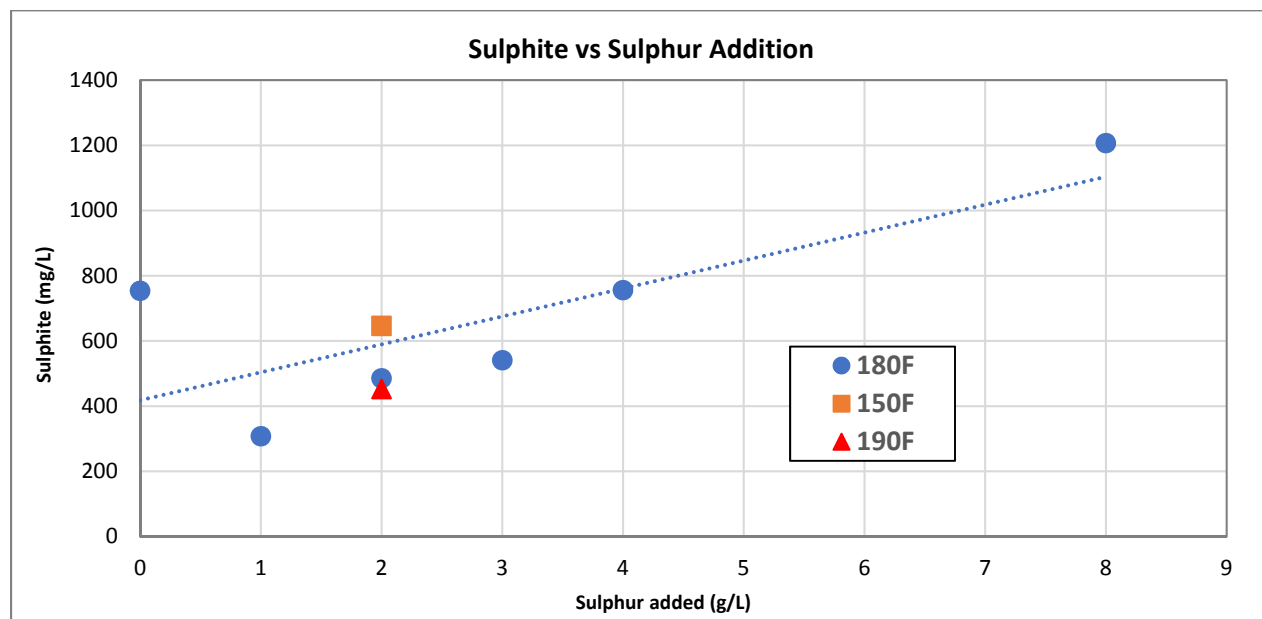


Figure 5 The sulphite concentration increased slightly as a result of partial sulphur oxidation

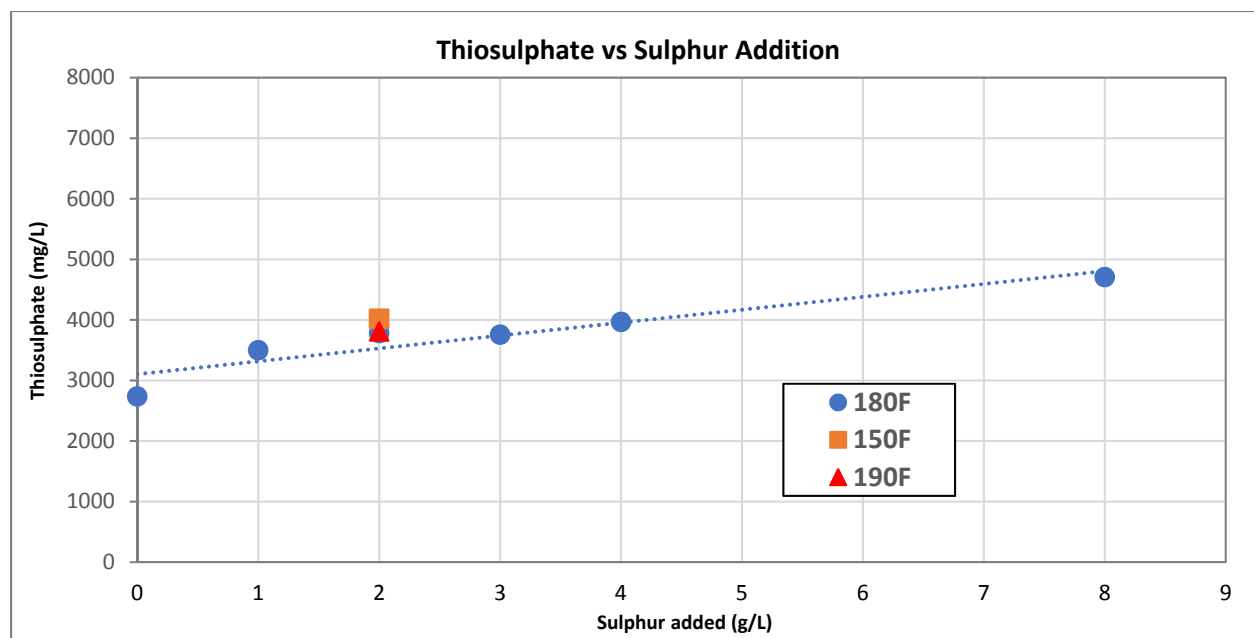


Figure 6 The thiosulphate concentration increased slightly as a result of partial sulphur oxidation

Mill Scale Trial

The next step was scaling up the lab trial to a mill scale trial. The purpose of this trial was to confirm that the pelletized sulphur dissolved into the white liquor and did not cause any negative impacts to immediate downstream processes specifically the pressure filters and the kiln.

Sodium sesquisulphate addition was stopped 18 hours prior to sulphur addition. Sulphur was purchased in 25 kg bags and dumped into the 3rd causticizer tank (Figure 7) at a predetermined interval to obtain ~ 2 g/l concentration of polysulphide which was what was calculated to simulate mill sulphur demand in UKP operation.

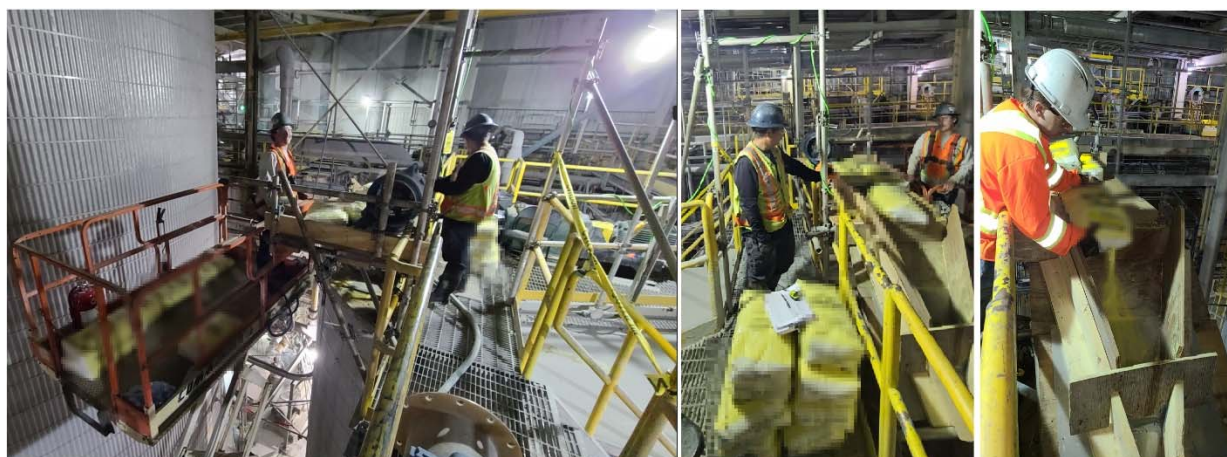


Figure 7 Pelletized Sulphur mill scale trial setup

There was no noticeable impact on recaust operations. Particularly, the motor loads on the causticizer train agitators (downstream of the addition point) and pressure filter differential pressures (DP) did not change (Figure 8). Furthermore, no impact was seen in lime kiln operation (Figure 9), where there was a concern that TRS emissions would have increased if the sulphur 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 (16 data points). During the trial the average of these values were 72.4%, 0.6% and 1.23% respectively, all of which are all were within 1.2 standard deviations 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 (since the average was 93.0% versus 93.3% during the trial). The discharged lime maintained regular node size and color.

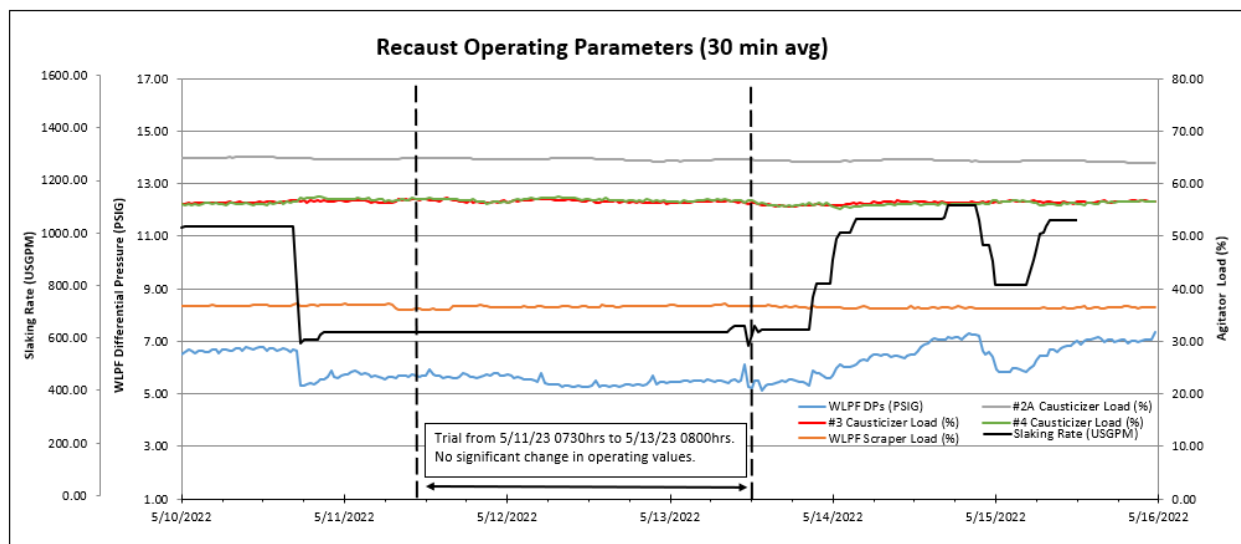


Figure 8 Recast operating parameters trends before, during and after mill scale trial

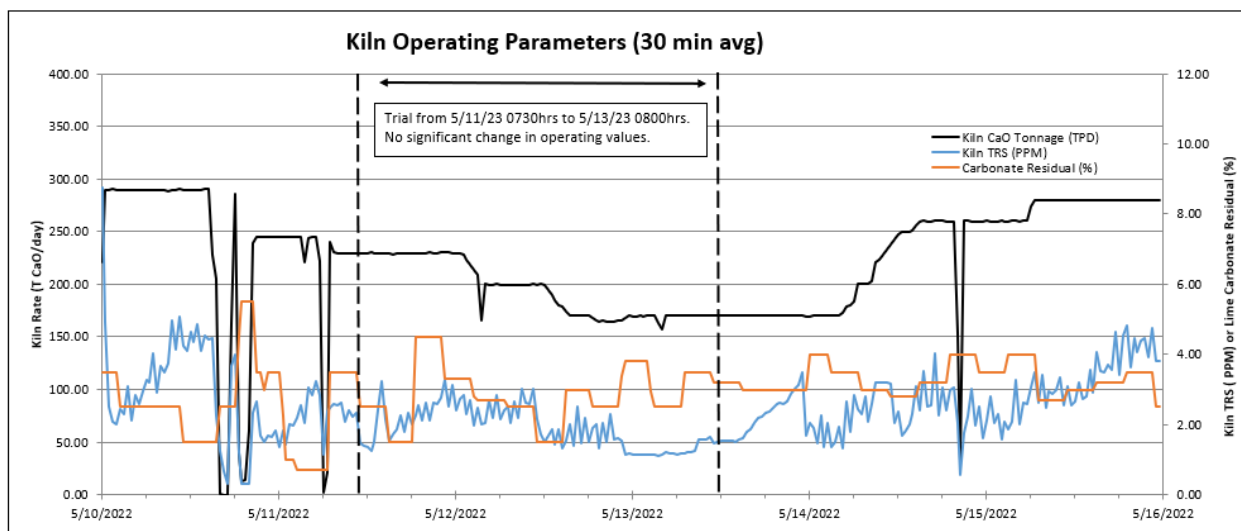


Figure 9 Kiln operating parameters trends before, during and after mill scale trial

The cooking liquor, however, changed significantly in color palette. Specifically, after the addition of pelletized sulphur the white liquor changed from an amber to dark orange in color, and the weak wash turned from colorless (similar to the color of kiln filtrate below) to yellow due to the presence of polysulphide in these two liquors. The mud itself, however, did not change color as shown in the picture of the settled mud (Figure 10).

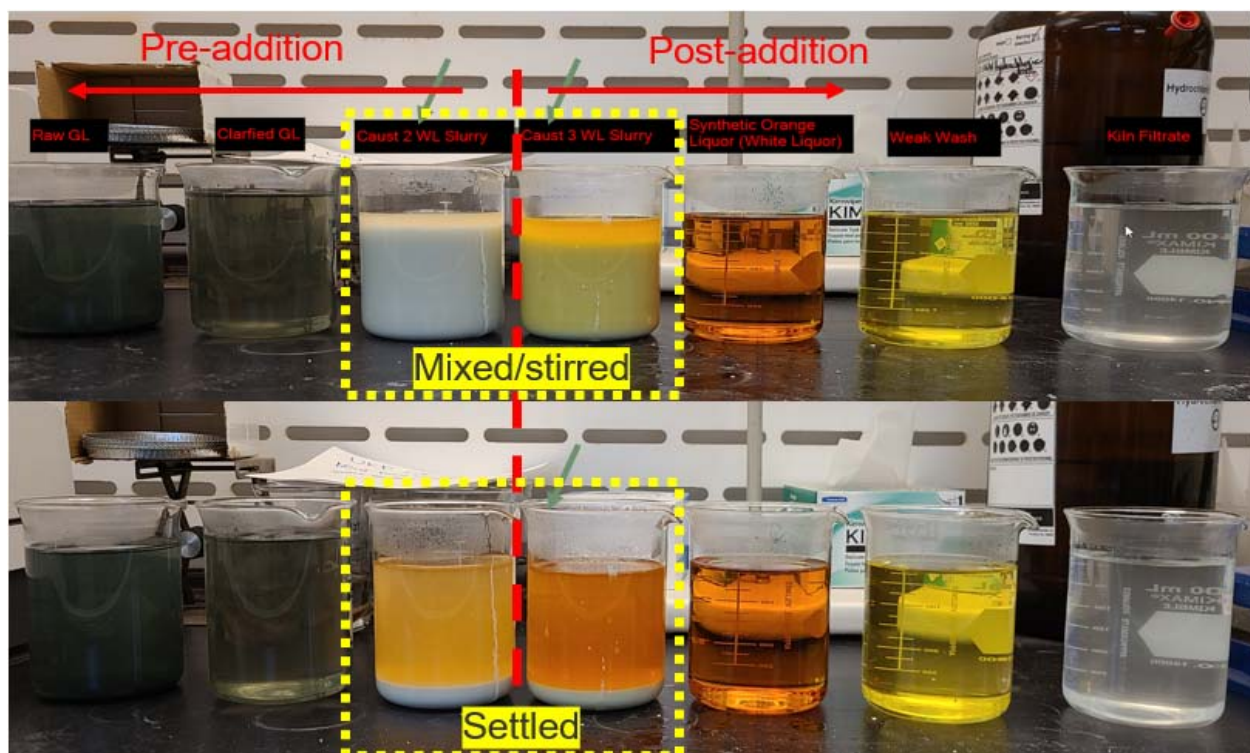


Figure 10 Picture of Recaust liquor during mill scale trial

The effective alkali (EA), sulphides, and carbonate content in selected white liquors (Figure 11) did not change during the trial and had normal values (EA 88 g/L; total sulphides 32 g/L and carbonate 13 g/L as Na_2O). Also, the sulphite and thiosulphate contents did not change (or slightly decreased), and had average values of 360 and 2770 ppm, respectively. However, the polysulphide content (Figure 11) measured gravimetrically ranged from 0.2 to 3.1 g/L (average 2.1 g/L during sulphur addition and 0.3 g/L without sulphur addition). Inductively coupled plasma spectroscopy (ICP) was used to determine the composition of the precipitate obtained in the polysulphide gravimetric (PSgrav) analysis (as shown in picture of Figure 12) – it was composed mainly of 83-86% sulphur during prilled sulphur addition and 62% sulphur prior to the prilled sulphur addition trial, suggesting that normal mill white liquor, i.e. prior to prilled sulphur addition contains 0.2-0.3 g/L polysulphide.

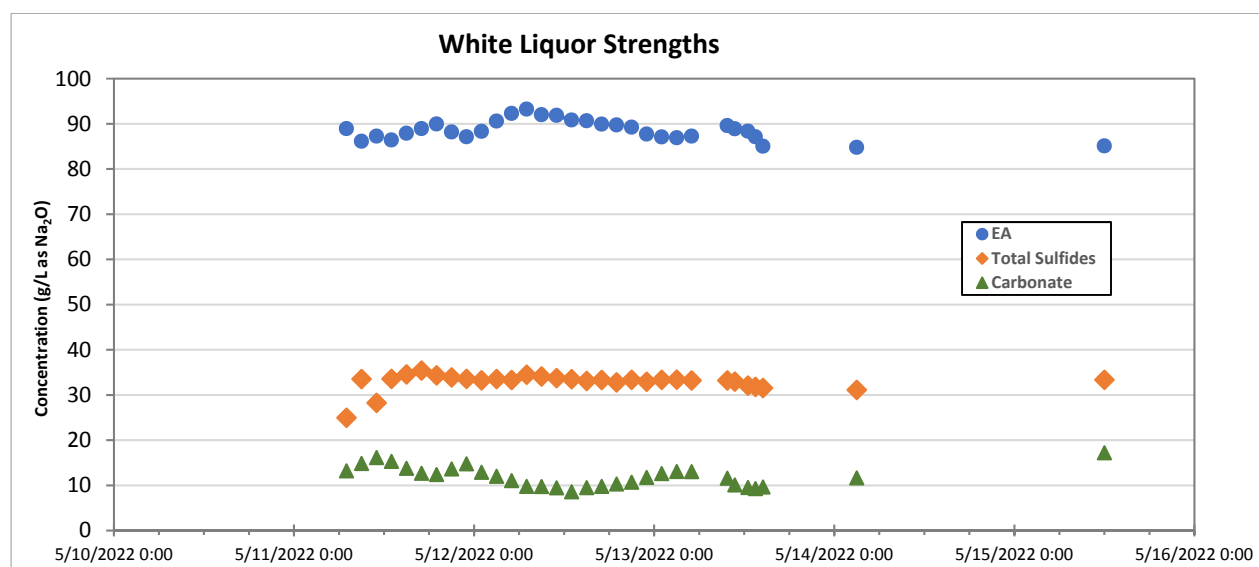


Figure 11 Chemical composition of white liquor during sulphur addition mill trial

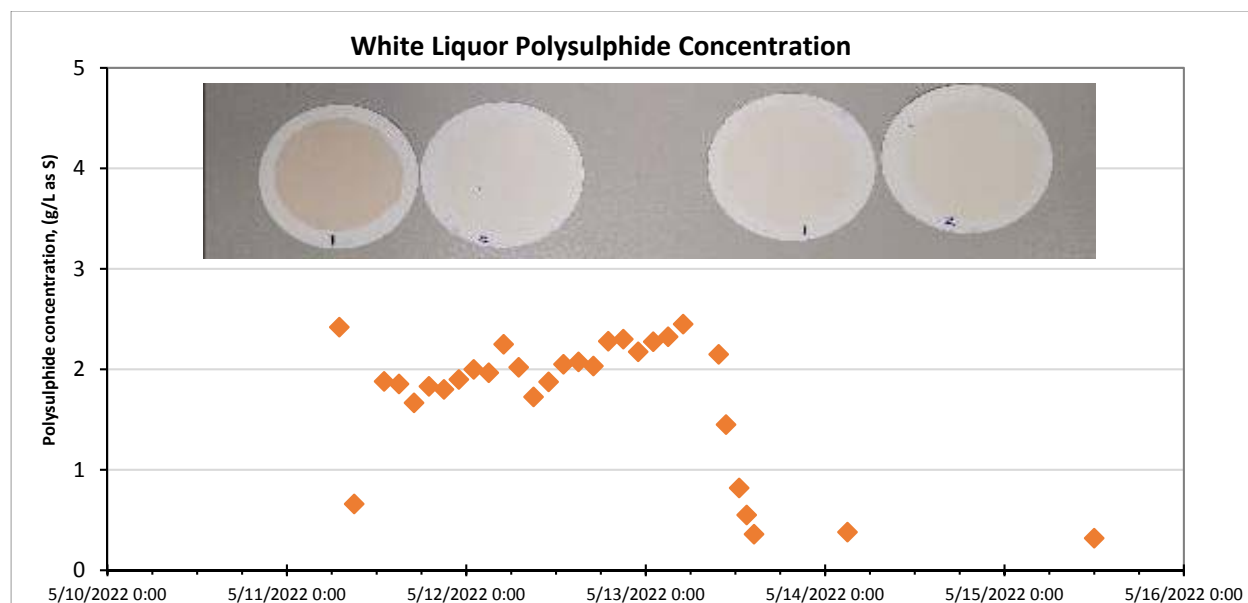


Figure 12 Polysulphide concentration, as measured gravimetrically, during the pelletized sulphur addition trial

IMPLEMENTATION

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

Mechanical

HIP found that the main driver of handling equipment selection with solid sulphur to be minimizing dust creation. While solid sulphur is not considered flammable the dust created in handling of the pellets is. Therefore, HIP decided to use “prilled” sulphur not granular sulphur, which is made in a specific and consistent shape that allows easier handling and promotes less degradation/dusting. Sulphur dust has a relatively low ignition point so the handling equipment must be gentle to prevent the creation of this dust but 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. HIP decided on using a bucket elevator to feed the pellets into the 3rd causticizer with the sulphur being metered into the bucket elevator by a vibratory feeder. This setup was in turn fed with sulphur via one-tonne (metric) 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 NFPA regulations for explosive dust hazards. HIP worked closely with the manufacturer of the equipment to ensure that regulations were met; equipment had to be dust-tight to keep all explosive dust contained, valves on the inlet and the outlet to allow for isolation of the equipment and equipped with a fire suppression system added to prevent personnel injury or damage to equipment in the event of an explosion. Figure 13 shows the sulphur addition system installed at HIP.



Figure 13 Sulphur addition system

At the time of this report, the setup has been running relatively smoothly for approximately 7 months. The only issue HIP 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 sulphur 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 Sulphur 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 sulphur 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 sulphur for sulphidity control using a combination of:
 - a. Feedforward Control: calculating the amount of sulphur required to maintain sulphidity based on the NaOH added in 1.)
 - b. Feedback Bias: biased up or down by the average sulphidity in the previous 24 hours

Feedforward control Equation 1 can be used to determine the amount of sulphur required to achieve target sulphidity (care should be taken with unit conversion when performing calculation). However, this amount of calculated sulphur will likely not be enough to control sulphidity. This is because sulphur is not always lost at this ratio to soda 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 non-condensable gases (NCG) in the form of TRS/SO₂ losses in the lime kiln, and boilers. Since certain sulphur compounds will be volatilized at lower temperatures than sodium compounds, the calculated amount of sulphur required to maintain the target sulphidity will likely require a bias. At HIP this bias is approximately 0.5 kg Sulphur/ADMT of pulp. Using boiler(s)/kiln emissions ppm measurements may assist in determining this offset. If electrostatic precipitator (ESP) ash saltcake is sewerred from the recovery boiler this will also have an offset effect (HIP 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 sulphidity 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 sulphidity. However, the sulphidity measurement using the ABC titration tests does not have the ability to measure Polysulphide content in the WL, and potentially throws off the sulphidity result. Furthermore, the hydrosulphide ions generated from the hydrolysis of Na₂S in white liquor would be consumed in the reaction that produces polysulphide, meaning that the sulphidity, even if accurate will not account for the polysulphide in the liquor.

Data was gathered to determine how much impact/offset might be required from a sulphidity result that came from an ABC titration test result to determine a new sulphidity setpoint to maintain 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 Sulphidity both increased by 0.03 lb/ft³ and 0.18% respectively. This is a discrepancy of less than 2% each and thus negligible. An error plot (Figure 14) with time showed the distribution of the error was random as a function of time (which was done to look for correlation with shift change and thus testing method). This residual plot showed no correlation. The mill gained confidence to use the ABC titration test results to measure and monitor sulphidity, and the sulphidity setpoint did not change.

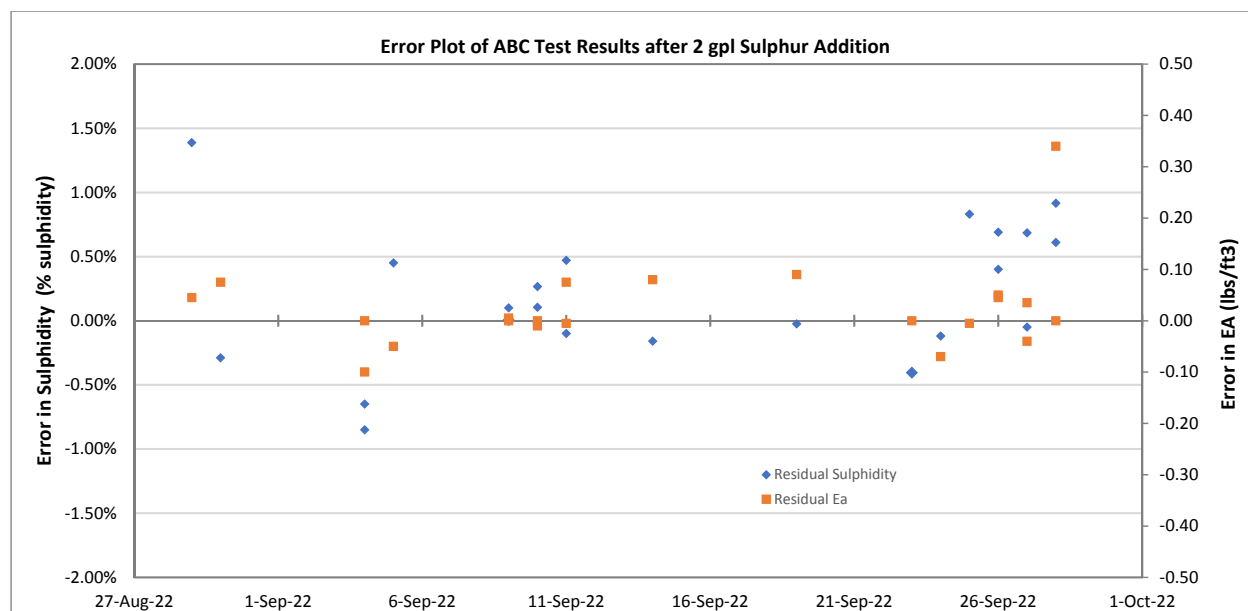


Figure 14 Error plot of the sulphidity values after the addition of 2 g/l of sulphur into WL

FINAL MILL RESULTS

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

Process Control

Using the method explained above the mill has achieved its target sulphidity. During a relatively normal operating 5-month window, the average and standard deviation of sulphidity had been 28.0% and 0.84% respectively versus 28.1% and 1.3% under the previous operating regime as shown in Figure 15 (when sesqui was used as makeup rather than pelletized sulphur). These are similar values thereby confirming the validity of this sulphur makeup approach. It is expected that the sulphidity variability will decrease as HIP is still optimizing the sulphur dosing system and working through issues that were noted in the mechanical implementation section.

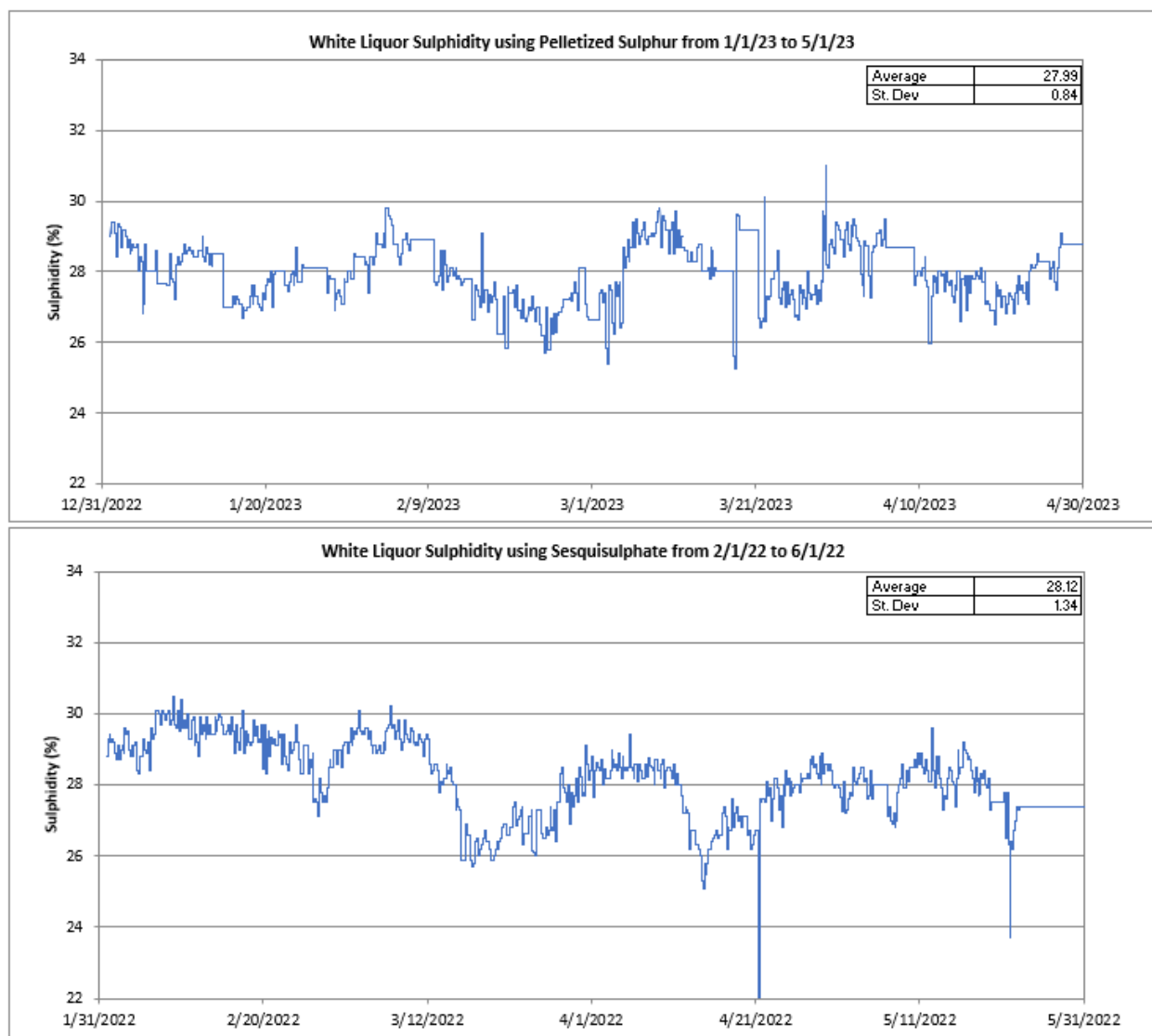


Figure 15 Sulphidity trend versus time before and after sulphur addition

Recausticizing Process and WL Quality Impact

As noted above, recaust and kiln operation were not impacted. Lab test results relating to lime mud filter operation since the addition of sulphur show the lime mud solids, %Na₂O and free lime content (14 samples) were 73.4%, 0.57% and 1.13% respectively compared to 74.7%, 0.61 wt% and 0.9 wt% for the previous 16 test results. Comparing 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 recaust or kiln operation. When the causticizer was opened during the turnaround 8 months after the addition of sulphur started there was no residual sulphur found. No anomalous scaling was found in Recaustr or Digester that could be traced back to Sulphur addition.

The WL quality and properties were not much affected by shifting from sodium sesquisulphate to elemental sulphur and sodium hydroxide as the sulphur and sodium make-up chemicals (Table 4). However, it appears that polysulphides get partially oxidized to thiosulphate. Furthermore, the sulphite and sulphate content of WL appear to be reduced. Further testing needs to be done to confirm that the thiosulphate concentration is appearing after the addition of sulfur and the creation of polysulphide, and it is not coming from the upstream green liquor which would suggest its increase is due the lower reduction efficiencies in the recovery boiler. If the increase in thiosulphate concentration occurs after the addition of sulphur, this may be due to the retention time of WL in storage before it is

pumped to the digester. The WL storages operate at ~180 °F, according to Olsson and Samuelson polysulphide may degrade into thiosulphate given sufficient time [10], especially in the presence of oxygen.

A possible solution to this problem would be to store the WL under nitrogen blanketing. Sodium thiosulphate 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 their bottleneck is in the liquor loop. Furthermore, thiosulphate, like polysulphide, may be a concern with respect to digester metallurgy. For HIP, 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.

Table 4 WL Properties Before and After Sulphur addition started

Parameter	Units	Pre-UKP Average (8 samples) Aug 22 –Sept 22	Post UKP Average (7 samples) Oct 22 to Nov 22	% Difference
EA	g/l as Na ₂ O	83.59	87.67	+4.89%
AA	g/l as Na ₂ O	100.66	104.94	+4.25%
TTA	g/l as Na ₂ O	115.88	120.86	+4.30%
Na ₂ CO ₃	g/l as Na ₂ O	15.18	15.68	+3.29%
NaOH	g/l as Na ₂ O	66.60	64.24	-3.55%
Na ₂ S	g/l as Na ₂ O	32.73	31.69	-3.17%
Na ₂ SO ₄	g/l	6.33	5.63	-11.01%
Na ₂ SO ₃	g/l	1.64	0.11	-93.22%
Na ₂ S ₂ O 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%

Recovery Boiler Process and HBL Quality Impact

The Heavy Black Liquor was analyzed (Table 5) to determine if the added sulphur (a) reduced organic loading to the recovery boiler due to higher polysulphide concentrations in WL improving the digester yield and/or (b) reduced the elemental sulphur and sodium content as the addition point of both soda and sulphur is upstream of previous location (in relation to recovery boiler). These potential changes may have an impact on the bed conditions of the recovery boiler, which HIP was already struggling with, even though the mill operated at a hearth heat release rate (HHRR) of ~0.9 MMBtu/ft²/hr during normal operation (which is lower than typical new recovery boilers at >1.1 MMBtu/ft²/hr). In particular, HIP 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 SO₂ emissions may be increased due to lower bed temperature. A reduction in sulphide 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 change slightly however the change was hard to ascribe to polysulphide 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 ending 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 HIP is). Furthermore, soap is not fired into the boiler under the new UKP operation, which also reduce the heating value of the HBL. The yield improvement due to polysulphide was expected to be too low in magnitude to measure/realize as the polysulphide concentration was low (between 1-2 g/l).

The elemental analysis of the liquor showed no significant change in comparison to pre-UKP including sulphur content. This is surprising as most of the sulphur loss in a pulp mill is expected to be lost through the brownstock

area. Pre-UKP the mill added its sulphur downstream of brownstock and post UKP the addition was after brownstock.

Table 5 HBL Properties Before and After Sulphur addition started

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, OD basis	5819	5766	-0.9%
Sulfur	% on OD basis	5.33	5.52	+3.5%
Chloride	% on OD basis	0.31	0.11	-65.2%
Carbon	% on OD basis	33.17	32.44	-2.2%
Hydrogen	% on OD basis	3.76	3.32	-11.7%
Nitrogen	% on OD basis	0.10	0.10	0.0%
Oxygen	% on OD basis	37.11	36.02	-2.9%
Sulfate	% on OD basis as Na ₂ SO ₄	8.65	7.66	-11.5%
Carbonate	% on OD basis as Na ₂ CO ₃	9.15	9.24	+1.0%
Sulfite	% on OD basis as Na ₂ SO ₃	0.13	0.14	+8.9%
Thiosulfate	% on OD basis as Na ₂ S ₂ O ₃	2.65	2.74	+3.4%
Organic/inorganic ratio		1.67	1.60	-4.0%
Effective Alkali	g/l as Na ₂ O	5.86	5.79	-1.2%
Active Alkali	g/l as Na ₂ O	8.58	8.91	+3.9%
Potassium, K	mg/kg, OD basis	17157	14700	-14.3%
Sodium, Na	mg/kg, OD basis	209285	207500	-0.9%
Tall Oil Content	% OD basis	1.24	0.68	-45.7%

Overall, the recovery boiler bed was not impacted by the sulphur 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 patter, and air distribution were adjusted. The consensus is that sulphur addition has had no significant impact on recover boiler operation.

IMPACT ON CORROSION

High concentrations of polysulphide and thiosulphate in pulp mill liquors can impact corrosion dynamics in vessels made of carbon steel [11]. HIP reviewed the metallurgy of the recaustisizing 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 polysulphide 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 is approximately 180 to 240 minutes before the pulp would be at the wash screens ready to be extracted and 45-60 minutes before the pulp is out the blowline. The temperature of the MC zone circulated liquor is 280-300 °F and that of the wash zone extraction liquor is 250-270 °F meaning the temperature the liquor and polysulphide sees at minimum for 180 minutes as it is moving through the MC zone down to the wash zone is 250 °F. According to experiments carried out by Olsson and Samuelson at a concentration of 2 g/l of polysulphide, this decomposed within 60 minutes (even when the cooking temperatures were less than 250 °F) [10]. Taking this into account the assumption of little to no polysulphide 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 HIP and thus required more frequent monitoring during annual turnarounds. In Recast 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 run time may not be enough to show a change following addition of sulphur make-up, however, suggests that no significant accelerated corrosion occurs.

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

CONCLUSION

Hinton Pulp found that pelletized/molten sulphur was the least expensive most abundant chemical that can be used to makeup sulphur in the recovery loop in its conversion to unbleached kraft pulping (UKP). Elemental Sulphur also held an advantage of requiring a small system which would require low capital cost, and less maintenance in comparison to Na_2SO_4 which is a typical sulphur makeup source in kraft pulp mills. Pelletized sulphur was confirmed to dissolve into white liquor within 12 minutes at operating temperatures seen in Recast. Almost all the sulphur converted into polysulphide as confirmed in lab and mill scale trials. When pelletized sulphur addition was implemented at the pulp mill, it was found that this polysulphide may partially decompose into thiosulphate which is a chemical that does not participate in cooking. The thiosulphate and polysulphide did not seem to impact corrosion dynamics at HIP 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 recast plant or digester that can be traced back to the sulphur addition. Finally, recast, kiln and recovery boiler operators have not noticed a noticeable change in operability of equipment.

For the future, HIP would consider using molten sulphur as it is cheaper than pelletized sulphur and would require virtually no operator intervention. This is because instead of coming in one-tonne tote bags which requires reloading bags numerous times a shift, an operator would simply have to unload a truck once a week or two. The feed would be controlled by a pump on a VFD and thus would have minimal components. Also, this would remove any combustible dust hazard. Furthermore, HIP would consider adding the sulphur into the WL storages to minimize any time the polysulphide has to degrade, which may provide a yield benefit and offload recovery boilers leading to higher production rate at the mill. Finally, it is paramount for HIP 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 (perhaps a similar review of different soda makeup options is also 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, 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/sulphur makeup methods and cost per tonne of pulp (especially coming out of shutdowns). Depending on this cost, consider pelletized sulphur as a makeup method. The cost dynamics will depend highly on location of the mill (and industries in its vicinity). Consider that molten and pelletized sulphur are directly or indirectly a feedstock/raw material for most if not all the makeup chemicals/compounds mills typically consider for sulphur makeup.

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