Modeling the Dynamics of Evaporator Wash Cycles

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Abstract

Kraft pulping is a process that utilizes white liquor, composed of Na_2S and NaOH, for wood delignification and pulp production. This process involves washing the dissolved organics and spent chemicals from the pulp, resulting in the generation of black liquor. Prior to its use as fuel in the recovery boiler, the black liquor is concentrated in multiple-effect evaporators. During the evaporation process, the inorganic salts present in the liquor become supersaturated and undergo crystallization. Fluctuations in liquor chemistry can give rise to severe evaporator scaling events, which significantly impact the thermal efficiency of the evaporators, and ultimately, pulp production.

Dynamic modeling provides insights into fluctuations in liquor chemistry in the evaporators. The primary objective of this study was to employ dynamic modeling to evaluate the effects of wash liquor recovery from evaporator wash cycles. The dynamics associated with wash cycles encompass variations in the concentrations of salts and solids in the recovered wash liquor, changes in the flow rate of wash liquor recovery, and fluctuations in liquor volume within the liquor tanks. The dynamic model was developed using Matlab Simulink and applied to the evaporation plant of a pulp mill in South America. By utilizing one month of mill process data, the model enabled the evaluation of fluctuations in liquor chemistry due to evaporator wash cycles. The developed model has demonstrated the potential to estimate the concentration of key ions responsible for scaling and to contribute to enhancements in evaporator washing strategies.

Introduction

Kraft pulping, the predominant pulping method in the pulp and paper industry, utilizes a combination of Na_2S and NaOH as active chemicals for the delignification of wood fibers and subsequent pulp production. Following this process, the resultant black liquor stream, consisting of dissolved organic matter and spent pulping chemicals, is separated from the pulp via washing procedures. The black liquor is then conveyed to a multi-effect evaporator system where it is subjected to a sequence of heat transfer surfaces. The condensation of steam on one side of the surface provides heat energy to the black liquor flowing on the other side. This process is repeated in multiple effect stages, where the vapor produced from the black liquor in one effect serves as the heating medium for the next effect at a lower pressure level [8]. In the current study, the evaporator system receives low and medium pressure steam from back pressure turbines, with the vapor from the concentrators flowing to evaporator 2A/B, followed by evaporator 3, and so forth. The evaporation process elevates the black liquor dry solids content from approximately 15% to 75% prior to firing in the recovery boiler.

Sodium salt scaling is a primary contributor to evaporator capacity limitations and evaporator downtime [1,4,10,11]. Scaling hinders heat transfer from steam to black liquor, necessitating evaporator washes or boilouts to dissolve the layer of scale and ensure proper evaporator performance. Three primary sodium double salts have been identified in black liquor, namely burkeite ($2Na_2SO_4 \cdot Na_2CO_3$) [11,18], sodium sulfate carbonate ($Na_2SO_4 \cdot 1.5Na_2CO_3$), and sodium sulfate dicarbonate, known as dicarbonate ($Na_2SO_4 \cdot 2Na_2CO_3$) [8]. Carbonate to sulfate ratio in black liquor can be used to predict the crystalized salt species [2, 20]. Carbonate rich salts form crystals at higher levels of supersaturation , which aggravates crystal adhesion onto heat transfer surfaces and exacerbates scaling issues [23]. In addition to the extensively investigated Na-CO_3-SO_4 salts, recent reports from several mills have indicated the presence of soluble scales containing sodium oxalate [5]. Studies have demonstrated that the wood species and rate of wash water recovery can influence the risk of oxalate deposition [5]. The impact of liquor temperature on the solubility of sodium oxalate, which demonstrates normal solubility, should be noted, as its solubility increases with a rise in temperature. In contrast, Na-CO_3-SO_4 double salts demonstrate a decrease in solubility with increasing temperature [12]. However, it is important to acknowledge that the dependence of Na-CO_3-SO_4 salts' solubility on temperature is relatively minor compared to that of liquor solids content.

Various studies have shown that fouling is dependent on liquor composition and nucleation events due to soluble sodium salts [2,7,9,12,14,16]. Liquor chemistry can fluctuate over time due to several factors, including wood species, pulp yield, brown stock washing efficiency, reduction efficiency (the extent of sulfide formation in the recovery boiler), and causticity (the extent of conversion from Na_2CO_3 to NaOH in the causticizing plant). Although online analytical tools have improved over the years particularly around the digester [21] and recausticizing plant [3,22], a substantial amount of information is still lacking regarding the black liquor chemistry at the evaporators. Tanks, piping, and evaporator bodies add to time lags and dampening effects to changes in liquor chemistry. In the absence of real-time information on liquor chemistry, accurately determining and predicting scaling periods becomes challenging. Studies have found that the frequency of evaporator wash cycles has a direct impact on scaling rates, with shorter periods between wash cycles leading to a higher rate of scaling [24,23]. The observed phenomenon can be ascribed to the utilization of weak black liquor or condensate in the wash cycle to dissolve the soluble sodium scale. Subsequently, the resulting liquor contains a higher concentration of sodium salts that initially caused scaling, which is then introduced back into the weak black liquor tanks. The impact on salt concentration is negligible when the wash liquor is recovered at a slow rate, however, quick recovery can lead to a surge in the concentration of salts responsible for scaling, thus, accelerating the scaling process [24].

Several modeling approaches have been employed to investigate the fundamental mechanisms underlying evaporator cleaning. In one such approach, a scale dissolution model was developed based on experimental work conducted in a laboratory setting [13]. Furthermore, a dynamic model, which simulated scale dissolution and mass flow over time, discretized in time and space, was implemented in Matlab [15]. In addition, a modeling methodology has been proposed that utilizes mill measurement data to enable automatic offline evaluation of scaling rates, thickness of scaling dissolution after a wash, and correlation analysis between operational parameters to scaling rate and washing performances [6]. A dynamic simulation study in liquor chemistry was also conducted using CADSIM software, which simulated sodium and sulfur balances and accumulation of non-process elements in the kraft recovery cycle [17]. Nevertheless, it is worth noting that the above-mentioned study did not take into account the liquor chemistry in the evaporator train, and the CADSIM software does not currently possess a dedicated function to model evaporator scaling.

Previous modeling studies have not included dynamic simulations of liquor chemistry along with evaporator scaling dissolution and wash liquor reclamation. This paper presents a dynamic modeling approach to evaluate the effectiveness of wash cycles and the impact of wash liquor recovery on black liquor dry solids and the concentration of inorganic components within the liquor solids. By accounting for the dynamic changes in liquor chemistry, our approach aims to provide an enhanced representation of the complex processes involved in evaporator scaling and washing.

Methodology

Step 1: Estimate Operational Parameters Through Mass and Energy Balance in the Evaporation Plant

Real-time data collected from the mill was utilized for mass and energy calculations. The data included steam pressure and flow

rate, condensate temperature, black liquor flow rate and dry solids content entering and exiting the evaporator train, black liquor recirculation temperature, vapor pressure in the evaporator bodies, and certain operating parameters of the stripper that are part of the vapor flow in the evaporator train. A simplified overall schematic of the multiple effect evaporator train that the simulation was based on is presented in Figure 1.

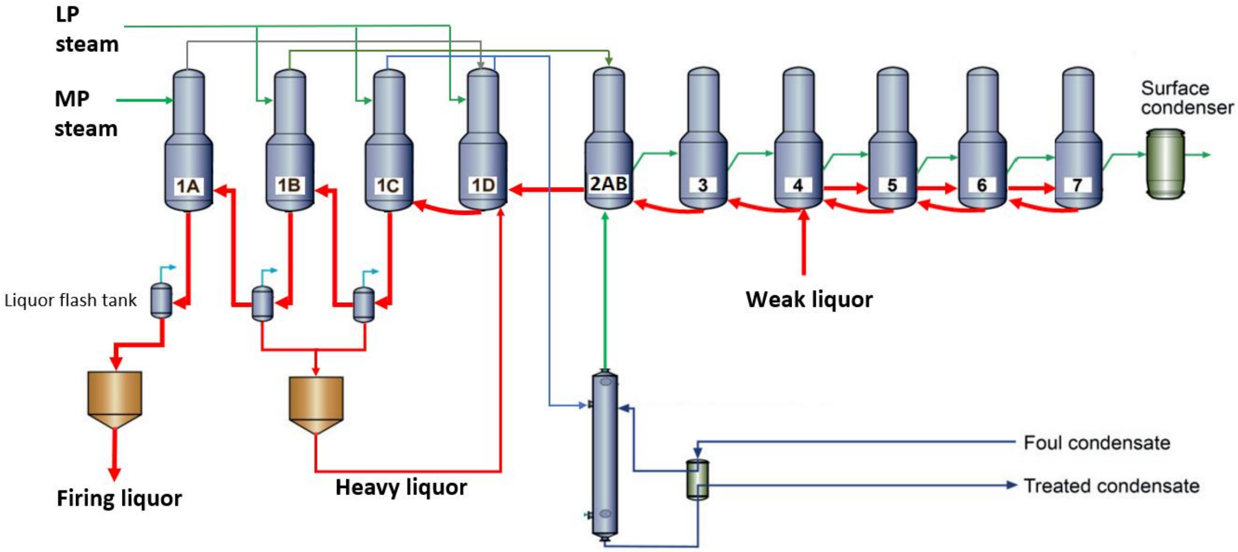

Figure 1: Simplified overall schematic of the evaporator train which the simulation was based on. This figure was modified from a general evaporator train schematic created by Valmet.

Mass and energy balances were then performed to determine the black liquor and vapor flow rates between the bodies in the evaporator train. These flowrates were necessary for calculating the heat transfer coefficients, thickness of scale dissolved, and mass of scale dissolved for various evaporator washes.

To calculate the black liquor mass flow rate in the evaporator train, the dry solids content of the black liquor was required. The dry solids content in each effect was obtained based on the boiling point rise in that effect. This was done using the correlation between boiling point rise (BPR) and black liquor dry solids mass fraction (DS) presented in equation 1 [25]:

$$DS = \frac{8.1 * BPR}{7.1 * BPR + 9.1 * BPR_{50}} \qquad \text{(Eq.1)}$$

The boiling point rise at 50% dry solids (BPR_{50}) was assumed to be 7.5°C [25]. BPR was calculated by taking the temperature difference between the black liquor and vapor temperatures, as the organic and inorganic contents in the black liquor contribute to a higher boiling point than water. By using known vapor pressure and black liquor temperature obtained from the real-time data, BPR, and ultimately DS, can be determined at specific time stamps.

Step 2: Identify Effects Washed and the Volume of Wash Water Used

As the mill data track wash water flow rates without specifying the evaporator body in the cleaning process, the liquor levels within the bodies can serve as an indicator to identify the particular evaporator undergoing the wash. Normally, the liquor level remains constant, but before a wash, it drops as some liquor is drained from the sump. During a wash, the level rises due to the addition of wash water, and towards the end of the cycle, it decreases as the wash water is drained out. These effects can be cross-checked with a drop in black liquor BPR in the evaporator bodies.

The wash liquor flow rate was measured at the mill, and with the known wash period, the total volume of wash water for a specific wash could be calculated, refer to Figure 2. Time stamps were taken at 2-minute intervals from recorded mill data to ensure accurate calculation, as evaporator washes usually last around two hours for this specific mill.

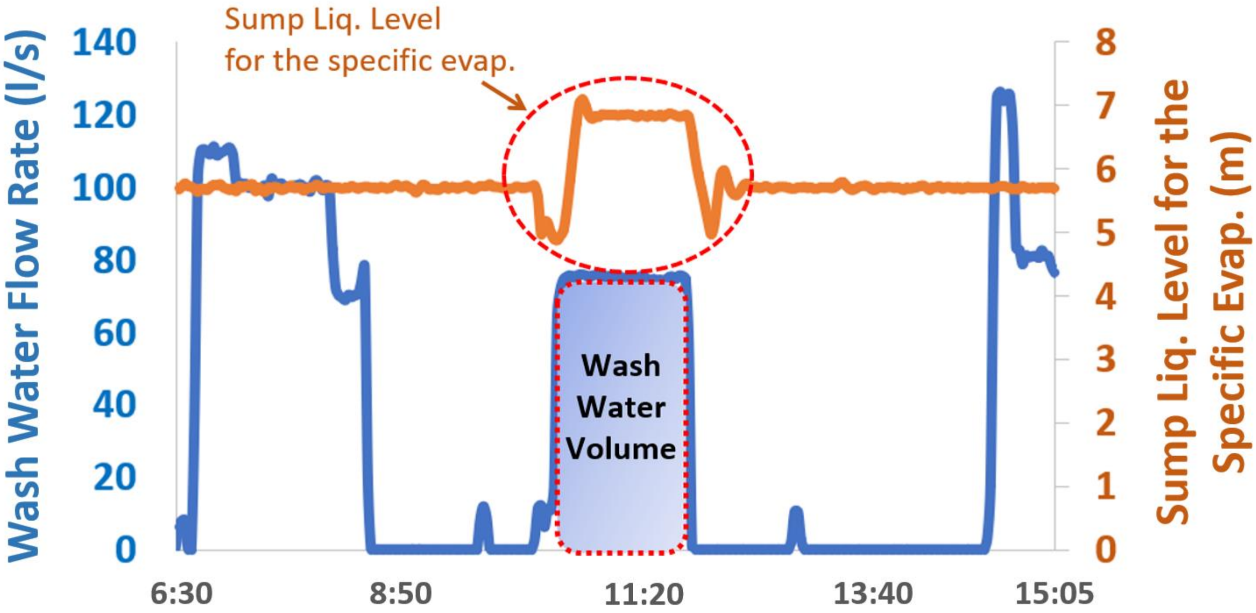

Figure 2. Identifying evaporator washed and wash water used by using wash water flow rate and liquid level curves.

Step 3: Estimate Mass of Scale Dissolved in the Wash Water

Scale thickness dissolution can be calculated from equation 2, which is derived from one-dimensional steady-state heat transfer equation:

$$\frac{\delta}{K_{scale}} = \frac{1}{U_{fouled}} - \frac{1}{U_{clean}} \qquad \text{(Eq.2)}$$

Where, δ is the thickness of scales (m), K_{scale} is the thermal conductivity of scales (W/mK), U_{fouled} is the heat transfer coefficient between steam to the black liquor before washing (W/m^{2}K), U_{clean} is the heat transfer coefficient after washing (W/m^{2}K). The value for K_{scale} used in this work is 1.73 W/mK [19].

To estimate the mass of scale on the heat transfer surfaces, it was assumed that the scale is evenly distributed across the full heat transfer area of the evaporator body, and with the calculated scale thickness and assumed density, the mass of scale can be found:

$$m_{DS_{scale}} = \delta * A_{heat\,transfer\,surface} * \rho_{scale} \qquad \text{(Eq.3)}$$

Where, $\rho_{scale} = \rho_{salt} * (1 - V_{void})$

The density, ρ_{scale}, is taken to be the product of salt density, ρ_{salt}, and the void volume, V_{void}, of the scale. The salt density used is 2.4 g/cm^3, considering the salt densities from various Na-CO_3-SO_4 salts that can scale the evaporator heat transfer surfaces, and V_{void} is assumed to be 30%. If V_{void} is assumed to be 15% or 45%, the resulting scale mass would increase or decrease by 21% respectively.

Heat transfer coefficients U_{fouled} and U_{clean} are calculated by analyzing the heat transferred from the steam to the black liquor:

$$\dot{q} = UA(T_{steam} - T_{BL}) = \dot{m}_{steam}\left(h_{vap} - h_{cond}\right) \qquad \text{(Eq.4)}$$

Where $\dot{q}$ is the heat transfer rate (kJ/s), $\dot{m}_{steam}$ is the mass flow rate of the steam condensate (kg/s), h_{vap} is specific enthalpy of the steam (kJ/kg), correlated to the real-time measured steam pressure from a steam table, and h_{cond} is specific enthalpy of the steam condensate (kJ/kg), correlated to the condensate temperature from a steam table.

The above equation was rearranged to calculate the heat transfer coefficient U (W/m^{2}K) between steam and the black liquor:

$$U = \frac{\dot{q}}{A\Delta T} = \frac{\dot{m}_{steam}\left(h_{vap} - h_{cond}\right)}{A(T_{steam} - T_{BL})} = \frac{\dot{m}_{steam}\Delta H_{vap}}{A(T_{steam} - T_{BL})} \qquad \text{(Eq.5)}$$

U_{fouled} was calculated from the average of U values (6 to 24 hours) before the wash (shown as blue squares in Figure 3), and U_{clean} was calculated from the average of U values (6 to 24 hours) after the wash (shown as red circles in Figure 3). Mill data such as steam pressure, mass flow rate, and black liquor temperature were used to calculate heat transfer coefficients. The sampling time for the PI data was at a 20-minute interval for adequate accuracy and acceptable computational time. For a fairly constant $\dot{m}_{steam}$ into the evaporator body before and after the wash, the heat transfer can often be improved after the wash, Figure 3.

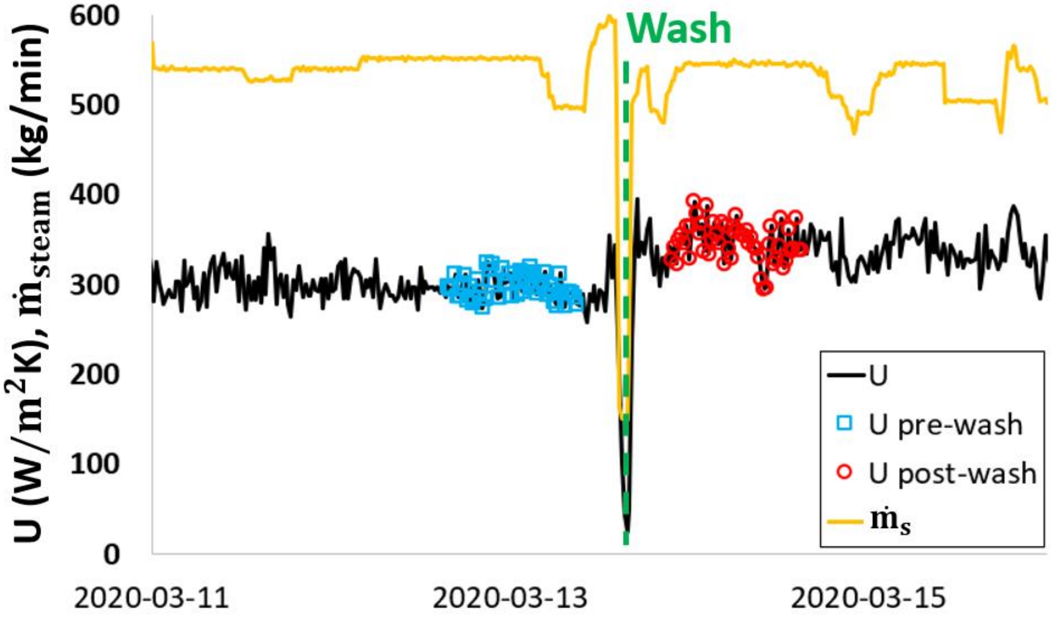

Figure 3. Example A of a fairly constant $\dot{m}_{steam}$ into the evaporator before and after the wash for a 2nd effect evaporator.

However, there are instances in the three-month data, where $\dot{m}_{steam}$ is lower after a wash due to operational fluctuations that correlated to a drop in flow rate of weak black liquor sent to the evaporation plant. In this case, the calculated U value decreases after the wash, which can lead to misrepresentation of scaling thickness in the dynamic model. It is caused by the decrease in $\dot{m}_{steam}$ after the wash, Figure 4. The calculated scaling thickness dissolved in this case is -1.23 mm, which represents a growth of 1.23 mm of scale during the wash, which is not possible.

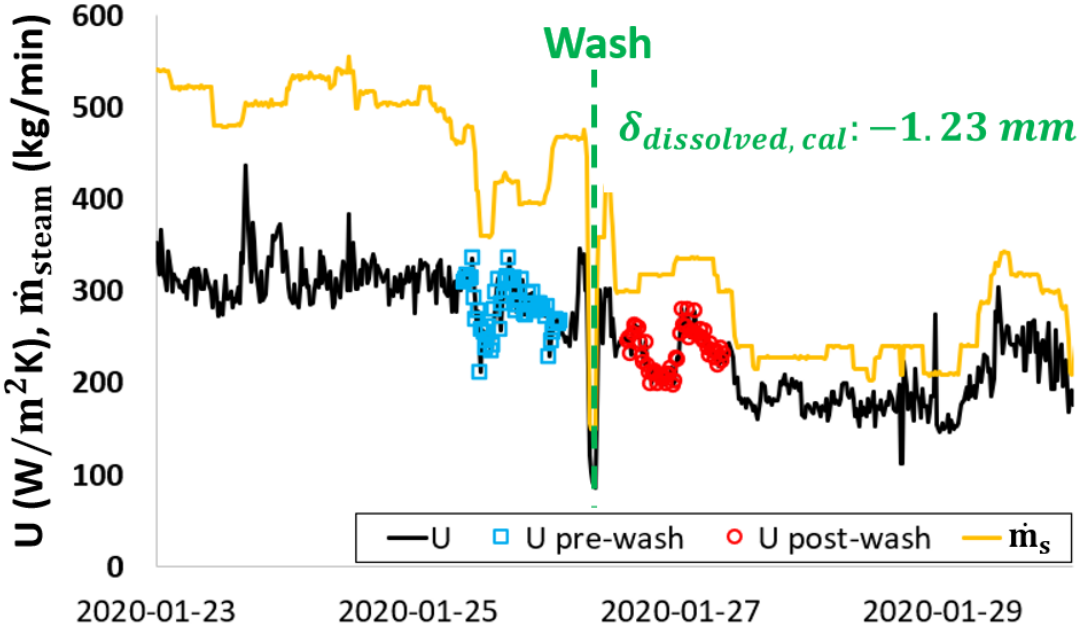

Figure 4. Example B of $\dot{m}_{steam}$ decreases after the wash for a 2nd effect evaporator, resulting in calculated scaling dissolution thickness to be negative in value.

To address this challenge, two different mitigation methods were employed. The first method involved taking the average values of $\dot{m}_{steam}$ for 18 hours, ranging from 24 hours before the wash to 6 hours before the wash. These average values were used to calculate both U_{fouled} and U_{clean}.

The second method involved taking the average mass flow rate of steam, $\dot{m}_{steam}$, for the entire calculation period and using this average to calculate both U_{fouled} and U_{clean}. When applying both mitigation methods 1 and 2, the calculated U values increased after the wash (refer to Figure 5 and Figure 6).

The first method resulted in a calculated scale thickness of 0.54 mm, while the second method yielded a scale thickness of 0.48 mm. Any negative values obtained for the calculated scale thickness removed were set to zero for the wash water recovery dynamic simulation.

An example of mass of scale dissolved for concentrator body 1A, calculated by using three different methods, refer to Figure 7. Here are the explanations for the three methods:

- Direct calculation method, using the steam mass flow rate values measured at various time stamps to calculate heat transfer coefficients and scale thickness at the respective time stamps (shown as black diagonal striped bars).
- 1st mitigation method, averaging the steam mass flow rate values from 6 to 24 hours prior to the wash (shown as pink confetti bars).
- 2nd mitigation method, using the overall average mass of steam flow rate over a longer time period, in this case a 3-month period without mill downtimes (shown as blue checkered bars).

The pink and blue bars (calculated from using mitigation methods) have values that are within 50% of each other. In contrast, the black bars do not always agree with the mitigation methods' results. The scale thickness calculations (eqn. 2) depend on the U values before and after washing, and $\dot{m}_{steam}$ is directly proportional to U (eqn. 5). Therefore, $\dot{m}_{steam}$ values directly affect the scale thickness calculations.

When using the $\dot{m}_{steam}$ value at a specific time stamp for the calculation, it assumes that there is no time lag for heat transfer from the steam to the black liquor. However, in reality, this is not the case. Due to the greatly varying mass flow rate of the steam, there is not enough time for the heat transfer between the steam and the black liquor to reach steady state. Thus, an average value of the mass of steam flow rate is required for the calculation, such as the mitigation methods used.

The 1st mitigation method was chosen for the dynamic simulation because the 2nd mitigation method can result in inaccurate scale thickness estimation if there are changes in $\dot{m}_{steam}$ values over time, periods of instrumentation issues, or mill downtime within the calculation period. Deviations in $\dot{m}_{steam}$ values due to the mentioned reasons affect the overall averaged $\dot{m}_{steam}$value. However, the advantage of the 2nd mitigation method is that, unlike the 1st mitigation method, a different set of U values needs to be calculated based on the average mass flow rate of steam before each wash. This saves computational time in the simulation, as only one set of U values needs to be calculated once. Ultimately, further research is required to address the variability in parameters, such as the $\dot{m}_{steam}$ values used for calculating the U values, enabling a more precise estimation of scaling growth and dissolution.

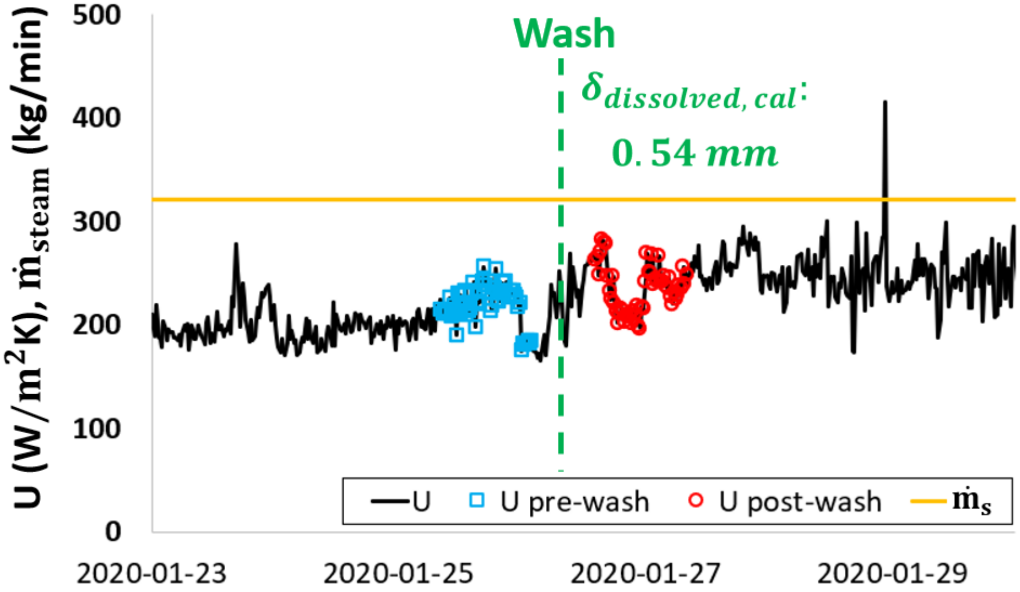

Figure 5. 1st mitigation method applied to Example B, averaging the steam mass flow rate values from 6 to 24 hours prior to the wash, resulting in positive calculated scale thickness dissolution.

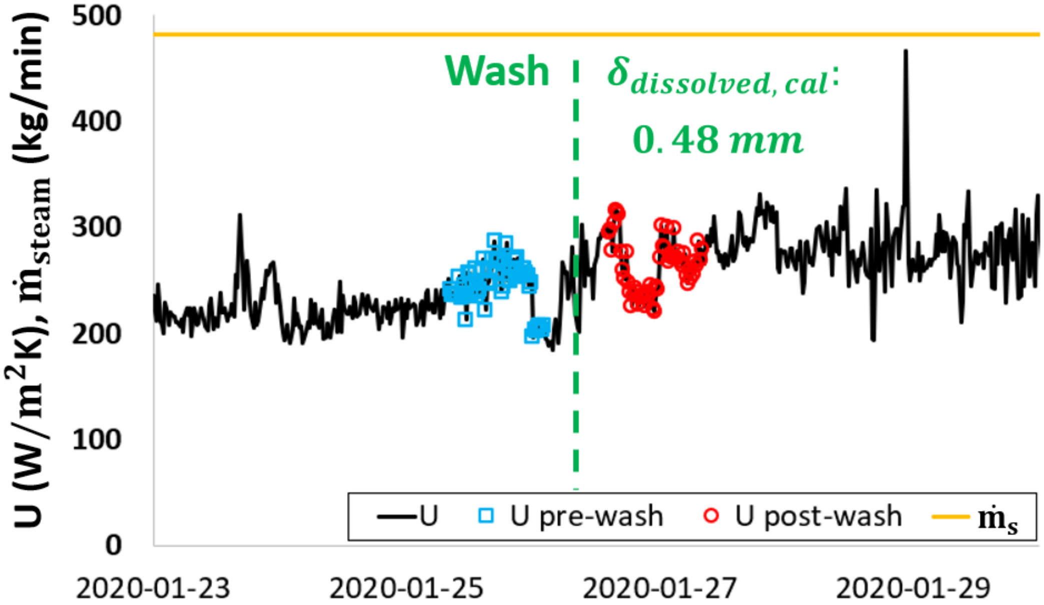

Figure 6. 2nd mitigation method applied to Example B, using the overall average mass of steam flow rate over a longer time period, in this case a 3-month period without mill downtimes, resulting in positive calculated scale thickness dissolution similar to the results from the 1st mitigation method.

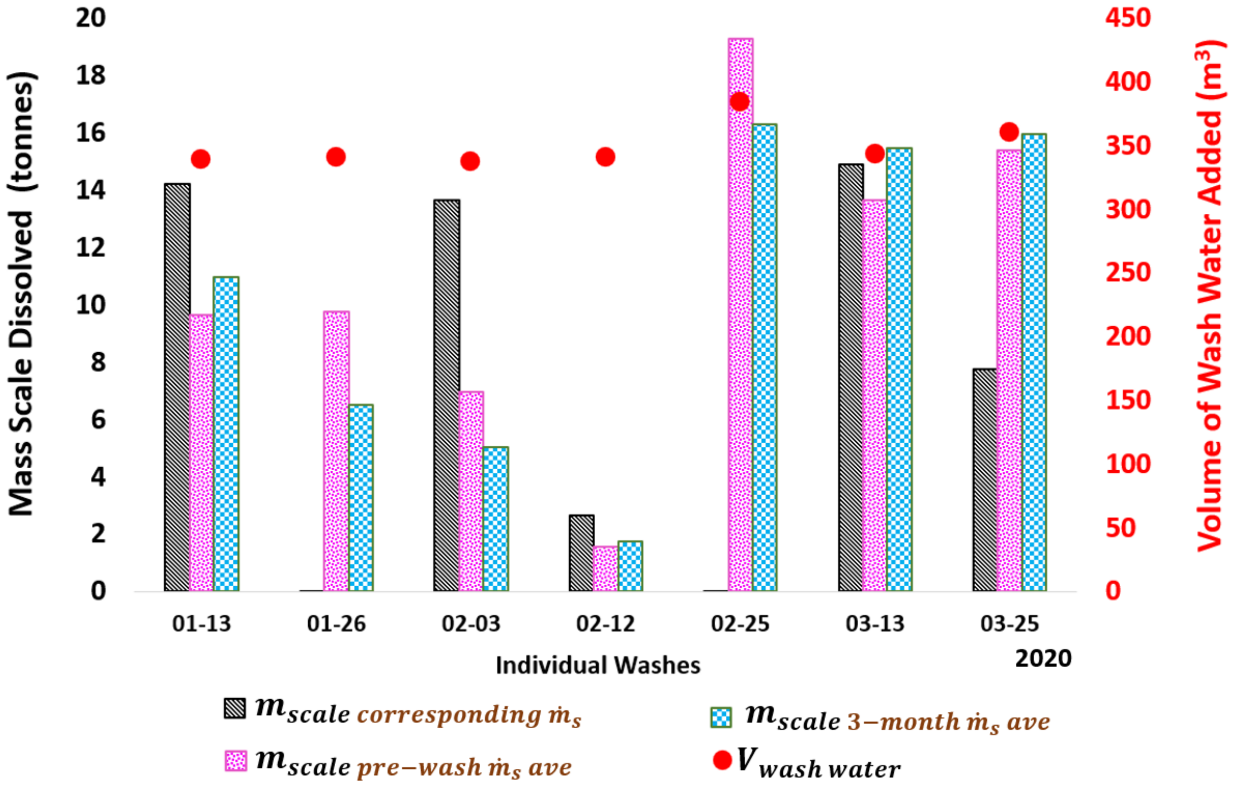

Figure 7. An example showing the volume of wash water used and mass of scale dissolved from 3 different calculation methods for concentrator body 1A over a 3-month period.

Step 4: Estimate Mass of Dry Solids Recovered from the Remaining Black Liquor in the System

At the beginning of a wash, there is black liquor present in various parts of the system, including the evaporator body, black liquor flash tank, and pipes, refer to Figure 8. Within the evaporator body, the remaining black liquor consists of the black liquor film flowing down the heat transfer surfaces, black liquor in the sump, and black liquor in the recirculation line. The volume of black liquor remaining in the system can be calculated based on the dimensions of the equipment and the sump level.

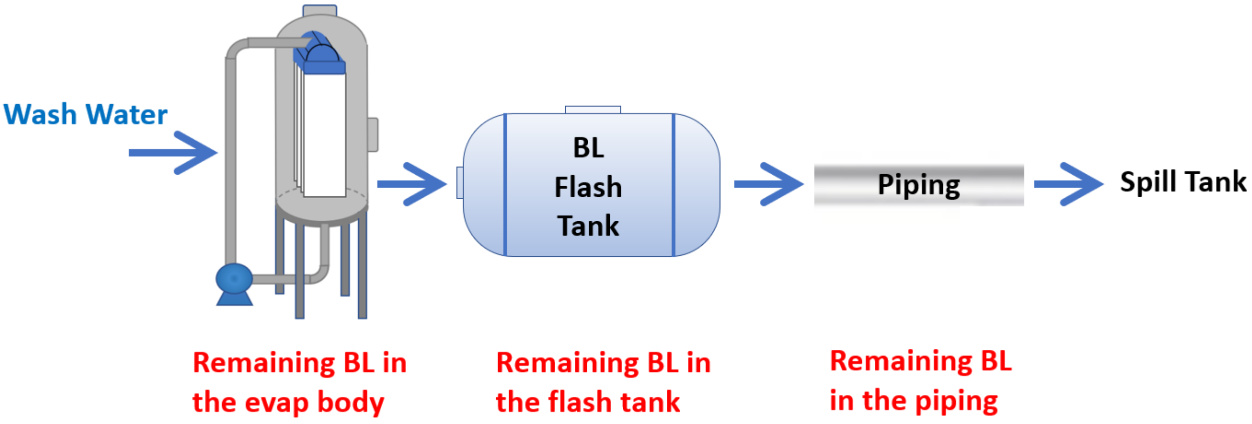

Figure 8. Simplified schematic to illustrate the black liquor remaining in the system prior to the wash comes from the evaporator body, flash tanks, and piping.

To estimate the mass of black liquor dry solids recovered with the wash water, the density of the black liquor and its dry solids content are taken into account. The boiling point rise, which is calculated from the black liquor temperature and vapor pressure, is used to determine the dry solids content. This dry solids content is then used to estimate the black liquor density using equation 6, which is valid for a temperature range between 20°C and 100°C, and dry solids content up to 65% [26].

It is important to acknowledge that the mill in this study has black liquor temperature that reaches up to 165°C, and dry solids content up to around 75% to 80%. This extends the density estimation beyond the specified range of equation 6.

The equation for calculating the black liquor density at a given temperature is as follows:

$$\rho_{BL,T} = [1 - 3.69 * 10^{-4} * (T - 25) - 1.94 * 10^{-6} * (T - 25)^2] * \rho_{BL,25°C} \qquad \text{(Eq.6)}$$

Where,

$$\rho_{BL,25°C} = 997 + 649 * DS$$

$\rho_{BL,T}$ represents the black liquor density (kg/m^3) at a specific temperature – T (°C), $\rho_{BL,25°C}$ represents the black liquor density at 25°C (kg/m^3), and DS represents the black liquor dry solids mass fraction.

Step 5: Estimate Mass of Chemical Species Recovered from Scale Dissolution, Weak Black Liquor, and Remaining Black Liquor

The concentration of salt in the recovered wash liquor contains dissolved scale, the remaining liquor prior to the wash, and the wash water added into the bodies for liquor dilution. Frequent sampling is required to compare sampled wash liquor dry solids and salt concentration with the theoretical wash liquor concentration that does not account for scaling dissolution. By taking this approach, the mass of scaling dissolution and the composition of the scales can be estimated. However, due to challenges encountered during the research regarding sample collection, it was not possible to develop a comprehensive salt concentration profile over the wash cycle. Nonetheless, educated estimations were made based on limited laboratory data from the collected wash samples. To improve the accuracy of the model input parameters, it is necessary to collect additional black liquor and wash liquor samples at frequent intervals. The estimated concentrations of sodium and oxalate in the liquor and dissolved scales can be found in Table 1.

Table 1. Chemical composition assumptions derived from black liquor and wash liquor lab analysis

Items		m_{Na}/m_{DS} (%)	$m_{C_2O_4}/m_{DS}$ (%)
Scale		20.7	3.4
Weak BL		18.05	1.04
Remaining BL in eff.	3	19.5	1.04
	2 A/B	20.0	0.51
	1 A/B/C/D		

Step 6: Modeling Multiple Washes with Constant Stirred Tank Reactor – CSTR Assumptions

To simulate the fluctuating concentration of dry solids and chemical species during the recovery of wash water back to the feed liquor tank and evaporators, the assumption is made that the spill and feed liquor tanks exhibit well-mixed conditions. It is further assumed that these tanks operate as continuous stirred tank reactors (CSTR's). The dynamic model incorporates CSTR equations derived from the fundamental CSTR design equation.

CSTR design equation in terms of volumetric flow rate for reactant A:

$$\frac{dn_A}{dt} = C_{A,in}\dot{V}_{in} - C_{A,out}\dot{V}_{out} - (-r_A)V \qquad \text{(Eq.7)}$$

Since we are assuming there is no reaction along wash liquor recovery back to the evaporator train, the reaction rate $r_A = 0$.

To simulate the temporal variation of dry solids as black liquor flows through a liquor tank, $\frac{d\frac{m_{DS}}{m_{BL}}}{dt}$, the same theory is applicable, refer to equation 8. V$_t$ is the volume of liquor in the tank at time t. Also, volumetric flow rate of black liquor into or out of a tank, $\dot{V}_{BL} = \frac{\dot{m}_{BL}}{\rho_{BL}}$, where the liquor mass flow rate, $\dot{m}_{BL}$ can serve as the input variable with known liquor density value, ρ_{BL}.

$$\frac{d\frac{m_{DS}}{m_{BL}}}{dt} = \frac{\dot{m}_{DS,in}}{\dot{m}_{BL,in}}\frac{\dot{V}_{BL,in}}{V_t} - \frac{\dot{m}_{DS,out}}{\dot{m}_{BL,out}}\frac{\dot{V}_{BL,out}}{V_t} \qquad \text{(Eq.8)}$$

The temporal variation of sodium content in black liquor, $\frac{d\frac{m_{Na}}{m_{BL}}}{dt}$, as it flows through a liquor tank can be expressed as follows:

$$\frac{d\frac{m_{Na}}{m_{BL}}}{dt} = \frac{\dot{m}_{Na,in}}{\dot{m}_{BL,in}}\frac{\dot{V}_{BL,in}}{V_t} - \frac{\dot{m}_{Na,out}}{\dot{m}_{BL,out}}\frac{\dot{V}_{BL,out}}{V_t} \qquad \text{(Eq.9)}$$

The temporal variation of oxalate content in black liquor, $\frac{d\frac{m_{C_2O_4}}{m_{BL}}}{dt}$, as it flows through a liquor tank can be expressed as follows:

$$\frac{d\frac{m_{C_2O_4}}{m_{BL}}}{dt} = \frac{\dot{m}_{C_2O_4,in}}{\dot{m}_{BL,in}}\frac{\dot{V}_{BL,in}}{V_t} - \frac{\dot{m}_{C_2O_4,out}}{\dot{m}_{BL,out}}\frac{\dot{V}_{BL,out}}{V_t} \qquad \text{(Eq.10)}$$

The "integrator" block in Matlab Simulink was used to solve the ordinary differential equations with user defined initial conditions, and the model computes outputs $\frac{m_{DS}}{m_{BL}}$, $\frac{m_{Na}}{m_{BL}}$, and $\frac{m_{C_2O_4}}{m_{BL}}$ at various time stamps.

To determine the sodium and oxalate concentrations per black liquor dry solids weight percent at a specific time stamp, simply divide the species concentrations by the dry solids content. The initial conditions for the spill liquor tanks were determined based on the average mass of dry solids, sodium, and oxalate recovered from the wash water over a one-month period. As for the feed black liquor tanks, the initial conditions were assumed to be the same as those for the weak black liquor listed in Table 1.

The turnover rate of the continuous stirred tank reactor (CSTR) is measured by the space-time parameter, τ, which can be estimated by dividing the tank liquor volume by the volumetric flow rate exiting the tank. The space-time for the spill liquor tank, τ_{spill}, is approximately 20 hours, while for the feed liquor tanks, τ_{feed}, it is around 4 hours. Comparatively, the time periods for τ_{spill} and τ_{feed} are minimal when compared to the one-month simulation period, which includes time stamps recorded every 2 minutes. Consequently, the definition of the initial conditions has a negligible impact on the simulation outputs.

Integrating the dynamic model

The previous simulation steps enabled the calculation of several parameters, including the mass of dissolved scale, volume of wash water utilized, and the mass and dry solids content of the black liquor in the evaporator effect prior to washing. To determine the mass flow rate $\dot{m}_{BL,in}$ and dry solids flow rate $\dot{m}_{DS,in}$ entering the spill liquor tank, the total mass of recovered wash liquor and dry solids in the wash liquor are divided by the duration of the wash.

The total mass of solids in the recovered wash liquor is determined by summing the mass of dissolved scale, the dry solids mass in the black liquor at the beginning of the wash, and the dry solids in the weak black liquor used for washing. The total mass of sodium and oxalate is calculated based on the compositions provided in Table 1. This yields the mass flow rates of sodium $\dot{m}_{Na,in}$ and oxalate $\dot{m}_{C_2O_4,in}$.

The recovered wash liquor is directed into the spill liquor tank, and real-time PI data inputs are provided at 2-minute intervals. These inputs include the volume of liquor in the feed and spill liquor tanks, the flow rate of wash water from the spill liquor tank, weak black liquor from the brown stock washer, and weak black liquor from the feed liquor tanks to the evaporators. These data inputs are utilized to determine the fluctuations in the sodium and oxalate compositions within the spill liquor and weak black liquor tanks. The input signals to Simulink are composed of real-time mill data measurements (illustrated in yellow boxes in Figure 9), and the parameters calculated from methodology steps 1 to 5, including the mass flow rate of liquor, dry solids, and chemical concentrations (illustrated in the red circle in Figure 9).

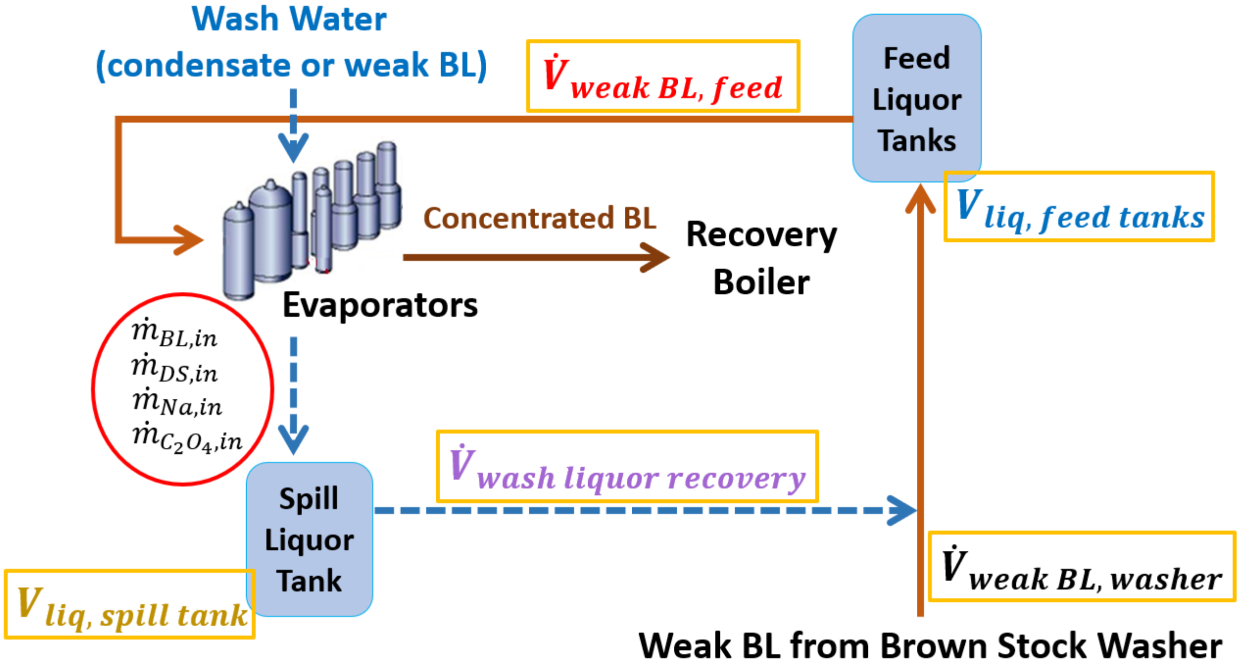

Figure 9. Schematic of dynamic simulation overview with input parameters.

To utilize the dynamic model, one-month worth of evaporator wash data was simulated. To provide a visual representation of the washes happened during the simulated month, the wash water flow rate towards the evaporator train (illustrated as dotted lines), and the specific evaporator bodies that were washed (illustrated as colored dots), after implementing Step 2 in the Methodology section, is illustrated in Figure 10. The highlighted periods in the figure illustrate periods of when 1A/B/C/D were washed within hours from each other. The real-time one-month input parameters of the liquor mass flow rates and tank volumes (parameters in the yellow boxes in Figure 9) are illustrated in Figure 11.

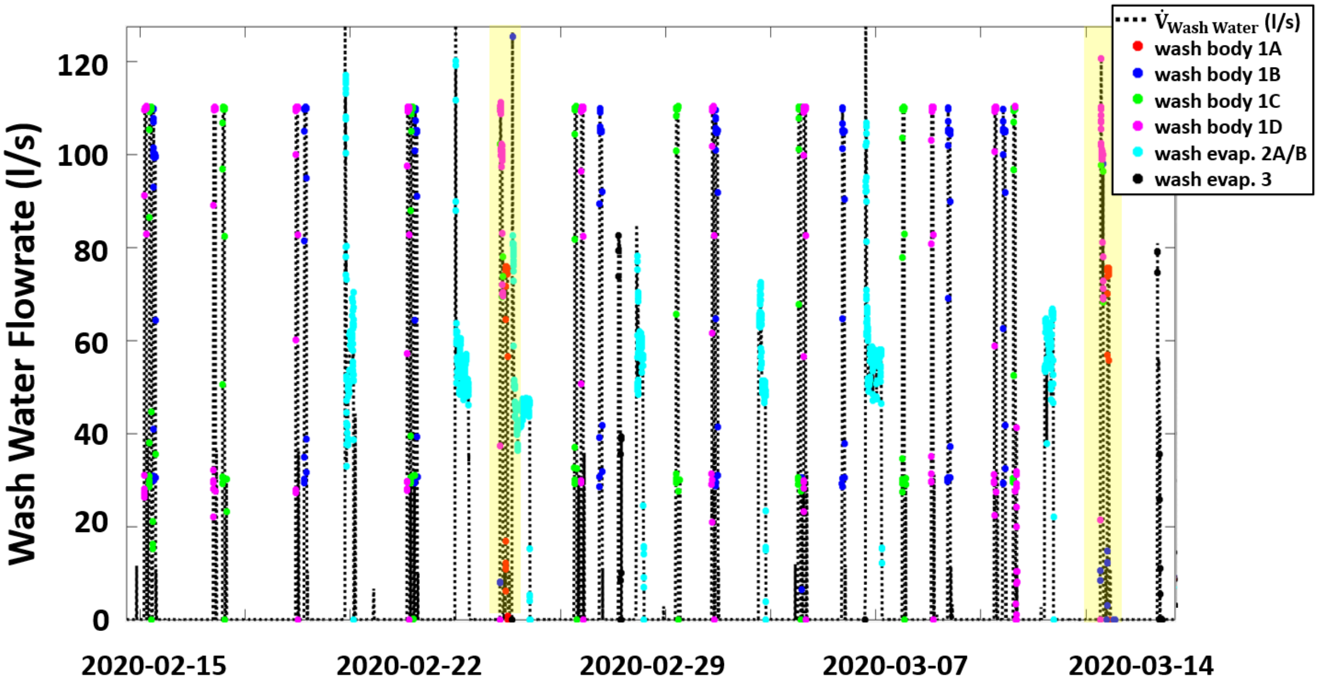

Figure 10. The wash water flow rate to the evaporators over the course of a month is depicted with dotted lines, and the specific evaporators that the wash water flowed to are depicted with colored dots. The highlighted periods illustrate when 1A/B/C/D were washed within hours from each other.

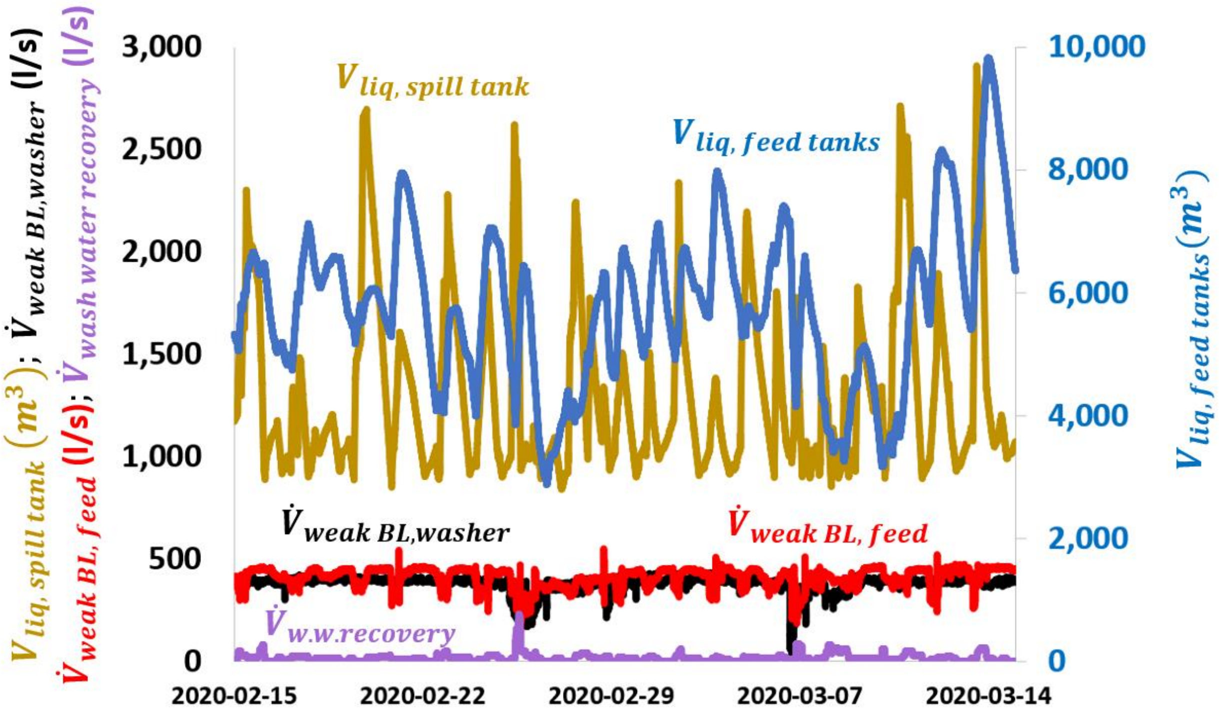

Figure 11. Input parameters from real-time PI data in the same month period during the washes

Results and Discussion

The dry solids calculated in effects 1A/B/C/D, 2A/B, and 3 over a one-month period are presented in Figure 12. The simulated black liquor dry solids content is essential for conducting mass balances and determining black liquor and vapor flow rates, which are necessary for scale dissolution calculations. It is also utilized to calculate the mass of the remaining black liquor dry solids recovered back into the evaporator train.

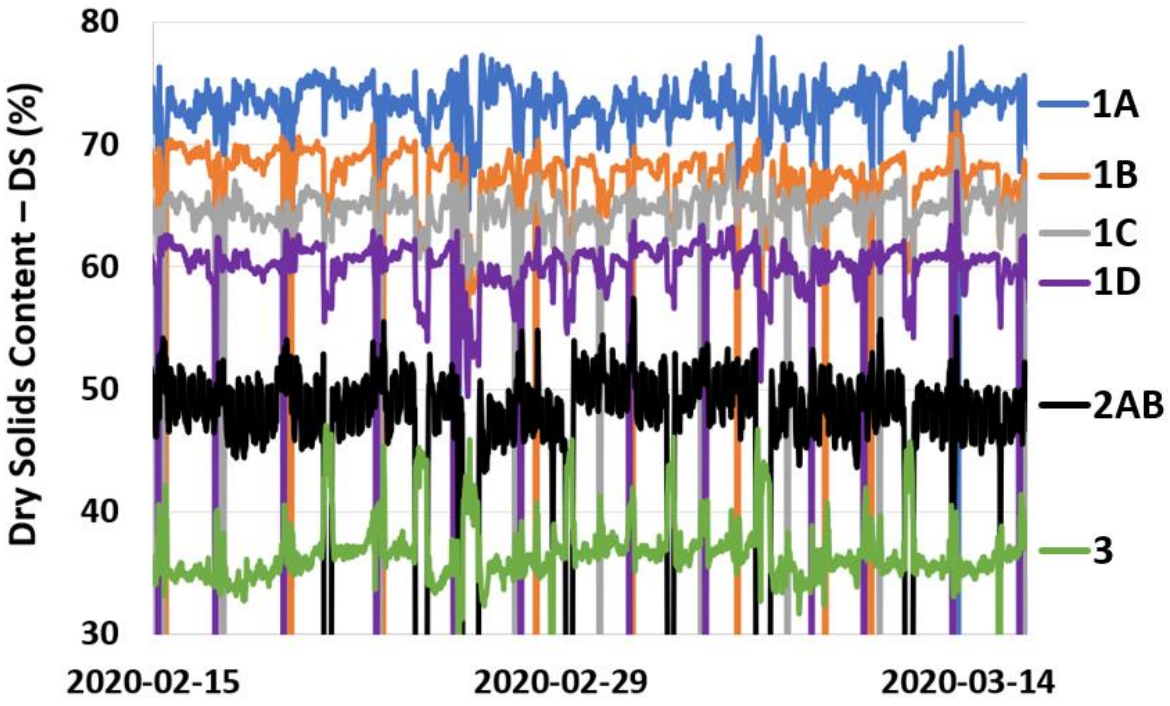

Figure 12. Liquor DS% in evaporator bodies 1A/B/C/D, 2A/B, and 3, calculated from liquor boiling point rise

Several noteworthy observations can be made. Firstly, in evaporator 2A/B, the dry solids content fluctuated above and below 50 wt%, which is the "critical solids content" known to trigger Na-CO_3-SO_4 precipitation [12]. On the other hand, effect 3 consistently exhibited dry solids content fluctuations within the range of 32% to 42%, remaining below the critical threshold. Regarding the issue of oxalate scaling, the researchers at the University of Toronto had developed an oxalate solubility model [16], which was applied in this study. The model indicated that the solubility limits of oxalate were periodically exceeded in both 2A/B and effect 3. Wash water sampling results supported these findings, indicating that 2A/B experienced sulfate-rich Na-CO_3-SO_4 and oxalate scaling, while effect 3 had only minor occurrences of oxalate scaling.

With regards to the outputs from Step 3 mentioned in the Methodology section, The thickness of the scale removed during the washes were calculated using the heat transfer coefficients (U) before and after the wash. Four different washes for 2A/B are shown in Figure 13. The U values were calculated by using the 1st mitigation method, and for every wash, there is a different set of U values calculated based on the average mass of steam flow rate before the wash. The blue squares represent the U values 6 to 24 hrs before the wash, while the red circles represent the U values 6 to 24 hrs after the wash. This specific example demonstrates that the washes improve the heat transfer between the steam and the black liquor , and the dissolved scale thickness corresponds to the degree of improvement in the heat transfer coefficient following the wash. According to the methodology employed, three out of the four wash cycles were found to be effective in removing scale, while minimal to no scale was removed during the fourth wash. However, as alluded to in the Methodology section, additional investigations are necessary to verify the actual amount of scale dissolved.

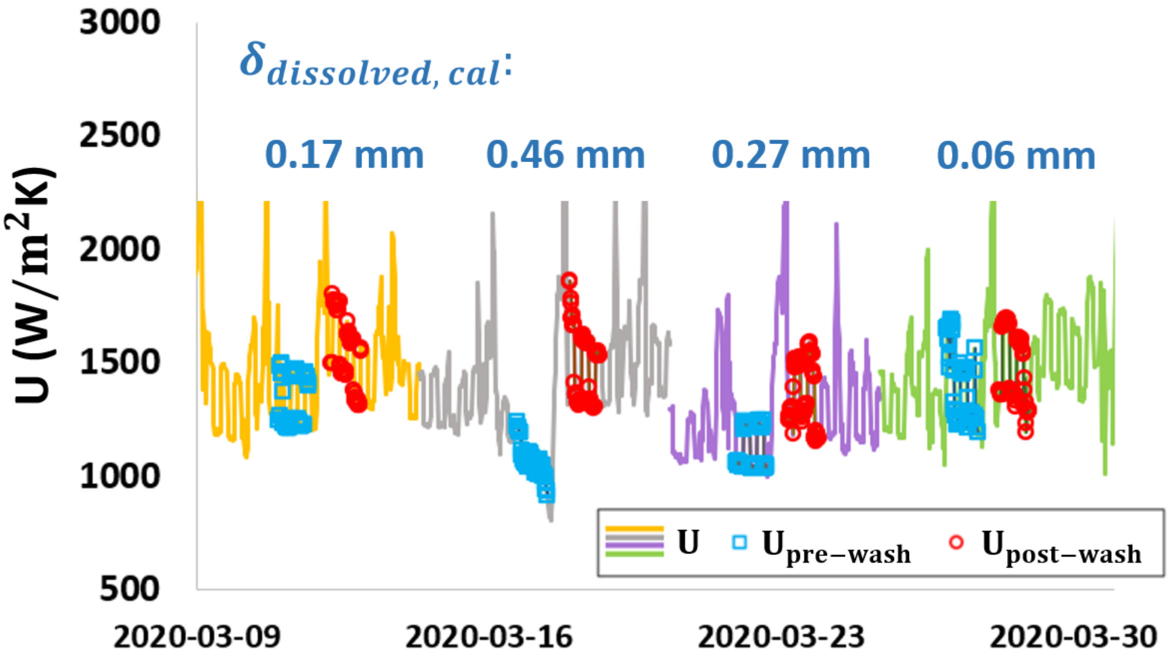

Figure 13. U values calculated by using the 1st mitigation method. Each color for the U value illustrates a different set of U values calculated corresponding to the average mass of steam flow rate before the wash. Dissolved scale thickness calculated are illustrated directly above the 4 washes.

In addition to recovering scale dissolution through the wash water, the washing process also reclaims the remaining black liquor in the system prior to the addition of the wash water. The primary source of the remaining black liquor is from the evaporator body, as shown in Figure 14.

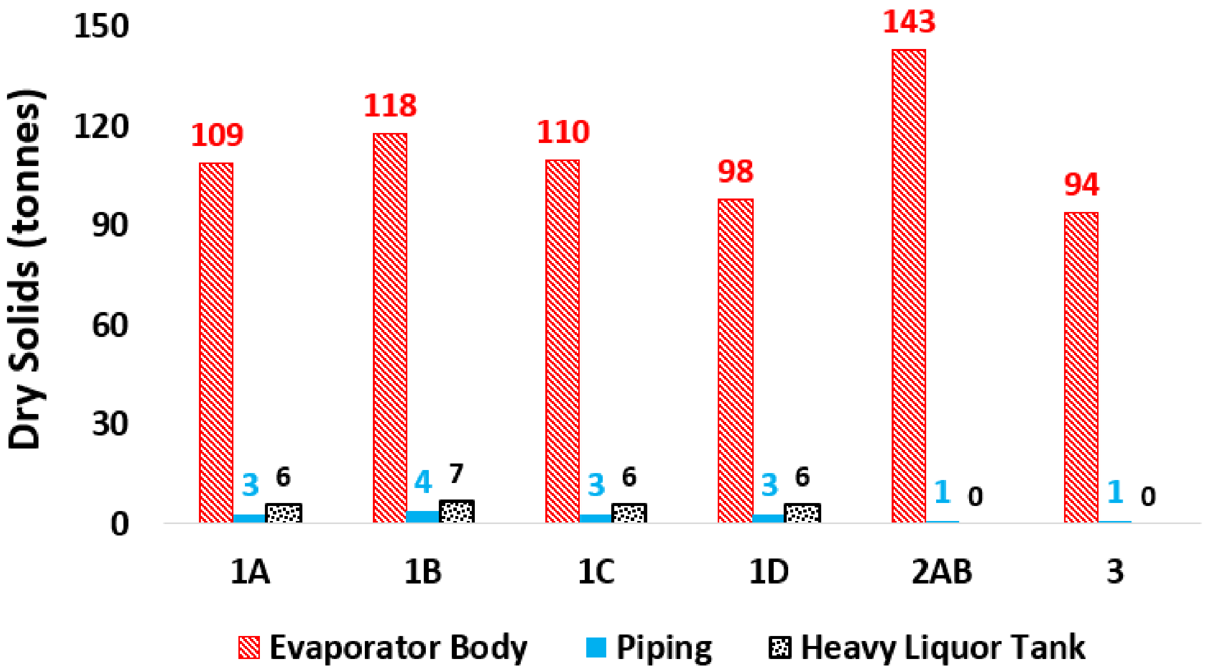

Figure 14. Distribution of mass of dry solids from the remaining black liquor in the system.

Comparing the amount of liquor dry solids from the remaining liquor and the scale dissolutions from each evaporator body, in this particular case study, during a wash, the main source of solids in the wash water reclamation is the remaining black liquor, rather than scale dissolution. Scale dissolution has a minimal impact on the overall dry solids content, as depicted in Figure 15.

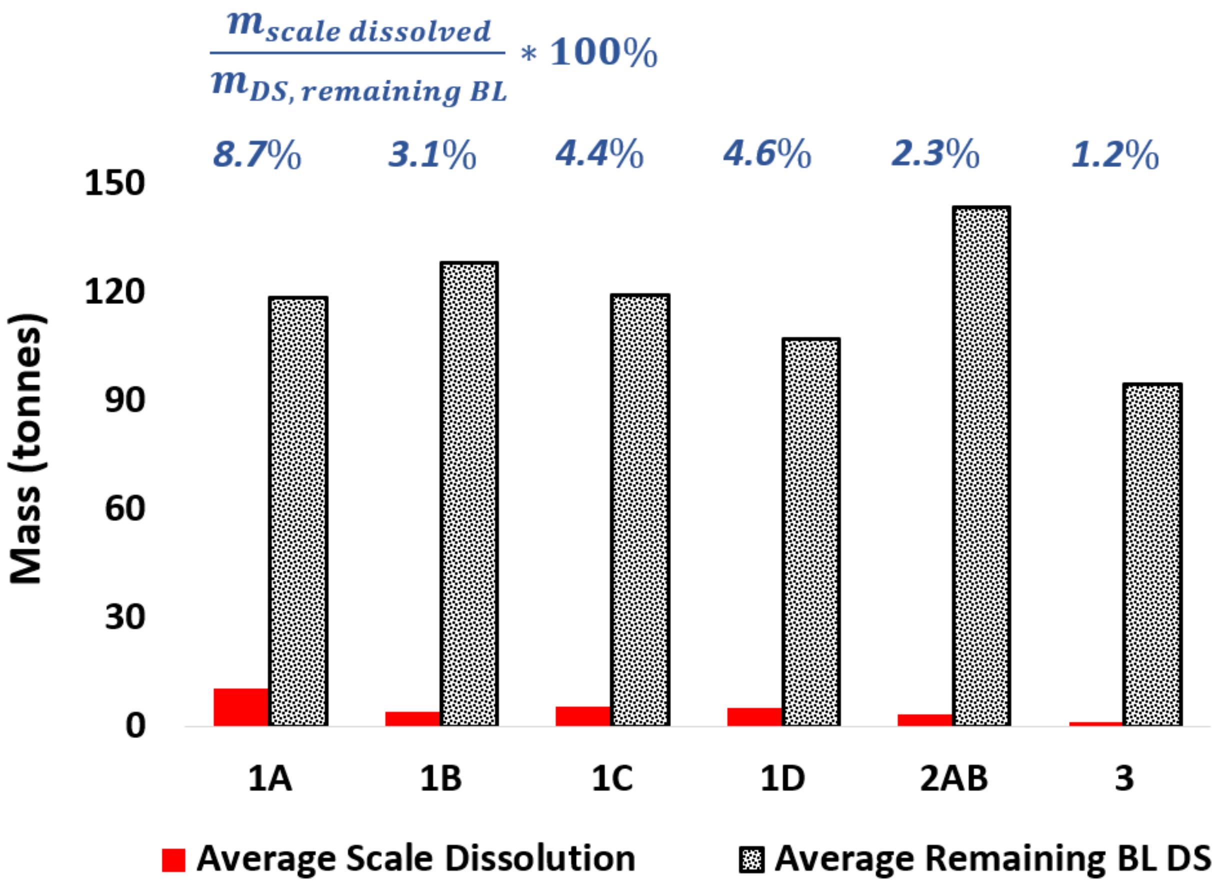

Figure 15. Comparison of the contribution of dry solids to the recovered wash water between scale dissolution and the remaining black liquor.

Since around 55% of black liquor dry solids consists of organics [25], to better illustrate the contribution of soluble sodium scale dissolution in comparison to the inorganic portion of the remaining black liquor. The significance of sodium salts' contribution to the inorganics in the remaining black liquor is illustrated in Figure 16. Scale dissolution (solid red bars) accounts for approximately one-third of the sodium salts of the remaining black liquor (blue checkered bars) in body 1A, 15% in bodies 1B/C/D, 8% in 2A/B, and 4% in effect 3.

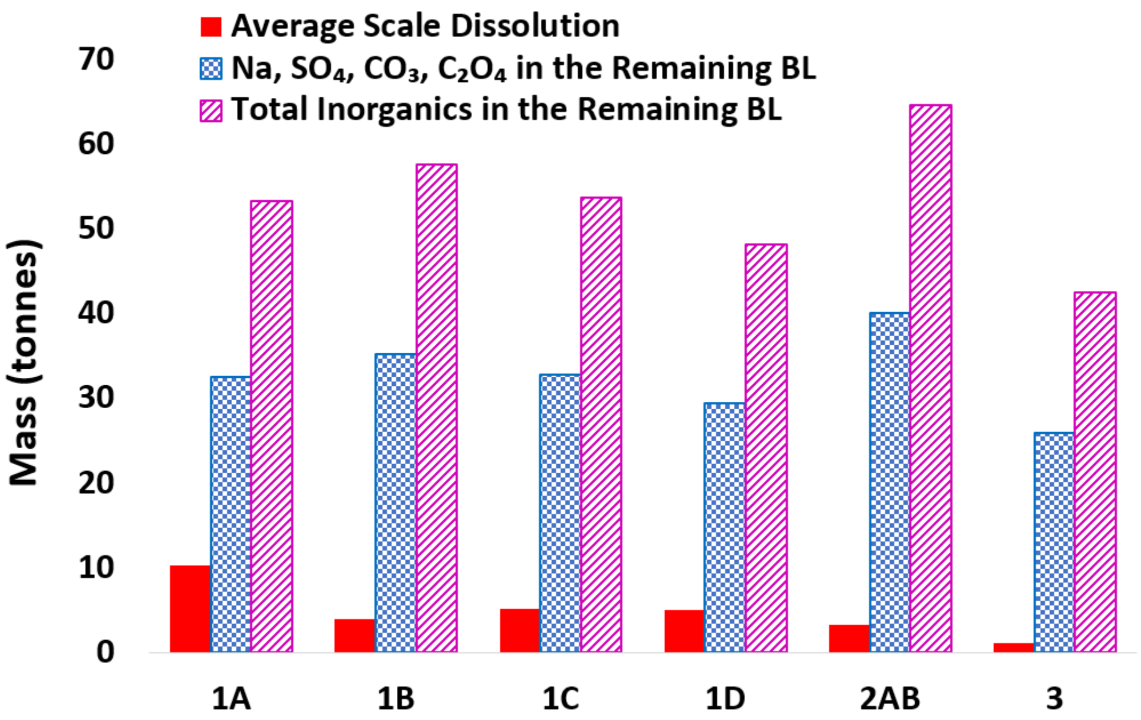

Figure 16. Comparison of average mass of scale dissolution with the mass of sodium, sulfate, carbonate, oxalate, and overall inorganics in the remaining black liquor.

The dynamic portion of the Simulink model provides output shown in Figures 17 to 19, which illustrate the fluctuations in liquor dry solids and chemical species. These fluctuations occur due to a combination of factors, including changing liquor flow rate and tank levels, varying quantities of scale dissolution and black liquor recovery, different amounts of wash water used, and varying salt concentrations in the scale and liquor.

During the modeled time period, the dry solids content in the spill liquor tank ranges from 8% to 28% (Figure 17). The lower end of the range corresponds to the washing of evaporator 2A/B, where condensate was used instead of weak black liquor. The higher solids range is observed in the washing of the concentrators, particularly in 1A with residual black liquor having a dry solids content of around 74%, and between 60% and 70% in 1B/C/D. The effect of dry solids from wash water recovery is attenuated in the black liquor exiting the feed liquor tanks. This is because the mass flow rate of wash water recovery from the spill tank is approximately 5% of the mass flow rate of weak black liquor from the brown stock washer, and the volume of liquor in the feed liquor tanks is relatively high compared to the recovered wash water flow rate (refer back to Figure 11).

The dampening effect can also be observed in the sodium and oxalate concentration plots per black liquor dry solids (Figure 18, Figure 19). The two small spikes in sodium concentration (indicated by periods highlighted in Figure 18) were results of washing 1A/B/C/D bodies within hours from each other, where the wash water brought back dissolved scale and remaining black liquor with higher sodium content compared to the lower sodium content in the weak black liquor from the brown stock washer. On the other hand, the oxalate concentration in the feed liquor tank is higher than in the spill liquor tank due to the higher oxalate concentration in the weak black liquor from the brown stock washer. The two noticeable drops in oxalate concentrations (indicated by the highlighted periods in Figure 19) corresponded to the same periods pointed out in Figure 18, where 1A/B/C/D were washed within a short time frame of each other, as the remaining black liquor in the concentrator had a lower oxalate concentration than the weak black liquor. Overall, the combinations of the amount of scale dissolved, the amount and type of wash water used, and tank liquor volumes, led to the results that in this mill, dry solids and chemical fluctuations in the feed liquor are unlikely to cause significant sodium salt scaling in the evaporators.

It is important to note that the chemical compositions assumed for scale, remaining black liquor, and weak black liquor were based on limited chemical analysis, and further mill sampling is required to validate the model inputs and outputs. The suggested future work includes collecting and analyzing additional samples of wash liquor at frequent intervals to enhance the accuracy of model inputs regarding the mass and composition of scales washed out from different effects, as well as sampling in and out of the liquor tanks and the evaporator train to validate the model outputs from the dynamic simulation.

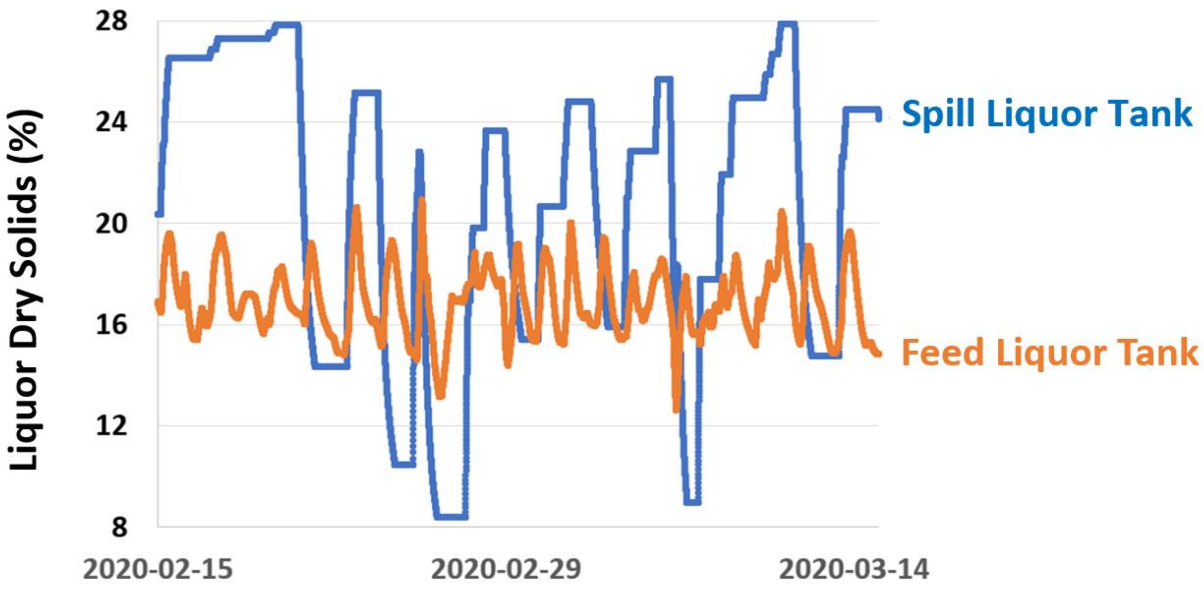

Figure 17. The dynamic simulation output of liquor dry solids content out of the spill and feed liquor tanks.

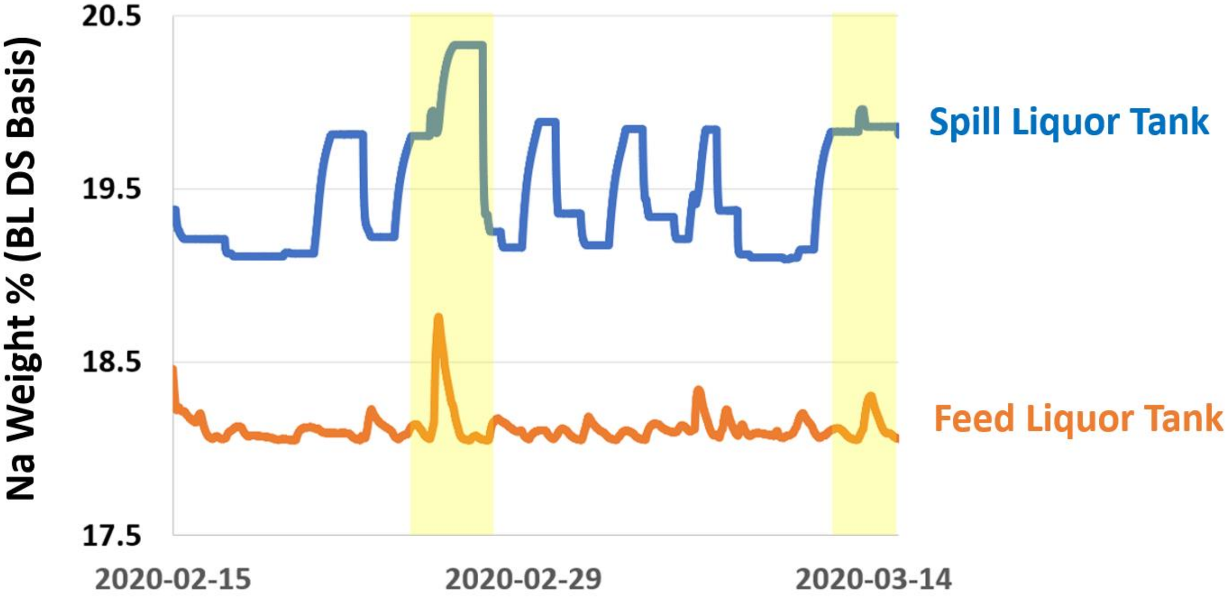

Figure 18. The dynamic simulation output of sodium content. The highlighted periods correspond to periods of when 1A/B/C/D were washed within hours from each other. It led to higher Na in the recovered liquor due to scale dissolution and the remaining liquor in 1A/B/C/D.

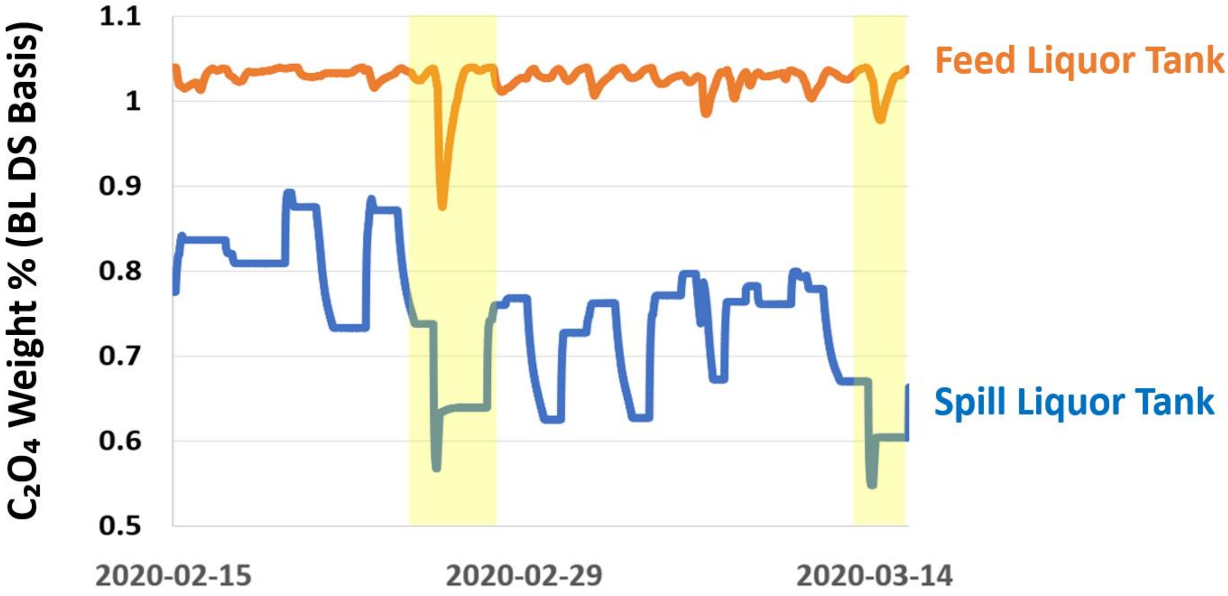

Figure 19. The dynamic simulation output of oxalate content. The highlighted periods correspond to periods of when 1A/B/C/D were washed within hours from each other. It led to lower oxalate content in recovered liquor due to no oxalate scaling in 1A/B/C/D and low oxalate content in the remaining liquor in those bodies.

Conclusions

A dynamic modeling approach assessed the impact of wash liquor recovery on black liquor chemistry by integrating real-time PI data, scale composition, and liquor property under the CSTR assumption.

For this mill, the simulation suggests that the combination of scale dissolution, wash water flow rate, wash liquor recovery rate, and tank volumes is unlikely to result in significant sodium salt scaling in the evaporators. In mills with notable evaporator fouling, smaller tanks, and rapid wash liquor recovery, fluctuations in feed liquor properties are more likely to lead to swift fouling events.

Future research work involves collecting and analyzing wash liquor at frequent intervals to improve model inputs regarding the mass and composition of scales washed out from various effects. Additionally, conducting liquor analysis on streams in and out of liquor tanks and the evaporator train to validate dynamic simulation model outputs.

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