Effects of varying total titratable alkali and causticizing efficiency targets on kraft pulp mill productivity

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ABSTRACT: The kraft mill causticizing area is often overlooked and undervalued when it comes to mill optimization; however, the operation of the causticizing plant has downstream effects on the entire liquor cycle. Setting the right targets for the causticizing plant can have a tremendous effect on mill operating costs, as well as push the production bottleneck from one unit operation to another. The key performance parameters associated with the causticizing plant itself are liquor total titratable alkali (TTA) and causticizing efficiency.

Individual facilities choose their TTA and causticizing efficiency targets based on their goals, the limits of their equipment, and past experiences. This gives a variety of operating strategies in practice, but what are the implications for optimizing total titratable alkali and causticizing efficiency, and what level of optimization can be achieved through implementation of modern technology? This paper reviews the results of several different operational strategies and models the effects of these different approaches on kraft mill liquor cycle.

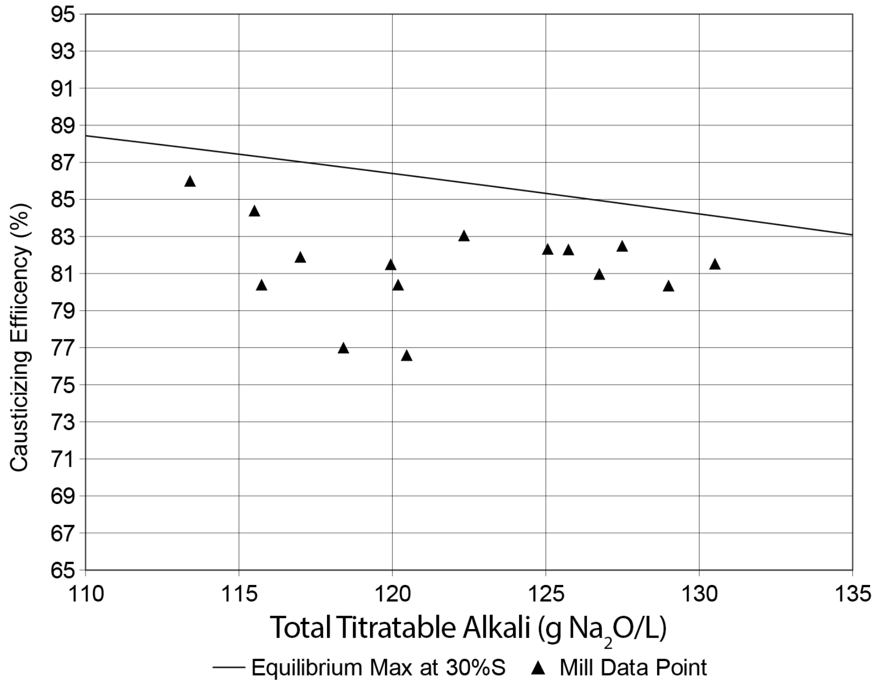
Application: This paper describes the effects of changing the targets for kraft liquor total alkali and causticizing efficiency on the different unit operations in the pulp mill. The value of maximizing both total alkali and causticizing efficiency, as well as a method of optimizing both key performance variables, is described.

The primary function of the kraft mill causticizing plant is to convert the inactive sodium carbonate in green liquor to active sodium hydroxide, which is an active cooking chemical component of white liquor. The chemical conversion starts in the slaker where lime is dosed into the clarified green liquor. The resulting slurry flows to the causticizer train where the causticizing reaction is ideally completed. The primary control points and key performance indicators for the causticizing plant are total titratable alkali (TTA) and causticizing efficiency or active chemical concentration. Total titratable alkali concentration is initially controlled by regulating dissolving fluid flow to the recovery boiler smelt dissolving tank. Sometimes, an additional control point is implemented where trim dilution is added to green liquor going to the slaker to reduce green liquor quality variability for improved causticizing plant control. The control lever for the causticizing reaction is lime dosage, either by directly regulating lime screw speed or adjusting the setpoint for a mass of lime per volume of green liquor controller. Either way, the lime screw speed is adjusted to regulate the reaction, and the lime-to-green liquor ratio just helps maintain a constant liquor quality as the slaker flow production is changed [1].

A variety of methods for controlling these two levers have been implemented. Total titratable alkali is often controlled based on manual laboratory measurements, density measurements, process analyzers, or a combination of such techniques. Mills may choose between targeting effective alkali concentration or causticizing efficiency as the quality measurement for the white liquor product. Causticizing efficiency is a measurement of conversion of sodium carbonate to sodium hydroxide as described by Grace [2] in the equation below where NaOH is the concentration of sodium hydroxide and Na_2CO_3 is the concentration of sodium carbonate. These concentrations are typically expressed in North America on a sodium oxide (Na_2O) basis in units of g/L, lb/ft³, or lb/gal.

$$\text{Causticizing Efficiency} = CE\,\% = \frac{NaOH}{NaOH + Na_2CO_3} \times 100\,\%$$

Controlling lime addition to a causticizing efficiency target is useful because the target can be set relative to maximum achievable according to liquor sulfidity and TTA, along with the available equilibrium data. However, controlling to an effective alkali target is also understandable as the end goal is to charge the digester based on the desired ratio of effective alkali mass to wood mass. The problem with targeting effective alkali without regard to equilibrium is that as mill sulfidity or, more commonly, the TTA is changing, the equilibrium maximum will change. Thus, the operators may be doing a fantastic job controlling to the effective alkali target but could still find themselves over liming and fighting the mud separation equipment, or they could be far from the equilibrium maximum,



1. Example results of white liquor causticizing efficiency (CE) and total titratable alkali (TTA) for 15 North American mills. Mill data points are plotted against maximum achievable equilibrium curve, known as the Goodwin curve, at 30% sulfidity on an active alkali basis (Na_2O: sodium oxide).

leading to high chemical deadload and downstream process inefficiencies.

Regardless of the selected control method, each individual facility's targets for TTA and causticizing efficiency necessarily evolve to meet their ever-changing goals for production and costs according to the limits of their equipment capability and lessons learned from past experiences. Thus, although kraft chemical recovery is essentially the same chemical process at most kraft pulp mills, actual TTA concentrations and causticizing efficiencies vary greatly from mill to mill, as shown on the example equilibrium curve, known as the Goodwin curve, in **Fig. 1**. A discussion of why this occurs follows below.

The TTA concentration and causticizing efficiency (CE) are not independent of each other. As shown on the example equilibrium curve in Fig. 1, as TTA increases, the achievable equilibrium maximum causticizing efficiency decreases. Thus, mills that target higher TTA concentrations tend to target lower causticizing efficiencies, and mills that target lower TTA concentrations can safely target higher causticizing efficiencies. Thus, targeting lower TTA can be seen as an advantage, because running higher CE means that there is less sodium carbonate deadload. Reducing the chemical deadload in the liquor cycle is commonly known to be advantageous in terms of energy efficiency by reducing heating requirements of the chemical deadload in cooking and evaporation, as well as increasing efficiency of recovery boiler combustion. However, perhaps more importantly, reducing chemical deadload reduces the total solids throughput required to meet mill production goals [3]. This can be noted as reduced black liquor solids firing required per ton of pulp produced. This gives an apparent advantage for recovery boiler debottlenecking, although the resulting value of the debottlenecking will depend on what the black liquor solids throughput bottleneck of the recovery boiler itself is. Decreasing the chemical deadload does not decrease the organics to be burned; it decreases the inorganic loading and total loading. If the boiler is running at the steaming limit, the boiler solids throughput will simply have to decrease, as more steam will be generated per pound of black liquor solids. Similarly, if the boiler is limited by forced draft flow capacity, decreasing the chemical deadload may not help. The required forced draft air depends on the stoichiometric requirement of combustion, so if the same amount of organic solids needs to be burned, the same amount of air should be needed. However, if the boiler is running to environmental limits or flue gas flow limits, reduced chemical deadload could help. Not only does less deadload mean less inorganics to boiler, it also means there will not be the water that comes with the chemical deadload, so the flue gas volumetric flow will be reduced.

A strategy of lower TTA to potentially increase CE can have unexpected consequences. There are advantages to running higher TTA concentrations. Lowering TTA means adding more dilution to green liquor and, in turn, means that the final white liquor product will also have lower TTA, as there normally is no method of increasing TTA after the recovery boiler dissolver other than adding concentrated chemical makeup. Thus, lower TTA means lower white liquor active alkali concentration. Lower active alkali concentration means that more white liquor flow is required to meet the digester alkali-to-wood mass requirement. If one draws a circle around the cooking and washing processes, one should find that if more white liquor volume is added to the digester, more black liquor volume is passed on to the evaporators. This happens because the liquid volume-to-wood ratio in the digester should also be controlled, either by adjusting recirculation of black liquor back to the digester or by reducing extraction of black liquor from the digester. Thus, lower TTA concentration increases the white liquor flow through cooking and black liquor flow through evaporation [3]. This is hydraulic deadload on the liquor cycle. White liquor going to cooking must be heated to get to cooking temperature, so thermal efficiency is lost there. The extra volume of black liquor to evaporation will either increase steam use at the evaporator, or perhaps more critically, reduce the capability of the evaporator set to meet production needs.

The hydraulic deadload also shows up in the causticizing process as reduced residence times for causticizing equipment. It may be straightforward to see that if we further dilute the green liquor to reduce TTA, flow through the slakers and causticizers must go up to support the same mass flow of chemical. This hydraulic deadload increases the strain on the slakers and causticizers since they are designed to have the correct residence time for completing the slaking and causticizing reactions [2]. Dilution of green liquor can, therefore, either limit mill productivity or force operators to run the causticizing plant outside of design specifications, which tends to lead to more challenging operation of filters and clarifiers.

METHOD

We can observe these effects in an imaginary mill model. Consider a 1000 metric tons/day pulp mill. If we assume 50% pulp yield per mass of dry wood, we can calculate the mass flow requirements of active chemical based on the desired alkali-to-wood ratio. In this case, we will use an example charge of 13.5% effective alkali as Na_2O per ton of dry wood. In this way, we will hold the cooking alkali mass flow requirement constant but make changes to the TTA and causticizing efficiency conditions. We will also hold sulfidity constant at 30% on an active alkali basis. This will vary the volumetric flow requirements of white liquor to cooking and black liquor to evaporation, as well as the sodium carbonate deadload in the liquor cycle. We will also hold the recovery boiler reduction degree constant at 90%. This means, however, that as we change the TTA and causticizing efficiency, the sodium sulfide concentration will change, so the sodium sulfate deadload concentration will also be changing. For calculating the effects on evaporation, we will start with a baseline of 16.6% solids from the washroom to the evaporators. The weak liquor solids to evaporation changes slightly for each case as the chemical deadload is changing, but keep in mind that the bulk of the change in evaporation demand is from reducing the flow of water through cooking and washing to evaporation. We will keep the heavy liquor target constant at 70% solids and the evaporator specific heat of consumption 0.46 GJ/ton of water evaporated so that the changes in hydraulic and chemical deadload are seen as changes in water evaporation requirements.

For this paper, we will use a simple model employed by Valmet Automation to compare a base case TTA and CE to varying targets for TTA and CE that are within the range of actual mill results shown in Fig. 1. In the model, the aforementioned variables are held constant and the results of changing TTA and CE targets are based on mass and energy balances. As a reference, we will use recommendations from 1990 [3] and 1991 [4] of TTA at 120 g/L as the base case. We can see in Fig. 1 that some mills follow this recommendation, while some are higher or lower. In 1990, Dorris [3] also recommended a causticizing efficiency of 80% at this TTA concentration. We will set the base case at 79% CE, since some mills target 79% or even lower, as we can see in Fig. 1. Thus, all scenarios in the following tables we will discuss are compared to base case of 120 g/L TTA and 79% CE.

RESULTS AND DISCUSSION

We will start with scenarios increasing TTA only while holding causticizing efficiency constant, as shown in **Table I**. In these scenarios, a 2.5% increase directly results in a 2.5% increase in white liquor effective alkali. This is hopefully clear, since increasing the TTA concentration should increase active chemical concentration. Likewise, the liquor is 2.5% stronger, so the flow through the causticizing area is 2.5% lower. Since multiple effect evaporators are designed to be efficient at their work, we do not see the full hydraulic debottlenecking effect, but if we can increase the TTA by 7.5%, we can debottleneck the evaporators by more than 3%.

The downside of increasing the TTA at constant CE is that we are also increasing the concentration of the deadload, and higher deadload means more black liquor solids per ton of pulp and increased risk of evaporator fouling [5]. We also need to recognize that as we increase TTA, we change where we are operating on the equilibrium curve, so it will be more difficult to achieve a higher CE; however, we can see in Fig. 1 that mills are able to achieve more than 79% CE even at TTA greater than 129 g/L. Still, there are other factors to consider before we raise green liquor TTA through the dissolving tank roof. As green liquor TTA increases, the concentration of sodium carbonate in the green liquor increases; therefore, running higher TTA increases the risk of forming pirssonite scale in the dissolver and green liquor piping [6]. Pirssonite is formed from sodium

TTA, g/L	TTA Change	CE, %	CE Change	White Liquor EA Concentration Increase	Na_2CO_3 Deadload Reduction	Causticizing Hydraulic Debottlenecking	Evaporator Hydraulic Debottlenecking
123	2.50%	79	0.00%	2.50%	-2.50%	2.50%	1.09%
126	5.00%	79	0.00%	5.00%	-5.00%	5.00%	2.12%
129	7.50%	79	0.00%	7.50%	-7.50%	7.50%	3.13%

TTA: total titratable alkali; CE: causticizing efficiency; EA: effective alkali; Na_2CO_3: sodium carbonate.

I. Scenarios increasing TTA only and compared to baseline of 120 g/L TTA and 79% CE.

TTA, g/L	TTA Change	CE, %	CE Change	White Liquor EA Concentration Increase	Na_2CO_3 Deadload Reduction	Causticizing Hydraulic Debottlenecking	Evaporator Hydraulic Debottlenecking
120	0.00%	80	1.27%	0.94%	5.07%	0.94%	0.30%
120	0.00%	81	2.53%	1.88%	10.10%	1.88%	0.59%
120	0.00%	82	3.80%	2.81%	15.10%	2.81%	0.87%

TTA: total titratable alkali; CE: causticizing efficiency; EA: effective alkali; Na_2CO_3: sodium carbonate.

II. Scenarios increasing CE only and compared to baseline of 120 g/L TTA and 79% CE.

carbonate as well as calcium carbonate. Most mills periodically swap recovery boiler green liquor and weak wash lines to allow the weak wash to redissolve the sodium carbonate. However, the calcium carbonate is left behind; thus, repeated high TTA excursions grow the scale over time [7]. Therefore, a high TTA target requires good control of TTA to prevent high TTA excursions. The target also needs to be picked with consideration of liquor chemistry, as the relative amount of sodium carbonate in green liquor is changing over time as parameters like mill sulfidity and weak wash quality are changing, which changes the amount of sodium sulfide and sodium hydroxide in the green liquor [1]. A higher TTA has also been seen to reduce the causticizing reaction rate [4].

Next, we look at the effects of increasing causticizing efficiency while holding TTA constant at 120 g/L, as shown in **Table II**. As the causticizing efficiency is increased, the relative amount of sodium carbonate deadload in white liquor is significantly decreased. The hydraulic deadload is also decreasing, which leads to some causticizing and evaporator debottlenecking since the effective alkali concentration is increasing. Causticizing efficiency also has a great effect on evaporator scaling, as it determines the amount sodium carbonate deadload in the liquor cycle [5]. Sodium carbonate content, in combination with sodium sulfate content, largely dictates at what black liquor solids concentration burkeite precipitates in the evaporators [8]. Thus, manipulating CE can influence where in the evaporation process burkeite begins to form. For example, a low CE increases the sodium carbonate deadload, which may lower the burkeite precipitation critical solids point towards the operating target for a long tube vertical (LTV) evaporator set where the rapidly forming scale will severely limit throughput capacity [8].

So, clearly, every mill would run at the equilibrium limit of causticizing efficiency if they could. The well-known problem is that the closer the lime dose runs to achieving maximum CE, the greater the risk of over liming. Over liming, or being too close to over liming, leads to small lime mud particles that are difficult to separate from white liquor [9]. For clarifier operation, over liming can lead to poor settling mud that is difficult to thicken and pump away from the clarifier underflow, leading to possible equipment plug ups and damage. Still, clarifier mills can often get away with a little over liming compared to mills with white liquor filters. Over liming leads to rapid blinding of filters and increased need for acid washing cycles. Mills with white liquor filters in operation are typically more risk averse to running higher causticizing efficiencies compared to clarifier mills. Either way, the average causticizing operator will not appreciate being asked to run a higher lime dose than typical based on past experiences.

In fact, this is where most control schemes fall short on true causticizing process optimization. Without accurate information of how close the operation is to the chemically dictated maximum, the operation risks a process variation swinging the TTA concentration or suddenly changing the lime quality. The causticizing efficiency approaches the maximum, and the operator does not have the information required to make a change in time. A great day at work suddenly turns to back-breaking labor. Yet in Fig. 1, we see that several mills maintain TTA and CE targets that keep

TTA, g/L	TTA Change	CE, %	CE Change	White Liquor EA Concentration Increase	Na_2CO_3 Deadload Reduction	Causticizing Hydraulic Debottlenecking	Evaporator Hydraulic Debottlenecking
123	2.50%	83	5.06%	6.33%	18.07%	6.33%	2.20%
126	5.00%	82	3.80%	7.95%	10.86%	7.95%	2.94%
129	7.50%	81	2.53%	9.52%	3.36%	9.52%	3.66%

TTA: total titratable alkali; CE: causticizing efficiency; EA: effective alkali; Na_2CO_3: sodium carbonate.

III. Scenarios with different TTA and CE targets at approximately 3% CE below equilibrium maximum compared to base case of 120 g/L TTA and 79% CE.

them quite close to the limit compared to others. We will compare some scenarios where the TTA and CE targets are set to approximately 3% below the equilibrium maximum CE as shown in **Table III**.

By increasing the TTA and then pushing CE to near 3% of the equilibrium limit at that TTA, we achieve the greatest process debottlenecking. In the case of 129 g/L TTA and 81 g/L TTA, nearly 10% causticizing plant debottlenecking and over 3% evaporator debottlenecking is achieved. Keep in mind this is compared to 120 g/L, but as we can see in Fig. 1, TTA is often as low as 115 g/L. We can see that maximizing both CE and TTA is directionally correct, so we will explore what stops every mill from doing as well as some of the mills shown in Fig. 1.

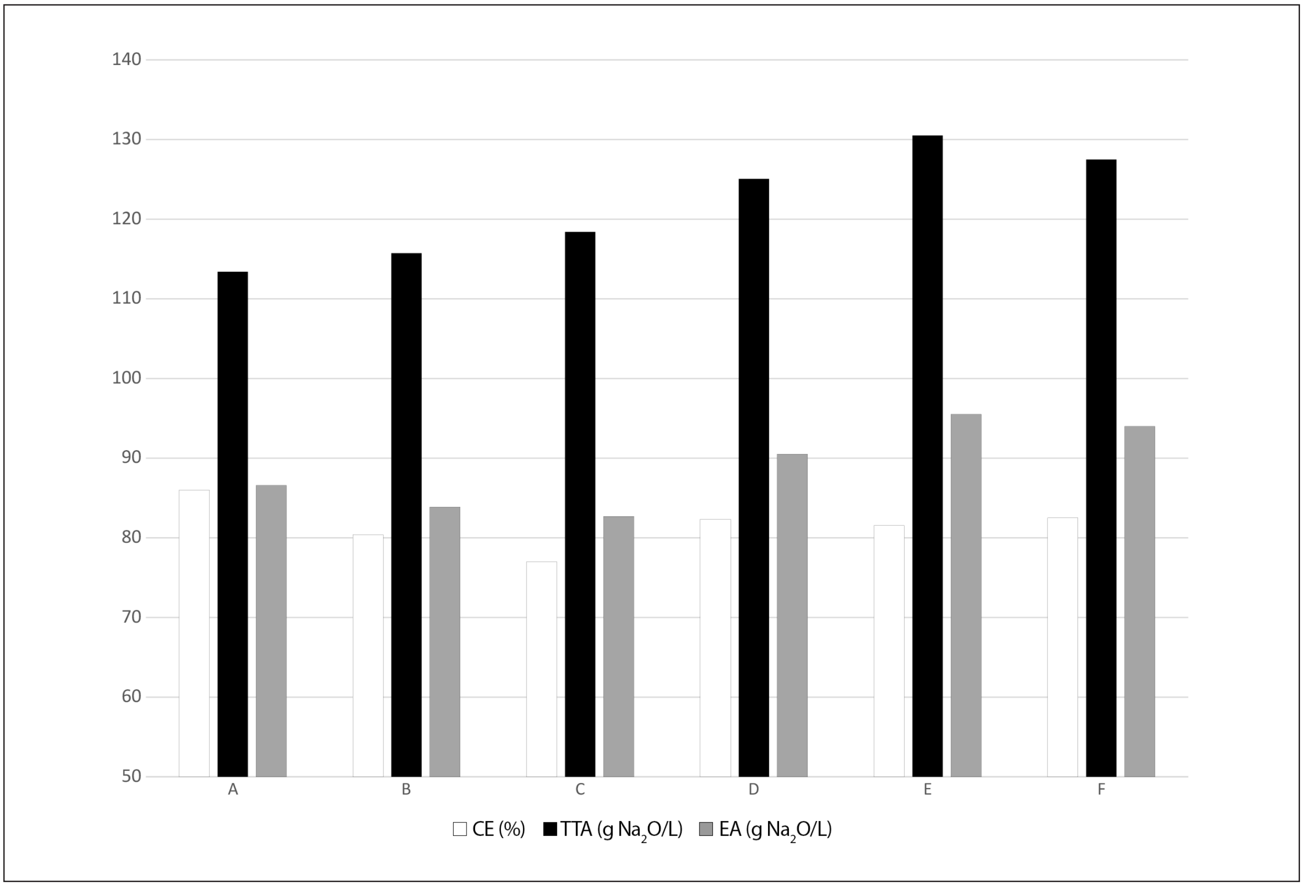
We must keep in mind the limits of the available equipment. Raising the TTA decreases the green liquor flow, and raising the CE requires increasing the lime dose per gallon green liquor. The net lime use for the same mill production rate remains the same, since volumetric flow requirement is equivalently decreasing as the active cooking chemical concentration increases; however, the amount of heat absorbed from the slaking reaction per gallon of green liquor will also increase, so there is an increased risk of boiling the slaker. This is not a problem for some mills, depending on their inlet green liquor temperature and whether they are equipped with a green liquor cooler, but something to consider when setting targets. Similarly, reaction time is needed for slaking and causticizing. We can achieve causticizing hydraulic debottlenecking with optimized targets, but a grossly undersized causticizing train simply may not have enough residence time to move the reaction far enough along to reach a desired efficiency, regardless of how accurate the lime dosing is. As an observation, a well-sized causticizing train can make up for a fair amount of control error in terms of running high TTA and CE targets without incurring downstream upsets from over liming.

However, there are two main factors that drive conservative TTA and causticizing efficiency targets: process variability and data accuracy. For a manually operated causticizing plant, the final CE standard deviation is typically around 5%. For our 120 g/L TTA base case, 80% CE compared to a CE maximum between 86% and 87% may make sense to avoid over liming if variability is high. Likewise, if our control scheme does not consider how close the operation is to the equilibrium limit, such as when using a simple control method alone like differential temperature or conductivity, a conservative target must naturally be chosen. This is because a low TTA event will eventually occur, and the operator will have a bad day with an over liming event. Even if TTA is constant, the green liquor quality can be changing, as the amount of sodium hydroxide and sodium sulfide in the weak wash going to the dissolver is varying [1]. Perhaps this base case is derived from 1990 conventional wisdom, and conventional wisdom may often be the best kind of wisdom for the unchanging ways of the world. Green liquor is comprised mainly of sodium carbonate, sodium hydroxide, and sodium sulfide in 2023, just as it was in 1990. But what has changed is the availability of accurate measurement devices for green and white liquor chemistry, and the successful implementation of advanced controls using the data from process analyzers for causticizing controls [10-14].

Figure 2 shows the differences in TTA and CE targets for six of the mills from Fig. 1. Mill A runs a quite high CE, over 86%, but does so at a lower TTA than all others. Mill C runs a more aggressive TTA than Mill A and Mill B, but clearly must be conservative with causticizing efficiency to avoid over liming. These mills suffer from high variability and limited or inaccurate data. Mills D, E, and F have aggressive TTA targets but still maintain a high CE of at least 81%. These mills combine process analyzers with advanced controls to continuously optimize causticizing plant operation. The combination of aggressive TTA and CE yields the greatest effective alkali concentration to cooking. This gives these mills optimized conditions for hydraulic deadload and chemical deadload reduction, yielding benefits in terms of operational costs and productivity.

CONCLUSION

The causticizing plant often gets less attention and resources than the paper or board machine. After all, we need to make the paper to make the money. However, the health of the causticizing plant affects the health of the entire



2. Total titratable alkali (TTA), causticizing efficiency (CE), and effective alkali (EA) results at six mills from Fig. 1. The combination of aggressive TTA and CE targets shown for Mills D, E, and F yields the highest EA strength to cooking, as well as optimum conditions for hydraulic deadload and chemical deadload reduction.

pulping process, and a well-managed causticizing plant can make the difference between a mill meeting its goals or falling short.

Total titratable alkali and causticizing efficiency targets should be carefully considered to support the pulp mill's needs. The plant can be optimized to alleviate strains on the various operating units in the liquor cycle. Past practices have called for conservative TTA and causticizing efficiency targets to avoid the unknown causing process upsets; however, the implementations of process analyzers and advanced control systems are becoming increasingly widespread in North America as these technologies make the unknown known and allow for more aggressive targets that maximize profitability and productivity. **TJ**

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ABOUT THE AUTHORS

Total titratable alkali (TTA) and causticizing efficiency (CE) optimization is a valuable tool for improving productivity in North American mills. This paper seeks to prove the value of maximizing both TTA and CE and show that it is possible to optimize both, which many others have challenged in the past.

Conventional wisdom suggests that the TTA and CE targets shown in this work are not achievable. I sought to prove these targets can be achieved and should be targeted for optimum mill operation. Three years ago, when I joined Valmet, I had a difficult time believing in maximizing both TTA and CE, because I was used to operating a causticizing plant based off manual lab tests. However, once I saw the results of the best available measurement and control strategies, I saw that I was living in the past. The operational strategies employed in North American pulp mills today are largely dictated by limits that were established 30 years ago. These limits can be overcome with modern technology.

Causticizing plant optimization is often underappreciated, but maximizing TTA and CE can allow mills to meet production goals that were previously unachievable with the same operational units. As a next step in this research, the modeled data presented here could be validated with advanced software tools.

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