Chemical and Energy Savings by Efficient Brownstock Washing – Mill Experiences

Carlos Alberto dos Santos, Mathiesen Group, csantos@grupomathiesen.com
Hannu Hämäläinen: Nopco Paper Technology, Finland, hannu.hamalainen@nopco.fi
Ariel Lamonato, Mathiesen do Brazil, alamonato@grupomathiesen.com
Ramon S. Dorronsoro: Nopco Paper Technology, Spain, ramon.dorronsoro@nopco.es

Abstract

This paper discusses developments and mill experiences pertaining to usage of state-of-art brown stock chemistries capable for improving productivity with robust design. Examples are provided how different unique methods are utilized to design appropriate washing chemistries, to improve drainage and for safe operations. Recent mill experiences are provided show casing compelling ideas how to gain significant energy and chemical savings through unorthodox ways to operate brown stock washing.

Keywords: kraft pulping; eucalyptus; silicone defoamer; drainage; washing efficiency, chemical savings.

Introduction

At the pace of steadily increasing energy prices worldwide, which impact chemical costs, savings associated with higher performing operations at kraft pulp mills have grown of importance for the total economy of a pulp mill. In fact, a kraft pulp mill is a significant producer of bioenergy with its black liquor. Brownstock washing (BSW) is an important step where two valuable products are separated: the pulp fibre, and the black liquor recoverable for energy. BSW is thus a crucial process area but today it is often neglected. For a deeper understanding of BSW there is abundant knowledge available in literature [1,2].

From chemistry viewpoint, brownstock washing is a heterogenous process involving solid state fibre and liquid media. Additionally, mixed phase systems incorporating soaps, surface active particles and abundancy of hydrophobic and hydrophilic substances makes it even more complex to manage. Traditionally the brownstock area layout has been designed to remove lignin with as compact machine design as possible, whereas less emphasis has been focused on managing the chemistry. Currently a somewhat standard chemistry design is to use dispersants to control pitch removal, and defoamers to eliminate foam in process.

The development of brownstock defoamers dates back to early stages of Kraft pulping and has evolved since then through improvements in application chemistry, changes in pulping process design and regulations. Silicone emulsion defoamers, pioneered by Nopco since 1980's, set the standard of today's brownstock washing operations. As of late, the importance has shifted from killing the foam into enhanced drainage and robust operation to maximize production and secure clean pulp.

Robust process chemistry not only requires an understanding of process control, usually measured as wash loss (COD or soda loss), conductivities of filtrates, black liquor solids to evaporation, etc., but also profound understanding of process design & limitations, ways of operation, automation & control, as well as understanding deeply enough surface chemistry and washing phenomena. Lack of overall view is often seen as sub-optimization of brownstock area with further productivity potential being suppressed. A one-eyed articulation of sub-optimization is using cheapest possible defoamer at lowest possible unit cost. The end result may be seen as dirtier pulp with higher bleaching cost, or lower generation of energy.

To assess the whole system, one must take into consideration:

- Wood (fibre) type
- Operational parameters
- Chemistry
- Application know-how
- Equipment design (washer types)

While we concentrate on chemistry in this paper, the other parameters are closely linked to it. For example, wood type plays two roles: fiber length affects equipment design and fibre mat behavior in washing. Hardwood (short fibre) and softwood (long fibre) have not only different lignin chemistry but importantly, different surfactant chemistry too. Softwoods bring with soap and conditions more prone to foaming.

Operational parameters are much linked to equipment design: production rates, consistencies, dilution factor, tank levels, filtrate flow levels, dilution levels, pressures, vat levels, temperature, process stability etc. all effect the final result if not directly, at least indirectly.

Equipment design is usually inherent to original design applied when a mill was constructed. Later upgrades are possible, but there is historically a grand variation in types of washers used, which all have their unique optima in terms of operation parameters. The most common washer type today is perhaps Drum Displacer (DD), followed by wash presses, drum filters, compaction baffle washers, diffusers and chemiwashers. Experience and literature tell the different washer types have their own best practices of operating parameters, some of which are universal from one washer type to another. For example, while for an atmospheric drum filter it is advisable to run a reasonably low rpm, keep vat level suitably high and inlet consistency low, a DD-washer clocks highest washing efficiency values with higher inlet consistencies and the important parameters to manage are inlet pressure and filtrate flows. A press requires to maintain stable consistency and pressure. A pressure diffuser benefits from higher dilution, not so much with atmospheric diffuser.

Chemistry, given its multitude of possibilities, has to be designed keeping in mind the above framework. However, certain chemical phenomena are universal and can be theoretically applied to any washing process. In fact, a lot of analogy can be sought in detergent or laundry industry for example. Semantics aside, defoamer is the common nominator today to describe a chemical additive to improve BSW. Not fully correct as a state-of-art defoamer is more than a mere foam killer, but it serves as a nominator here as foam and entrained air play key roles in BSW after all. We need to look first at the environment where BSW is operating, namely a liquor media which has tendency to foam. Conditions to produce foam can be identified as:

- Mechanical energy input into the system to expand the total surface area (agitation, pouring, shaking, stirring, depressurizing, aeration by blowing or injecting gas)
- Presence of a surface active agent (soap, tenside) to lower the surface tension
- Rate of foam formation greater than rate of foam collapse

Defoamers work through puncture and rupture of air or foam bubbles: a defoamer spreads on interfaces and penetrates between bubble lamellas. The water and surfactants make way to the defoamer in the bubble film, thinning the lamella until it breaks and collapses. Silicone emulsions have additionally higher capability of reducing the local surface tension by forming a very thin film on the interface and allow the tiny particle on the surface of oil droplets to faster migrate between lamellas and penetrate and break the film.

The same effect applies to entrapped air at liquor-fibre interface where tiny air bubbles hamper drainage, thus making silicone defoamers more effective compared to oil-based ones. For a deeper understanding of defoaming theory and applications, there are excellent books available in literature [3].

Traditionally defoamers were only used to break down visible surface foam. In the pulp industry, products used were easy at hand like kerosene, fuel oil or other light oil products. In the 1970s, EBS (ethylene bis stearamide) wax boosted oil based pulp defoamers came into use. Experiments with silicone based defoamers started already around 1950's, based on polydimethylsiloxane (silicone oil) dispersed in water or light oil. First defoamers with hydrophobic particles (hydrophobic silica) in light oil were patented in 1960's.

Early 1970s, hydrophobic waxes like ethylene bis stearamide (EBS) dispersed in oils were developed into efficient defoamers, but these became expensive and resulted in a push for reduction of the oil content, together with other problems of EBS, mostly its affinity with pitch to create deposits in hardwood lines. The development of silicone based defoamers has continued, using different emulsifiers and modified silicone oils.

Early 1990s, pioneered by Nopco Paper Technology, silicone emulsion defoamers that caused less surface disturbances were used in the wood pulping industry with great success. These improved chemistries allowed better washing, reduced chemical and biological oxygen demand (COD and BOD) in effluent and cleaner pulp.

A good defoamer to counteract foam formation and act as washing aid has to possess several capabilities: insolubility in foaming media, surface tension lower than media, dispersing properties in media, fast and even spreading in media to name but a few. Numerous chemicals are capable of these, with varying efficiency, but in general we have two established groups of chemistries used today in BSW, "oil-based" and "silicone emulsion" defoamers.

Oil-based defoamers are efficient foam killers at temperature range of 0-100C. They typically contain ethylene bistearamine (EBS) or hydrocarbon waxes, mineral oil, hydrophobic silica and surfactants. They are proven, cheap foam killers, but insufficient wash aids as they lack capability to improve drainage in pulp washer mat.

Silicone emulsions are excellent foam killers and wash aids at 0-100C. They are typically emulsions containing polydimethylsiloxane backbone (PDMS) which is a chemically inert, very low surface tension, flexible polymeric frame allowing fast and even spreading on foaming media. In addition, silicone emulsions contain hydrophobic silica and surfactants in various proportions. Silicone emulsions allow lower dosing than oil-based defoamers.

When formulated right, they have lower tendency towards fibre and hydrophobic material such as resin and soap. Silicone emulsions are pre-emulsified for easier dosage. Nopco silicone emulsions are formulated to follow filtrates and not fibres or soap to eliminate carry-over and allow safe operation.

The key is selection of raw materials and appropriate formulation in a given BSW system with required knowledge of emulsification chemistry. For example, PDMS as such is highly hydrophobic and sparsely soluble in water, but can be formulated with reactive/functional groups for desired properties. It is however easy to design a cheap and powerful defoamer; take kerosene as example. It takes an art however to design a robust and efficient defoamer or wash aid which is also safe from regulatory aspect (not contain wax, mineral oil or precursors to dioxin), does not interfere with soap and other tacky or hydrophobic substances, thus enabling trouble free operations and clean pulp.

Kraft Pulp Brown Stock Washing Efficiency

BSW efficiency is typically measured by COD carryover (Chemical Oxygen Demand in pulp carried over from BSW to next stage). Mills sometimes correlate COD carryover with soda loss (sometimes expressed as sulfate loss) or just with conductivities in filtrate from pulp leaving BSW plant. These measurements are not adequate either, since conductivity is dependent on state of ions present in solution and COD is a sum parameter describing all oxidizable material, not only lignin and sulfur compounds, but also carbohydrates, methanol and other stuff that doesn't relate well with washing performance and subsequent bleachability of pulp. Leaching of washable material out of pulp into filtrates is a highly dynamic process too, affecting the real wash result [4].

Further, individual washer efficiencies can be calculated, but cannot be directly compared between different equipment at differing consistencies, therefore a so called E10 value (a more sophisticated measurement more recently applied) is sometimes referred to, but not as a daily operative control parameter. After all, here we refer to mainly COD and conductivity as parameters to highlight the impact on total cost of chemicals, since they are anyhow the readily available measurements in place at most of the mills and easily related to in practice.

Experimental

Industrial full-scale mill trials were carried out at number of kraft pulp mills, where Nopco and Mathiesen provided state-of-the-art silicone defoamer chemicals and application service. Before trials, each case was designed to follow Nopco - Mathiesen CleanPulp philosophy, which is a systematic process starting from auditing a mill process design, ways of operation, technical performance and process limitations to screening suitable chemical additives in laboratory, finally selecting & tailoring best product candidates for mill trials given the desired improvement targets for the mills.

Each step of the approach constitute an integral part of the process and none of them is to be neglected, since one need to take into account equipment design, operating parameters, chemistry and application know-how as described earlier. The concept is centered on maximizing productivity through following measures:

- Maximise production rate (through high drainage ability and stability/robustness)
- Increase BSW efficiency (through elevated stability and robustness)
- Reduce bleaching chemical cost and total operation cost
- Formulate defoamer NOT to produce deposits, safe operation instead
- In the light of the concept, the least and last consideration is minimization of defoamer dosage.

To unlock any improvement potential in BSW, this approach was adopted, where BSW efficiency is maximized chemistry-wise through turning upside-down the conventional thinking of minimizing defoamer unit consumption. Practical *experience and earlier literature show that a 1% increase in black liquor solids into evaporation can generate 1 MUSD energy surplus for an average mill.*

It is well documented in literature as well that reduction of 1 kg COD wash loss translates to reduction of 0,5 to 1 kg active chlorine consumption in bleaching, which would mean significant production cost reduction in bleaching plant by improving brown stock washing chemistry. This reduction also will reduce the effluent treatment load (COD, BOD, AOX, etc). Caustic and sulfur make up, poor soap separation and fouling of evaporators are another examples of poorly managed BSW, all of which proposing to have a proper look on BSW chemistry management. This philosophy has paved the way for the high share of Nopco defoamers in pulp industry.

The methods and data presented in this paper were done according to known standards of TAPPI [5], SCAN, ISO etc. unless otherwise stated.

Background mill results

Following mill cases present results that supported development of products and applications for pulping processes using different raw materials other than pine, like eucalyptus.

Mill case A

Case A is a typical kraft pulp mill which was earlier optimized for lowest possible defoamer unit cost. The mill had somewhat periodical issues with kappa variation, production disturbances with abrupt stops of varying periods. We identified the BSW was “too optimized” chemistry-wise, allowing little playroom for any minor upset. With a 180-degree turn in chemical philosophy, we switched current silicone defoamer to another one with more robust chemistry, applied a new dosing point alongside the existing old ones, and increased the total dosage with higher defoamer unit cost as such. In turn, the impact on total cost and productivity was remarkable.

With an elevated chemical dosing level and revised dosing points, we could allow more robust playroom for BSW with lower tendency to disturbances, which lead to more stable and augmented production level. A significant downwards trend was noted in online measurement of conductivity in filtrates.

Notable was the relatively long time to stabilize and optimize the system with associated change of liquor volumes in filtrate tanks until a new balance was established in the whole BSW plant. It took roughly a week to come down into new level, something of a fact that is often neglected when doing trials of too short time period (1-4 days or sometimes even less than a day). The conductivity trend translated also to cleaner pulp for easier bleaching. The savings in bleach chemicals more than offset the higher unit cost of defoamer in BSW. The additional revenue from increased pulp sales was even more important.

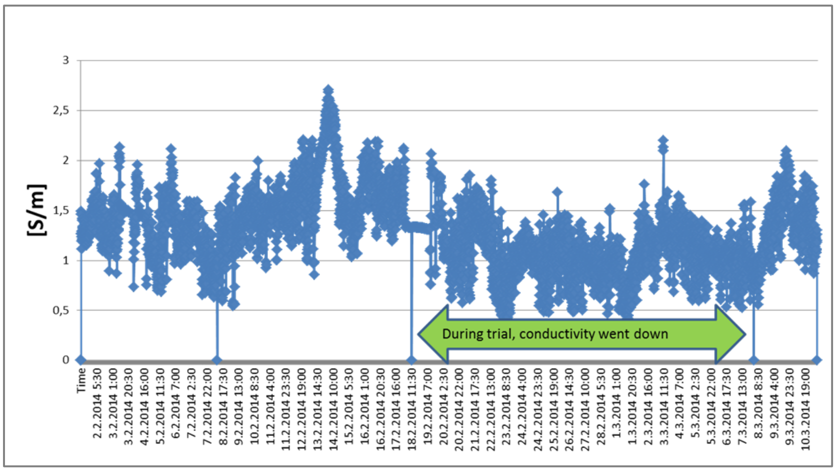


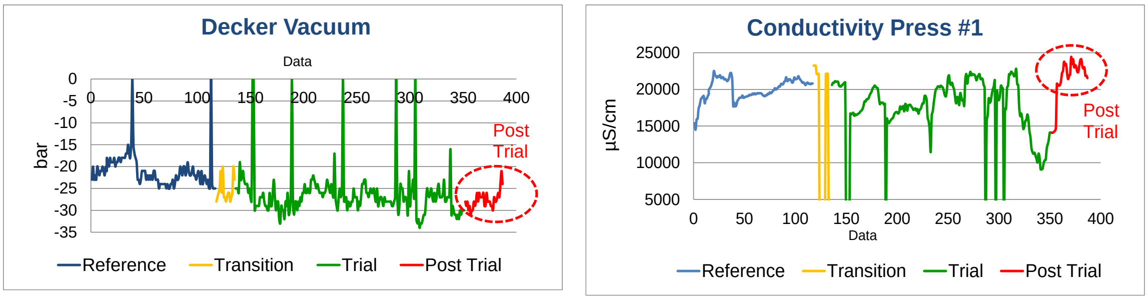
Figure 1. Conductivity of brownstock filtrate showing improved washing operations , which lead to cleaner pulp easier to bleach.

Mill case B

Case B highlights another brown stock washing improvement by increasing drainage rate of filtrates through the washer by using proper silicone defoamer or washing aid with drainage effects, replacing regular defoamer product without said effect, as showed on figures 2a,b and 3.

Likewise the previous mill case, “Mill B” bleaching operation was influenced positively by cleaner pulp entering first bleaching plant stage. Higher BSW efficiency was possible by higher drainage rate through the washer and presses. Evidence of this effect was showed by higher vacuum rates through deckers, with improved discharge. When trial stopped decker vacuum reduced instead. Wash press operations were also benefited by higher drainage effects through BSW.

Overall BSW efficiency improvement resulted in 10 to 15% lower conductivity in pulp carried out to bleaching plant. Savings in first month operation achieved an average of 1,0 kg ClO_2 / ADT, measured as chlorine dioxide. These savings would pay out several times cost of silicone defoamer as washing aids.



Figures 2 a, b: Other mill trial example of increased drainage to increase vacuum for higher washing efficiency, which is showed by reduced conductivity of brown stock filtrate, which led to cleaner pulp easier to bleach.

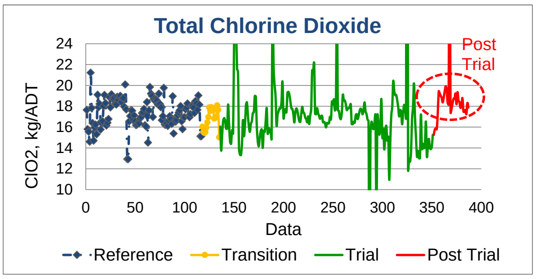


Figure 3. Chlorine dioxide savings.

Results and Discussion

Mill case C

Mill case C is a Brazilian eucalyptus kraft pulp mill, with conventional washing plant, whereas achieved brown stock washing improvement also by increasing drainage rate of filtrates through the washers by using proper silicone defoamer and washing aid formulated in same product with drainage effects, replacing regular silicone defoamer product.

First figure 4a below presents graphs of relative mill production on percent of production targets for reference and trial periods, both periods were on same level of 97% of target production. Second figure 4b shows the dilution factor profile, showing similar levels on reference and trial periods. Trial results were divided into two periods because second part of trial was done with significant increase on carryover from digester (Alkaline loss and COD), due to limitations on extraction screen in digester not related to trial.

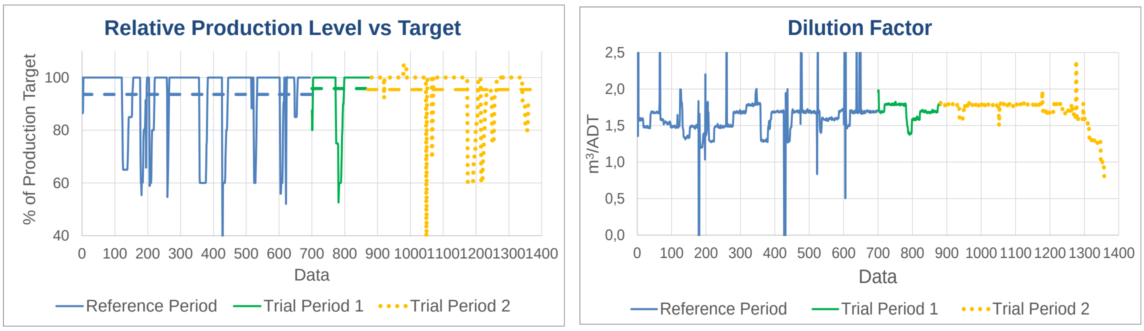


Figure 4 a,b: Production level and dilution factor on trial versus reference.

Following figure 5 shows the significant improvement on vacuum level of two brown stock washers promoted by filtrate drainage effects increase. Additional vacuum allowed gains on discharge consistency level, this higher consistency is confirmed by higher valve opening for pulp consistency control to feed oxygen delignification reactors, as showed on figures 6 a, b.

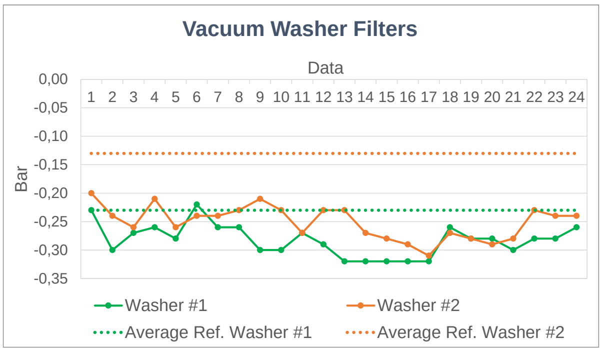


Figure 5: Vacuum washer filter increase.

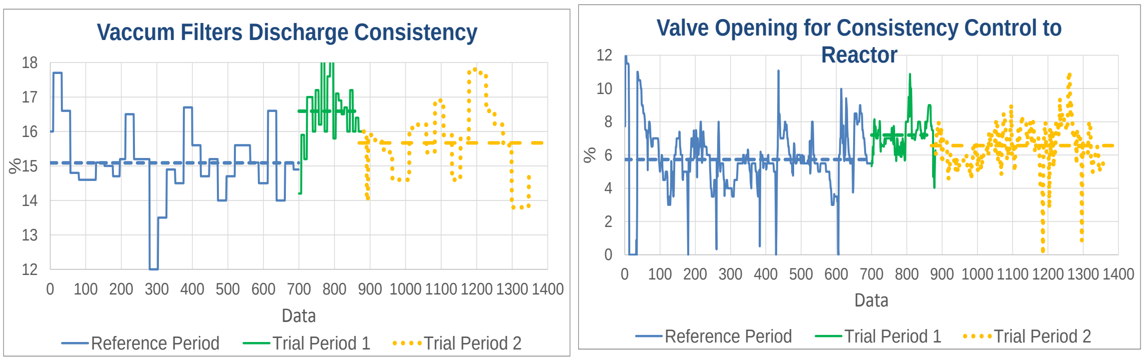


Figure 6 a, b: Vacuum washer discharge consistency and valve opening increase for consistency control to oxygen reactor.

Above vacuum effect is a firm evidence that filtrate drainage profile was improved significantly through vacuum washer, which would also positively benefited other types washers of BSW plant, like diffusers, presses or pressure washers. This improved drainage profile led to gains on washing efficiency which allowed higher removal backwards of the additional carryover digester.

Following figures 7 a, b show such additional higher alkaline carryover from digester and higher removal on Brown Stock Washing (BSW) during trial compared with reference. This higher carryover from digester was caused by limitations on digester extraction screens not related to trial. Similarly COD removal during trial was higher during trial compared with reference.

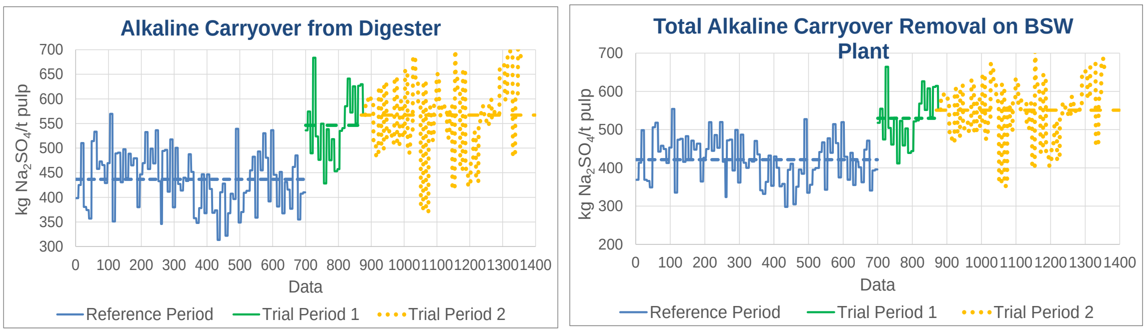


Figure 7 a,b: Alkaline carryover from digester and its washing removal.

Similarly to alkaline carryover, following figures 8 a, b show additional higher COD carryover from digester and also higher removal on Brown Stock Washing (BSW) during trial compared with reference. Similarly COD removal during trial was higher during trial compared with reference.

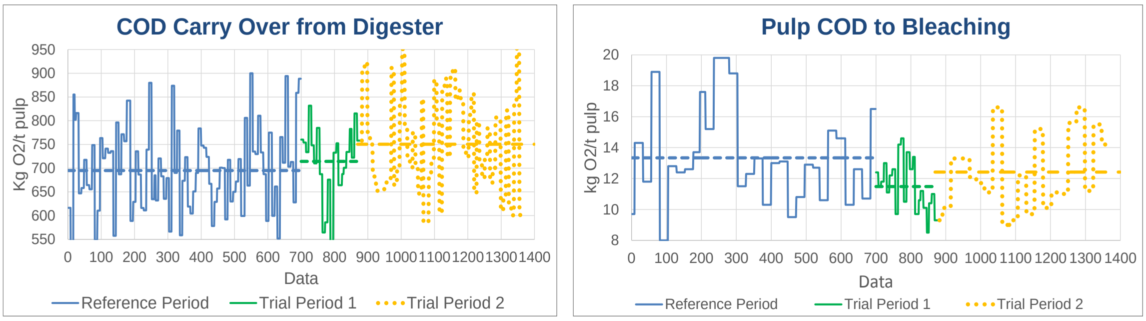


Figure 8 a,b: COD carryover from digester and its washing removal.

Likewise the previous mill case, “Mill C” bleaching operation was influenced positively by cleaner pulp entering first bleaching plant stage. Following figures show reductions on kappa factor and chlorine dioxide consumption during first phase of trial, even with somewhat higher alkaline and COD carryovers from digester above discussed. Second phase of trial the kappa factor and chlorine dioxide consumption were minimized even with much higher carryovers.

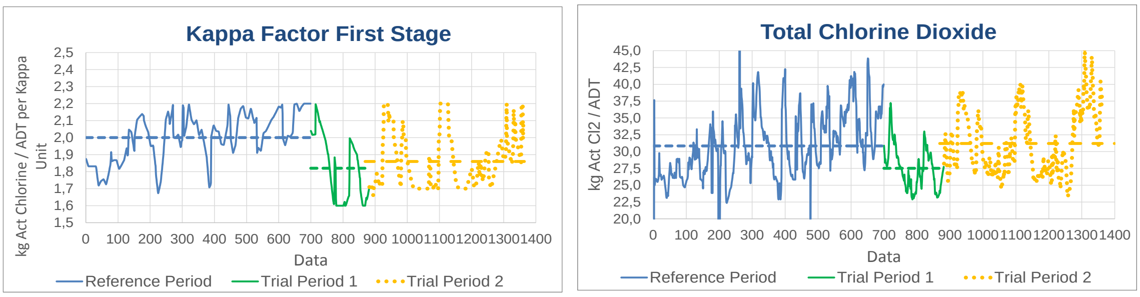


Figure 9 a,b: Kappa factor and total chlorine dioxide consumption.

Regarding other bleaching parameters, results were similar in terms of final brightness and other chemical consumptions, like caustic soda, hydrogen peroxide and sulfuric acid, following figures illustrate these results.

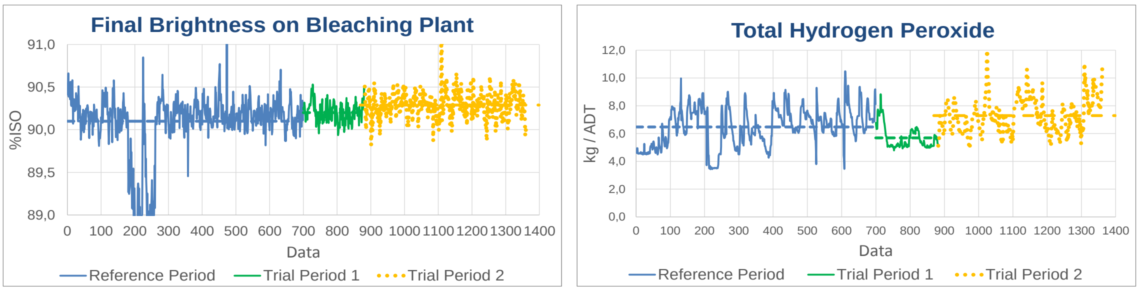


Figure 10 a,b: Final Brightness and hydrogen peroxide consumption.

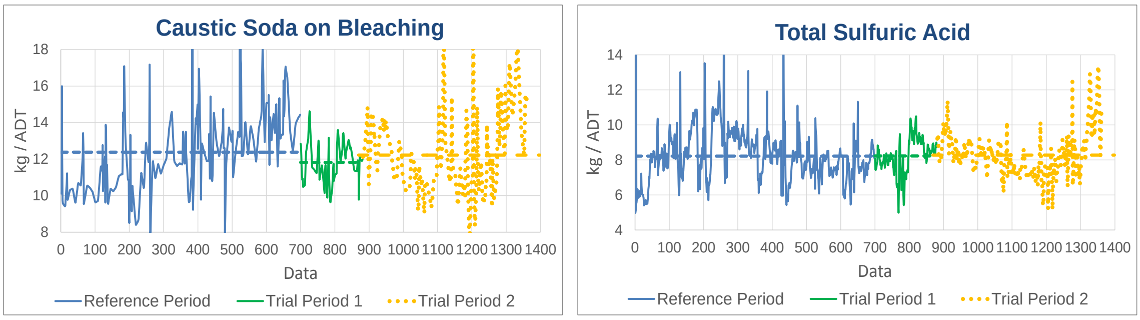


Figure 11 a,b: Caustic soda and sulfuric acid consumptions.

Mill case D

Mill case D is a Brazilian eucalyptus kraft pulp mill, with modern pressure washers (DDW), whereas also achieved brown stock washing improvement by increasing drainage rate of filtrates through the washer by using proper silicone defoamer and washing aid with drainage effects in same product, replacing regular silicone defoamer product.

Figure 12 below presents graph of relative mill production on percent of production targets for reference and trial periods, reference period was on average level of about 97% of target production, while trial period was close to 100% of production target.

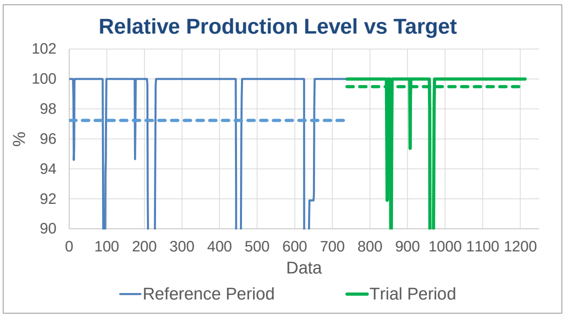


Figure 12: Production level.

Figure 13 show in first and final parts of trial higher level or peaks of COD carryover from digester, trial period was on average of about 10% higher COD than reference period. Following figures 14 a, b show higher removal on BSW during trial compared with reference. As result COD carryovers to Oxygen Delignification and to Bleaching were reduced compared with reference.

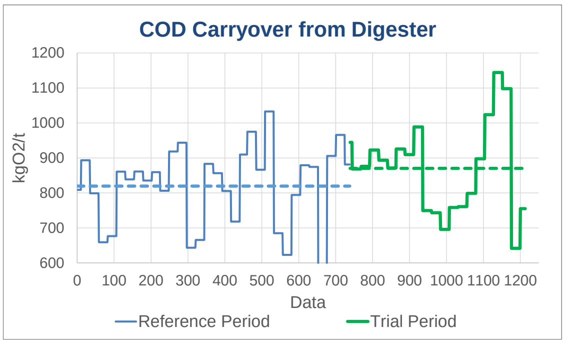


Figure 13: COD carryover from digester.

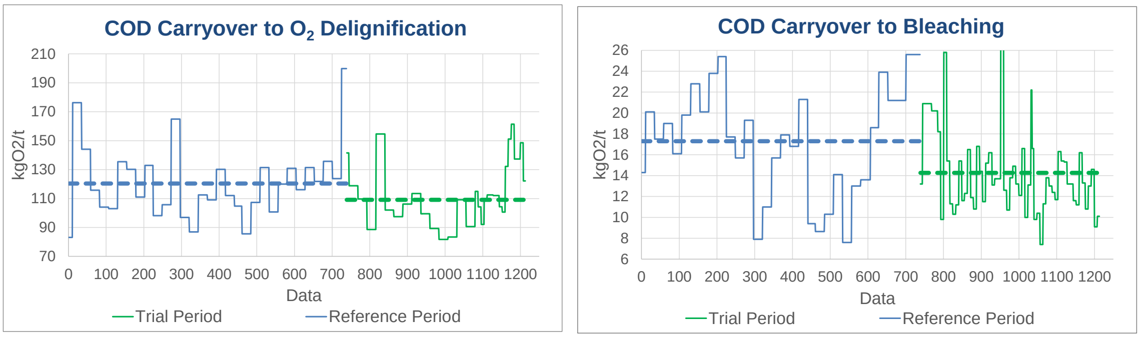


Figure 14: a, b. COD carryover to Oxygen Delignification and to Bleaching.

Figure 15 show Dilution Factor (DF) on reference versus trial period. Above better washing efficiency on trial period versus reference, about 10% lower COD, was achieved on about 14% lower DF, which is remarkable.

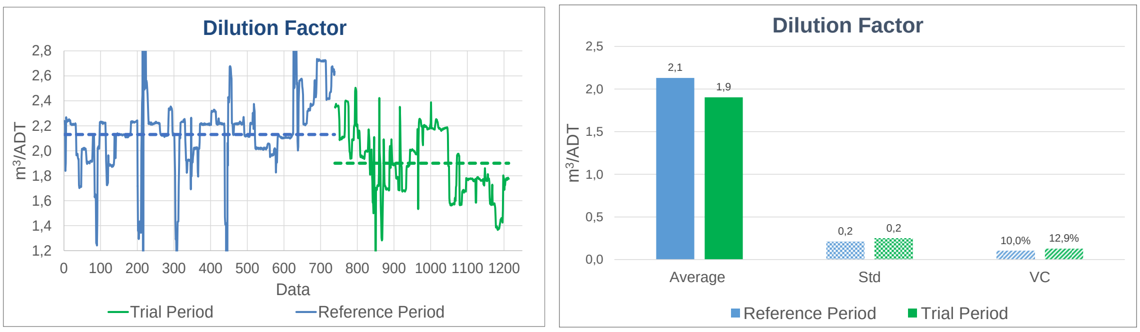


Figure 15: a, b. Dilution Factor and statistics on reference and trial periods.

Conclusions

Recent experiences demonstrate there is further potential to chemistry-wise unlock higher productivity in brownstock washing area which has reached machinery-wise the limits of capacity. Appropriately designed state-of-art silicone defoamer can successfully serve as washing aid to elevate washing performance of current BSW equipments. A revised BSW chemistry, even with higher dosage and unit cost, can translate into significant payback in bleaching and recovery costs without compromising pulp quality. However, it requires a decision making by switch from defoamer unit cost minimization to total cost savings perspective with following guidelines:

- Focus on improving process stability
- Designing robust chemistry with state-of-art wash aids
- Instead of unit cost, focus on total operational cost
- High-quality formulated products to avoid carry-over, guarantee safe operation instead

References

1. Pikka, O., Vesala, R., Carlsson, J. G., Steffes, F., Gullichsen, J., Pulp washing applications. In: Chemical Pulping (Ed: Papermaking Science and Technology series), ISBN 952-5216-06-03, Fapet Oy, Finland, pp. 573-601, (2000).
2. Kopra, R., Application of the refractometer in the measurement and monitoring of brown stock washing, Doctoral Thesis, MKKK, Finland, (2015).
3. Garret, P.R., ed. (1992). "3". Defoaming. Theory and Industrial Applications. Surfactant Science Series 45. CRC Press. pp. 151-175. ISBN 0-8247-8770-6.
4. Ala-Kaila, K., Modeling of mass transfer phenomena in pulp-water suspensions. Doctoral Thesis, Helsinki University of Technology, Helsinki, Finland, ISBN 952-5148-70-
5. Perking, J. K, How to improve kraft brown stock washing efficiency. Paper Trade Journal, v. 153(8), p. 30-34, (1969).
6. Rogers, J., Funo, P.K., Nery, J. ,A lavagem da polpa. São Paulo: ABTCP Conf.(1995).
7. Bryntesson, J., Dahlöff, H., Petterson, E. A. K., Ragnar, M., New concept technology for washing of chemical pulp. Proceedings African Pulp and Paper Week, Durban, (2002)
8. Tappi Standard Procedures. Tappi Press. Atlanta, USA.

Acknowledgements

Kind support provided by pulp mill personnel for providing data, Nopco Paper Technology and Mathiesen Group for support this paper and experts from both companies for helping to write the paper are greatly appreciated.