Determining wash loss levels in the brownstock pulp washing line using different methods

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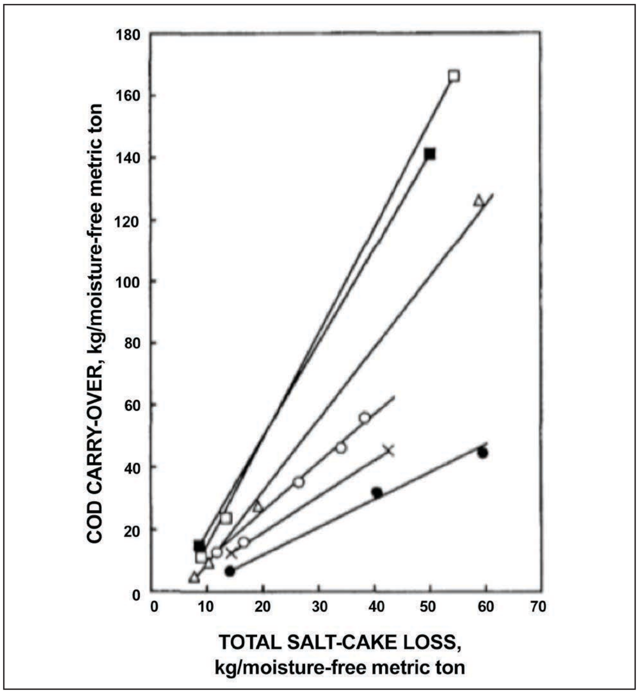
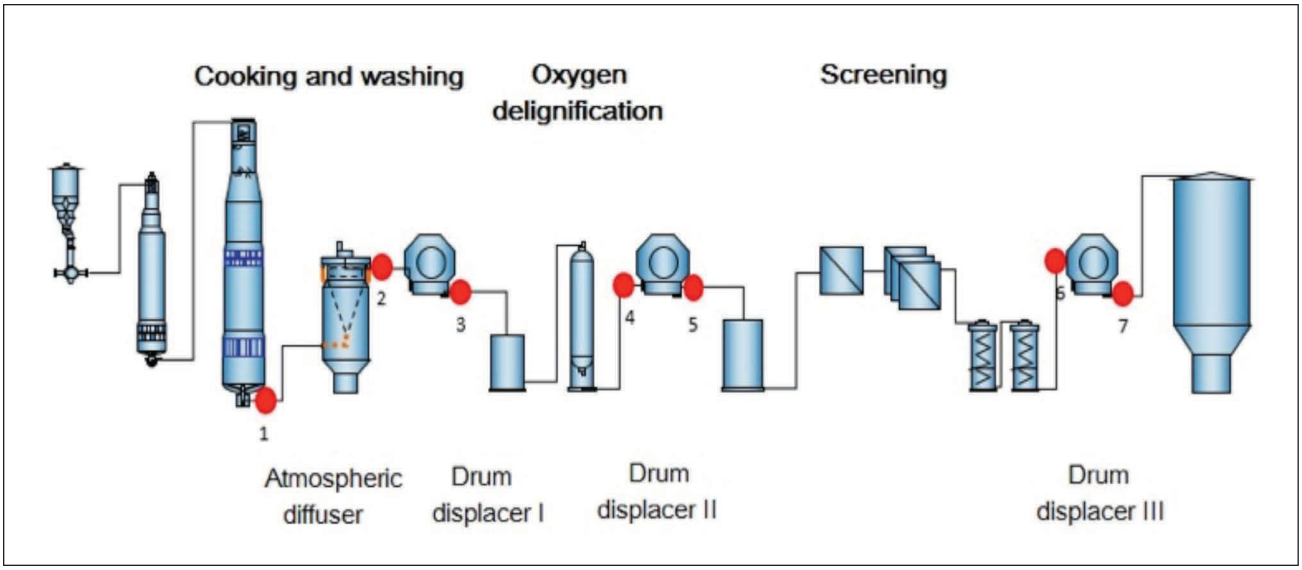
ABSTRACT: The purpose of brownstock pulp washing is to recover the maximum amount of dissolved inorganic and organic material using a minimal amount of water. Brownstock washing is a notable subprocess in chemical pulping because it has effects on the subsequent treatments of the pulp and is also the first step in the chemical recovery cycle. Without effective washing, the economic viability of chemical pulp production is affected. The performance of washing can be described in two main ways: using wash loss, which describes the amount of washable compounds in the pulp suspension that could have been removed in washing; or the dilution factor, which represents the net amount of water that is added during washing. The amount of sodium in the pulp suspension after washing has typically been used as an indicator of wash loss, usually expressed as kg sodium sulfate/ovendry ton of washed pulp. Other common measurement methods are conductivity, chemical oxygen demand (COD), total organic carbon (TOC), dissolved dry solids (DDS), and lignin concentration. Scandinavian pulp mill softwood and hardwood fiber lines were investigated using various measurement methods in the pulp phases to gain better understanding of wash loss. The concentration of DDS in the streams was measured using a refractometer and laboratory scale. The pH, conductivity, lignin content, TOC, and COD were measured to look for any correlations. Using different methods, the level differences remain constant, but it is difficult to control the washing process with sufficient precision using individual measurements. The measurement methods must also be continuous and reliable to be used to monitor and control washing.

Application: Proper measurement techniques can help mills detect a wash line's problem areas; predict wash efficiency in real-time; and control washers' operation, water usage, and chemical consumption, which have a direct impact on the economics of other processes.

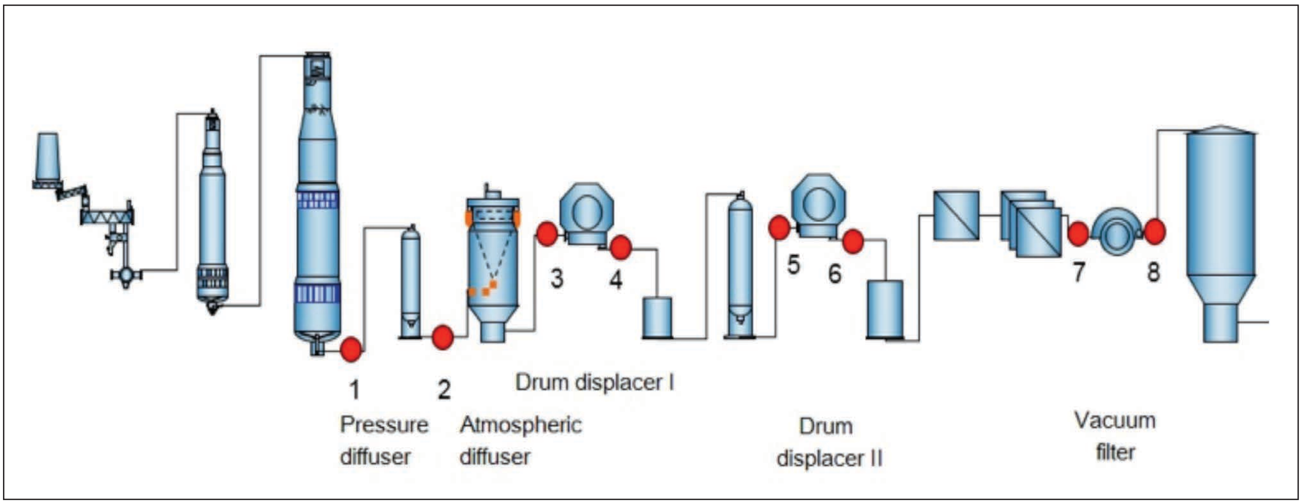
Wash loss (or carryover) is the amount of soluble (washable) inorganic and organic compounds that remain in the pulp suspension after washing. Wash loss can originate from the pulp itself (reaction products) or from the wash water used (e.g., condensates, recirculated washing filtrates). Traditionally, wash loss is measured on a laboratory scale as the amount of sodium that leaves the washer with the pulp. The method for evaluating wash loss in brownstock washing as the amount of sodium (SCAN-C 30:73 "Sodium content of wet pulp") was considered obsolete in 2003 and is no longer a standard method. Nowadays, wash losses are evaluated by measuring individual parameters such as chemical oxygen demand (COD), total organic carbon (TOC), sodium content, and conductivity [1]. Of these, COD has partly replaced sodium measurement as an indicator in both brownstock washing and bleaching as the most-used wash loss method; this is because the constituents of COD are totally dissolved in water [2]. In bleaching, COD is a better way to measure wash loss than amount of sodium because organic compounds causing wash loss may also have an effect on the consumption of bleaching chemicals [3]. The most important chemical compounds causing COD in filtrates are lignin, carbohydrates, methanol, low molecular weight organic acids, and extractives [4].



1. Correlation between chemical oxygen demand (COD) carryover and salt-cake loss for washed pulp from six kraft mills.



2. Hardwood pulp fiber line; 650,000 a.d. metric tons/year. Sample points: red circle indicates pulp sample.



3. Softwood pulp fiber line; 250,000 a.d. metric tons/year. Sample points: red circle indicates pulp sample.

Figure 1 presents the wash loss correlation between COD and salt-cake loss from six different kraft mills [3]. The ratio of salt-cake loss and COD wash loss can vary greatly from mill to mill. Variations of this magnitude complicate the estimations of bleaching chemical consumption on the basis of salt-cake wash loss, especially in a new mill or after major process or equipment changes. Dissolved sodium and dissolved organic material also behave differently in the wash line. Therefore, changes in a mill's operations, such as to the production ratio, dilution factor, and kappa number target, can affect the ratio between sodium and COD. Nowadays, the recommendation is to measure either all dissolved solids as a sum parameter, for example with a refractometer, or the organic and inorganic matter separately.

The traditional online method is to measure the filtrates' conductivity, which has an acceptable correlation with the amounts of sodium [5]. The recently generalized online method involves measuring dissolved dry solids (DDS) using a refractometer. From a practical standpoint, the evaluation of washing efficiency on the basis of dissolved solids is simple and repeatable and has been used widely by washer manufacturers and researchers for experiments on and troubleshooting of brownstock washing systems [6]. All methods have their advantages and disadvantages. For example, measuring the amount of sodium or conductivity does not take into consideration other substances retained in the pulp suspension, such as lignin and other organic compounds. In brownstock washing, disadvantages of using the COD method include the complexity of the test, which makes it less attractive for the continuous monitoring of operations, and the difficulty of repeating results accurately, especially at the low end of the range (less than 10 kg/ton COD) [7].

Studies [8-12] investigating the composition and certain components of wash loss have shown that several compounds cause organic load (COD) in the wash waters, but only some of them are detrimental or harmful to the process. In oxygen delignification, kraft lignin and inorganic sulfur compounds (sodium thiosulfate and sodium hydrogen sulfide) could be mentioned as real wash loss compounds. Real wash loss compounds are certain chemical compounds that have an impact on the pulp quality responses (i.e., kappa number, brightness, and viscosity). Similarly, low molecular weight organic compounds such as methanol (which cause a high COD load) were harmless compounds in the washing and following bleaching stages. Thus, in the future, several of the measurements might have to be used. For example, DDS could be measured by refractometer and inorganic compounds by conductometer; regarding the remaining organic materials, possible dissolved lignin could also be measured separately. New measurements would increase costs, but a combination of measurements would open up new possibilities for more accurate monitoring and controlling of washing.

MATERIALS AND METHODS

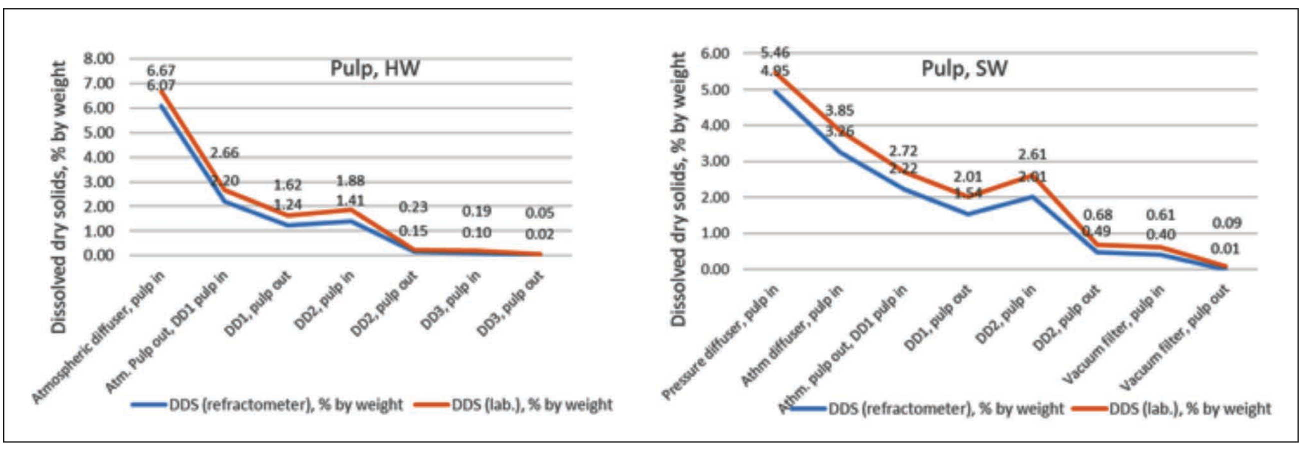
The research was carried out in the hardwood (HW) and softwood (SW) pulp brownstock washing lines at a Scandinavian kraft pulp mill. The HW pulp brownstock washing line consists of high-heat washing, an atmospheric diffuser, one DD-washer before 1-stage oxygen delignification, and two DD-washers after the oxygen stage. Production was about 2000 a.d. metric tons/day during research; kappa number targets were 17 after digester and 11 after oxygen delignification. The SW pulp brownstock washing line consists of high-heat washing, a pressure diffuser, an atmospheric diffuser, one DD-washer before 1-stage oxygen delignification, a second DD-washer after the oxygen stage and the last washer before bleaching is a vacuum filter. The SW pulp line production was 700 a.d. metric tons/day; kappa number targets were 32 after digester and 22 after oxygen delignification. Pulp samples were taken from the washer's inlet and outlet pulp. Three sample laps were taken from both lines. The fiber lines and sample points are shown in **Figs. 2** and **3**.

From the pulp lines, the filtrate sample was extruded from the pulp through wire gauze about 15 min after sampling. The pH, conductivity, and amount of DDS of all samples were determined using a refractometer on the spot. In the refractometer analysis, the temperature of the samples was controlled to 40°C using a thermostat. The DDS by laboratory standard, COD, TOC, and dissolved lignin of all samples were determined afterwards in the laboratory. The consistency and kappa number of the pulp samples were also determined afterwards. The COD and dissolved lignin were determined from the HW line samples 3 weeks after sampling and from the SW line samples 2 weeks after sampling. This could reduce the COD analysis results slightly according to the presence of volatile organic compounds and easily degradable organic material.

Analytical determinations

Analyses were made to define the chemical situation of the washing line. The samples were analyzed using the following methods:

- Determination of dry matter content (analytical) (ISO 638 "Paper, board and pulps—determination of dry matter content—oven-drying method")
- Determination of dry matter content (on site), refractometer
- Conductivity (on site), conductometer (Mettler Toledo; Columbus, OH, USA)
- COD liquor, COD liquor samples were filtrated using 1000 μm paper and then analyzed in a COD analyzer (ISO 15705 "Water quality determination of the chemical oxygen demand index [ST-COD] small-scale sealed-tube method")
- TOC, total organic carbon analyzer (Shimadzu Corp.; Kyoto, Japan) (ISO 8245:1999 "Water quality—guidelines for the determination of total organic carbon [TOC] and dissolved organic carbon [DOC]")
- Dissolved lignin, ultraviolet (UV) measurement at 280 nm, UV 2550 Spectrophotometer (Shimadzu Corp.) using an absorptivity value of 19.8 L/(g·cm)
- Pulps (ISO 302 "Determination of kappa number")



4. Hardwood (HW) and softwood (SW) pulp filtrate fractions of dissolved dry solids (DDS) measured by refractometer and standard methods in whole brownstock washing line.

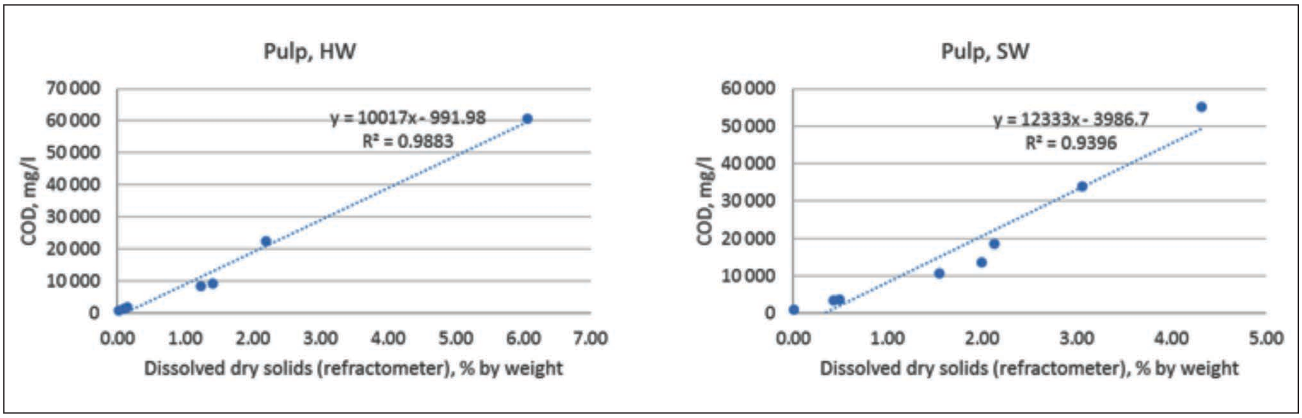
RESULTS AND DISCUSSION

Brownstock washing works well in both fiber lines. The washing loss to bleaching in the HW line was about 5 kg COD/a.d. metric tons of pulp and in the SW line about 6 kg COD/a.d. metric tons of pulp, both at the target level. However, the measurement results showed differences between the washing of different fractions. The results for both washing lines are presented in the following.

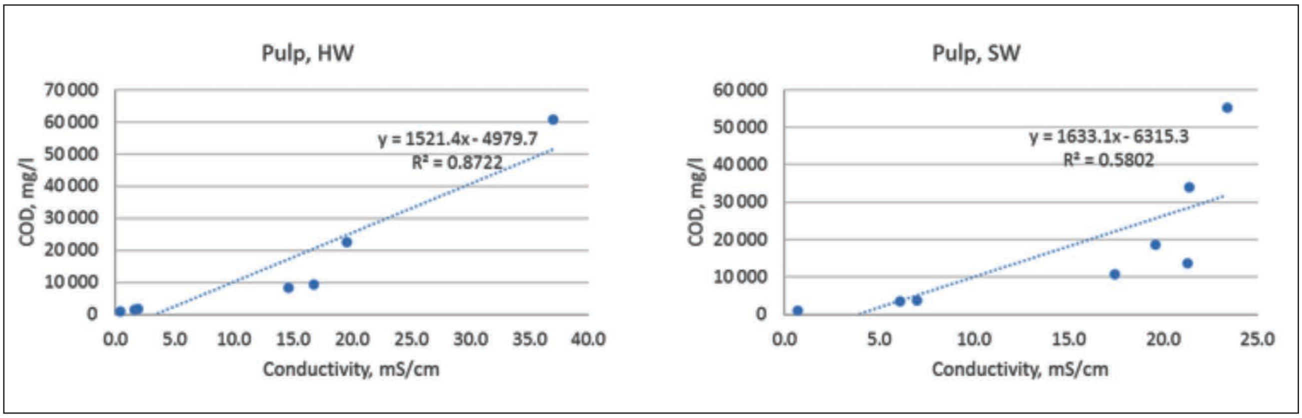
Figure 4 represents the level changes in the pulp suspensions' real-time DDS, measured by refractometer and laboratory standard. The refractometer results are regularly lower than the standard results. This is caused by the lack of field calibration of the refractometer. When using the refractometer, calibrations should be done for the wood species and the specific installation location, while considering the concentration of the solution. Oxygen delignification occurs between drum displacer 1 and 2, which explains the increase at sample point DD2, pulp in, in Fig. 4. Otherwise, the pulp logically becomes cleaner as it moves forward through the fiber line.

Figure 5 presents the relation between COD content and DDS content measured in real time by a refractometer for HW and SW pulp filtrates. **Figure 6** shows the correlation between COD and conductivity. **Figure 7** shows the correlation between COD and lignin content. **Figure 8** shows the correlation between COD and TOC. The results indicate that measurement of dissolved organics and inorganics by a refractometer has excellent correlation to COD (HW 0.9883 and SW 0.9396) because of the high portion of organic matter present in the filtrates. Conductivity's correlation with COD is satisfactory with HW (0.8722) and weak with SW (0.5802). The reason for the difference in wood species in this case is unknown. This phenomenon can perhaps be explained by the different proportions of potassium chloride or potassium hydroxide concentration in the measured solution, as the pH was equal in both cases. TOC has a naturally excellent correlation with COD (HW 0.9996 and SW 0.9998). Lignin, which caused significant organic load, also followed the COD value levels (HW 0.9947 and SW 0.9969). For the COD and dissolved lignin analysis, the samples must be diluted with plenty of water, which in turn can cause measurement errors and make real-time measurements difficult to implement. Components measured with COD or conductivity or dissolved solids wash away differently.

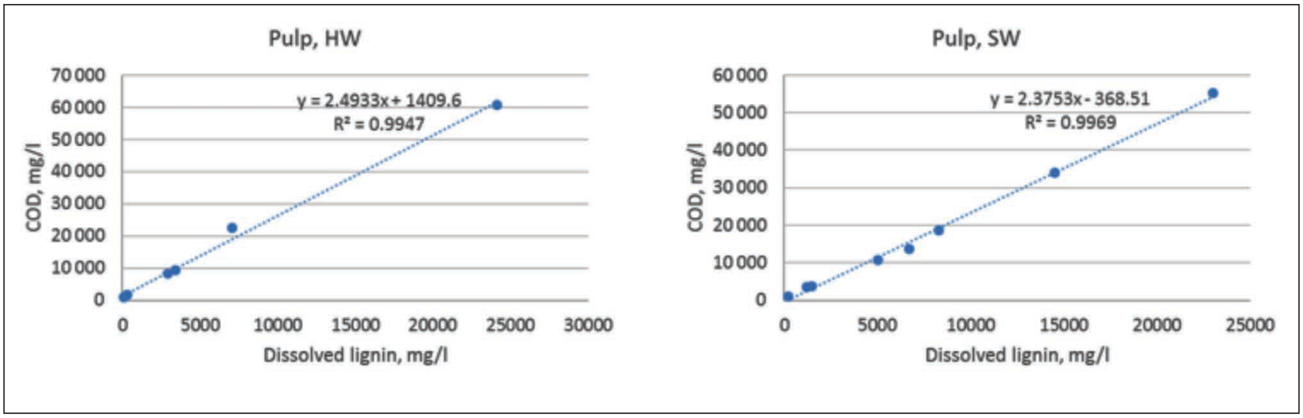
According to Shackford [6], it is important to measure dissolved organic wash loss because it has detrimental effects on viscosity, delignification efficiency, chemical consumption, and organochlorine formation in the bleach plant. Otherwise, measuring inorganic content using conductivity is important



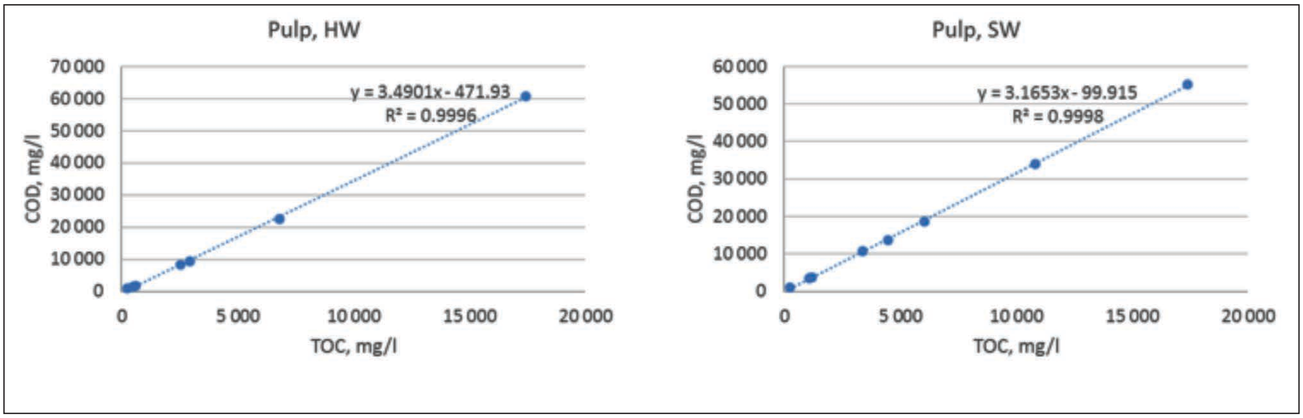
5. COD content of HW and SW pulp filtrate fractions analyzed in laboratory versus DDS measured by a refractometer.



6. COD content of HW and SW pulp filtrate fractions analyzed in laboratory versus conductivity.



7. COD content of HW and SW pulp filtrate fractions analyzed in laboratory versus dissolved lignin analyzed in laboratory.



8. COD content of HW and SW pulp filtrate fractions analyzed in laboratory versus total organic carbon (TOC) analyzed in laboratory.

because of the chemical recovery system. Targets for washing efficiency generally are based on conductivity because simple, robust sensors have not been available to monitor the wash loss of dissolved organics.

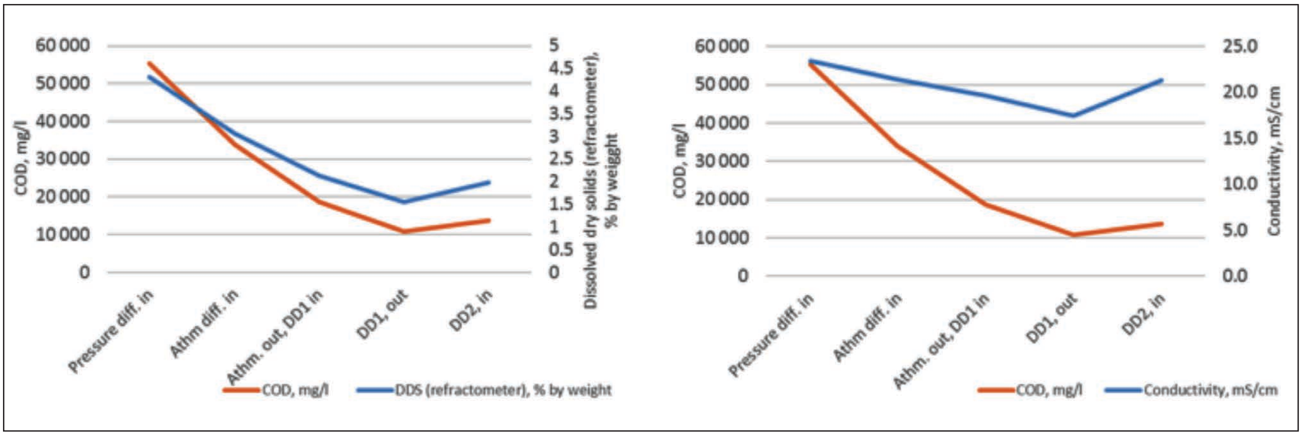
Nowadays, total dissolved solids (TDS) is of interest for several reasons, as concluded by Brown and Hart [5]. Most methods to evaluate the efficiency of brownstock washing use dissolved solids in their calculations. All washer material balance calculations must use dissolved solids mass, and it is a relatively easy test to run. Furthermore, knowing the dissolved solids losses at the washers can help account for changes in daily solids burned in the recovery boiler and even the steam used to evaporate the water associated with those solids. As discussed in the following, the results confirm that measurement of either organic or inorganic material does not give a holistic view of washing.

Figure 8 shows that COD and TOC values follow each other relatively, as they should. Carbon combustion consumes oxygen at the ratio of 2.667, so the COD/TOC ratio should be at this level. Experimentally, it has been stated that the ratio is usually between 2.6 and 3.2. Most of our measurement results were between 2.9 and 3.4. A partial explanation for the larger variation can be found from the TOC analyzed. The analysis also oxidizes some of the inorganic matter.

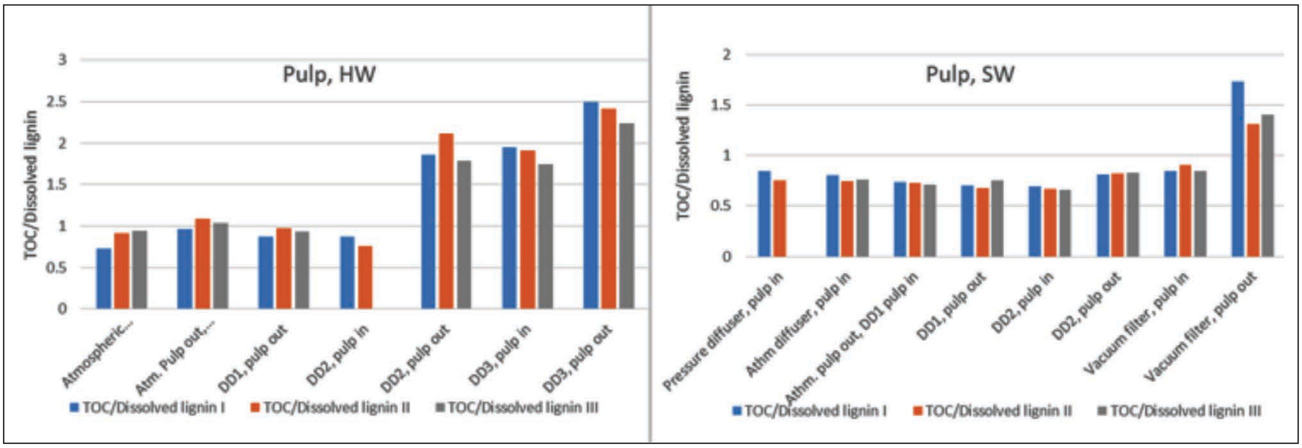
From the results, it can also be stated that organic materials (COD) wash away relatively faster than inorganic material (conductivity) at the beginning of the washing line. Relative efficiency can be a function of process variables, e.g. pH, and washer type, as well. Especially at the beginning of the SW line, inorganic material washes away inefficiently from the diffuser washers (**Fig. 9**).

The measurements were repeated three times and results were codirectional/repeatedly consistent, thus eliminating any measurement errors. Insufficient wash results arise from low feed consistency to the diffuser. It was not possible to completely understand a clear reason for the better washability of the organic matter. However, the organics were in a soluble form and in a higher proportion relative to the inorganics, whereas inorganic matter could be adsorbed in the surface of the fibers because of the charges. This being so, conductivity would not give representative wash result information and COD would also give good wash results and be influenced by the nonwashable components. Measurement by a refractometer shows the TDS content of washable compounds in the filtrate, which describes washing success relatively well.

Figure 10 represents the TOC values per dissolved lignin from every three sample laps. The closer the ratio is to 0.7, the



9. COD content of SW pulp filtrate fraction compared with DDS measured with a refractometer and conductivity at the beginning of the line.



10. HW and SW pulp filtrate fractions of laboratory-analyzed TOC per laboratory-analyzed dissolved lignin.

more lignin represents a significant part of the organic carbon. Regarding the results, a clear change of ratio occurs after oxygen delignification, especially in HW. This is probably because the oxygen stage removes more hemicellulose (sugars) than lignin when using HW, whereas with SW, the ratio of hemicellulose and lignin is more even. Furthermore, with SW, magnesium sulfate is used to limit the loss of hemicellulose.

The results present the one precise occasion and give the direction of the performance of the washing. However, the choice of sampling time has a major impact on the values obtained. In addition, the dilution of the samples and the measurement errors caused errors in the results. Reliable monitoring of the washers' effectiveness required real-time measurements.

CONCLUSIONS

The results indicated that when using different methods for measuring wash loss, the level differences remain quite constant. The results also showed clear differences between, for example, how organic and inorganic materials are washed away and how the oxygen stage affects soluble materials. The wash results for the HW and SW lines also differed from each other at the pulp mill. Using a range of measurements would allow more information on the washing status to be obtained. Conductivity alone does not give an accurate account of the washing lines, and COD cannot be measured in real time; therefore, TDS could be one potential way to measure the performance of brownstock washing. In the future, different types of measurement might be combined and used more frequently for adjustment purposes. It is difficult to properly control the washing process using individual measurement. The measurement methods must also be continuous and reliable to be used to monitor and control the washing.

These types of study on the basis of a hand-picked samples will necessarily include both sampling and analysis errors. Furthermore, the results represent a temporary status when the process itself might have momentarily deviated significantly from the mean value. **TJ**

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ABOUT THE AUTHORS

Without efficient brownstock washing, kraft pulp production is not economically viable. Because effective brownstock washing requires reliable and real-time monitoring and controlling equipment, we compared several types of available measurements. We have studied brownstock washing for a number of years, published articles in several journals, and presented our findings at conferences. However, this study has helped us to understand the benefits and advantages of different measurement techniques. In particular, each measurement technique detects very different components in the washable matter and provides different information on washing performance.

The most difficult aspect of this study was to find the causes for certain behaviors of different measurements. For example, we noticed that one of the measurement techniques gave deviant results when comparing hardwood and softwood lines. Drawing conclusions required research and understanding of process chemistry. The results indicate that inorganic and organic matter can be washed out with different methods. Thus, a single measurement, be it focusing on the inorganic or organic, can reflect a very diverse image of washing success.

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Mills can benefit from the comparison of several different types of available measurements or tests to predict brownstock washing performance. In addition, the data were comprehensively collected and tested, bringing distinct value to the readers. For the next step, we will focus on the performance of oxygen delignification by using total dissolved solids measurements and on how dissolved solids behave when process conditions change.

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