Multi–component control of brownstock washing

William E. Josephson, Gopal A. Krishnagopalan, and Harry T. Cullinan

ABSTRACT: Stringent effluent standards require improved washing efficiency and control. The organic content of streams from the washing process affects the formation of chlorinated organics. Current washing control strategies focus on inorganic materials recovery and measure organics recovery only by inference. A laboratory displacement cell simulates a washing stage to measure inorganics concentration, total dissolved solids, and dissolved lignin. Using ultraviolet absorbance and refractive index techniques with conductivity to measure washing performance can detect otherwise unnoticed problems.

KEYWORDS: Conductivity, refractivity, simulation, ultraviolet spectra, unbleached pulps, washing.

The first step in the kraft recovery cycle is the separation of black liquor from pulp using a washing operation. The black liquor as it leaves the digester is a solution containing about 25% dissolved solids of which approximately 50% are organic compounds. These organic compounds include partially fragmented lignin (solubilized as phenolates or carboxylates), cellulose and hemicellulose degradation products and their solubilized derivatives, and other reaction byproducts such as sodium soaps. Inorganics present in the black liquor are primarily cooking chemicals in ionic form. After washing, the recovered pulp is then ready for subsequent processing steps such as bleaching and papermaking or both. The term for black liquor separated from the pulp is weak black liquor. This contains about 15% dissolved solids. The weak black liquor goes to recovery operations for reclamation of chemicals and reformation into cooking liquor. The organics in the weak black liquor are a source of energy to the mill when burned in the recovery boiler.

Brownstock washing separates the dissolved organic and inorganic chemicals present in the brownstock stream from the pulp fibers. Organics that proceed with the pulp to subsequent processing steps are sources of biological oxygen demand, chemical oxygen demand, and color in pulp mill effluent streams *(1)*. In addition, poorly washed pulp is a source of precursors for dioxins and chlorinated furans during the bleaching operation *(2)*. Since organics are a source of energy, improving washing efficiency provides improved energy recovery. Finally, inorganics that remain with the pulp require increased chemicals. This last effect has traditionally been the impetus for washing control. Salt cake loss is still the grading method for washer performance.

There are various methods to achieve brownstock washing. A system using dilution, extraction, and displacement finds predominant use in the pulp and paper industry. It consists of staged rotary drum washers using either vacuum or pressure for aiding the filtration. Although the basic concept is over 60 years old, multi–stage vacuum filter washing systems constitute the majority of systems in North America. **Figure 1** shows the elements of a typical rotary vacuum filter stage.

The rotary drum washer consists of a wire covered cylinder rotating in a vat containing the black liquor and pulp mixture. Internal valving and a drop leg apply vacuum to the inside of the cylinder. As the cylinder passes through the vat liquor, a layer of pulp builds on and clings to the drum surface. When the cylinder surface leaves the vat, there is a shower of weaker liquor applied to the pulp layer. Under the influence of the vacuum, this wash water displaces the black liquor that is present with the pulp. Before the sur-

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face can dip into the vat again, the vacuum releases for removal of the washed pulp. Because the efficiency for one stage seldom exceeds 80%, a typical washing system will have at least three washers in the countercurrent flow sequence of **Fig. 2**. Such an arrangement is usually sufficient to give a recovery level of about 99% of the incoming washable solids.

Two parameters typically determine the performance of washing systems: the dilution factor (DF) and the displacement ratio (DR). The DF is the amount of wash water over that required for total displacement. Equation 1 provides the mathematical expression:

$$DF = (W_S - W_M)/W_P \qquad (1)$$

where

W_S = mass of shower liquor

W_M = mass of liquor in mat leaving washer

W_P = mass of dry pulp.

Other investigators originally proposed the DR term *(3)*. It is the ratio of the actual solids reduction in a single stage to the maximum possible reduction in that stage. Equation 2 is the mathematical expression:

$$DR = (C_V - C_M)/(C_V - C_S) \qquad (2)$$

where

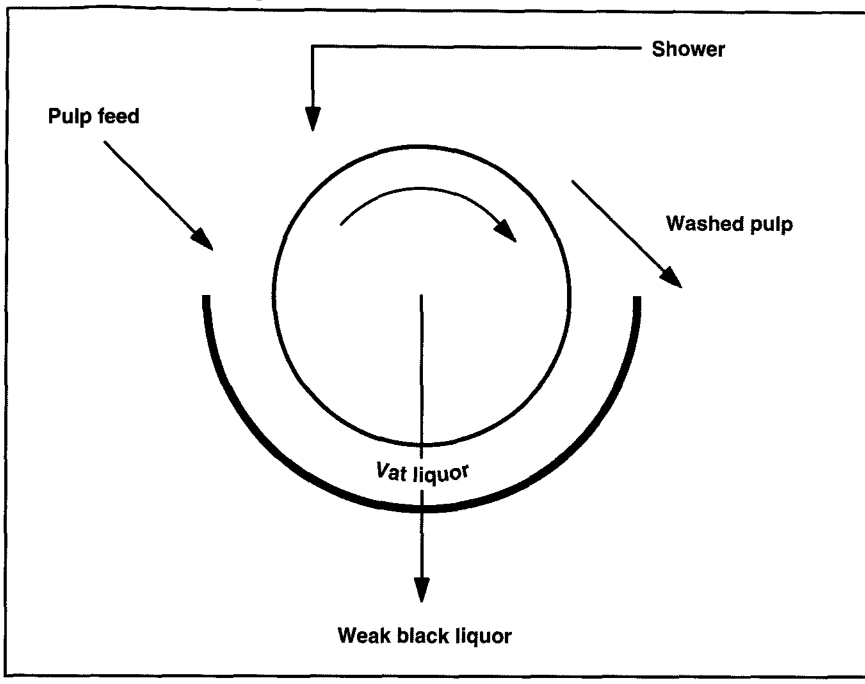
C_V = vat liquor solids concentration

C_S = shower liquor solids concentration

C_M = solids concentration in mat liquor leaving washer.

The goal of any washing system is to achieve high cleaning with low water usage. In terms of the above equations, one wants to maximize DR while minimizing DF. The two terms relate to each other. Use of a high DF will result in a large percentage of solids removal. Lowering DF will decrease DR. The DF is a controllable variable. Consideration of evaporator steam costs, wash water cost, evaporator condensate savings, salt cake losses, organic losses, and effluent treatment costs will optimize the DF.

1. Rotary vacuum filter stage

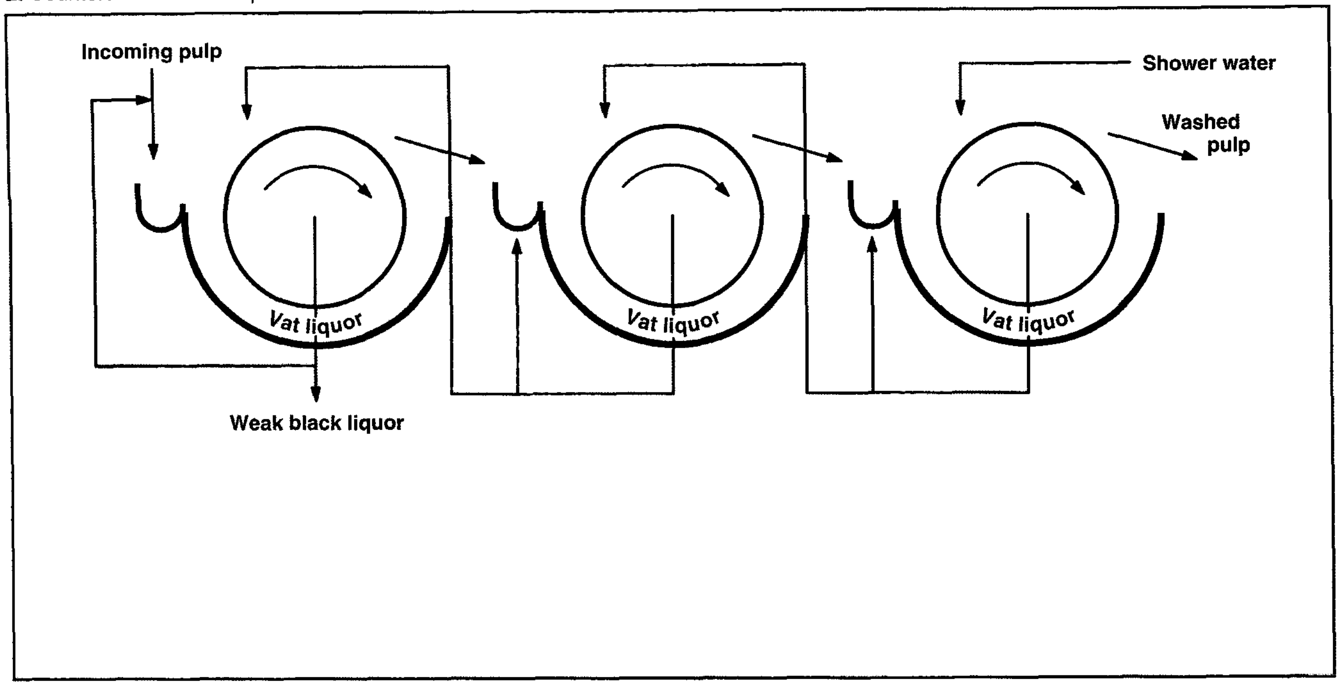


Adjusting shower flow based on first-stage filtrate Baumé or last-stage conductivity or both are the historical control methods for brownstock washers. The first measurement provides an indication of the total dissolved solids in the filtrate stream. The conductivity measurement is proportional to the amount of ionic materials in the measured stream and relates directly to inorganic losses. There have been recent advances in washer control using computerized data analysis *(4–7)* and sensors *(8, 9)*. The vast majority of control systems in place, however, do not specifically consider organic losses. Studies have shown that organics and inorganics wash out of pulp at different rates because there are different mechanisms. On a theoretical basis, lignin losses can be five times the sodium losses at the same DF *(10)*. Lignin losses are a contributor to increased effluent treatment costs and bleaching chemicals consumption. Actual mill data has shown that the ratio of organic losses to inorganic losses can vary by a factor of 4 between mills *(11)*. Under some circumstances, it is possible that the optimum DF will change considerably if one considers lignin losses. To examine the entire picture, it is necessary to consider lignin content as well as total solids and inorganic content of liquor streams when studying brownstock washing performance.

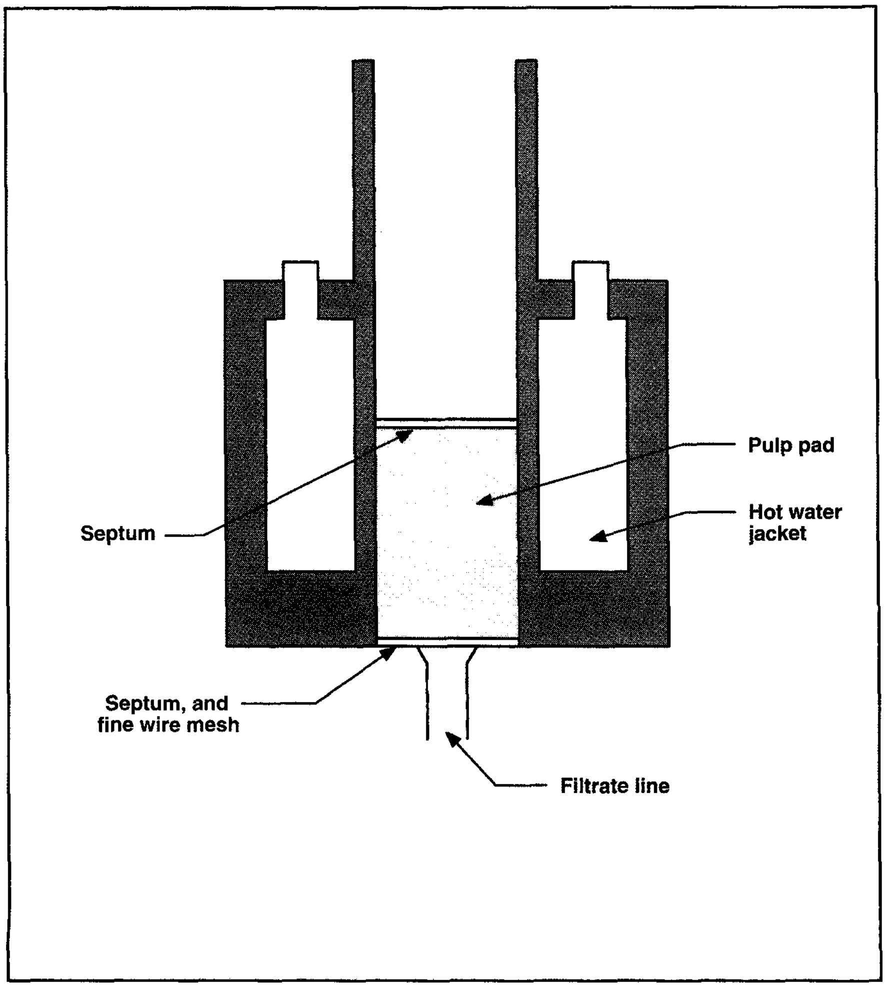
Experimental procedures

Initial experiments involved a laboratory washing cell that simulates a single stage of an actual washing system. The cell consists of a jacketed 8.5-cm diameter cylinder as in **Fig. 3**. To conduct an experiment, one places a pulp slurry in the cell on top of a perforated rubber septum and fine wire screen. The slurry consists of a measured amount of pulp soaked in black liquor of known strength 24 h before an experiment. The soaking allows the pulp and black liquor to come to equilibrium and thus approximate the feed stream to a washing vat. A piston then compresses the slurry in the cell to the desired pad height and consistency. Then another perforated septum goes on top of the pad. This septum allows even distribution of wash liquor across the pulp surface. The filtrate line at the bottom of the cell connects to a vacuum pump through a filtrate receiver. Shower liquor enters the top of the pulp pad

2. Countercurrent flow sequence for three washers



3. Laboratory washing cell simulating the single stage of an actual wash system

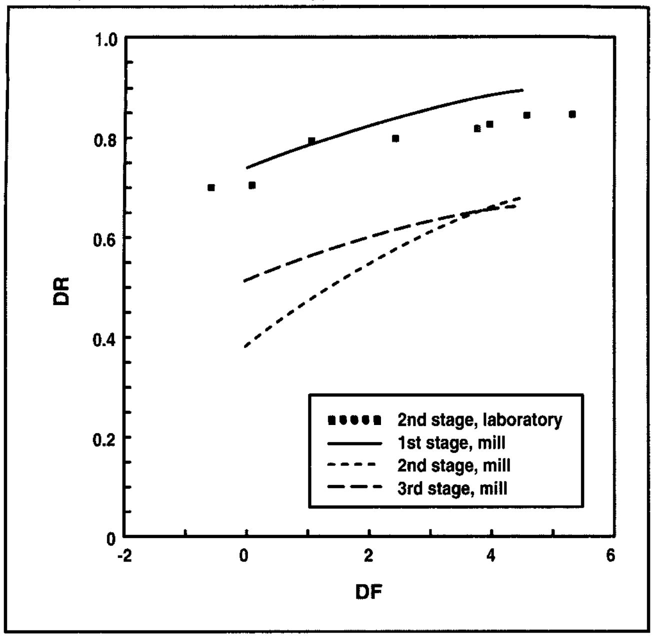


while an equal amount of filtrate liquor departs.

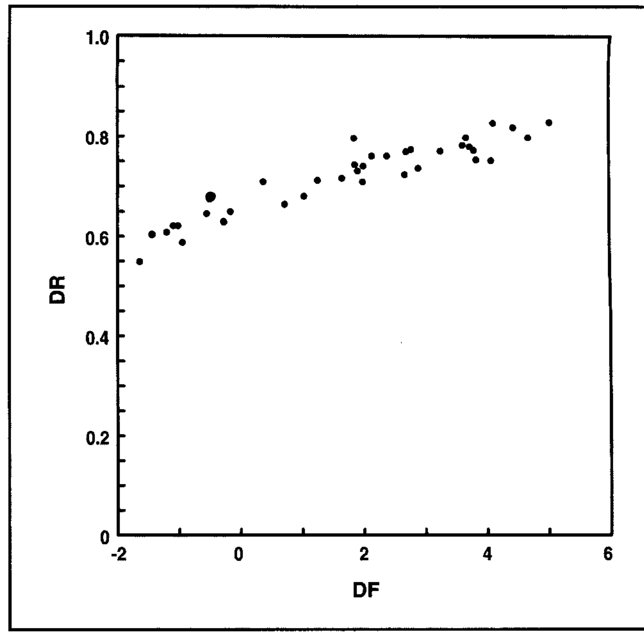
Each experiment allows for the manipulation of many process variables. Adjusting the amount of slurry in the cell controls pad height. Since the amounts of filtrate liquor and shower liquor are the same, the pad consistency remains constant throughout an experiment. It is possible to control the amounts of filtrate and shower liquor as well as the consistency of the pulp pad. Therefore one can achieve any desired DF in an experiment. Varying the compositions of the shower and vat liquors approximates different stages of a washing system. One can control the temperature of washing, since it is possible to heat the shower liquor and pulp slurry to any desired temperature. Water circulation through the cell jacket maintains this temperature.

The pulp pad at the beginning of an experiment corresponds to the mat on a drum washer before it encounters shower liquor. The composition of the pad liquor at this point is that of the vat liquor in the drum washer. At the end of a run, the pulp pad is comparable to the sheet leaving the washer. One squeezes the pad at the end of the experiment.

4. Comparison of cell data with typical mill data



6. Effect of DF on DR based on inorganics



The experimenter saves samples of all four liquors (vat, shower, filtrate, and squeezed pad) for analysis.

Relevance to mill washers

Conductivity analysis of the vat, shower, and pad liquors provides the calculation of DR. **Figure 4** provides a comparison of cell data with typical mill data *(3)*. As the figure indicates, the DR for a given DF of a first stage washer operating in a mill setting can be markedly higher than that of subsequent washers. This decrease in DR results from uneven mixing *(3)* and foaming after the first stage. Figure 4 shows that the DR values for the cell experiment (which attempted to simulate a second-stage washer) are comparable to the actual first-stage washer. One would expect this, since there are no foaming or mixing problems in using the displacement cell. Displacement cell data for a first-stage simulation is comparable to that of the second-stage simulation. While the displacement cell is unable to predict the effects of physical macro–phenomena such as foaming, it can accurately simulate other aspects of the washing process.

Liquor analysis

The relationship between conductivity and inorganics concentration is linear for most concentrations of interest. Sodium, the most prevalent inorganic component of black liquor, usually represents all inorganics. Atomic absorption spectrophotometry determined absolute levels of sodium ions and generated conductivity calibration curves for the pulp system. Since the relationship of conductivity to inorganics is linear, knowledge of absolute sodium levels is not necessary in calculations of the DR. Such information would be necessary, however, to determine the economic impact of control decisions.

Kraft lignin has a local absorption maximum at UV wavelength of 280 nm *(12)*. Equation 3 is Beer's law, which states that the absorbance of a solution at a particular wavelength is linear with respect to concentration:

$$A = \varepsilon c b \qquad (3)$$

where

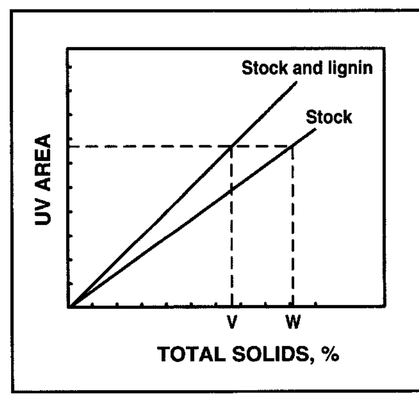
A = absorbance

ε = absorptivity at the wavelength

c = concentration

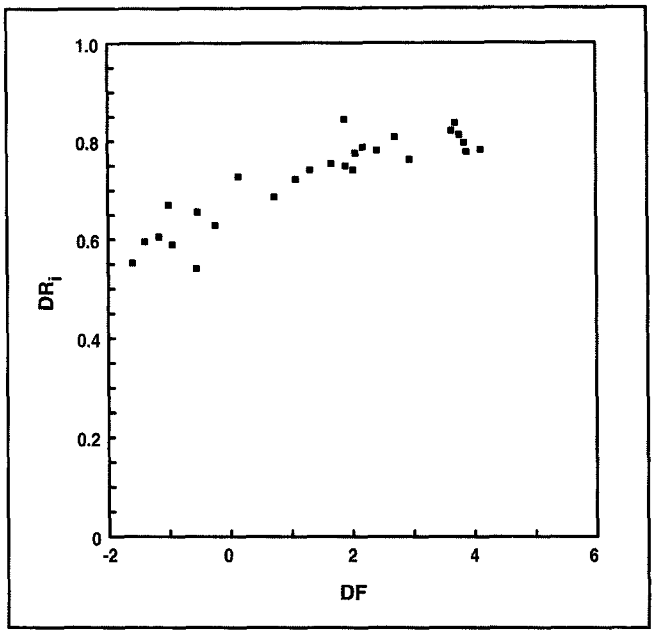
b = light path length.

5. UV calibration curves

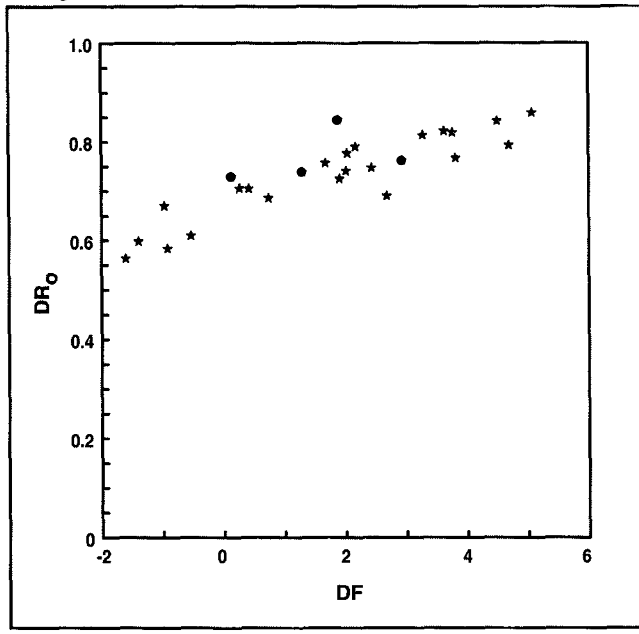


Other investigations *(13–16)* have confirmed the linearity of the relationship and have generated estimates for ε in the range of 15–25 L/g·cm. To determine absolute amounts of lignin, it would therefore seem possible to measure UV absorption vs. precipitated lignin from kraft black liquor redissolved in solvent. Some of these investigations have noted, however, that there is a difference in the absorbance characteristics of isolated lignin and the lignin occurring in kraft liquors. The present study confirms this. Isolated pine lignin had an absorptivity of 24.5 L/g·cm while ε for lignin in its natural environment was 22.8 L/g·cm. A methodology was therefore

7. Measured DR based on total solids



8. Organics DR as a function of DF



necessary to determine absolute lignin levels using only black liquor. Such a method consists of adding precipitated lignin back to kraft black liquor. It is possible to calculate the fraction of total solids that is lignin after one has UV calibration curves for both solutions as shown in **Fig. 5.** To use Fig. 5, let Z equal the fraction lignin in solids of stock solution. Add α g lignin per 100 g total solids. This is stock and lignin solution. Then the fraction lignin in solids of stock and lignin solution is $(\alpha + 100Z)/(100 + \alpha)$. Since the lignin concentrations are the same at the same UV signal, Eq. 4 applies:

$$ZW = V(\alpha + 100Z)/(100 + \alpha) \quad (4)$$

where

V = % total solids of the stock and lignin solution at a given UV signal

W = % total solids of the stock solution at the same UV signal.

Since α, V, and W are known terms, one can calculate Z. It is then possible to find absolute lignin levels for any solution of the same lignin type.

Measurement of the refractive index (RI) of the liquor determines the total dissolved solids in the liquor. The relationship between RI and total solids is linear for the ranges of interest. Oven drying the samples provides easy calibration of the RI line. Use of RI as a measurement technique suffers from two disadvantages, however. First, the RI of a solution depends on its temperature. This is also true for conductivity. Second, the RI calibration can change if the nature of the components that comprise the solids changes. Previous work *(17)* has established the feasibility of using this analytical technique in digester control for any specific black liquor. One can readily account for the temperature dependence. RI calibration is accurate, if the nature of the components does not change too drastically. The present study has extended this method for brownstock washing operation.

These two methods of analysis allow for the definition of additional DR based on inorganics and organics as shown in Eqs. 5 and 6:

$$DR_i = (C_{Vi} - C_{Mi})/(C_{Vi} - C_{Si}) \quad (5)$$

$$DR_o = (C_{Vo} - C_{Mo})/(C_{Vo} - C_{So}) \quad (6)$$

where

DR_i = DR for inorganics

DR_o = DR for organics

C_{Vi} = vat liquor inorganics concentration

C_{Vo} = vat liquor organics concentration

C_{Si} = shower liquor inorganics concentration

C_{So} = shower liquor organics concentration

C_{Mi} = inorganics concentration in mat liquor leaving washer

C_{Mo} = organics concentration in mat liquor leaving washer.

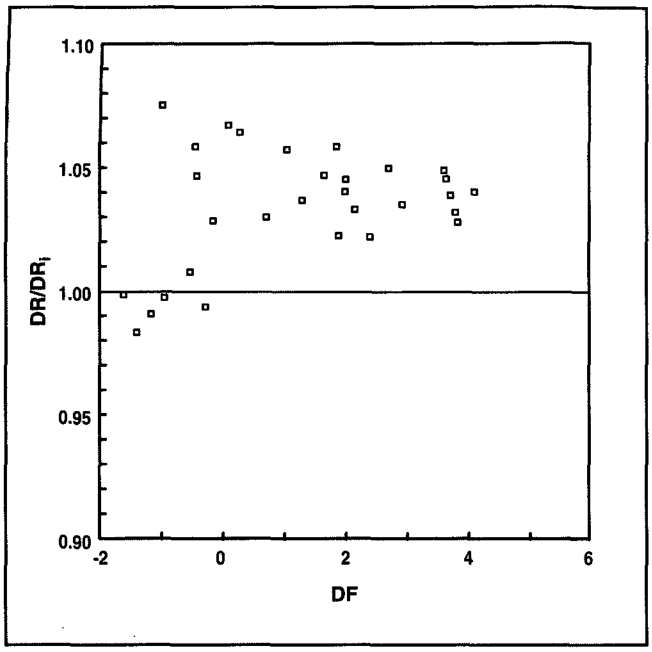
One computes DR_i directly from conductivity measurements. DR_o comes from UV analysis. RI will calculate the conventional DR. One can therefore directly measure the washing of total solids rather than using inference from conductivity measurements.

Although it is not necessary in the calculation of DR, it is also possible to analyze the filtrate liquor samples using the above methods. One can then perform a material balance verification (MBV) on each experiment based on the premise that anything going in as a liquor component must come out. Equation 7 is a mathematical expression for this:

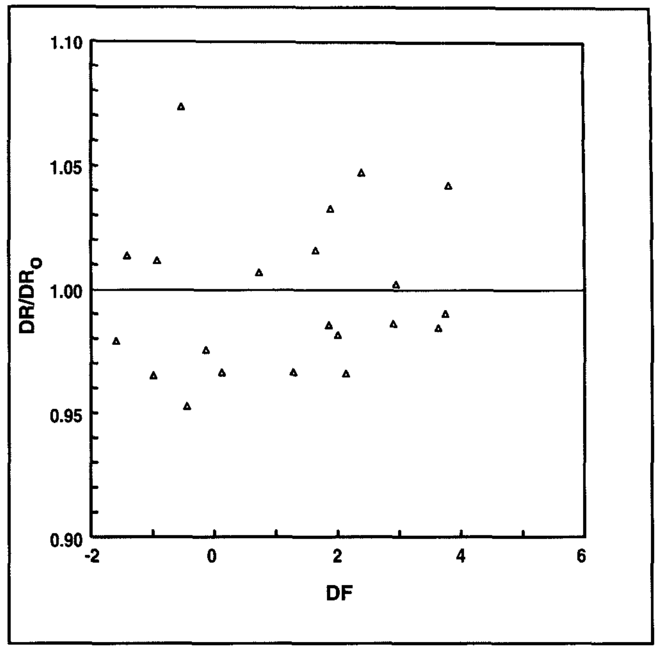
$$MBV = 100[(x - y)/MIN(x,y)] \quad (7)$$

Equations 8 and 9 provide the expressions for x and y:

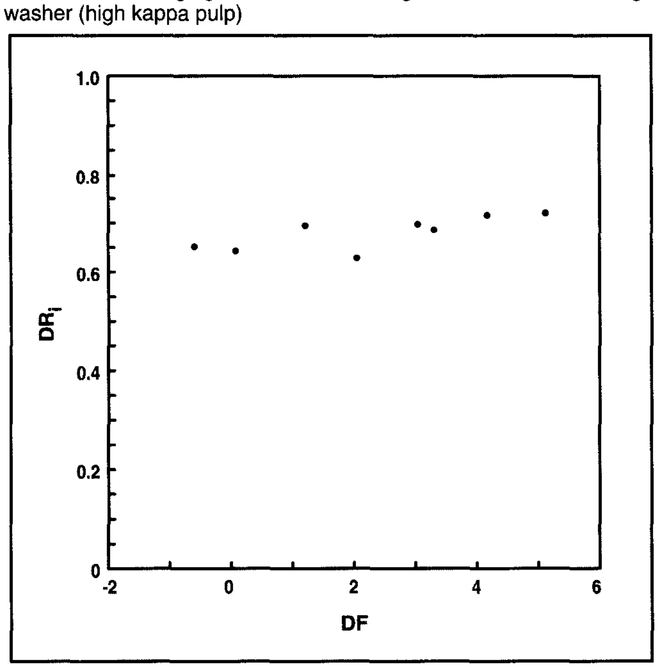
9. Relationship between DR/DR_i and DF



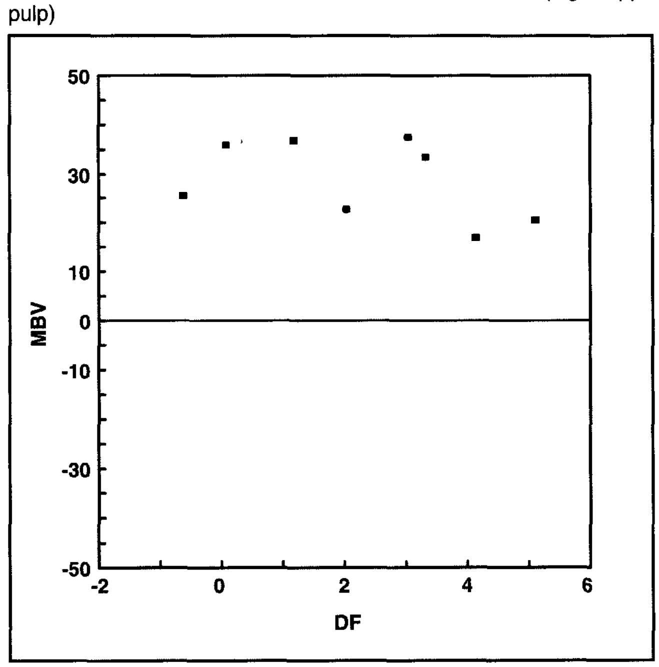
10. Relationship between DR/DR_o and DF



11. Effect of changing the DF on the inorganics DR of a third stage washer (high kappa pulp)



12. Effect of DF on material balance based on total solids (high kappa pulp)



$$x = W_V C_V + W_S W_S \quad (8)$$

$$y = W_F C_F + W_M C_M \quad (9)$$

where

C_V = vat liquor solids concentration

C_S = shower liquor solids concentration

C_F = filtrate liquor solids concentration

C_M = solids concentration in mat liquor leaving washer

W_V = mass of vat liquor

W_S = mass of shower liquor

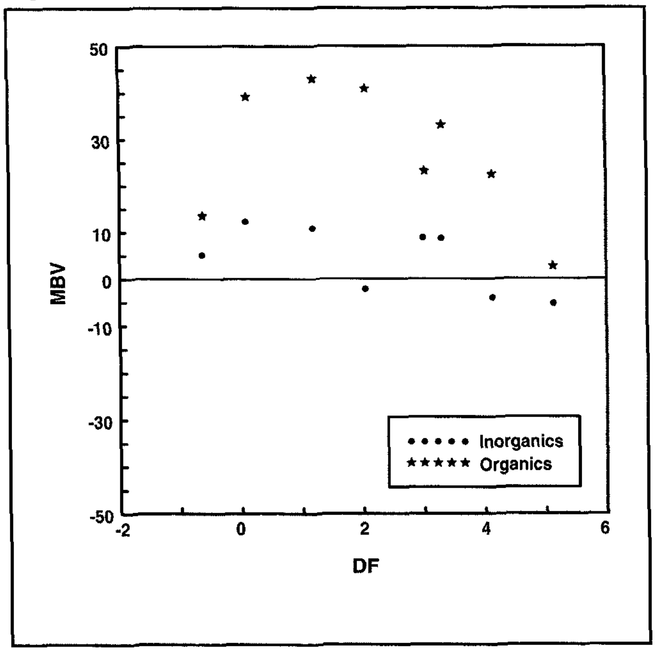
W_F = mass of filtrate liquor

W_M = mass of liquor in mat leaving washer

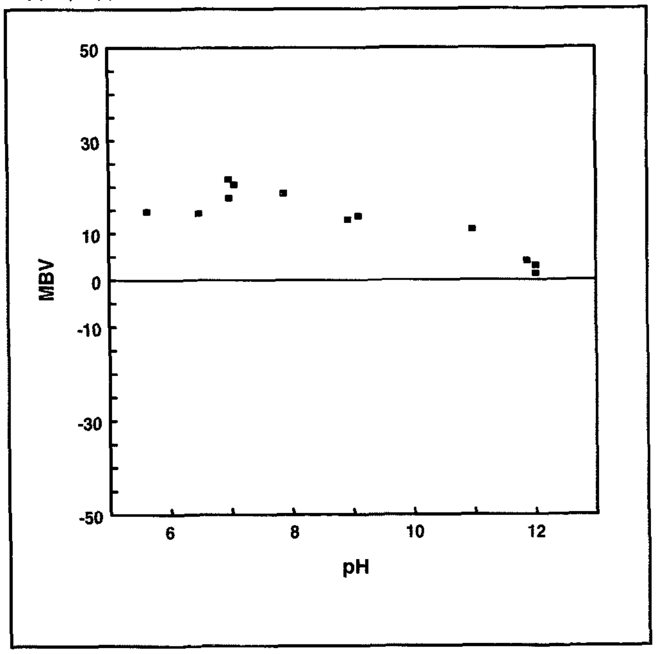
MIN(x,y) = the smaller of either x or y.

It is possible to construct the MBV using the total solids as above as well as organics or inorganics as a basis.

13. Effect of DF on inorganics and organics based material balance (high kappa pulp)



14. Effect of shower pH on material balance based total solids (high kappa pulp)



The MBV form is such that positive numbers indicate that some of the component in question is staying with the pulp fibers instead of leaving with filtrate or pad liquors. Negative numbers indicate that more component than anticipated has left the system.

Results

Low kappa system

A first set of experiments involved a low kappa softwood pulp and its liquor. Parameters such as DF, pad consistency, pad height, stage, and temperature were varied while all other parameters were held constant. **Figures 6–10** present typical plots. Figure 6 shows the effect that changing the DF has on the inorganics DR. This corresponds to the DR calculated in a mill setting and extrapolated to all total solids. Figure 7 shows the measured DR based on total solids, and Fig. 8 shows DR_0 vs. DF data. Plotting various ratios of the DR values indicates the relative washing effectiveness. Figure 9 depicts the relationship between DR/DR_i and DF. Figure 10 plots DR/DR_0 vs. DF. The latter plot indicates that organics and total solids washed with the same effectiveness. Figure 9 shows that inorganics washed with slightly less efficiency than that of total solids. This discrepancy is within the bounds of experimental error, however. All experiments with the low kappa system gave similar indications, i.e., all components wash with equal efficiency no matter which parameter varies. For this pulp system, therefore, the industry practice of inferring total solids losses from inorganics measurements is valid.

The effect of changing other parameters in this system gave results similar to that of previous displacement cell experiments *(18, 19)*. Increasing pad consistency from 8% to 12% decreases the DR. Changing pad height in the cell from 1 cm to 6 cm has relatively little effect. Washing is best at higher temperatures ranging from 70°C to 90°C. There is little difference in the washing effectiveness of different stages. The MBV was close to zero for each experiment. This indicated that the materials entering the system in a liquor stream with low kappa number departed in the liquor stream.

In summary, there were no differences in washing efficiency among the liquor components for the low kappa system. Since all components acted similarly, UV and IR can be useful to indicate washing performance.

High kappa system

Another set of experiments involved a high kappa softwood pulp and its liquor. Initial examination of the results seems to indicate no qualitative difference from those of the low kappa system. **Figure 11** shows the effect that changing the DF has on the inorganics DR of a third-stage washer. Again, this would be similar to observations in a mill setting. DR from UV and RI data are similar. Further analysis of the data, however, indicates that particularly for the MBV parameter normal washing does not occur. **Figures 12 and 13** show the results of computing material balances for all components in the system. The vast majority of MBV parameters for the organics and total solids are consistently above a value of 20. Inorganics MBV scatter around a value of zero. None are above 10 which is the bound of experimental error. These data indicate that more organic materials are entering the washing system in the form of vat and shower liquor than are leaving it in the form of filtrate or pad liquor. These results would not occur if the sole method of liquor analysis was conductivity testing. The important conclusion from these observations is that a significant fraction of the organics remains with the pulp over the duration of the washing operation.

Parameters other than DF were varied with the high kappa system. All experiments except one gave indications that organic materials were staying with the pulp. The pH of the shower liquor was a variable that influenced the MBV parameter. As **Fig. 14** shows, the total solids MBV gradually decreases with increasing shower liquor pH. At a pH of 11, however, the MBV parameter is still above a value of 10. This indicates significant amounts of material staying with the pulp fibers. At a shower liquor pH of 12, which is also the vat liquor pH, the total solids MBV is close to zero. The organics relationship for MBV and pH is similar. Since changing the pH of the third-stage shower liquor involved addition of acid or base to water, it is not possible to calculate reliably the nature of the relationship of conductivity and inorganics. RI and oven drying techniques calculated the total solids MBV. Both provided similar results indicating that the relationship of RI to total solids did not substantially change.

This material balance failure relates to a number of events. One possibility is that the relationship between free lignin in solution and lignin adsorbed on pulp changes with pH. The quantity of the sodium adsorbed on pulp depends on pH *(20)*. It seems reasonable to expect that the lignin relationship also depends in some way upon pH. An alternative to the adsorption argument is that the mobility of free lignin in solution may be so low that the duration of the washing experiments, simulating the residence time of the pad in the wash zone, is not long enough for the lignin to diffuse from the pulp to the filtrate or pad liquor.

For the high kappa system, therefore, UV and RI analysis indicated a potential washing problem that conventional conductivity analysis would not detect. There are systems, however, in which conductivity can detect washing problems that UV and RI cannot. Such systems are characterized by ionic materials behaving in an undesirable manner, while the organic materials behave ordinarily. Some combination of the three sensing mechanisms may well be best to gauge washer performance in all circumstances.

Conclusions

These experiments have confirmed previous studies that displacement cell techniques can accurately simulate some aspects of brownstock washing. In addition, UV absorbance and RI techniques act as sensing mechanisms in gauging washing performance. The efficiency of washing various components was approximately equal in the systems studied. UV and RI analysis, however, did determine the presence of undesirable lignin adsorption or transport behavior in a high kappa pulp system. Conventional conductivity analysis could not detect the behavior. The pH difference between the shower liquor and vat liquor was a significant factor in this phenomenon.

Future work will focus on a pilot scale washer. This system will allow the continued study of major variables and will provide a more practical system for the study of parameters that displacement cells do not adequately simulate. It is probable that some combination of the three sensing mechanisms will provide the best opportunity for optimum total control. TJ

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