# Washing for low bleach chemical consumption

**C. Bertil Stromberg**

*Chlorine consumption can be reduced by using a pulp washer that provides a long retention time in the wash zone.*

Environmental concerns are driving mills to reduce their consumption of bleaching chemicals, especially chlorine. One way of accomplishing this objective is to thoroughly wash the pulp, thereby reducing the black-liquor carry-over to the bleach plant.

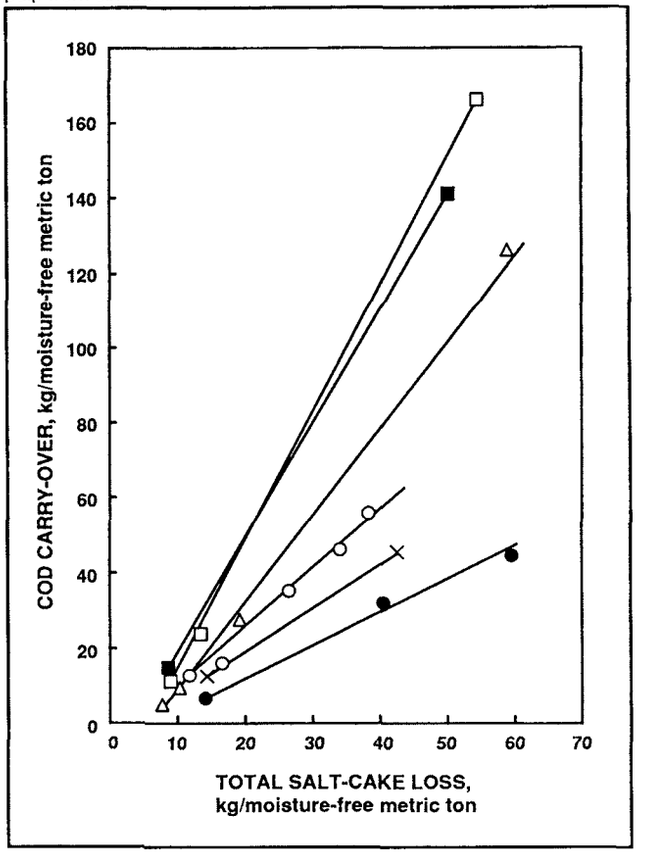
Kraft mills have long been evaluating washer performance by measuring salt-cake loss—the amount of sodium in the pulp after the last washing stage. Virtually all data generated and published have dealt with the pulp washer's ability to remove sodium from the pulp. The only real drawback to using sodium as a measure of washing efficiency is its ability to adsorb to the cellulose and other larger molecules present in the pulp. This adsorption strongly affects the measured amount of sodium, depending on whether the test is performed on squeezed liquor, diluted pulp, or acidified pulp. The consequent variation in measured sodium content makes it difficult to compare results from different mills. Sodium, moreover, does not consume bleaching chemicals. Bleach chemicals are consumed by the dissolved organic substance carried over with the pulp.

**Figure 1** shows that at the same salt-cake loss, the dissolved organic solids loss (expressed as chemical oxygen demand, COD) can vary by as much as a factor of four between different mills. Variation of this magnitude makes it very hard to predict bleach chemical consumption from salt-cake carry-over in a new mill or after major process and/or equipment changes. On the other hand, the individual curves in Fig. 1 appear to indicate that it is possible to establish a correlation between sodium and organic substance once these data are collected for an individual mill. However, the data in Fig. 1 were collected under stable operating conditions. We will show that dissolved sodium and dissolved organic solids behave differently in a wash line. Because of this, changes in mill operating conditions (e.g., production rate, dilution factor, and target kappa number) can affect the relationship between sodium and organic solids.

Salt-cake loss is thus an unreliable predictor of the amount of dissolved organic substance in the washed pulp. Since it is these dissolved organics that consume bleach chemicals, it is apparent that some other way of measuring the carry-over of organic solids is needed. There are many ways of indirectly measuring the dissolved organic content: Roe number on the liquid, kappa number on the liquid, dissolved lignin concentration in the liquid, difference in kappa number between unwashed and thoroughly washed pulp, etc. Most work has been carried out using COD of the liquid, which is an established test that is normally used to determine effluent quality.

COD is a collective measurement of all compounds that can be oxidized by boiling in an acid bichromate solution.

**1.** Correlation between COD carry-over and salt-cake loss for washed pulp from six kraft mills

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These compounds include virtually all organic substances and many reduced inorganic substances. Sulfides in black liquor will contribute to the COD number, but at the end of a wash line, and especially after an oxygen delignification stage, the COD contribution from sulfides should be negligible.

**Figure 2** shows the impact of COD carry-over on the active chlorine consumption in the chlorination stage. One kilogram of COD consumes about 0.4–0.8 kg of active chlorine. As the target kappa number after chlorination and alkali extraction (CE kappa number) is lowered, the amount of chlorine consumed by each kilogram of COD increases. If excessive carry-over prevents the chlorination stage from achieving the target CE kappa number, chemical consumption in the D-stage also will be affected because of the higher CE kappa number.

If we are to predict the effect of carry-over on consumption of bleach chemicals, we must be able to predict accurately the amount of COD in the carry-over. This cannot be done by simply using a ratio between sodium and COD. We need to know how the organic substances behave when exposed to the different unit operations in a wash line.

## Principles of washing

Cellulose fiber is a heterogenous mass with several layers of cellulose molecules (lamellae) and a large central cavity (lumen). Cellulose fibers also bond to each other, creating a network of fibers and cavities. When suspended in water, the fiber network swells, and movement of liquid from one cavity to another is relatively easy. As the pulp consistency is lowered, communication becomes even easier, as demonstrated by Wong and Reeve (*1*).

Communication among the lumen cavity, the liquor between the lamellae, and the liquor surrounding the fiber is limited to what can pass through the pores in the fiber wall. Liquor outside the fiber can be displaced or mixed with cleaner liquor by breaking up the fiber network. However, the liquor inside the fiber can only be affected by diffusion through the pores in the fiber wall.

The washing operation can be divided into two major principles:

- Dilution of the pulp with a cleaner liquid and then thickening to remove the liquor with contaminants
- Displacement of liquor with a cleaner liquid without changing the consistency.

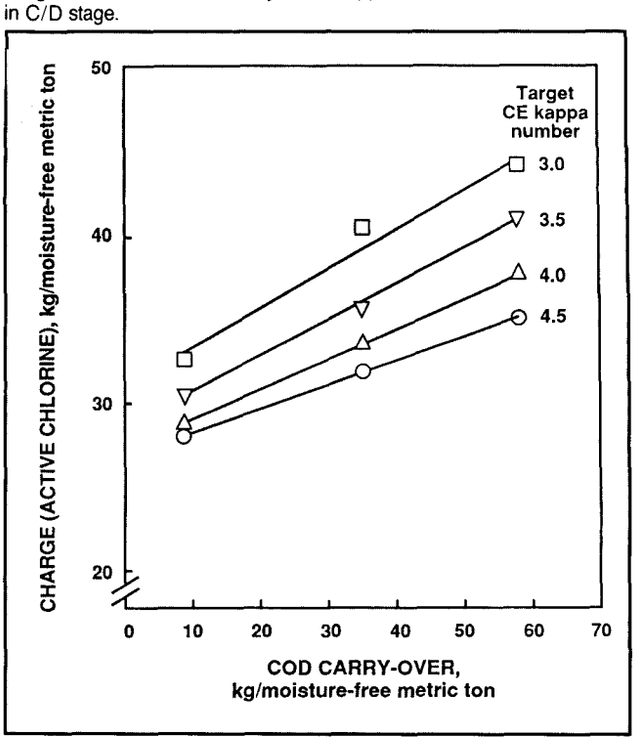
## Diffusion

Diffusion occurs whenever there is a difference in liquor concentration between the inside and the outside of a fiber, e.g., when pulp is diluted or displaced with a cleaner liquid. The speed at which diffusion takes place is a function of the difference in concentration between the inside and the outside of the fiber, temperature, turbulence in the liquor surrounding the fiber, and the size of the molecule that is subject to diffusion. The rate of diffusion is highest when the difference in concentration is large, the temperature is high, the turbulence is intense, and the molecule undergoing diffusion is small.

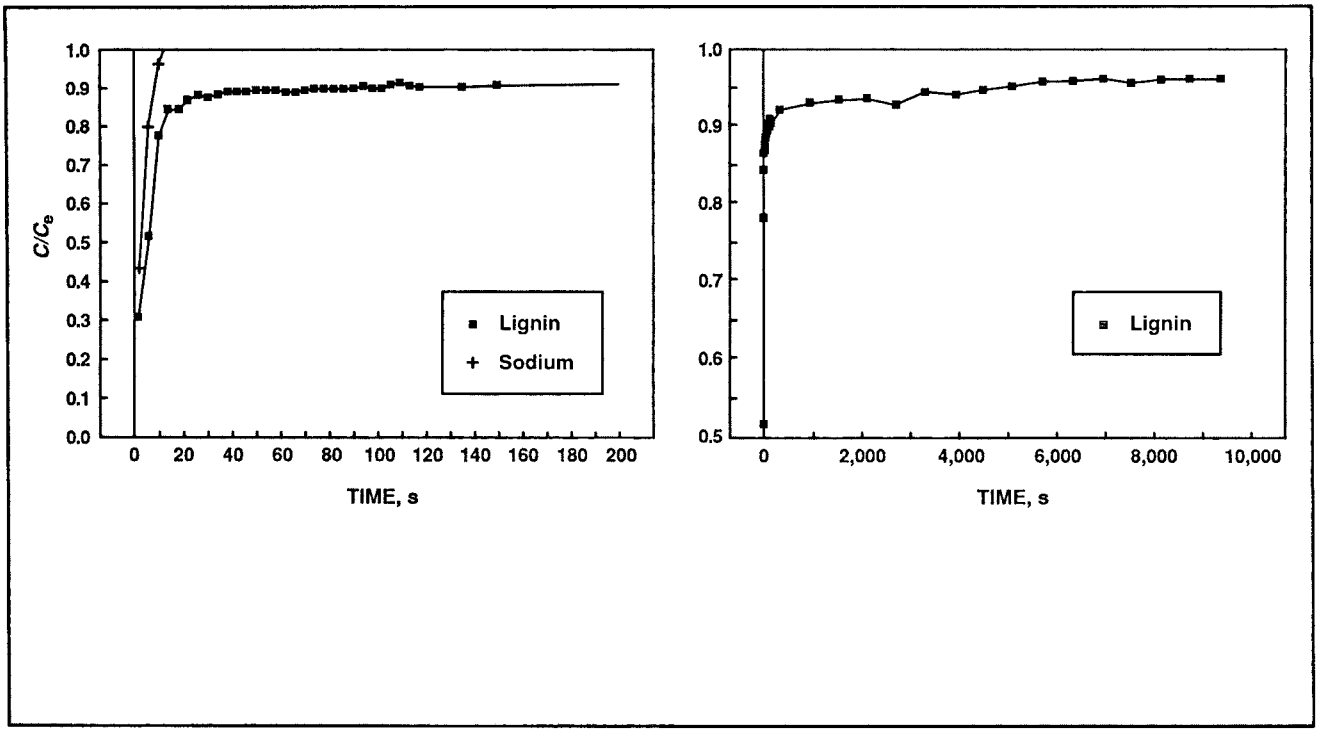
Several authors have addressed the issue of lignin diffusion from wood pulp suspended in water. Trinh and Crotogino (*2*) used softwood pulp with dilute dissolved lignin and sodium concentrations to simulate the last washing stage. The lignin and sodium concentrations in the suspension were measured at close intervals initially, and then at longer intervals, up to a total time of about 2.5 h. A similar technique was used by Edwards and Rydin (*3*), but their reported time periods were relatively short, about 2 min. Favis *et al.* (*4*) removed all free liquid and measured the diffusion of lignin out of the fiber wall for time periods up to several weeks. Eriksson and Gren (*5*) used a technique similar to that of Favis by washing the pulp shortly before suspending it in water and measuring lignin concentration for about 2.3 h. All authors used some type of stirred vessel in which the pulp consistency was 1% or lower.

Trinh and Crotogino (*2*) made the assumption that a part of the liquor entrained in the fiber is not available for immediate dispersion of lignin in the free-liquor phase and that all liquor is available for immediate dispersion of sodium. They thus came to the conclusion that lignin and sodium diffused at about the same rates, a conclusion also drawn by Edwards and Rydin (*3*). In both works, the authors used the measured lignin and sodium concentrations after 1-2 min as a reference point. The raw data developed by Trinh and Crotogino (*2*) suggest that desorption of sodium from the fibers influenced this reference point. Different conclusions can be made by using a calculated equilibrium point based on the dilution ratio in the experiments and the known sodium and lignin concentrations in the undiluted pulp. This approach eliminates the problem of desorption and the question of

**2.** Impact of COD carry-over on chemical consumption in the chlorination stage. Results based on softwood pulp after oxygen delignification in the laboratory, initial kappa no. 17.8, 20% substitution in C/D stage.



**3.** Relative concentrations of sodium and lignin in the free-liquor phase. $C_e$ is the theoretically calculated equilibrium concentration based on pulp dilution. Data provided by Trinh and Crotogino (*2*).




whether or not the entrained liquor is accessible for lignin diffusion.

Trinh and Crotogino's data (*2*) are depicted in **Fig. 3**, where the lignin and sodium concentrations ($C$) are shown as a fraction of the calculated equilibrium point ($C_e$) versus time. **Figure 4** presents these data as a first-order reaction model, as suggested by Trinh and Crotogino (*2*) and Edwards and Rydin (*3*). In Fig. 4, $\ln[(C_e-C)/C_e]$ is plotted versus time, and the slope of the curve provides the time constant for the reaction (in this case, the diffusion). The sodium data show a straight line with a slope of 2.95 s. Since the measured time constant for the mixing in the tank was 2.75 s, it can be concluded that the unsorbed sodium diffuses out of the fibers almost instantaneously. The time constant is in the order of 0.2 s. Additional sodium is removed from the fiber at slower rates, as demonstrated by Trinh and Crotogino (*2*) and Edwards and Rydin (*3*). This sodium is most likely attached to larger organic molecules, which diffuse at substantially slower rates than sodium, as seen in Fig. 4.

The lignin data in Fig. 4 show four distinct regions, with fairly sharp break points at about 15 s, 40 s, and 300 s. The first break point at 15 s is due to the time it takes to get the fibers uniformly distributed within the vessel used in the experiment. The other points can be interpreted as liquor entrained in three different areas of the fiber, with diffusion in each area essentially complete at one of the break points.

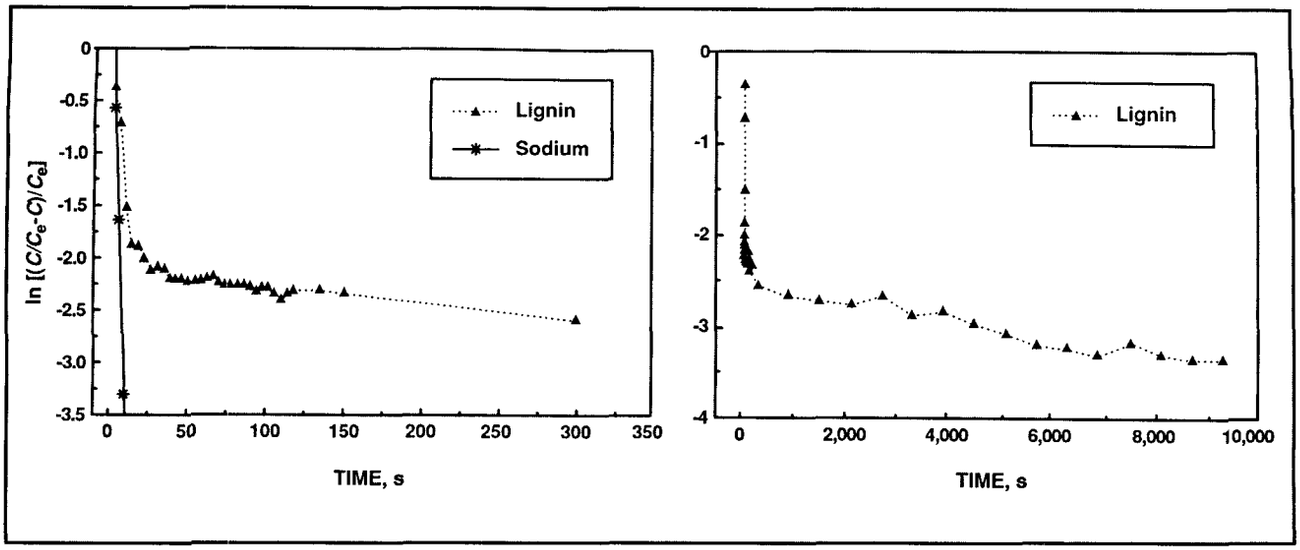
A model was constructed to describe the diffusion of lignin from these three areas within the fiber to the surrounding liquor. The volume of liquor entrained within each area and the diffusion time constants for each area were adjusted to obtain the best fit with the data in Fig. 4. The resulting volumes and diffusion time constants are shown in **Fig. 5**, and the fit to experimental values is shown in **Fig. 6**.

The total amount of entrained liquor in each moisture-free gram of fiber is about 2.25 g, of which 1.2 g is subject to relatively fast lignin diffusion ($L_1$), while 0.4 g is one order of magnitude slower ($L_2$), and 0.65 g is two to three orders of magnitude slower ($L_3$). The calculated time constants are 15 s, 300 s, and 7500 s for diffusion of lignin out of the respective entrained liquor volumes $L_1$, $L_2$, and $L_3$.

The calculated entrained liquor volumes are well within the range reported by other authors (2-3 g total entrained liquor in each moisture-free gram of fiber and 1-2 g entrained liquor in the fiber wall for each moisture-free gram of fiber) and summarized by Wong and Reeve (*1*). It is probably reasonable to assume that the $L_1$ volume (1.2 g liquor/moisture-free g fiber) includes the liquor in the lumen and between the fibers in fiber bundles that are not broken up. The $L_2$ and $L_3$ volumes represent different parts of the fiber wall. Choi *et al.* (*6*) reported a different behavior in the secondary wall from the rest of the fiber wall, which could explain the observation of the two volumes ($L_2$ and $L_3$) that appear to be affected by different resistance to diffusion.

The data presented by Edwards and Rydin (*3*) show the same order of magnitude for diffusion during the first 2 min. Data from Favis *et al.* (*4*) and Eriksson and Gren (*5*) show the same order of magnitude for the long-term diffusion. Exact diffusion time constants for the last three sources (*6-8*) cannot be calculated because there is no way to determine the theoretical equilibrium concentration. The relatively small differences among the various

4. Data from Fig. 3 expressed as a first-order reaction




experiments can be explained by differences in wood species, fiber history, pH, temperature, and other factors. Thus the diffusion model is valid only at 30°C and pH 9, the conditions used by Trinh and Crotogino (*2*).

It is likely that differences in the rate of lignin diffusion for different areas of the fiber are the result of physical differences in the fiber wall rather than changes in the size of the lignin molecules throughout the course of the experiment. If the latter were the case, a more continuous curve would be the result, rather than the fairly rapid changes in diffusion rate that take place at certain points during the experiment.

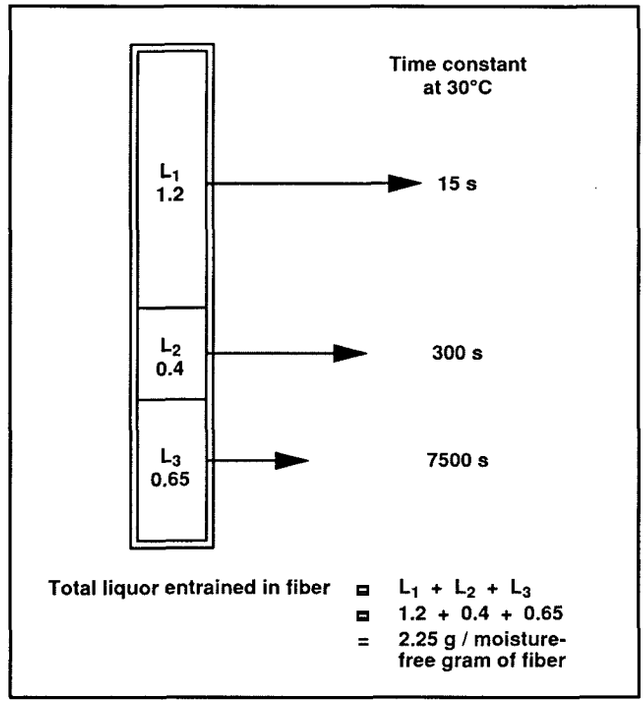
Because of the slow diffusion out of $L_3$, most of the lignin contained in this part of the fiber will likely be measured as kappa number of the pulp, depending on how long after sampling the kappa number test is run

## Effect of temperature and pH on lignin diffusion

Goring (*7*) reports a predictable (and almost linear) increase in lignin diffusion at temperatures between 20°C and 70°C. The long-term (several hours) diffusivity increased by a factor of 1.5 when temperature was increased from 30°C to 70°C. Trinh and Crotogino (*2*) observed no change in lignin diffusion rates between 30°C and 45°C, either over the short or long term. Goring (*7*) observed a sharp increase in diffusivity for temperatures 80°C and higher, with diffusivity increasing by a factor of 5.5 from 50°C to 90°C. This observation is supported by Eriksson and Gren (*5*), who observed long-term diffusion increase by a factor of four and short-term (up to 6 min) diffusion increase by a factor of 2.5 between the same temperatures.

Temperature also has a large effect on the hydraulic capacity of the washing equipment and can therefore greatly affect the overall washing result. Washing at temperatures above 80°C can have a considerable impact on the amount of lignin removed from the pulp. Eriksson and Gren (*5*) show a one-unit drop in kappa number in a pulp washed for 5 min at 90–100°C.

5. Diffusion model based on data from Fig. 3. $L_1$, $L_2$, and $L_3$ represent three phases for liquor entrained within the fiber.

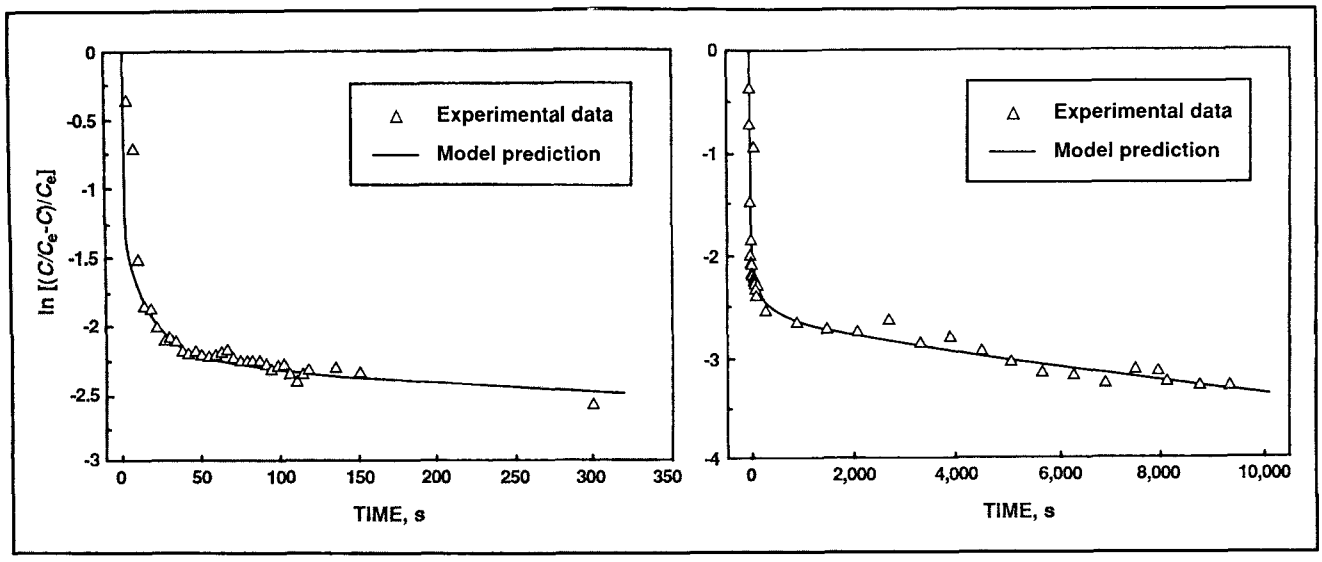



The effect of pH on lignin diffusion was studied by Wilcox and Goring (*8*), who found an increasing diffusion rate with increasing pH, especially when the pH was above 7. The effect is most likely the result of increased swelling of the fiber.

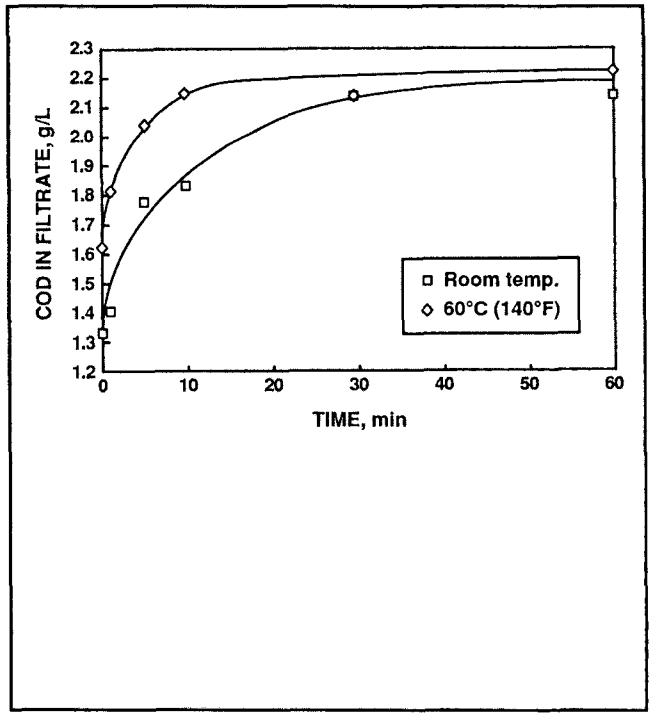
## Comparison between lignin and COD

Experiments performed by our company show that COD and lignin behave similarly. **Figure 7** shows the concentration of COD in wash filtrate over 1 h at two temper-

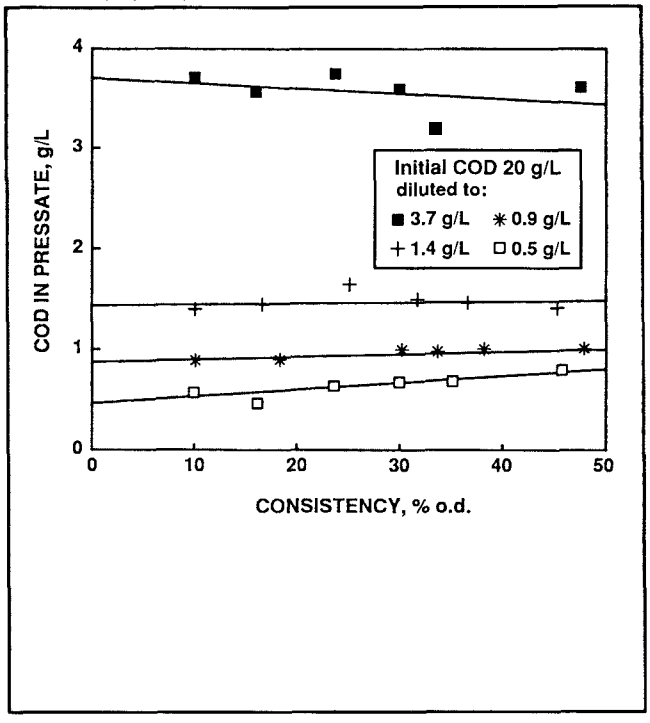
**6.** Comparison of laboratory results in Fig. 4 with predicted values from diffusion model




**7.** COD concentration in filtrate of pulp (1% consistency) at room temperature and at 60°C




**8.** COD concentration in pressate of never-washed, oxygen-delignified pulp after dilution and equilibration. Each data point represents COD concentration in the incremental pressate for each of the four pulp suspensions.




atures. At room temperature, the pulp suspension reaches an apparent equilibrium after about 30 min. At 60°C, however, it takes only about 10 min to reach the same apparent equilibrium point. These data fit well with the $L_2$ phase reaching equilibrium in Trinh and Crotogino's experiments on lignin diffusion (*2*). The three-time-faster diffusion rate at 60°C also fits well with Goring's data on lignin (*7*). We can thus draw the conclusion that lignin and COD are similar in their diffusion behavior, and we can use experiences with one compound to predict the other.

## Pressing

When pulp is diluted with cleaner liquor, the free liquor mixes with the dilution liquor. The liquor inside the fiber is affected by diffusion only. Provided the enclosed and free liquors reach equilibrium, thickening the pulp, even to very high consistencies, does not affect the concentration in the liquor that remains with the pulp. This is shown in **Fig. 8**, where never-washed pulp was diluted to different dissolved organic solids concentrations (measured as COD), allowed to stand overnight for equilibra-

tion, and then pressed to consistencies up to 45–50% o.d. The incremental pressate samples show small differences in COD concentration at various levels of pressing. This means pressing has no extra effect on COD removal beyond simply removing the liquor. If the retention time between dilution and thickening is short, the enclosed liquor will be dirtier than the free liquor, and the cleaner liquor will preferentially be removed in the thickening step, thus leaving the dirtier liquor inside the pulp fibers.

We can thus conclude that efficient removal of a swiftly diffusing compound like sodium can be accomplished in a washer designed for short retention times. Efficient removal of compounds that diffuse more slowly, such as the compounds that create COD, requires a washer with a long retention time in the wash zone.

## Measured efficiencies on operating equipment

We have laid a theoretical ground that a washer designed to efficiently remove COD from pulp should have a much longer retention time than is required to efficiently remove sodium. **Table I** lists the measured displacement ratios (DR numbers) for sodium and COD on identical liquor and pulp samples for three types of pulp washers. The data are presented without considering operating conditions (consistencies, loadings, temperatures, and dilution factors). However, these variables are not important when we are just looking at the difference in washing performance on different compounds in the same samples.

Table I shows a clear trend toward a decreasing efficiency in COD removal compared with sodium removal as the retention time in the wash zone is decreased. The atmospheric diffuser with 5–10-min retention time is equally effective at removing COD and sodium, with COD removal arguably better than sodium removal. The pressure diffuser at 90–120-s retention time is slightly less efficient on COD than sodium. The wash press, with 4–5 s in the wash zone, gives about 6 DR units less efficiency for COD than sodium. The drum washer—with only 2–3 s in the wash zone—has an average DR number that is 12 units lower for COD than for sodium. Comparable differences for drum washers were measured by Smedman and Jamieson (*9*).

All washing-efficiency measurements made on the commercial equipment shown in Table I were made on liquor squeezed out of the pulp within a few minutes after the samples were taken. This method of testing slightly disfavors the atmospheric diffuser, since it takes the pulp about 10 min to reach the sampling point and some diffusion takes place during this time period. For pressure diffusers, drum washers and displacement wash presses, the time between washing and sampling is only a few seconds.

**I.** Measured DR numbers for sodium and COD on different pulp washers

| Mill | Pulp type[a] | DR no.[b] COD | DR no.[b] Na | Difference in DR no. (COD–Na) | Average difference in DR no. |
|---|---|---|---|---|---|
| **Atmospheric diffusers (retention = 5–10 min per stage)** | | | | | |
| One stage | | | | | |
| A | SW | 0.90 | 0.90 | 0 | |
| Two stage | | | | | |
| C | SW | 0.98 | 0.96 | +2 | |
| C | SW | 0.97 | 0.93 | +4 | |
| D | SW | 0.93 | 0.91 | +2 | |
| E | SW (post $O_2$) | 0.98 | 0.97 | +1 | +1 |
| F | HW | 0.98 | 0.98 | 0 | |
| J | SW | 0.97 | 0.97 | 0 | |
| Three stage | | | | | |
| K | SW (post $O_2$) | 0.97 | 0.98 | -1 | |
| **Pressure diffusers (retention = 90–120 s)** | | | | | |
| G | SW | 0.92 | 0.94 | -2 | |
| H | SW (post $O_2$) | 0.90 | 0.91 | -1 | -2 |
| I | SW (post $O_2$) | 0.91 | 0.94 | -3 | |
| **Wash presses (retention = 3–4 s)** | | | | | |
| A | SW (post $O_2$) | 0.48 | 0.47 | +1 | |
| H | NSSC | 0.24 | 0.28 | -4 | |
| H | NSSC | 0.27 | 0.31 | -4 | -6 |
| H | SW (post $O_2$) | 0.29 | 0.36 | -7 | |
| I | SW (post $O_2$) | 0.40 | 0.56 | -16 | |
| **Drum washers (retention = 2–3)** | | | | | |
| C | SW | 0.58 | 0.65 | -7 | |
| C | SW | 0.31 | 0.74 | -43 | |
| F | HW | 0.81 | 0.87 | -6 | |
| H | SW | 0.81 | 0.88 | -7 | -12 |
| H | SW | 0.78 | 0.74 | +4 | |
| H | SW | 0.53 | 0.60 | -7 | |
| H | SW | 0.43 | 0.59 | -16 | |

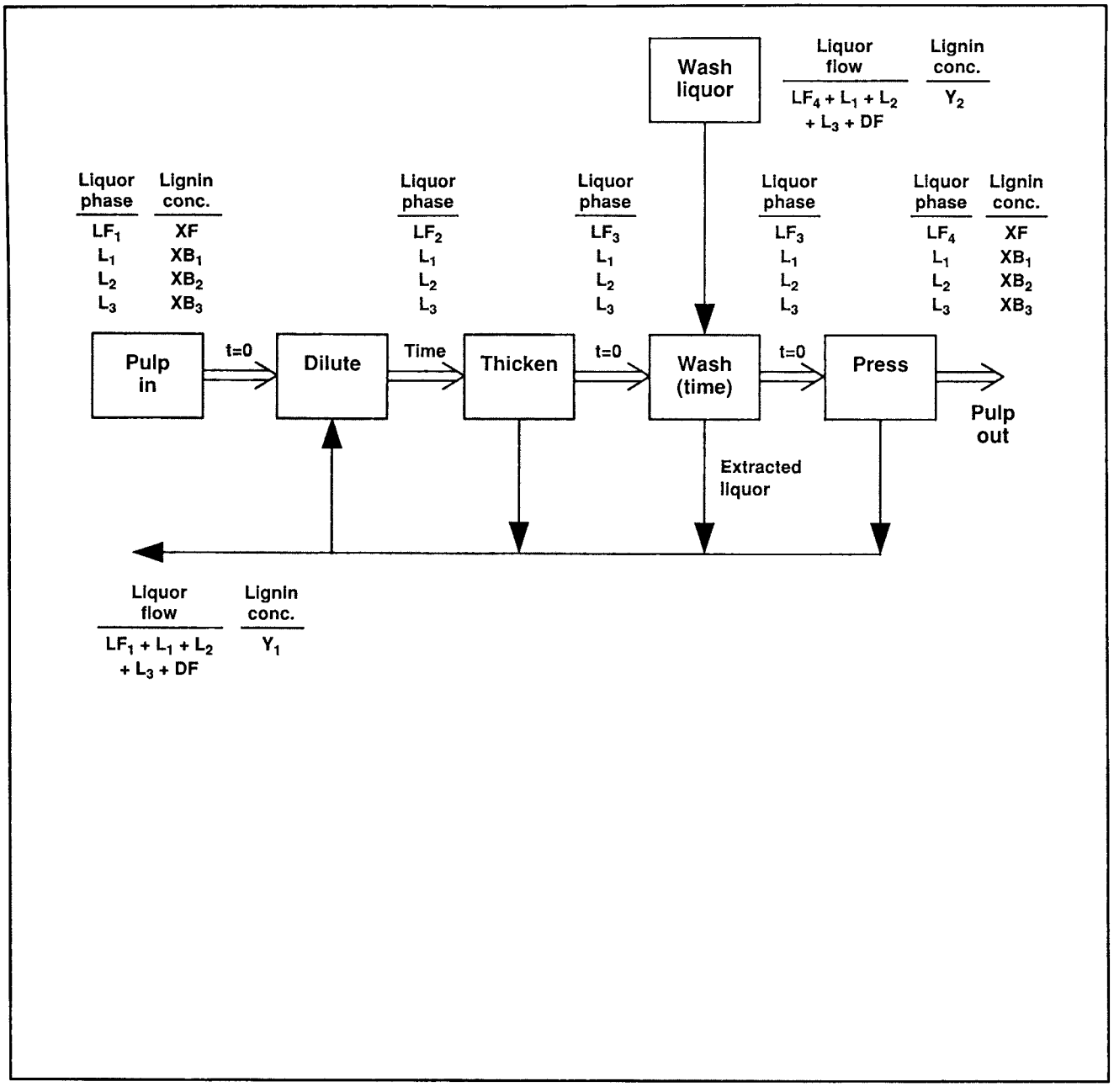
[a] SW = softwood; HW = hardwood; NSSC = neutral sulfite semichemical; post $O_2$ = post-oxygen-stage washing

[b] $DR = (x_0 - x_1) / (x_0 - y_2)$; $x_0$ = concentration in pulp entering washer; $x_1$ = concentration in pulp leaving washer; $y_2$ = concentration in wash liquid.

## Predicting the washing efficiency for organic solids

We have created a computer model that can simulate one stage of washing, including dilution, thickening, displacement washing, and pressing. Four liquor phases are assumed to flow with the fiber. Three phases are enclosed within the fiber, and one "free" liquor phase surrounds the fiber. Diffusion takes place between the different liquor phases as soon as there is a concentration gradient. The model also incorporates retention times in and between the different unit operations. In the displacement washing calculation, the model consists of a pulp mat that moves through the displacement zone. The mat thickness is divided into several elements. Wash liquor is introduced into the top element, where it displaces free liquor only. Diffusion starts between the entrained liquor phases and the "new" free liquor. The displaced liquor from the first element displaces liquor from the second element, and so on, until free liquor from the last element is removed from the pulp pad. The pulp mat is then exposed to another increment of wash liquor until the desired amount of wash liquor has been added.

**9.** Flow diagram showing the basis for the washer model used to predict dissolved organic solids losses. $LF_i$, $L_1$, $L_2$, and $L_3$ are the free liquor and the three entrained liquor phases, respectively. XF, $XB_1$, $XB_2$, and $XB_3$ are the COD concentrations in the respective liquor phase. DF is the dilution factor (wash liquor in excess of liquid in pulp stream).

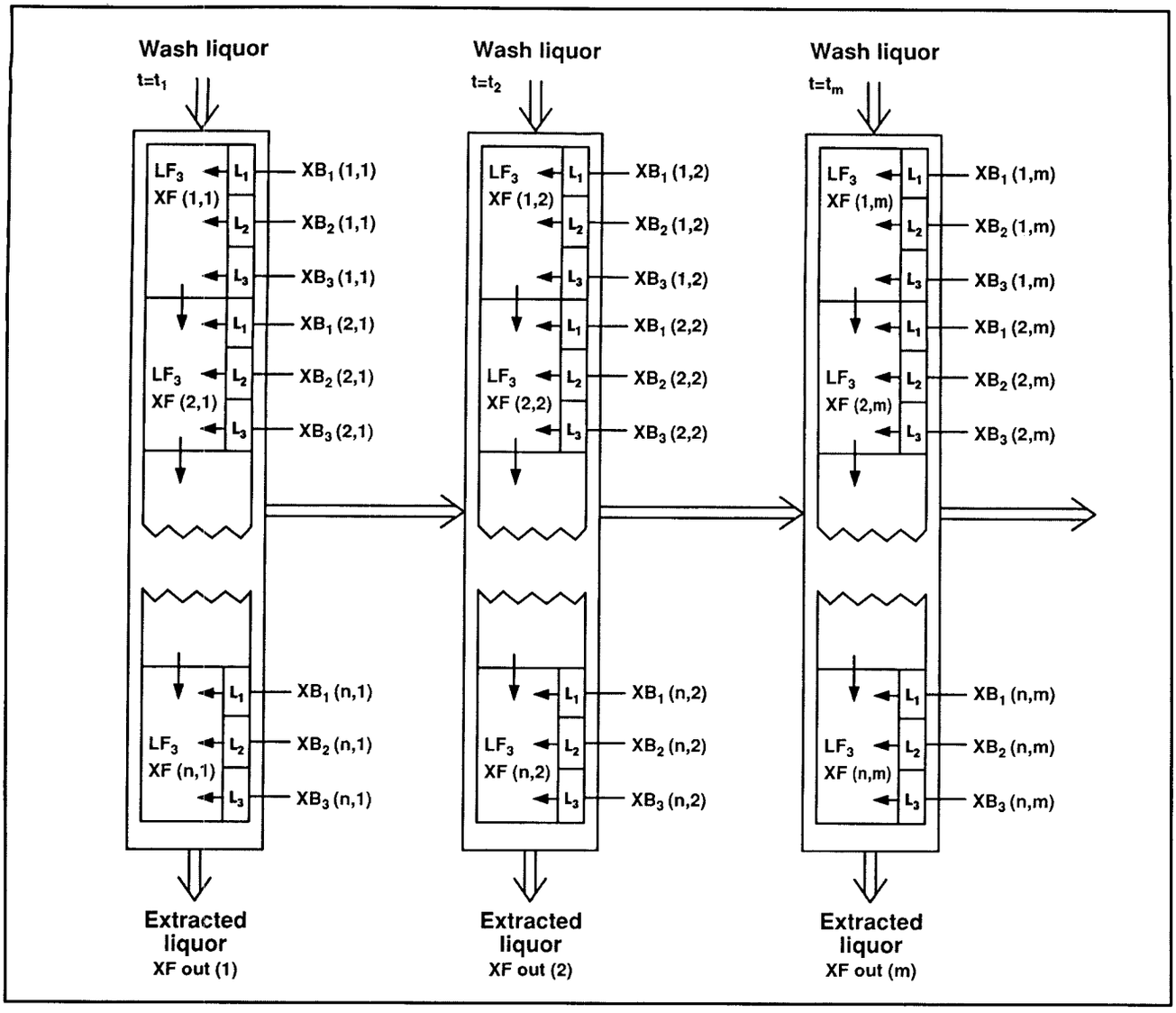



A simplified flow schematic of our hypothetical washer is shown in **Fig. 9**. The displacement washing zone is illustrated in **Fig. 10**.

**Table II** lists the chosen parameters for three different types of common pulp washers. The parameters were chosen to give the vacuum drum washer, the displacement wash press, and the one-stage atmospheric diffuser exactly the same performance on unsorbed sodium, as seen in **Table III** (sodium data). There are probably some minor variations between these washers, but this parameter selection will clearly show the differences in the washing of organic solids. The result that is of particular interest in determining washer efficiency is how much substance is left in the pulp leaving the washer. As seen in Table III (sodium data), the drum washer, displacement wash press, and one-stage atmospheric diffuser in our model all leave 11% of the sodium in the pulp. The calculated DR numbers for sodium are close to the results measured on the industrial equipment, shown in Table I.

We calculated the values for the dissolved organic substance using the diffusion constants developed from Trinh and Crotogino's data (*2*) and then corrected them for temperature according to Goring (*7*). We simulated washer performance at 70°C, so we took the diffusion constants for 30°C and divided them by a correction factor of 2.5. We also increased the simulation pH to 10, compared with pH 9 for Trinh and Crotogino (*2*). This increased the overall correction factor to about 3. We assumed that this

**10.** Displacement model




correction is valid for the short-term diffusion out of $L_1$ based on the fact that the measured effect of temperature reported by Goring (*7*) agreed well with what would be theoretically expected. Temperature and pH are constant throughout the entire washing stage. The free and entrained liquor have the same concentration when the pulp enters the washing stage.

For a typical commercial pulp washing system, the resulting time constants will then be

$L_1$ (1.25 ton/moisture-free ton) = 5 s

$L_2$ (0.4 ton/moisture-free ton) = 100 s

$L_3$ (0.65 ton/moisture-free ton) = 2500 s

The calculated results for lignin are presented in Table III (all-liquor data). It is clear that the efficiency of all the washers is considerably less for lignin than for sodium, but the reduction is much more pronounced for the drum washer and displacement wash press, which have much shorter retention times than the atmospheric diffuser.

**II.** Operating conditions for the three washers used in the simulation model

| | *Vacuum drum washer* | *Displacement wash press* | *Atmospheric diffuser* |
|---|---|---|---|
| Incoming pulp consistency, % | 10 | 10 | 10 |
| Pulp consistency after dilution, % | 1 | 4 | 10 |
| Time at this consistency, s | 30 | 300 | 1200 |
| Pulp consistency in displacement zone, % | 12 | 15 | 10 |
| Retention time in displacement zone, s | 3 | 5 | 450 |
| Outgoing pulp consistency, % | 12 | 30 | 10 |
| Dilution factor, ton/moisture-free ton | 2.78 | 2.78 | 2.78 |

**III.** Washing efficiencies for sodium and for dissolved organic solids as calculated by the simulation model[a]

| | *Vacuum drum washer* | *Displacement wash press* | *Atmospheric diffuser* |
|---|---|---|---|
| **Sodium data (unsorbed sodium only)** | | | |
| Displacement ratio (DR), % | 81 | 47 | 89 |
| Equivalent displacement ratio (EDR)[b], % | 81 | 81 | 81 |
| Yield, % | 89.0 | 89.0 | 89.0 |
| Left in pulp, % | 11.0 | 11.0 | 11.0 |
| **Lignin data (all liquor accessible for washing)** | | | |
| Displacement ratio (DR), % | 60 | 10 | 84 |
| Equivalent displacement ratio (EDR), % | 60 | 67 | 71 |
| Yield, % | 79.1 | 82.1 | 84.3 |
| Left in pulp, % | 20.9 | 17.9 | 15.7 |
| **Lignin data (all liquor except $L_3$ accessible for washing)** | | | |
| Displacement ratio (DR), % | 71 | 24 | 91 |
| Equivalent displacement ratio (EDR), % | 71 | 72 | 85 |
| Yield, % | 85.3 | 88.5 | 90.9 |
| Left in pulp, % | 14.7 | 11.5 | 9.1 |

[a]Washer operating conditions as listed in Table II. Temp. = 70°C. Diffusion constants $L_1$, $L_2$, and $L_3$ are 5 s, 100 s, and 2500 s, respectively.

[b]EDR represents the equivalent washing efficiency, expressed as a DR-number, of a washer if it were operating with % inlet and 12% discharge consistency (*10*).

The results in Table III are based on the assumption that the entire liquor volume is accessible to be washed out of the fiber bed. This was shown to be the case for sodium, where the diffusion out of the entrained liquor is very fast. It takes a retention time that is 4-5 times greater than the diffusion time constant to get within 99% of the equilibrium concentration. This means that it will take 20-25 s at operating temperature and pH for $L_1$ to get to this point. For $L_2$ and $L_3$, the times are 6-8 min and 3-3.5 h, respectively. At room temperature, it would take three times longer to achieve equilibrium. At the time of testing, most of the dissolved organic substance contained in $L_3$ will therefore be part of the kappa number of the pulp. Table III shows the results for lignin if the $L_3$ phase is excluded.

## Testing

The diffusion of dissolved organic substance continues after the pulp leaves the washer. Therefore, the testing result is affected by the following parameters:

- Method of removing the liquor sample from the pulp
- Time elapsed after washing
- Consistency of the pulp during the time lapse
- pH during the time lapse
- Temperature during the time lapse.

No general statements can be made as to which of these parameters is more important. It depends on the time interval and how close to equilibrium the pulp got in the washing stage.

### Liquor sampling method and time

There are two methods to get a liquor sample out of the pulp suspension: squeezing or soaking.

Squeezing the pulp will preferentially remove the free liquor. Using mechanical devices for pressing in the lab will probably make it possible to remove the $L_1$ fraction as well. To get any of the $L_2$ and $L_3$ fractions should probably be regarded as impossible by squeezing, since the resulting consistency would have to be over 50%. The time lapse after the pulp leaves the displacement zone will affect the concentration of COD in the free liquor. This is illustrated in **Fig. 11**, which shows actual data and predicted results for a pulp sample taken off a two-stage diffuser in a post-oxygen washing position. The COD loss increases from 3.4 kg/moisture-free metric ton to 5.0 kg/moisture-free metric ton in 24 h. The predicted curve does not completely agree with the data but shows a similar trend.

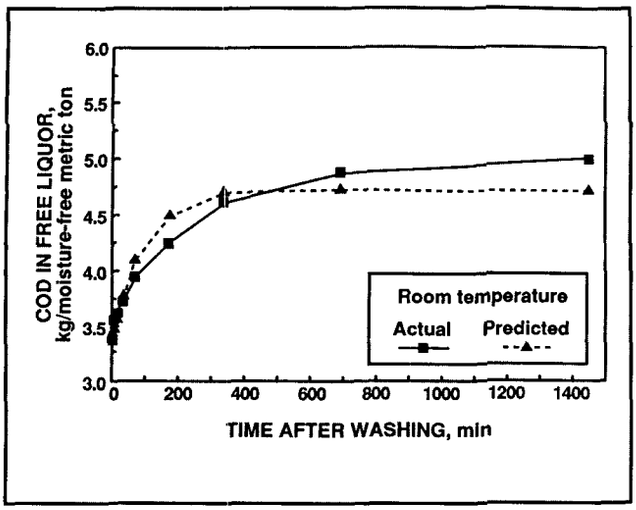
**Figure 12** shows the predicted variation in lignin concentration in the free liquor within the first 2 h after the pulp leaves each of the washers described in Table II. Temperature and pH after washing are assumed to be the same as in the washer. The free liquor concentration at time zero for the atmospheric diffuser is set as reference. The resulting DR numbers for the three washers are shown in **Fig. 13**. The DR number in this case is calculated as if the free-liquor phase represents all the liquor with the pulp, which would actually be the case if the pulp were squeezed by hand.

The displacement wash press would not be expected to have any free liquor into which diffusion can take place. Squeezing the liquor out of the pulp leaving the press would remove the $L_1$ liquor phase. This liquor concentration would not be expected to change over time. For the displacement wash press, the expected concentrations in the $L_1$ phase are shown in Figs. 12 and 13. The DR numbers predicted for the different washers within a few minutes after the pulp leaves the displacement zone agree well with the DR numbers for industrial washers presented in Table I.

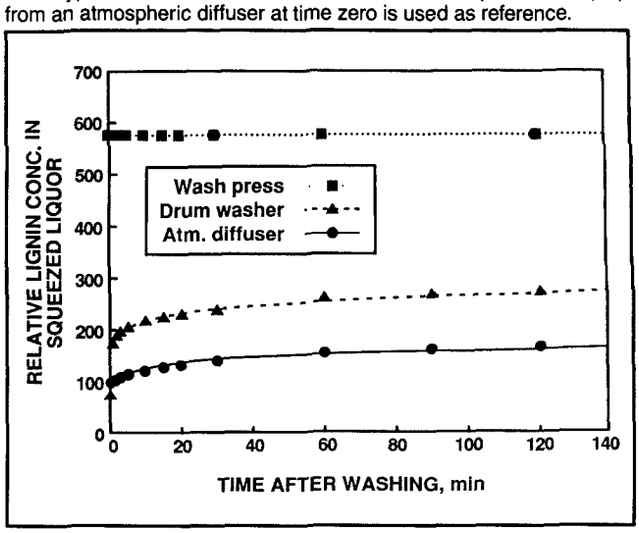
### Suggested test method

Instead of squeezing the pulp, we think that the pulp should be soaked in a mildly stirred tank for a defined period of time at a defined consistency, temperature, and pH. All of this should be done at a defined period of time after the pulp sample has been collected. The kappa number of the pulp should be determined on the same pulp sample that was used to determine the dissolved organic solids concentration, after the pulp has been soaked. The kappa number and COD loss determined this way should give a very good indication of the expected bleach chemical consumption.

**11.** COD concentration in free liquor as a function of time after pulp leaves the washer. Actual and simulated results for pulp sample taken off a commercial two-stage atmospheric diffuser.




**12.** Predicted results for relative lignin concentration in squeezed liquor as a function of time after pulp leaves displacement zone for three types of washer. The concentration in free liquor for the pulp from an atmospheric diffuser at time zero is used as reference.

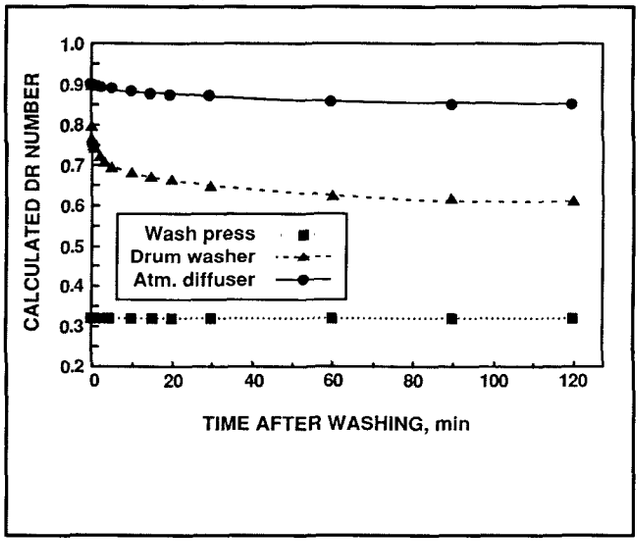



## Conclusions

The results support the following conclusions:

- Diffusion for dissolved lignin and COD is slower than for unsorbed sodium.
- Pulp washers with long retention times have a better opportunity to remove dissolved lignin and COD than washers with short retention times.
- Temperature and pH have a major impact on the rate of diffusion of dissolved lignin and COD and could alter the way future wash lines are designed.
- Testing procedures can greatly affect the perceived washing result. There is a need for a standardized procedure to determine dissolved organic substance in pulp.□

**13.** Calculated DR numbers as a function of time after pulp leaves the displacement zone for three types of washer. DR number based on COD in the free-liquor phase only.

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