Enhanced lignin removal in brownstock washing

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ABSTRACT: Concerns about the effects that chlorine bleaching effluent may have on the environment have made the paper industry more interested in lowering pulp lignin levels before bleaching. Current industry alternatives include oxygen delignification and extended cooking, but both processes require a significant capital investment. This project was designed to study lignin removal during kraft brownstock washing and screening and to assess the feasibility of modifying the brownstock washing unit operation to maximize the leaching of freeable lignin.

KEYWORDS: Feasibility, leaching, lignins, removal, screening, unbleached pulps, washing.

Given the high capital investment required to implement current industry alternatives for lowering lignin levels before bleaching, we decided to study the behavior of lignin in mill brownstock washing situations and to determine the process conditions that have the greatest effect on lignin removal and hence should be controlled. Analysis of the washing variables should suggest a feasible means to augment delignification prior to bleaching. The identified method could then be implemented through configurational changes in an existing mill wash line.

Brownstock washing theory and variables

The purpose of brownstock washing is to separate the pulp from the black liquor solution, sending clean pulp to the bleach plant and black liquor to chemical recovery. Regardless of the type of washer used, the separation is accomplished with a combination of displacement and diffusion processes. An ideal displacement washing process would have a plug flow of wash liquor moving through a stationary pulp pad, completely replacing the previous solution. Real washing processes exhibit several departures from this ideality, such as viscous fingering and axial diffusion or back-mixing. Some of the solute will be contained in stagnant areas between fibers, in the fiber lumen, and within the fiber walls. This material must diffuse out of the stagnant areas before it can become available for displacement.

Viscous fingering, axial diffusion, and even diffusion from stagnant areas between fibers all occur on a relatively short time scale and must be controlled using washer variables: shower water application method and volume, vat consistency, machine speed, etc. Diffusion of inorganics, degraded lignin, and other pulping byproducts out of the fiber lumen and walls occurs on a longer time scale and is less dependent on machine variables. Several researchers have shown that sorption and diffusion effects must be taken into account when calculating soda losses in washing (*1–3*).

Lignin behavior during washing has been studied on a fiber level by Choi *et al.* (*4*). In their study, washing was performed for varying lengths of time, and then the lignin concentration of the filtrate was measured. Two phases of lignin removal were found: an initial quick phase, during which lignin was removed, and a slower, apparently diffusion-controlled phase. The main mechanism proposed for lignin removal is degradation of protolignin and diffusion through the cellulose hydrogel, with diffusion controlling.

Favis, the author of five published papers on lignin removal during washing, found the total lignin available for leaching to be approximately 1.6% of the fiber weight (*5*). Increasing tem-

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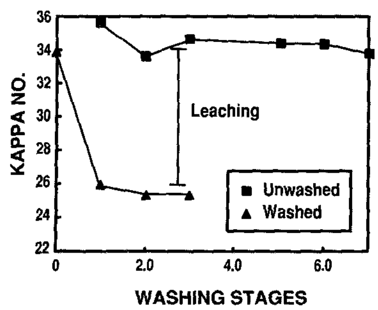
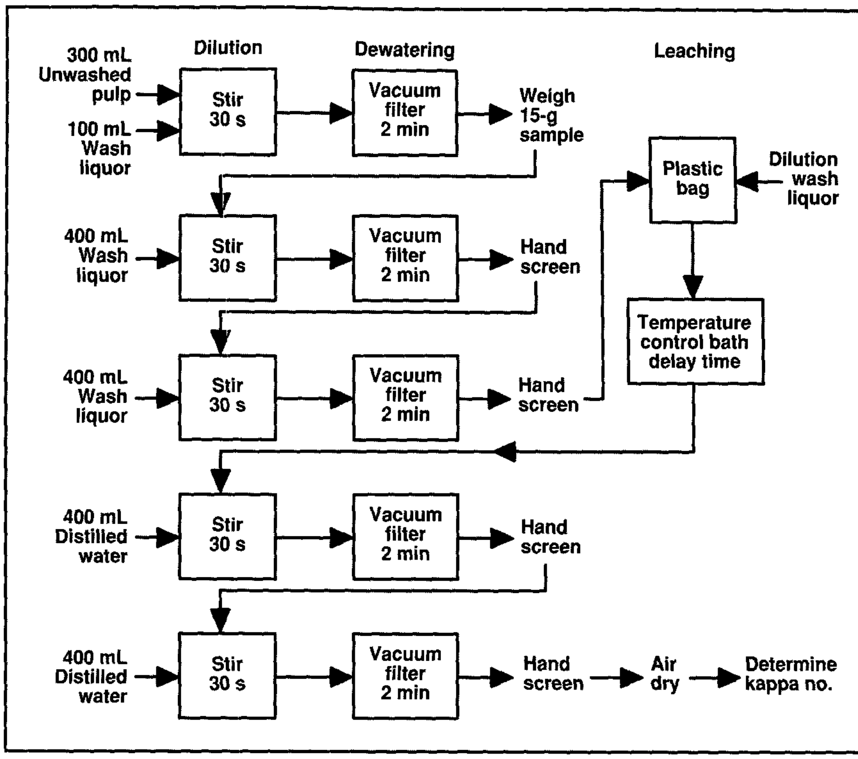
1. Change in kappa number as a function of leaching and washing stages



2. Method used in leaching experiments



perature was found to enhance leaching, while the presence of electrolytes greatly inhibited lignin removal.

Hagstrom-Nasi *et al.* performed experiments similar to those of Favis and found similar results (*6*).

Experimental

Preliminary trials

The practicality of using leaching to augment brownstock delignification is determined by the amount of time required for the process to reach a reasonable degree of completion. Several studies on diffusion of dissolved substances from pulp fibers have been performed, but the results have been inconsistent with regard to the absolute time requirement and the relative mass transfer rates of different solutes (*7–9*). Preliminary trials in this study were performed to estimate the time required for lignin removal within the constraints of a commercial brownstock pulp washer system. Douglas-fir pulp samples for the trials were taken from the inlet and the outlet of the washer train at Weyerhaeuser's Everett, WA, kraft pulp mill.

In the preliminary trials, samples of the mill-washed and unwashed pulps were washed with distilled water by dilution and filtration through a different number of washing stages. Both the mill-washed and unwashed pulp samples had been in the cold room for 60 days, and it was observed that the mill-washed pulp yielded a brown filtrate when pressed. The mill-washed pulp was carefully dried for use as the zero-wash-stage sample so that none of the dissolved material was lost. No zero-stage test was run on the unwashed pulp. The results of this test, shown in **Fig. 1**, demonstrate that there is a significant difference between the two samples. The kappa number for both pulp samples leveled out quickly with washing, but storage of the mill-washed pulp at 10% consistency allowed a substantial additional amount of lignin to enter the wash solution and be removed from the pulp.

Based on these preliminary trials and previous research in the literature, a hypothesis was made that a significant amount of lignin can leach out of the fibers but that the short time scale of washing is insufficient to significantly change the kappa number of the pulp. Other preliminary trials indicated that wash liquor pH would be an important controlling factor. The in-depth leaching studies were then designed with an emphasis on tests with liquors having high alkali concentration.

In-depth leaching trials

Pulp was taken from the inlet to the washers for the leaching experiments. The leaching measurements were made with reference to a sample of the unwashed pulp that had been washed in the laboratory with distilled water without allowing additional time for leaching. This reference, called the "initial kappa number" of the pulp, allowed the total amount of lignin removed from the fibers by leaching to be determined. Care was taken to ensure that the conditions of washing for each sample were similar by controlling wash liquor volume, pulp weight, mixing time, and filtration time. Mill-washed samples were used to compare the laboratory leaching results to the mill process. These samples were screened by hand and air dried.

The experiments were designed with leaching conditions that could realistically be implemented in an existing mill. Most of the experiments were performed following the method shown in **Fig. 2**. A sample taken from the washer inlet was first diluted and dewatered to produce a pulp mat with consistent characteristics so that weighing would produce samples of uniform size. The two subsequent washings removed black-liquor solids from the surface of the fibers and evenly applied the wash-liquor solution to the pulp. The samples were diluted with wash liquor to 8% consistency in a resealable plastic bag and immersed in a water bath at the temperature of interest for the appropriate time. When the samples were removed, they were washed twice with distilled water. Shives were removed by hand after each dewatering step so they would not interfere with the measurement of lignin in the pulp. The samples were then air dried and the lignin content of the pulp determined by the kappa number test (TAPPI Test Method T 236 cm-85).

The method shown in Fig. 2 allowed the total amount of lignin leached from the pulp to be repeatably determined and allowed a comparison with the performance of the mill system. The relative effects of retention time, wash liquor pH, temperature, electrolyte concentration, and initial kappa number on the lignin leaching rate after washing were tested using this method.

Results and discussion

Effect of pH

For the first leaching tests, four different wash-liquor NaOH concentrations and seven different retention times were used to study the effects of pH and retention time on the amount of lignin removed from pulp by leaching. These tests were run at 70°C with pulp of initial kappa no. 36. The results of these experiments are shown in **Fig. 3**. The tests were repeated using a different sample of Douglas-fir pulp of initial kappa no. 33. The results of these tests are shown in **Fig. 4** and verify the previous results. Results similar to those in Figs. 3 and 4 were observed by Hagstrom-Nasi *et al.* (*6*).

The results in Figs. 3 and 4 show that diffusion of lignin out of the fiber wall is a significant consideration in evaluating the efficiency of washing with respect to lignin removal and that higher retention time can benefit washing of bleachable-grade brownstock. At higher pH, lignin leaching was significant even with moderate retention time, medium consistency, moderate temperature, and initial low kappa number.

The results of experiments to determine the effects of pH on leaching of lignin from pulps at three different initial kappa numbers are summarized in **Fig. 5**. The 24-hour kappa number is a measure of the lignin remaining in the pulp after 24 hours of leaching. The results show that high pH is required to remove a significant amount of lignin. There does not appear to be, based on these results, a maximum of leaching relative to pH.

Effect of temperature

Previous work has shown that increasing the temperature during leaching could dramatically increase the rate of lignin removal (*10*). Studies of temperature variation were performed to determine if elevated temperature would significantly increase leaching in alkaline wash liquors.

The temperature was varied between extremes of 20°C and 90°C, a range representative of conditions feasible on a vacuum-drum washer line. The results of two temperature studies are shown in **Fig. 6**. The first test was performed by leaching a sample of mill-washed pulp initially at kappa no. 32 in a solution of 0.01*N* NaOH (pH 12) for 24 hours. The second test was performed by washing and leaching a sample of unwashed pulp initially at kappa no. 48 in a solution of 0.1*N* NaOH (pH 13) for 24 hours. Both tests show an approximately linear increase in lignin leached with temperature.

Effect of electrolyte concentration

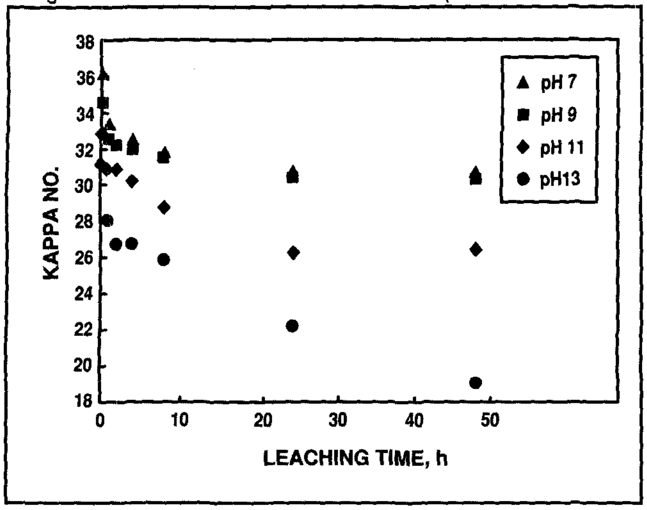
Electrolytes in wash liquor have previously been shown to inhibit lignin removal and fiber swelling (*11–15*). Studies were performed to investigate the effect of additional electrolytes on leaching in alkaline wash liquors.

A wide range of electrolyte concentrations was tested, since the electrolyte content of the wash water in a pulp mill is variable. The results of the electrolyte concentration trials are shown in **Fig. 7**. This plot of kappa number vs. leaching time shows that the five different trials are experimentally indistinguishable. These trials were run at 70°C in solutions of 0.01*N* NaOH plus NaCl or $MgCl_2$. Tests also were run comparing leaching with 0.1*N* NaOH to leaching with a combination of 0.1*N* NaOH and 0.1*N* NaCl. Again, the results were indistinguishable. No tests were run at neutral pH, so direct comparison with previous work (*14*) is impossible. The results in Fig. 7 indicate that the hindering effect of electrolytes seen previously was not present under the conditions of high alkalinity used in this study.

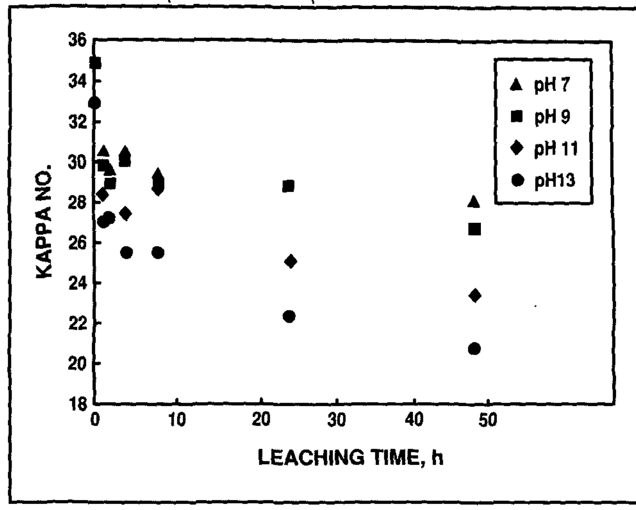
Effect of initial kappa number

The initial kappa number affects fiber swelling and leaching rate in pulp fibers (*6, 11, 15*). Pulps cooked to five different initial kappa numbers were tested to measure the effect of initial kappa number on leaching rate. **Figure** 8 shows the kappa number change associated with 24-hour leaching in the laboratory for these pulps and the change accomplished in the current mill washing system for four of the samples. Leaching for the initial kappa no. 33 test was run with 0.01*N* NaOH. The other tests were run with solutions of 0.1*N* NaOH. Retention time, temperature, and consistency for all five runs were held constant. Figure 8

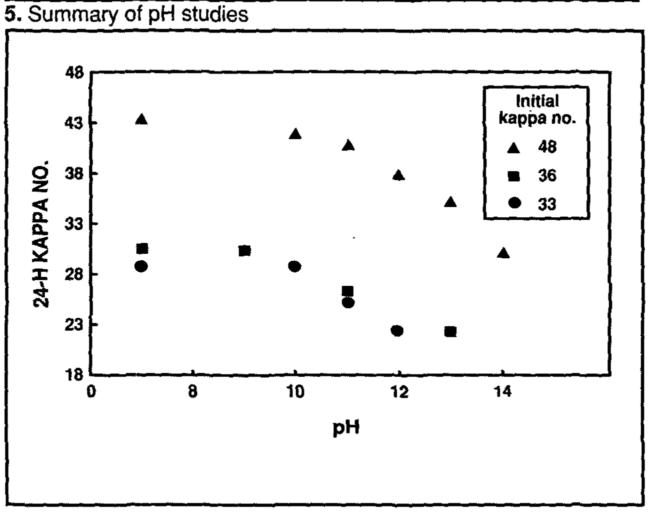
3. Lignin removal vs. retention time for various pH values



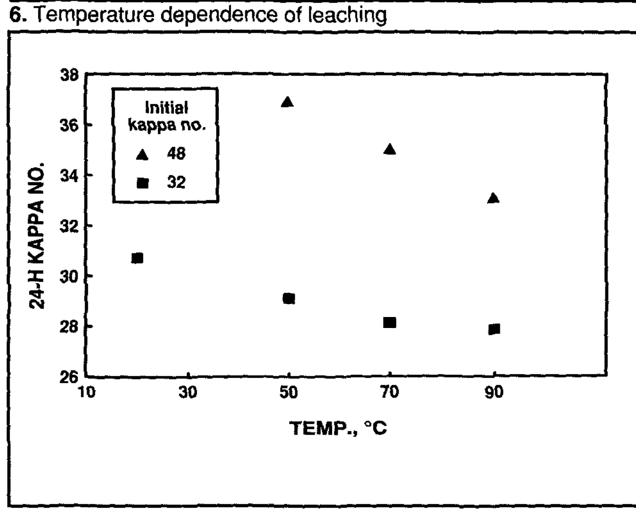
4. Verification of pH and time dependence



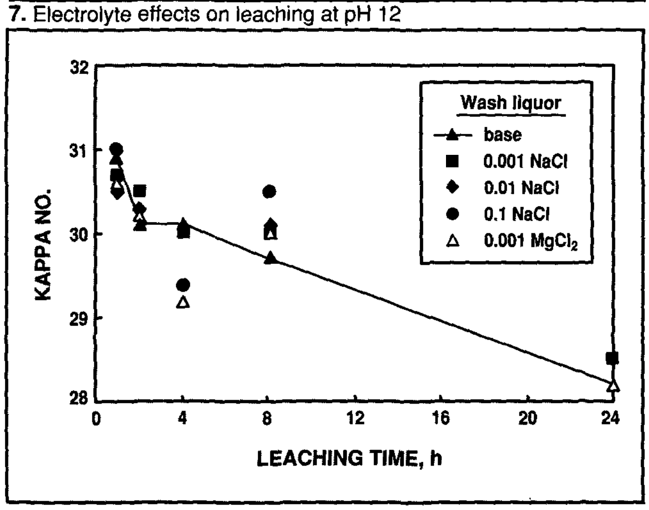
5. Summary of pH studies



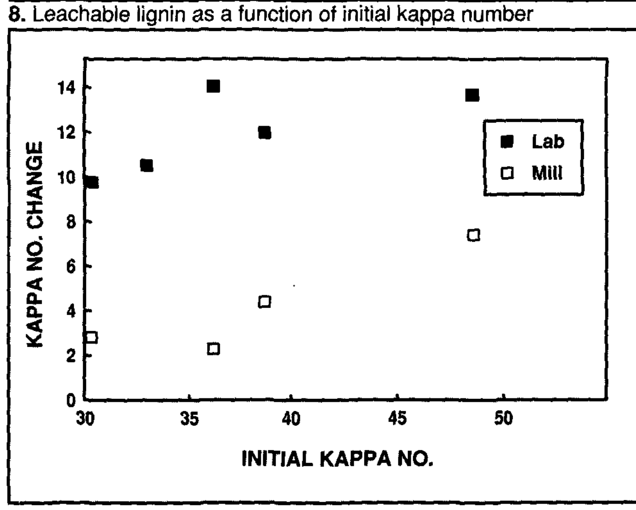
6. Temperature dependence of leaching



7. Electrolyte effects on leaching at pH 12



8. Leachable lignin as a function of initial kappa number



shows the relationship between 24-hour leachable lignin and initial kappa number to be linear and flat in the range covered by these data. In all cases much more lignin was removed in the laboratory leaching than in the mill washing.

Analysis of results

The comparison of unwashed and washed pulp shown in Fig. 1 illustrates that a significant amount of lignin can be removed even from well-washed pulp. The studies of pH and time dependency shown in Figs. 3 and 4 show that most of this removal is accomplished in under 4h, a reasonable amount of time for mill considerations. The remainder of the experiments help to find the controlling variables in this process and also to suggest modifications to the pulping and washing system that will enhance lignin removal.

Many variables affect the mass transfer of the large lignin molecules out of the fiber walls during washing, and it is unlikely that a single dominant variable can be isolated. Previous investigators have proposed that the rate of leaching is limited by pore restrictions in the fiber walls, the size of which are controlled by the chemical environment and fiber swelling (*5, 6, 16, 17*). Other variables that control diffusion, like the concentration-gradient driving force and the characteristics of the diffusing substance, also must be considered.

Fiber swelling may be important when evaluating diffusion from pulp fibers, but the pH and electrolyte tests performed in this study indicate that swelling is probably not a controlling factor. Literature sources agree that swelling of unbleached kraft pulps is at a maximum near pH 9. The addition of electrolytes, including higher concentrations of alkali, inhibits swelling, probably through a shielding of the charged carboxyl and phenolic hydroxyl groups in unbleached kraft pulp (*11–13*). If fiber swelling were the controlling variable for leaching, a maximum leaching rate with respect to pH should have occurred near pH 9, and addition of electrolytes to the high-pH wash liquors should have inhibited leaching. Instead, no maximum leaching rate was found as alkali concentration was increased, and electrolytes had no observable effect on the rate of leaching.

The variable with the most significant effect on leaching appears to be the alkali concentration of the wash liquor, as shown in Fig. 5. Temperature variation had a lesser effect. We hypothesize that the increase in leaching with alkali concentration and temperature is primarily attributable to higher lignin solubility. Lignin precipitates from solution near pH 10. As long as the pH of the liquor in and around the fiber is maintained above this value, lignin will be soluble. A lignin concentration gradient then will be maintained across the fiber wall as the wash liquor is replaced from stage to stage.

Application

The results of this study suggest process modifications to increase washing efficiency with respect to lignin. Temperature, pH, and retention time should all be increased to maximize lignin washing efficiency. Stromberg makes similar conclusions (*18*). By increasing the retention time, temperature, and pH of washing, a mill should be able to reduce bleaching and effluent treatment costs, without excess capital expense, because of the lower lignin content of the pulp entering the bleaching stage. Sodium loss also may be reduced because sodium associated with removed lignin phenolic hydroxyl groups will be recovered (*2*).

In pulp mills with chlorination as the first bleaching stage, the pulp must be neutralized to avoid the need for additional chlorine. If an oxygen delignification stage is in place, optimization of brownstock washing for lignin leaching is simpler to apply because the oxygen stage is operated under alkaline conditions. The entire wash line then can be maintained at high pH. Regardless of the bleaching sequence at the mill, NaOH added to facilitate leaching must be recovered after the leaching tank or oxygen stage. Since sodium equilibrium is achieved very quickly in pulp (*2*), neutralization should be possible in one or two post-leaching displacement washing stages.

An example of how leaching could be implemented is shown by considering the Weyerhaeuser pulp mill in Everett, WA. **Figure 9** is a schematic of the equipment in the brownstock washing and screening room at Everett. The pulp enters the wash room from the blow tank at about 75°C and is cooled to about 45°C when it reaches the screen-room surge tank at the end of the washer train. The wash-water supply is fresh water heated to 45°C. The surge tanks have approximate retention times of 45 min before screening and four hours before bleaching.

In the Everett mill, the pulp in the first surge tank is at pH 9. Figure 3 shows that very little leaching should occur under these conditions. If the pH were raised to 12 or 13 and the residence time increased to four hours, the effect of leaching would be sufficient to reduce the bleaching chemical demand by as much as 10%. This could be accomplished, as shown in **Fig. 10**, by moving the larger surge tank and screen room forward in the process, so they are positioned after washer 2 or washer 3. The smaller surge tank then would be used to control the feed of pulp to the bleach plant. The screen room would need to be included in the wash-liquor recycle process to allow for recovery of the added caustic and additional organics.

Conclusions

Leaching experiments have been run on Douglas-fir pulps initially at five different kappa numbers. Tests have been run to study the effects of pH, temperature, electrolyte concentration, starting kappa number, and retention time on removal of lignin during washing.

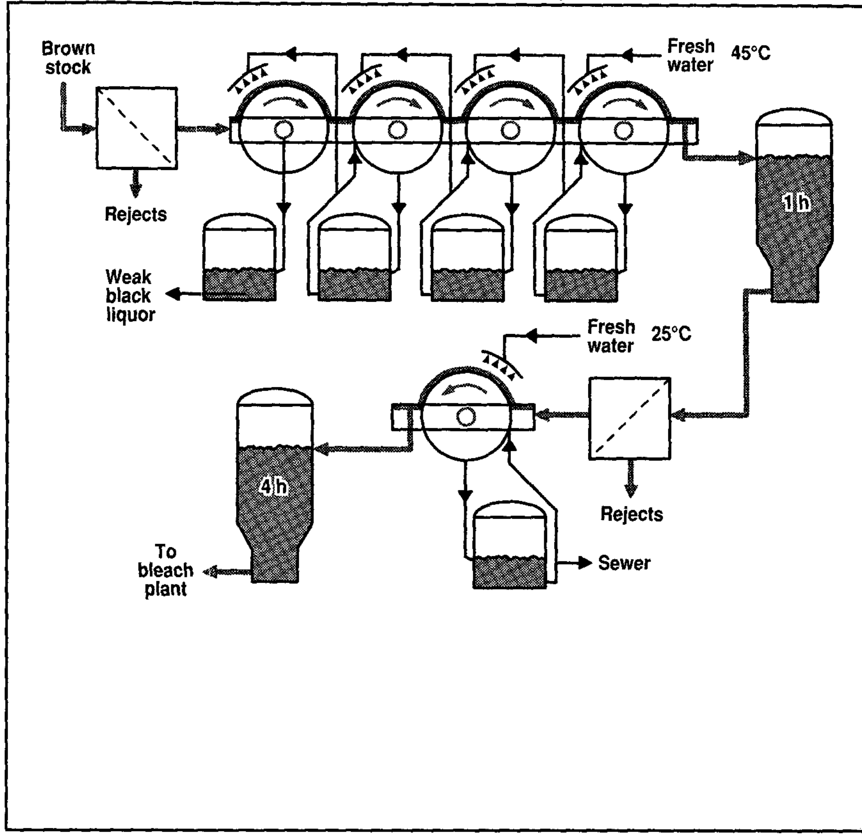
The rate of leaching increased dramatically with increasing pH and increased linearly with temperature in the range of 20°C to 90°C.

Electrolytes in solution were found to have no effect on leaching when using wash liquors of elevated pH.

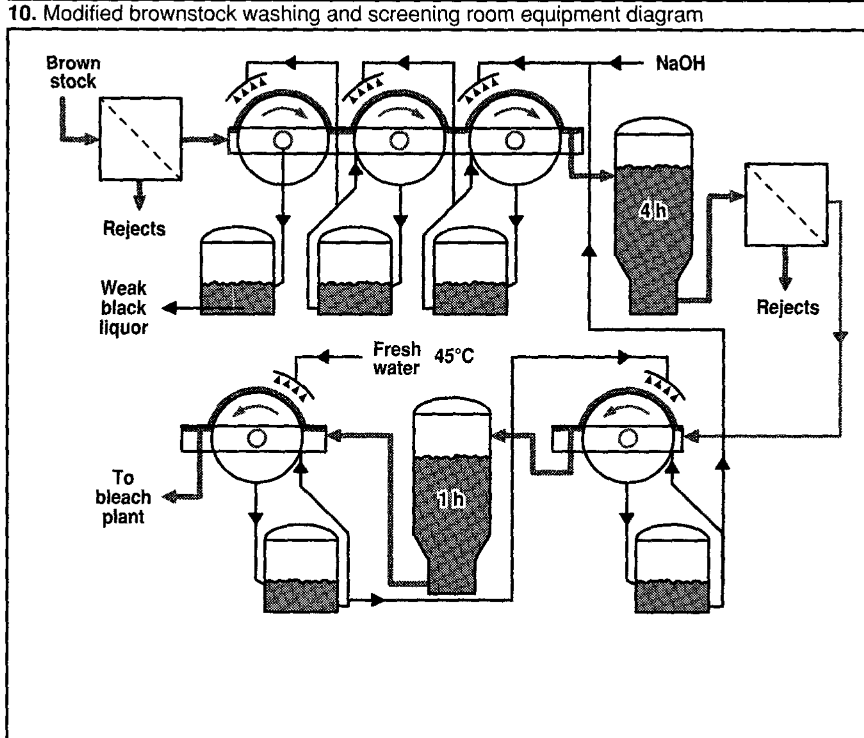
The kappa number of pulps, in the range of initial kappa no. 30–48, could be reduced 25% by leaching 24 h with 0.1N NaOH.

Moderate process modifications would allow a reduction in kappa number of 10% over that achieved with the current washing system if the pH in storage were raised to 13 and the temperature were maintained at 70°C. The optimum retention time is probably in the range of four to eight hours. ■

9. Brownstock washing and screening room equipment diagram



10. Modified brownstock washing and screening room equipment diagram



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