The role of penetration and diffusion in nonuniform pulping of softwood chips

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ABSTRACT *Investigating the mode by which kraft pulping liquor penetrates a commercial softwood chip, we derived a pulping model that accounts for penetration, diffusion, and reactions. The shrinking penetration core is modelled as a one-dimensional moving front. Simulations with the pulping model show under what conditions incomplete penetration or inadequate diffusion influence pulping uniformity.*

KEYWORDS
Diffusion
Kinetics
Kraft pulping
Modelling
Penetration
Pulp uniformity

Nonuniform pulp has a deleterious effect on the performance of downstream operations such as bleaching and papermaking. Kappa variability, for example, increases the amount of bleaching chemicals required to achieve a specific brightness.

In batch digesters, nonuniform pulp results from inter- or intra-batch variability. Chemical mischarges and errors in determining chip moisture are potential sources of inter-batch variability. Intra-batch variability can result from heterogeneous conditions within the digester or from nonuniform cooking within the chips themselves. A common source of digester heterogeneity is cooking liquor channelling through the chip bed.

One or more of these sources of pulping nonuniformity can be important depending on the particular operating conditions. Our paper focuses on pulping nonuniformity that occurs because of heterogeneous conditions within the pulp chips. This represents an ideal case because the digester itself is rarely homogeneous. Therefore, the results of this research could be construed as a "best case" scenario.

Knot or reaction wood, incomplete penetration, and inadequate diffusion are sources of intra-chip pulping heterogeneity. The pulping characteristics of knot and reaction wood have not been well quantified, so it is difficult to assess the effect of their presence on pulping homogeneity. However, the impact of diffusion and penetration can be examined, especially if a comprehensive pulping model is available.

Adequate movement of cooking liquor into wood is an essential first step in the pulping process. Removal of sufficient lignin for fiber liberation requires that the pulping liquor penetrate into the chip and that chemicals dissolved in the liquor be distributed uniformly throughout the wood (*1*).

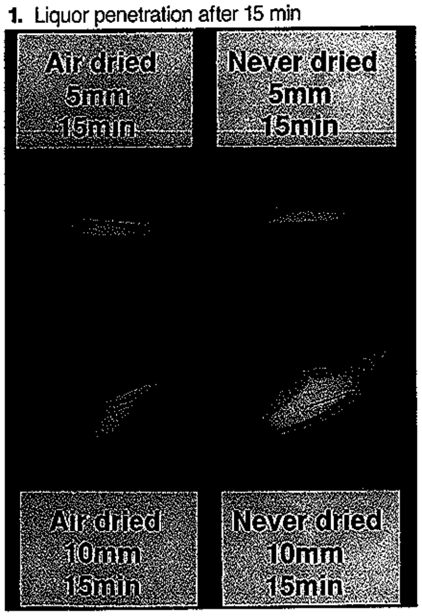
Two mechanisms move cooking chemicals into wood: penetration and diffusion. Penetration is the flow of cooking liquor into the wood pores while under the influence of a pressure gradient. Diffusion is the transport of dissolved chemicals as a result of a concentration gradient (*2*).

The importance of thorough liquor penetration prior to cooking is widely recognized in the pulping industry. Deficient impregnation results in higher screenings and shives in the final pulp, a higher lignin content at a given yield, and inferior bleachability and end-use properties (*3*). On the other hand, complete penetration reduces cooking time, increases pulp uniformity, and prevents undesirable lignin reactions (*4*).

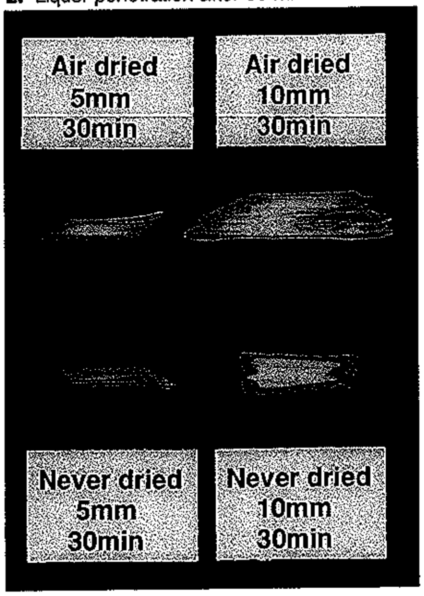
Nonuniform pulping can occur in chips completely impregnated with liquor. Roughly two-thirds of the alkali required for complete delignification must diffuse into the chip from the surrounding bulk liquid. If the chips are too thick, a more heterogeneous pulp is produced because the alkali in the chip center is consumed faster than it can be replaced by diffusion. Generally, avoiding diffusion limitations requires chips no more than 3 mm thick (*5*).

The results of this study can have an impact on the industry because diffusion and penetration limitations are probably both present in commercial pulping. The extent to which one is more important than the other

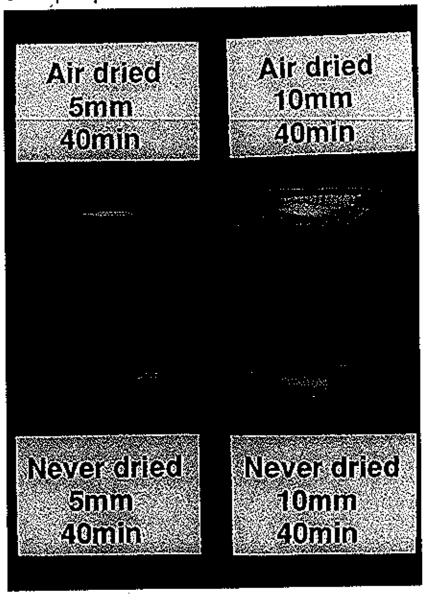
1. Liquor penetration after 15 min



2. Liquor penetration after 30 min



3. Liquor penetration after 40 min



depends on the wood species, chip pretreatment, chip thickness, and pulping conditions. One of our goals is to elucidate the relative effects of incomplete liquor penetration and inadequate diffusion on pulping uniformity. If, for example, slow alkali diffusion dominates pulping nonuniformity, then equipment that reduces chip thickness (such as screens and slicers) may be more effective in improving uniformity than equipment that improves liquor penetration (presteaming vessels, for example). If penetration is more significant, then presteaming or other preimpregnation equipment should be considered.

Here, we describe the development of a pulping model that includes the effects of reaction kinetics, chemical diffusion, and liquor penetration on kraft pulping. Applications of the pulping model to a study on the relative importance of diffusion and penetration as a function of pulping conditions are also presented.

Results and discussion

Penetration mode of kraft liquor

The manner by which kraft pulping liquor penetrates a chip must be determined before the penetration process can be modelled or the effect of incomplete penetration assessed. There have been many studies on the penetration of chemicals into wood (*6, 7, 8*) but, surprisingly, none that show the penetration of kraft liquor into a commercial chip. Transport studies on hand-cut chips are not generally applicable to commercial chips because of their fractured structure (*9*).

The following experiment was performed to study the mode by which kraft liquor penetrates commercial chips. Four sets of Douglas-fir chips were pulped with the conditions shown in **Table I**. Air-dried or never-dried 5-mm and 10-mm chips were pulped. Chip samples were taken from the digester at 15, 30, and 40 min, split open, and examined to see how the penetration progressed during the cook. Some chips were sprayed with phenolphthalein to enhance the contrast between the penetrated and unpenetrated part of the chip.

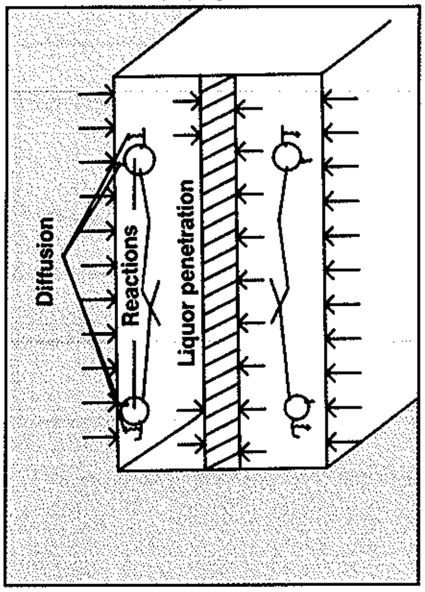
Figure 1 shows the extent of penetration in the chips after 15 min into the cook. There is very little liquor impregnation except in never-dried 5-mm chips. After 30 min (**Fig. 2**), the penetration has proceeded further but is still far from complete. Figure 2 also shows the unpenetrated area to be a shrinking elliptically shaped core. A shrinking core-type penetration pattern is consistent with the perception that penetration is controlled by the dissolution and diffusion of air trapped in the chip center (*4*). Since chip thickness is the critical dimension for diffusion, we anticipate it to be the critical dimension for liquor penetration. Chip thickness has been shown to be the critical dimension in kraft pulping (*5, 10*).

I. Pulping conditions for penetration mode experiments

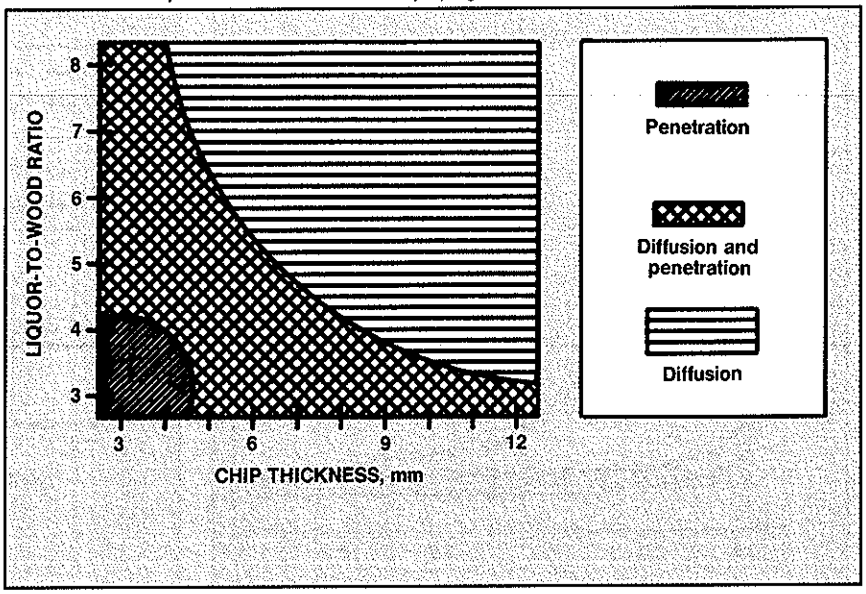
Effective alkali, % on wood as Na_2O	16
Sulfidity, %	25
Liquor-to-wood ratio, L/kg	4:1
Initial temperature, °C	25
Final temperature, °C	170
Heat-up time, min	40

After 40 min, the digester is at 170°C. The liquor penetration in the chips is shown in **Fig. 3**. The penetration still proceeds as a shrinking core. The only completely impregnated chip is the never-dried 5-mm chip. In the air-dried chips, the penetration is only about three quarters complete when the digester reaches the top cooking temperature. The center of these chips will almost certainly produce screen rejects. In Figures 1–3 the penetration occurs by a single shrinking core of trapped gas despite the random network of fissures induced by the chipper. We observed a cleavage of the shrinking core by the accelerated penetration of liquor into a fissure in only a few cases. Figures 1–3 represent general behavior of many chips examined during this study.

4. Model of kraft pulping



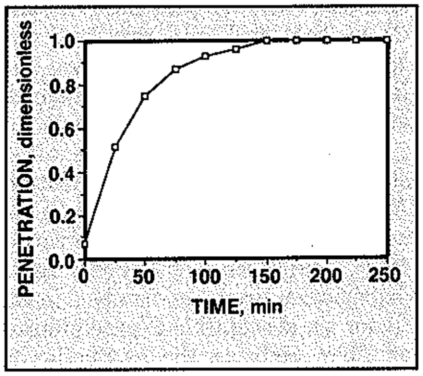
6. Dominant transport modes as a function of pulping conditions



II. Pulping conditions for penetration and diffusion simulations

Effective alkali, % on wood as Na_2O	16
Sulfidity, %	25
Liquor-to-wood ratio, L/kg	3:1 to 8:1
Initial temperature, °C	25
Final temperature, °C	170
Heat-up time, min	45
Total pulping time, min	250
Chip thickness, mm	3-12

5. Penetration curve used in model simulation



Pulping model

Following our studies on the liquor penetration mode, we modified the University of Washington Kraft Pulping Model (*11*) to account for the effect of incomplete penetration on pulp properties. Model development details are presented elsewhere (*12*) but a brief review is given here for completeness.

In the pulping model, the chip is assumed to be a semi-infinite symmetrical slab whose thickness is equal to that of a pulp chip. Liquor penetration is modeled as a front moving from the edge of the chip to the center (**Fig. 4**). The "shrinking core" occupies the center region of the chip.

At the beginning of the cook, the chip phase will be partially impregnated with liquor; the alkali and sulfide concentrations are uniform throughout the bulk liquid phase. As the digester heats up, the penetration front will move into the chip; pulping reactions will begin, producing degradation products that neutralize alkali as they diffuse out of the wood. No reactions are assumed to take place ahead of the penetration front. Alkali is transported from the bulk to the chip surface and then is transported by diffusion and convection with the penetrating liquor into the chip. The sulfide ion concentration in the liquor is assumed to remain constant (*11*). At some point in the cook, the penetration is essentially complete. After that time, the transport of alkali into the chip occurs strictly by diffusion. At the end of the cook, and after the pulp has been washed, all that remains in the fibers are the bound wood components.

Differential equations that describe the coupled kinetics, diffusion, and penetration make up the pulping model. The solution to the model provides the intra-chip alkali, lignin, and carbohydrate profiles and the bulk phase alkali concentration as a function of pulping time. Those interested in the details of the numerical methods used in the model should consult Jiménez *et al.* (*12*).

The role of penetration and diffusion in kraft pulping of softwood chips

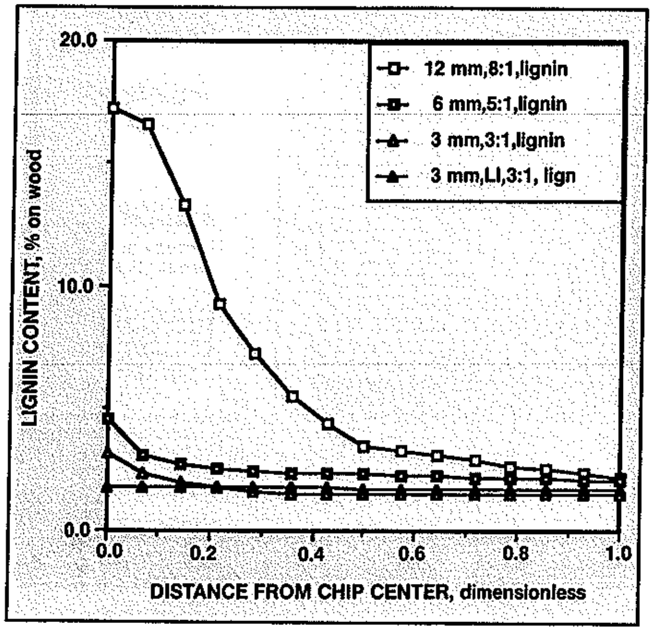
We first applied the pulping model to investigate the relative effect of diffusion and penetration on kraft pulping nonuniformity. We ran a series of simulations with the model to investigate the effect of chip thickness and liquor:wood ratio on pulping behavior, with particular emphasis on the relative importance of diffusion and penetration.

The pulping conditions used in the simulations are shown in **Table II**. In these simulations, the chip thickness was varied from 3 mm to 12 mm and the liquor to wood ratio from 3:1 to 8:1. In each simulation, however, one chip thickness and one liquor-to-wood ratio was selected. The extent of liquor penetration for all the simulations was assumed to follow the equation

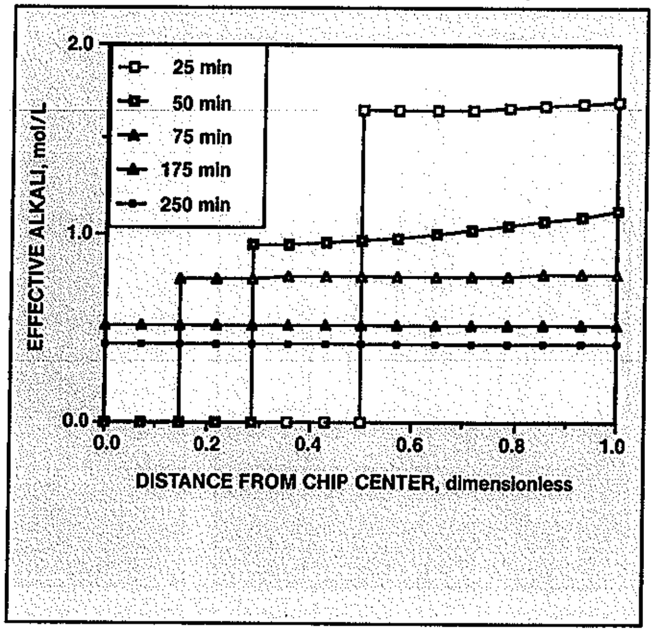
$$\delta = 0.07 + 0.93(1-e^{6.5t}) \quad (1)$$

where

7. Lignin profile at the end of pulping (250 min)



8. Intra-chip alkali profiles. Liquor-to-wood = 3:1, 3-mm chip.



δ = extent of penetration

t = pulping time.

Figure 5 shows the penetration curve generated by Eq. 1. Equation 1 was selected on the basis of preliminary penetration experimental results.

The pulping of a 3-mm chip completely impregnated with white liquor at the beginning of the cook and with a liquor-to-wood ratio of 3:1 was also simulated as a base case free of penetration and diffusion limitations. The following results are qualitative descriptions of the behavior inside the chips during pulping. Work is in progress at the University of Washington to improve the kinetics, diffusion, and penetration equations so the model will have true quantitative capacity over a broad range of pulping conditions.

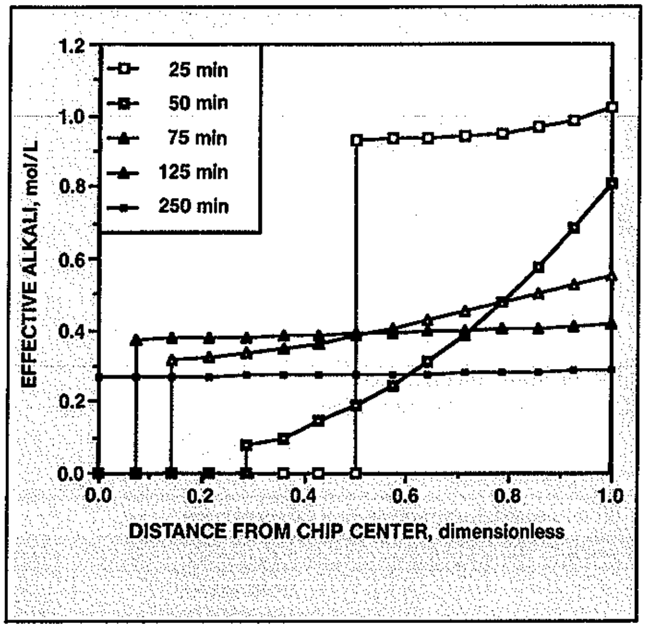
Analysis of the simulation results shows that the pulping behavior can be divided into three regimes. In the first pulping regime, the alkali concentration across the penetrated portion of the chip remains uniform. That is, the diffusion of alkali is faster than the rate of penetration. In these chips, pulping nonuniformity is penetration-rate controlled. In the second regime, both diffusion and penetration affect the pulping nonuniformity. In these chips, diffusion is slower than penetration, and the alkali concentration at the penetration front is depleted during pulping. However, alkali is not exhausted at the penetration front. Chips that fall into the first two categories will pulp much more uniformly if preimpregnation methods are used before cooking the chips.

In the third pulping regime, diffusion is much slower than penetration. As a result, all the available alkali has been consumed at the penetration front. Under these conditions, lignin degradation products dissolved in the liquor are susceptible to precipitation on fiber surfaces; the production of bleached pulp will be more difficult because of its higher chemical requirements in bleaching (*13*). Furthermore, if the liquor immediately behind the penetration front becomes acidic, carbohydrates may hydrolyze (*14, 15*), resulting in lower yield and poorer bleachability.

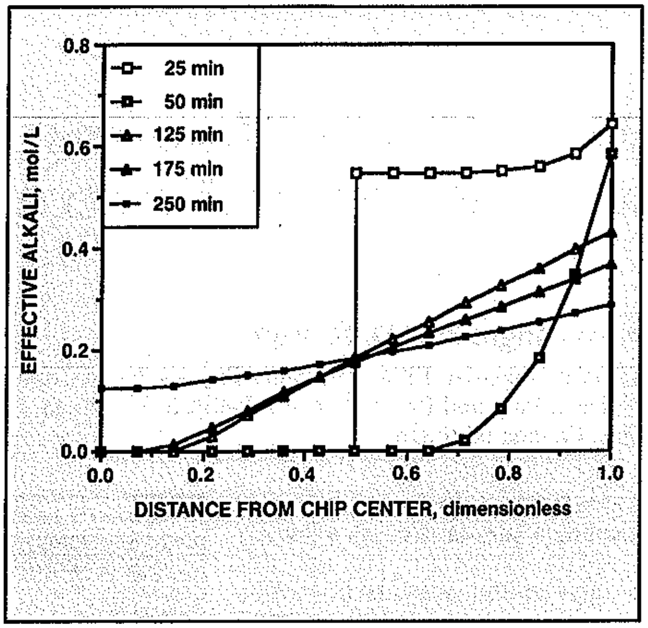
Figure 6 shows a "map" of the pulping conditions with respect to the three pulping regimes. As chips become thicker and as the liquor-to-wood ratio increases, the impact of diffusion becomes greater. Figure 6 also shows that a significant portion of chip sizes found in commercial digesters fall into the diffusion controlled category. Diffusion is particularly dominant at higher liquor-to-wood ratios. Implementation of higher liquor-to-wood ratios such as those proposed recently for modified pulping systems (*16*) may require extra measures such as chip screening to ensure uniform pulping.

To better understand the pulping in each regime, the intra-chip lignin and alkali profiles from representative simulations are shown in **Figs. 7-10.** These representative simulations lie along the diagonal (lower left to upper right) of Fig. 6. Specifically, they include the pulping of 3-mm chips at a liquor-to-wood ratio of 3:1, 6-mm chips at 5:1, and 12-mm chips at 8:1. In Fig. 7, the lignin profile at the end of the cook for all three cases is shown. For comparison, the lignin profile for the perfectly impregnated 3-mm chip is also shown. Increasing the chip thickness and liquor-to-wood ratio from 3 mm and 3:1 to 6 mm and 5:1 (moving from the penetration into the penetration/diffusion regime) results in a moderate increase in the average kappa and kappa range of the pulp. Differences in the final lignin profile of the 3-mm and 6-mm chips are mitigated somewhat in this particular case because the pulping is well into residual delignification. When the pulping enters the diffusion regime, as shown for the 12-mm chips (liquor-to-wood 8:1), the pulping becomes extremely nonuniform. This severe nonuniformity is a consequence of the penetration front being completely devoid of alkali. No delignification occurs at the center of these chips until the cook is almost complete. Figure 7 shows that roughly 20% of the chip will have a lignin content well above that required for fiber liberation. The

9. Intra-chip alkali profiles. Liquor-to-wood = 5:1, 6-mm chip.



10. Intra-chip alkali profiles. Liquor-to-wood = 8:1, 12-mm chip.



9-mm chips pulped in our laboratory with a liquor-to-wood ratio of 8:1 and the conditions shown in Table II produced rejects of 24%.

The intra-chip alkali profiles for the three representative simulations are shown in Figs. 8-10. Pulping the 3-mm chip with a 3:1 liquor-to-wood ratio results in an alkali profile that is very uniform behind the penetration front (Fig. 8). All of the nonuniformity observed in this pulping occurs because the center of the chips are not exposed to the liquor until the middle of the cook. In Fig. 9, the penetration front for the 6-mm chip is still obvious, but the alkali profile behind the penetration has become more pronounced. Such a chip will yield a less uniform pulp than the thinner chip that is free of concentration gradients.

Figure 10 shows the intra-chip alkali profiles for the 12-mm chip during pulping. In Fig. 10, it is impossible to locate the penetration front because, due to inadequate diffusion, the alkali remains depleted well behind the front. The center of the 12-mm chip is not exposed to any alkali until 220 min into the cook. There is not enough time for lignin at the chip center to be removed sufficiently for fiber liberation (Fig. 7). The depletion of alkali will result in hydrolysis and condensation reactions in the region where the penetration front precedes the alkali diffusion front. These undesirable reactions will also increase the nonuniformity of the pulping.

Conclusions

The penetration of kraft liquor into a commercial softwood chip takes place as an elliptically shaped shrinking core. The highly fissured structure of commercial chips does not appear to affect the mode of penetration, but it may affect the penetration rate. We derived a pulping model that accounts for penetration, diffusion, and reactions. The shrinking penetration core is modelled as a one-dimensional moving front. Simulations with the model show under what conditions incomplete penetration or inadequate diffusion influence pulping uniformity.□

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