Alkali impregnation of hardwood chips

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ABSTRACT: Alkali impregnation can be thought of as a process of reactive diffusion in which a moving front separates a reacted, swollen outer zone from an intact inner zone. In the alkaline impregnation of hardwood, the reaction zone becomes wider, and its movement slows, but the mechanism is always the same. The advance of the impregnation front can be determined as a function of time for a given hardwood material, a given wood chip thickness, and a given set of cooking conditions. Experiments carried out on eucalyptus wood and poplar wood reflect changes in the pattern that take place as impregnation progresses.

Application: It should be possible to predict the time needed for a complete alkali impregnation of hardwood chips based on the chip thickness distribution.

The distribution of pulping chemicals has to be uniform within the wood chip for optimal pulping efficiency and pulp uniformity. For chemimechanical processes, the uniformity of chip impregnation determines the uniformity of the pulp produced. For chemical pulping, the benefits brought about by a proper impregnation stage depend on the cooking conditions of the whole process. For kraft pulping of pine, even under ideal laboratory conditions, the nonuniformity of pulp begins when the chips are thicker than 2 mm. Nonuniform delignification results in significantly lower pulp yield and strength than obtained under uniform delignification [1].

The effect of proper impregnation in pine kraft pulping has been recently shown by Malkov *et al.*, who determined the kappa numbers of individual cooked fibers [2]. After an efficient impregnation, a pulp of kappa no. 30 showed a more narrow distribution in kappa number and a higher percentage of fibers at the average level. Complete profiles of the lignin content of the cooked chips were also more uniform under more favorable impregnation conditions [2]. On the other hand, better impregnation leads to a lower consumption of bleaching chemicals [3].

For eucalyptus pulping, an extended impregnation stage in modified kraft cooking leads to a more efficient delignification [4]. In other words, the alkali requirement is lower, and the pulp yield is higher. Extended delignification is generally used in kraft pulping today. Among other practices, the black liquor is used in the impregnation stage to reduce the concentration of hydroxide ions at the beginning of the initial cooking stage [5]. This lower alkali concentration slows the impregnation process.

It would be useful to be able to predict the time needed for the complete impregnation of the wood chips. The critical dimension for alkali impregnation is chip thickness. For alkaline impregnation of hardwoods, according to Stone and Green [6], liquid flow across the grain (penetration) is negligible, and impregnation takes place by diffusion across the cell wall.

As we have previously shown [7], the alkali impregnation of poplar wood at temperatures below 100°C in both transverse directions (tangential and radial) can be considered a process of reactive diffusion. Deacetylation is the main reaction, and it can be considered an index of the chemical action of the alkali. During impregnation, an advancing front separates a growing, reacted, swollen outer zone from an intact inner zone. A similar impregnation pattern is established for fresh as well as dry and water-saturated poplar wood.

Here, we first discuss the results of eucalyptus wood treatment and present further evidence of the mechanism for the alkali impregnation of hardwoods. Second, we analyze changes in the pattern as the impregnation front reaches deeper positions in the wood (poplar). Differences in the front position are presented for different alkali concentrations and wood moisture conditions. This work is useful for predicting the time needed for a complete alkali impregnation of a wood chip.

EXPERIMENTAL

Materials

Wood sample. We used green, freshly felled 7-year-old cottonwood and 8-year-old *Eucalyptus grandis* wood. The densities were 0.388 g/cm³ for poplar and 0.433 g/cm³ for eucalyptus. Samples were supplied by two paper companies from Argentina (Papel Prensa S.A. and Celulosa Argentina S.A.).

Logs were cut into discs about 30 mm high. We used a carpentry saw to obtain four cubes with sides 30 mm long from each disc. The cube faces corresponded to the tangential and transverse planes and approximately to the radial plane. We prepared these cubes with a microtome to obtain parallel faces, taking care to avoid drying the wood. For the radial impregnation studies, cubes were prepared so that latewood was excluded from the reaction zone.

Alkaline treatment

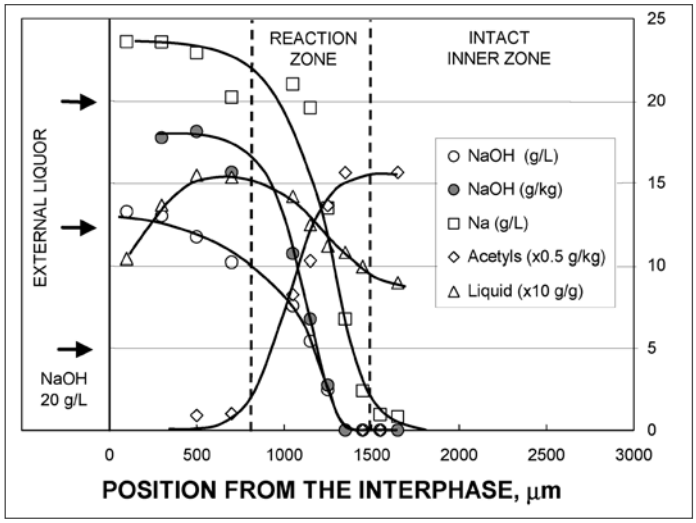
For isothermal treatment, the cubes were preheated in a microwave oven. To keep the cubes from drying, we wrapped them with polyethylene film during this stage. None of the cube faces were sealed. As a result, impregnation could take place simultaneously in all directions, and air could be released when the cubes were soaked in the solution of alkali.

After treatment, the cubes were immersed in liquid nitrogen. After two hours in liquid nitrogen, they were stored in a freezer.

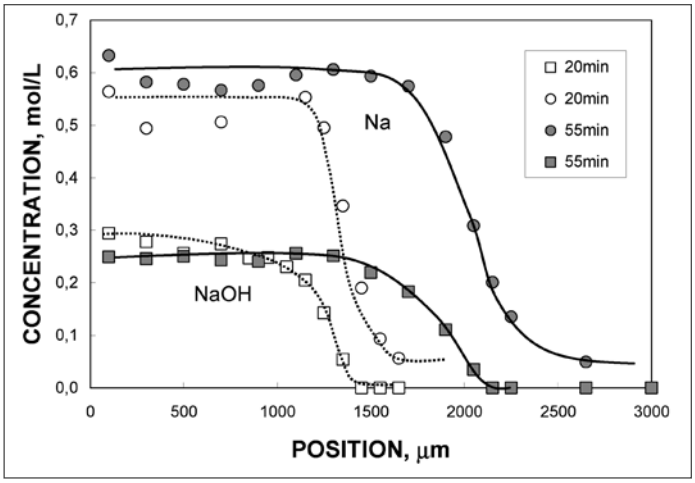
In other experiments, we treated fresh wood, dry wood, and wood that had been saturated with water. To saturate cubes, we applied a vacuum on them when they were immersed in water.

Determination of profiles

The frozen cubes were sliced by microtome to remove the layers of impregnated wood, with the exception of the faces of interest. These faces were cut into 100-µm-thick slices, which were immediately weighed, immersed in water, and quantitatively neutralized. To determine the alkaline charge, we carried out the titration while allowing alkali to diffuse from the slices, where the end-point was



1. Profiles of alkali impregnation of fresh eucalyptus wood. (Alkali content as g NaOH per kg of o.d. wood, acetyl group content as × 0.5 acetyls per kg of o.d. wood, and liquid content as × 10 g liquid per g of o.d. wood.)



2. Profiles of alkali impregnation of fresh eucalyptus wood. Alkali and elemental sodium concentrations as functions of position from the liquor-to-wood interface (tangential direction).

indicated by the color change of phenolphthalein. The slices were later air-dried end weighed. More details are given elsewhere [8].

The content of elemental sodium was calculated from its concentration in the titration volume, which was determined by atomic absorption spectroscopy. It is reported here as g Na/L or mol Na/L of liquid in wood.

The acetyl group content was determined on air-dry slices by the chromatographic method proposed by Solár *et al.* [9]. The content of the original wood was 33.0 g of acetyl groups per kg of o.d. wood for poplar and 31.0 g of acetyl groups per kg for eucalyptus.

RESULTS AND DISCUSSION

Impregnation of eucalyptus wood

Figure 1 shows results for the impregnation of fresh eucalyptus wood with 20 g NaOH/L at 90°C for 20 min. The profiles of alkali concentration, alkali content, liquid content, and acetyl content in wood are presented, each as a function of position from the liquor-to-wood interface.

The actual alkali content of the wood is considered here. We determined the alkali by titrating the solution that contains the wood sample. Hence, the wood is neutralized. In the figures, we have not included the consumption attributable to the absorbed alkali or the ionization of the phenolic hydroxyl group or other groups.

The general pattern coincides with patterns found for the impregnation of poplar wood [7], given the differences in the chemical concentration and the depth of penetration. The profiles of alkali, elemental sodium concentration, and acetyl group content are rather steep. A zone between 750 μm and 1400 μm can be defined where the deacetylation reaction occurs. There is no alkali in front of this zone. As the profile of the liquid content shows, an important liquid uptake takes place as a consequence of alkali action, and there is no increase in liquid content in front of the reaction zone.

Figure 2 shows the profiles of alkali concentration and elemental sodium concentration as functions of the distance to the external surface of the wood. The wood was treated with 20 g NaOH/L at 90°C for 20 min and for 55 min.

As the figure shows, the profile of elemental sodium concentration is in front of the alkali concentration profile. The reason is that alkali consumption is taking place in the reaction front. In the external outer zone, the plateau of elemental sodium is higher than the plateau for the alkali concentration. The concentration of sodium is close to 0.5 mol/L, which is its concentration in the external liquor. Nevertheless, sodium hydroxide has a lower concentration. This difference can be ascribed to the competition between the hydroxyl ion and the anions created by the reaction with wood. Both the elemental sodium and hydroxyl concentration profiles, as well as the acetyl content profile, could be useful in following the pace of the impregnation front, provided that the significance of each were considered.

Changes of pattern as impregnation proceeds

The general pattern of impregnation can change as the liquor penetrates the chips. **Figure 3** shows profiles of alkali concentration and acetyl content for different treatment periods. We obtained these profiles by impregnating poplar in the tangential direction. The reaction zone grows wider as impregnation proceeds. An amplitude of around 400 μm at 5–7 min increases up to 1000 μm by 80 min.

The profile is increasingly less steep, undoubtedly because the diffusive restrictions increase. However, a traveling zone always exists where the reaction takes place.

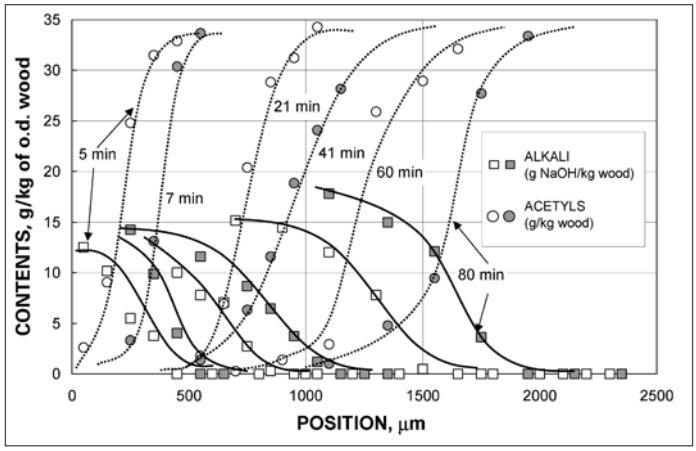
Effects of conditions on the process rate

Both alkali and acetyl profiles present similar general patterns throughout the impregnation of a given wood [7]. Hence, the position of one point in these profiles could be enough to characterize the depth of impregnation.

Figure 4 shows the position of the impregnation front in poplar wood for different treatment conditions as a function of time. The depth of the point at which hydroxyl concentration starts to increase in the corresponding profiles (not shown here) was taken into consideration to build this figure.

As the figure shows for the wood under study, the pace slows as impregnation proceeds. On the other hand, as can be expected, a higher alkali concentration in the liquor speeds up the impregnation because the diffusion pressure is proportionally higher.

The time needed for impregnation can be determined from Fig. 4. Given a wood chip with a half thickness of 2.0 mm, a 10-g/L impregnation triples the time needed for a 40 g/L impregnation, as we see by comparing Curves 1 and 3. The time needed for a 5 g/L impregnation triples the time required by a 10 g/L impregnation, as we can see by comparing Curves 3 and 6.



3. Profiles of alkali impregnation of fresh poplar wood with 10 g NaOH/L at 90ºC for different times from 5 min to 80 min. Alkali and acetyl contents (g per kg of o.d. wood) as functions of the position from the interface (tangential direction).

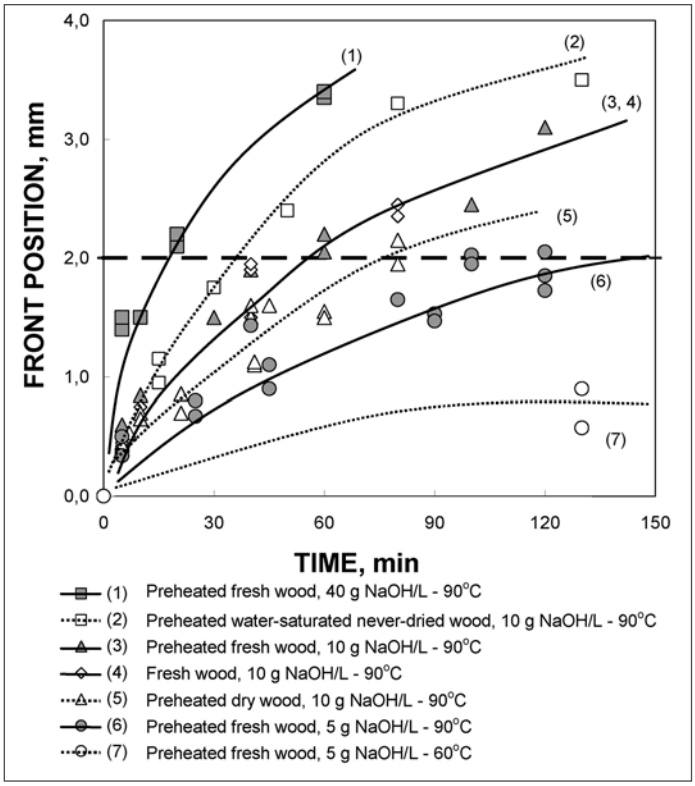
The moist state of the wood increases the impregnation speed. As we can see by comparing Curves 2 and 5, air-dry wood requires twice as much impregnation time as the never-dried, water-saturated wood requires.

CONCLUSIONS

The general pattern found for the alkali impregnation of eucalyptus wood coincides with patterns that were found for poplar wood. The profiles of alkali, elemental sodium concentration, and acetyl group content are steep, which indicates a reactive process. There is no alkali in front of the reaction zone, where there is also no increase in either the elementary sodium concentration or the liquid content.

The general profile of alkali impregnation is increasingly less steep when impregnation reaches greater depth in the wood, which can most likely be attributed to increasing diffusive restrictions. At any rate, a moving reaction zone defines the front of the impregnation.

For a given hardwood material, the advance of the impregnation front can be determined as a function of time. This information allows us to predict the period of time needed to impregnate a wood chip under given conditions. For a 4.0 mm wide chip of poplar wood, for example, a 10 g/L impregnation triples the time needed for a 40 g/L impregnation at 90°C, and an air-dry wood requires twice as much impregnation time as a never-dried, water-saturated wood requires. **TJ**



4. Rate of impregnation of poplar wood under different conditions. A possible half-thickness of 2.0 mm is indicated.

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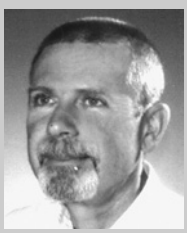
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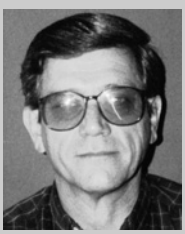
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