

Pattern of Alkali Impregnation of Poplar Wood at Moderate Conditions

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Keywords

Alkali impregnation
Poplar
Alkaline pulping
Acetyl groups
Alkali concentration
Alkali content
Liquor uptake
Shrinking core model
Swelling
Liquor penetration

Summary

The impregnation pattern of alkali in fresh Cottonwood is analysed. Isothermal process, medium alkali-concentration, temperature below 100 °C and tangential direction are considered. The degree of deacetylation in the wood is taken as an indicator of the whole chemical action of the alkali. Profiles of alkali concentration, alkali content, liquid content and acetyl content in the wood are experimentally determined. The results show that wood behaves rather like a glassy polymeric solid placed in contact with a solvent. An advancing boundary zone is established which separates an intact inner part from the outer swollen zone. Alkali concentration and acetyl groups content profiles can approximately be described by a model used to analyse the reaction of solids: the shrinking core model. The chemical reaction in the front is the controlling mechanism. The swelling of the cell walls together with the occupation of the hollow cavities of the wood by the liquor make it possible for the wood liquid content to increase up to almost 3 g liquid g wood⁻¹.

The procedure here adopted and the impregnation pattern proposed are valuable tools to analyse the effect of wood direction and process variables such as temperature, alkali concentration and initial wood moisture. They could also be very useful to build a model for alkaline impregnation of wood under moderate conditions.

Introduction

Penetration and diffusion of chemicals in wood is of utmost importance in many wood processings. For example, in both chemical and chemimechanical pulping, the level of impregnation of the chips determines the uniformity of the chemical treatment and thus affects the time periods needed for the process and the pulp quality.

Wood impregnation involves both mass flow and diffusion. Further, in the case of alkaline liquor, chemical reactions occur during penetration.

In the tangential direction of the wood, there are not exist radial cells nor vessels that allow for liquid penetration. However, the phenomenon is more complicated than impregnation of a rigid material with an inert solvent. The arrival of alkali and subsequent chemical reactions cause wood swelling which increases cell wall thickness and thus increases the amount of liquid absorbed in the wall.

Alkali reactions are especially significant for moderate conditions like those corresponding to alkaline chemimechanical pulping processes. In this case, the analysis of the impregnation pattern should consider chemical reactions because the alkali charge is low and thus a high proportion of alkali is consumed by these reactions.

The alkali swelling of willow-poplar wood can achieve a great magnitude. It has been shown that the increase in wall thickness can almost close the fibre lumen for high alkali concentration and low temperature conditions (Maximino *et al.* 1988).

The study of alkali diffusion in wood has been frequently approached as a simple Fickian diffusion process in an inert solid. However, as was shown by Burazin (1986), the wood diffusion coefficient varies as the alkali concentration changes. Stone (1957) found a considerable increase in the so-called effective capillary in the transverse direction of aspen wood as the pH increases from 12.8 to 13.5 and he ascribed this to changes in the swelling level brought about by changes in the alkali concentration.

Talton (1986) applied the method of McKibbins (1960) based on the unidirectional isothermal extraction of alkali from an impregnated piece of wood applying mathematical solutions of Fick's first law of diffusion to determine diffusion coefficients for NaOH under different conditions. Jacobs-Young *et al.* (1998) applied the same principle and determined the diffusion coefficient of different woods in longitudinal and transverse directions. Lönnberg and Robertsen (1992) proposed a direct method to calculate the diffusion coefficient by determining alkali flow through a thin wood piece of pine that separates two solutions of different concentration.

All these articles dealt with diffusion in previously completely soaked wood, a condition for which the consideration that wood is inert and has an invariant geometry can be acceptable. When the preliminary phase, i.e. the impregnation process, is analysed, this assumption can be misleading. In fact, when chemical reactions, as well as swelling effects and liquid penetration in wood voids were left aside by Kazi *et al.* (1997) to study spruce wood impregnation,

a pour fitting of the alkali concentration profiles by the theoretical Fickian equations was obtained.

For the detailed modelling of Kraft pulping carried out by Jiménez *et al.* (1989) and Gustafson (1989), an impregnation pattern different from a simple pure diffusion model was considered, since a penetration front was adopted as alkali concentration profile. Owing to the non-existence of specific studies on the subject, the authors used an empirical equation for the rate of advance of this front.

Alfrey (1966) analysed the diffusion in glassy polymeric solids. The pattern in this case is clearly distinguishable from a Fickian diffusion and even from those corresponding to the generalised Fick's second law, which considers concentration-dependent diffusion coefficient. According to several references cited by the author, when a glassy polymer is placed in contact with a solvent, a sharp advancing boundary is established which separates the inner glassy core from the outer swollen shell.

There is abundant practical qualitative evidence that wood treated with alkali under certain conditions shows a penetration front. For these cases, we understand that it is of interest to analyse the description of the phenomenon by the "shrinking core" model that is used in chemical engineering to describe solid reactions. In wood, under moderate conditions, alkali reacts with acid groups but it is deacetylation the most important reaction that takes place. It has been recently shown for poplar wood meal that this reaction accounts for most of the alkali consumption (Zanuttini *et al.* 1998).

In this paper, profiles of alkali concentration, alkali content, liquid content and acetyl content in tangential direction for poplar wood treated under moderate and isothermal conditions are experimentally studied. A general pattern of alkaline impregnation of poplar wood in tangential direction is analysed.

Materials and Methods

Wood sample

Green, freshly felled cottonwood (*Populus deltoides* cv. I-63-51) was used for the study. Logs from 7 year old trees were supplied by a newsprint-paper producer company (Papel Prensa S.A., San Pedro, Argentina). They were cut into disks of about 2.5 cm high and then stored in polyethylene bags at -16°C . Four cubes (2.5 cm side length) were obtained from the sapwood of each log section using a carpentry saw, with the cube faces corresponding to the tangential, transverse, and radial planes approximately. These cubes were prepared with microtome to obtain parallel radial faces. The other faces (tangential and transverse) were sealed by applying two layers of rubber screw-thread sealant, being careful to avoid drying the wood. The radial faces were kept bare, so that alkali penetration in only the tangential direction occurred.

Other cubes were prepared to get parallelism in the three directions. These cubes were alkali treated to observe simultaneously impregnation rates from all directions.

The average moisture content of the original wood was 0.95 g water g wood⁻¹.

Alkaline treatment

In order to obtain an isothermal treatment, the cubes, wrapped with polyethylene film to avoid drying, were preheated in a microwave oven with control of maximum temperature. This control was car-

Table 1. Treatment conditions

Temperature (°C)	Alkali Concentration (g l ⁻¹)	Time (minutes)
60	5.0	180
90	5.0	40, 80, 120
90	10.0	40

ried out on other similar cubes used as reference and obtained from the same log section. The temperature probe of the oven was inserted in four successive reference cubes, which were previously drilled, and later this device was wrapped as were study cubes.

The preheated cubes were unwrapped and immediately immersed in the thermostatised liquor.

The conditions of the alkaline treatments presented in this paper are displayed in Table 1.

The treatment times corresponded to a similar extent of the alkaline penetration.

Time periods are longer than usual for treatments applied in industrial chemimechanical pulping processes but they were adopted to allow a better observation of the phenomenon pattern.

After completion of the treatment, the cubes were immersed in liquid nitrogen during a period of at least two hours in order to stop the reaction and, then, stored at freezer temperature.

Frozen cubes were cut in 100 µm thick serial slices parallel to the radial face. In the case of excessively softened materials the slice thickness was increased to 200 micrometers in order to increase the possibility for obtaining unbroken slices. The slices were immediately weighed, immersed in 20 ml of water containing phenolphthalein and quantitatively neutralised with HCl 0.005 M to determine its alkaline charge. The neutralisation time was enough to allow the alkali diffusion from slices, as was indicated by the colour change of phenolphthalein. The slices were later air-dried. The dry weight of each slice allowed to determine the liquid content of the treated wood expressed as g liquid g o.d. treated wood⁻¹, as well as to calculate the alkali charge as g NaOH g o.d. treated wood⁻¹ and the alkaline concentration as g NaOH l liquid⁻¹. The alkali content of slices defined the depth of advance of the slicing applied.

It must be emphasised that this procedure requires operator ability because the slice must be obtained complete and unbroken so that it can be weighed, neutralised, air dried and weighed again. The incomplete, broken slices should be discarded. The methodology applied presents the restrictive aspect of not being able to appreciate smaller distances than 100 (or 200 micrometers) which corresponds to the slice thickness.

The penetration distance considered for each slice corresponded to its central plane.

Determination of acetyl content

The acetyl group content was determined on air dry slices using the chromatographic method proposed by Solár *et al.* (1987). The technique involves a deacetylation of the material in oxalic acid and a quantification by GC of the released acetic acid, using propionic acid as internal standard. Conditions were the same as those applied in a previous work (Zanuttini *et al.* 1998).

In this work, the weight of slices was only between 13 and 20 mg, which is substantially lower than the 300 mg used as sample in the technique proposed by Solar. The content of the original wood was 33 g acetyl groups per kg o.d. wood⁻¹.

Results

The profiles obtained for 90 °C and 5 g NaOH l⁻¹ liquor concentration are indicated in Figure 1. The profiles of wood alkali content, wood acetyl content and alkali con-

centration, all as a function of position from liquor/wood interface, are displayed on the left Y-axis. On the right Y-axis the liquid content of the wood is represented. The profiles of alkali content, alkali concentration and liquid content were fitted to Boltzman's sigmoidal curves.

Figure 1 shows that the method used, i.e. determination of alkali profiles by means of weighing and quantitative neutralisation of slices is a reliable procedure. It is worth mentioning that others have used a different method to experimentally determine alkali profile in impregnated wood. Kazi *et al.* (1997) traced alkali concentration directly by determining Na-element concentration using SEM-EDAX on wood surfaces parallel to the direction of penetration. This method is not accurate because these concentrations (Na-element and alkali) are not the same due to chemical reactions. Moreover, it does not allow one to know the local liquid contents in wood, this data being necessary to express the alkali content ($\text{g NaOH g wood}^{-1}$) as alkali concentration ($\text{g NaOH l liquor}^{-1}$).

The results shown in Figure 1 indicate that profiles of alkali and acetyl content are steep. A transition zone between 1000 and 1600 μm can be defined. These limits are indicated in the plot by dashed vertical lines. In front of this zone, alkali does not exist and acetyl content takes the level of $33.0 \text{ g kg wood}^{-1}$ which corresponds to untreated wood. Behind this zone, acetyl groups do not exist. It is clear that almost the whole reaction between alkali and acetyl groups takes place in this zone.

A useful model used for studying noncatalytic heterogeneous solid reactions is the unreacted-shrinking-core model (Levespiel 1972). Although in our case, the reaction zone is not a sharp boundary the pattern can be rather well described by the shrinking core model considering solid reactant exhausted in the outer zone.

According to the deacetylation stoichiometry, 40 g of NaOH reacts with 43 g of acetyls. Nevertheless, the consumption of alkali is somewhat higher due to other reactions (Zanuttini *et al.* 1998).

Two typical controlling mechanisms can be considered in the shrinking core model, i.e., reactant diffusion in the outer zone and the reaction in the boundary (Levenspiel 1972). Figure 1 shows that the alkali concentration in the outer zone is constant which indicates that, from these two mechanisms, the chemical reaction is the controlling one. The alkali concentration level of this plateau (5 g NaOH l^{-1}) is the same as that of the bulk solution.

Each content and concentration value reported corresponds to an average for a slice that has a section of about $25 \times 25 \text{ mm}$ and a thickness of 0.1 (or 0.2) mm. Since this section corresponds to a radial plane of the wood, it can be accepted that differences in density and reactivity along this section can exist mainly due to the presence of annual rings. During the slicing of the cubes, dark areas extended along the longitudinal wood direction were visually observed in sections corresponding to the penetration front which indicated a non-uniform arrival of alkali to the plane (Fig. 2). It is to be hoped that smaller sections of the slice (lower sides of the working cubes) would lead to the determination of a narrower reaction zone. Regrettably, practical limitations to

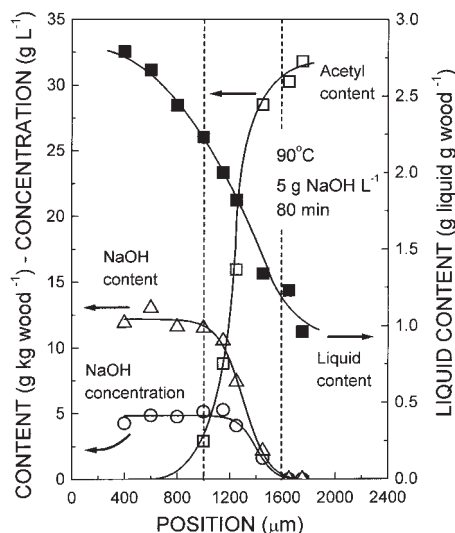


Fig. 1. Profiles of alkali impregnation (90°C , 5 g NaOH l^{-1} , 80 min): Wood alkali content, wood acetyl content, alkali concentration and wood liquid content (the last on the right Y-axis) as a function of position from the liquor/wood interface.

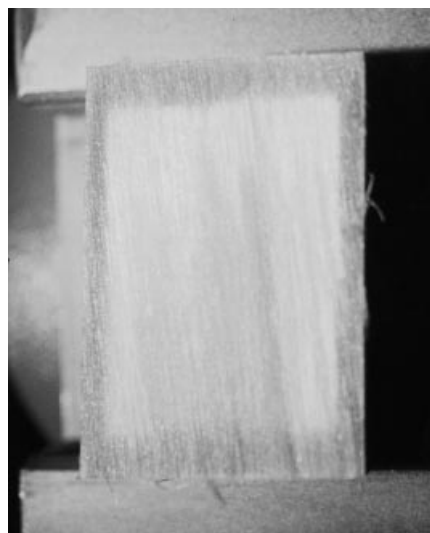


Fig. 2. Radial face of a cube simultaneously impregnated in the three directions (90°C , 5 g NaOH l^{-1} , 95 min). In the frozen-state, it was cut in serial slices up to the transition zone. The presence of areas coloured by alkali and areas that seem to be intact indicates the non-uniform advance of the penetration front. The dark borders show the penetration in radial and longitudinal wood directions. It can be noted that the longitudinal penetration is larger but not more than double in comparison with penetration in a transverse direction.

working with smaller cubes and the lack of precision of the analytical determinations applied does not allow such size reduction.

The profile of liquid content shows that alkali impregnation involves an important liquid uptake since from a value of $0.95 \text{ g liquid g wood}^{-1}$ in the intact interior of wood, the liquid content increases up to about 2.1 through the reaction zone. This uptake continues behind the reaction front and thus the liquid content increases up to $2.8 \text{ g liquid g wood}^{-1}$ in the outermost zone of the wood.

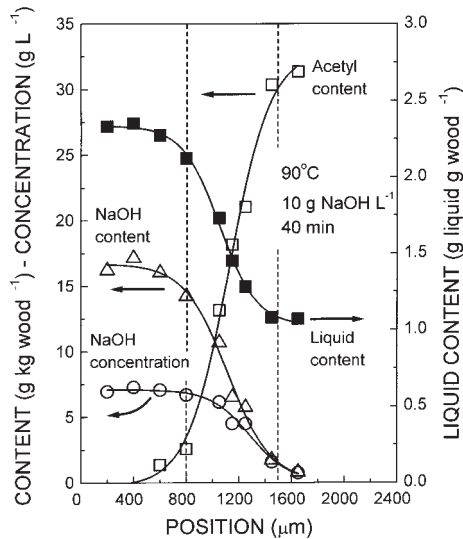


Fig. 3. Profiles of alkali impregnation at 90 °C, 10 g NaOH l⁻¹ and 40 min.

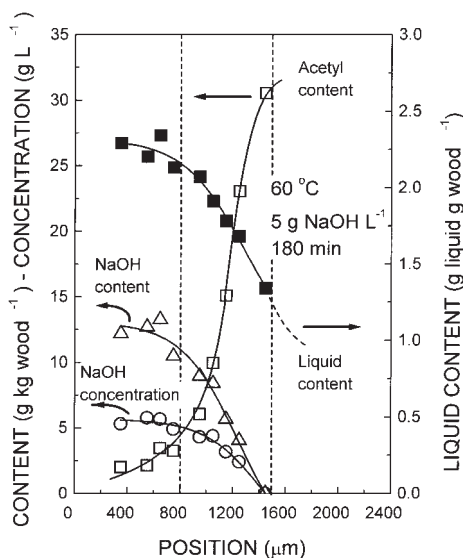


Fig. 4. Profiles of alkali impregnation at 60 °C, 5 g NaOH l⁻¹ and 180 min.

The results obtained at 90 °C and 10 g NaOH l⁻¹ are displayed in Figure 3. All these profiles were fitted to sigmoidal curves.

The impregnation pattern in this case is similar to that found for 5 g l⁻¹. The reaction zone can be considered here between 800 μm and 1500 μm, which is lightly wider than the previous one. Alkali concentration of 7.5 g NaOH l⁻¹ and liquid content of 2.3 g liquid g wood⁻¹ combine to make alkali content reach a value of 17 g kg wood⁻¹ in the outermost zone.

The results obtained at 60 °C and 5 g l⁻¹ are displayed in Figure 4. All profiles, with the exception of the acetyl content one, were fitted to sigmoidal curves.

For these conditions, although the deacetylation is not completed in the reaction zone, it is here where the major part of the process occurs. The impregnation pattern can be considered similar to those found for higher temperatures.

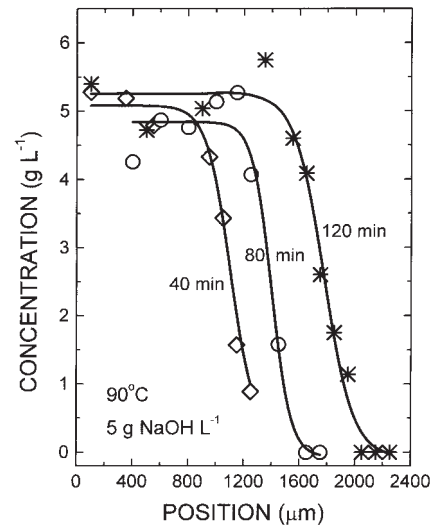


Fig. 5. Profiles of alkali concentration at 90 °C and 5 g NaOH l⁻¹ for three different times.

The reaction zone in this case can be considered between 800 μm and 1500 μm.

A concentration that tends to 5.5 g NaOH l⁻¹ and a liquid content that tends to 2.3 g liquid g wood⁻¹ combine to give an alkali content that tends to 15 g NaOH kg wood⁻¹ toward the outermost zone.

Figure 5 shows alkali concentration profiles obtained at 5 g l⁻¹ and 90 °C for three different times (40, 80 and 120 min). It can be noted that, concentration front penetrates toward the interior of the wood keeping a similar shape.

Discussion

Results indicate that, under these conditions, poplar wood behaves similarly to a glassy polymeric solid in contact with a solvent. An advancing boundary separates an intact inner part of the particle from a swollen outer zone. The thickness of this boundary zone is similar for these three conditions.

In the fully-swollen and fully-impregnated zone, near to the wood-bulk solution interface, the alkali concentration, alkali content and liquid content tend to the levels indicated in Table 2.

The alkali concentration inside swollen wood is similar to the concentration in the bulk solution when this is 5 g NaOH l⁻¹ for 60 and 90 °C. Nevertheless, the concentration inside wood is lower when the bulk solution concentration is 10 g l⁻¹ and temperature is 90 °C.

It must be taken into account that when wood is treated with alkali, the OH concentration in the external liquor can be different from that inside the fibre wall, according to the theoretical ionic balance established by Grignon and Scallan (1980). At equilibrium, the OH concentration in the wall is lower than that in the liquid phase and the difference depends on the carboxyl groups concentration in the wall and the OH concentration in the liquid phase.

An important liquid uptake has been found inside the reaction zone as well as behind it.

Table 2. Alkali concentration, alkali content and liquid content at outermost wood layer

Impregnation Conditions	60 °C 5 g NaOH l ⁻¹	90 °C 5 g NaOH l ⁻¹	90 °C 10 g NaOH l ⁻¹
Alkali Concentration (g NaOH l liquid ⁻¹)	5.5	5.0	7.3
Alkali Content (g NaOH kg treated wood ⁻¹)	14	12.5	17.0
Liquid Content (g liquid g treated wood ⁻¹)	2.3	2.8	2.3

Two factors contribute to this uptake: 1) Alkaline swelling which implicates an increase in fibre wall thickness and 2) Penetration in the hollow cavities of the wood such as vessels and fibre lumens. The relative contribution of each factor cannot be determined by the present experimental method.

Even green, pulpwood is generally in a state of three-phase system: Wood substance, liquid and air (Rydholm 1965). The air entrapped by impregnating liquors in a wood particle produces a back-pressure that checks additional penetration (Rydholm 1965). In the present case that pressure can affect the filling of vessels and lumina and in this way can prevent the liquor uptake. However, this resistance should not affect the advance of the alkaline action front, which takes place in the solid phase and is controlled by the chemical reaction mechanism.

The model explains the frequent practical observation of non-uniform alkali impregnation of wood specimens that show a well-impregnated outer zone and an intact core. This non-uniformity can produce definitive consequences when the alkali concentration or the alkali charge are low as it happens for chips in chemimechanical pulping processes.

For poplar, the reactions that take place under conditions of alkaline chemimechanical pulping consume between 4 and 5 % NaOH on wood (Zanuttini *et al.* 1999). This consumption is higher than the whole alkali charge normally applied in the process and hence alkali affects only the outer zone of chips.

Results obtained indicate that impregnation profiles could be approximated to a step-form pattern. Under this assumption, the level of impregnation could be characterised by only one parameter, i.e., the position of alkali concentration front or, alternatively, acetyl content front. It is clear that the determination of the front position as a function of time for different conditions of the treatment and wood directions could be very useful to build a model for predicting impregnation levels of alkaline treatments carried out under moderate conditions.

Conclusions

Alkali impregnation of fresh poplar wood in the tangential direction, under moderate conditions, cannot be considered as a pure diffusive problem. The fast kinetics of the chemi-

cal reactions, the relatively high level of alkali consumption and the high uptake of liquor as a consequence of alkaline swelling and liquid penetration in wood cavities play fundamental roles in the phenomenon.

Instead of following an unsteady-state fickian diffusion, wood behaves like a glassy polymeric solid. An advancing boundary zone separates an intact inner part of the particle from a swollen outer shell. The existence of an advance boundary indicates that the complex process of diffusion with chemical reaction and swelling can be in great part described by the shrinking core model. The concentration profile that is established in the interior of the wood approaches to a step-form pattern indicating that the chemical reaction is the controlling mechanism and that there are no diffusive restrictions.

The alkaline swelling of the cell wall and the liquor penetration in the hollow cavities can increase the liquid content of wood up to values as high as 2.8 g liquid g wood⁻¹.

The procedure used here, and the impregnation pattern proposed, appears to be useful when analyzing the effect of wood direction and process variables such as temperature, alkali concentration and initial wood moisture. They could also be very useful to build a model for alkaline impregnation of wood under moderate conditions.

Acknowledgements

Financial support was provided by ANPCyT (Proyect N° 14-00000-00047, BID 802 OC-AR) and UNL (CAI+D 96 Program).

The authors thank Elsa Grimaldi for the linguistic revision.

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Received August 10th1999

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