

# PROJECT REPORT FORM

cc: The Files  
MacLaurin  
Stone

PROJECT NO. ✓ 1710  
COOPERATOR Institute  
REPORT NO. 1  
DATE April 23, 1953  
NOTE BOOK 1219  
PAGE 6  
SIGNED John E. Stone  
John E. Stone

## A STUDY OF SOME OF THE FUNDAMENTALS OF PULPING

It was originally intended to open the attack on some of the problems of pulping by measuring the force required to shear a piece of wood which had been acted upon by various pulping reagents. While the apparatus was being built it was decided to study effective capillary cross section and internal swelling of wood which had been saturated with a number of different solutions. Using poplar, this has been done for KCl,  $\text{NH}_4\text{Cl}$ ,  $\text{CaCl}_2$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$ , diethylamine and pyridine, all at  $25^\circ\text{C}$ . and at a number of different concentrations. The results obtained with the first seven reagents are shown below:

		Longitudinal	Radial	Tangential
KCl	M/100	.60	.19	.16
	M/10	.50	.11	.075
	M	.52	.11	.07
$\text{NH}_4\text{Cl}$	M/10	.47	.11	.083
	M	.48	.11	.077
$\text{CaCl}_2$	M/10	.47	.08	.06
	M	.41	.10	.06
	4M	.38	.10	.07
$\text{Na}_2\text{SO}_3$	M	.53	.076	.05
$\text{Na}_2\text{CO}_3$	M	.47	.08	.07
$\text{Ba}(\text{OH})_2$	.12M (Saturated)	.53	.30	.24
NaOH	M/10	.33	.11	.08
	M/5	.43	.16	.18
	M/2	.38	.29	.27
	M	.43	.32	.29
Stamm N/10 KCl Sweetgum sapwood		.46	.055	.027

The figures represent the ratio of the conductivity through the wood to the conductivity through the bulk solution and give a measure of the rate at which the ions would diffuse in the various directions. (A value of unity would indicate that the wood structure offered no resistance to the passage of ions.) There are no values in the literature relating to poplar so the above results cannot be checked directly; however, work of Stamm on M/10 KCl and various softwoods and hardwoods gave results of the same order as those given above, but differing by a factor of 2-3 in the transverse directions. The different wood and different technique could largely account for these divergences. Examining the present results it is seen that the first five salts give very similar values (the most concentrated  $\text{CaCl}_2$  solution shows a viscosity effect). The sodium carbonate and sulphite have perhaps slightly lower diffusibilities in the transverse direction. Considerable differences are seen with the strong alkalies, however, and the four concentrations of NaOH illustrate this quite well. It indicates that with increasing concentration the transient cell wall capillaries and pit membrane pores open up and allow a more easy passage of ions. Presumably with still higher concentrations, the values for the three directions would approach one another and support the contention that diffusion of NaOH into wood is equal in all directions.

The results obtained with the weak bases ( $\text{NH}_4\text{OH}$ , diethylamine, and pyridine) were rendered unintelligible due to their rapid reaction with the wood to form salts(?) of higher conductivity than the free base. It is clear that diffusion results, whether obtained by classical methods or by the

conductivity method, are of limited value when the solute reacts with or is adsorbed on the membrane, and yet it is precisely these solutes which could produce interesting results from a pulping point of view. It is intended to follow this up, possibly by carrying out a conductometric "titration" of weak base solution with wood meal. The behavior of ammonium hydroxide toward wood is particularly worthy of investigation.

Work in the immediate future will consist of studying the effect of temperature on the effective capillary cross-section of poplar, using KCl as solute. Then I believe it would be logical to obtain values of

$K_{\text{wood}} / K_{\text{bulk liquid}}$  for all species of wood of which samples can be obtained, using KCl at room temperatures. Such values could be obtained very rapidly, with no trouble, and while not of immediate use to us they would provide a background of information which might be correlated with something else later on and would also provide greater justification for a publication.

It became very evident during this work that there are large gaps in our knowledge concerning some of the fundamental physical chemistry of pulping. I will give several examples. Considerable work has been done on the adsorption of NaOH by cellulose; less on the adsorption by wood. In all cases the ratio of liquid to solid has been quite high, although in actual practice it is about 2:1 in the interior of the wood. The reason for not using ratios of 2:1 is that no free liquid can be extracted from wood meal which has this amount of liquid mixed with it, and it is necessary

to obtain some of this free liquid in order to measure the decrease in NaOH concentration. This decrease in NaOH concentration will be naturally quite different for a ratio of 2:1 to a ratio of say 10:1. Values for a ratio of 2:1 can be obtained by a method described by Freundlich, but so far no one has done it on wood. The importance of knowing more about this subject can be seen by considering the kinetics, or rate of pulping. Inside the chip the ratio of solid to liquid is 1:2 and at first the reaction will be quite rapid. As the chemical is used up the concentration decreases and the rate of the reaction will decrease. When all the chemical is consumed the reaction ceases as far as the chemical is concerned. I believe some pure adsorption work and some straight pulping (delignification) studies might well be carried out using ratios of 2:1 just to see what happens inside a wood chip if conditions are such that no bulk liquid gets in or out and there is no diffusion of ions. (This might be the case for short-term cooks.)

and  
Another example of work that could/certainly should be done is a study of the rates of swelling, imbibition, diffusion, and adsorption. These are particularly important in cooks which last just a few minutes but are quite important for all cooks. Take the cold NaOH "cook" for example. It is stated that a basic principle of the process is the fact that the rate of swelling varies inversely with the temperature; hence, they keep the temperature low. As far as I know, the rate of swelling does not vary inversely with temperature; it actually increases somewhat. It is the equilibrium amount of swelling which varies inversely with temperature. Thus, although there might be more swelling in 2 hours at 25°C, than in 2 hours at 100°C., there might be more in 30 minutes at 100° than during the same period at 25°C. It should be investigated. Swelling, imbibition, etc. can be studied very nicely by

Weighing the wood after various times, in fact this is the usual method for gels, but in order to obtain the most valuable information, it would be desirable to make these measurements at pulping temperatures and pressures. It has been proposed to use the autoclave under construction for this purpose but I suggest that to supplement this apparatus, a quartz helix be purchased to cover the lower ranges of weight change. Such a helix costs \$45.00 and covers the range 0 to 2 grams with sensitivity of about a milligram. It will support one wood chip. All the work with it would be, in effect, sinkage studies, but would measure liquid uptake after sinking as well as before.

Note: Chip would be weighted down so that it was below liquid even when density is less than one. One would then be measuring decrease of buoyancy. By weighing when suspended in the liquid and also when suspended in air (vapor) the density and hence external volume or degree of swelling could be measured. When studying rates, the variables would be (1) amount of pre-evacuation, (2) moisture content during pre-evacuation, (3) temperature, (4) chemical, (5) pressure, (6) wood, (7) etc.

Work at atmospheric pressure and moderate temperatures could be done using an ordinary balance but I feel that at elevated temperatures and pressures, conditions could be made very similar to those existing in a digester and would be of more interest. A quartz helix also permits complete sealing of solutions at room temperatures and eliminates troubles due to evaporation.

The necessity for work along these lines became apparent during the present study of effective capillary cross-section. I have been measuring equilibrium values, but it took a considerable period (up to several hours) to reach this equilibrium, even after 2 hours pre-evacuation of sample at  $1/2$  mm pressure. A "rate" study should have come before an "equilibrium" study.

Although not important with a solute which does not react with wood, i.e., KCl, it is of paramount importance with one that does, i.e., NaOH,  $\text{NH}_4\text{OH}$ , etc.

Future work, or work that might be considered for a student thesis, is the effective capillary cross-section of wood after various degrees of pulping; the diffusibility of large ions and molecules (lignin) through partially delignified wood and through cellophane membranes; etc.

# PROJECT REPORT FORM

cc: The Files  
Dr. May  
Dr. Stone (2)  
Mr. Weiner

✓ PROJECT NO. 1710  
COOPERATOR Institute  
REPORT NO. 21  
DATE April 26, 1956  
NOTE BOOK 1328  
PAGE 7 TO 186  
SIGNED J. E. Stone

## STUDIES OF PENETRATION AND DIFFUSION INTO WOOD

### INTRODUCTION

A great deal of work has been carried out on the penetration and diffusion of various liquors into wood, and while much has been learned through these experiments there is ample evidence that considerable confusion still exists with regard to the mechanisms involved. Moreover, in a practical situation in a mill, where some particular species of wood of a certain moisture content is to be pulped by one of the recognized processes using a set of operating conditions more or less controlled by the limitations of existing equipment, it remains true that it is still often necessary to "try it and see." So many factors are involved that this is inevitable, but it is hoped that the following discussion will go a short way toward bridging the gap between practice and theory and aid the pulping man in his analysis of his local problems.

It is necessary to say a word here about nomenclature. The term "penetration" is often used to describe any movement of chemical into wood, whether the mechanism is a flow of solution into the wood voids or is a diffusion of solute ions into water already present in the wood. Actually, these two mechanisms for chemical movement into wood are entirely different and operate in response to quite different laws, so in order to avoid ambiguity, the following nomenclature will be used. The term "penetration" will be restricted to the flow of liquor into wood under the influence of a hydrostatic

pressure gradient. The liquor moves as such. The term "diffusion" will be used in its physico-chemical sense for describing the movement of ions or other solute through water under the influence of a concentration gradient.

The lack of precise terminology may be the source of several misconceptions which exist in this field. For example, it is quite widely believed that alkaline solutions are able to penetrate wood considerably faster than acidic ones, and that alkaline solutions can penetrate wood at approximately equal rates in the three structural directions--longitudinal, radial, and tangential. In the sense that the word "penetration" is used here, this is definitely not the case. In fact, alkaline solutions penetrate wood more slowly than acidic ones. What is meant is that alkaline solutions swell the cell walls of the wood, producing wider and more numerous diffusion paths across the fibers, and permitting a diffusion of solute at approximately equal rates in the three structural directions.

Diffusion is a very much slower process than penetration and is therefore unsuitable for the transport of chemical into large pieces of wood. Thus, in the chemigroundwood process where logs several feet long and many inches in diameter are to be cooked whole before grinding, a diffusion process is out of the question, and conditions must be chosen which are most suitable for rapid penetration. This raises the question as to just what factors are involved in penetration and diffusion, and to what extent these factors are under the control of the operator. Listed, the chief factors are:

Wood	Liquor
Capillary structure	Composition
Presence of moisture	Temperature
Presence of air	Pressure
	Viscosity
	Surface tension



## CAPILLARY STRUCTURE OF WOOD

This is too well known to need much elaboration here. Briefly, however, it may be stated that penetration rate is exceedingly sensitive to the diameter of the individual capillaries, whereas diffusion rate is controlled more by the total cross-sectional area of the capillaries, ~~whereas diffusion rate is controlled more by the total cross-sectional area of the capillaries~~ rather than their individual diameters. In practice, this means that penetration takes place only through the larger pores such as the fiber lumen in series with the pit membrane pores, or through the vessels, in the case of hardwoods. The cell walls themselves are ineffective for liquid movement as the individual capillaries are too small. This leads to the result: that longitudinal penetration is always much more rapid than transverse penetration, the ratio of one to the other being perhaps 100:1 in the case of conifers to 10,000:1 or more in the case of hardwoods. By contrast, diffusion involves the capillaries of the cell wall as well as the larger pores, and the ratio of longitudinal to transverse diffusion is much less than is the case for penetration. It may be about 5:1 up to perhaps 30:1 for neutral or acidic solutions, and approach 1:1 in the strongly alkaline regions.

Because of the sensitivity of penetration rate to the diameter of the individual capillaries, changes in wood structure affect penetration very strongly. Thus the plugging of pit membrane pores in the case of softwoods, or the formation of tylosic membranes across the vessels in the case of hardwoods, can have such a very considerable affect on penetration rate that the whole nature of wood as a porous medium can be said to have changed.

In another paper (\_\_\_) a discussion is given of the penetrability of wood, and it is shown to vary up to many thousand-fold in going from sapwood to heartwood, or from one species to another. Diffusion rate is much less influenced by changes in wood structure, variations from sapwood to heartwood, or from one species to another being only of the order of several fold.

The penetrability of a wood can be demonstrated by taking chips or blocks of fairly low moisture content, pulling a vacuum and flooding with water. An easily penetrated wood will sink in a few seconds, whereas a very difficultly penetrated wood will not sink even after many hours or days. In some cases the application of 2000 p.s.i. hydrostatic pressure will still not give complete penetration. It is clearly necessary to know into which of these two categories a wood falls, for without such knowledge of the nature of the medium being worked with, much time may be wasted attempting the virtually impossible.

Structural differences between softwoods (conifers) and hardwoods must be clearly distinguished. The natural channels for water movement in hardwoods are the vessels, and these very wide pores run longitudinally through the wood for a more or less indefinite distance. If these vessels are unblocked by tyloses, the wood can be any length in the fiber direction without seriously affecting the efficiency of penetration. On the other hand, there are no large pores such as the vessels running transversely through hardwoods, which means that transverse penetration rates are negligibly small. If the vessels are plugged with tyloses, penetration rate is exceedingly small in all directions. The fibers of hardwoods are inter-connected by pit pairs, but because they are few in number, the fiber system in hardwoods is a poor medium for liquid movement.

Coniferous woods do not have vessels, the tracheids and their inter-connecting pit system taking over the function of liquid transfer. This is less effective than the vascular system but more effective than the fibers of hardwoods. Longitudinal penetration through softwoods is therefore much slower than through easily penetrated hardwoods, but transverse penetration on the other hand is just the reverse--i.e., more rapid through softwoods than hardwoods.

Diffusion takes place into water, not into wood. Solute particles can therefore diffuse through wood wherever water is present but cannot do so where water is absent, leading to the conclusion that wood should be water-saturated for diffusion to be most effective. Although diffusion is a slow process, it is an efficient one when the distances involved are small, for the wood substance itself--i.e., the cell wall material--is a comparatively open network so far as a diffusing ion is concerned. Thus the effective capillary cross-sectional area of wood--that is, the ratio of the area available for diffusion to the area which would be available if no wood at all were present--may be as high as 50% for a low density wood in the longitudinal direction, and still as much as 10% in the transverse directions. In strongly alkaline solutions the effective capillary cross-sectional area may approach 50% in all three directions (—). Barriers to penetration, such as tyloses, gummy deposits, and bordered pits closed by the torus, are considerably less effective in reducing diffusion rate because diffusion can take place through the cell wall itself and is not limited to those passages where the barriers occur. If a wood is very difficult to penetrate, therefore, (beech or white oak may be cited as examples), it is probably better to use chips as nearly water-saturated as possible, permitting diffusion to carry the chemical into the interior of the wood, rather than use drier chips and attempt to penetrate

liquor under pressure.

#### PRESENCE OF AIR

Air is detrimental to both penetration and diffusion and should be removed as far as possible. This may be done by evacuation, steaming, or replacement with a water-soluble gas. Steaming is the least suitable method if the wood is easily penetrated, for the wood increases in moisture content and there is consequently less room for the entering liquor. For a difficultly penetrated wood on the other hand, where diffusion is to be relied upon and the wood should be as wet as possible, steaming is probably the most satisfactory method for removing air.

#### LIQUOR FACTORS

Penetration rate will increase with an increase in pressure, and also with a reduction in liquor viscosity such as occurs when the temperature rises. The nature of the electrolyte is of small importance except in so far as it affects pH. Acidic liquors (below pH 7.0) penetrate faster than slightly alkaline liquors for the same reason that pulp slurries drain faster when acidic than when alkaline. Liquors which are sufficiently alkaline to swell the cell walls beyond their water swollen dimensions, e.g., soda or kraft liquors, penetrate very slowly.

In contrast to penetration, diffusion is strongly influenced by liquor composition since in the latter case it is the mobility and concentration gradient of the ions which determines rate. Also, ionic mobility increases substantially with increasing temperature and there is probably at least a ten-fold increase in rate for 100°C. rise, a larger temperature coefficient

## SIMULTANEOUS PENETRATION AND DIFFUSION

Wood as cooked is seldom either oven-dry or water saturated. This means that in practice a combination of both penetration and diffusion will occur when chips of normal moisture content are treated with liquor at elevated temperatures and pressures. It then becomes unreasonable to expect that a simple law which applies to one mechanism will be valid when the system is subjected to both. Actually, the system is exceedingly complex, for the whole balance between penetration and diffusion is constantly shifting as the temperature and pressure rise, the moisture content of the wood increases, and the chemical concentration and temperature gradients within the wood are continually changing. It is this complexity which has forced the use of empirical approaches to problems in this field, and the work to be described below is no exception.

## EXPERIMENTAL

It was desired to compare the relative rates of movement of sodium sulphite and ammonium sulphite into aspenwood. If only penetration were involved it might be predicted that there would be little difference in rate, for the viscosities of the two solutions are very similar. If only diffusion were involved, it might be predicted that ammonium sulphite would move into wood about one and a half times as fast as sodium sulphite, for this is the ratio of their diffusion coefficients at room temperature.

When there is a combination of penetration and diffusion, the relative rates of movement of the two sulphites should lie somewhere between 1:1 and 3:2, unless (a) the temperature coefficients of diffusion of the

two salts are widely different, or (b) the mobilities of the various ionic species through a wood membrane are markedly different than through water.

The empirical method adopted to study this system, under what might approximate a real set of conditions, was to take advantage of the well-known fact that wood which is heated in the absence of cooking liquor turns brown. That is, it is "burnt." If, therefore, two similar pieces of wood are taken, and one is heated in ammonium sulfite solution while the other is heated in sodium sulfite solution, and after heating the wood is split open, the specimen with the smallest area of brown is the one penetrated (or diffused into) most efficiently.

The wood used was the sapwood of aspen (Populus tremuloides) with a specific gravity of 0.33. It contained few, if any, tyloses and could be considered to be an easily penetrated wood. Its penetration factor (\_\_\_) was about  $2000 \times 10^{-10}$ .

The wood was cut into blocks with the following dimensions: 1/2-inch radial, 1/2-inch tangential, and 1/4, 1/2, 1, and 2 inches longitudinal.

The moisture content of the wood was adjusted to four ranges: oven-dry, water-saturated—(230% moisture, oven-dry basis), and two intermediate moisture contents—43 and 100% on the oven-dry basis.

The cooking temperature chosen was 170°C. and two different times-to-temperature adopted, viz., 16 and 90 minutes. The time at temperature was fixed at 2 hours. The vessels used for the cooks consisted of 200-ml. stainless steel bombs. These bombs were brought up to temperature at the desired rate in an electrical preheater and the temperature maintained at 170°C. in a thermostatically controlled oil bath. There was no relief of

pressure during the cook and no agitation or circulation of the cooking liquor.

The cooking liquors consisted of 0.25 molar solutions of sodium and ammonium sulphites. Each of the two solutions contained 16 g./l. of sulphur dioxide and had a pH of 8.1. No buffer was used for either solution since the buffers themselves have their own diffusion coefficients which would interfere with the comparison of the sodium and ammonium sulphites. Instead, a large liquor-to-wood ratio was used (about 25:1) which effectively prevented the liquor dropping in pH below 7.

Each cook was carried out in duplicate. One of the two wood specimens obtained under each set of conditions was split to show a tangential face; the other was split to show a radial face. Photographs were taken to show the extent of burning inside the wood and these photographs form the only record of the results which were obtained.

## RESULTS AND DISCUSSION

The results are shown in Figures 1-4. The specimen on the left of each pair shows the tangential face with the radially split specimen on the right. The interpretation given below is based on an examination of the original specimens which showed up the differences more clearly than the photographs. The photographs do, however, show the pattern of penetration and diffusion in a pictorial way which would be difficult to duplicate in any other manner.

### Effect of Wood Length

Only the 1/4-inch specimens were unburned under all conditions. The 2-inch specimens always showed some burning.

### The Effect of Moisture Content

It appears that for both sodium- and ammonium-base liquors and for both slow and fast rates of rise to temperature, water-saturated wood shows less burning than oven-dry wood or wood of intermediate moisture contents. Oven-dry wood appears to be more satisfactory than partially dry wood.

### Effect of Time-to-Temperature

As would be expected, the specimens heated to 170°C. in 16 minutes showed more burning than those heated to 170°C. in 90 minutes. The effect of varying the time to 170°C. was very marked with the water-saturated and oven-dry specimens. Thus, the water-saturated 1-inch long specimens were quite unburned using a 90-minute heat-up period, whereas with a 16-minute heat-up period, the unburned section extended only about 1/4-inch into the wood, leaving the central 1/2-inch badly burned.

### Effect of Base

Very little difference could be seen between the ammonium- and the sodium-base liquors, regardless of wood moisture or time-to-temperature. If a difference did exist, it was most evident in the 16-minute time-to-temperature experiments, where the wood cooked with ammonium sulphite showed a little more white and a little less black area than did the wood from the sodium-base cooks.

### Effect of Radial and Tangential Directions

If wood rays help the radial movement of cooking liquor, the width of the white border should be greater on the right hand specimens than on the left. The photographs show some evidence of this, but it is obviously not a very important factor. In many cases, the width of the white border is



sufficient to suggest that with chips of normal thickness there would be little burning in the center even though very considerable burning occurred with the 1/2-inch thick specimens used in the present experiments.

It should be mentioned that for comparison, a number of aspen sapwood specimens considerably larger than those used in the above experiments were evacuated in the air-dry condition (20% moisture, oven-dry basis) and flooded with cooking liquor under atmospheric pressure. These wood blocks could be heated to 170°C. as rapidly as desired—5 minutes, for example, in one experiment—with no trace of burning.

The advantage of choosing conditions which result in burning when studying penetration and diffusion is that a simple visual examination is all that is necessary to compare one set of conditions with another. Thus, two wood species could be compared, or sapwood with heartwood, or an alkaline liquor with a neutral liquor, or steaming with evacuation, or any of countless other comparisons which might be useful in anticipating the results of changes which are contemplated in a mill. If conditions are not chosen so that burning occurs, for example if small wood chips are used, there may still be differences in penetration and diffusion between two sets of conditions but these differences will now show up as chips with undercooked centers, and it is necessary to obtain data on screened yield, per cent screenings, and pulp quality in order to make a comparison. This of course is the ultimate test of a procedure, but much valuable preliminary information may be obtained by the "burning" method outlined.

#### ADDITIONAL EXPERIMENTS

It will be noted from Figures 2 and 4 that the 2-inch water-saturated specimens were less burnt at one end than the other. This, or similar effects, were found quite frequently in many miscellaneous experiments not recorded here, the following example being typical. Two 2-inch water-saturated blocks of wood were placed in a bomb so that one rested on the other and the fiber direction was vertical. Neutral sulfite liquor was added and the bomb heated to 170°C. in 90 minutes and maintained there for 2 hours. There was no circulation or agitation of the liquor. When split open, the top half of each block was white and unburned whereas the bottom half of each block was burned. At the junction of the two blocks therefore the liquor apparently moved down into the bottom piece but did not move up into the top piece. Horizontally oriented blocks showed no such effect. The tentative explanation for this effect was that the free liquor in the bomb heated up faster than the water in the wood and acquired a lower density. This produced circulation through the wood by means of the cold, dense water flowing out of the bottom of each block and the hot, less-dense liquor flowing down into the top. In a horizontally oriented specimen no such effect is possible. This hypothesis was tested on blocks of birch sapwood 4 inches long and 2-inches by 2-inches in the transverse directions. The wood was thoroughly water saturated, preheated to 70°C. in a water-bath, and then immersed in a sodium sulphite solution also at 70°C. The liquor is now more dense than the water in the wood, being at the same temperature, and if the mechanism postulated actually operates, the liquor should flow up into the bottom of a vertically placed block. The temperature was too low to show burning, so the blocks were cut into nine equal segments and analyzed. The results are shown in Figure 5.

The vertical block is seen to have taken up most chemical, the horizontal least, and the 45° one an intermediate amount. The bottom end of the blocks had more electrolyte in it than the top end, as predicted. The vertical block had actually almost reached equilibrium with the surrounding solution, whereas the horizontal block was still far from this condition.

The very uneven character of the salt distribution will be noticed. No explanation can be given for this. About 200 separate blocks were used for a corresponding number of diffusion experiments, using various electrolytes and temperatures, and an irregular distribution of chemical proved to be the rule rather than the exception. The conclusion was reached that, notwithstanding the very fine capillaries involved, a fairly ready interchange of liquor inside and outside the blocks must be possible in the case of wood containing tylose-free vessels. Thus it was found that stirring the bath of solution in which the blocks were immersed introduced considerably more chemical into the wood in a given period than did no stirring.

A different type of experiment confirms the hypothesis that density differences between liquor and water in the wood can cause appreciable convection currents through wood. It was decided to increase the effect of density differences by using a centrifuge. Blocks of wood, 1/2" by 1/2" by 1" in the fiber direction were cut from the sapwood and the heartwood of poplar, birch, beech, and maple. One set was water-saturated and another set left air dry. Thus, four species of wood, sapwood and heartwood, at two different moisture contents were obtained. One complete set of these blocks was immersed in a sodium chloride solution for 15 minutes, the blocks being vertical, while the other set was centrifuged for 15 minutes in the same concentration of salt solution. At the end of 15 minutes the centrifuged

and non-centrifuged blocks were removed, wiped free of surplus solution, and ashed. The results are given in Table I.

(Table I)

It is seen that the centrifuged blocks took up considerably more salt than the blocks which had merely stood in a beaker of the solution. The increase in uptake due to centrifuging was from 5-10 times and in some cases the centrifuged blocks took up almost the maximum theoretically possible for complete equilibration.

The easily penetrated woods--that is, the sapwood ~~and~~ of all four species and the heartwood of birch--took up more solution than the difficultly penetrated heartwoods of beech, poplar, and maple. This is to be expected. It is interesting, however, that the easily penetrated woods were apparently most effectively penetrated (by centrifuging) when in the water-saturated condition, whereas the difficultly penetrated woods were most effectively penetrated by centrifuging when in the airdry state.

The value of these results lies possibly in their demonstration that a unidirectional driving force through wood is remarkably effective in increasing the rate of liquor uptake. The air, instead of being forced to retreat to the center of the wood and be compressed there, opposing further penetration, can be swept out of one end of the wood by the liquor moving in from the other end. Whether or not such a mechanism could be adapted for commercial use is problematical, but it may well be that this mechanism operates to a limited extent in any digester and cannot be entirely ignored as a possible factor in the already complicated field of penetration and diffusion into wood.

TABLE I  
 EFFECT OF CENTRIFUGING ON PENETRATION

Wood Used	<u>Airdry</u>		<u>Water Saturated</u>		Maximum Theoretical Ash, %
	Not Centrifuged	Centrifuged	Not Centrifuged	Centrifuged	
Birch sapwood	0.26	3.93	1.17	5.21	6.20
Birch heartwood	0.02	2.90	0.91	5.00	6.20
Beech sapwood	0.69	3.78	0.86	4.28	6.55
Beech heartwood	0.42	2.78	0.29	0.38	5.75
Maple sapwood	1.45	4.68	1.56	5.48	7.10
Maple heartwood	0.93	3.40	1.12	1.32	7.70
Aspen sapwood	2.00	7.55	3.88	8.12	12.70
Aspen heartwood	0.57	3.51	0.81	1.20	13.10

References

1. J.<sup>E.</sup> Stone. Pulp Paper Mag. Canada (to be published)
2. J. E. Stone. Unpublished work (to be published 1956)

# PROJECT REPORT FORM

cc: The Files

Dr. May

PROJECT NO. 1710  
COOPERATOR Institute  
REPORT NO. 3  
DATE January 28, 1957  
NOTE BOOK 1219  
PAGE 118 159  
SIGNED J. E. Stone  
J. E. Stone

## COMPARISON OF SODIUM AND AMMONIUM BASE LIQUORS ON ASPEN AND SPRUCE AT VARIOUS pH

This work was presented by D. J. MacLaurin at the Tappi meeting in New York on February \_\_, 1955.

It has not been written up in report form or for publication as Mr. MacLaurin took the responsibility for this and has not completed the report yet.

jes/jh

# PROJECT REPORT FORM

cc: The Files

Dr. May

PROJECT NO. 1710  
COOPERATOR Institute  
REPORT NO. 4  
DATE January 28, 1957  
NOTE BOOK 1328  
PAGE 7 JO 106  
SIGNED J. E. Stone / J. E. Stone

## STUDIES OF PENETRATION AND DIFFUSION INTO WOOD

Only a small part of the work performed is contained in this publication. The remainder has not been published because of uncertainty about the data.



# Studies of Penetration and Diffusion into Wood

J. E. STONE and CARL FÖRDERREUTHER

The rates at which sodium and ammonium sulphites move into aspen sapwood have been compared under conditions approximating commercial practice. The comparison was based on the relative amounts of "burning" which took place with each of the two salts when the wood was cooked for 2 hr. at 170°C. Little, if any, difference between sodium and ammonium sulphite—regardless of chip length, wood moisture content, or time-to-temperature—could be distinguished. With a given salt and varying wood moisture content, "burning" increased in the order water-saturated, oven-dry, intermediate moisture content. The amount of "burning" increased with a decrease in heat-up time, as expected. Additional experiments showed that wood blocks which had the fibers oriented vertically took up more chemical in a given time when immersed in liquor than did blocks where the fibers lay horizontally. The centrifuging of blocks of several different species immersed in a salt solution showed a considerable increase in salt uptake over similar blocks immersed but not centrifuged. It is suggested that density differences between ambient liquor and water in the wood can cause a circulation through the wood when the vessels are vertical.

A GREAT deal of work has been carried out on the penetration and diffusion of various liquors into wood, and while much has been learned through these experiments, there is ample evidence that considerable confusion still exists with regard to the mechanisms involved. Moreover, in a practical situation in a mill, where some particular species of wood of a certain moisture content is to be pulped by one of the recognized processes using a set of operating conditions more or less controlled by the limitations of existing equipment, it remains true that it is still often necessary to "try it and see." So many factors are involved that this is inevitable, but it is hoped that the following discussion will go a short way toward bridging the gap between practice and theory and aid the pulping man in his analysis of his local problems.

It is necessary to say a word here about nomenclature. The term "penetration" is often used to describe any movement of chemical into wood, whether the mechanism is a flow of solution into the wood voids or is a diffusion of solute ions into water already present in the wood. Actually, these two mechanisms for chemical movement into wood are entirely different and operate in response to quite different laws, so in order to avoid ambiguity, the following nomenclature

will be used. The term "penetration" will be restricted to the flow of liquor into wood under the influence of a hydrostatic pressure gradient. The liquor moves as such. The term "diffusion" will be used in its physico-chemical sense for describing the movement of ions or other solute through water under the influence of a concentration gradient.

The lack of precise terminology may be the source of several misconceptions which exist in this field. For example, it is quite widely believed that alkaline solutions are able to penetrate wood considerably faster than acidic ones, and that alkaline solutions can penetrate wood at approximately equal rates in the three structural directions—longitudinal, radial, and tangential. In the sense that the word "penetration" is used here, this is definitely not the case. In fact, alkaline solutions *penetrate* wood more slowly than acidic ones. What is meant is that alkaline solutions swell the cell walls of the wood, producing wider and more numerous diffusion paths across the fibers, and permitting a diffusion of solute at approximately equal rates in the three structural directions.

Diffusion is a very much slower process than penetration and is therefore unsuitable for the transport of chemical into large pieces of wood. Thus, in the chemigroundwood process where logs several feet long and many inches in diameter are to be cooked whole before grinding, a diffusion process is out of the question, and conditions must be chosen which are most suitable for rapid penetration. This raises the question as to just what factors are involved in penetration and diffusion, and to what extent these factors are under the control of the operator. The chief factors are:

Wood	Liquor
Capillary structure	Composition
Presence of moisture	Temperature
Presence of air	Pressure
	Viscosity
	Surface tension

## Capillary Structure of Wood

This is too well known to need much elaboration here. Briefly, however, it may be stated that penetration rate is exceedingly sensitive to the diameter of the individual capillaries, whereas diffusion rate is controlled more by the total cross-sectional area of all the capillaries, rather than their individual diameters. In

J. E. STONE, Research Assistant, The Institute of Paper Chemistry, Appleton, Wis., and C. FÖRDERREUTHER, Research Fellow, The Institute of Paper Chemistry, 1954-55; present address Feldmühle Papier- und Zellstoffwerke, A/G., Dusseldorf, Germany.

practice, this means that penetration takes place only through the larger pores such as the fiber lumen in series with the pit membrane pores, or through the vessels in the case of hardwoods. The cell walls themselves are ineffective for liquid movement as the individual capillaries are too small. This leads to the result that longitudinal penetration is always much more rapid than transverse penetration, the ratio of one to the other being perhaps 100:1 in the case of conifers to 10,000:1 or more in the case of hardwoods. By contrast, diffusion involves the capillaries of the cell wall as well as the larger pores, and the ratio of longitudinal to transverse diffusion is much less than is the case for penetration. It may be about 5:1 up to perhaps 30:1 for neutral or acidic solutions, and approach 1:1 in the strongly alkaline regions.

Because of the sensitivity of penetration rate to the diameter of the individual capillaries, changes in wood structure affect penetration very strongly. Thus, the plugging of pit membrane pores in the case of softwoods, or the formation of tylosis membranes across the vessels in the case of hardwoods, can have such a very considerable effect on penetration rate that the whole nature of wood as a porous medium can be said to have changed. In another paper (1) a discussion is given of the penetrability of wood, and it is shown to vary up to many thousandfold between the sapwood and heartwood of a given species or in going from one species to another. Diffusion rate is much less influenced by changes in wood structure, variations from sapwood to heartwood, or from one species to another being only of the order of several fold.

The difference in the penetrability of various woods can be demonstrated by taking chips or blocks of fairly low moisture content, pulling a vacuum, and flooding with water. An easily penetrated wood will sink in a few seconds, whereas a very difficultly penetrated wood will not sink even after many hours or days. In some cases the application of 2000 p.s.i. hydrostatic pressure will still not lead to complete penetration. In any practical problem, therefore, it is clearly necessary to know into which category a wood falls, for without such knowledge of the nature of the medium worked with, much time may be wasted attempting the virtually impossible.

Structural differences between softwoods (conifers) and hardwoods must be clearly distinguished. The natural channels for water movement in hardwoods are the vessels, and these very wide pores run longitudinally through the wood for a more or less indefinite distance. If these vessels are unblocked by tyloses, the wood can be almost any length in the fiber direction without seriously affecting the efficiency of penetration. On the other hand, there are no large pores such as the vessels running transversely through hardwoods, which means that transverse penetration rates are negligibly small. If the vessels are plugged with tyloses, penetration rate is exceedingly small in all directions. The fibers of hardwoods are interconnected by pit pairs, but because they are few in number, the fiber system in hardwoods is a poor medium for liquid movement.

Coniferous woods do not have vessels, the tracheids and their interconnecting pit system taking over the function of liquid transfer. This is less effective than the vascular system but more effective than the fibers of

hardwoods. Longitudinal penetration through softwoods is therefore much slower than through easily penetrated hardwoods, but transverse penetration on the other hand is just the reverse—i.e., more rapid through softwoods than hardwoods.

Diffusion takes place into water, not into wood. Solute particles can therefore diffuse through wood wherever water is present but cannot do so where water is absent, leading to the conclusion that wood should be water-saturated for diffusion to be most effective. Although diffusion is a slow process, it is an efficient one when the distances involved are small, for the wood substance itself—i.e., the cell wall material—is a comparatively open network so far as a diffusing ion is concerned. Thus, the effective capillary cross-sectional area of wood—that is, the ratio of the area available for diffusion to the area which would be available if no wood at all were present—may be as high as 50% for a low density wood in the longitudinal direction, and still as much as 10% in the transverse directions. In strongly alkaline solutions, the effective capillary cross-sectional area may approach 50% in all three directions (2). Barriers to penetration, such as tyloses, gummy deposits, and bordered pits closed by the torus, are considerably less effective in reducing diffusion rate because diffusion can take place through the cell wall itself and is not limited to those passages where the barriers occur. If a wood is very difficult to penetrate, therefore (beech or white oak may be cited as examples), it is probably better to use chips as nearly water saturated as possible, permitting diffusion to carry the chemical into the interior of the wood, rather than use drier chips and attempt to penetrate liquor under pressure.

#### *Presence of Air*

Air is detrimental to both penetration and diffusion and should be removed as far as possible. This may be done by evacuation, steaming, or replacement with a water-soluble gas. Steaming is the least suitable method if the wood is easily penetrated, for the wood increases in moisture content and there is consequently less room for the entering liquor. For a difficultly penetrated wood, on the other hand, where diffusion is to be relied upon and the wood should be as wet as possible, steaming is probably the most satisfactory method for removing air.

#### *Liquor Factors*

Penetration rate will increase with an increase in applied hydrostatic pressure, and also with a reduction in liquor viscosity such as occurs when the temperature rises. The nature of the electrolyte is of small importance except insofar as it affects pH. Acidic liquors (below pH 7.0) penetrate faster than slightly alkaline liquors for the same reason that pulp slurries drain faster when acidic than when alkaline. Liquors which are sufficiently alkaline to swell the cell walls beyond their water swollen dimensions, e.g., soda or kraft liquors, penetrate very slowly.

In contrast to penetration, diffusion is strongly influenced by liquor composition since, in this case, it is the mobility and concentration gradient of the ions which determine rate. Also, ionic mobility increases substantially with increasing temperature and there is probably at least a tenfold increase in rate for 100°C.

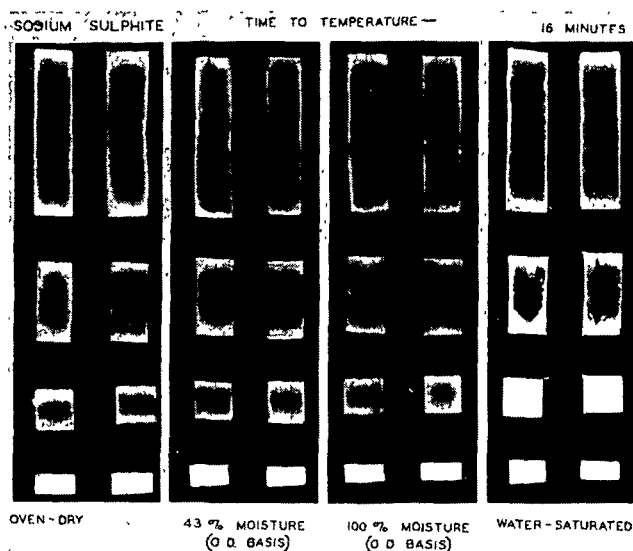


Fig. 1

rise, a larger temperature coefficient than can be expected for penetration.

#### Simultaneous Penetration and Diffusion

Wood as cooked is seldom either oven-dry or water-saturated. This means that in practice a combination of both penetration and diffusion will occur when chips of normal moisture content are treated with liquor at elevated temperatures and pressures. It then becomes unreasonable to expect that a simple law which applies to one mechanism will be valid when the system is subjected to both. Actually, the system is exceedingly complex, for the whole balance between penetration and diffusion is constantly shifting as the temperature and pressure rise, the moisture content of the wood increases, and the chemical concentration and temperature gradients within the wood are continually changing. It is this complexity which has forced the use of empirical approaches to problems in this field, and the work to be described below is no exception.

#### EXPERIMENTAL

It was desired to compare the relative rates of movement of sodium sulphite and ammonium sulphite into aspenwood. If only penetration were involved it might be predicted that there would be little difference in rate, for the viscosities of the two solutions are very similar. If only diffusion were involved, it might be predicted that ammonium sulphite would move into wood about one and a half times as fast as sodium sulphite, for this is the ratio of their diffusion coefficients at room temperature.

When there is a combination of penetration and diffusion, the relative rates of movement of the two sulphites should lie somewhere between 1:1 and 3:2, unless (1) the temperature coefficients of diffusion of the two salts are widely different, or (2) the mobilities of the various ionic species through a wood membrane are markedly different than through water.

The empirical method adopted to study this system, under what might approximate a real set of conditions, was to take advantage of the well-known fact that wood which is heated in the absence of cooking liquor turns brown. That is, it is "burnt." If, therefore, two similar pieces of wood are taken, and one is heated in

ammonium sulphite solution while the other is heated in sodium sulphite solution, and after heating, the wood is split open, the specimen with the smallest area of brown is the one penetrated (or diffused into) most efficiently.

The wood used was the sapwood of aspen (*Populus tremuloides*) with a specific gravity of 0.33. It contained few, if any, tyloses and could be considered to be an easily penetrated wood. Its penetration factor (1) was about  $2000 \times 10^{-10}$ .

The wood was cut into blocks with the following dimensions:  $\frac{1}{2}$  in. radial,  $\frac{1}{2}$  in. tangential, and  $\frac{1}{4}$ ,  $\frac{1}{2}$ , 1, and 2 in. longitudinal.

The moisture content of the wood was adjusted to four ranges: oven-dry, water-saturated (230% moisture, oven-dry basis), and two intermediate moisture contents—43 and 100% on the oven-dry basis.

The cooking temperature chosen was 170°C. and two different times-to-temperature adopted, viz., 16 and 90 min. The time at temperature was fixed at 2 hr. The vessels used for the cooks consisted of 200-ml. stainless steel bombs. These bombs were brought up to temperature at the desired rate in an electrical pre-heater and the temperature maintained at 170°C. in a thermostatically controlled oil bath. There was no relief of pressure during the cook and no agitation or circulation of the cooking liquor.

The cooking liquors consisted of 0.25 molar solutions of sodium and ammonium sulphites. Each of the two solutions contained 16 grams per liter of sulphur dioxide and had a pH of 8.1. No buffer was used for either solution since the buffers themselves have their own diffusion coefficients which would interfere with the comparison of the sodium and ammonium sulphites. Instead, a large liquor-to-wood ratio was used (about 25:1) which effectively prevented the liquor dropping in pH below 7.

Each cook was carried out in duplicate. One of the two wood specimens obtained under each set of conditions was split to show a tangential face; the other was split to show a radial face. Photographs were taken to show the extent of burning inside the wood and these photographs form the only record of the results which were obtained.

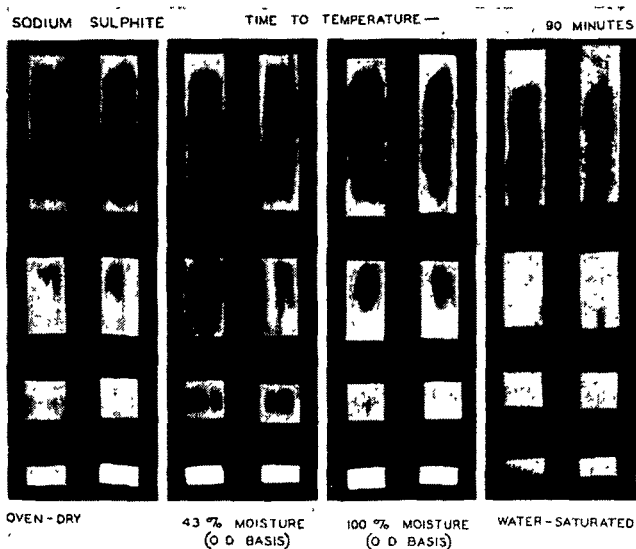


Fig. 2

## RESULTS AND DISCUSSION

The results are shown in Figs. 1 to 4. The specimen on the left of each pair shows the tangential face with the radially split specimen on the right. The interpretation given below is based on an examination of the original specimens which showed up the differences more clearly than the photographs. The photographs do, however, show the pattern of penetration and diffusion in a pictorial way which would be difficult to duplicate in any other manner.

Only the  $\frac{1}{4}$ -in. specimens were unburned under all conditions. The 2-in. specimens always showed some burning.

### Effect of Moisture Content

It appears that for both sodium and ammonium-base liquors and for both slow and fast rates of rise to temperature, water-saturated wood shows less burning than oven-dry wood or wood of intermediate moisture contents. Oven-dry wood appears to be more satisfactory than partially dry wood.

As would be expected, the specimens heated to 170°C. in 16 min. showed more burning than those heated to 170°C. in 90 min. The effect of varying the time to 170°C. was very marked with the water-saturated and oven-dry specimens. Thus, the water-saturated 1-in. long specimens were quite unburned using a 90-min. heat-up period, whereas with a 16-min. heat-up period, the unburned section extended only about  $\frac{1}{4}$  in. into the wood, leaving the central  $\frac{1}{2}$  in. badly burned.

Very little difference could be seen between the ammonium and the sodium-base liquors, regardless of wood moisture or time-to-temperature. If a difference did exist, it was most evident in the 16-min. time-to-temperature experiments, where the wood cooked with ammonium sulphite showed a little more white and a little less black area than did the wood from the sodium-base cooks.

If wood rays help the radial movement of cooking liquor, the width of the white border should be greater on the right-hand specimens than on the left. The photographs show some evidence of this, but it is obviously not a very important factor. In many cases, the width of the white border is sufficient to suggest that

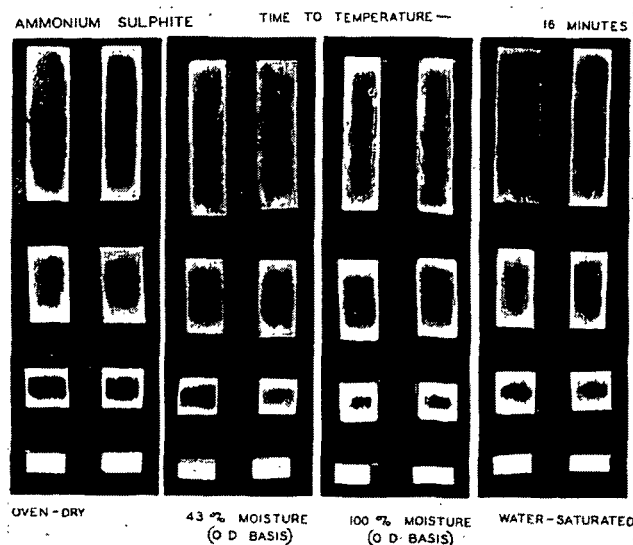


Fig. 3

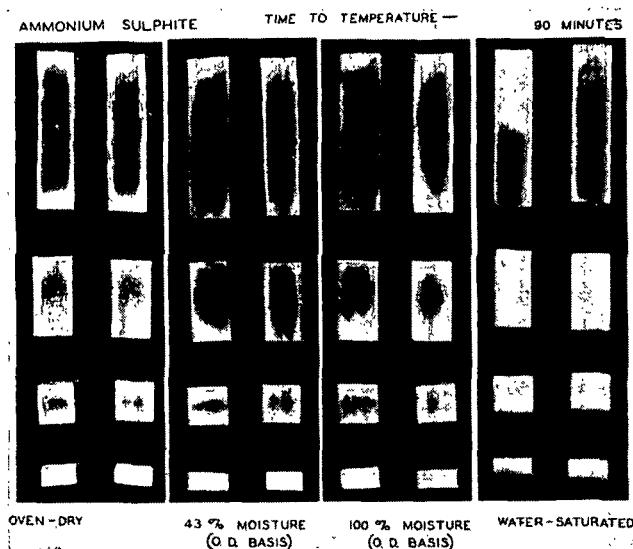


Fig. 4

with chips of normal thickness there would be little burning in the center even though very considerable burning occurred with the  $\frac{1}{2}$ -in. thick specimens used in the present experiments.

It should be mentioned that for comparison, a number of aspen sapwood specimens considerably larger than those used in the above experiments were evacuated in the air-dry condition (20% moisture, oven-dry basis) and flooded with cooking liquor under atmospheric pressure. These wood blocks could be heated to 170°C. as rapidly as desired—5 min., for example, in one experiment—with no trace of burning.

The advantage of choosing conditions which result in burning when studying penetration and diffusion is that a simple visual examination is all that is necessary to compare one set of conditions with another. Thus, two wood species could be compared, or sapwood with heartwood, or an alkaline liquor with a neutral liquor, or steaming with evacuation, or any of countless other comparisons which might be useful in anticipating the results of changes which are contemplated in a mill. If conditions are not chosen so that burning occurs, for example if small wood chips are used, there may still be differences in penetration and diffusion between two sets of conditions but these differences will now show up as chips with undercooked centers, and it is necessary to obtain data on screened yield, per cent screenings, and pulp quality in order to make a comparison. This, of course, is the ultimate test of a procedure, but much valuable preliminary information may be obtained by the "burning" method outlined.

### ADDITIONAL EXPERIMENTS

It will be noted from Figs. 2 and 4 that the 2-in. water-saturated specimens were less burnt at one end than the other. This, or similar effects, were found quite frequently in many miscellaneous experiments not recorded here, the following example being typical. Two 2-in. water-saturated blocks of wood were placed in a bomb so that one rested on the other and the fiber direction was vertical. Neutral sulphite liquor was added and the bomb heated to 170°C. in 90 min. and maintained there for 2 hr. There was no circulation or agitation of the liquor. When split open, the top half of each block was white and unburned whereas the

bottom half of each block was burned. At the junction of the two blocks, therefore, the liquor apparently moved down into the bottom piece but did not move up into the top piece. Horizontally oriented blocks showed no such effect. The tentative explanation for this effect was that the free liquor in the bomb heated up faster than the water in the wood and acquired a lower density. This produced circulation through the wood by means of the cold, dense water flowing out of the bottom of each block and the hot, less-dense liquor flowing down into the top. In a horizontally oriented specimen no such effect is possible. This hypothesis was tested on blocks of birch sapwood 4 in. long and 2 by 2 in. in the transverse directions. The wood was thoroughly water-saturated, preheated to 70°C. in a water-bath, and then immersed in a sodium sulphite solution also at 70°C. The liquor is now more dense than the water in the wood, being at the same temperature, and if the mechanism postulated actually operates, the liquor should flow up into the bottom of a vertically placed block. The temperature was too low to show burning, so the blocks were cut into 9 equal segments and analyzed. The results are shown in Fig. 5.

The vertical block is seen to have taken up most chemical, the horizontal least, and the 45° one an intermediate amount. The bottom end of the vertical and 45° blocks had more electrolyte in them than the top end, as predicted. The vertical block had actually almost reached equilibrium with the surrounding solution, whereas the horizontal block was still far from this condition.

The very uneven character of the salt distribution will be noticed. No explanation can be given for this. About 200 separate blocks were used for a corresponding number of diffusion experiments, using various electrolytes and temperatures, and an irregular distribution of chemical proved to be the rule rather than the exception. The conclusion was reached that, notwithstanding the very fine capillaries involved, a fairly ready interchange of liquor inside and outside the blocks must be possible in the case of wood containing tylose-free vessels. Thus, it was found that stirring the bath of solution in which the blocks were immersed introduced considerably more chemical into the wood in a given period than did no stirring.

A different type of experiment confirms the hypothesis that density differences between liquor and water in the wood can cause appreciable convection currents through wood. It was decided to increase the

Table I. Effect of Centrifuging on Penetration

Wood used	Air-dry		Water saturated		Maximum theoretical ash, %
	Not centrifuged <sup>a</sup>	Centrifuged <sup>b</sup>	Not centrifuged <sup>a</sup>	Centrifuged <sup>b</sup>	
Birch sapwood	0.26	3.93	1.17	5.21	6.20
Birch heartwood	0.02	2.90	0.91	5.00	6.20
Beech sapwood	0.69	3.78	0.86	4.28	6.55
Beech heartwood	0.42	2.78	0.29	0.38	5.75
Maple sapwood	1.45	4.68	1.56	5.48	7.10
Maple heartwood	0.93	3.40	1.12	1.32	7.70
Aspen sapwood	2.00	7.55	3.88	8.12	12.70
Aspen heartwood	0.57	3.51	0.81	1.20	13.10

<sup>a</sup> Blocks immersed in 1 M NaCl solution for 15 min. Grain direction vertical.

<sup>b</sup> Blocks held below surface of 1 M NaCl solution and centrifuged for 15 min. Grain direction vertical.

effect of density differences by using a centrifuge. Blocks of wood, 1/2 by 1/2 by 1 in. in the fiber direction were cut from the sapwood and the heartwood of poplar, birch, beech, and maple. One set was water-saturated and another set left air-dry. Thus, four species of wood, sapwood and heartwood, at two different moisture contents were obtained. One complete set of these blocks was immersed in a sodium chloride solution for 15 min., the blocks being vertical, while the other set was centrifuged for 15 min. in the same concentration of salt solution. At the end of 15 min. the centrifuged and noncentrifuged blocks were removed, wiped free of surplus solution, and ashed. The results are given in Table I.

It is seen that the centrifuged blocks took up considerably more salt than the blocks which had merely stood in a beaker of the solution. The increase in uptake due to centrifuging was from 5 to 10 times and in some cases the centrifuged blocks took up almost the maximum theoretically possible for complete equilibration.

The easily penetrated woods—that is, the sapwood of all four species and the heartwood of birch—took up more solution than the difficultly penetrated heartwoods of beech, poplar, and maple. This is to be expected. It is interesting, however, that the easily penetrated woods were apparently most effectively penetrated (by centrifuging) when in the water-saturated condition, whereas the difficultly penetrated woods were most effectively penetrated by centrifuging when in the air-dry state.

The value of these results lies possibly in their demonstration that a unidirectional driving force through wood is remarkably effective in increasing the rate of liquor uptake. The air, instead of being forced to retreat to the center of the wood and be compressed there, opposing further penetration, can be swept out of one end of the wood by the liquor moving in from the other end. Whether or not such a mechanism could be adapted for commercial use is problematical, but it may well be that this mechanism operates to a limited extent in any digester and cannot be entirely ignored as a possible factor in the already complicated field of penetration and diffusion into wood.

#### LITERATURE CITED

1. Stone, J. E., *Pulp Paper Mag. Can.* 57, No. 7: 139-145 (June, 1956).
2. Stone, J. E., unpublished work (to be published 1956).

RECEIVED July 2, 1956. Presented at the Ninth Alkaline Pulping Conference of the Technical Association of the Pulp and Paper Industry, Chattanooga, Tenn., Oct. 19-21, 1955.

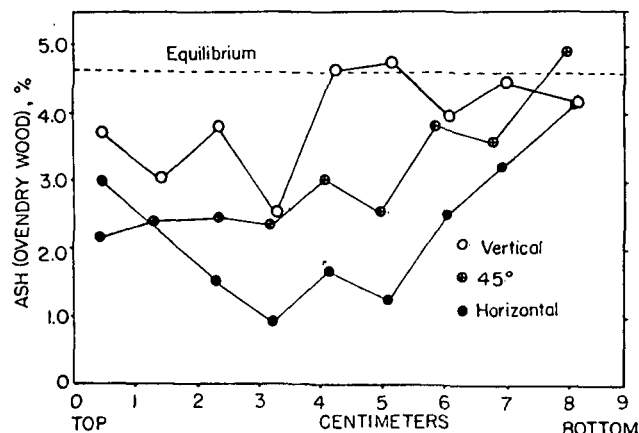


Fig. 5. Effect of wood orientation on liquor uptake by water saturated brick blocks

# PROJECT REPORT FORM

PROJECT NO. ✓ 1710  
COOPERATOR Institute  
REPORT NO. 5  
DATE January 28, 1957  
NOTE BOOK 1328  
PAGE 107 TO 111  
SIGNED J. E. Stone

cc: The Files  
Dr. May

## A STUDY OF THE LIGNIN REMOVED DURING A NEUTRAL SULPHITE COOK OF ASPEN

(Please see attached reprint).

# A Study of the Lignin Removed During a Neutral Sulphite Cook of Aspen

J. E. STONE

Cooking liquors withdrawn from the digester at various times during a neutral sulphite cook of aspen have been oxidized with alkaline nitrobenzene. The vanillin and syringaldehyde so formed were determined and their ratio found to change continually throughout the cook. The syringaldehyde yield was zero at the start of the cook, but increased until the final liquor yielded twice as much syringaldehyde as vanillin. When calculated as a percentage of the lignin in the liquor (the lignin being determined by ultraviolet spectrophotometry), the yield of vanillin was approximately constant throughout the cook whereas the syringaldehyde yield continually increased.

A RECENT study in these laboratories by Quick (5) was concerned with the carbohydrate material removed from aspen (*Populus tremuloides*) at the various stages of a neutral sulphite cook. This study made available a series of liquors taken from the digester at various times during the cook and it appeared of interest to make a brief study of these liquors from the point of view of the lignin present. Of chief concern was the question as to whether pronounced differences could be found between the lignin removed during the early stages of the cook and that removed later.

The question immediately arose of how to isolate the lignin. Quick (5) had found that the material precipitated from the liquors with acid represented only a fraction of the lignin as determined by ultraviolet absorption measurements or by subtracting the lignin in the pulp from the lignin in the wood. This is not surprising in view of the fact generally accepted today that some lignin is acid soluble. Rather than risk any separation scheme, therefore, which might fractionate the lignin and yield only one of the fractions, it was decided to use the whole cooking liquor. The characterization of the lignin in the various liquors would be made by carrying out an alkaline nitrobenzene oxidation followed by a determination of the vanillin and syringaldehyde so formed.

## EXPERIMENTAL

The cooking conditions used by Quick were similar to commercial practice. The maximum temperature was 171°C. and the yield after a total cooking time of 210 min. was 76.3%. The initial pH was 8.3 and the final pH, 7.05. Liquor was removed from the digester after 30, 60, 90, 120, 150, 180, and 210 min. from start-up, the temperatures at these times being 64, 100, 133, 164, 171, 171, and 170°C.

The oxidation of the liquors and determination of aldehydes was carried out by the micro-method of Stone and Blundell (6). The first four liquors—i.e., at 30, 60, 90, and 120 min., were concentrated to about

half volume. The others were used (after filtration) just as they came from the digester. One milliliter of liquor was made up to 2 normal in sodium hydroxide by adding 0.5 ml. of 6 N NaOH, 0.15 ml. of nitrobenzene was added, and the small bombs containing this mixture heated at 160°C. for 2 hr. with agitation. Aliquots of the liquors were then chromatographed and the vanillin and syringaldehyde determined spectrophotometrically at the appropriate wavelengths. For comparison, an oxidation was also carried out on the original wood (*Populus tremuloides*), ground to a 60–80 mesh meal.

## RESULTS

The results are shown in Table I and Fig. 1. The ratio of vanillin to syringaldehyde obtained from the various liquors changes throughout the course of the cook. Both aldehydes increase in amount but syringaldehyde, which could not be detected in the 30-min. liquor, increases much more rapidly than the vanillin, until it predominates by a factor of more than two. Basing the aldehyde yield on the amount of lignin in the liquor (the lignin being determined by ultraviolet absorption measurements), the yield of vanillin is seen to stay approximately constant whereas the yield of syringaldehyde steadily increases.

## DISCUSSION

The conclusion cannot be escaped that the lignin removed from the wood at the early stages of the cook is different in composition to that removed later. As the cook progresses the lignin found in the liquor approaches the composition of the total lignin in the wood so far as vanillin and syringaldehyde production is concerned. The reason for the differences between the liquors may be either that there is a different ratio of guaiacyl to syringyl groups actually present or that there is a different ratio of the oxidizable bonds joining these groups to the parent molecule.

The constancy of the vanillin yield when based upon the ultraviolet lignin is remarkable in view of the calculations involved and the very large differences in absolute amount of lignin present in the various liquors—forty-fold in going from the first to the last liquor. The constancy of vanillin yield even extends to an oxidation of the wood meal itself. It seems very unlikely that this situation is fortuitous and based upon compensating errors. The result suggests the existence of a comparatively uniform guaiacyl polymer which appears in the liquor in increasing amounts during the course of the cook, giving a certain absorption in the ultraviolet, and which is oxidizable to a definite yield of vanillin regardless of the amount present. It may be that the absorbance of ultraviolet light at 280 mμ, used in the

J. E. STONE, Research Assistant, The Institute of Paper Chemistry, Appleton, Wis.

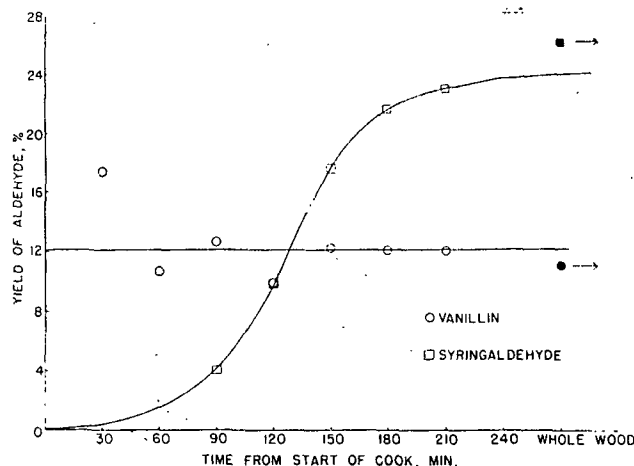


Fig. 1. Aldehyde yield from alkaline nitrobenzene oxidation of liquors from neutral sulphite cook of aspen

determination of "lignin," is due to the presence of the same groups and bonds which are susceptible to oxidation. A constant ratio of "lignin" to vanillin would therefore not be surprising because they would be two different ways of measuring the same thing. This hypothesis is greatly complicated by the amounts of syringaldehyde formed. The syringaldehyde yield, based on the ultraviolet lignin, increases from zero to 23.0% of the lignin in the course of the cook, suggesting that the polymer containing syringyl groups is less soluble than that containing guaiacyl groups, either because of structural differences or a different location in the cell wall, and therefore does not appear in the liquor until much later in the cook. Alternatively, the "syringyl lignin" does appear in the liquor at the start of the cook but contains no bonds capable of being oxidized to an aldehyde group. This will be discussed later. If it is the syringyl groups which are absent in the early stages of the cook, it appears to follow that the "syringyl lignin" does not contribute to the ultraviolet absorption. If it did, the yield of vanillin should decrease as more and more syringyl lignin appeared in solution. Furthermore, if the ultraviolet absorption of the lignin represents both guaiacyl and syringyl groups, then the sum of the two aldehyde yields rather than just one of them should be proportional to the lignin content. The data show quite clearly however that the sum of the two aldehydes bears no simple relationship to the ultraviolet lignin in the liquor. The question arises as to the validity of basing calculations on a lignin content obtained solely from ultraviolet measurements. There is naturally some doubt about

values obtained in this way but no better alternative presents itself. At four times during the cook, pulps were obtained which permitted a Klason lignin determination, and through a knowledge of the lignin content of the original wood and the liquor-to-wood ratio, it is possible to calculate the amount of lignin lost from the wood and entering the liquor at any stage of the cook. These values are given in Table I. They, too, depend on an ultraviolet measurement, however, for the acid-soluble lignin obtained during the Klason lignin analysis is determined spectrophotometrically and represents a considerable portion of the total lignin. This method of calculating lignin cannot therefore be considered superior to the ultraviolet measurement on the cooking liquor itself. In any case, the use of a "lignin by difference" value for the lignin in the cooking liquor does not make the lignin in the liquor proportional to the amount of vanillin and syringaldehyde obtained from the liquor. Although a number of hypotheses might be advanced to explain the nonequivalence of ultraviolet lignin (or any other lignin) and aldehyde yield, there is really insufficient evidence at present to warrant too much speculation.

Returning now to the question of the changing ratio of vanillin to syringaldehyde during the course of the cook, it was previously suggested that this could be due to either a change in the number of syringyl groups actually present or only to a change in the number of oxidizable bonds joining the syringyl groups to the parent molecule. A methoxyl determination should settle this question if the lignin could be freed from methylated carbohydrates. It seems likely that an absence of syringyl groups rather than oxidizable bonds is responsible for the low syringaldehyde yield from the early liquors. Kudzin and Nord (3) found that the native lignin from oak, birch, and maple—i.e., the more soluble lignin which might be expected to appear in a cooking liquor at an early stage of the cook—gave a much lower syringaldehyde yield (nil in the case of oak and birch) and had a lower methoxyl than the total lignin from the whole wood. The lower methoxyl suggests a reduction in the number of syringyl groups present. Lovell and Hibbert (4) obtained a native lignin from aspen and separated it into three fractions with methoxyl contents of 16.0, 17.7, and 18.4%, all of which are lower than the methoxyl content of Klason lignin obtained from the wood. This again suggests a lower syringyl content in the more soluble lignin fraction. Buchanan, Brauns, and Leaf (2) obtained a "crude" aspen native lignin with a methoxyl content of 17.6% which, when purified, had 19.5% methoxyl.

Table I. Yield of Vanillin and Syringaldehyde from Liquors Obtained During Neutral Sulphite Cook of Aspen

Time from start of cook, min.	Lignin in liquor, g./100 ml.		Vanillin, g./100 ml.	Syringaldehyde, g./100 ml.	Aldehyde yield, %				Ratio of vanillin/syringaldehyde
	By ultraviolet	By difference <sup>a</sup>			Based on ultraviolet lignin	Based on lignin by difference <sup>a</sup>	Vanillin	Syringaldehyde	
30	0.052	0.025	0.009	Not detectable	17.4	...	36.0	...	...
60	0.112	...	0.012	Not measurable	10.6	...	...	...	...
90	0.284	0.500	0.036	0.012	12.6	4.2	7.2	2.4	3:1
120	0.763	...	0.075	0.075	9.8	9.8	...	...	1:1
150	1.15	1.55	0.141	0.202	12.2	17.6	9.1	13.0	1:1.4
180	1.47	...	0.177	0.316	12.0	21.6	...	...	1:1.8
210	2.20	2.28	0.264	0.504	12.0	23.0	11.6	22.0	1:1.9
Wood-meal, 46.5 mg.	...	9.86 mg. <sup>b</sup>	1.08 mg.	2.56 mg.	Vanillin: 11.0 <sup>b</sup> Syringaldehyde 26.0				1:2.4

<sup>a</sup> Lignin in wood minus lignin in pulp, each lignin being the sum of Klason plus acid-soluble lignin. Quick (5).

<sup>b</sup> Based on sum of Klason plus acid-soluble lignin in wood.



This "purification" consists in part of precipitation from alcohol by water, and this procedure necessarily eliminates the water-soluble fraction which is therefore quite possibly lower in syringyl groups than the water-insoluble material since its removal raises the methoxyl content of the remainder. It is likely to be the water-soluble lignin which is removed during the early stages of a cook. Aaltio and Roschier (1) obtained a series of lignins from a butanol-water cook of aspen (*Populus tremula*) buffered around pH 6 to 7, and found that the methoxyl content steadily decreased with increasing lignin removal. This appears to be in direct conflict with the present findings. However, their first cook removed over 40% of the lignin with the

rest of the series of lignins being obtained during the removal of the remaining 60%. In the present work the lignin studied was that from zero to 40% removal.

#### LITERATURE CITED

1. Aaltio, E., and Roschier, R. H., *Paper and Timber (Finland)* 36, No. 4a: 157-174 (1954).
2. Buchanan, M. A., Brauns, F. E., and Leaf, R. L., *J. Am. Chem. Soc.* 71: 1297-1299 (1949).
3. Kudzin, S. F., and Nord, F. F., *J. Am. Chem. Soc.* 73: 690 (1951).
4. Lovell, E. L., and Hibbert, H., *J. Am. Chem. Soc.* 63: 2070-2073 (1941).
5. Quick, R. H., Doctor's Dissertation, Appleton, Wis., The Institute of Paper Chemistry, 1955. (To be published.)
6. Stone, J. E., and Blundell, M. J., *Anal. Chem.* 23: 771 (1951).

RECEIVED June 8, 1955.

# PROJECT REPORT FORM

cc: The Files  
Dr. May

PROJECT NO. ✓ 1710  
COOPERATOR Institute  
REPORT NO. 6  
DATE January 28, 1957  
NOTE BOOK 1328  
PAGE 119 TO 142  
SIGNED J. E. Stone / JES  
J. E. Stone

THE PENETRABILITY OF WOOD

(Please see attached reprint).

# The Penetrability of Wood

J. E. STONE

Research Assistant  
The Institute of Paper Chemistry

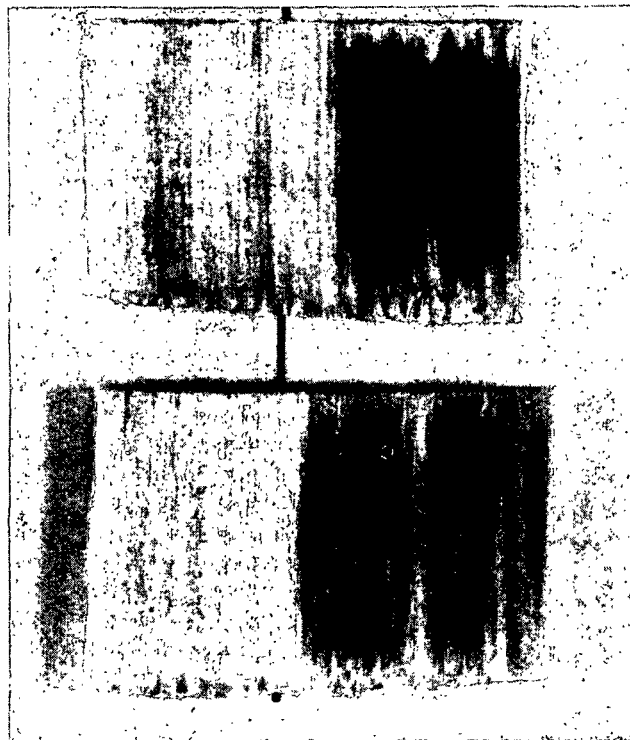
## ABSTRACT

Wood varies in its ease of penetration over a very wide range, depending on species and whether or not it is sapwood or heartwood. Obtaining adequate liquor movement into woods widely differing in permeability constitutes two separate problems of quite different orders of magnitude which may require different methods of attack for optimum results. It is only by knowing the actual permeability of the wood being studied that a penetration problem can be seen in proper perspective, or the results obtained related to the data of other workers in this field using some other species of wood. A simple method of measuring wood permeability is given, and it is suggested that a useful form for recording permeabilities is the fourth power of the radius of a single capillary which would give the same rate of flow as all the capillaries in one sq. cm. cross section of the wood. A number of pulpwoods have been so rated, and the penetration factors listed. A discussion is given of the tyloses which are largely responsible for poor penetration in many deciduous woods.

## INTRODUCTION

An adequate movement of cooking liquor into wood is an essential first step in the pulping process, and has deservedly received much attention from experimenters who are concerned with speeding up the cook and improving the uniformity of delignification throughout the chip. Cooking chemicals move into wood by two mechanisms — (1) diffusion of the dissolved chemical into water already in the wood under the influence of a concentration gradient, and (2) movement of the liquor itself into the wood voids under the influence of a hydrostatic pressure gradient. The term "penetration" will be used here to describe the second mechanism.

The rate of penetration of liquors into wood is controlled not only by the operating conditions used — e.g. the pressure applied, the temperature and viscosity of the liquor, etc., but also by the permeability of the wood itself, and it may not be an exaggeration to say that of all the factors involved in penetration rate, the internal structure of the wood — which controls its permeability — is the factor of chief importance. Examples of the effect of differences in wood permeability are shown in Figs. 1—3. In Fig. 1 are shown two chips of aspen (*P. tremuloides*) which have been cooked in a neutral sulphite liquor and then split open to show the pattern of penetration. Where the wood is white, the liquor has penetrated properly, whereas the brown areas show in-



SAPWOOD

HEARTWOOD

Fig. 1. Chips of aspen, part sapwood and part heartwood, cooked in neutral sulphite liquor. Chip thickness: Upper,  $\frac{1}{8}$ "; lower,  $\frac{1}{4}$ ".

adequate penetration and darkening ("burning") due to the action of wood acids at high temperature. These chips were sawn from a disk of an aspen log so that one-half of the chip was sapwood and the other half heartwood. The chips were  $\frac{3}{4}$  in. long in the fibre direction and of two different thicknesses, viz.,  $\frac{1}{8}$  and  $\frac{1}{4}$  in. The cooking conditions were as follows: The wood was air-dried (10 per cent moisture, oven-dry basis), evacuated for two hours using a good laboratory vacuum pump, neutral sulphite liquor flooded in, the flooded chips placed in a bomb with a considerable excess of liquor and heated to 170 deg. C. in 15 min. This temperature was maintained for 40 min. It is evident that these pretreatment and cooking conditions are quite adequate for penetrating aspen sapwood, but are inadequate for the heartwood and it can be easily demonstrated that considerably less favourable conditions are still perfectly adequate for penetrating the sapwood whereas much more drastic conditions are still not adequate for getting liquor into the heartwood.

The difference between aspen sapwood and heartwood

Paper presented at the Annual Meeting of the Technical Section, Canadian Pulp and Paper Association, held in Montreal, Que., January 25, 26, 27, 1956.

NOTE: Not to be reproduced without permission.

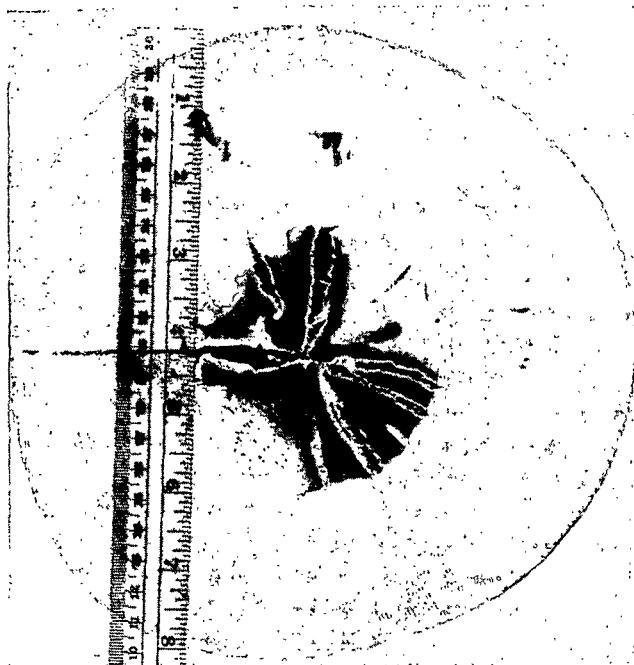


Fig. 2. Disk cut from aspen log cooked under chemigroundwood condition.

is shown in a different way in Fig. 2. This is a disk cut from an aspen log 2 ft. long, which had been evacuated for an hour, flooded with neutral sulphite liquor, 150 p.s.i. hydrostatic pressure applied for 30 min. to help force the liquor into the wood, and the log then cooked at 150 deg. C. for several hours. This operation is similar to the chemigroundwood process. There are several noteworthy features here. The first is that the heartwood is burned, whereas the sapwood is unburned. It will also be noted that one pie-shaped section of the heartwood is unburned, showing adequate penetration in this area. Just why the tree should develop a resistance to penetration in an unsymmetrical way like this is not clear. Another feature of note is that the heartwood shows radial cracks\* and the edges of these cracks are unburned, showing that penetration (or diffusion) occurred to a slight extent in the transverse direction. Evidently, however, transverse movement of chemical was very slow, for the unburnt region adjacent to the crack is only a few fibres thick, even though it had been exposed to liquor at 150 p.s.i. for 4 hours.

The pattern of liquor penetration into a beech log is shown in Fig. 3. The log (4 ft. long) was cooked in a neutral sulphite liquor under chemigroundwood conditions and a disk cut from the cooked log. The well-penetrated and well-cooked sapwood was cut away, leaving the heartwood with its concentric rings of burnt and unburnt wood as shown in the photograph. It is tempting to explain this behaviour of beech heartwood, a behaviour typical of this species, on the basis of periodic changes in growing conditions, but the "bridge" of unpenetrated wood crossing a ring of penetrated wood means that such explanations must be treated with caution.

The foregoing illustrations of the variability of penetration characteristics within a single log of a given species give visual qualitative proof of the well-known fact

\*These cracks formed during the early stages of cooking due to swelling of the dry sapwood when liquor penetrated it and nonswelling of the unpenetrated heartwood. The cracks widened and became distorted when the cooked disk dried before being photographed.

that the heartwood of many species is more difficult to penetrate than the sapwood. It is also well-known that penetrability varies between species, the case of the red and white oaks often being cited. Red oak is easy to penetrate, whereas white oak is exceedingly difficult. However, although the variation of penetrability is well-known, it does not seem to have received the attention it deserves, particularly in the various pulping studies which have been made in which penetration rate is one of the factors influencing the results. There are probably two reasons for this neglect: one is that in most cases a species of wood is chosen because of its availability, and its internal structure has to be accepted for what it is, easily or difficultly penetrated, so that the only real area for improving penetration is in the operating conditions of steaming, evacuation, etc. The second reason is that there is no method at present, so far as is known, for determining and expressing penetrabilities on a quantitative basis.

The purpose of the present paper is to meet the second of these two objections by suggesting a simple, rapid method for determining and expressing the penetrability of a wood on a reasonably quantitative basis. The value of this lies in the fact that in any experimental work in which penetration rate is a factor, the characteristics of the wood itself in this regard are of the utmost importance. Thus, the penetration of aspen sapwood and aspen heartwood are problems of two entirely different orders of magnitude and it is only by a knowledge of the limitations imposed by the wood itself that the problem can be seen in a proper perspective. If, for example, a series of experiments is carried out on some wood specimen designed to show the effect of evacuation, or pressure, or temperature, on the rate at which liquids will flow into it, the information so obtained is only useful if it is also known just how that particular piece of wood stands in relationship to other wood so far as its penetrability is concerned. Results obtained for aspen sapwood would be comparatively meaningless as far as the heartwood is concerned, for it is not a twofold or a threefold increase in rate that is required for the heartwood, but something possibly in the order of a hundredfold increase. In other words, it is not the *increase* in rate but the *absolute* rate that we are concerned with in pulping, and it is the characteristics of the wood itself which will



Fig. 3. Beech heartwood, showing concentric rings of "burnt" and "unburnt" wood.

largely determine what the maximum rate will be.

The problems involved in penetrating wood with cooking liquor show up in an exaggerated form in the chemigroundwood process. Diffusion is out of the question for chemical movement through such large pieces of wood, and penetration only need be considered. Also, in the case of deciduous woods, penetration in the transverse direction is negligible, liquor movement occurring only in the longitudinal direction. With easily penetrated wood, liquor will flow in to the centre of a log several feet long in just a few minutes, or even seconds, but with a very intractable wood, there is no known method by which the liquor can be made to penetrate an adequate distance in a reasonable time. Even pressures as high as 2000 p.s.i. are ineffective.

It was while carrying out a study of the penetration of liquor into logs, as in the chemigroundwood process, that a need was felt for being able to classify wood according to its ease or difficulty of penetration. A single log was used for each experiment and it was soon found that there was little or no correlation between changes in procedure and the amount of liquor taken up by the log. The reason was that the logs varied so much in penetrability that in some cases better penetration was obtained using poor conditions — e.g., low pressures — than when better conditions were used — e.g., high pressures. It therefore became necessary to classify the logs in terms of penetrability and use only logs of the same or similar penetration characteristics for each series of experiments.

## EXPERIMENTAL

### SINKAGE TIME

Two methods of classification were tried. The first involved the measurement of sinkage time, a procedure used by others (1—4) to determine the ease with which wood can be flooded with liquor. In this test, 1-in. cubes of oven-dry wood were evacuated at about 1 mm. mercury for 1 hour, flooded with deaerated water while under vacuum, and the time required for the specimen to sink noted after the vessel was opened to atmospheric pressure. The results of a few experiments are shown in Table I.

All the sapwood samples sank in a very short time and the heartwood of birch averaged only 16 minutes, so these woods are evidently quite easy to penetrate. The heartwood of aspen, however, took an average of 8 days to sink, and in a number of cases more than three weeks. Aspen heartwood may thus be considered to be perhaps several thousand times more difficult to penetrate than the sapwood. It should be noted that a dense wood needs to absorb less water than a light wood in order to sink. Thus, beech will sink when a gram of the wood has absorbed about one-half gram of water, whereas a gram of aspen must take up about two grams of water before it will sink.

### AIR-FLOW METHOD

There are several drawbacks to the sinkage-time method for determining penetrability. For one thing, it is difficult to ensure reproducible evacuation and flooding conditions. For another, it may take a considerable time to complete an experiment.

A better method would seem to be that based on the rate at which air will flow through the wood under certain specified conditions. This is a commonly used method for determining the permeability of porous media, and has been used for wood by Stamm (5). Stamm was concerned with finding the size distribution of the various capillaries within white pine and Western hemlock heartwood, and measured the flow rate of air of various relative humidities through wood membranes of different moisture contents. With slight modifications, a similar apparatus to Stamm's was used for the present work, and is shown in Fig. 4.

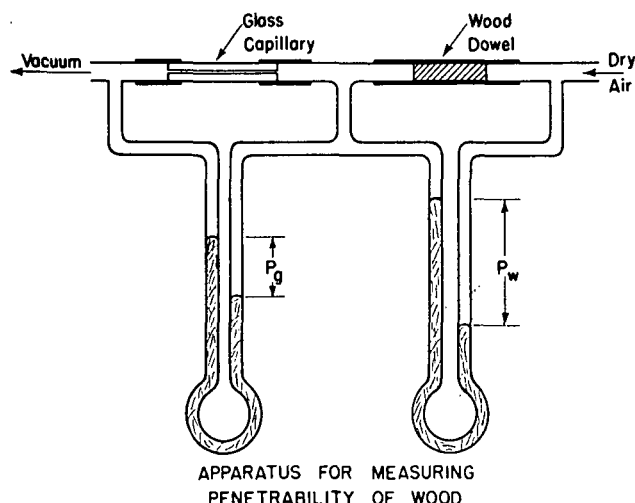


Fig. 4. Apparatus for measuring permeability of wood to air.

*Apparatus.* Essentially, the apparatus (Fig. 4) consists of two flowmeters in series, the restriction in one being a glass capillary of known dimensions and the restriction in the other being a dowel of the wood being tested. A word should be said about this wood dowel, for one of the features of penetration studies of wood is the difficulty of arranging for the membrane or block of wood to be leakproof around the edges. A dowel-cutting drill was used to obtain a dowel  $\frac{3}{8}$  in. in diameter and any length up to about 3 inches. The dowel could be cut in any of three structural directions of the wood with equal ease and could be obtained from whole logs with little more difficulty than from prepared cubes. To insert the dowel in the apparatus it was rubbed with stop-cock grease and pushed into tightly-fitting rubber lining. Leaks were never experienced with this arrangement and

TABLE I

### SINKAGE TIME FOR SEVERAL HARDWOODS

Species	Sp. Gr.	No. of Trees Sampled	Sinkage Time, min.					
			Sapwood			Heartwood		
			Min.	Max.	Av.	Min.	Max.	Av.
Aspen ( <i>P. tremuloides</i> ).....	0.33	35	3	9	5	1,800	42,000	12,000 (8 days)
Beech ( <i>F. grandifolia</i> ).....	0.5—0.6	35	<0.1	0.5	<0.1	1	5,000	700 (12 hours)
Maple (mixed).....	0.5—0.6	35	0.5	3	0.5	1	1,000	90
Birch ( <i>B. papyrifera</i> ).....	0.5—0.6	40	2	5	3	3	60	16

TABLE II

## VARIATION OF PENETRABILITY WITHIN A SINGLE LOG

Species	No. of Samples	Sapwood			Heartwood		
		Min.	Max.	Av.	Min.	Max.	Av.
Aspen ( <i>P. tremuloides</i> )...	40	1600	2200	1800	10	0.1	2.0
Birch ( <i>B. papyrifera</i> )....	56	370	2600	850	15	90	900
Beech ( <i>F. grandifolia</i> )...	21	300	2800	1400	12	0.16	1.4
Maple ( <i>Acer rubrum</i> )....	34	150	400	300	11	110	670

it is recommended to anyone studying the flow of liquids or gasses through wood under low pressures.

By application of the Poiseuille equation, the following relationship is obtained:

$$r_w^4 = r_g^4 / (N \times A) \times P_g / P_w \times l_w / l_g = \text{const.} \times P_g / P_w$$

where the subscripts w and g refer to wood and glass, respectively, and

$r$  = radius of capillary

$l$  = length of capillary

$P$  = pressure drop

$N$  = number of capillaries per unit cross-section of wood

$A$  = cross-sectional area of wood

Everything here is known except  $r_w$ , the average radius of the wood capillaries, and  $N$ , the number of capillaries per unit cross section.

To obtain a penetration factor from this equation, all the capillaries in 1 sq. cm. of wood are considered to be gathered together into a single capillary which gives the same rate of flow. Then  $N$  equals 1, and  $r_w$  is the radius of this hypothetical capillary. The penetration factor is the fourth power of this radius.

For any given glass capillary and length of wood dowel, the penetration factor  $= r_w^4 = \text{const.} \times P_g / P_w$ ; i.e., penetration factor is proportional to the pressure-drop ratio between the glass capillary and wood dowel. In practice, in order to correct for the change of volume due to the differences in pressure, the pressure-drop ratio  $P_g / P_w$  is measured at several total pressures and extrapolated back to zero total pressure. It is the value of  $P_g / P_w$  at zero pressure differential found by extrapolation in this way which is substituted in the above equation.

There are many other ways of determining the resistance to air flow of a wood section, a good one being a modification of the instrument used for determining the porosity or air resistance of paper (TAPPI Method T 460 m). Whatever the method, however, it is suggested

that a useful form in which to express the permeability of the wood is the one outlined, i.e., the fourth power of the radius of a single capillary which would permit the same rate of flow as one sq. cm. of wood.

## RESULTS

The results obtained with a number of different woods are given in Tables II, III, and IV, but it should be emphasized that the values given are nothing more than a guide and an illustration of the sort of values which might be expected using this method on various wood species.

The data recorded in Table II were obtained as follows: A disk was cut from a log and  $\frac{3}{8}$ -in. dowels drilled out at various locations in the sapwood and heartwood. Thus, in the case of birch, 56 dowels were cut from the sapwood and 15 from the heartwood. There was no obvious pattern in the penetration factors obtained, the distribution of high and low values being quite random. It might be expected that beech heartwood would show concentric circles of high and low permeabilities, but either insufficient samples were taken to show this or the particular tree chosen did not have this characteristic.

High penetration factors indicate an easily penetrated wood; low factors show the reverse. With the logs chosen, all the sapwoods, and the heartwood of birch and maple are seen to have high values, whereas the heartwoods of aspen and beech have values under  $1 \times 10^{-10}$ .

In Table III, which records the penetration factors for several trees of each of the above four species, the same pattern is evident. The heartwoods of aspen and beech have generally very low penetration factors, whereas the heartwoods of birch and maple, and all the sapwoods, have comparatively high factors.

In Table IV are the results from testing a number of different species, both conifers and hardwoods. In each case two samples were cut from the sapwood and two from the heartwood of each log tested. In most cases several trees of each species were tested and the average values recorded in the table.

TABLE III

## VARIATION OF PENETRABILITY WITHIN A SPECIES

Species	No. of Trees Sampled <sup>1</sup>	Sapwood			Heartwood		
		Min.	Max.	Av.	Min.	Max.	Av.
Aspen ( <i>P. tremuloides</i> ).....	20	800	3000	2000	0.2	10	1
Birch ( <i>B. papyrifera</i> ).....	11	550	3500	1300	100	700	440
Beech ( <i>F. grandifolia</i> ).....	10	500	3000	1000	0.1	5	0.5
Maple ( <i>A. rubrum</i> ).....	20	150	1000	400	10	300	120

<sup>1</sup>Two sapwood and one heartwood dowel cut from each tree.

TABLE IV

VARIATION OF PENETRABILITY  
BETWEEN SPECIES

Species	Penetration Factor $\times 10^{10}$	
	Sapwood	Heartwood
Black spruce ( <i>Picea mariana</i> ).....	—	2
Engelmann spruce ( <i>Picea engelmanni</i> ).....	5	3
Slash pine ( <i>Pinus caribaea</i> ).....	6000	10
White pine ( <i>Pinus monticola</i> ).....	100	10
Shortleaf pine ( <i>Pinus echinata</i> ).....	120	5
Longleaf pine ( <i>Pinus palustris</i> ).....	4000	2
Lodgepole pine ( <i>Pinus contorta</i> ).....	300	—
Douglas-fir ( <i>Pseudotsuga taxifolia</i> ).....	70	5
Elm ( <i>Ulmus americana</i> ).....	400	70
Box elder ( <i>Acer negundo</i> ).....	1300	400
Hickory ( <i>Caryax</i> ?).....	4000	400
Sycamore ( <i>Platanus occidentalis</i> ).....	4000	4000
Willow ( <i>Salix nigra</i> ).....	4000	—
Birch ( <i>Betula papyrifera</i> ).....	1300	450
Beech ( <i>F. grandifolia</i> ).....	1000	1/2
Sweetgum ( <i>Liquidambar styraciflua</i> ).....	1200	850
Ash ( <i>Fraxinus nigra</i> ).....	80	—
Maple ( <i>A. rubrum</i> ).....	400	120
Red oak ( <i>Q. falcata</i> ).....	4000	5
Scarlet oak ( <i>C. coccinea</i> ).....	1000	400
Post oak ( <i>Q. stellata</i> ).....	67	5
White oak ( <i>Q. alba</i> ).....	0.7	—
Cottonwood ( <i>P. deltooides</i> ).....	4000	500
Balm of Gilead ( <i>P. lacamahaca</i> ).....	800	300
Aspen ( <i>P. tremuloides</i> ).....	2500	1
Aspen (Finland) ( <i>P. tremula</i> ).....	5000	4
Triploid Aspen (Finland) ( <i>P. tremula</i> ).....	1000	2000

## DISCUSSION

Theoretically, a wood with a penetration factor of say  $100 \times 10^{-10}$  is ten times more difficult to penetrate than one whose value is  $1000 \times 10^{-10}$ . Since the measurements were made with air on oven-dry wood, such a quantitative relationship probably will not apply exactly to water flowing into swollen wood. Experience has shown, however, that the permeability of wood obtained by the air flow method gives a useful indication of the way in which wood can be expected to take up liquor in a typical pulping operation. For example, there is never any doubt that wood with a rating of  $1 \times 10^{-10}$  or less will be exceedingly difficult to penetrate with liquor, even under such favourable conditions as when dry wood is used, and is pre-evacuated in the digester before admitting the cooking liquor. Difficulty may, in fact, be experienced with any wood which rates below about  $50 \times 10^{-10}$ . Between  $50$  and  $500 \times 10^{-10}$  successful penetration is possible if appropriate operating conditions are chosen, whereas above  $500 \times 10^{-10}$  a minimum of difficulty should be experienced. In many cases a difficultly penetrated heartwood and an easily penetrated sapwood will be cooked together in the same digester. The heartwood chips may appear at the end of the cook as "floaters" with rather hard, uncooked centres, and it then has to be decided whether the percentage of heartwood is sufficient to warrant taking the extreme measures which may be necessary to secure adequate penetration of this fraction. The same problem is encountered in the chemigroundwood process where aspen logs with easily penetrated sapwoods and difficultly penetrated heartwoods are cooked before grinding.

By measuring the permeability of the heartwood it becomes clear that this part of the log is so impenetrable that there is little chance of forcing liquor into it. As yet there is no solution to the problem, but the measurement of the heartwood permeability has, at least, brought an awareness of the magnitude of the task, and a realization that a solution to the problem, if one exists, lies in the direction of changing the permeability of the wood and not in the adoption of extreme operating conditions such as a higher vacuum for a longer time followed by higher hydrostatic pressures.

The measurement of permeability will be useful not only in studying woods currently being pulped, but also in evaluating new species such as tropical hardwoods for their resistance to penetration. In addition, when new varieties of species are developed for the paper industry through the tree-breeding programs now being carried out by geneticists in various parts of the world, it may be as well to study the permeability of the wood as one of the characteristics which are important for a good pulpwood.

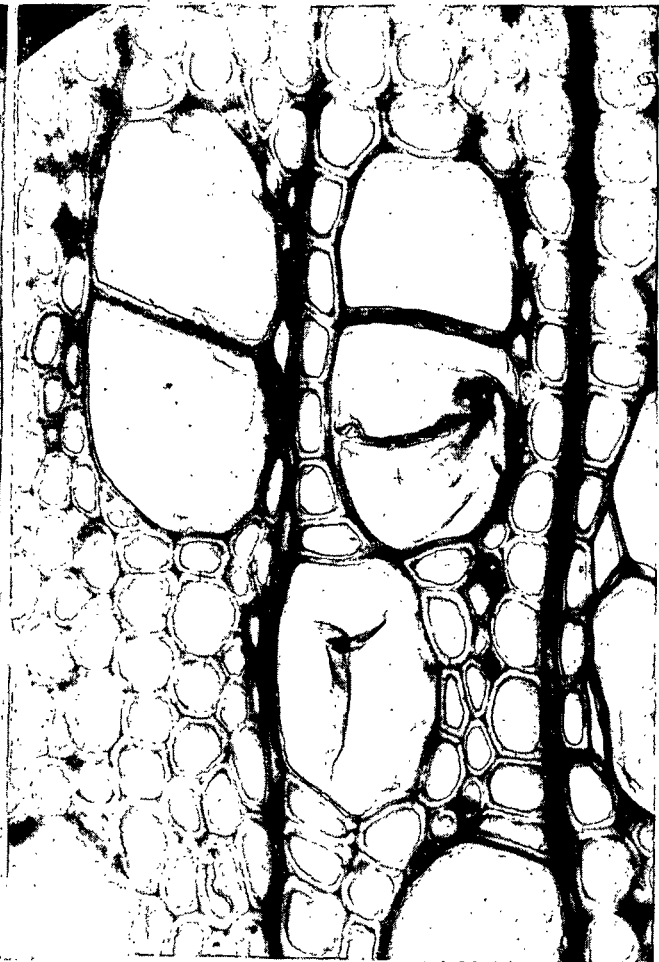
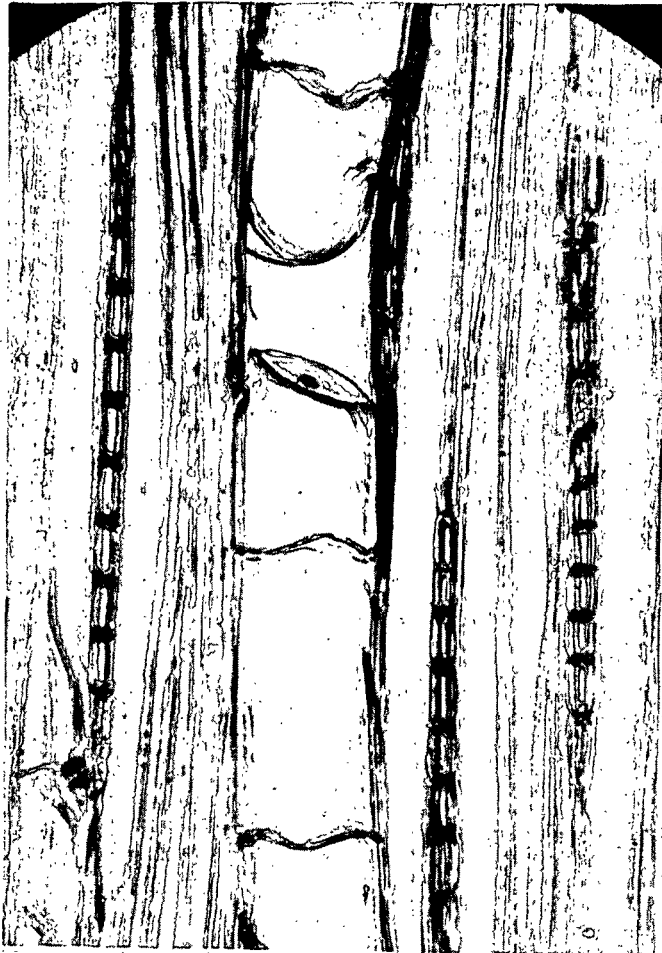
**Reasons for poor penetrability:** One of the major causes of poor penetration in deciduous woods is the occurrence of tyloses in the vessels. Tyloses are bladder-like growths in the vessel cavities caused by adjacent parenchyma cells growing through the semibordered pit membranes and enlarging to fill or partly fill the vessel. Since, in the case of hardwoods, the vessels are the natural channels for water movement, the blockage of these passages by tyloses causes a very marked decrease in the rate at which liquids can be forced through the wood.

In Fig. 5 is shown a section cut from aspen at the juncture of sapwood and heartwood, and it can be seen that the change from one to the other is very abrupt. The sapwood vessels appear to be completely open, whereas the heartwood vessels contain a profusion of tylosic membranes. The effect on penetration can be seen from Fig. 1, which is a wood chip cut from the same position in the log. The penetration factor of the sapwood was about  $2000 \times 10^{-10}$ , whereas for the heartwood it was  $1.4 \times 10^{-10}$ .

In Figs. 6 and 7 the tyloses of aspen are shown at greater magnification, while in Fig. 8, the tylosic forma-



Fig. 5. Juncture between sapwood and heartwood in aspen, showing tyloses in latter and absence of tyloses in former.



(Top Left)

Fig. 6. Tyloses in vessel of aspen heartwood.

(Top Right)

Fig. 7. Cross-section showing tylosic membranes in vessels of aspen heartwood.



(Bottom Left)

Fig. 8. Tyloses in vessels of beech heartwood.



(Bottom Right)

Fig. 9. Cluster of tyloses in vessel of white oak.



tion of beech heartwood is seen. In Fig. 9 the tyloses of white oak are seen to have entered the vessel from all sides, leaving a small opening in the centre, and it is clear that such a wood will vary in its ease of penetration according to the size of the opening which remains within the cluster of tyloses.

According to Isenberg (6), tyloses are composed of typical cell wall material — i.e., lignin and carbohydrate, varying somewhat in percentage of cellulose according to species. It would seem, therefore, that there is little hope of finding a selective solvent for the tyloses, and cooking liquor itself is probably as good a reagent as any.

A solution to the problem of very impermeable wood, which in the case of angiosperms is the problem of breaking down tyloses, is not easy to find. The only true solution to the problem it would seem, admittedly a long-range solution, is to develop trees in which tyloses are absent or few in number. In this connection it is interesting that a sample of a triploid aspen found growing in Finland was recently tested and proved to have a heartwood quite free of tyloses and as easily penetrated as the sapwood (see Table IV). The fact that the tree was 14-in. in diameter when 15 years old was another feature not unattractive to the paper industry.

#### ACKNOWLEDGMENT

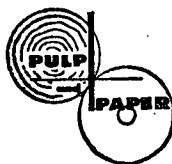
The author wishes to thank the Great Northern Paper Company, Millinocket, Maine, for supplying some of the wood used in these studies; for permission to use the specimen of beech shown in Fig. 3; and for allowing a discussion of certain problems of the chemigroundwood process which were investigated under a co-operative research project.

Grateful thanks are also due to Mrs. Janice Hein for carrying out much of the experimental work reported herein.

#### REFERENCES

1. SCARTH, G. W. *Can J. Research* 3:107-114 (1930).
2. RICHARDSON, R., and MAASS, O. Forest Products Labs. *Can. Pulp Paper Lab. Quart. Rev.*, 6:31-42 (1931).
3. SAUNDERSON, H. H., and MAASS, O. *Can J. Research*, 10: 24-35 (1934).
4. LUSBY, G. R., and MAASS, O. *Can. J. Research*, 10: 180-189 (1934).
5. STAMM, A. J., *Physics*, 6:334-342 (Oct., 1935).
6. ISENBERG, I. H., *J. Forestry*, 31:961-967 (1933).

Reprinted from



MAGAZINE OF CANADA.

June, 1956.

# PROJECT REPORT FORM

cc: The Files

Dr. May

PROJECT NO. 1710  
COOPERATOR Institute  
REPORT NO. 7  
DATE January 28, 1957  
NOTE BOOK  
PAGE  
SIGNED J. E. Stone / JA  
J. E. Stone

## STUDIES OF PENETRATION AND DIFFUSION INTO WOOD

(Please see attached reprint.)

# Studies of Penetration and Diffusion into Wood

J. E. STONE and CARL FÖRDERREUTHER

The rates at which sodium and ammonium sulphites move into aspen sapwood have been compared under conditions approximating commercial practice. The comparison was based on the relative amounts of "burning" which took place with each of the two salts when the wood was cooked for 2 hr. at 170°C. Little, if any, difference between sodium and ammonium sulphite—regardless of chip length, wood moisture content, or time-to-temperature—could be distinguished. With a given salt and varying wood moisture content, "burning" increased in the order water-saturated, oven-dry, intermediate moisture content. The amount of "burning" increased with a decrease in heat-up time, as expected. Additional experiments showed that wood blocks which had the fibers oriented vertically took up more chemical in a given time when immersed in liquor than did blocks where the fibers lay horizontally. The centrifuging of blocks of several different species immersed in a salt solution showed a considerable increase in salt uptake over similar blocks immersed but not centrifuged. It is suggested that density differences between ambient liquor and water in the wood can cause a circulation through the wood when the vessels are vertical.

A GREAT deal of work has been carried out on the penetration and diffusion of various liquors into wood, and while much has been learned through these experiments, there is ample evidence that considerable confusion still exists with regard to the mechanisms involved. Moreover, in a practical situation in a mill, where some particular species of wood of a certain moisture content is to be pulped by one of the recognized processes using a set of operating conditions more or less controlled by the limitations of existing equipment, it remains true that it is still often necessary to "try it and see." So many factors are involved that this is inevitable, but it is hoped that the following discussion will go a short way toward bridging the gap between practice and theory and aid the pulping man in his analysis of his local problems.

It is necessary to say a word here about nomenclature. The term "penetration" is often used to describe any movement of chemical into wood, whether the mechanism is a flow of solution into the wood voids or is a diffusion of solute ions into water already present in the wood. Actually, these two mechanisms for chemical movement into wood are entirely different and operate in response to quite different laws, so in order to avoid ambiguity, the following nomenclature

will be used. The term "penetration" will be restricted to the flow of liquor into wood under the influence of a hydrostatic pressure gradient. The liquor moves as such. The term "diffusion" will be used in its physico-chemical sense for describing the movement of ions or other solute through water under the influence of a concentration gradient.

The lack of precise terminology may be the source of several misconceptions which exist in this field. For example, it is quite widely believed that alkaline solutions are able to penetrate wood considerably faster than acidic ones, and that alkaline solutions can penetrate wood at approximately equal rates in the three structural directions—longitudinal, radial, and tangential. In the sense that the word "penetration" is used here, this is definitely not the case. In fact, alkaline solutions *penetrate* wood more slowly than acidic ones. What is meant is that alkaline solutions swell the cell walls of the wood, producing wider and more numerous diffusion paths across the fibers, and permitting a diffusion of solute at approximately equal rates in the three structural directions.

Diffusion is a very much slower process than penetration and is therefore unsuitable for the transport of chemical into large pieces of wood. Thus, in the chemigroundwood process where logs several feet long and many inches in diameter are to be cooked whole before grinding, a diffusion process is out of the question, and conditions must be chosen which are most suitable for rapid penetration. This raises the question as to just what factors are involved in penetration and diffusion, and to what extent these factors are under the control of the operator. The chief factors are:

Wood	Liquor
Capillary structure	Composition
Presence of moisture	Temperature
Presence of air	Pressure
	Viscosity
	Surface tension

## Capillary Structure of Wood

This is too well known to need much elaboration here. Briefly, however, it may be stated that penetration rate is exceedingly sensitive to the diameter of the individual capillaries, whereas diffusion rate is controlled more by the total cross-sectional area of all the capillaries, rather than their individual diameters. In

J. E. STONE, Research Assistant, The Institute of Paper Chemistry, Appleton, Wis., and C. FÖRDERREUTHER, Research Fellow, The Institute of Paper Chemistry, 1954-55; present address Feldmühle Papier- und Zellstoffwerke, A/G., Düsseldorf, Germany.

practice, this means that penetration takes place only through the larger pores such as the fiber lumen in series with the pit membrane pores, or through the vessels in the case of hardwoods. The cell walls themselves are ineffective for liquid movement as the individual capillaries are too small. This leads to the result that longitudinal penetration is always much more rapid than transverse penetration, the ratio of one to the other being perhaps 100:1 in the case of conifers to 10,000:1 or more in the case of hardwoods. By contrast, diffusion involves the capillaries of the cell wall as well as the larger pores, and the ratio of longitudinal to transverse diffusion is much less than is the case for penetration. It may be about 5:1 up to perhaps 30:1 for neutral or acidic solutions, and approach 1:1 in the strongly alkaline regions.

Because of the sensitivity of penetration rate to the diameter of the individual capillaries, changes in wood structure affect penetration very strongly. Thus, the plugging of pit membrane pores in the case of softwoods, or the formation of tylosis membranes across the vessels in the case of hardwoods, can have such a very considerable effect on penetration rate that the whole nature of wood as a porous medium can be said to have changed. In another paper (1) a discussion is given of the penetrability of wood, and it is shown to vary up to many thousandfold between the sapwood and heartwood of a given species or in going from one species to another. Diffusion rate is much less influenced by changes in wood structure, variations from sapwood to heartwood, or from one species to another being only of the order of several fold.

The difference in the penetrability of various woods can be demonstrated by taking chips or blocks of fairly low moisture content, pulling a vacuum, and flooding with water. An easily penetrated wood will sink in a few seconds, whereas a very difficultly penetrated wood will not sink even after many hours or days. In some cases the application of 2000 p.s.i. hydrostatic pressure will still not lead to complete penetration. In any practical problem, therefore, it is clearly necessary to know into which category a wood falls, for without such knowledge of the nature of the medium worked with, much time may be wasted attempting the virtually impossible.

Structural differences between softwoods (conifers) and hardwoods must be clearly distinguished. The natural channels for water movement in hardwoods are the vessels, and these very wide pores run longitudinally through the wood for a more or less indefinite distance. If these vessels are unblocked by tyloses, the wood can be almost any length in the fiber direction without seriously affecting the efficiency of penetration. On the other hand, there are no large pores such as the vessels running transversely through hardwoods, which means that transverse penetration rates are negligibly small. If the vessels are plugged with tyloses, penetration rate is exceedingly small in all directions. The fibers of hardwoods are interconnected by pit pairs, but because they are few in number, the fiber system in hardwoods is a poor medium for liquid movement.

Coniferous woods do not have vessels, the tracheids and their interconnecting pit system taking over the function of liquid transfer. This is less effective than the vascular system but more effective than the fibers of

hardwoods. Longitudinal penetration through softwoods is therefore much slower than through easily penetrated hardwoods, but transverse penetration on the other hand is just the reverse—i.e., more rapid through softwoods than hardwoods.

Diffusion takes place into water, not into wood. Solute particles can therefore diffuse through wood wherever water is present but cannot do so where water is absent, leading to the conclusion that wood should be water-saturated for diffusion to be most effective. Although diffusion is a slow process, it is an efficient one when the distances involved are small, for the wood substance itself—i.e., the cell wall material—is a comparatively open network so far as a diffusing ion is concerned. Thus, the effective capillary cross-sectional area of wood—that is, the ratio of the area available for diffusion to the area which would be available if no wood at all were present—may be as high as 50% for a low density wood in the longitudinal direction, and still as much as 10% in the transverse directions. In strongly alkaline solutions, the effective capillary cross-sectional area may approach 50% in all three directions (2). Barriers to penetration, such as tyloses, gummy deposits, and bordered pits closed by the torus, are considerably less effective in reducing diffusion rate because diffusion can take place through the cell wall itself and is not limited to those passages where the barriers occur. If a wood is very difficult to penetrate, therefore (beech or white oak may be cited as examples), it is probably better to use chips as nearly water saturated as possible, permitting diffusion to carry the chemical into the interior of the wood, rather than use drier chips and attempt to penetrate liquor under pressure.

#### *Presence of Air*

Air is detrimental to both penetration and diffusion and should be removed as far as possible. This may be done by evacuation, steaming, or replacement with a water-soluble gas. Steaming is the least suitable method if the wood is easily penetrated, for the wood increases in moisture content and there is consequently less room for the entering liquor. For a difficultly penetrated wood, on the other hand, where diffusion is to be relied upon and the wood should be as wet as possible, steaming is probably the most satisfactory method for removing air.

#### *Liquor Factors*

Penetration rate will increase with an increase in applied hydrostatic pressure, and also with a reduction in liquor viscosity such as occurs when the temperature rises. The nature of the electrolyte is of small importance except insofar as it affects pH. Acidic liquors (below pH 7.0) penetrate faster than slightly alkaline liquors for the same reason that pulp slurries drain faster when acidic than when alkaline. Liquors which are sufficiently alkaline to swell the cell walls beyond their water swollen dimensions, e.g., soda or kraft liquors, penetrate very slowly.

In contrast to penetration, diffusion is strongly influenced by liquor composition since, in this case, it is the mobility and concentration gradient of the ions which determine rate. Also, ionic mobility increases substantially with increasing temperature and there is probably at least a tenfold increase in rate for 100°C.

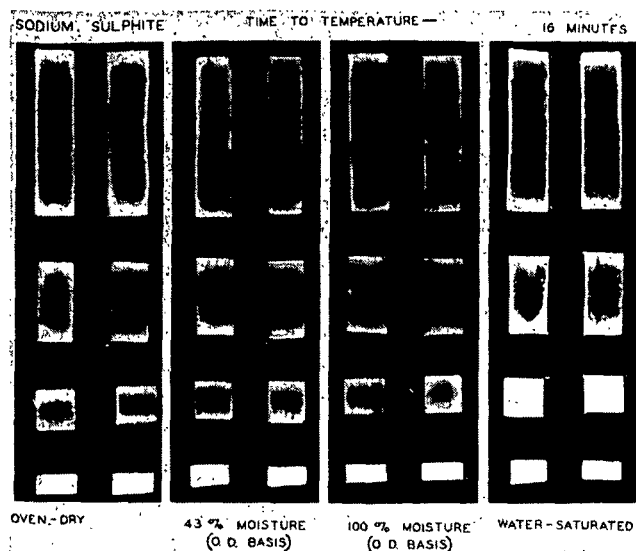


Fig. 1

rise, a larger temperature coefficient than can be expected for penetration.

#### Simultaneous Penetration and Diffusion

Wood as cooked is seldom either oven-dry or water-saturated. This means that in practice a combination of both penetration and diffusion will occur when chips of normal moisture content are treated with liquor at elevated temperatures and pressures. It then becomes unreasonable to expect that a simple law which applies to one mechanism will be valid when the system is subjected to both. Actually, the system is exceedingly complex, for the whole balance between penetration and diffusion is constantly shifting as the temperature and pressure rise, the moisture content of the wood increases, and the chemical concentration and temperature gradients within the wood are continually changing. It is this complexity which has forced the use of empirical approaches to problems in this field, and the work to be described below is no exception.

#### EXPERIMENTAL

It was desired to compare the relative rates of movement of sodium sulphite and ammonium sulphite into aspenwood. If only penetration were involved it might be predicted that there would be little difference in rate, for the viscosities of the two solutions are very similar. If only diffusion were involved, it might be predicted that ammonium sulphite would move into wood about one and a half times as fast as sodium sulphite, for this is the ratio of their diffusion coefficients at room temperature.

When there is a combination of penetration and diffusion, the relative rates of movement of the two sulphites should lie somewhere between 1:1 and 3:2, unless (1) the temperature coefficients of diffusion of the two salts are widely different, or (2) the mobilities of the various ionic species through a wood membrane are markedly different than through water.

The empirical method adopted to study this system, under what might approximate a real set of conditions, was to take advantage of the well-known fact that wood which is heated in the absence of cooking liquor turns brown. That is, it is "burnt." If, therefore, two similar pieces of wood are taken, and one is heated in

ammonium sulphite solution while the other is heated in sodium sulphite solution, and after heating, the wood is split open, the specimen with the smallest area of brown is the one penetrated (or diffused into) most efficiently.

The wood used was the sapwood of aspen (*Populus tremuloides*) with a specific gravity of 0.33. It contained few, if any, tyloses and could be considered to be an easily penetrated wood. Its penetration factor (1) was about  $2000 \times 10^{-10}$ .

The wood was cut into blocks with the following dimensions:  $\frac{1}{2}$  in. radial,  $\frac{1}{2}$  in. tangential, and  $\frac{1}{4}$ ,  $\frac{1}{2}$ , 1, and 2 in. longitudinal.

The moisture content of the wood was adjusted to four ranges: oven-dry, water-saturated (230% moisture, oven-dry basis), and two intermediate moisture contents—43 and 100% on the oven-dry basis.

The cooking temperature chosen was 170°C. and two different times-to-temperature adopted, viz., 16 and 90 min. The time at temperature was fixed at 2 hr. The vessels used for the cooks consisted of 200-ml. stainless steel bombs. These bombs were brought up to temperature at the desired rate in an electrical pre-heater and the temperature maintained at 170°C. in a thermostatically controlled oil bath. There was no relief of pressure during the cook and no agitation or circulation of the cooking liquor.

The cooking liquors consisted of 0.25 molar solutions of sodium and ammonium sulphites. Each of the two solutions contained 16 grams per liter of sulphur dioxide and had a pH of 8.1. No buffer was used for either solution since the buffers themselves have their own diffusion coefficients which would interfere with the comparison of the sodium and ammonium sulphites. Instead, a large liquor-to-wood ratio was used (about 25:1) which effectively prevented the liquor dropping in pH below 7.

Each cook was carried out in duplicate. One of the two wood specimens obtained under each set of conditions was split to show a tangential face; the other was split to show a radial face. Photographs were taken to show the extent of burning inside the wood and these photographs form the only record of the results which were obtained.

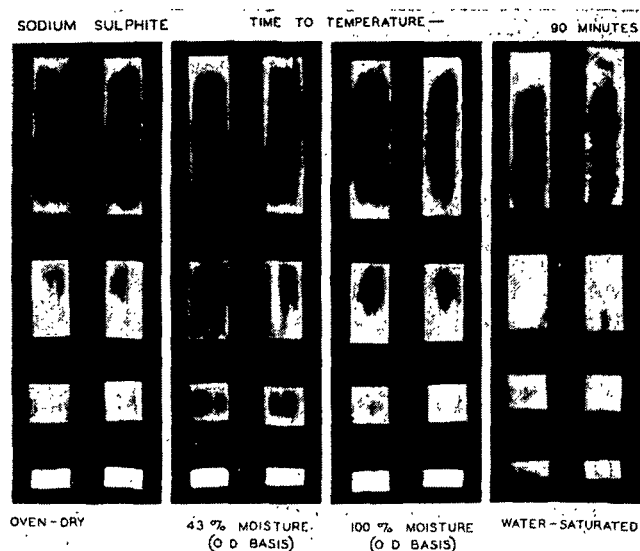


Fig. 2

## RESULTS AND DISCUSSION

The results are shown in Figs. 1 to 4. The specimen on the left of each pair shows the tangential face with the radially split specimen on the right. The interpretation given below is based on an examination of the original specimens which showed up the differences more clearly than the photographs. The photographs do, however, show the pattern of penetration and diffusion in a pictorial way which would be difficult to duplicate in any other manner.

Only the  $\frac{1}{4}$ -in. specimens were unburned under all conditions. The 2-in. specimens always showed some burning.

### Effect of Moisture Content

It appears that for both sodium and ammonium-base liquors and for both slow and fast rates of rise to temperature, water-saturated wood shows less burning than oven-dry wood or wood of intermediate moisture contents. Oven-dry wood appears to be more satisfactory than partially dry wood.

As would be expected, the specimens heated to 170°C. in 16 min. showed more burning than those heated to 170°C. in 90 min. The effect of varying the time to 170°C. was very marked with the water-saturated and oven-dry specimens. Thus, the water-saturated 1-in. long specimens were quite unburned using a 90-min. heat-up period, whereas with a 16-min. heat-up period, the unburned section extended only about  $\frac{1}{4}$  in. into the wood, leaving the central  $\frac{1}{2}$  in. badly burned.

Very little difference could be seen between the ammonium and the sodium-base liquors, regardless of wood moisture or time-to-temperature. If a difference did exist, it was most evident in the 16-min. time-to-temperature experiments, where the wood cooked with ammonium sulphite showed a little more white and a little less black area than did the wood from the sodium-base cooks.

If wood rays help the radial movement of cooking liquor, the width of the white border should be greater on the right-hand specimens than on the left. The photographs show some evidence of this, but it is obviously not a very important factor. In many cases, the width of the white border is sufficient to suggest that

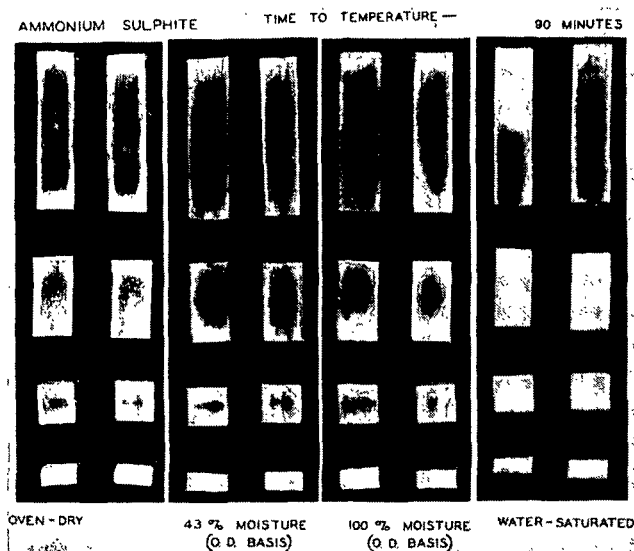


Fig. 4

with chips of normal thickness there would be little burning in the center even though very considerable burning occurred with the  $\frac{1}{2}$ -in. thick specimens used in the present experiments.

It should be mentioned that for comparison, a number of aspen sapwood specimens considerably larger than those used in the above experiments were evacuated in the air-dry condition (20% moisture, oven-dry basis) and flooded with cooking liquor under atmospheric pressure. These wood blocks could be heated to 170°C. as rapidly as desired—5 min., for example, in one experiment—with no trace of burning.

The advantage of choosing conditions which result in burning when studying penetration and diffusion is that a simple visual examination is all that is necessary to compare one set of conditions with another. Thus, two wood species could be compared, or sapwood with heartwood, or an alkaline liquor with a neutral liquor, or steaming with evacuation, or any of countless other comparisons which might be useful in anticipating the results of changes which are contemplated in a mill. If conditions are not chosen so that burning occurs, for example if small wood chips are used, there may still be differences in penetration and diffusion between two sets of conditions but these differences will now show up as chips with undercooked centers, and it is necessary to obtain data on screened yield, per cent screenings, and pulp quality in order to make a comparison. This, of course, is the ultimate test of a procedure, but much valuable preliminary information may be obtained by the "burning" method outlined.

### ADDITIONAL EXPERIMENTS

It will be noted from Figs. 2 and 4 that the 2-in. water-saturated specimens were less burnt at one end than the other. This, or similar effects, were found quite frequently in many miscellaneous experiments not recorded here, the following example being typical. Two 2-in. water-saturated blocks of wood were placed in a bomb so that one rested on the other and the fiber direction was vertical. Neutral sulphite liquor was added and the bomb heated to 170°C. in 90 min. and maintained there for 2 hr. There was no circulation or agitation of the liquor. When split open, the top half of each block was white and unburned whereas the

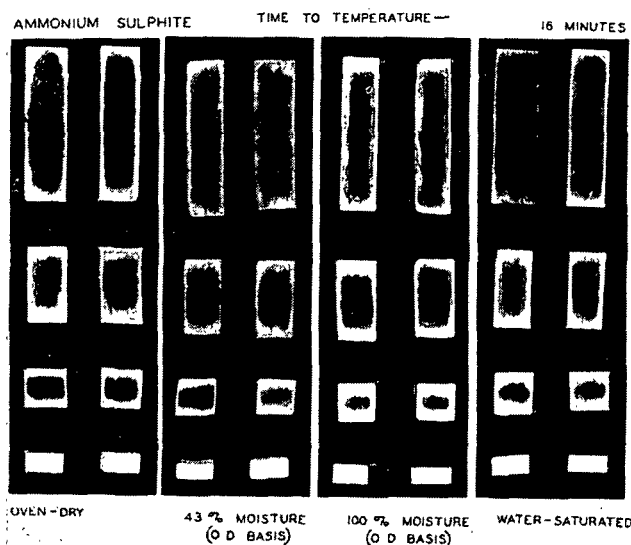


Fig. 3

bottom half of each block was burned. At the junction of the two blocks, therefore, the liquor apparently moved down into the bottom piece but did not move up into the top piece. Horizontally oriented blocks showed no such effect. The tentative explanation for this effect was that the free liquor in the bomb heated up faster than the water in the wood and acquired a lower density. This produced circulation through the wood by means of the cold, dense water flowing out of the bottom of each block and the hot, less-dense liquor flowing down into the top. In a horizontally oriented specimen no such effect is possible. This hypothesis was tested on blocks of birch sapwood 4 in. long and 2 by 2 in. in the transverse directions. The wood was thoroughly water-saturated, preheated to 70°C. in a water-bath, and then immersed in a sodium sulphite solution also at 70°C. The liquor is now more dense than the water in the wood, being at the same temperature, and if the mechanism postulated actually operates, the liquor should flow up into the bottom of a vertically placed block. The temperature was too low to show burning, so the blocks were cut into 9 equal segments and analyzed. The results are shown in Fig. 5.

The vertical block is seen to have taken up most chemical, the horizontal least, and the 45° one an intermediate amount. The bottom end of the vertical and 45° blocks had more electrolyte in them than the top end, as predicted. The vertical block had actually almost reached equilibrium with the surrounding solution, whereas the horizontal block was still far from this condition.

The very uneven character of the salt distribution will be noticed. No explanation can be given for this. About 200 separate blocks were used for a corresponding number of diffusion experiments, using various electrolytes and temperatures, and an irregular distribution of chemical proved to be the rule rather than the exception. The conclusion was reached that, notwithstanding the very fine capillaries involved, a fairly ready interchange of liquor inside and outside the blocks must be possible in the case of wood containing tylose-free vessels. Thus, it was found that stirring the bath of solution in which the blocks were immersed introduced considerably more chemical into the wood in a given period than did no stirring.

A different type of experiment confirms the hypothesis that density differences between liquor and water in the wood can cause appreciable convection currents through wood. It was decided to increase the

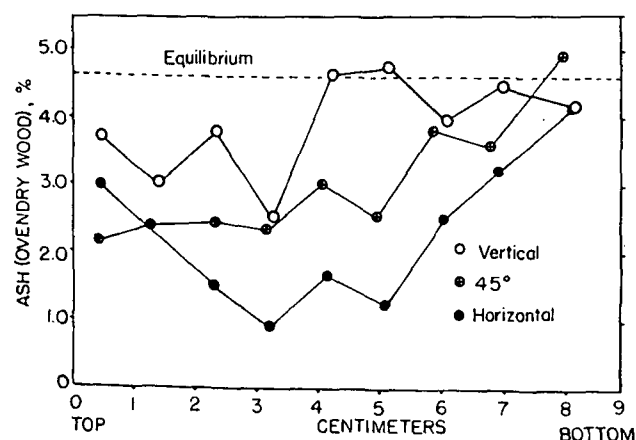


Fig. 5. Effect of wood orientation on liquor uptake by water saturated brick blocks

Table I. Effect of Centrifuging on Penetration

Wood used	Air-dry		Water saturated		Maximum theoretical ash, %
	Not centrifuged <sup>a</sup>	Centrifuged <sup>b</sup>	Not centrifuged <sup>a</sup>	Centrifuged <sup>b</sup>	
Birch sapwood	0.26	3.93	1.17	5.21	6.20
Birch heartwood	0.02	2.90	0.91	5.00	6.20
Beech sapwood	0.69	3.78	0.86	4.28	6.55
Beech heartwood	0.42	2.78	0.29	0.38	5.75
Maple sapwood	1.45	4.68	1.56	5.48	7.10
Maple heartwood	0.93	3.40	1.12	1.32	7.70
Aspen sapwood	2.00	7.55	3.88	8.12	12.70
Aspen heartwood	0.57	3.51	0.81	1.20	13.10

<sup>a</sup> Blocks immersed in 1 M NaCl solution for 15 min. Grain direction vertical.

<sup>b</sup> Blocks held below surface of 1 M NaCl solution and centrifuged for 15 min. Grain direction vertical.

effect of density differences by using a centrifuge. Blocks of wood, 1/2 by 1/2 by 1 in. in the fiber direction were cut from the sapwood and the heartwood of poplar, birch, beech, and maple. One set was water-saturated and another set left air-dry. Thus, four species of wood, sapwood and heartwood, at two different moisture contents were obtained. One complete set of these blocks was immersed in a sodium chloride solution for 15 min., the blocks being vertical, while the other set was centrifuged for 15 min. in the same concentration of salt solution. At the end of 15 min. the centrifuged and noncentrifuged blocks were removed, wiped free of surplus solution, and ashed. The results are given in Table I.

It is seen that the centrifuged blocks took up considerably more salt than the blocks which had merely stood in a beaker of the solution. The increase in uptake due to centrifuging was from 5 to 10 times and in some cases the centrifuged blocks took up almost the maximum theoretically possible for complete equilibration.

The easily penetrated woods—that is, the sapwood of all four species and the heartwood of birch—took up more solution than the difficultly penetrated heartwoods of beech, poplar, and maple. This is to be expected. It is interesting, however, that the easily penetrated woods were apparently most effectively penetrated (by centrifuging) when in the water-saturated condition, whereas the difficultly penetrated woods were most effectively penetrated by centrifuging when in the air-dry state.

The value of these results lies possibly in their demonstration that a unidirectional driving force through wood is remarkably effective in increasing the rate of liquor uptake. The air, instead of being forced to retreat to the center of the wood and be compressed there, opposing further penetration, can be swept out of one end of the wood by the liquor moving in from the other end. Whether or not such a mechanism could be adapted for commercial use is problematical, but it may well be that this mechanism operates to a limited extent in any digester and cannot be entirely ignored as a possible factor in the already complicated field of penetration and diffusion into wood.

#### LITERATURE CITED

1. Stone, J. E., *Pulp Paper Mag. Can.* 57, No. 7: 139-145 (June, 1956).
2. Stone, J. E., unpublished work (to be published 1956).

RECEIVED July 2, 1956. Presented at the Ninth Alkaline Pulping Conference of the Technical Association of the Pulp and Paper Industry, Chattanooga, Tenn., Oct. 19-21, 1955.