

# EXPRESSION OF WATER FROM CELLULOSIC FIBRES UNDER COMPRESSIVE LOADING

G. CARLSSON, T. LINDSTRÖM and C. SÖREMARK, Swedish Forest Products Research Laboratory, Stockholm, Sweden

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**Synopsis** Experiments have been performed in order to demonstrate that water is expressed from small cavities in the fibre matrix during the pressing operation.

The gel water\* in the fibre was tagged by mixing a fibre suspension with a solution of a polysaccharide (dextran) with a known relative molecular mass, capable of entering only cavities greater than its molecular diameter. When a fibre mat is subjected to an external pressure under these conditions, the water expressed from smaller cavities dilutes the polysaccharide solution. By using solutions of polysaccharides of different relative molecular masses, it was possible to demonstrate from which cavities the water was expressed.

Pressing experiments were performed with different kinds of fibres. Bleached and unbleached fibres, a mechanical pulp and viscose fibres were used.

The effects of beating, drying and de-crilling were investigated.

## **Introduction**

THE physical properties of cellulosic fibres in water are normally described by referring to the fibre as a swollen gel. In a series of papers,<sup>(1-6)</sup> Stone and Scallan have described the porous structure of cellulosic fibres in water. By equilibrating a fibre slurry with a polymer solution the water inaccessible to the polymer can be experimentally determined. This technique, commonly referred to as the 'solute exclusion technique', has its analytical analogue in gel permeation chromatography (GPC). This paper describes the expression of gel water during static pressing.

## **Experimental**

THE pressing device used in the experiments is shown in Fig. 1. Basic components are a 6 cm steel piston fitted in a steel cylinder with adequate

\* In this context, gel water is defined empirically as the water inaccessible to a polymer with a specified relative molecular mass. The amount of gel water is thus dependent on the size of the chosen polymer.

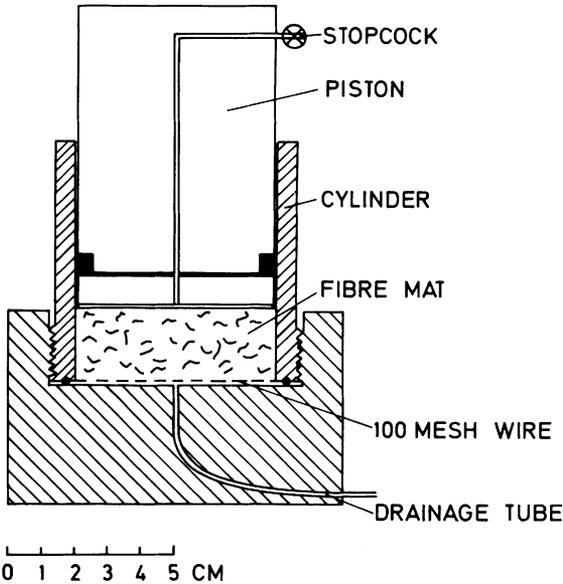


Fig. 1—The pressing device

packing arrangements to sustain a fluid pressure up to at least 3 MPa. The pressing chamber was equipped with a 100 mesh wire and a Teflon drainage tube (diam. = 1.0 mm). A small hole (diam. = 1.0 mm) was drilled in the piston in order to permit liquid to be flushed through the whole apparatus from a hand pump to which this hole was connected. At the highest static pressures (70 MPa) on the fibre bed, a pressure of about 1 MPa was needed for flushing.

During operation, the pressing device was inserted in a plate press in order to maintain the high pressures required in the pressing experiments.

The polymers used in this work were dextran fractions with different relative molecular masses ( $M_w = 2 \times 10^4 - 2 \times 10^6$ , Pharmacia Fine Chemicals, Uppsala, Sweden). One fraction ( $M_w = 3 \times 10^3$ ) was kindly donated by Dr Kirsti Granath (Pharmacia). The corresponding radii of gyration for these polymers were calculated from data according to Grotte.<sup>(7)</sup>

In most experiments it was convenient from an analytical standpoint to use the high relative molecular mass polysaccharide 'Blue Dextran' ( $M_w = 2 \times 10^6$ ).

The concentration of blue dextran was determined in a Beckman Grating Spectrophotometer at 620 nm and for the other dextrans in a Knauer

differential refractometer model 2000 (with thermostatic control to  $\pm 0.005^\circ\text{C}$  at  $25.0^\circ\text{C}$ ).

The solute-exclusion values were determined according to the procedure reported by Stone and Scallan.<sup>(2)</sup>

The characteristics of the pulps used in this investigation are shown in Table 1.

TABLE 1

<i>Pulp</i>	<i>Characteristics</i>
Bleached sulphate $\alpha$ -pulp (bleached sulphate)	$\kappa$ -number: 30 (Scotch pine) $\alpha$ -cellulose: 97.5% (Scotch pine) Visc. Scan (11): 20.3 cp Extract in methanol: 0.01% Ash content: 0.06% SiO <sub>2</sub> : 25 ppm Ca: 20 ppm Fe: 2 ppm
Unbleached sulphate Viscose fibres	$\kappa$ -number: 72 (Scotch pine) Length: 3 mm Diameter: 12 $\mu\text{m}$
Thermomechanical pulp	Freeness: 107 CSF (Norwegian spruce)

The fibres were beaten in a PFI-Mill.<sup>(8)</sup> Water retention values (WRV) were determined by centrifugation at 1 900 times the gravitational force for 15 minutes.

### **Experimental procedure**

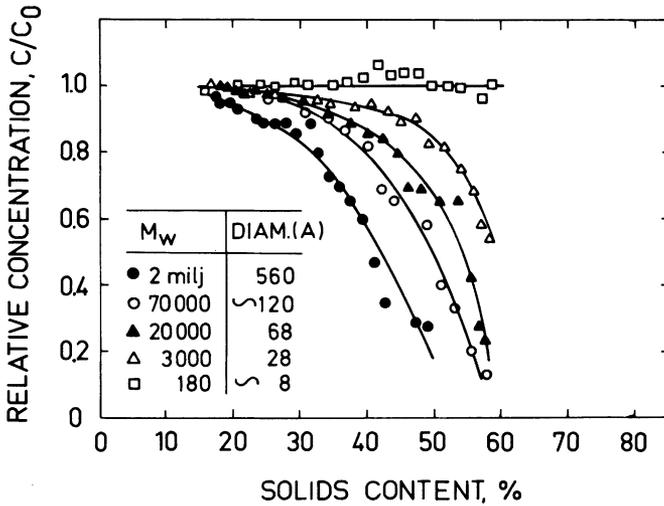
100 g of wet pulp representing about 20 g of dry fibres was mixed with 150 ml of a 5 g/l blue dextran solution (unless otherwise stated). The mixture was then allowed to stand for 1 hour.

The concentration of blue dextran and the contact time were chosen from initial experiments (see 'Results' and 'Discussion').

Fibre mats were then made in a sheet former equipped with a 100 mesh wire. After the fibre mat had been made, it was transferred to the pressing device, and inserted in the plate press.

The grammage of the mats was about 7 000 g/m<sup>2</sup>, so that even at the lowest moisture contents sufficient water would be expressed to permit satisfactory analysis.

The pressure in the plate press was successively increased in small steps, and the water expressed was collected in test tubes. At each step, the pressure was kept constant for 5 minutes to ensure equilibrium in the system. At the highest pressures, a true equilibrium situation is probably not set up, due to plastic flow in the fibre material. On the other hand, this small deviation from a true equilibrium situation is not considered to be of importance for the results, since initial experiments showed



**Fig. 2**—Effect of polymer relative molecular mass on the relative concentration of dextran at different solids contents

that the results were also reproducible if the increments were prolonged for more than 5 minutes. From the final moisture content and the amount of expressed water, the moisture content in each step could be calculated.

The highest pressure employed by the end of an experiment was 70 MPa.

In all experiments, distilled and ion-exchanged water was used.

## Results

### *Effect of polymer molecular weight*

FIG. 2 shows how the relative concentration of dextran in the water expressed from the fibre mat decreases at successively higher dry contents. In this case, the fibre material was a bleached kraft pulp beaten to 20° SR in a Valley beater.<sup>(9)</sup>

It is believed that the concentration of dextran decreases when water inaccessible to the polymer molecule is expressed from the gel matrix and successively dilutes the polymer solution. As can be seen from the figure, water is expressed from smaller cavities the higher the solids content. For glucose, no decrease in concentration could be found even at the highest solids contents.

### *Effect of contact time*

One factor to take into consideration is the possible effect of contact time between blue dextran and the fibre material before it was inserted in the press.

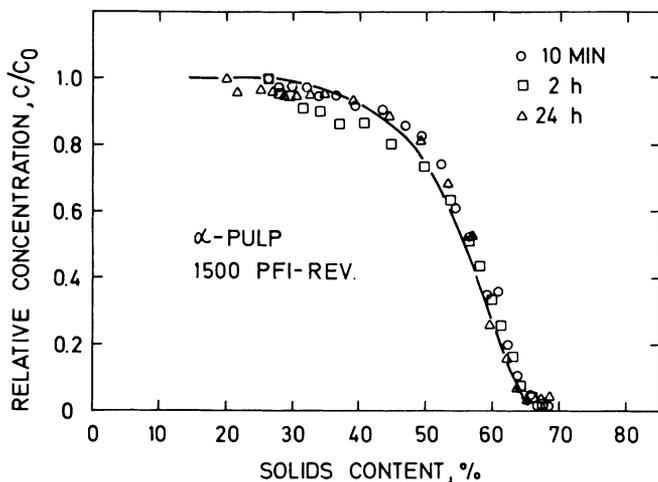


Fig. 3—Effect of contact time on the relative concentration of blue dextran at different solids contents

It might be imagined that diffusion of the high relative molecular mass polymer into the fibre lumen and inter-lamellar cavities in the fibre might be a slow process.

A bleached kraft pulp ( $\alpha$ -pulp) beaten to 1 500 revolutions in a PFI-mill was used. As is evident in Fig. 3, the contact time between the polymer and

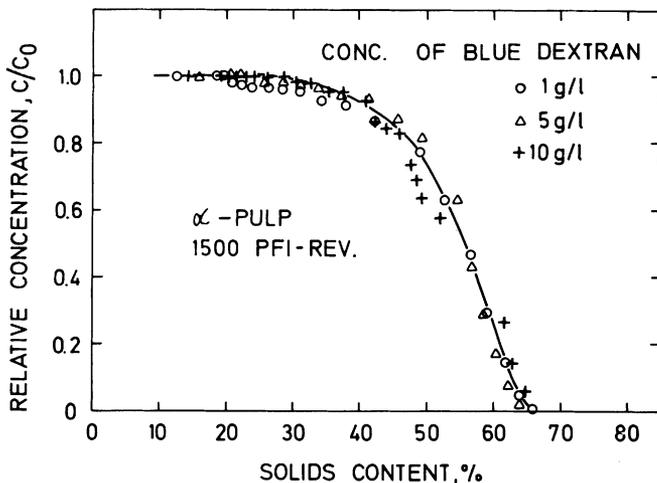


Fig. 4—Effect of polymer concentration on the relative concentration of blue dextran at different solids contents

the fibre material was not of importance, and a real equilibrium situation with respect to diffusion of the polymer into larger fibre pores has been established during these experimental conditions. It should be noted that each step in the pressing sequence took 5 minutes in addition to the contact times quoted in Fig. 3.

#### *Effect of dextran concentration*

If blue dextran is extensively adsorbed onto the fibre material, a desorption could take place as the concentration of the polymer decreased at the lowest average moisture contents of the fibre mat.

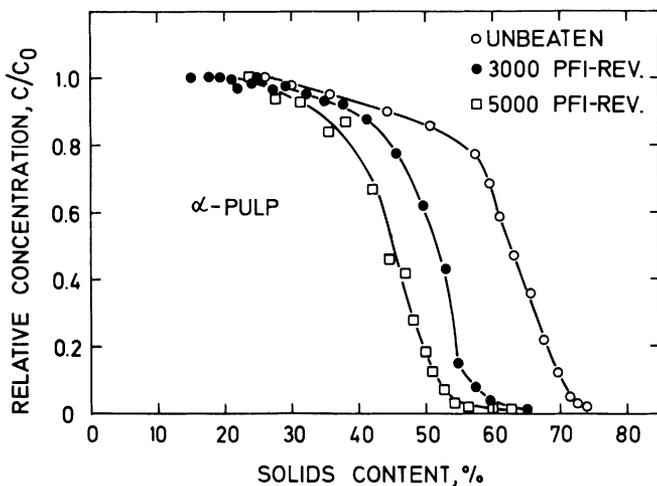
In order to elucidate the possible influence of this effect upon the pressing results, experiments were performed where the concentration of blue dextran was varied from 1 to 10 g/l.

The results are given in Fig. 4. The pulp was the same as that used in the experiments reported in the previous figure.

Within the experimental limits, coincident results were obtained over the investigated range of concentrations. Separate sorption experiments revealed that the sorption of blue dextran to this fibre material was less than 0.02 per cent, which was the experimental limit in these experiments. Thus the effect of polymer concentration needs no further attention.

#### *Effect of beating*

The effect of beating on the expression of gel water from the fibre material is shown in Fig. 5. In this case, the bleached kraft pulp was beaten to different



**Fig. 5**—Effect of beating on the relative concentration of blue dextran at different solids contents

levels in a PFI-mill. As can be seen in the figure, beating decreases the solids content level at which expression of gel water takes place.

These data have been interpreted as showing that there is an increase in the amount of water inaccessible to blue dextran when fibres are beaten.

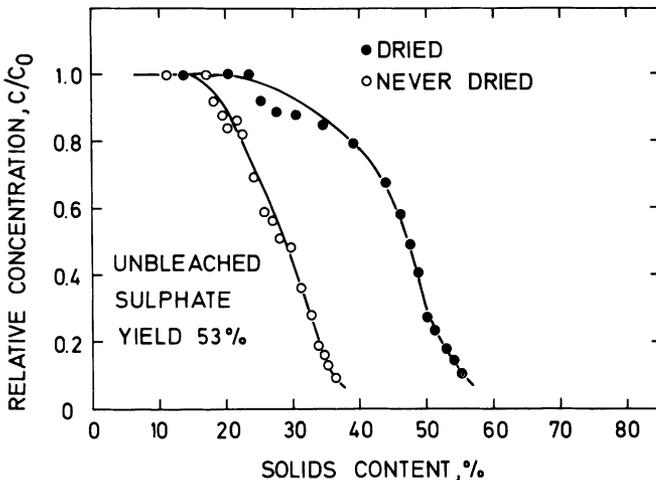
#### *Effect of drying the fibres*

Drying of fibres is known to decrease the amount of gel water in the fibre. In one set of experiments, a laboratory unbleached kraft pulp (53 per cent yield) was beaten to 5 000 revolutions in a PFI-mill and subsequently dried at 105° C overnight. Pressing experiments were carried out before and after the drying operation and the results are given in Fig. 6. As can be expected, the decreased amount of gel water in the dried fibres leads to an increase in the solids content at which inaccessible water is expressed from the fibres.

#### *Effect of fines*

It is well-known to the papermaker that the fines fraction of the pulp contains a large amount of gel water on a weight basis than does the coarse fibre fraction.

In one experiment, the highly swollen fine fibre material was removed on a McNett fractionator<sup>(10)</sup> and the coarse fibre material that did not pass a 100 mesh screen was collected. The pulp ( $\alpha$ -pulp) had been beaten 5 000



**Fig. 6**—Effect of drying on the relative concentration of blue dextran at different solids contents

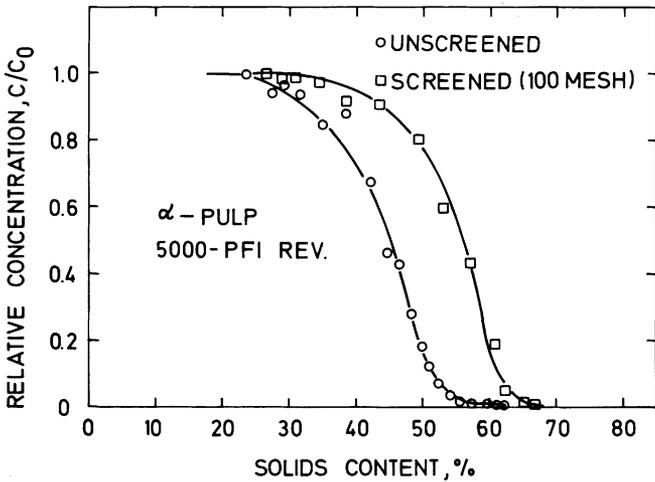


Fig. 7—Effect of fines removal on the relative concentration of blue dextran at different solids contents

revolutions in a PFI-mill before the fines were removed. The effect of fines removal is given in Fig. 7.

The decreased amount of inaccessible water in the de-cripled pulp shows up as an increase in the solids content at which the concentration of the polymer decreases.

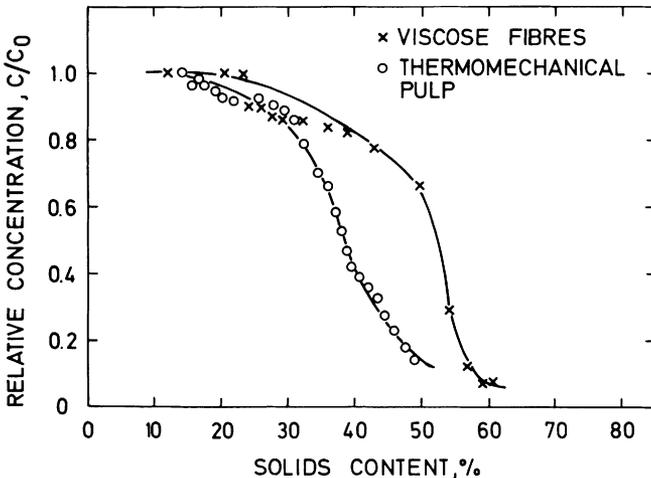


Fig. 8—Effect of different fibre materials on the relative concentration of blue dextran at different solids contents

*Effect of different fibre materials*

The behaviour described for the expression of gel water during pressing is quite general for different kinds of fibre materials. In Fig. 8 an example is given where viscose fibres and thermomechanical pulp were used. As can be deduced from the figure, these fibres also show the expected behaviour during pressing.

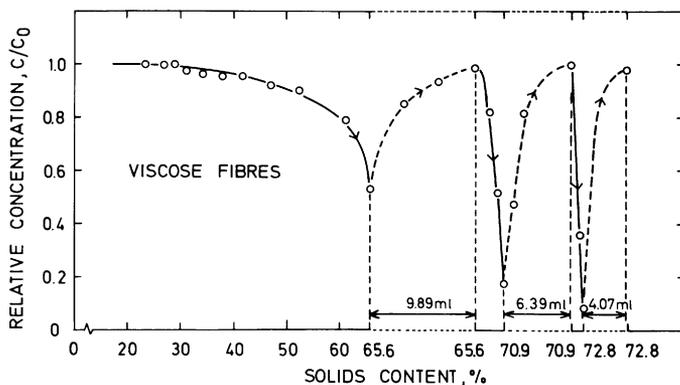
In one experiment, PVC-fibre (diam. = 10  $\mu\text{m}$ ) was used which has no inaccessible water. No decrease in polymer concentration could be found and a moisture content of 6 per cent was obtained at the highest pressing level.

*Discussion*

THERE is still one question which remains to be answered and that is whether these experimental results can be interpreted in terms of an ultra-filtration effect. In order to test this hypothesis, a hole was drilled in the piston in the pressing apparatus (Fig. 1) and this hole was connected to a hand pump which could give a hydrostatic pressure of 1 MPa. With this arrangement, a polymer solution could be flushed through the fibre mat at any desired moisture content of the fibre mat.

A typical run is recorded in Fig. 9. In this experiment viscose fibres were employed. It may be noted that these viscose fibres were not from the same batch as those in Fig. 8.

In the first sequence the pressure was increased until the calculated dry solids content was 65.6 per cent. At this point the pressure was kept constant and a fresh solution of blue dextran was flushed through the fibre bed until the relative polymer concentration had increased to 1.0. The flushing loop was then closed and pressure was increased until the solids content was 70.9 per cent.



**Fig. 9**—Effect of flushing blue dextran through the fibre mat

At this stage, the expressed water had a relative polymer concentration of 0.17. Again, the pressure was kept constant and fresh polymer solution was flushed through the fibre bed until the relative concentration was nearly 1.0. The sequence was then repeated again as indicated by the figure.

If the experiments could be explained by an ultrafiltration mechanism it would be expected that the blue dextran would be collected on the fibre mat. Analysis of the amount of blue dextran in the fibre mat after a flushing experiment rejected this hypothesis. It is believed that these additional experiments support the expression mechanism outlined in this paper.

The question then arises as to what is the relationship between the amount of inaccessible water in the fibre and the expression of gel water during pressing?

In principle, if all fibres were identical and all individual fibres were subjected to the same static pressure, a critical dryness level corresponding to the point of solute exclusion should exist and a drastic decrease in polymer concentration should be detected, when the pressure was increased beyond this level. It is assumed here that the total void space (accessible to the specific polymer) between the fibres is negligible in comparison with the total inaccessible volume.

In practice, however, this is certainly not the case, because all fibres are not expected to have the same amount of inaccessible water. Secondly, the fibre mat is not ideally uniform and a complicated stress distribution is set up in the mat. Thirdly, the polymer samples are not mono-disperse and finally, non-ideal experimental conditions always limit the results obtained. Such statistical

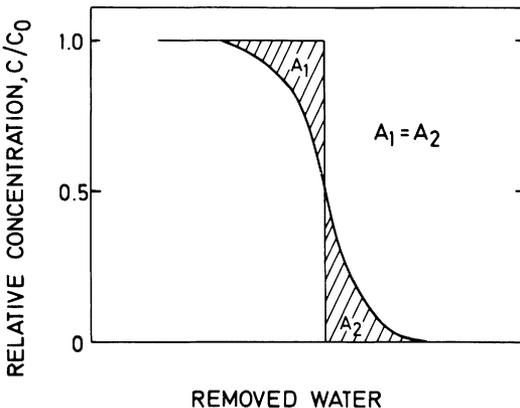


Fig. 10—Method of calculating the critical dryness point

errors may be taken care of by different methods. One might for example correlate the dryness value at a relative concentration  $c/c_0 = 0.5$  with dryness values from solute exclusion experiments with the same polymer and fibre material. Another method is to equalise the two areas  $A_1$  and  $A_2$  in a diagram of the type shown in Fig. 10.

This second method was found to yield better correlations than the former. The dryness value calculated according to this method is here termed 'calculated critical dryness'.

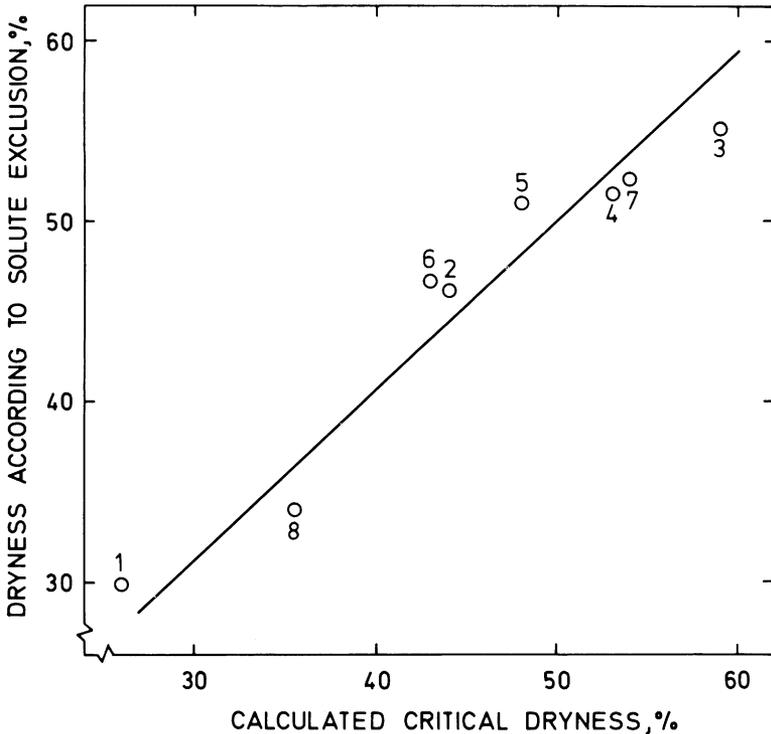


Fig. 11—Correlation between dryness calculated from the WRV and calculated critical dryness.

- 1 = Unbleached kraft, never dried
- 2 = Unbleached kraft, dried
- 3 = Bleached kraft ( $\alpha$ -pulp), unbeaten
- 4 = Bleached kraft ( $\alpha$ -pulp), 1 500 PFI-rev.
- 5 = Bleached kraft ( $\alpha$ -pulp), 3 000 PFI-rev.
- 6 = Bleached kraft ( $\alpha$ -pulp), 5 000 PFI-rev.
- 7 = Bleached kraft ( $\alpha$ -pulp), 5 000 PFI-rev., screened (100 mesh)
- 8 = Thermomechanical pulp

Fig. 11 illustrates that a linear relationship exists between the dryness calculated from solute exclusion values and the calculated critical dryness.

Instead of solute exclusion values, the water retention value can be used and this correlation is shown in Fig. 12. A correlation between solute exclusion values and water retention values has also been reported by Scallan and Carles.<sup>(6)</sup>

Fig. 13 also shows that the same type of correlation can be obtained with the different relative molecular mass dextrans if the calculated critical dryness is compared with inaccessible water. (In this case, the calculated critical

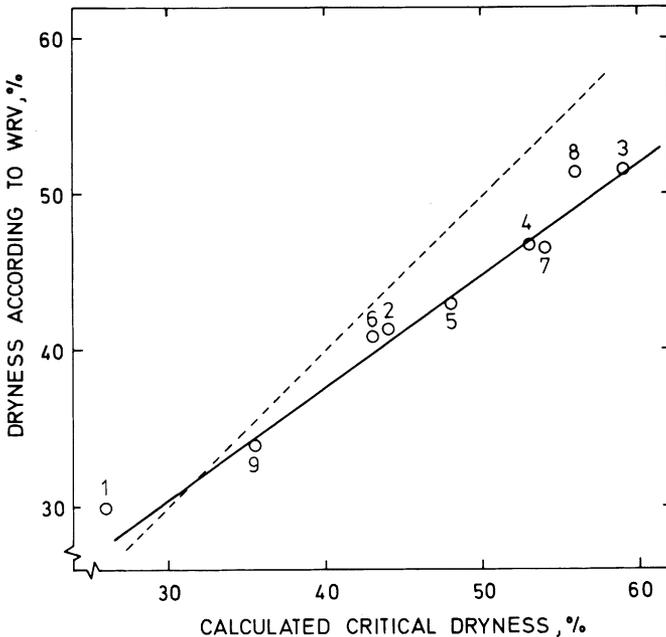
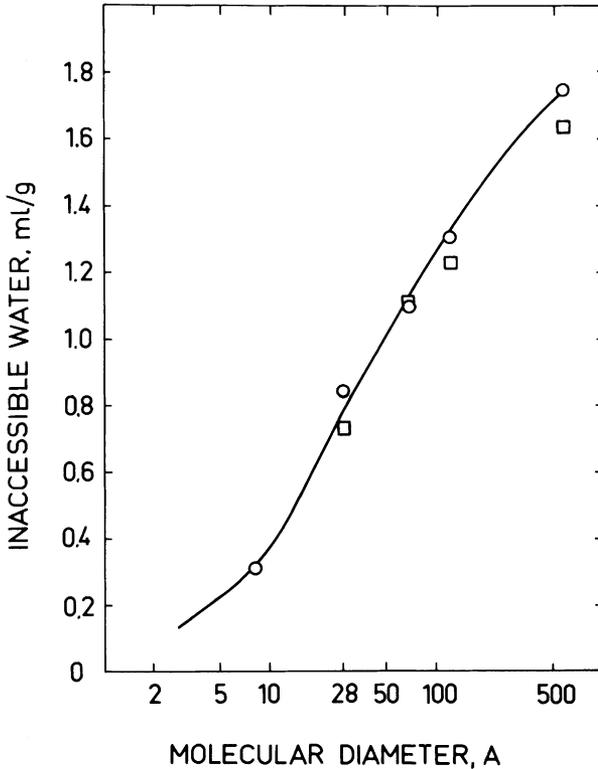


Fig. 12—Correlation between dryness calculated from the WRV and calculated critical dryness.

- 1 = Unbleached kraft, never dried
- 2 = Unbleached kraft, dried
- 3 = Bleached kraft ( $\alpha$ -pulp), unbeaten
- 4 = Bleached kraft ( $\alpha$ -pulp), 1 500 PFI-rev.
- 5 = Bleached kraft ( $\alpha$ -pulp), 3 000 PFI-rev.
- 6 = Bleached kraft ( $\alpha$ -pulp), 5 000 PFI-rev.
- 7 = Bleached kraft ( $\alpha$ -pulp), 5 000 PFI-rev., screened (100 mesh)
- 8 = Viscose fibres
- 9 = Thermomechanical pulp



**Fig. 13**—Comparison of inaccessible water as determined from solute exclusion experiments and from pressing experiments

- = solute exclusion  
 □ = pressing experiments

dryness was estimated by taking the dryness value at a relative concentration = 0.5 for the dextran with a relative molecular mass of 3 000.)

The quoted figures thus strongly support the hypothesis that gel water is expressed under the performed experiments.

Throughout this experimental investigation (and in pressing experiments other than those reported here) it was noted that the higher the equilibrium swelling, the higher was the final moisture content at the highest pressure level (70 MPa). The apparatus used was not, however, built to establish such relationships.

### Acknowledgement

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10. According to SCAN-M 6:69
11. According to SCAN-C 15:62