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THE ROLE OF HYDRATION IN PAPERMAKING SUSPENSION

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The study summarizes the present knowledge on the role of hydration in concentrated papermaking suspensions, and describes the influence of the aqueous medium, characterized by the determination of the so-called relative hydration factor on :
— initial tensile strength of the wet paper web :
— permeability of the pulp bed for different aqueous media, as well as the pulps refining process.
Determination of the relative hydration factor is based on the different orientation of water molecules in the hydration layers, affecting the so-called hydration forces.

Die Zusammenfassung von unseren gegenwärtigen Erkenntnisen über Rolle von Hydratation in konzentrierter Papierstoffsuspension.
Der Einflus von Wasserumbedung charakterisiert mit dem sog. rel. Hydrationsfaktor auf :
— der initialen Nasfestigkeit von Papierblatt,
— der Permeabilität von Zellstoffbett in verschiedener Wasserumgebung und besonders auf dem Mahlungsprozess von Zellstoff wird gescheben. Die Beurteilung von rel. Hydratationsfaktor wird auf Konzeption verschiedene Orientation die Wassermolekülen in der Hydratationschichten und mit dem verbindete wechselwirkende sog. Hydratationskräfte begründet.

INTRODUCTION

No doubt, nowadays, water or water medium play quite an important role in paper production. It is not only a problem of transport, but mainly of an important influence upon the behaviour and properties of dilute paper stocks from the wet paper web up to finished paper. The most decisive problem is the influence of water on the bond system of paper. The behaviour of pulp suspensions at low concentrations is quite known.

Another problem, however, appears after removing free water from the pulp suspension, i.e. from concentrations about 10% and higher. In these cases, the relative mobility of individual fibres is fairly lowered and mutual distances between interacting fibre configurations are so small

that other effects than the electrokinetic ones are functioning here. Water or water medium, respectively, continue their influence, but in another sense. There is presumed that the influence will be similar in all hydrated hydrophilic systems and will operate with the same mechanism. This water medium can be characterized, and its influence on some qualities of pulp suspensions of higher concentration can be studied, if a suitable phenomenon is designed, that is easy to observe and is sensible to changes of this water medium. Such a phenomenon, called relative hydration factor is based on the idea of hydration forces forming a hydration bonding system among hydrated hydrophilic components.

We have followed the influence of the water medium upon :

— the initial tensile strength of paper
— the permeability of the fibrous pulp bed
— the energy requirement for beating pulps.

1. MODELLING SYSTEM OF HYDRATION FORCES

A phenomenon where, according to our observations, the hydration forces play the main role is the so-called critical degree of dilution (CDD),[1] an untypical case of a limited dilution ability characteristic for some concentrated hydrophilic systems, e.g. some polyesters, urea-formaldehyde resins, etc. The volume of the original hydrated hydrophilic system V_0 being gradually diluted with water or water solutions, respectively, it does not undergo any changes until the moment when the volume of added water or of its solutions exceeds the critical value V_k (Fig. 1). Now,
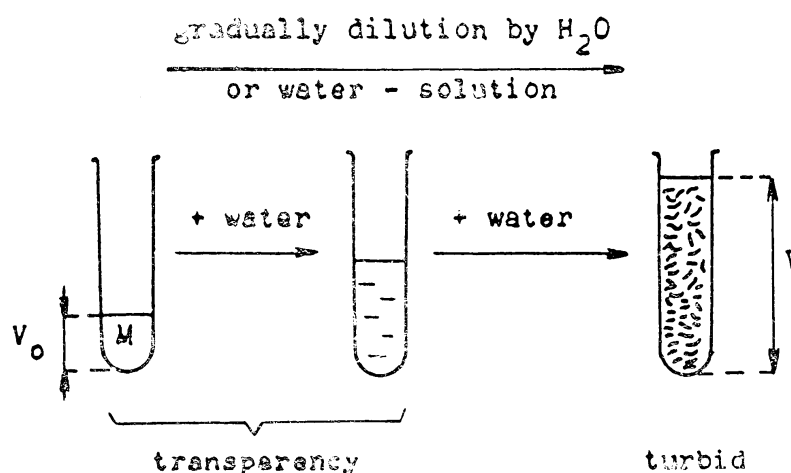

Fig. 1. — Evaluation of the effect of hydration forces by means of hydration hydrophilic modelling system.

M — Modelling system; $CDD = \dfrac{V}{V_0}$; $V = V_0 + V_k$

CDD_0 — Critical degree of dilution in distilled water;
CDD — Critical degree of dilution in water — solution;

$g - 1 = f_H = \dfrac{CDD - CDD_0}{CDD_0}$; g — Relative hydration factor.

If $g < 1$ or $f_H < 0$ — increasing of the attractive forces influence in the bonding system of hydration forces.
If $g > 1$ or $f_H > 0$ — increasing of repulsive forces influence in the bonding system of hydration forces.

the originally transparent liquid becomes turbid due to precipitated microgel particles. The value CDD $= (V_k + V_0)/V_0$. The turbidity is caused by the coacervation of the originally homogeneous system with the addition of water or water solutions.

The super-molecular chemical phenomenon can be simply explained by the so-called hydration forces functioning among interacting hydrophilic molecules or their fragments in water (Figs. 2, 3).[1,2] The condition of such behaviour is the presence of hydrated hydrophilic anisometric oligomer molecules. The parts or ends of these molecules influence each other by the attractive hydration forces, while other parts of molecules by the repulsive forces. The effect of the attractive forces among interacting molecules must however prevail to that of repulsive hydration forces. The uniform distribution of oligomer molecules is thus reached in all the volume of the water medium. When these systems are diluted, the molecules, their parts and ends are drawn away from each other and their mutual force action is thus weakened. After exceeding the critical concentration or the critical volume of added diluting water V_k, resp., coacer-
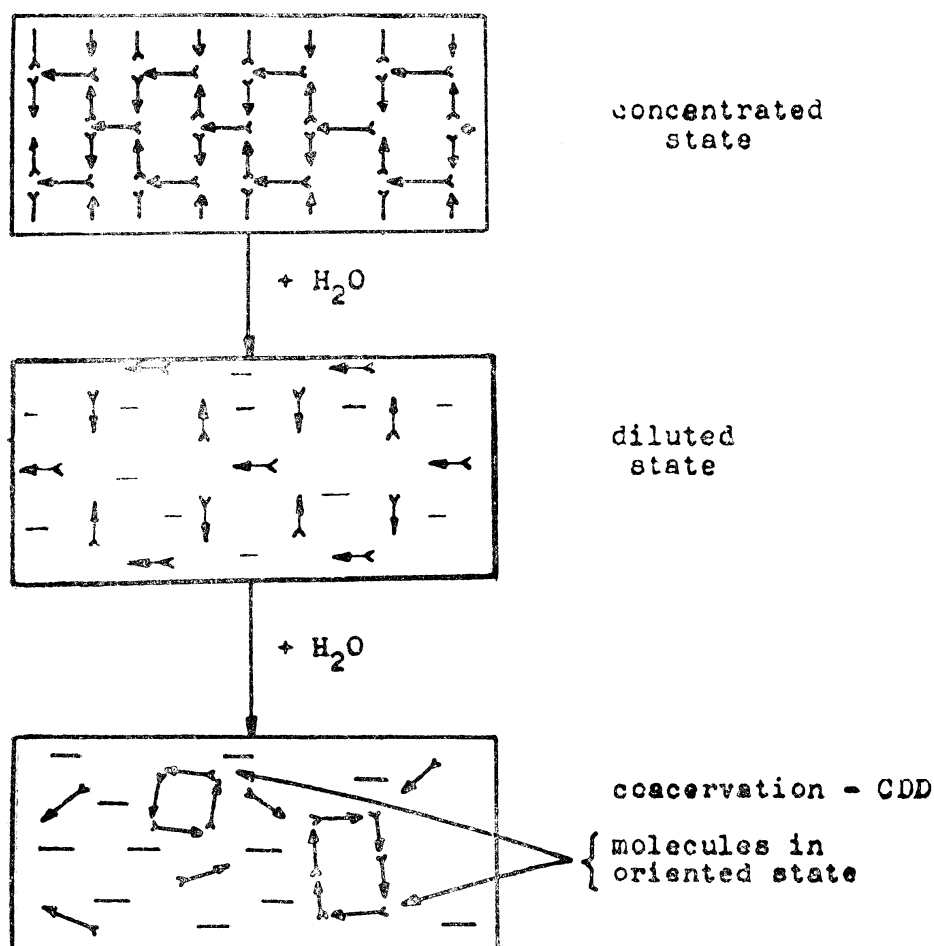

Fig. 2. — Schematic representation of the behaviour mechanism of the bipolar, hydrated oligomer system on its dilution with water.
← = Schematic representation of the "bipolarity" of a hydrated oligomer molecule caused by different orientations of the water molecules at both ends of the molecule
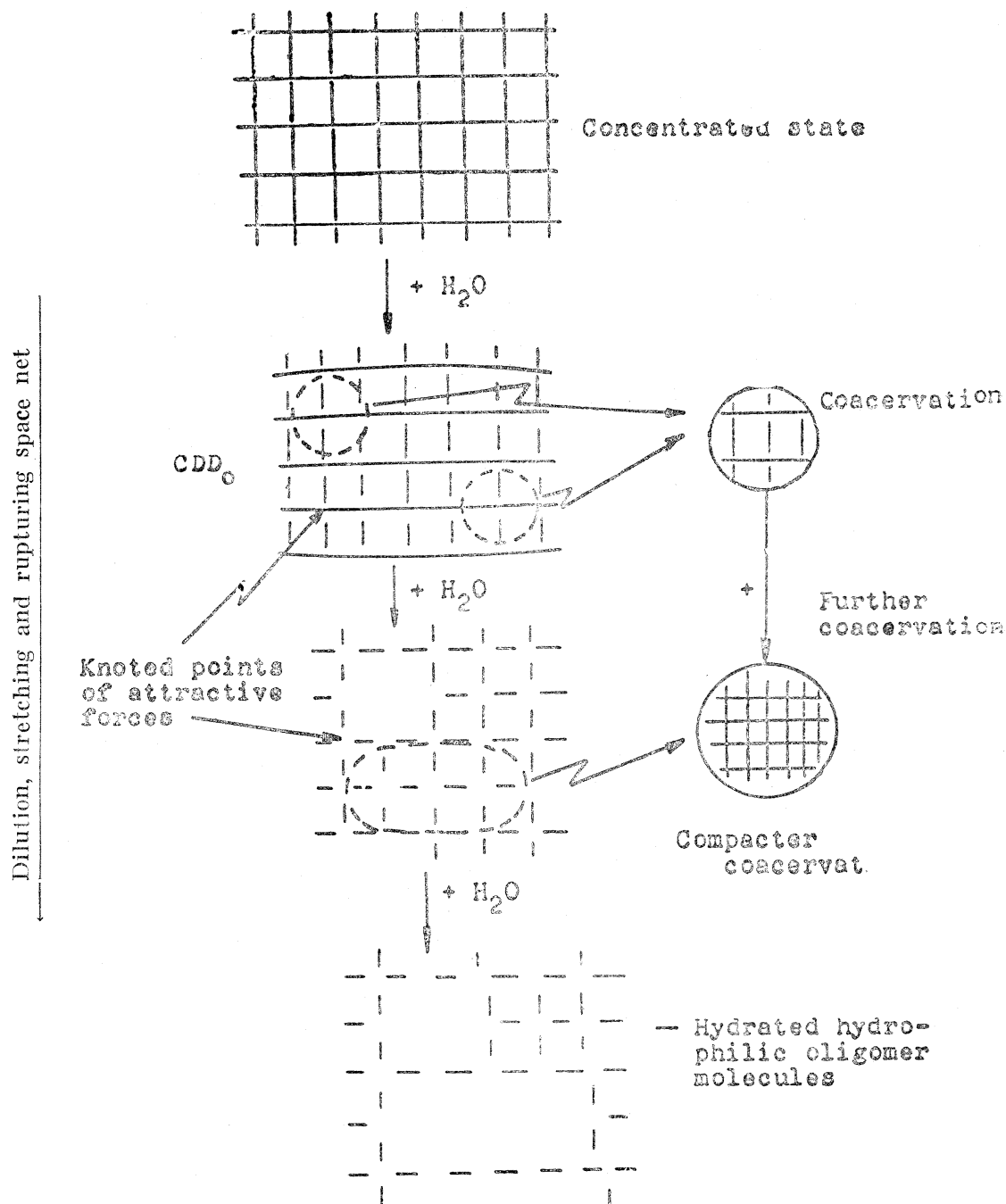— = Free water molecules outside the hydration spheres.

Fig. 3. — Rupture mechanism of the stretching space net by gradual dilution.

vation takes place, owing to the fluctuation of the affecting mutual forces and the kinetic energy of interacting oligomer molecules. In this case, the composition and properties of the separated coacervates correspond to the original concentrated system. The influence rate of the added substances upon hydration forces can be evaluated by means of the so-called hydration factor $g = CDD/CDD_0$, where CDD_0 means the CDD value in a standard medium, e.g. in distilled water. The value $g > 1$ means that when compared with the original medium, the added substances decrease the attractive forces or increase the repulsive hydration forces, resp.,

and reversely (see Fig. 1). Thus, the system enables us to simulate the influence of different components in water upon hydration bonding system, among hydrated hydrophilic molecules, particles etc.

2. PRACTICAL ASPECTS OF THE RELATIVE HYDRATION FACTOR

Influence of the water medium on the initial wet strength of paper[2]

It is known that the strength of wet paper web (initial strength) or its bond system resp., is determined by the mechanical entanglement of fibrous formations and by mutual physical bonds between them. The degree of mutual bonding abilities increases with increasing the beating degree to the detriment of the mechanical entanglement. If a constant contribution to mechanical entanglement is assured in the bond system of wet paper (for instance, by a constant beating degree), the changes of initial strength will then indicate the changes in fibre bonds.

The dependence of the initial strength of paper, I_p, measured at comparable conditions with a relative hydration factor — g (g = = CDD/CDD_0, CDD_0 is the CDD value in the water from paper stock without any other additives) is plotted in Figure 4. It shows clearly that the initial strength of paper web falls with the rise of repulsive hydration forces to the detriment of the drop of its attractive component the increase of g values). The hydration bonding system among hydra-
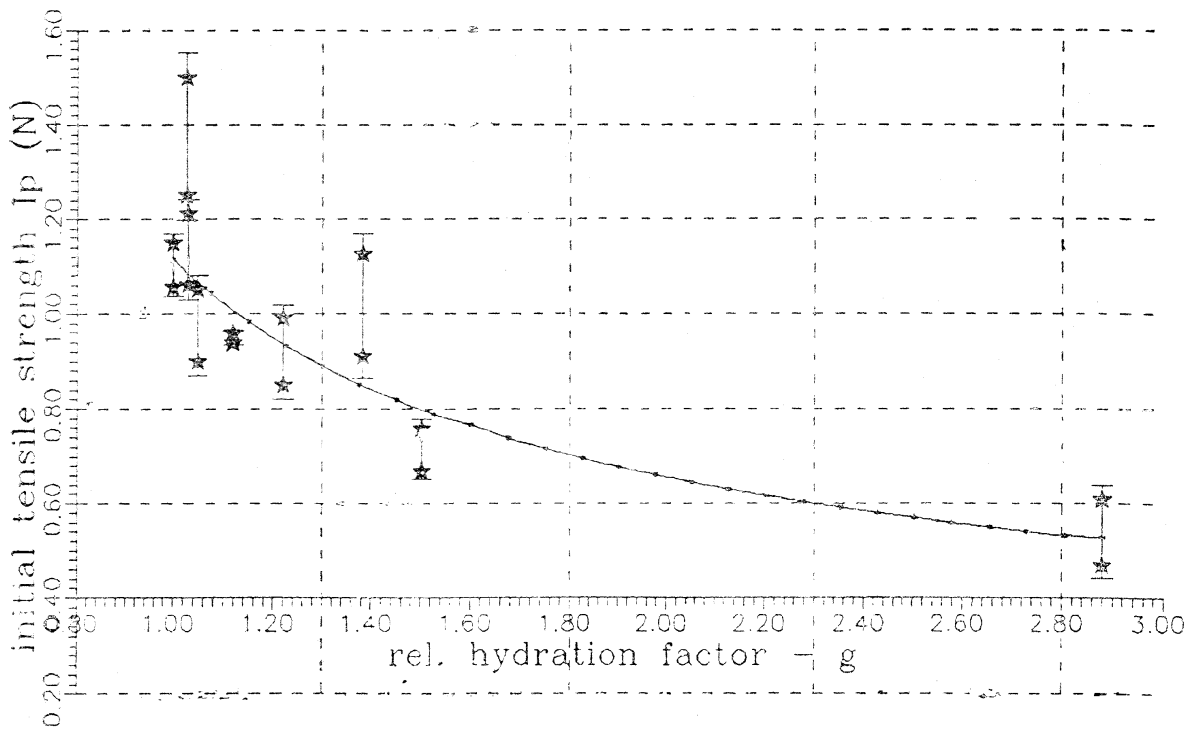

Fig. 4. — Relationship between the initial tensile strength — I_p of paper on the hydration factor — g relation. The hydration factor — g relation was measured over a range extending from pulp slurries without other components (g = 1.00, where CDD = CDD_0) to water from pulp slurries with other components (g > 1.00), I_p = (1.5213 g — 0.7184) $^{0.4986}$ (in N); Correlation coef. = 0.90122.

ted fibers is getting weaken. The linear relationship has the form $I_p =$ $= 1.4 - 0.32.g$, $r_{xv} = 0.754$, which can be taken as a semiquantitative proof of the existence of hydration forces.

The initial strength of wet paper web (I_p) was determined using the method and apparatus by Brecht-Heiniger.[3-4] The dispersion variance of the values around the calculated dependence was caused in this case by a greater error in determining the initial strength (about 10% on the average).

Relation of the permeability of pulp bed to the water medium

One of the important aspects of paper stock draining is the filtration resistance of the drained bed, which is characterized by its permeability. Ingmanson's method [6] is often used to evaluate the permeation properties of pulp. The relations of the permeability of the fibre bed B to the g value characterizing the water medium are plotted in Fig. 5 (CDD_0 corresponds to CDD in water, without any other additives). Table 1 shows the relations of the parameters characterizing fibrous pulp bed (K — Kozeny's constant, S_0 — specific surface, x — specific volume of fibre bed) and the permeating water medium (g).
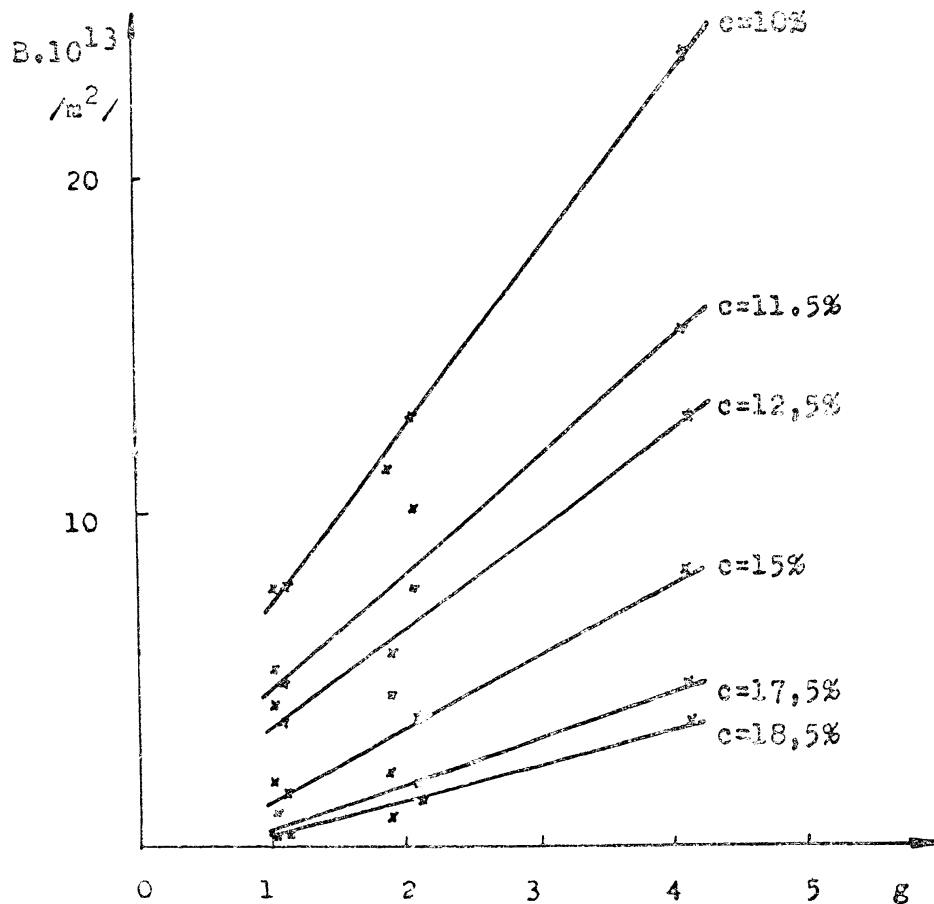

Fig. 5. — Relation of the permeability of fibre pulp bed to the relative hydration factor. B — Permeability; g - Relative hydration factor/CDD_0 corresponds to the CDD value determined in water without additives; c — Concentration of fibre bed.

TABLE 1

Relation of parameters characterizing fibre pulp bed with the relative
hydration factor -- g

Rel, hydrat. factor g	$S_0 K^{0.5} \cdot 10^{-6}$ (m^{-1})	$\alpha \cdot 10^3$ (m^5/kg)
1.000	1.962	3.24
1.866	2.057	2.94
2.044	1.776	2.84
4.044	2.192	2.09

$$\alpha \cdot 10^3 = -0.3789, g + 3.623, \quad r_{xy} = -0.99979$$

Figure 5 explicitly shows that the permeability of fibre pulp bed B
increases in such a water medium in a linear way, which supports the
effect of repulsive hydration forces between hydrated phase interfaces.
It is such water medium, that supports only one direction in the orien-
tation of molecules near the by-passed walls of individual pulp fibres. As
the specific volume of the fibre bed, α, falls with the increase of the rela-
tive hydration factor g (see Table 1) and the specific surface of the bed
$S_0 K^{0.5}$ is practically constant, it is clear that the corresponding in-
crease of permeability B is connected with a drop of the so-called
immobilized water in the bed, in its interfibre space. In other words,
the amount of water closely connected at these measuring conditions
to pulp fibres forming the fibre bed is decreased, with rising the effect
of repulsive hydration forces in the bed.

This phenomenon can be explained as follows (see Fig. 6) : the
zones around the phase interfaces where attractive hydration forces are
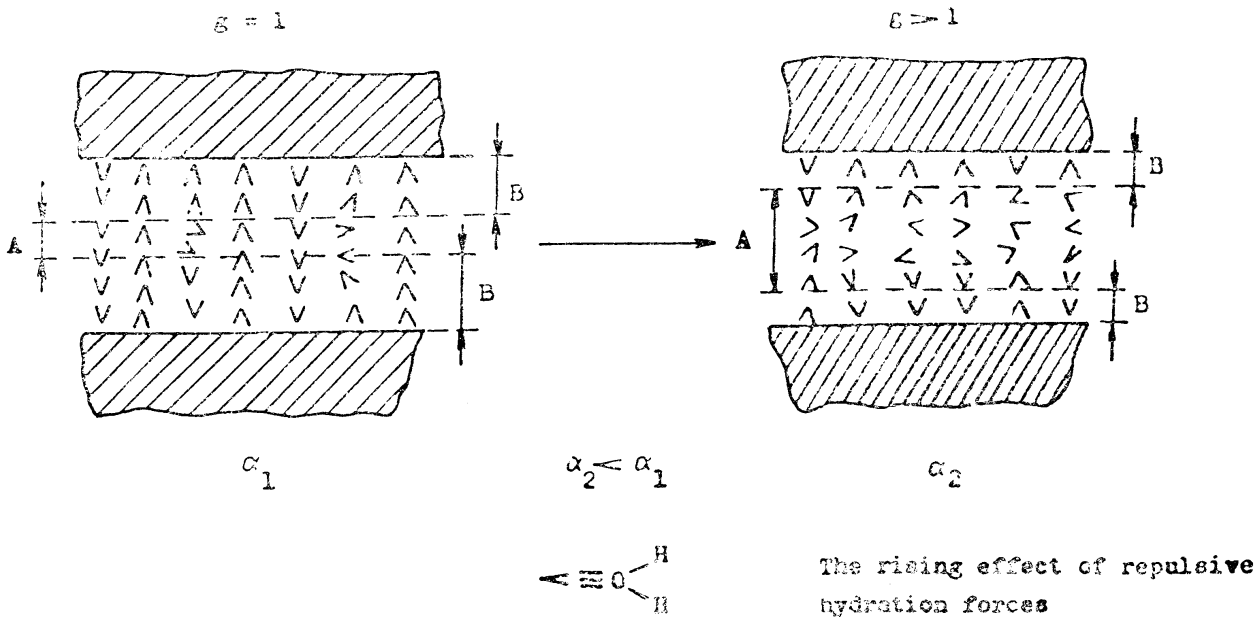operating are filled up with more strongly bound and less mobile water

Fig. 6. — Schematic presentation of lowering the content of immobilized water around pulp
fibres in fibre bed due to the increase of the repulsive hydration forces action among interacting
fibres. A — Zone of mobile water; B — Zone of immobilized water; α — Specific volume of
fibre bed.

molecules and, on the contrary, the zones of repulsive hydration forces are filled up with less bound and thus more mobile water molecules. The decrease of the action of repulsive hydration forces results in the rise of the content of immobilized water and thus in a drop of permeability of the fibre bed for the given water medium, and reversely.

To carry out these experiments, the chosen water medium was forced through the fibrous pulp bed of a definite concentration c, which was placed in an apparatus especially designed for this purpose. The results were treated by Ingmanson.[6] The pulp material used was bleached softwood sulphite MgBi pulp beaten to 35 SR.

The influence of water medium on the refining process

If we accept the conception of hydration forces as right, it becomes evident that water medium must play an important part in pulp beating, which destroys its super-molecular structure to form fine fibres, fibrils, microfibrils, etc. Without any appropriate theoretical explanation, several substances have been already known for a longer time whose presence in the water medium of pulp shortens its beating time or lowers the requirements of refining energy resp., e.g. some azodyes (Kongo Red is typical).[7]

The dependence of the relative specific energy consumption needed for refining pulp to 50 SR (regarding distilled water) upon the relative hydration factor given in Figure 7 fully confirms the theoretical concept of hydration forces forming hydration bonding system among fiber components of pulp. The increase of the relative hydration factor means a rise in the action of repulsive hydration forces to the detriment of the attractive ones. This becomes evident with refining, in that the creation of new surfaces, particles or structural damage and/or modifications of pulp fibres are more easily performed. Figure 7 also shows that, beside substances having a positive effect on the refining process, there are also substances acting in the opposite sense. Their effect can even change, depending on their dosed amount. A relative dispersion variance of the experimental data is caused by a worse reproducibility of refining experiments and, in some cases, by the qualitative differences in the behaviour of the pulp system and of the model system used to determine the value of the relative hydration factor g.

In all experiments, the hydration factor g was changed only with some low molecular additives that did not affect the flocculation of the paper stock.

3. CONCEPT OF HYDRATION FORCES

The idea of the origins and effect of hydration forces is based upon the typical dipole character of water molecules and on their possible orientation in hydration spheres around the hydrophilic phase interface depending upon its nature.[8] The possible orientations of water molecules with regard to the phase interface vary essentially between the following extreme positions (see Fig. 8) :[1,8]
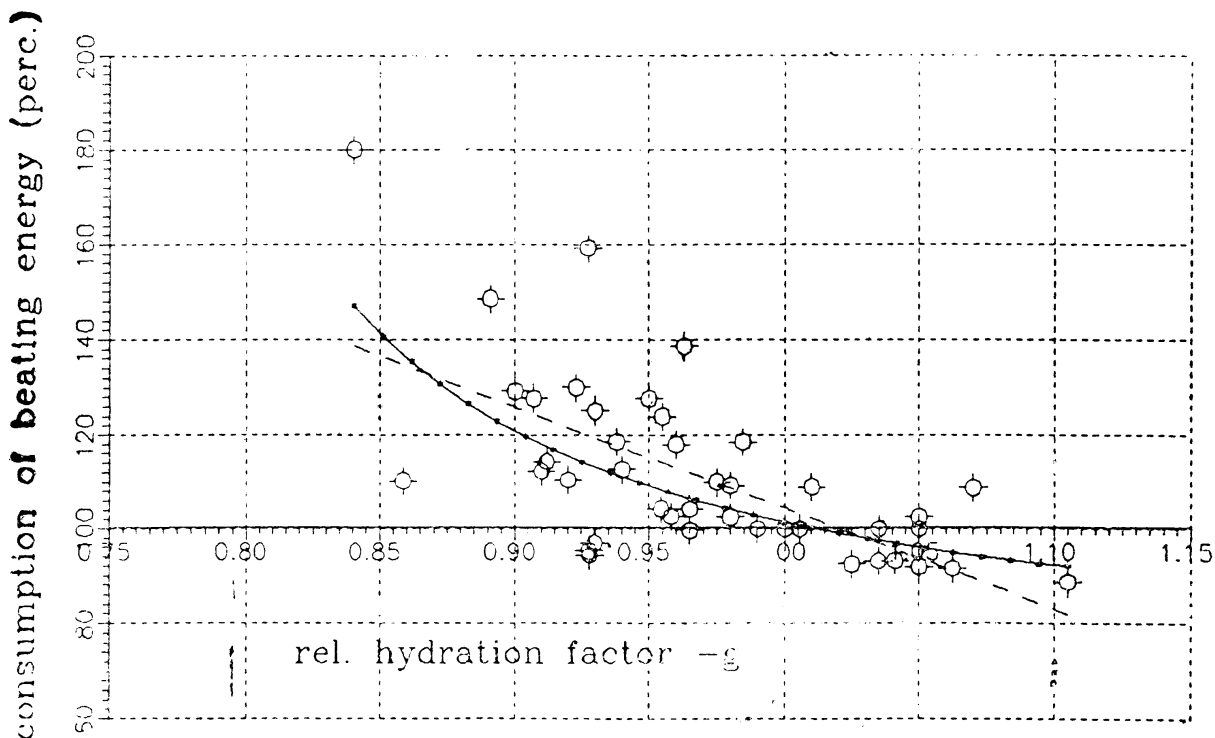
Fig. 7. — Relationship between the consumption of beating energy (on 50 SR) — C on relative
hydration factor — g.
g = CDD/CDD₀ (CDD₀ and the consumption of beating energy = 100 % was measured in dis-
    tilled water.)
1) C = 65.105 + 1/(0.096 · g — 0.0687);
Correlation coef. = 0.70158
2) Linear relationship :
C = 318.85 — 214.43 · g; Correlation coef. = — 0.66147.

— orientation with the H-atoms of water molecules to the surface
of the phase interface,

— orientation with the O-atoms of water molecules to the surface
of the phase interface.

Owing to this orientation of water molecules, caused by the formed
H-bonds of water molecules to the groups of the phase interface, a strong
force field arises and extends due to other water molecules within the hy-
dration sphere, inducing decreased diffusion, until it has a zero value inside
water. This effect serves as origin of the force action between interacting
phase interfaces — i.e., of the hydration forces. If the orientation of water
molecules is equal to each of the interacting phase surfaces, the two phase
interfaces will affect each other with repulsive hydration forces. In the
opposite case, when the orientation of water molecules to each of the
phase interfaces is different, the two surfaces will affect each other with
attractive forces. From theoretical considerations there follows, under the
same conditions, that the repulsive forces extend their effect to larger
distances than the attractive hydration forces, and the effect of attractive
hydration prevails on short distances (probably smaller than 4 nm)[2,8]-see
Figure 9. In the case of heterogeneous phase interfaces (e.g. pulp fibres),
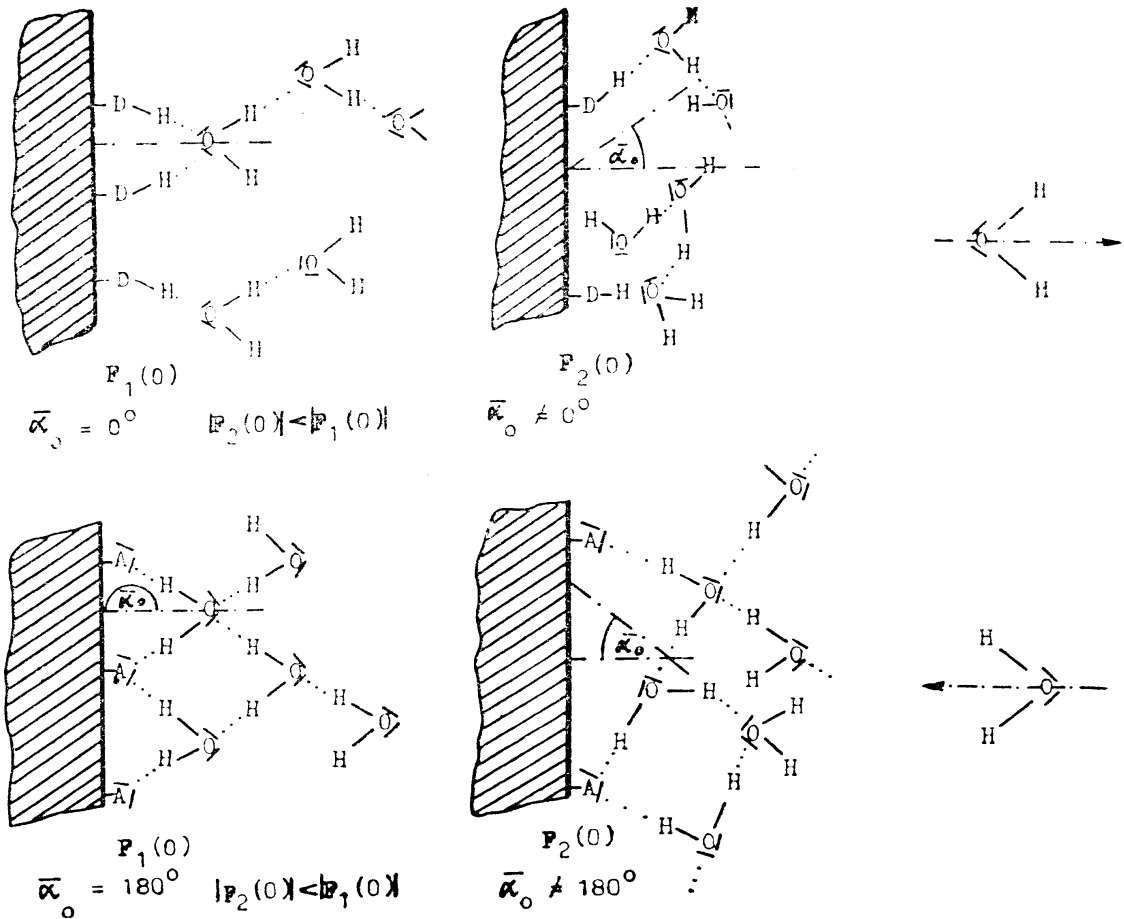when repulsive and attractive hydration forces are functioning simulta-

Fig. 8. — Conception of water molecules orientation on various types of phase interfaces.
$\bar{\alpha}_0$ — Average axis angle of water molecules related to the phase interface normal at its close vicinity;
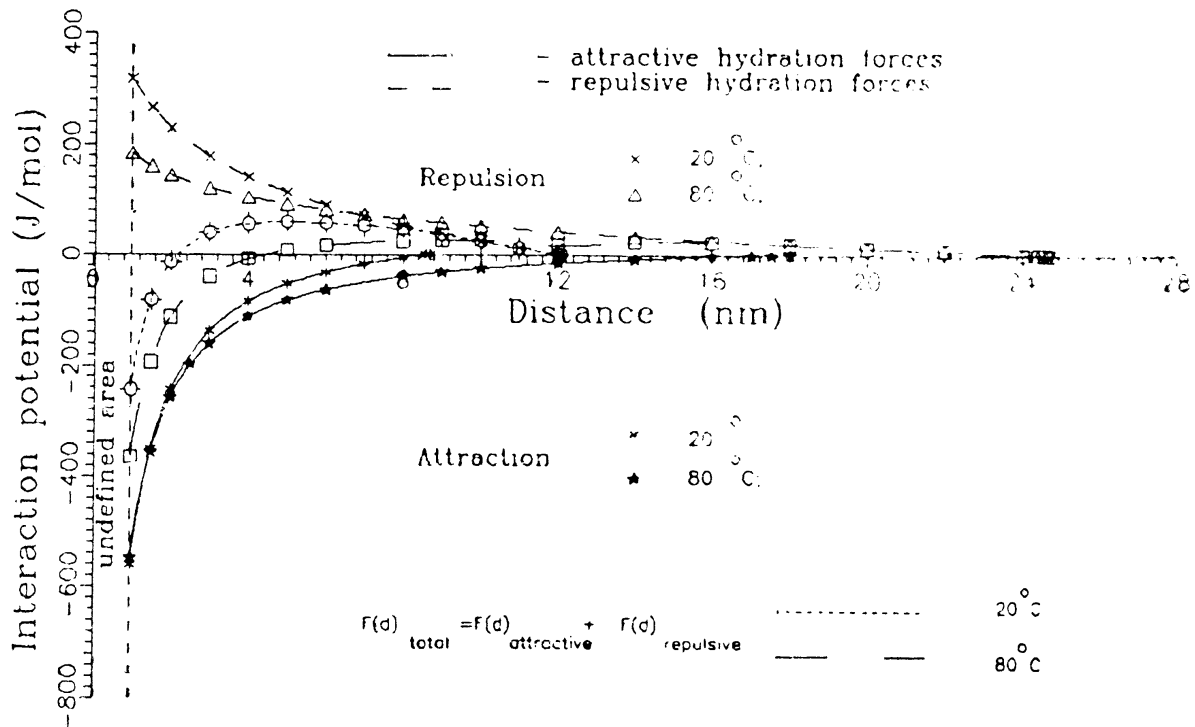F(0) — Potential energy of water molecule in distance d = 0.

Fig. 9. — Dependence of interaction potentials (F(d) (absolute value) upon the distance d of interacting homogeneous and quantitative equally flat formations.
Attraction $F(d) = - (7.\ 782.F(0)^{0.5}/(a.d) - F(0).0.297).N_A$
Repulsion $F(d) = - (6.52.F(0).\ln (0.0274\ F(0)^{0.5}.a) + \ln d).N_A$ where F(0) — interactiong potential at distance $d = 0$ by 20°C (F(0) = $4.068.10^{-22}$, J/mol; 80°C F(0) = $1.826.10^{-22}$, J/mol and parameter a = $1.496.10^{-22}$, $N^{-0.5}.m^{-3/2}$ by 20°C; a = $= 1.093.10^{20}$, $N^{-0.5}.m^{-3/2}$ by 80°C, N_A — Avogadro's number. All F(0), F(d) are in J/mol of water in the first adjancent layer.

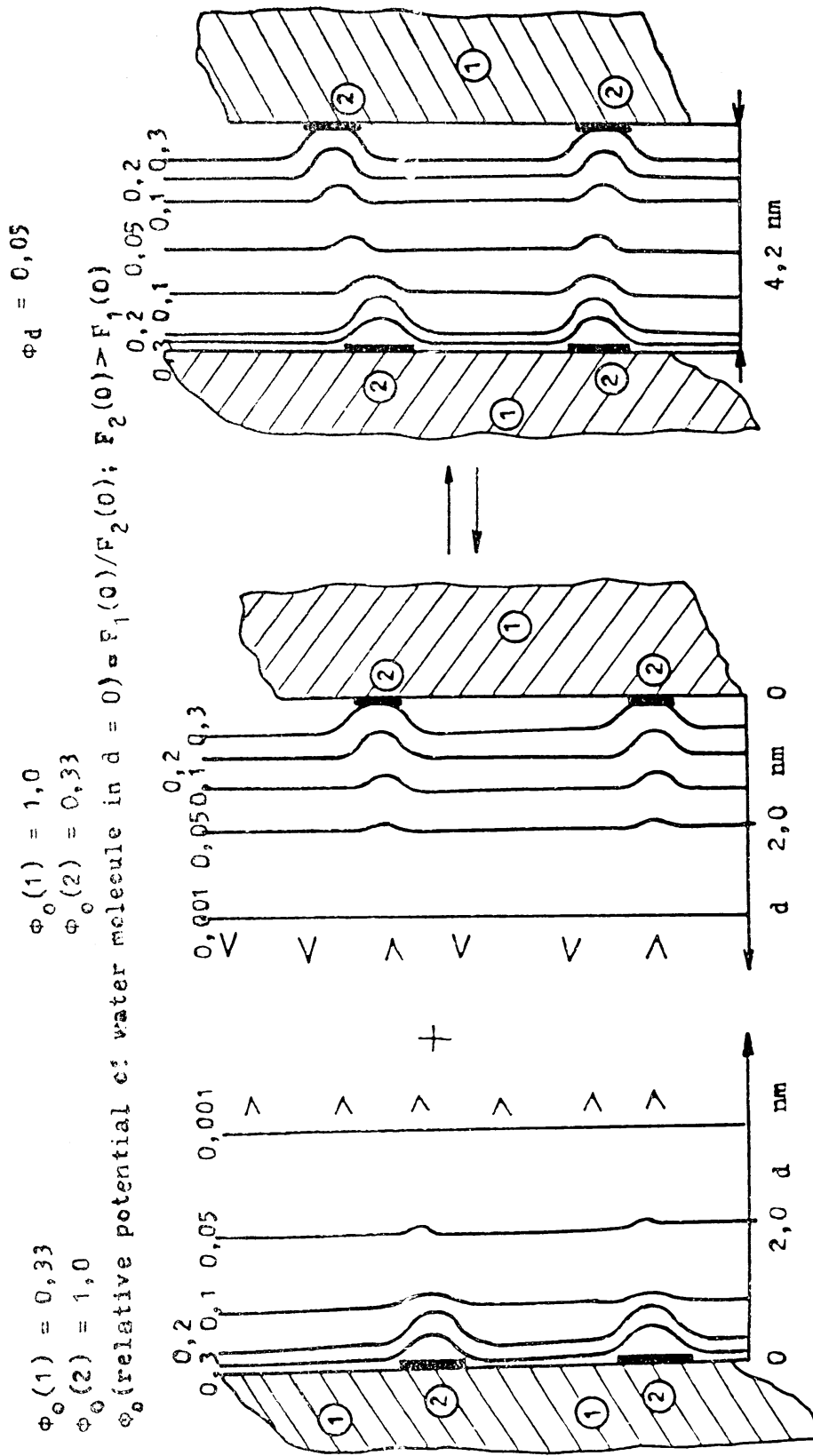Fig. 10. — The course and dependence of isopotentials upon the distance from interacting heterogeneous surfaces attraction $<$; $\wedge$ — Plot of the prevailing orientation of water molecules in the hydration layers ; d — Distance from the phase boundary.

neously in the interaction, a certain equilibrium is established, at which the two surfaces are in a definite optimum distance from each other (see Fig. 10). The interaction thus leads to mutual diffusion of their hydration spheres, which is connected with a change of their structure. These structural changes take place at the molecular level, being accompanied by appropriate heat effects.[9]

As we can see from Figure 9, the action of the hydration forces is strongly influenced by temperature.[8]

CONCLUSION

Although the conception of hydration forces has a main importance in the intensification of refining and other processes, it can be used in other fields of paper and pulp industry, too. It is proved that the principles of hydration bonding system make possible to explain and develop the precipitations (coacervation) of lignosulphonates from spent sulphite liquors, of hemicelluloses from alkaline pulp eluates, and to utilize some synthetic coating pigments as so-called co-binders, etc. Highly important, this conception may be applied to the rheological behaviour of the high concentrated paper stocks and high concentrated hydrated hydrophilic dispersion systems, such as glues, coating colors, impregnation systems, etc

LITERATURE

[1] M. Milichovský, *Zellstoff und Papier*, **38**, 15 (1989).
[2] M. Milichovský, *Tappi J.*, **73**, 221 (1990).
[3] Zellcheming-Merkblatt VI/1/66 : Prüfung von Holzstoffen.
[4] K. Weishaupt, *Wochenblatt für Papierfabrikat.*, **85**, 627 (1957).
[5] C. Skalicky, M. Milichovský, *Cellulose Chem. Technol.*, **25**, 6 (1991) — in print.
[6] W. L. Ingmanson, *Chem. Eng. Prog.*, **49**, 577 (1953).
[7] J. E. Laine T. Sloan, and G. G. Allan, Intern. Symp. "Fundamental Concepts in Refining', Appleton, Wisconsin, Sept. 16—18, 1980.
[8] M. Milichovský, Scientific Papers, Inst. of Chemical Technology, Pardubice, 51, 115 (1988).
[9] M. Milichovský and Vr. Velich, *Cellulose Chem. Technol.*, **23**, 588 (1989).