

VYSOKÁ ŠKOLA CHEMICKO-TECHNOLOGICKÁ PARDUBICE
UNIVERSITY OF CHEMICAL TECHNOLOGY PARDUBICE

SBORNÍK VĚDECKÝCH PRACÍ
SCIENTIFIC PAPERS
57 (1994)

BEHAVIOUR OF HYDROPHILIC COMPONENTS IN PAPER
MAKING SUSPENSIONS - PART III.
PRACTICAL ASPECTS AND BEHAVIOUR OF REAL HIGHLY
CONCENTRATED PAPER MAKING SYSTEMS

Miloslav Milichovský
Department of Wood, Pulp and Paper

Received October 4, 1992

The characterization of influence of water medium on the level of hydration forces enables an evaluation of its influence upon the initial tensile strength of paper, the permeability of the fibrous pulp bed and, particularly, the refining process of pulps. The level of hydration forces in a hydrophilic system is measured by means of determination of the so-called relative hydration factor.

Introduction

From previous parts of this series^{1,2} resulted the important role of so-called hydration forces on the behaviour of the

hydrated hydrophilic dispersion systems. The concept of hydration forces follows from the so-called SCHL theory³⁻⁵ and is based on different possible orientations of water molecules around the hydrophilic phase interface¹. As we can see from Fig. 1 for the interactions of the heterogeneous hydrated surfaces, the hydration forces come into existence on relatively short distances, i.e. they are evoked in highly concentrated systems. The term "high concentration" is understood with respect to the hydration forces, i.e. the concentration of hydrated hydrophilic components in the system where a mutual permeation of the immobilized water layers around all hydrated hydrophilic phase interfaces takes place. In the pulp suspensions this occurs after removing of free water, i.e. when the concentrations of about 10 % and higher are reached.

Practical Significance

From what has been said it also follows that this phenomenon will be important in most real situations in pulp and paper industry. For example by action of these effects the following phenomena will be influenced:

- the transport of high concentrated pulp suspensions,
- the destroying of hyper-molecular pulp structure by pulp beating and chip refining in the production of mechanical pulp etc.,
- the permeability of the wet paper web, i.e. its drainage properties at the press section of paper machine,
- the initial strength of paper, i.e. its behaviour in wet section of paper machine and runnability of the latter,
- some wet-web properties of paper such as wet-web strength etc.
- the rheological properties of highly concentrated hydrated hydrophilic coating colours, glues, impregnants etc.

For good understanding of this phenomenon and for controlling its influence in the majority of processes of pulp and paper technology we have to characterize the water medium from this point of view.

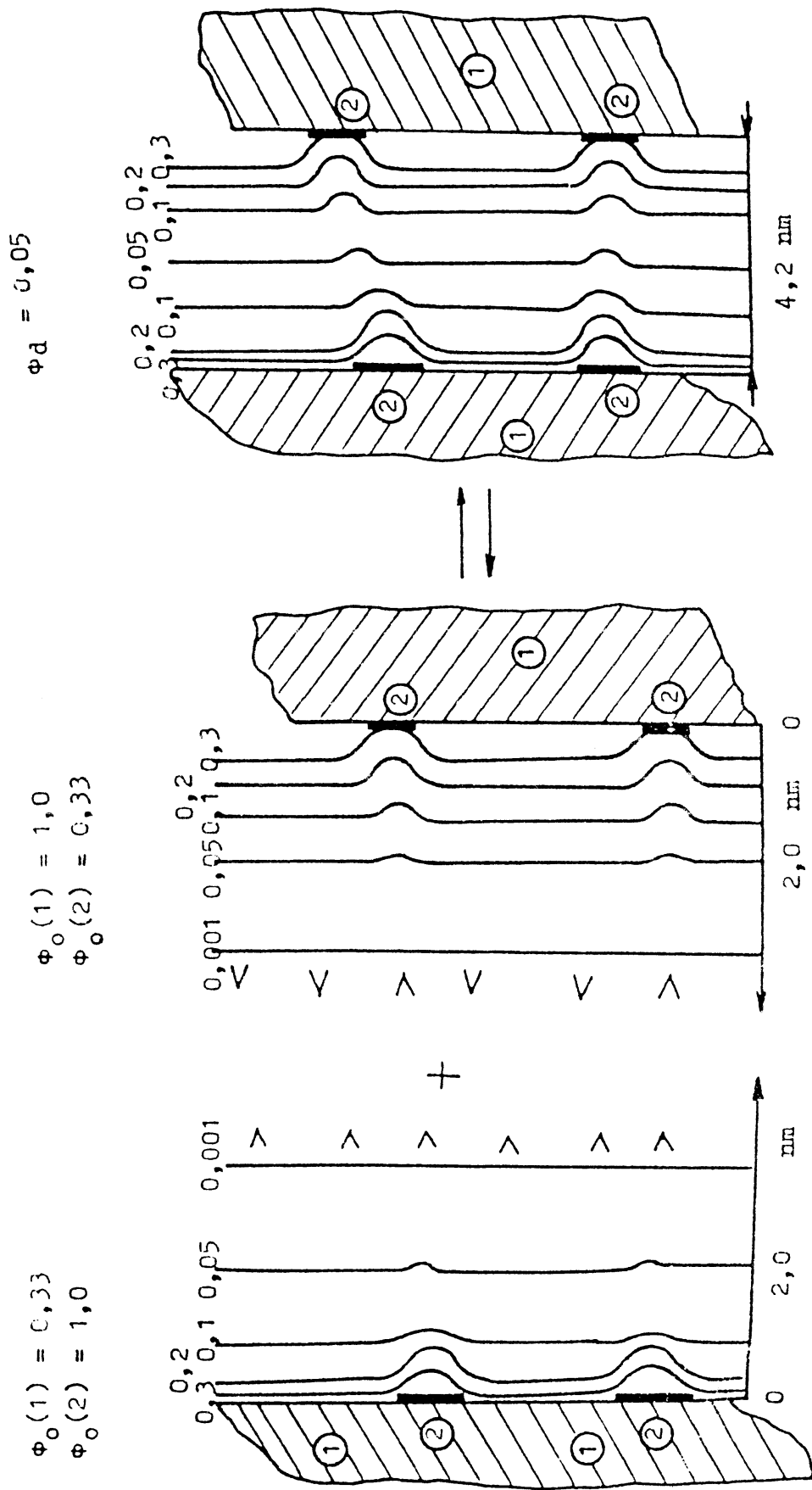


Fig. 1 Course and dependence of isopotentials upon the distance from interacting heterogeneous surfaces - attraction: < ; > - plot of the prevailing orientation of water mole cules in the hydration sphere

Characterizing of Water Medium by Colloid Titration⁶⁻⁷

The effort to characterize the influence of the water medium on electrokinetic behaviour of diluted pulp suspensions or paper slurries is well known. The methods used for this characterization are referred to as colloid titration methods or sometimes as polyelectrolyte titrations and they measure cationic or anionic demands of the real water medium to achieve the isoelectric point.

Characterizing of Aqueous Medium by Relative Hydration Factor³

As it was said in part² II of this series a modelling system was developed whose properties (characterized by rel. hydration factor) make it possible to simulate the influence of different water media on the behaviour of hydration forces or hydration bonds, i.e. on the behaviour of hydrated hydrophilic highly concentrated systems. This influence is given by the value of the so-called rel. hydration factor - g .

If $g > 1$ (in comparison to the blank water), then real water medium acts in negative sense on the level of hydration bonds, i.e. decreases an action of attractive hydration forces. If $g < 1$, then the real water medium acts in positive sense on the level of hydration bonds, i.e. it increases the action of attractive hydration forces.

Influence of Water Medium on Wet Paper Web.

Influence on the Initial Tensile Strength of Wet Paper Web³

Theoretical Assumptions

The strength of bonding system of the wet paper web is defined by mechanical entanglements of the fibres and by the mutual physical bonds between them. The extent of the ability of fibers to bind increases with increasing degree of beating. If a constant contribution to mechanical entanglements is assured in the bonding system of the wet paper web, such as with a constant degree of beating, then the changes in the initial tensile strength of the wet paper web will indicate the changes of in-

terfibre bonds. When these mutual bonds result from the mentioned hydration bonds due to hydration forces, then the initial strength will directly indicate their changes, and the final strength of the wet web will depend upon them.

Experimental

The initial tensile strength of wet paper web (I_p) was determined by the method and with the apparatus described by Brecht-Heiniger^{8,9}. Bleached softwood sulfite pulp was used for these experiments. The results for initial tensile strength were then converted to uniform 15 % dry matter and to basic weight of 100 g/m².

Verification of Experiment

This theory was verified (Fig. 2) by the relationship between initial tensile strength of paper I_p (N) and the relative hydration factor $g = CDD/CDD_0$, where CDD_0 is the critical degree of dilution in paper stock water without other additives. In Fig. 2 the experimental dependences found can be described by the linear relationship given in Eq. (1)

$$I_p = 1.4 - 0.32g, \quad \text{with } r_{xy} = - 0.754 \quad (1)$$

Alternatively, we may use the non-linear relationship of Eq. (2) which better agrees with the dependence:

$$I_p = 1/(1.52g - 0.715)^{0.5}, \quad \text{with } r_{xy} = 0.901 \quad (2)$$

The dispersion variance of experimental values around the calculated relation was caused, in this case, by a lower reproducibility in determining the initial tensile strength³.

Conclusions

If we accept the theoretical concept of hydration forces in hydration bonding system of interacting hydrated hydrophilic pulp fibres, then these results can be taken for a semi-

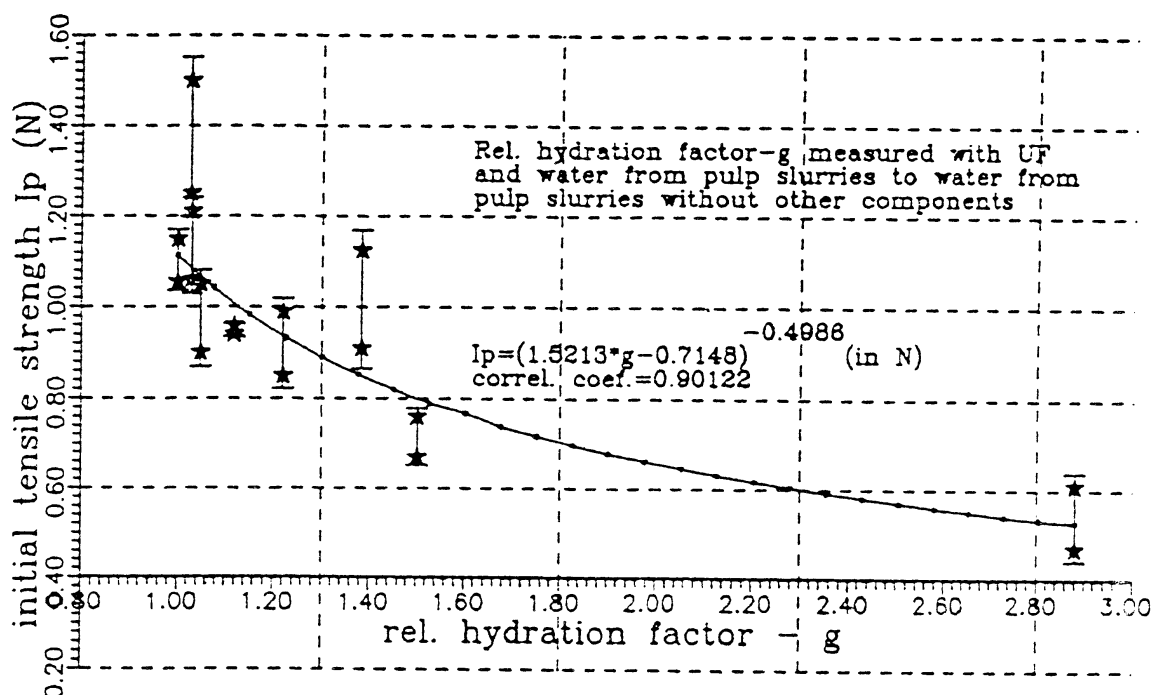


Fig. 2 Relationship of the initial tensile strength, I_p , of paper on rel. hydration factor g : $g = CDD/CDD_0$ (water from slurries without other components); Dry matter substance = 15 %; bleached sulphite pulp beated on 48 SR

quantitative proof of existence of the hydration forces.

Relation of the Permeability of Pulp Bed to the Water Medium¹⁰.

One of important aspects of paper stock draining is the filtration resistance of drained bed which is characterized by its permeability. Ingmanson's method is often used to evaluate the permeation properties of pulp. The relations of the permeability of fibre bed B to the g value characterizing the water medium are plotted in Fig. 3 (CDD_0 corresponds to CDD in water without any other additives). Table I shows the relations of parameters characterizing the fibrous pulp bed (K - Kozeny's constant, S_0 - specific surface, α - specific volume of fibre bed, i.e. volume fraction of fiber bed in m^3 which is presented in 1 kg o.d. matter through which no water can flow) and the properties of permeating water medium characterized with value

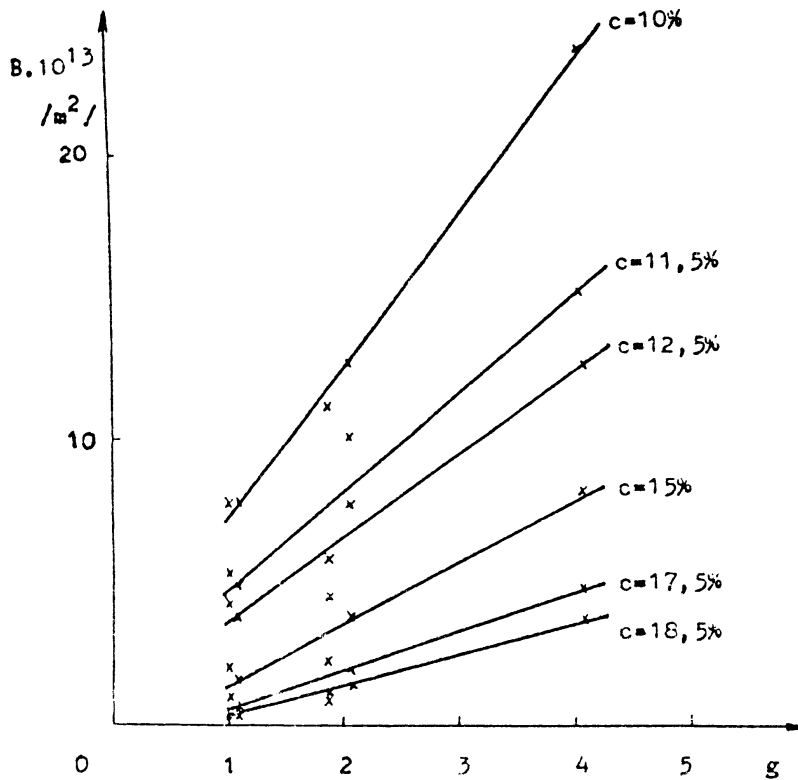


Fig. 3 Relation of permeability of fibre pulp bed to the relative hydration factor: B - Permeability; g - Relative hydration factor (CDD_0 corresponds to the CDD value determined in water without additives); c - Concentration of fibre bed

of rel. hydration factor - g .

Experimental¹⁰

In these experiments the chosen water medium was forced through the fibrous pulp bed of a definite concentration - c which was placed in a suitable apparatus adapted for this purpose. The results were treated according to Ingmanson¹¹.

The pulp material used was a sample of bleached softwood sulfite MgBi pulp.

Table I Relation of parameters characterizing fibre pulp bed to the relative hydration factor - g

Rel. hydrat. factor g	$S_0 K^{0.5} \times 10^{-6}$ m^{-1}	$\alpha \times 10^3$ $m^3 kg^{-1}$
1.000	1.962	3.24
1.866	2.057	2.94
2.044	1.766	2.84
4.044	2.192	1.09

$$\alpha \times 10^3 = -0.3789g + 3.623$$

$$r_{xy} = -0.99979$$

$$g = 1$$

$$g > 1$$

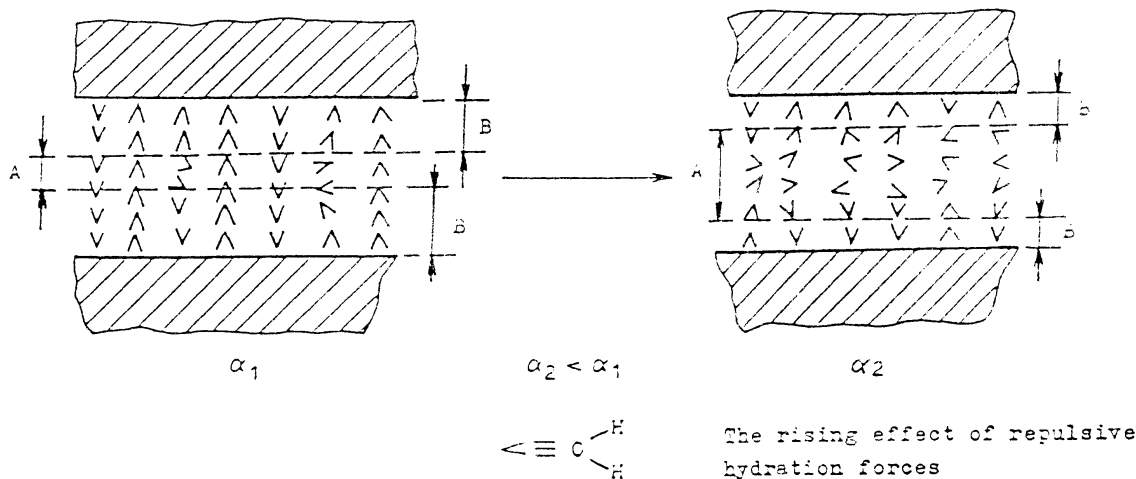


Fig. 4 Scheme of lowering the content of immobilized water around pulp fibres in fibre bed due to the increase of the action extent of repulsive hydration forces among interacting fibres: A - Zone of mobile water; B - Zone of immobilized water; α - Specific volume of fibre bed

Results and Discussion

From Fig. 3 it explicitly follows that the permeability of fiber pulp bed B increases in a linear way in such a water medium that supports the effects of repulsive hydration forces between hydrated phase interfaces or, in other words, it weakens the hydration bonding system. This is such a water medium which supports only one direction in the orientation of water molecules near the by-passed walls of individual pulp fibres. As the

specific volume of fibre bed α falls with the increase of the relative hydration factor g (see Table I) and specific surface of the bed $S_0 K^{0.5}$ is practically constant, logically, the corresponding increase in permeability B is connected with a drop of the so-called immobilized water in the bed or in its inter-fibre space. In other words, the amount of water closely connected to pulp fibres forming the fiber bed at these measuring conditions is decreased with increasing effect of repulsive hydration forces in the bed.

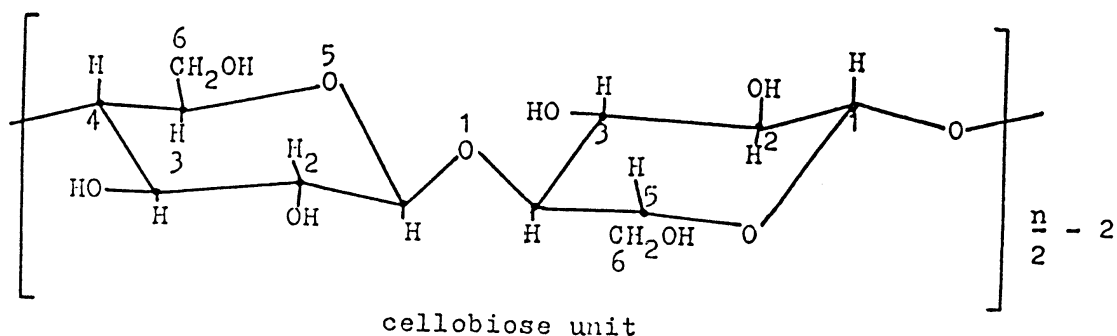
This effect can be explained as it follows from Fig. 4. The zones around the phase interfaces where attractive hydration forces are operating - i.e. the strong hydration bonding system - are filled up with more strongly bound and less mobile water molecules. On the other hand, the zones of the repulsive hydration forces are filled up with less bound and thus more mobile water molecules. The decrease in the action of repulsive hydration forces results in increasing content of immobilized water and thus in a drop of permeability of fiber bed for the given water medium, and vice versa.

The Influence of Water Medium on the Refining Process^{3,5}

The purpose of pulp beating is a disintegration of the hyper-molecular structure of pulp fibres to a maximum extent with minimum destruction of macromolecular cellulose chains. If we accept the concept of hydration forces, then it becomes evident that the water medium plays an important role in pulp beating. Without any appropriate theoretical explanation several substances have been known for a certain time already, whose presence in the water medium of pulp shortens its beating time or lowers the requirements on the refining energy, e.g. some azo dyes (Kongo Red is typical¹).

Cellulosic H-bond System^{3,13}

The hyper-molecular structure of cellulose as the main pulp constituent is formed by an abundant system of hydrogen bonds holding together separate cellulose chains and their segments in



Intramolecular H-bonds: C'(2)OH - C(6)OH; C'(3)OH - O(5);

Intermolecular H-bonds:

- 1) H-bonds linking up single cellulose chains in the planes located one above the other
 C'(2)OH - O(5); C'(3)OH - O(5); C'(6)OH - O(5); C'(2)OH - C(3)OH, C'(6)OH - C(2)OH; C'(6)OH - C(6)OH; C'(6)OH - O(1)
- 2) H-bonds linking single cellulose chains located in the same plane
 C'(6)OH - C(6)OH; C'(6)OH - C(2)OH; C'(6)OH - O(5)

The strength order of particular H-bonds:

Intra C(6)OH - C'(2)OH > C'(3)OH - O(5) ÷ Inter C'(6)OH - C(2)OH ÷ C'(6)OH - C(6)OH ÷ C'(3)OH - O(5) ÷ C'(2)OH - O(5) ÷ C'(6)OH - O(1) > C'(6)OH - C(2)OH in the plane > C'(3)OH - O(5) > > C'(2)OH - C(3)OH

Fig. 5 Main types of H-bonds possible forming the hypermolecular structure of cellulose

more or less oriented zones. The cellulose molecule is wound to a helix due to intramolecular and intermolecular H-bonds, to form the fibre structure of an elementary fibril. These elementary fibrils are joined into microfibrils forming the fibrillar pulp system together with other constituents of polysaccharide and lignin origin. Main H-bond types forming the above molecular cellulose structure, such as follow from molecular models, are presented in Fig. 5. Intramolecular H-bonds are formed either between different planes or on the same plane in which separate

cellulose chains are located that occupy the most advantageous so-called "C1" conformation.

Two or three types of qualitatively different H-bonds can be distinguished^{3,13}, following the scheme presented in Fig. 5:

1. H-bonds of irreversible nature:
 - Glycosidic oxygen with hydrogen atoms of several hydroxyl groups [C'(6)OH - O(1)],
 - Hemiacetal oxygen with hydrogen atoms of several hydroxyl groups [C'(3)OH - O(5), C'(2)OH - O(5), C'(6)OH - O(5)].
2. Reversible H-bonds between amphoteric primary and secondary hydroxyl groups: [C'(2)OH - C(3)OH, C'(6)OH - C(6)OH].
3. Slightly irreversible type: between primary and secondary hydroxyl groups such as C'(6)OH - C(2)OH.

These qualitatively different H-bonds then cause an oriented (crystalline), less oriented, and amorphous zones to occur in native cellulose. Transitions among these portions are not smooth, but the orientation and the degree of coherence in various parts of fiber differ. There can exist different arrangements even in oriented zones. (Three arrangement degrees of oriented portions are usually distinguished¹³).

According to part II of this series, for the behaviour of some hydrated hydrophilic systems CDD (the critical degree of dilution) is a typical quality. We suppose that the hydrated cellulosic materials can also be classified as similar systems but with very low value of CDD.

The destruction of H-bonds with water and water solutions will depend not only on their strength but also on the nature of the H-bonds. As it follows from the first theoretical chapter of this series¹, the destruction can be reversible or irreversible. The H-bonds produced from H-amphoteric groups are usually reversible H-bonds, while the groups of donor or acceptor nature usually form the irreversible H-bonds.

Mechanism of Destruction of H-Bonds Systems by Water^{3,5}

In this mechanism, the water molecules first destroy the H-bonds of reversible nature in such a way that these water molecules are oriented to each of two surfaces in similar manner.

Both the surfaces then become affected with relatively strong repulsive hydration forces. The strengths of these forces are determined by the amount and size of these centers referred to the total area of destroyed surfaces.

Swelling Mechanism

As it was mentioned earlier, the repulsive effects of these forces extend over larger distances than the effects of attractive forces. Consequently, the water molecules penetrate like a kind of wedge between irreversible H-bonds to destroy them, which does not mean that the attractive action evoked by them is lost. In this mechanism the water molecules are oriented to each of the surfaces mostly in the opposite direction. For this reason, attractive hydration forces result between them to prevent the surfaces from moving further away. The interaction of these repulsive and attractive forces results in a kind of equilibrium that maintains the two surfaces at certain distances, separated by hydration spheres of various width. In practice, this action is called "swelling". Further actions of repulsive hydration forces or of outer forces, such as those produced by mechanical beating, may lead to their full removal and to a stabilization of this process - for instance, with diluting.

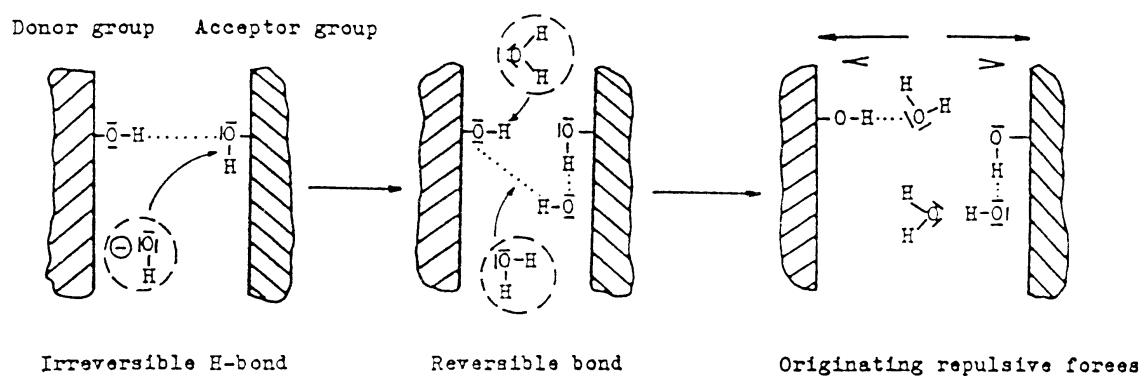


Fig. 6 Schematic representation of the assumed mechanism of destroying irreversible H-bonds by action of OH-ions in alkaline medium

Destruction Mechanism of Irreversible H-bonds with OH⁻ Ions^{5,13}

If we want to increase the destruction ability of water in such a bonding system it is necessary to provide a greater number of H-amphoteric groups in it. Alkaline medium, i.e. OH⁻ ions can be considered to be such an amphoterizing agent (see Fig. 6). The strongly active OH⁻ ions attack the proton - acceptor groups of the irreversible H-bond giving rise to a transition complex which is mutually linked to the still unstable reversible H-bond (see Fig. 6). The latter is then usually attacked with water molecules to produce relatively strong repulsive hydration forces.

Note 1:

The occurrence of H-amphoteric groups in the system causes a decrease of the crystallinic zones. On the other hand, due to the presence of water molecules which are penetrating between the bonds it appears a change of the rheological qualities of such a system. Amphoteric unoriented portions have a more viscous character. With mechanical disintegrating of such a bond system, e.g. with beating, an increase in dissipation energy will occur.

Mechanism of Facilitating the Beating Process^{3,5}

Coincident Orientation of Water Molecules around Beating Aids

A possibility for facilitating the disintegration of the H-bond system in pulp beating is offered by the use of substances that carry some groups on their surfaces that are evenly arranged in space. These substances are able to accept H-bonds that are qualitatively coincident with water. This includes such groups that maintain or cause the coincident orientation of the sheaf of water molecules surrounding them. Fig. 7 presents this mechanism.

Occurrence of Repulsive Hydration Forces between Fiber Surfaces

If these substances, their molecules or aggregates are small enough, or if they have a form suited to the disintegrated system, they penetrate into the interfibrillar or interfibrous space during beating. In the pulp, at disintegrating fiber surfaces, they become linked to the phase of the interface that contains suitably oriented water molecules. The orientation of these water molecules would evoke the hydration forces which attract the penetrating hydrated substance. The other part of this substance - the averted part - will then give rise to repulsive hydration forces, because the orientation of water molecules on this substance is the same as that on the fiber surface to be destroyed. An example of substance having these effects is Congo Red (see Fig. 7). On the basis of the SCHL theory, the capability of Congo Red and similar compounds to improve beating is determined by their convenient structure.

Convenient Structure of Congo Red¹⁴

The structure of Congo Red molecule makes it possible for the molecule to take the linear configuration because the individual molecular fragments have a limited mobility. This mobility is more pronounced for the intramolecular H-bond of the primary amino group to the electron pair on nitrogen adjacent to a benzidine group. This linear configuration makes it easier for the Congo Red molecule to approach closer and cling to the cellulose surfaces. The *trans*-configuration of the azo group secures the formation of chelate H-bond and a convenient linking and orientation of water molecules around the Congo Red molecule and its aggregates. Other beating aids are characterized by structural properties similar to those of Congo Red.

Relationship between Interactions in Dry and Wet State

It follows from the SCHL theory that the mechanisms of phase interaction are different in the dry and wet states of fibrous pulp formations. On the other hand, the two mechanisms depend on each other. The wet action is necessary for the bonds to form in the dry state, and vice versa.

An example of beating aids
Congo Red

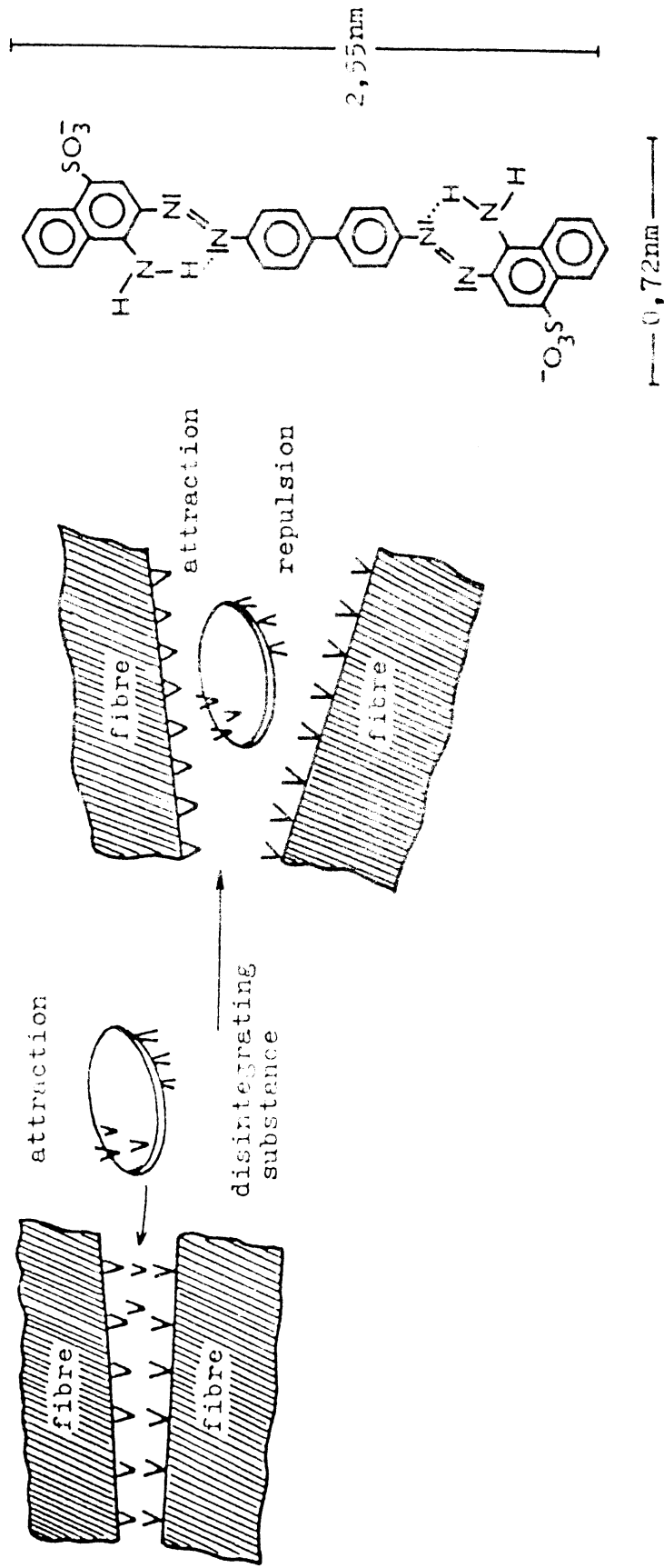


Fig. 7 Schematic representation of the action mechanism for substances facilitating the mechanical destroying of pulp in beating process

Evaluation of the Influence of Hydrated Hydrophilic Substances on the Beating Process³

Relationship between g and Beating Energy

By simulating hydrated, hydrophilic systems with model system we have a chance to examine the influences of the medium and various beating aids on hydration forces and thus on the beating process. Substances that increase the hydration factor f above the value of zero - that is $g > 1$ in comparison to distilled water - will then decrease the effect of attractive hydration forces, i.e. the hydration bonded system, and thus the beating energy. Figs 8 and 9 show the relationships of the relative hydration factor g and the beating energy consumed, both of which serve as evidence.

Verifications of Experimental Results

The relationship of the beating energy consumption C with respect to the beating energy in fresh water to the rel. hydration factor g is given in Fig. 8. This relationship can be des-

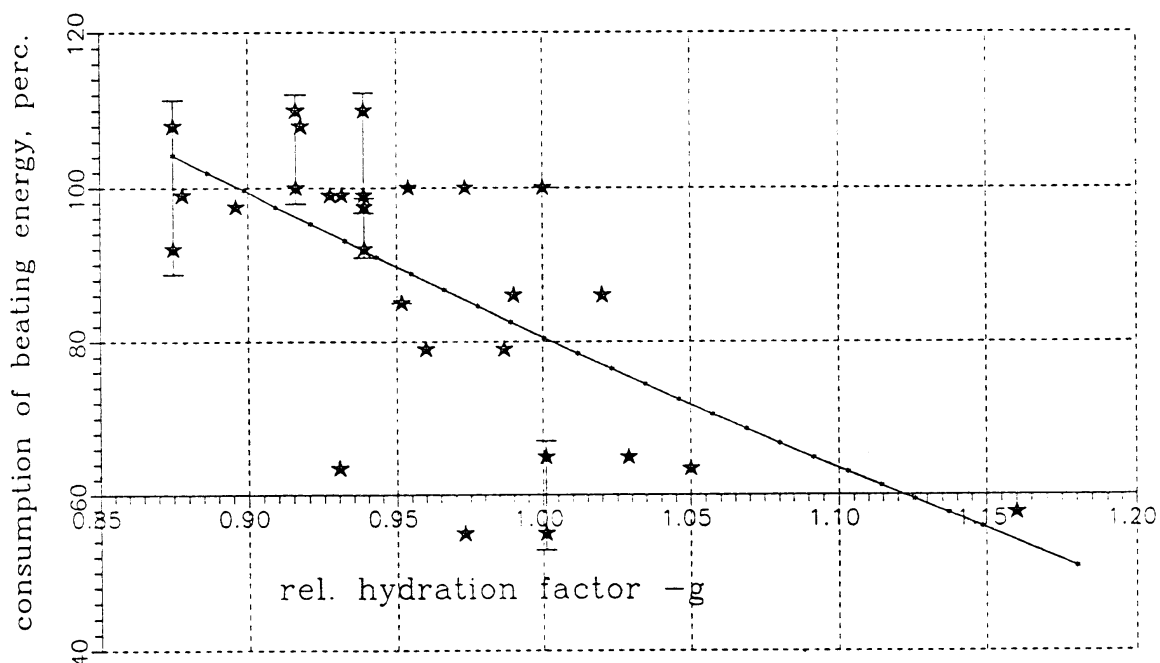


Fig. 8 Relationship the consumption of beating energy, C , on relative hydration factor - g : $g = CDD/CDD(\text{water from nonbeated pulp slurries without other components})$

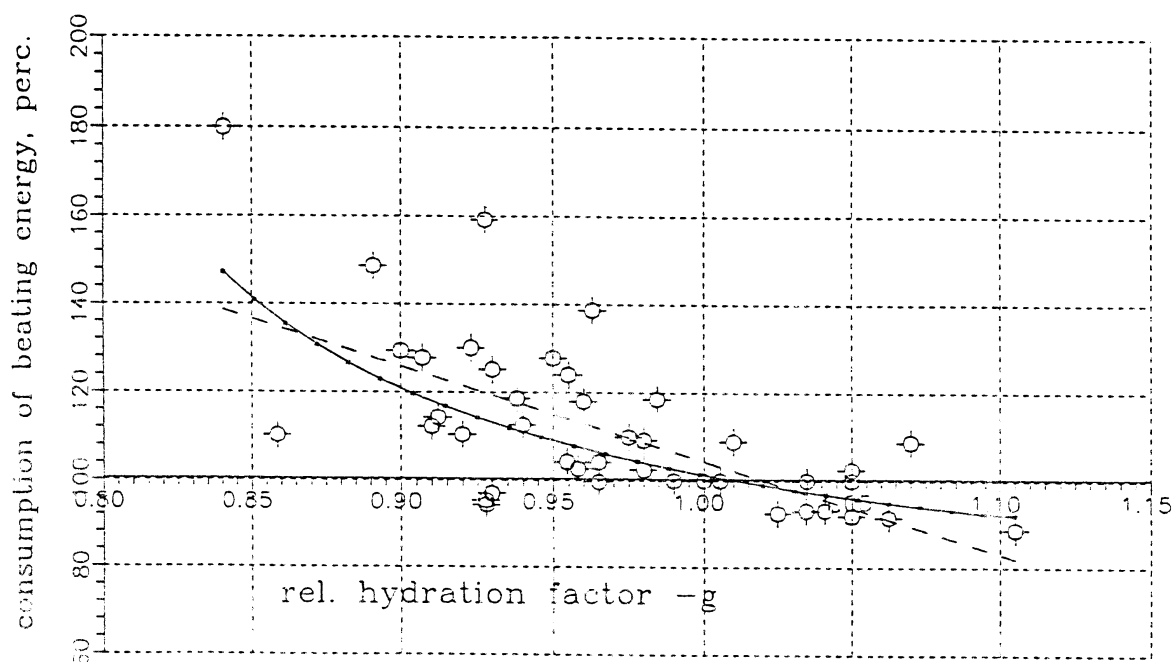


Fig. 9 Relationship the consumption of beating energy (to 50 SR), C , on relative hydration factor, g : $g = CDD/CDD$ (in distilled water).

cribed by Eq. (3) or (4).

$$C(\%) = 260.1 - 178.2g, \quad \text{with } r_{xy} = -0.6067 \quad (3)$$

Preferably, a non-linear relation could be used:

$$C(\%) = (26.75 - 14.87g)^{1.77}, \quad \text{with } r_{xy} = -0.6072 \quad (4)$$

The dependence of consumption of beating energy C with respect to the beating energy in distilled water on the rel. hydration factor g is given in Fig. 9. This relationship can be described by Eq. (5) or (6).

$$C(\%) = 318.85 - 214.43g, \quad \text{with } r_{xy} = -0.66147 \quad (5)$$

Preferably, a non-linear relation could be used:

$$C(\%) = 65.105 + 1/(0.096g - 0.0687),$$

$$\text{with } r_{xy} = 0.70158 \quad (6)$$

A considerable dispersion variance of the values around the calculated relationships is caused not only by the error in measuring the beating energy consumption and factors that can influence it (such as pulp consistency etc). It is caused mainly by possible differences in the distribution of hydration forces in the pulp and in the simulated system of UF-precondensate. The decrease in relative energy for pulp beating varies with the degree of beating (freeness³). The relative decrease in beating energy grows to a lesser extent in the range of 25 - 55 SR and is greater at higher freeness, i.e. above 60 SR. For this reason, the data on beating energy consumption are related to the universal beating degree of 50 SR.

Differences in Experiments with Distilled and Fresh Water as Blank Experiment

The consumption of energy needed for beating pulp to 50 SR with respect to the beating energy in fresh water can be estimated from the dependence shown in Fig. 8 or from Eqs (3) and (4). Notice that the value of g at 100 % of the beating energy consumed does not equal 1 but about 0.9. This means that the synergistic effect of the soluble substances released from pulp and other additives has a positive influence on beating energy requirements. This is not the case in Fig. 9 with distilled water as blank experiment.

Note 2:

The relative hydration factor g in all sorts of experiments was changed only with some low molecular additives which are non-effective in the flocculation of paper stock.

- - - - -

Conclusion

The results from simulated investigations were verified with beating experiments in the laboratory, pilot plant, and on the commercial process scale. A lot of substances exist that

have an influence on beating process in positive and negative sense. Some of these may be seen in Table II. The analysis shows that the effect of beating aids - some of these are colourless compounds (see Tab. II) - is highly dependent on the composition of process water. It may happen that, while a good results are reached with the use of a particular beating aid in one paper mill, anyway the results could be substantially less satisfactory in another one. The badly washed pulps and alum dosage usually deteriorate the beating process. For these reasons, for satisfactory results we have to watch and control the quality of the process water. On the basis of the described theoretical concepts, a simulated system can be prepared to serve as a simple tool for evaluating the action of beating aids and the influence of a water medium on beating, runability of paper machine, transport of highly concentrated pulp suspensions etc.

Table II Influence of several auxiliary substances upon hydration forces in a simulated system formed by UF pre-condensate

Substance	f	Increase of hydration forces	Dosage %
Congo Red	0.70	repulsive	1.0
K ₂ SO ₄	- 0.11	attractive	3.0
Al ₂ (SO ₄) ₃	- 0.15	attractive	6.0
Process water	- 0.11	attractive	-
NaCl	0.07	repulsive	3.0
Acetamide	0.60	repulsive	20.0
Na Polystyrene	- 0.24	attractive	1.0
Maleinate			
Na Polystyrene	0.29	repulsive	10.0
Maleinate			
2,4,6-triamino	0.025	repulsive	0.5
-s-triazine			
Distilled water		-	-

References

1. Milichovský M.: Part I. of this Series, Sb. Věd. Prací, Vys. Škola Chem. Technol., Pardubice 56, (1992/93).
2. Milichovský M.: Part II. of this Series, Sb. Věd. Prací, Vys. Škola Chem. Technol., Pardubice 56, (1992/93).
3. Milichovský M.: Tappi J. 73, 221 (1990).
4. Milichovský M.: Sb. Věd. Prací, Vys. Škola Chem. Technol., Pardubice, 51, 71 (1988).
5. Milichovský M.: Zellstoff und Papier 38, 15 (1989).
6. Horn D.: Progr. Colloid & Polymer Sci. 65, 251 (1978).
7. Brouwer P.H.: Tappi J. 74, 170 (1991).
8. Zellcheming - Merkblatt VI/1/66: Prüfung von Holzstoffen.
9. Weishaupt K.: Wochenblatt für Papierfabrikat 85, 627 (1957).
10. Skalický Č., Milichovský M.: Cellulose Chem. Technol. 26, 85 (1992).
11. Ingmanson W.L.: Chem. Eng. Prog. 49, 577 (1953).
12. Laine J.E., Sloan T., Allan G.G.: Inter. Symp. "Fundamental Concepts in Refining", Appleton, Wisconsin, Sept. 16-18, 1980.
13. Milichovský M.: Sb. Věd. Prací, Vys. Škola Chem. Technol., Pardubice, 51, 115 (1988).
14. Milichovský M.: Sb. Věd. Prací, Vys. Škola Chem. Technol., Pardubice, 51, 149 (1988).