Rheosedimentation – typical and characteristic phenomenon of paper matter

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Abstract

As well known, the hydrocohesive interbonding system among components of paper – predominantly among fibre components – is realized through H-bonds. Direct connection between paper suspension and paper is not because third state of paper matter exists between paper and paper suspension – the wet web of paper. As known, a bonding system of wet web state is realized through so called Campbell's effect being followed by origination of H-bonding system but only in water media, i.e. among paper components with so called hydrocohesive properties. It is well shown as typical for this behaviour an ability of these components in water medium to form a comprehensive fibre space net.

Behaviour of this third state of paper matter corresponds to general formula describing the movement of continuum and it is typical for components with marked papermaking properties. As evidence supporting this description is phenomenon being called as rheosedimentation because it is observable during sedimentation of diluted fibre slurries. The movement of fibre space net during rheosedimentation is described by equation

$$\frac{t}{(h_0-h)}=\alpha+\beta\cdot t$$

which follows from solution of general continuity equation.

Symbols h_0 and h is the high of boundary level a fibre space net – water at time t = 0 and t, respectively. Parameters α and β are characterizing a velocity of sedimentation at high h_0 and a final concentration of sedimented fibre space net, respectively.

It was shown that:

- The rheosedimentation is decisive for everyone fibre component in itself papermaking ability and it is useful as indicator of this one;
- Both sedimentation velocity and final concentration of sedimented fibre components are depending on fibre morphology;
- The final concentration is sensitive to interbonding ability of fibre components creating a fibre suspension – it appears that with increasing this ability the final concentration of sediment decreases;
- Both of these parameters, i.e. sedimentation velocity and final concentration of sediment are strongly dependent upon hydration ability of fibre components – with increasing this hydration ability both parameters decrease.

Introduction

It is well known that paper matter exist in the three forms:

- The suspension form;
- The wet web paper form;
- The dry web paper form.

As it can be seen on the Fig. 1, all of these forms are step by step connected by origin and destruction of paper. It is also well known that these processes are not quite reversible.

However, a suspension form of paper matter is existed in two phases (see Fig. 2) because pulp slurry is so called "rheo-sedimented" after reaching approximately the pulp concentration of 1 kg/m^3. At low concentration - the concentration of a pulp slurry is lower as 1 kg/m^3 – the individual fibres, fragments of fibres, particles etc. are free moving in suspension independently each of other – first phase of the suspension form of paper matter. At second phase of this one – the concentration of pulp slurry is higher as 1 kg/m^3 – the individual components in suspension are interacting so that they contact mutual and partly permeate with their water shells. There it is formed a network from pulp fibre components of pulp suspension enabling us to observe this behaviour during so called process of rheosedimentation (Milichovský[3-4]) because fibre network is sedimented due to itself compression respective subsiding (see Fig. 5) by gravity.

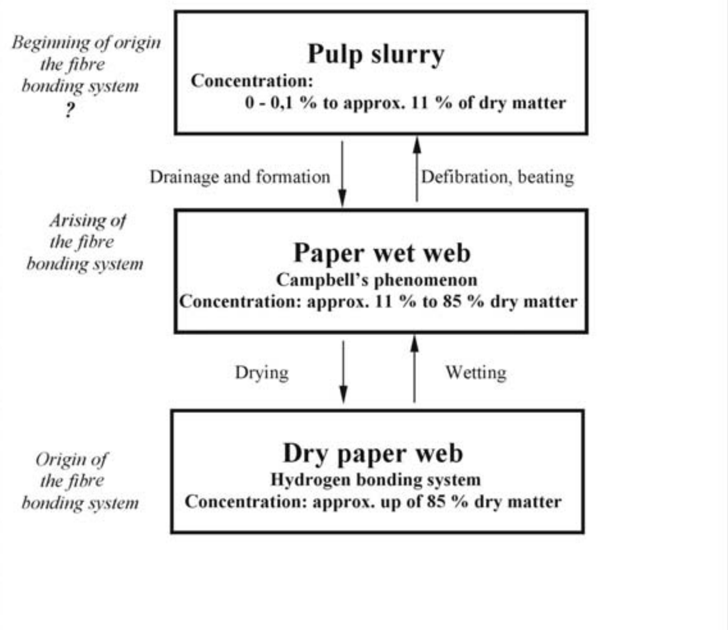

Fig. 1: Schematic representation of creation and destruction of a paper web.

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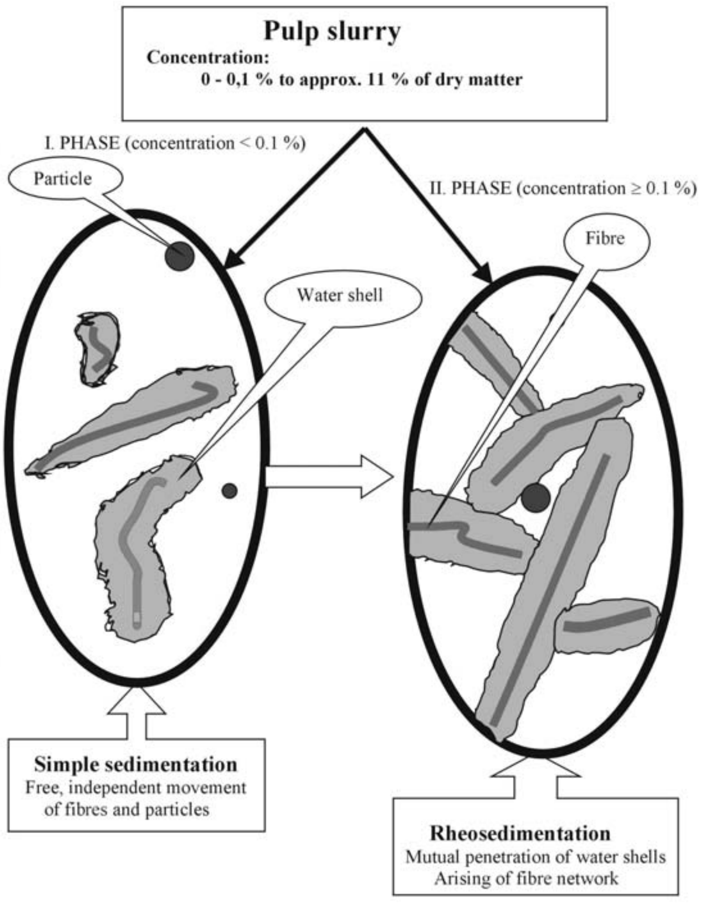

Fig. 2: Suspension form of paper matter.

The wet web form of paper matter holds together by adhesion of fibre and non-fibre components of wet web due to so called Campbell's effect[1] (see Figures 3 and 4). The bonding system of paper wet web is formed namely by presence of water among components of a paper web. At given constancy adhesion tension, an adhesion force (see Fig. 4) between surfaces increases hyperbolical with decreasing of depth of water layer between them. From it follows as well that an extent of bonding system is not really dependent on an water amount in paper web but depends only upon amount of vicinal water located in micro pores of paper web being characterized for instance by value of WRV. At constancy dry matter substance, the extent of paper web bonding system has to arise with increasing of its WRV and vice versa. This prediction was confirmed by lot of exactly executed experiments of Klepaczka at al[2]. It has been showed that characteristic dry matter substance of paper web, in which an measurable shrinkage of paper web is appeared, is strongly dependent only on WRV of pulp slurry and stretch tension of paper web during its drying – with WRV increasing of this characteristic dry matter is decreasing.

As also convenience, after removing last water molecules of water between fibres the firmly hydrogen-bonding system of paper web is originating (e.g. Nissan[6]) – the strongest form of paper matter, the dry web form. We can call this bonding system among particularly fibre components of paper web as hydrocohesion because it is originated only in presence and by help of water or water medium. Due to this one process, any strength properties of paper are given by magnitude and extent, i.e. by quality and quantity, of hydrocohesion among all components particularly fibres in dry state of paper matter.

Summarizing up of the all above mentioned facts, we can conclude that any confluence have to be between behaviour of dry form and suspension form of paper matter especially its second phase because the fibre network represents in fact a continuum from which is formed a proper paper web. In accordance with this matter of fact, any information of behaviour and properties fibre network continuum have to given us a meaningful information of mechanical, physical, strength etc. properties of paper. The simplest method as to observe the fibre network behaviour is so called method of the rheosedimentation.

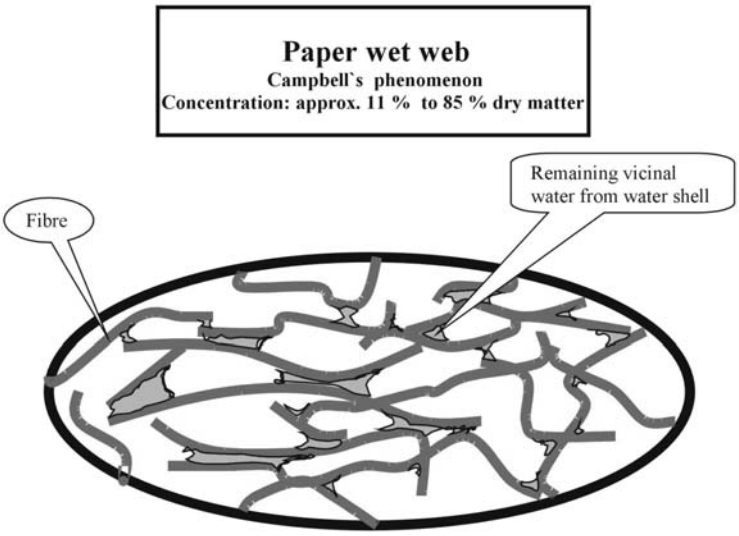

Fig. 3: Wet web form of paper matter.
Detailed description of paper bonding system in a wet state.

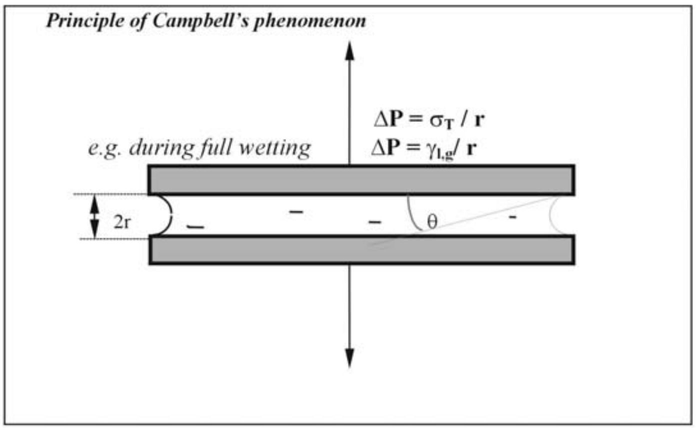

Fig. 4: Schematic representation of Campbell's adhesion between two wetted plates as model of bonding system arising among fibre and non-fibre components in paper wet web.

Notes:

σ_T - *adhesion tension between liquid and solid plate;*
for full wetting follows: $\sigma_T = \gamma_{l,g}$ *;*

$\gamma_{l,g}$ - *surface tension of used liquid;*

θ - *contact angel.*

Rheosedimentation

Fig. 5 presents the principle of rheosedimentation. A movement of rheosedimenting fibre network continuum is very well described (see Milichovský^4) by general equation of continuity (see Eq. /1/) as similar as Smellie and La Mer^7 used this equation to description of subsidence of uraniferous phosphate slime. As showed in Fig. 5, the observation of a proper rheosedimentation is very simple because rheosedimenting fibre network is characterized by high of this fibre network in cylindrical vessel. By use of Eq. /2/ which was received by solution of Eq. /1/ for given boundary condition, we can verify any dependences a height of rheosedimenting fibre network *h*, vs. time *t*, with satisfied uncertainty of calculation, i.e., correlation coefficient of verified data is at least 0.95.

<u>Notice.</u>

Generally speaking, lot types of curves h vs. t exists (Milichovský ^{4}*) because real papermaking suspensions do not consist only of fibre network forming components. Non-rheosedimenting components distort then a shape of h vs. t curves. This reality is often observable at beginning of rheosedimentation process. Owing to this fact, we have to eliminate a distorting initial data part of h vs. t curve from further verification by use of correlation coefficient as choice criterion.*

Compression of fibre network is described by general equation of continuity:

$$\frac{d\rho}{dt} + div(\rho \cdot v) = 0 \qquad /1/$$

ρ = volume density of fibre network, i.e., the volume of solid per unit volume of free water

$v = -(dh/dt) \rightarrow$ the rate of fall of the level between fibre network and clear water

for $t = 0$ is $h = h_0$

for $t > 0$ is $h < h_0$

Verification:

$$\frac{t}{(h_0 - h)} = \alpha + \beta \cdot t \qquad /2/$$

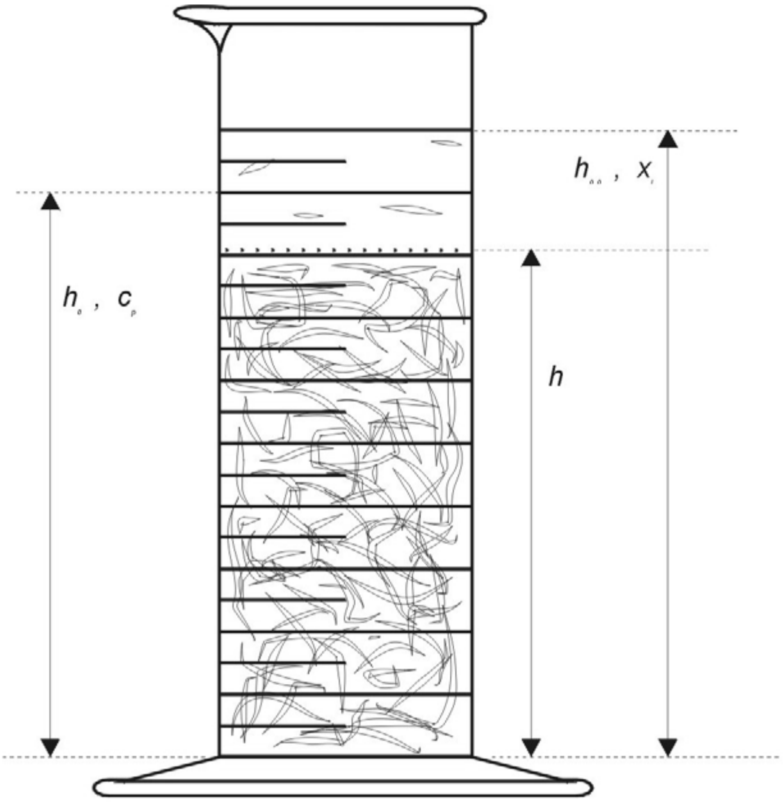

Fig. 5: Rheosedimentation principle

$\alpha = 1/v_0$ for initial fibre network concentration c_p

$v_s = 1/\alpha_s$ standardized rheosedimentation velocity for $c_p = 1$ kg/m^3

β characterised final concentration of fibre network - c_k because: $c_k = h_{00} \cdot x_1 \;/\; \left(h_0 - 1/\beta\right)$

Comment: *The tendencies of pulp slurry to rheosedimentation rapidly get worse with increasing of c_k and particularly v_s*

Simple sedimentation:

$$v = \frac{V \cdot (\rho_s - \rho_l) \cdot g}{f} = \text{constant} \qquad /3/$$

Rheosedimentation:

$$v = \frac{\alpha}{(\alpha + \beta \cdot t)^2} = f(t) \qquad /4/$$

The following equations /5/ and /6/ by use of constants independent of time α and β enable us to calculate an initial velocity v_s (mm/s) of rheosedimentation standardized on initial concentration of pulp suspension, $c_p^s = 1$ (kg/m^3)

$$v_s = \frac{1}{\alpha} = \frac{c_p^2 \cdot v_0 \cdot \left(c_k - c_p^s\right)^2}{\left(c_k - c_p\right)^2 \cdot \left(c_p^s\right)^2} \qquad /5/$$

and final concentration of rheosedimentation, c_k (kg/m^3)

$$c_k = \frac{h_{00}}{\left(h_0 - 1/\beta\right)} \qquad /6/$$

where $v_o = 1/\alpha$ and $c_p = (h_{oo} \,.\, x_1) / h_o$; h_{oo}, h_o and h is height of the water level, initial height of the subsidence level and height of the subsidence level after time t, respectively (see Fig. 5); x_1 is concentration of the pulp in a measured suspension.

As predicts Eq. /5/, if initial standard velocity of rheosedimentation, v_s achieves of an unlimited physical unrealistic value than it indicates no tendency of fibre slurry to rheosedimentation, i.e., the pulp forming of this fibre slurry behaves as non-rheosedimenting pulp fibre.

In contrast to a simple Stokes` sedimentation distinguishing itself by constancy velocity of subsidence of any individual particles being only dependent on their shape and density difference between clear liquid and the particles, the rate of movement of the boundary between clear liquid and the fibre network during rheosedimentation is not constant and a velocity of subsidence the fibre network decreases with prolonged time of rheosedimentation (compare Eqs. /3/ and /4/). If rheosedimentation is also occurring, then a free movement of individual fibres and particles is limited substantial by their mutual interactions in fibre network. On the other hand, due to a random movement of fibres, particles, etc. having a different shape and geometry during their sedimentation or agitation with pulp slurry, a haphazard association of these components exhibits any fibre network as well. However, the process of fibre network compression is in full deterministic manner depending only upon:

- the quality, quantity and distribution of in interface the attractive and repulsive forces acting among fibre and non-fibre components;
- the density of swelled fibre and non-fibre components;
- the mechanical properties as stiffness, sheet-yielding and persistence of fibre components;
- the shape and geometry of fibre and non-fibre components;

- the presence of flocculating agents in pulp slurry, their quality and amounts.

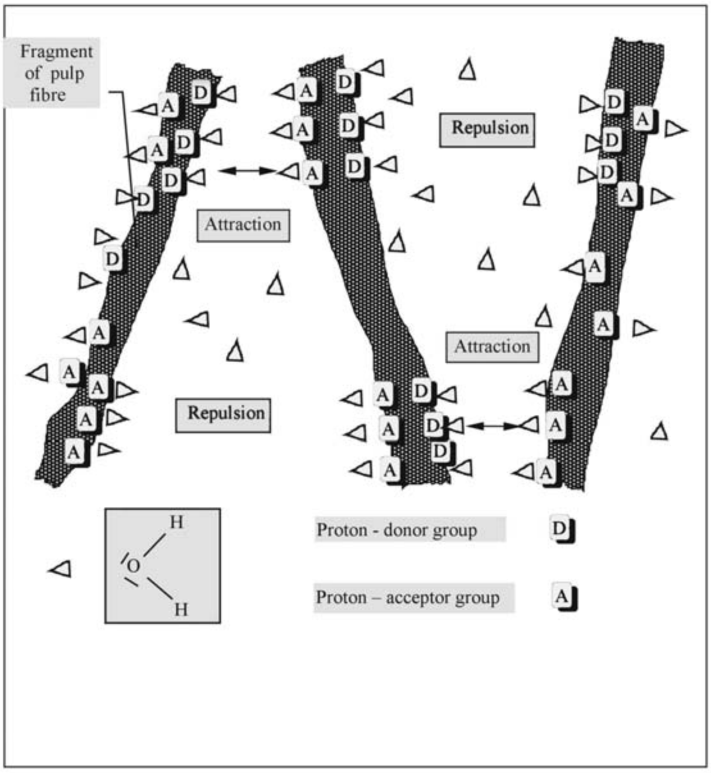

Fig. 6: Schematic representation of origin and character an action of repulsive and attractive hydration forces during interaction of cellulosic fibre materials in water.

The system of acting repulsive and attractive forces among micro-localities of paper-forming fibres is forming a weakest bonding system inside of paper matter. It is assumed that this bonding system is created by action of repulsive and attractive hydration forces (Milichovský[5]) as depicted in Fig. 6 – the hydration bonding system. The bonding system of hydration bonds is preceding to creation of proper bonding system inside of dry paper matter by means of H-bonds.

Formerly was shown (Milichovský[4]) that rheosedimentation is strongly dependent on intensity of pulp beating, i.e., with increasing a degree of beating the rheosedimentation gets slowly, and the standard rheosedimentation velocity can be used for determination of a character the beating process. It was found theoretically and proved by experiments that with increasing of pulp beating, the standard velocity of rheosedimentation is decreasing markedly faster for fibrillation than for fibre cutting. Further it was found that the course of the initial velocity of rheosedimentation is different for dried and never dried pulps, i.e. dried pulp rheo-sediments at comparable condition more rapidly than never dried pulp. This phenomenon was also depending on the degree of delignification, i.e., on a composition of tested the cellulosic material. The more the pulp was delignified, the deeper the phenomenon.

In the case of dried pulp, a decisive role in behaviour of rheosedimenting pulp slurry is played by time of pulp water soaking – with prolonged time of pulp soaking the standard velocity of rheosedimentation is decreasing. For this reason, it is recommended, any dried pulp is soaked before defibrillation in water at least 16 hours.

Theoretical background

It is meaningful to use following a simple hypothetical model to easy understand to process of rheosedimentation (see Fig. 7). Let us consider to following case of fibre suspension composed of equally rod fibres with reasonably flexibility and mutually bonding abilities. Due to gravity, the rod particles move in very diluted state independently each of other according to the Stoke's law, but their concentration is step-by-step increasing. As depicted in Fig. 7, after reaching the initial fibre network concentration, c_p (see Fig. 5), the independent movement is stopped, because bonding ability of micro localities localized in surfaces of end-parts of rod particles. Excluding interstitial mutual movement of the particles, a further movement of these ones is then possible only by compression of created fibre network,

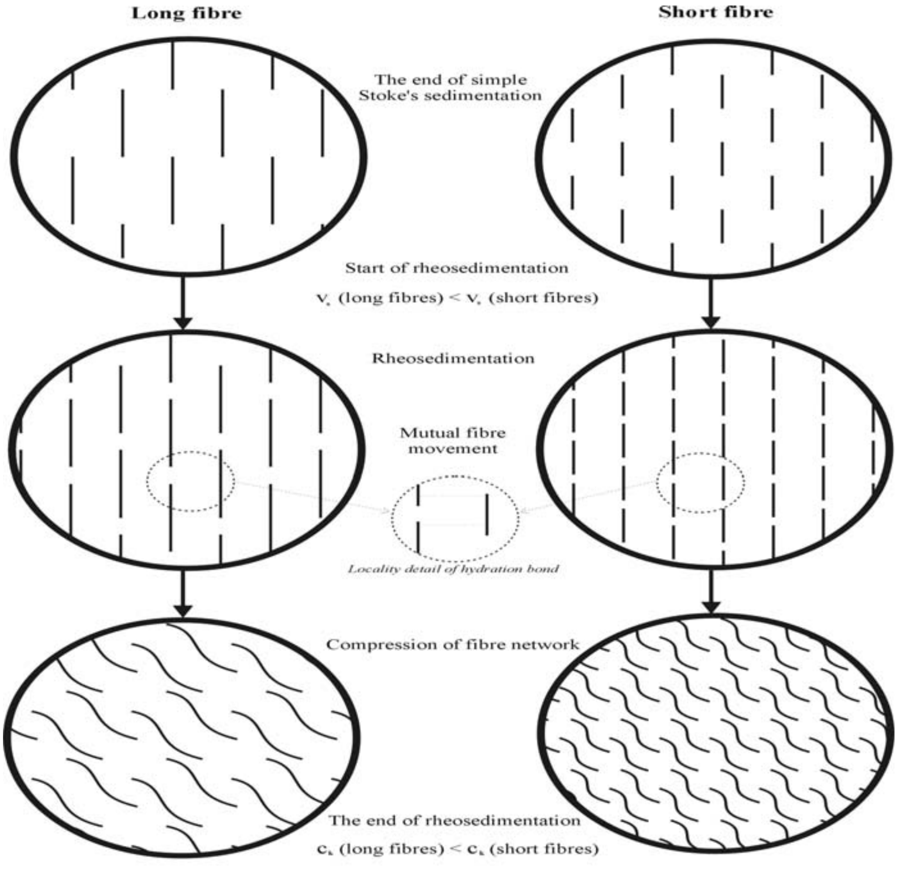

Fig. 7: Schematic representation of rheosedimentation mechanism

i.e. by rheosedimentation.
On basis of this hypothetical model we can conclude that:

1. Non-rheosedimenting fibres are distinguishing by
    - non-bonding abilities
    - bonding abilities but high rigidity of fibres enabling them no compression of created fibre network
    - non-bonding abilities and relatively high rigidity.
2. Compression of fibre network during rheosedimentation is possible due to flexibility of individual fibre.
3. More compact fibre network and faster rheosedimentation is achieved with short fibres than long fibres at comparable conditions (see Fig. 7), because the short fibres need shorter distance to achievement mutually close structure in network as long fibres.
4. Compression of fibre network during rheosedimentation gets slowly with increasing fibre stiffness and vice versa, i.e. both rheosedimentation parameters v_s and c_k decreases with increasing of fibre stiffness.

It was shown that for rheosedimenting fibres are important two papermaking significant properties:

- their bonding abilities
- their flexibility.

While the attractive forces approaching mutual the micro localities of interacting fibres are most important at start of rheosedimentation, the flexibility of fibres determines predominantly compression degree of fibre network at final stage of rheosedimentation, i.e. the standard velocity of rheosedimentation v_s is depended mostly of bonding abilities and final concentration of rheosediment, c_k is mostly influenced by flexibility of fibres in fibre network. At comparable condition an increase of v_s and a decrease of c_k indicates fibres with improving bonding abilities and persistence, respectively and vice versa.

Experimental Method

From comprehensible reason to ensure a good reproducibility of rheosedimentation experiments, we must very anxious control an amount of air in pulp suspension. For this reason, it has been used in all experiments inclusive a preparation of fibber suspension the diluting water being prepared by deaeration of distilled water by occasionally gentle agitation with glass rod during at least 24 hours at temperature of 22^o C. Before every rheosedimentation experiment, the diluting water was further cooled to temperature of 15^o C by dosed pieces of ice followed by dilution of pulp slurry to concentration of approximately 1 kg/m^3 with this diluting water and carefully agitation of this pulp suspension. The suspension agitation was realized in 2 l graduate cylindrical vessels with inner diameter 10 cm by up and down movement of special agitator having been made by connection of a rod and disc of diameter 8 cm with 1 cm holes. During up and down movement with agitator we must avoid to any pulling out of disc part of agitator from pulp suspension. Due to this one method of agitation we were able to ensure a full initial homogeneity of pulp slurry without its idle aeration.

In all experiments we used only pulp probes in dried form. For this reason, the pieces of bone-dry pulp probes were soaked over night with diluting water before every experiment.

Experimental Results and Discussion

Any measurements of the rheosedimentation indicate a closely connectivity of rheosedimenting phase of the suspension form of a paper matter with its dry web paper form, especially with strength and mechanical properties of paper. As results in Table 1 demonstrated, a lost of pulp slurry to rheosedimentation indicates the loss in ability of paper fibre components to form firmly bonding system of dry paper web, i.e., this pulp fibre has no paper-forming abilities. For this reason, a chemical modification of cellulose being presented in Table 1 by two sorts of nitrocellulose leads to loss in its ability to rheosedimentation although its water retention ability, WRV is relative high. As follows of Table 1, a lost of pulp fibres to rheosedimentation is well indicated by unrealistic values of standard velocity of rheosedimentation – v_s (more than 20 mm/s).

Table 1. Tendency of the pulp slurries to rheosedimentation vs. WRV and paper strength.

Pulp	**Burst strength of paper[*] (kPa)**	**Water retention ability of pulp WRV (%)**	**v_s ** (mm/s)**	**c_k *** (kg/m^3)**	**Tendency to rheosedimentation**
Bleached sulphite pulp, 17 SR	1500	120	10	6	excellent
Nitrocellulose (11,4% N), 85 % Bleached sulphate pulp, 15%	immeasurable	70	$1 \cdot 10^4$	27	insignificance
Nitrocellulose (13,3% N), 85% Bleached sulphate pulp, 15%	467	40	900	17	bad
Nitrocellulose (11,4%), 100%	none	63	∞	40	none

Notes:

* *The burst strength is recalculated to grammage of paper 1000 g/m^2;*

** v_s *- the standardized sedimentation velocity recalculated to initial suspension concentration, $c_p = 1$ kg/m^3;*

*** c_k *- the final concentration of sediment when $t \Rightarrow \infty$.*

Table 2. Rheosedimentation parameters obtained for different sorts of chemical pulps.

Pulp	**v_s ** *(mm/s)***	**c_k *** *(kg/m^3)***
Magnefite bleached hardwood pulp (Beech)	12.0 ± 0.2*	7.2 ± 0.2
Magnefite bleached softwood pulp (Spruce)	1.7 ± 0.1	3.6 ± 0.2
Magnefite bleached pulp (25% hardwood, 75% softwood)	2.6 ± 0.1	4.0 ± 0.1
Sulphite bleached pulp (MgBi) TCF	2.3 ± 0.2	4.2 ± 0.2
Sulphite bleached pulp (MgBi) ECF	2.6 ± 0.1	3.8 ± 0.1
Sulphite non-bleached pulp (CaBi)	2.2 ± 0.1	3.8 ± 0.1
Sulphite bleached pulp (CaBi)	1.9 ± 0.1	3.7 ± 0.2
Sulphite bleached pulp (NaBi)	2.1 ± 0.1	3.4 ± 0.1
Sulphate bleached hardwood pulp (Eucalyptus) NIST standard reference pulp 8494	3.9 ± 0.4	5.7 ± 0.1
Sulphate bleached softwood pulp, (68% White Spruce, 32% Lodgepole Pine, trace of Balsam Fir) NIST standard reference pulp 8495	1.2 ± 0.3	3.3 ± 0.2

Notes:

* *95% confidence limits;*

** v_s *- the standardized sedimentation velocity recalculated to initial suspension concentration, $c_p = 1$ kg/m^3;*

*** c_k *- the final concentration of sediment when $t \Rightarrow \infty$.*

The results collected in Table 2 are documenting the behaviour of typical chemical pulp during rheosedimentation. As follows from this Table 2:

- the final concentration of sediment, c_k approximately (roughly) increases with arising of the standard velocity of rheosedimentation;
- the lowest both value of rheosedimentation, v_s and the packing rate characterized by concentration, c_k are achieved by sulphate pulps being distinguished as well known by the highest stiffness and persistence;
- at comparable conditions, the short fibre pulp (hardwood) achieves higher values of v_s and c_k as compared with long fibre pulp (softwood);
- the stronger and stiffer a paper is, the rheosedimentation parameters v_s and c_k of the pulp composing of this paper are lower;
- any increase of the final concentration, c_k relative vs. standard rheosedimentation velocity, v_s indicates a weakening of cellulose skeleton matter of pulp characterized for instance by lowering of its mechanical properties (compare TCF Mg-bisulphite bleached pulp vs. Ca-bisulphite non-bleached pulp or Na-bisulphite bleached pulp).

Explanation of received results

It seems to be illogical that coarse and long fibres of softwood pulps subside slowly as well as they form network of small packing rate than short fibres of hardwood pulps. To explain this behaviour, it have to be supposed that individual fibres are connected mutual by help of relative firmly hydration bonds between micro-localities concentrated on their ends (see Fig. 7). Certainly, during separately movement of these fibres in pulp slurry evoked for instance by agitation, it is possible that the initial fibre orientation is controlled by action of attractive electrokinetical forces followed by attractive hydration forces in quiet rheosedimenting state.

For this reason, during rheosedimentation a network composing of pulp fibres is further only compressed without mutually straight-lined fibre movement. The fibres forming a fibre network predominantly only are bending with occasionally translation. Owing this fact, the subsidence velocity and final concentration of pulp slurry after rheosedimentation are strongly dependent on geometry and mechanical properties of fibres, i.e., upon their length and coarseness as well stiffness etc. Any weakening, or disturbing of cell-wall matter, e.g. by intensive chemical treatment, it appears particularly by increasing of final rheosedimentation concentration, c_k with regard to standard rheosedimentation velocity, v_s.

Conclusion

The existence of rheosedimentation proves an individuality and specialty of paper matter in which dry paper introduces only one part of its forms being in tune with complexity and conformity in behaviour and properties of paper matter, respectively. The different forms of paper matter are not given by any physical parameter, e.g. temperature, but any form of this one is only dependent upon amount of water in this fibre matter. For this reason, the non-rheosedimenting pulp slurry is not forming a really paper matter. Basic condition of rheosedimentation is an ability of pulp fibre to form a network with special behaviour, i.e., due to weak bonding system a fibre network is compressed by gravity.

Owing this fact, we are able to make, by help of simple rheosedimentation measurements, a prediction of paper strength and paper-forming properties of the rheosedimenting pulp. As a rule at comparable conditions, with decreasing both velocity of rheosedimentation and concentration of pulp sediment the strength and mechanical properties of paper being made of this pulp are increased. Further at comparable conditions, the velocity of rheosedimentation is more sensitive to fibre geometry and on the contrary, the concentration of pulp sediment is more sensitive to stiffness and persistence of individual fibre composing this sediment.

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