Fiber flocculation in pulp suspension flow

Part 1: Theoretical model

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ABSTRACT: *A theoretical model has been developed to provide quantitative relationships describing flocculation in pulp suspension flow. This model is based on the mass-action law and on the energy spectrum of the turbulent flow. Electrostatic contributions are calculated by minimizing the free energy of bound counterions using the Poisson-Boltzmann field.*

The model is supported by an experimental study based on digital signal analysis using light transmission through the flowing pulp. The experimental portion of this work will be presented in Part 2.

KEYWORDS
Analysis
Electrostatics
Flocculation
Mathematical models
Pulping
Simulation

Fiber dispersion in the papermaking process is an important phenomenon that has a critical effect on paper quality. The uniformity of optical and mechanical properties is affected by the small-scale distribution of mass in the sheet of paper. This distribution of mass is known as its "formation," which depends on the floc size distribution in that sheet.

The degree of fiber dispersion is controlled by a balance between several chemical and mechanical forces that act upon the fibers. Some of these forces enhance flocculation, such as (a) fiber-fiber attraction, (b) the minimization of water-fiber contact area vs. fiber-fiber contact area, and (c) the coalescence of the volume excluded to the water molecules by the formation of flocs. Other forces enhance dispersion, such as (a) changes in fiber density when flocculation occurs, (b) redistribution of the pulp electrostatic forces, and (c) turbulence. Summarized by Kerekes (*1*), literature is extensive on the effects of hydrodynamics, electrostatics, and fiber parameters on the building up and breaking of fiber networks.

The theoretical model developed in this study is based on the concept of "dynamic equilibrium," which was first formulated by Mason and further elaborated on by Kerekes (*1*). In the model, flocculation is considered as a reversible coalescence of fibers to which reaction equilibrium formulations can be applied (mass-action law). These formulations are coupled with the material and energy balances, resulting in descriptions of floc size distributions. The model has two experimentally determined parameters that are fitted to the experimental mean floc size and the variance of the distributions.

Theoretical model

The purpose of this model is to describe and to predict quantitatively the phenomenon of fiber flocculation in turbulent flows by accounting for all the chemical and mechanical forces that act upon the fibers. These forces, which include fiber surface properties, fiber-fiber and fiber-water interactions, electrostatics, density effects, and turbulence, are coupled with the material constraint on the overall fiber concentration in the pulp and the energy spectrum of the flow.

Energy balance

A pulp suspension is a two-phase system, and the derivation of its energy spectrum is a complex procedure. Al-Taweel and Landau (*2*) derived the dynamic equation of the kinetic energy, $E(K)$, for two-phase isotropic turbulent flows. That equation is used in our model:

$$d/dt\,[\ln E(K)] = 2/3\epsilon^{1/3} L^{5/3} - 2\nu K^2 - 36\nu/\zeta_0 \Sigma\,[X_{N,K}(t)/d_N^2]\, R_{K,N}^2 \quad (1)$$

The energy dissipation, ϵ, of the two-phase flow is:

$$\epsilon = \int_0^\infty \left\{15\nu K^2 + 36\nu/\zeta_0 \Sigma\,[X_{N,K}(t)/d_N^2]\, R_{K,N}^2\right\} E(K)\,dK \quad (2)$$

Experimentally measured energy spectra (*2, 3*) indicate that the energy $E(K)$ is related to the wavenumber K, by:

$$E(K) = E_o\, K^{E_s} \quad (3)$$

where

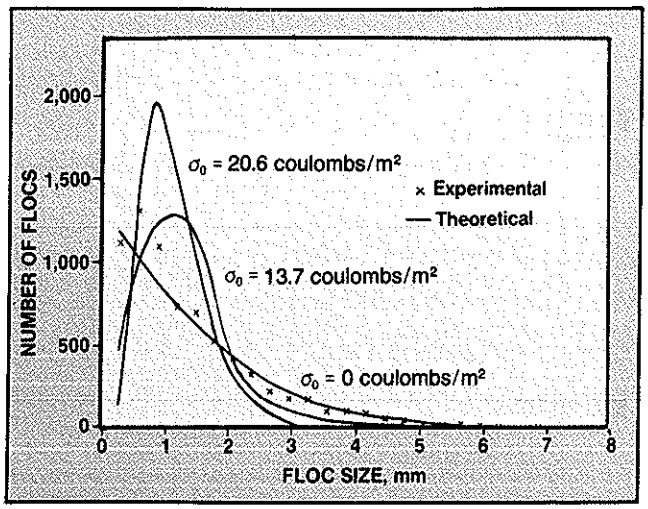
E_o = a constant

E_s = function of the suspended phase concentration

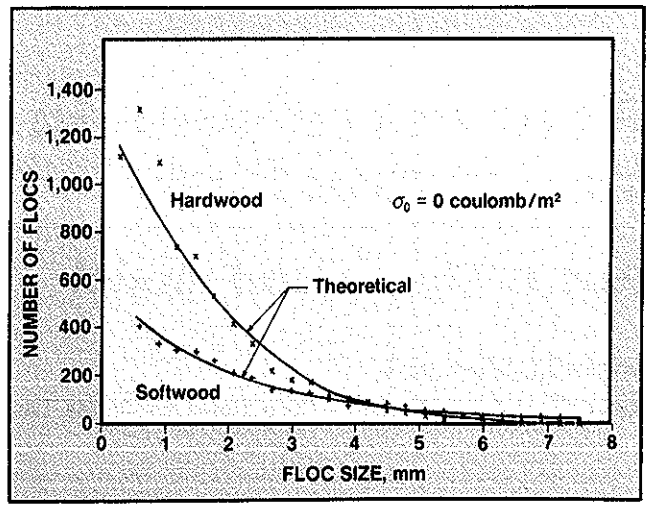
K = number of waves/cm.

The dependence of E_s on consistency is assumed to follow the experimen-

1. Electrostatic field effect on floc size distribution (hardwood pulp)



2. Floc size distribution at 300 ft/min, 0.5% consistency, 25°C



tal and theoretical functions given by Al-Taweel and Landau (*2*) for liquid-gas, solid-gas, solid-liquid, and gas-liquid systems.

To solve Eq. 1, we assumed there was a steady state in which turbulence neither decays nor increases with time, so that the time average energy of an eddy is constant at a fixed point of the flowing pulp. This assumption permits the use of equilibrium relationships. However, this average energy varies among different points of the flowing pulp, and Eq. 1 has to be applied separately for each point.

A second assumption deals with eddy size. Turbulent eddies are interface regions with relatively high shear, and the distribution of floc sizes is directly related to the distribution of the length scale of these eddies. The mean floc size was assumed to be equal to the mean eddy size:

$$\overline{K} = \text{length scale of } \overline{N} \qquad (4)$$

Material balance

The population density distribution of flocs can be obtained once the free energy change upon flocculation is determined. However, this distribution is constrained by the amount of fiber material present. As a weight fraction, this amount is:

$$X_T = \sum_N X_N \qquad (5)$$

The mean floc size, $\overline{N}$, where the size is expressed here in terms of number of fibers rather than in mm, and the variance, σ^2, can be found once the floc size distribution is determined:

$$\overline{N} = \sum_N N X_N / \sum_N X_N \qquad (6)$$

$$\sigma^2 = \sum_N (N - \overline{N})^2 X_N / \sum_N X_N \qquad (7)$$

The term X_N is related theoretically to the free energy description of the system.

The mean floc size and a corresponding variance are also represented by experimentally determined parameters, $\overline{F}$ and σ, respectively, on a length scale (in millimeters). (The experimental measurements will be discussed in Part 2.) To relate $\overline{N}$ to $\overline{F}$, the size of flocculated fibers has to be determined.

In this analysis, we have assumed that the length of hardwood fiber is 1 mm and that the length of softwood fiber is 4 mm. We have also assumed that the circular area corresponding to the smallest experimental scale of 0.3 mm is roughly equivalent to projected areas of 1 softwood fiber or 4 hardwood fibers. This viewing area might contain a fraction of a fiber but, for computational simplicity, we have not taken this circumstance into consideration.

Equilibrium balance

The "dynamic equilibrium" between fibers and flocs in pulp suspensions was assumed to follow the mass-action law, so the thermodynamic relations, properties, and the population density of each possible floc in the pulp can be evaluated. In the analysis, we consider flocs made of N fibers to be in reaction equilibrium with the dispersed fibers at fixed conditions. The floc charge depends on the number and valence of counterions bound to the floc. The floc and the dispersed fiber weight fractions, X_N and X_{fd}, respectively, are related to the free energy of formation, ΔG°_N, by the mass-action law (*4*):

$$X_N = \exp\{N[(-\Delta G^\circ_N/RT) + \ln X_{fd}]\} \qquad (8)$$

The weight fraction of counterions is assumed to be negligible compared to the fiber weight fraction in Eq. 8.

The value of ΔG°_N was found by modeling the property changes between dispersed fibers and flocs. The properties include fiber interactions and density changes, excluded volume, and structural changes of the water and electrostatic field effects:

$$\Delta G^\circ_N \sim \Delta G^\circ_{exv} + \Delta G^\circ_{sur} + \Delta G^\circ_{comp} + \Delta G^\circ_{ad} + \Delta G^\circ_{el} \qquad (9)$$

Each of the terms on the right-hand side of Eq. 9 was modeled independently.

Excluded volume free energy. One step of the flocculation process involves the collapse of the dispersed fiber cavities and the creation of an N-fiber floc cavity, where a cavity is the available volume (or space) for a chemical species to occupy in the solution. A universal correlation was developed for this term for a dispersed species in aqueous solutions (*5*):

$$-\Delta G^\circ_{exv,fiber}/RT = 93.64 - (1678.51/T) \qquad (10)$$

Equation 10 is applied to the floc cavity by using the ratio of the floc curvature to the fiber curvature:

$$-\Delta G^\circ_{exv,floc} = -\Delta G^\circ_{exv,fiber} f_r \quad \text{for } N >= 2 \qquad (11)$$

where f_r is the mean radius of curvature of N-fiber floc divided by N, divided by the mean radius of curvature of a fiber.

I. Electrostatic field effects on theoretical parameters

	Pulps			
	Hardwood,[a] coulombs/m²			
	0	13.7	20.6	Softwood
X_{fd}	0.55	0.99	0.98	0.89
E_0	4.40×10^{-6}	4.72×10^{-6}	3.50×10^{-6}	5.50×10^{-9}
$\Delta G_{sur,fiber}{}^{RT}$	76.1	73.2	73.2	76.7
B_0	0	-0.870	-1.474	0
B_1	0	0.516	0.503	0
B_2	0	0.0774	0.119	0
B_3	0	1.298	0.222	0
B_4	0	1.182	8.221	0
B_5	0	-1.631	-9.978	0
B_6	-1.0×10^{-4}	4.6×10^{-3}	8.0×10^{-3}	6.0×10^{-4}

Hardwood: F = 1.47 mm, σ = 1.20 mm. Softwood: F = 2.49 mm, σ = 2.40 mm. Flow conditions: 300 ft/min, 0.5% consistency, 25°C. Zeta potential = -25.5 mV.
[a] Three levels of surface charge density covering the range considered by Herrington (*8*).

The excluded volume free energy change is then equal to

$$\Delta G^\circ_{exv} = (-\Delta G^\circ_{exv,floc}) - (-\Delta G^\circ_{exv,fiber}) = -\Delta G^\circ_{exv,fiber}\,(f_r - 1) \quad (12)$$

For a spherocylindrical floc:

$$f_r = [1/(3^{1/3}\, r_{fiber}{}^2)]\,(V_{fiber}/4\pi)^{2/3} + 1/N$$
$$[2/3\, r_{fiber}\,(4\pi/3V_{fiber})^{1/3}] = a_r + (1/N)\, b_r \quad (13)$$

where

r_{fiber} = fiber radius

V_{fiber} = fiber volume.

Since the fiber radius and volume can have a wide range of values, we simplify Eq. 13 by assuming that $a_r \rightarrow 0$ and $b_r \rightarrow 1$. Any error introduced by that assumption is adjusted for the value of the surface free energy, since it is an experimentally fitted parameter.

Surface free energy. The intermolecular interactions between the solvent and the fibers are changed upon flocculation. More fiber-fiber contact and less fiber-solvent contact are occurring. The modeling of the surface free energy contribution in this analysis is done by experimentally fitting its effect:

$$-\Delta G^\circ_{sur,floc} = -\Delta G^\circ_{sur,fiber}\, f_s \quad (14)$$

$$\Delta G^\circ_{sur} = -\Delta G^\circ_{sur,fiber}\,(f_s - 1) \quad (15)$$

where f_s is the surface area of N-fiber floc divided by N, divided by the surface area of a fiber.

For a spherocylindrical floc:

$$f_s = V_{fiber}/[2\pi r_{fiber}\,(3V_{fiber}/4\pi)^{2/3}] + (1/N)$$
$$r^2{}_{fiber}/[3(3\,V_{fiber}/4\pi)^{2/3}] = a_s + (1/N)\, b_s \quad (16)$$

Again, we assume here that $a \rightarrow 0$ and $b \rightarrow 1$, as in the previous case.

Compression free energy. The free energy change associated with the compression of dispersed fibers to the floc density can be separated into energetic and entropic effects. The energetic effect has been accounted for in the surface free energy term. The entropic effect is dominated by the density increase of the fibers, which can be estimated by the use of a rigid body equation of state:

$$S_{comp}(\rho 2) - S_{comp}(\rho 1) = -\int_{\rho 1}^{\rho 2} \left(\frac{\partial \rho}{\partial T}\right)_V \frac{d\rho}{\rho} \quad (17)$$

Boublik's equation of state (*6*) is used for this term.

Electrostatic and adsorption free energy. For flocs which are ionically charged at their surface, the effects of concentrating the counterions must be accounted for. The fraction of bound counterions, β, can be obtained by minimizing the free energy with respect to β. This model separates the effects of bound counterions and electrostatic field effects into two terms, ΔG°_{ad} and ΔG°_{el}, respectively. The first accounts for excluded volume and ion-solvent effects:

$$\Delta G^\circ_{ad}/RT = B_0\beta \quad (18)$$

The electrostatic free energy dependence is obtained from the Poisson-Boltzmann theory (*7*):

$$\Delta G^\circ_{el} = (kT/e)^2\,(\kappa/4\pi) A_M \int_0^s y_0\, ds \quad (19)$$

where

A_M = surface area per charge

y_0 = dimensionless surface potential = $e\psi_0/KT$

s = dimensionless surface charge density = $4\pi\sigma_0\, e/\epsilon_0 \kappa KT$.

The theoretical results have been fitted for each floc size to:

$$\Delta G^\circ_{el}/RT = C_{0,N} + C_{1,N}\beta + C_{2,N}\beta^2 \quad (20)$$

The distribution minimum of the overall free energy with respect to β is identical to the minimum for each value of N, so β can be found from:

$$(-\partial/\partial\beta)\,\Delta G^\circ_{el}/RT + (-\partial/\partial\beta)\,(\Delta G^\circ_{ad}/RT) = 0 \quad (21)$$

The change of β with minimum free energy is correlated with N in the form:

$$\beta_{min} = B_1 + B_2 \ln N \quad (22)$$

This β_{min} is then used to calculate ΔG°_{el} from Eq. 20, which is finally correlated as:

$$\Delta G^\circ_{el}/RT = B_3 + B_4/N + B_5/N^2 \quad (23)$$

To determine $B_0 \ldots B_5$, the surface charge density on the fibers, σ_0, has to be known.

Substituting these five terms into Eq. 8, the floc-size distribution becomes:

$$X_N = \exp\{N[-(\Delta G^\circ_{exv,\,fiber}/RT)\,(1 - 1/N) - (\Delta G^\circ_{sur,\,fiber}/RT)\,(1 - 1/N) + (\Delta S^\circ_{comp}/R) - B_0\,(B_1 + B_2 \ln N) - B_3 - (B_4/N) - (B_5/N^2) + B_6 N + \ln X_{fd}]\} \quad (24)$$

where B_6 is a shape correction factor that accounts for deviations from spherocylindrical geometry.

All but two of the model parameters are determined by these derived equations. The unknown parameters are the surface free energy change and the correction factor, B_6. Experimentally determined floc size distributions (mean floc size and standard deviation) are used to fit these parameters. Equations 1 and 5 are solved iteratively to determine their unknowns: the kinetic energy term, E_0, and the concentration of dispersed fibers (unflocculated), X_{fd}.

The electrostatic parameters, $B_0 \ldots B_5$, can only be calculated if the surface charge density, σ_0, is known. The only available measurement which might relate to σ_0 is the zeta potential. However, Herrington (*8*) showed that the zeta potential is not a measure of surface charge and cannot be used to compare the surface

Nomenclature

Roman

d = diameter, cm
E = kinetic energy, cm
e = electron charge, coulomb
F = floc size, mm
G = free energy, calorie/mole
K = wavenumber, cm^{-1}
k = Boltzmann constant, calorie/°K
N = number of fibers in a floc
P = pressure, atm
R_{vr} = ratio of solid relative velocity to fluid fluctuating velocity
R = gas constant, calorie/(mole-°K)
S = entropy, calorie/(mole-°K)
T = temperature, °K
t = time, s
V = volume, cm^3
X = weight fraction

Greek symbols

β = fraction of counterion bound
Δ = denotes property change
κ = inverse Debye length, cm^{-1}
ρ = density, g/cm^3
σ = standard deviation
ν = kinematic viscosity, cm^2/s
ζ_0 = ratio of density of solid-liquid phases
ϵ = energy dissipation, cm^2/s^3
ψ_0 = surface electrostatic potential, mV
σ_0 = surface charge density, coulomb/m^2
ϵ_0 = dielectric constant

Subscripts

N = index of number of fibers in a floc
T = total concentration
K = index of wavenumber
fd = dispersed fiber
c = counterion
cxv = cavity
sur = surface
comp = compression
ad = adsorption
el = electrostatic

charges of even similar materials. This conclusion requires dealing with the electrostatic forces in one of two different approaches. First, electrostatic forces were assumed negligible—i.e., $B_0 = \ldots = B_5 = 0$. Second, the surface charge densities reported by Herrington for bleached sulfate pulp were used to calculate the electrostatic parameters and to determine their effects on the theoretical floc size distribution determined by the iterative technique.

This approach was used on two flowing pulps, one composed of only hardwood and one composed of softwood fibers. The results are shown in **Table I**, and theoretical and experimental distributions are compared in **Figs. 1 and 2**. These figures show that pulp used in this study had negligible electrostatic field effects even though the zeta potential measurements of that pulp indicated otherwise (Table I), supporting Herrington's conclusions. Also, the floc size distribution shifted from "negative exponential" form to "log-normal" as the surface charge density increased to 20.6 c/m^2 deviating from the good fit with the experimental data when σ_0 was zero.

Conclusions

The optimum conditions for formation improvement depend on the individual paper machine and pulp furnish. We have provided a theoretical framework to study flocculation in turbulent suspension flow by deriving quantitative relationships with determined quantitative parameters. With this method, we can now quantify floc size distribution, which has an essential influence on the uniformity of paper properties.

This method also has the capability of accurately predicting flocculation. The strategy of applying theory with experimental data provides a unique diagnostic technique capable of characterizing and predicting flocculation behavior with changes in pulp furnish, paper grades, broke levels, and other operating conditions.

Literature cited

1. Kerekes, R. J., J. Pulp Paper Sci. 9(4): 86(1983).
2. Al-Taweel, A. M. and Landau, J., Int. J. Multiphase Flow 3(3): 341(1977).
3. Baw, P. S. H. and Peskin, R. L., J. Basic Engineering 93 (Section D, No. 4): 631(1971).
4. Hall, D. G. and Pethica, B. A., Nonionic surfactants (M. J. Schick, Ed.), M. J. Marcel Dekker, New York, 1970, Ch. 6.
5. Hourani, M. J., A molecular thermodynamic model for surfactant aggregate formation, Ph.D. dissertation, Univ. of Florida, 1984.
6. Boublik, T., J. Chem. Phys. 63: 4084(1975).
7. Mitchell, D. J. and Ninham, B. W., J. Phys. Chem. 87: 2996(1983).
8. Herrington, T. M., Transactions of the Eighth Fundamental Research Symposium, Mechanical Engineering Publications Ltd., London, Vol. 1, 1985, p. 165.

I would like to thank A. H. Nissan for valuable and stimulating discussions concerning this work.

Received for review April 29, 1987.

Accepted Aug. 31, 1987.