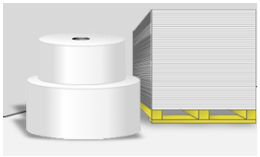
logging → barking → chipping → washing → straining → bleaching → sieving → cooking

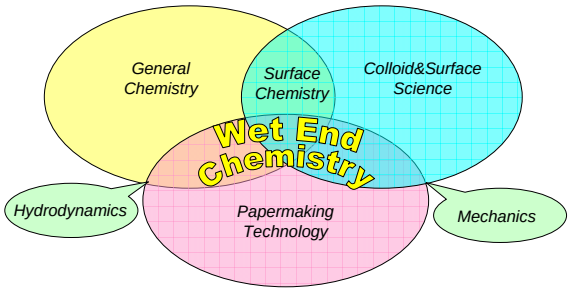
RETENTION AND FORMATION IN PAPERMAKING

Dr Boris Zhmud, Sveacon Consulting

wet pressing → drying → calendering →



Genealogical Tree of the Wet End Chemistry

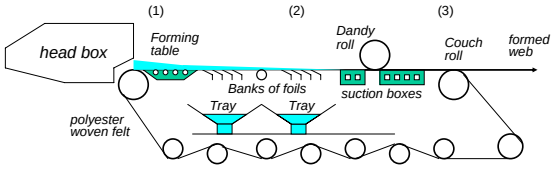


Papermaking

Drainage is:
- The process of straining the dilute suspension of fibers through the wire.

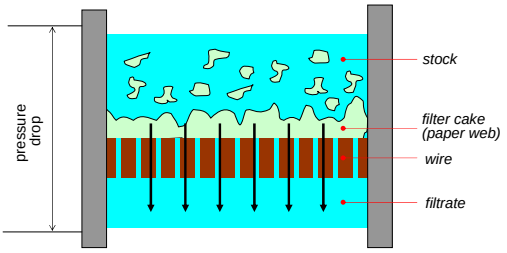
Formation is:
- The build-up of a coherent web from fibers retained on the wire during the straining.

1. The stock (1-10 g/kg solids, 6 to 18 mm layer thickness) gets on the wire.
2. Drainage is assisted by foils (upto ~ 20 g/kg) and then by suction boxes.
3. The formed web leaves the "couch" at 100-200 g/kg solids.



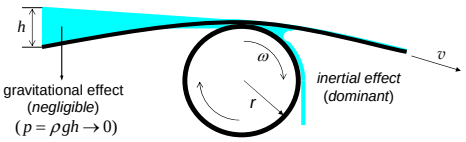
The elements of a Fourdrinier wire part

Formation Viewed as Filtration

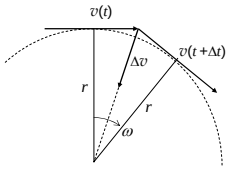


Rate of the Process = Pressure Drop x Filter Cake Permeability

Origin of the Pressure Drop



Streamlines change their direction in the nip between the table roll and the wire,



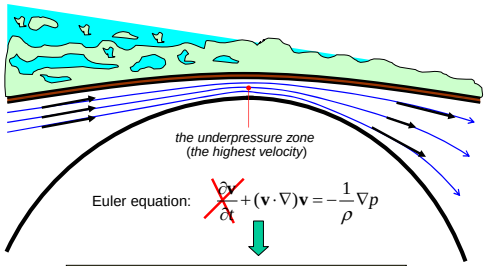
$$\Delta v = v(t+\Delta t) - v(t) = r\omega^2 \Delta t = \frac{v^2}{r}\Delta t$$

$$F = m\frac{\Delta v}{\Delta t} = \rho S h \frac{v^2}{r}$$

$$p = \frac{F}{S} = \rho \frac{h}{r} v^2$$

p - pressure
v - velocity
ω - angular velocity
ρ - density
g - acceleration of gravity

Origin of the Pressure Drop (Revisited)



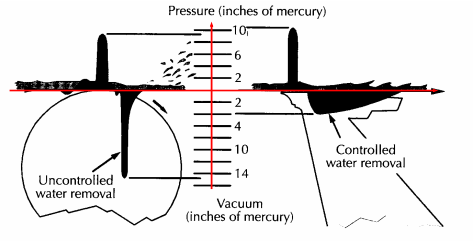
Euler equation: $\cancel{\frac{\partial \mathbf{v}}{\partial t}} + (\mathbf{v}\cdot\nabla)\mathbf{v} = -\frac{1}{\rho}\nabla p$

Bernoulli equation: $p + \frac{\rho v^2}{2} = const$

In the nip between the roll and the wire, water moves together with the confining surfaces. Hence, the steamlines shown are identical to the streamlines of an inviscid fluid.

Pressure Profile in the Nip

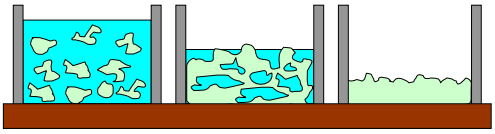
Table Roll vs. Foil



Advantages of foils:

- No speed limits
- More sustained low-amplitude pressure profile
- Customized drainage profile

Filter Cake Permeability



high medium low

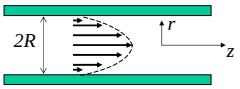
The Kozeny-Carman equation:

$$\text{Rate of Dranage } = const\,\frac{(1-C)^3}{S^2C^2}\,\frac{\nabla p}{\eta}$$

C - volume fraction of solids
S - specific surface area of solids (10-50 cm²/g)
η - viscosity of liquid
∇p - pressure drop

Physics Behind the Kozeny-Carman Equation

Poiseuille equation for the flow in a cylindrical tube:



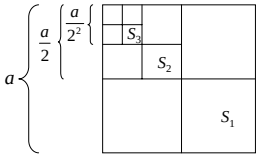
$$v_z(r) = \frac{R^2}{4}\left(1-\frac{r^2}{R^2}\right)\frac{\nabla p}{\eta}$$

$$Q = 2\pi\int_0^R r v_z(r)\,\mathrm{d}r = \frac{\pi}{8}\frac{\nabla p}{\eta}R^4$$

$$S_0 = a^2;\ S_1 = \left(\frac{a}{2}\right)^2;\ S_2 = \left(\frac{a}{2^2}\right)^2;\ \ldots$$

$$S_n = \frac{a^2}{2^{2n}} = \frac{S_0}{2^{2n}}$$

$$Q = 2^{2n}Q_n \propto 2^{2n}S_n^2 \propto \frac{S_0^2}{2^{2n}}$$



$$\frac{Q}{S_0} \propto S_n \times \underbrace{P(\text{pores are empty})}_{1-\phi} \times \underbrace{P(\text{pores are interconnected})}_{(1-\phi)^2}$$

Some Preliminary Remarks

The process of forming the web of paper may be represented as an example of the unit operation of solid/liquid separation by filtration.

It proceeds at a rate which is approximately proportional to the pressure drop and inversely proportional to the basis weight already formed.

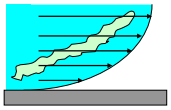
As is often the case, the progress of technology in the field of papermaking overtakes the need for detailed understanding of the original process.

Theoretical models more complex than those presented are legion but are of limited use because of the process complexity, e.g.:

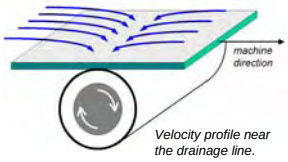
- the fibres are non-uniform in size and shape;
- the flow is not laminar;
- the web is not incompressible;
- plus many other unaccountable/stochastic factors.

Web Structure Building

Fibre Orientation



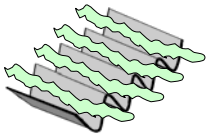
Velocity profile near the slice wall and in the jet impact point



Velocity profile near the drainage line.

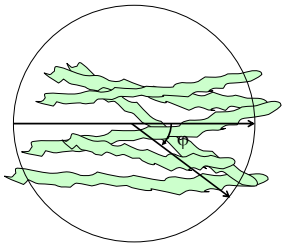
Fibres are aligned parallel to the machine direction in the slice, in the jet impact point and on the drainage elements; the overall felt motion plays no role here.

The preferential orientation of fibres causes the "grain" (i.e. the anisotropy of the mechanical properties of paper).

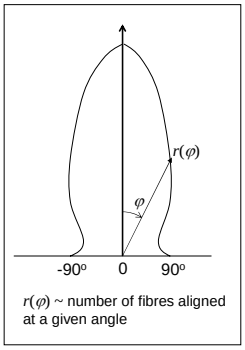


Templating (combing-out) effect.

Characterization of the Fibre Orientation Using the Polar Diagram

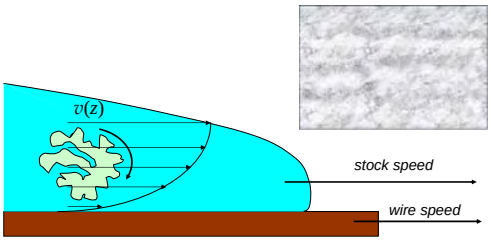


The number of intersections with the scanning line is counted.



$r(\varphi)$ ~ number of fibres aligned at a given angle

"Rolling" Flocs

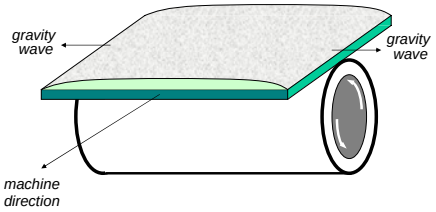


Flocs getting a torque due to an excessive jet/wire speed ratio

N.B. Bizarre terminology:

"Formation" or "Look-Through" is the visual inspection of the web of paper for small-scale non-uniformity. It is not the same as the "mass density distribution".

In-Plane Non-Uniformity

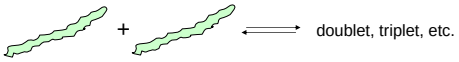


"Light edges" due to the gravity wave spreading outwards on the wire table.

Fibre Flocculation

Flocculation is the formation of relatively dense aggregates, or "flocs", of fibres.
Flocculation is the most important cause of uneven distribution of basis weight.

Mason's (mechanistic) theory (1954):
Flocculation is viewed as a result of mechanical entanglement of fibres.



Critical concentration by Mason: $C \simeq \frac{3}{2}\left(\frac{d}{L}\right)^2 <<$ the real value

d - diameter; L - length

The Concept of a Coherent Fibre Network

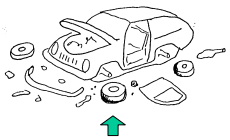
A fibre may only become a part of a network if it is in contact with at least three other fibres

Critical concentration by Wahren: $C \simeq 108\pi\left(\frac{d}{L}\right)^2$ (good agreement)

The Effect of Surface Forces on Flocculation

It is clearly an oversimplification to attribute the formation of flocs merely to the action of locked-in fibres straining against each other, and to disregard the contribution of adhesion and frictional forces at points of contact between fibres.

(B.Radvan, "Forming the Web of Paper", in the Handbook of Paper Science, 1980)



No flocculation ⇒ poor retention

Overflocculation ⇒ bad formation and uneven sheet

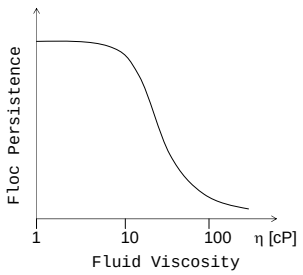
Controlled Flocculation

Controlled flocculation means that flocs can be easily broken without impairing retention

Flocculation of the stock cannot be avoided. Retention agents promote flocculation.

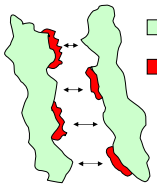
Rather than attempting to prevent it, the efforts should instead be aimed at providing conditions for dispersing flocs.

Remedies: High shear (use of shear-thickening agents), small turbulence, shaking the wire.



Common Flocculation Mechanisms

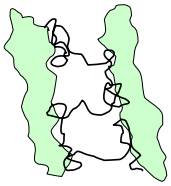
1. Patch Flocculation



negative charge
positive charge

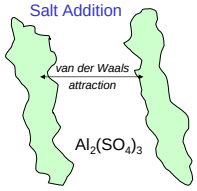
(high charge density low molecular weight polyelectrolytes)

2. Bridging Flocculation

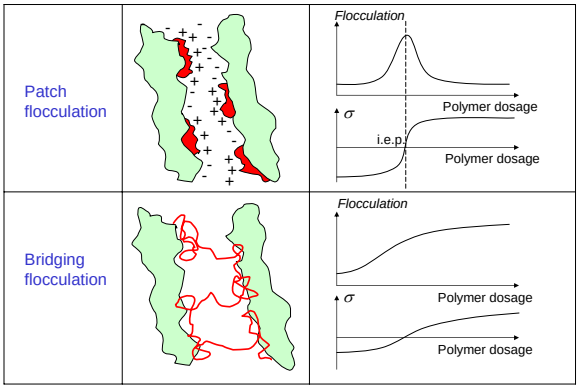


(low charge density high molecular weight polymers)

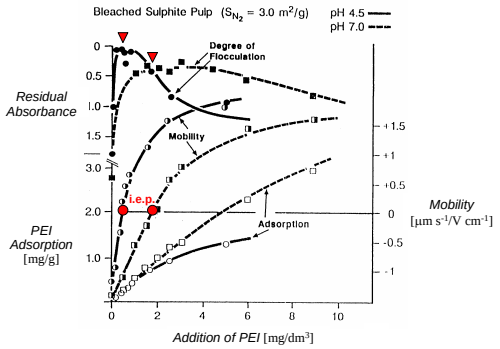
3. Flocculation by Salt Addition



Relation between the Polymer Adsorption and Flocculation Efficiency

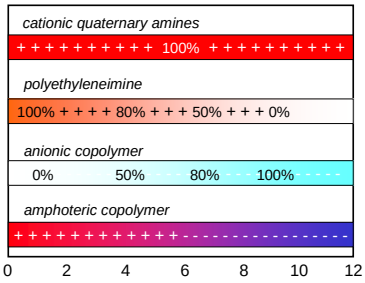


Relation between the Polymer Adsorption and Flocculation Efficiency (cont'd)



Flocculation of bleached sulphite pulp due to adsorption of PEI at pH 4.5 and 7.0.

Effect of pH on the Charge of Polyelectrolytes



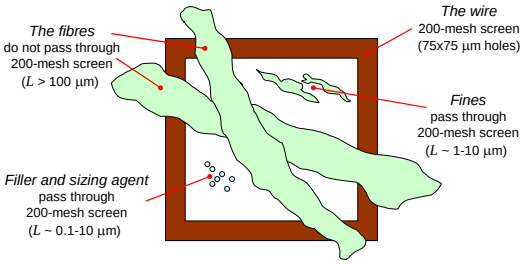
$$B + H^+ \rightleftarrows BH^+ \qquad K = \frac{1}{K_{base}} = \frac{[BH^+]}{[B][H^+]}$$

$$AH \rightleftarrows A^- + H^+ \qquad K = K_{acid} = \frac{[A^-][H^+]}{[AH]}$$

$$\Rightarrow \quad pH_{1/2} = pK_{\text{acid or base}}$$

Retention

I. Fibres are retained on the wire forming the paper web.
II. Fines and additives (fillers, sizing agents, wet strength agents) are (expected to be) retained by the fibres.



N.B. What isn't retained is lost increasing the production cost and adding to the environmental load.

First-pass Retention and True Retention

- Retention is a measure of raw material utilization.
- First-pass retention relates to the efficiency of the wet end.
- True retention relates to the efficiency of the total papermaking system.

$$\text{FPR} = \frac{\text{total solids in headbox - total solids in tray}}{\text{total solids in headbox}} \times 100\%$$

$$\text{TR} = \frac{\text{tonnage conveyed to the press}}{\text{tonnage discharged by the headbox}} \times 100\%$$

Terminology note:
"Consistency" = "Total Solids" in the slurry determined by filtration and drying

The Surface Forces that Control Retention

Force type / origin	Action range	Influenced by
Hydrodynamic shear	$L \sim (\eta t/\rho)^{1/2}$	Headbox hydrodynamics; Machine speed; Stock viscosity
Polymer-induced	$L \sim 10$ nm	Polymer type and M_w; ion strength of the stock
Electrostatic	$L \sim 0.3 / I^{1/2}$ nm (I - *ion strength*)	Ion strength of the stock water; pH; type of pulp; amount of ionic additives
van der Waals	$L \sim 1$ nm	-
Hydration (hydrophobic)	$L \sim 1$ nm	Hydrophobe/hydrophile balance; surface energy

N.B. Role of surface effects is proportional to the surface to bulk ratio,

$$\frac{\text{Surface}}{\text{Volume}} \propto \frac{\pi dL}{\pi d^2 L} \propto \frac{1}{d} \to \infty \quad \text{as } d \to 0$$

Common Types of Retention Aids

Alum(inium sulfate)

Hydrolysis

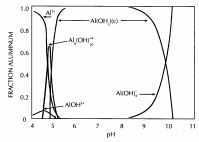
$Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$

$Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^+$

$AlOH^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+$

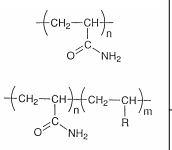
$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+$

$Al(OH)_3 + nOH^- \rightarrow Al(OH)_{3+n}^{n-}$



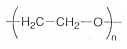
✓ Efficiency depends on pH.

Polyacrylamides
(20-70% of cation.subst.)



✓ Efficacy depends on M_w (high M_w is required).
✓ High viscosity.
✓ Weak chelating properties

Polyethylene oxide



✓ Efficiency depends on M_w (very high M_w required).
✓ High viscosity (handling).
✓ Non-charged.
✓ Little affected by ionic composition of stock.

Network flocculants

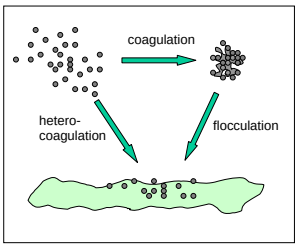
(SiO_2 or Clay)/(PAA or PEO)

Major types of RA's: (i) Inorganic, (ii) Synthetic Polymers, and (iii) Mixed

Dual Component Coagulant / Flocculant Systems

Usual combinations:

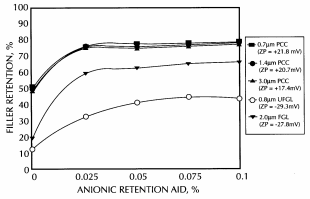
- Alum + PAM
- Cationic starch + PAM
- PAC + PAM
- Polymine + PAM
- PEI + PAM
- poly-DADMAC + PAM



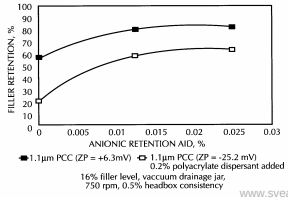
Glossary for non-technologists:
PAM = polyacrylamide (cationic or anionic)
PAC = polyaluminium chloride
PEI = polyethyleneimine
DADMAC = di-allyl di-methyl ammonium chloride

Retention is always affected by a great number of difficult-to-predict factors, e.g.

filler's mineralogy



16% filler level, vaccuum drainage jar, 750 rpm, 0.5% headbox consistency



and dispersing agent used in filler

… so it's more art than science.

Examples of Retention Systems

Poly(hydroxy styrene) / polyethylene oxide system for retaining fine particles (US pat. 5,472,570)

- M_w of PHS ~ 1,000 - 2,000
- M_w of PEO ~ 4,000,000 - 7,000,000
- Weight ratio PHS / PEO ~ 0.5 to 10
- Addition level ~ 0.01 to 0.1% by the weight of dry pulp.

Cationic galactomannan / bentonite system for retaining mineral fillers such as clay, chalk, calcium carbonate, titanium oxide, or bentonite (US pat. 6,270,626)

- Degree of cationic substitution ~ 0.01 to 1%; M_w ~ 2,000,000
- Bentonite/galactomannan ratio ~ 1 to 10 by weight
- Addition level ~ 0.01 to 5% by the weight of dry pulp.

Note: cationic substitution may be done by reacting hydroxyl groups of the parent polymer (polyhydroxystyrene, polygalactomannan, starch) with quaternary ammonium compounds.