Pulp Quality – Not Only Chemistry

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Guiding Thoughts…

• Wood fibre is a complex toroidal composite
  – It is not just a macromolecular structure

• We need ”thinking models”, thus, in stead of a polymer, think about a brick wall
  – Long stiff bricks … cellulose microfibrilles
  – Filling mortar … hemicellulose+lignin
  – Bonding between the elements
The Strength of a Brick Wall ... a Fibre Wall

Length of one brick...

Viscosity i.e. DP of cellulose
is not very important

Amount and strength of mortar...

Hemicellulose and lignin
Is not very important

But it is absolutely necessary that
the components are tightly bonded and the structure is
intact ... unbroken
It is easy to destroy a loose wall, but still have the bricks intact...
Pulp and Paper Technology – from scale one to thousand million

Importance of the scale

Nano m  Molecule monomer
Micro m  DP1500 cellulose
Milli m  Fibre length
Centi m  Paper web structure
Meters  Paper making
        Runnability
        End product quality

Chance from chemical interactions to physical phenomena and material properties
Fiber and Paper Physics

Classic Wood and Organic Chemistry

One and Multiple Fibres

Figure 2. Schematic picture of how the cellulose is organized on different levels in the fibre (Fellers and Norman 1996).

Nobody’s Land
From Nano to Milli
Origin of most Fibre Properties
Fibre Wall Structure

Bricks & Mortar thinking may not be far fetched…

IF:
DP1000 cell-fib = 1 brick
1 fiber = 450 m x 3m x 3m “brick wall”

Figure 8. Schematic picture of the interpretation of the cell wall structure made by Stone and Scallan (Stone and Scallan 1968) describing how the microfibrils are surrounded on all sides by an amorphous hemicellulose-lignin gel.
The wall may contain more or less porous areas by nature

“Honeycomb” structural cell wall model, proposed by Scallan
Composition Profile

• Cooking dissolves layers differently:
  • ML disappears
  • Most of S1
  • Almost half of S2
  • Differences much bigger in the microfibrille level
The Effect of Chemical Pulping

The wall is badly broken

At the end of cooking
50% of the wall volume is dissolved and free liquid
... full of holes

Does the wall still hold?
... not necessarily, the wall gets vulnerable
Fibre Wall Structure Changes in Cooking

- The fibre wall porosity increases significantly.
- The new free space is macropores.
- Note: The increase of FSP indicates the growth of macropores.

Figure 7. The change to the cell wall pore structure in kraft pulping of spruce wood [IV].

FSP Fiber Saturation Point

(T. Maloney)
Strength of the Porous Fibre at the End of Cooking

Kraft cooking

Cooling to 80°C pulp in Black Liquor

Washing @80°C @10% cons.

Wet disintegration by propeller:
5 min, 80°C, 4% cons in water

Wet zero-span strength: 115

Keep in BL @80°C @10% cons.

Wet disintegration by propeller:
5 min, 80°C, 4% cons in BL

Wet zero-span strength: 99

A simple lab experiment shows that the black liquor filled fibre is very vulnerable

A mild mechanical action on the fibre clearly lowers strength of the fibres
Possible load carrying structures of fibre wall composite

Schematic picture of a composite material where the components are coupled in parallel (a), in series (b) and in a combination of parallel and series (c).
Single Fibre Strength as a proof of fibre wall composite structure

- At very high lignin content both cellulose and lignin layers carry load
- Small amount lignin dissolved weakens the lignin layer
- Cellulose structures carry load over a very wide delignification range
- The fibre’s load carrying capacity finally collapses
- Chemically modified cellulose structure carries less load

(Ehrnrooth, 1984)
The Influence of Cooking Conditions on Fibre Wall Structure

Alkalinity, HO- ions, i.e. pH have a tremendous impact on the fibre wall properties and loosening of the structure. It is a beneficial factor to develop strength...especially after refining. Simultaneously it sensitizes fibre to get damaged, i.e. to loosen and open too much.
The Influence of Cooking Conditions on Paper Strength

- Alkali cooked fibres make strong sheet
- Too much alkali or mechanical damage cause strength losses

(J.Sundqvist)
How does it look inside? Fibre Wall Layers

Figure 6. Different layers in a fiber building up the cell wall (Salmén 1985).
How does it look inside? Fiber Wall Damage

Organized "tight" Wall Structure

Damaged "loosened" Wall Structure
Is this all? … Secondary wall hit

• No, it seems not to be all
• Many deficits in paper properties are due to fibre deformation, curl, kink, twist
  – Wide and complicated area of causalities
  – Worth of its own lecture
• New findings further indicate that, besides S2 layer, S1 may be damaged as well
The Origins of Fiber Damage

- S1 (transverse) layer is like casing around S2 layer (longitudinal)
- Damaged S1 lets S2 to get damaged and loosened very early in the process

Schematic diagram of the microfibril orientation in the primary wall and different layers of the secondary wall in tracheids and fibers: P0, P1 outer and inner surfaces in the primary wall, S12, S23, intermediate layers between S1 and S2 and between S2 and S3. Modified from the model of Wardrop and Harada, 1965.
Eucalyptus Pulp Quality
Steps from Microfibrilles

1. The microfibrillic structure ("the brick wall") chances by loosening and forming macropores
2. The fibre saturation behaviour and fibre web rheology chance, affecting a wide spectrum of paper technical properties
   • Basic measurements: WRV, FSP, pore volume, pore size distribution
Symptoms in the Pulp Mills

• The consequences of fiber damages are normally seen first at the end customer, paper made or used somewhere far away from the pulp mill.
• The pulp quality must be understood at the pulp mill on a broad basis with reference to benchmarking and quality performance of the main unit processes, drying and the whole mill.
Typical Quality Problems

- Situation at the door of the paper making:
  - Fast development of CSF (SR) but slow tensile development
  - High SEC for reasonable PM runnability
  - More fines, fiber length decrease
  - Low wet-strength, tear, toughness, zero-span tensile
  - Need to increase chemical pulp percentage
  - Low bulk, low tensile stiffness, high density
  - High hygro expansion, bad dimensional stability

- A long research dilemma, "fast refining but low strength"
The Fiber Damage Pathway

- Chipping, chip damage
- Digester quality delivery
  - Some measurable in cooked pulp
  - Some latent damage occurring later
- All MC-pumps, control valves, manifold tubes, mixers, reactors, blow valves, presses ... over-and-over-again
- Drying process, hornification
- Refining and refining targets
What to do?
Modern Research Methods

The first thing to do is to do some own research. How does this concern my mill, my pulp, my customers? Where and how do a loose quality?

The main idea is to combine a purposeful pulp mill fiberline study (audit) with fibre and paper physics study.
The target of the mill study is

1. To prepare reliable samples
   Chips - Digester Pulp - O2 Pulp - D2 Pulp - Dry Sheets
2. To analyse the fibre line quality profile

The target of the lab study is

1. To lab cook and lab bleach to prepare the ideal, undamaged reference pulps
2. To carry out fiber and paper physical study
   • Standard SEC based lab refining and hand sheet testing
   • Special sheet rheology measurements
   • Special fiber physics measurements, FSP, Pore issues
Now we don’t have to hit our heads on fibre wall anymore....
We Have Conclusions

• *On one hand*: Kraft cooking makes flexible and bonding fibers which after refining make very strong fibre web
• *On the other hand*: Creating macropores by dissolution and loosening of the structures by mechanical forces decrease mill pulp quality in many ways
• The softwood strength and quality delivery loss paradigm is valid for modern eucalyptus pulp mills as well!
• The mechanisms behind kraft pulp quality problems have been uncovered. The main culprits are: Digester, O2delig and drying machine. The digester makes the first, ever deteriorating chance and fiber damage.
We Have More Conclusions

- Eucalyptus laboratory made pulps, whether cooked by conventional or mill-actual process, are often dramatically better than mill pulps
- Chemistry as such does not explain observed pulp quality
- Chemistry opens the fibre structure for physical chances, be very cautious about reason-consequence causality
- Changing cooking chemistry without changing the physical performance of the process has only minor effect on pulp quality
- Changing the physical performance of cooking has significant effect on pulp quality
- There is a huge improvement potential in the quality efficiency of eucalyptus pulping-refining-paper value chain
We now know how the wall gets damaged and preventing it to happen we can get much better pulp and make the entire value chain more profitable!

Thanks for Attention!!

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