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DWP application and support

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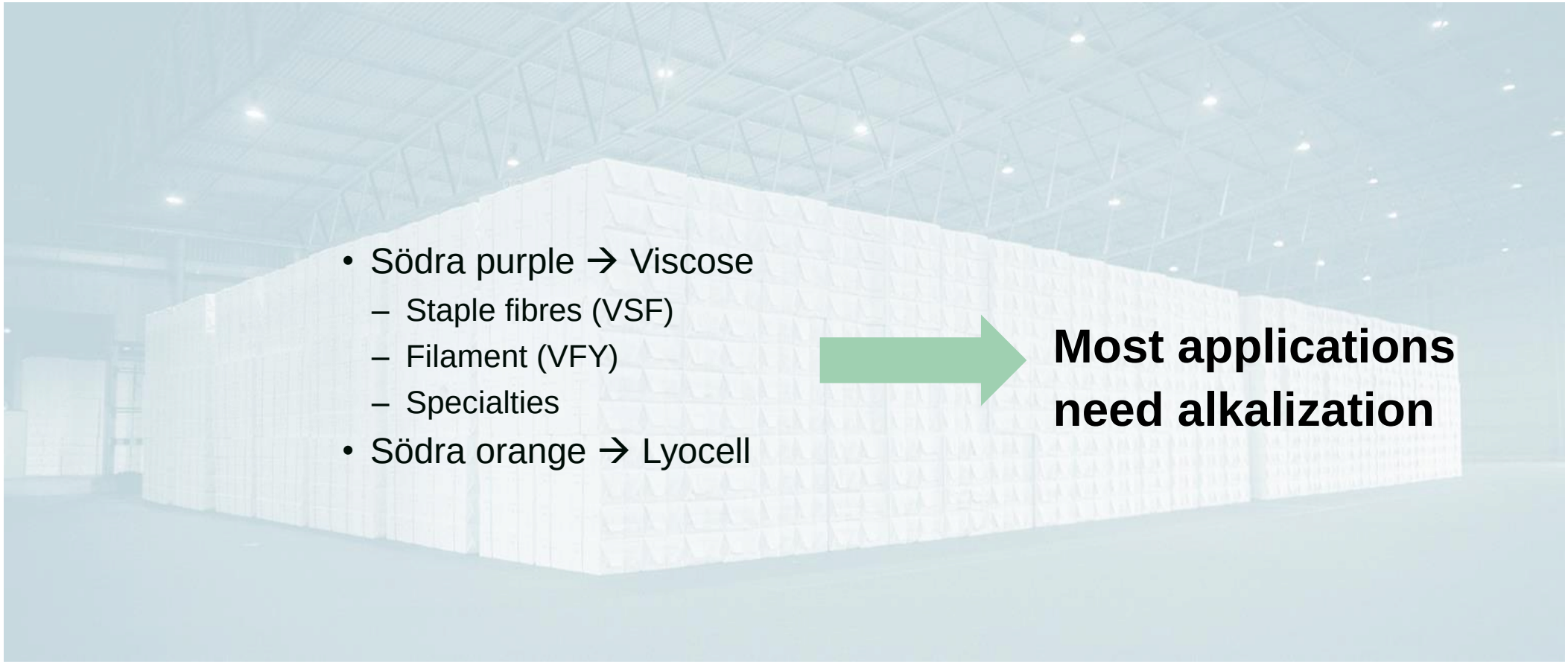
Agenda

- Product segments
- Aspects on alkalization
- Application support - What can we offer ?

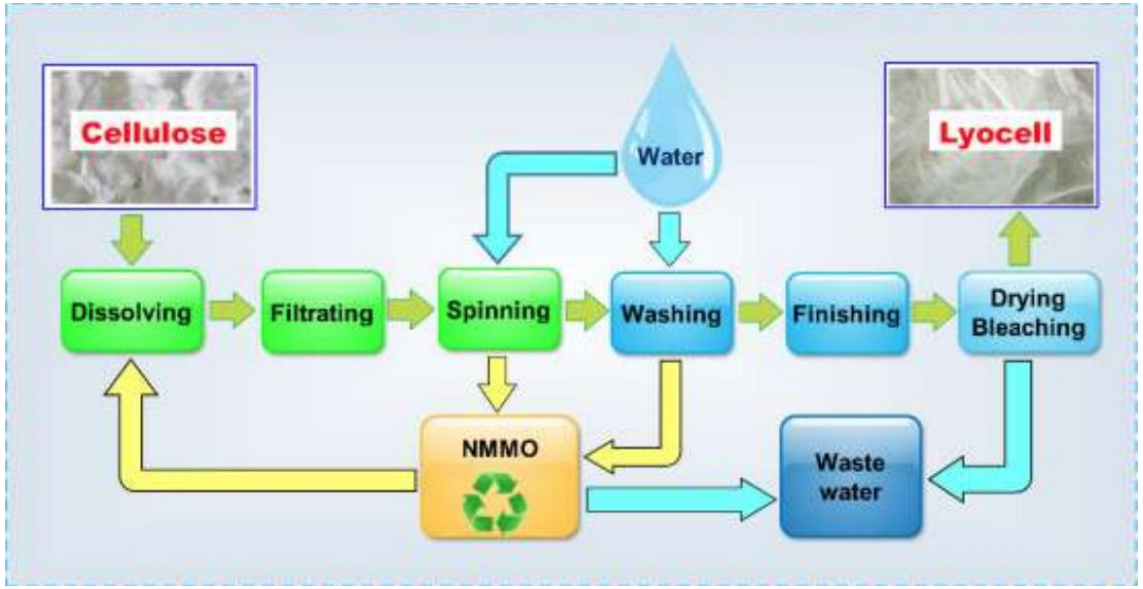
Product segments

Södra Cell – applications for Södra´s dissolving pulp



Lyocell process

Process	Lyocell process/ fibers	Viscose process/ fibers
Dissolution	**NMMO direct dissolution** Physical dissolution Without chemical reactions	**NaOH /CS_2** Mercerization/ xanthation Chemical reaction
Spinning	**Dry-jet wet spinning** Direct dissolution to form highly viscous dopes Fibers are formed *via* a) an orifice spinneret in a dry form into an air gap, b) then in a coagulation bath. Irregular molecules arrangement to form crystallites laminas (Wendler *et al.* 2011; Ramamoorthy *et al.* 2014;).	**Wet spinning** Dopes with relatively low viscosity Fibers are formed using spinneret immersed in an aqueous bath containing sulfuric acid and additives. Stretching is done after the regeneration. The formed fibers are relatively amorphous, with low-tenacity (Wendler *et al.* 2011; Ramamoorthy *et al.* 2014).
Environment	**Environmentally friendly** > 99% of the solvent recovered No harmful by-products formed High energy demand for solvent recycling	**Heavy environmental loads** CS_2 (about 25-30%) not recovered (may also be converted to by-product) High demand for water

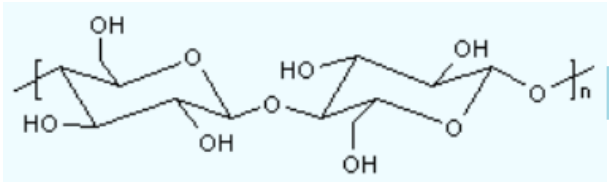


Zhang et al (2018)

Aspects on alkalization

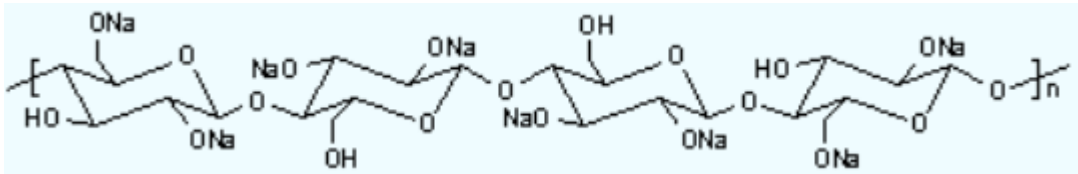
Chemial stages of the viscose process

Cellulose



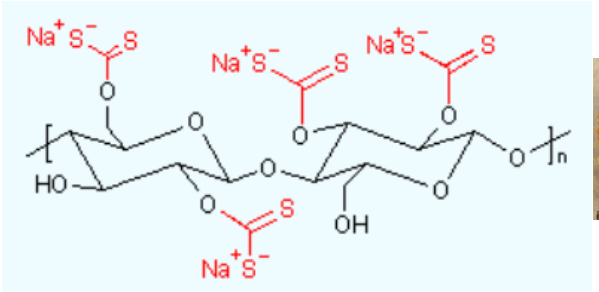
+ 18 % NaOH

Alkali cellullose



+ CS2

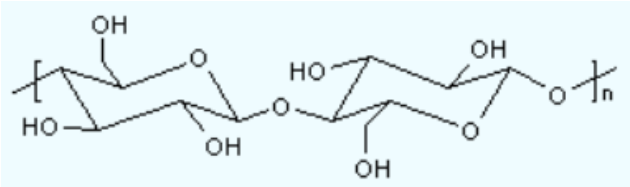
Cellulose derivative ”Xantate” / ”Viskose”



+ NaOH

+ H2SO4

Regenerate”Viskose fiber”



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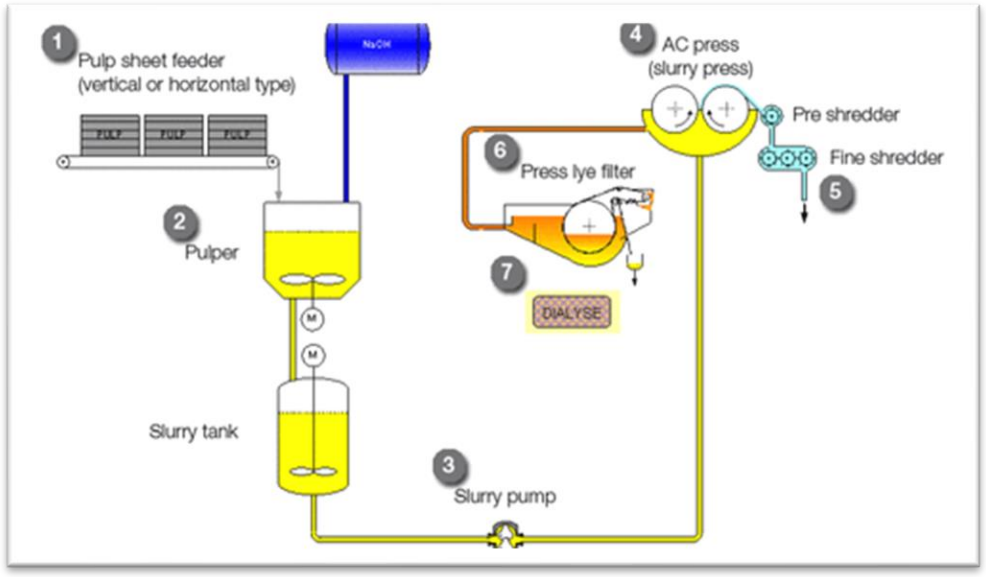
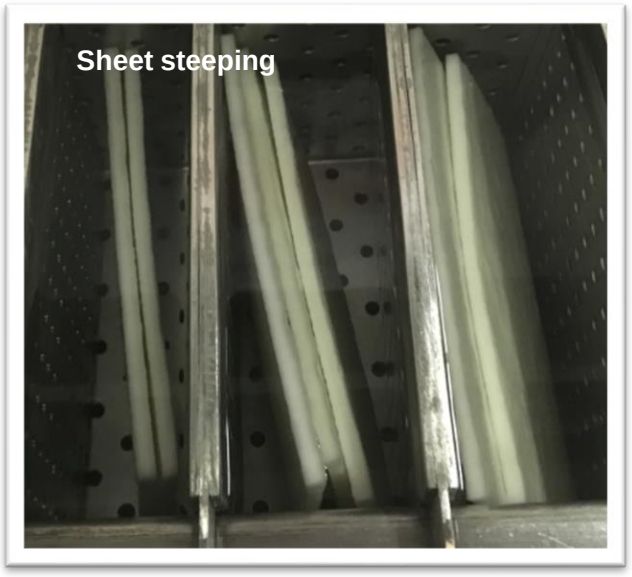
Slurry versus sheet alkalization





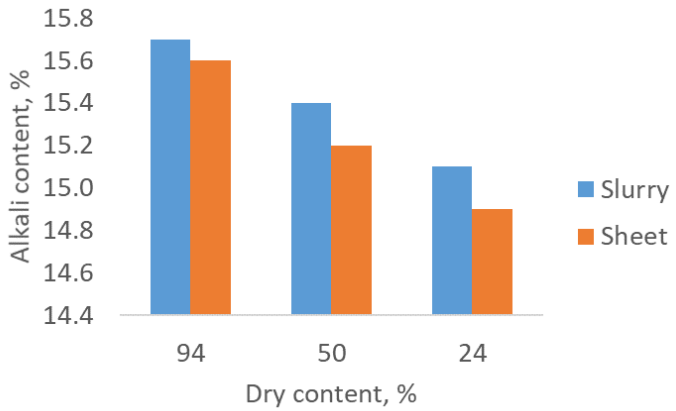


Figure: Alkali content in pressed alkali cellulose produced from pulp with different dry content alkalized in 18 wt% aq. NaOH using the technique of slurry and sheet alkalization.

Less chemical uptake in sheets.

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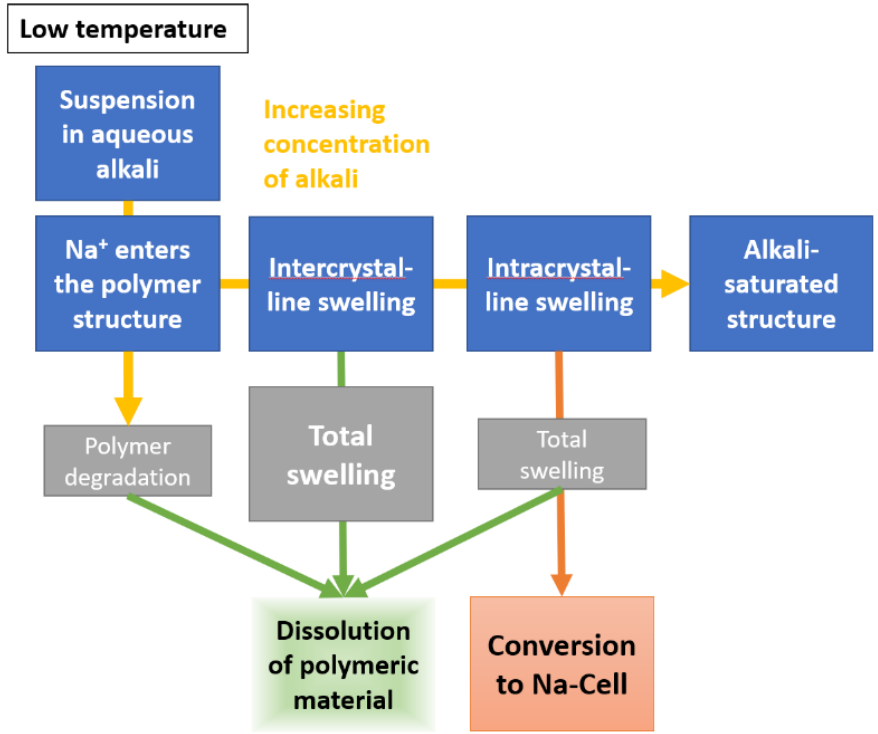
Alkalisation

- **Industrial established process operation**
  - Upgrade of pulp by extraction
  - Activation of pulp prior to processing by transformation to alkali cellulose
  - aka steeping and mercerization
- **R18**
  - Residue R after extraction with 18 wt% aq. NaOH and neutralization



Schematics for alkali treatment of cellulosic material at increasing alkali concentration.
(Götze 1967, Rydholm 1965, Wyatt 1966, Fengel and Wegener 1989, Woodings 2001, Sixta 2006a, Reyes et al. 2016)

Alkalization of pulps with increasing initial intrinsic viscosity

Loss of viscosity

Intrinsic viscosity decreases by alkalization and pressing.

The difference increases the higher the initial intrinsic viscosity is.

The decrease in intrinsic viscosity due to alkalization and pressing is important when predicting the course of preaging of specific pulps.

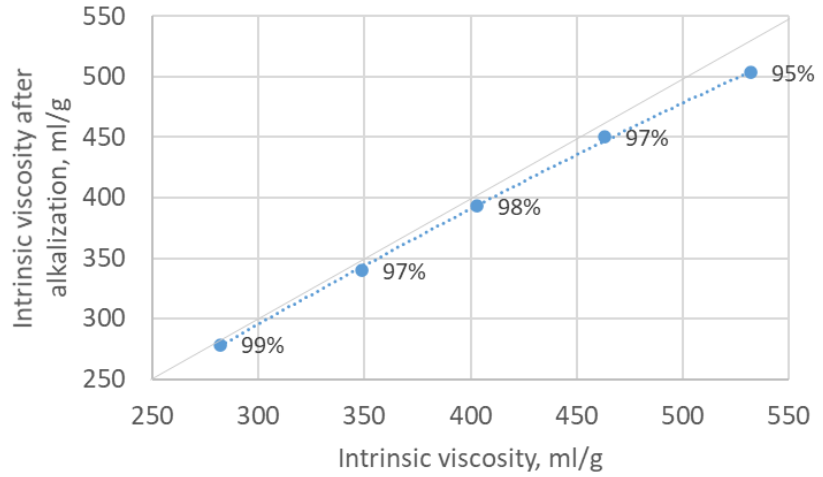


Figure: Intrinsic viscosity of a hardwood kraft dissolving pulp before and after alkalization with 18 wt% aq. NaOH at 50 °C (R18/50) (results taken from Eklund 2021). The data points are marked with the relative decrease in intrinsic viscosity due to alkalization.

Alkalization of pulps with increasing initial intrinsic viscosity

Decrease of PDI

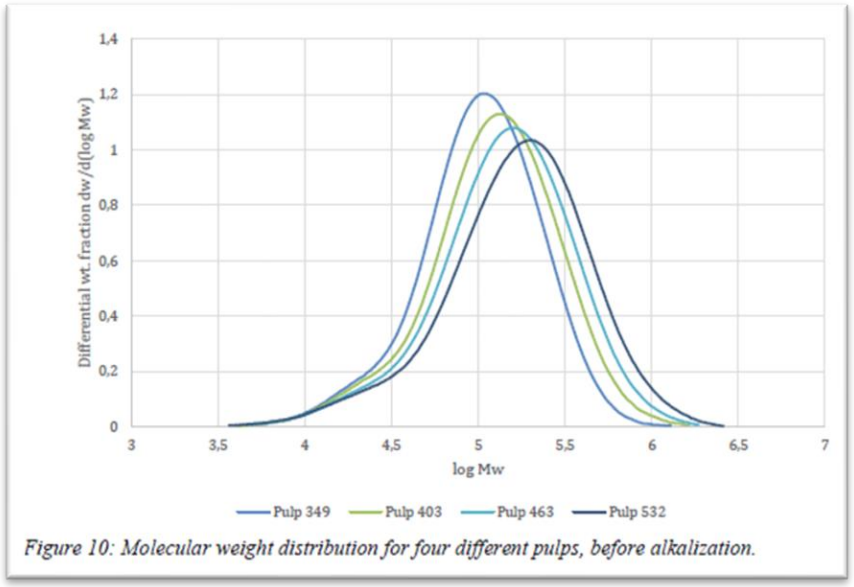


Figure 10: Molecular weight distribution for four different pulps, before alkalization.

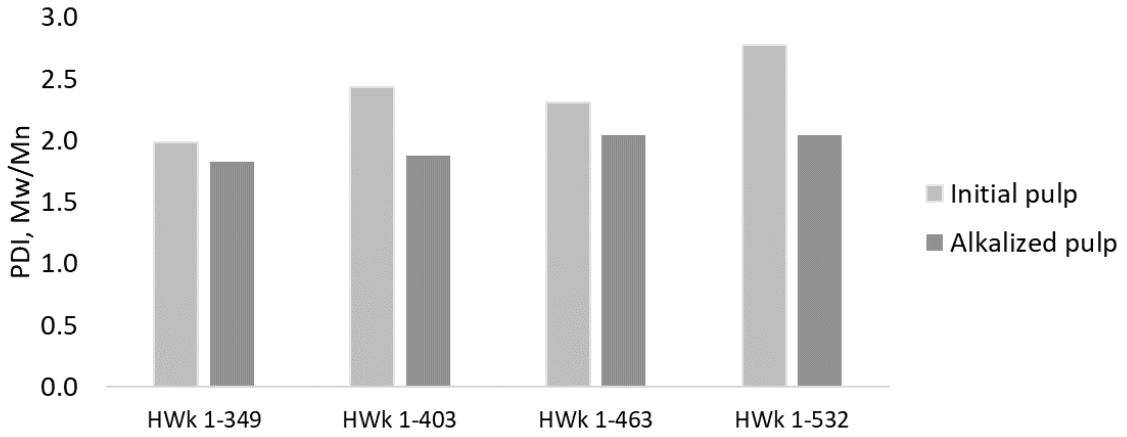


Figure: Polydispersity index (PDI) of a hardwood kraft dissolving pulp (HWk) before and after alkalization (R18/50) (results taken from Eklund 2021). The suffix indicates the initial intrinsic viscosity of the test series.

Higher initial viscosity comes with higher Mw/Mn (PDI).

Alkalization decreases PDI.

Alkalization of pulps with increasing initial intrinsic viscosity

Increase of residue

Lower availability increases residue

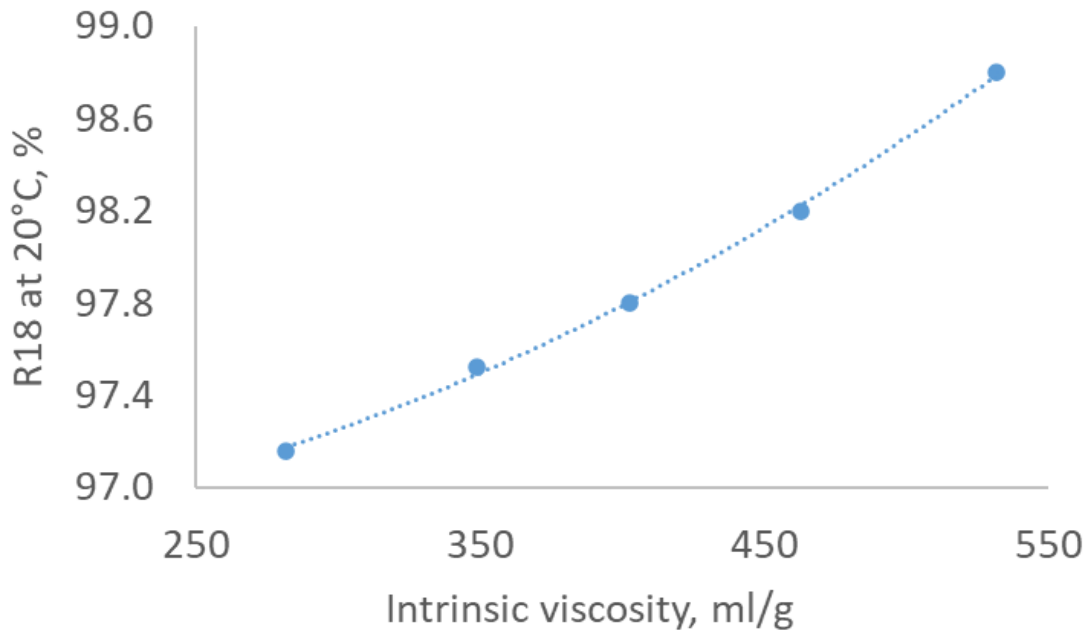
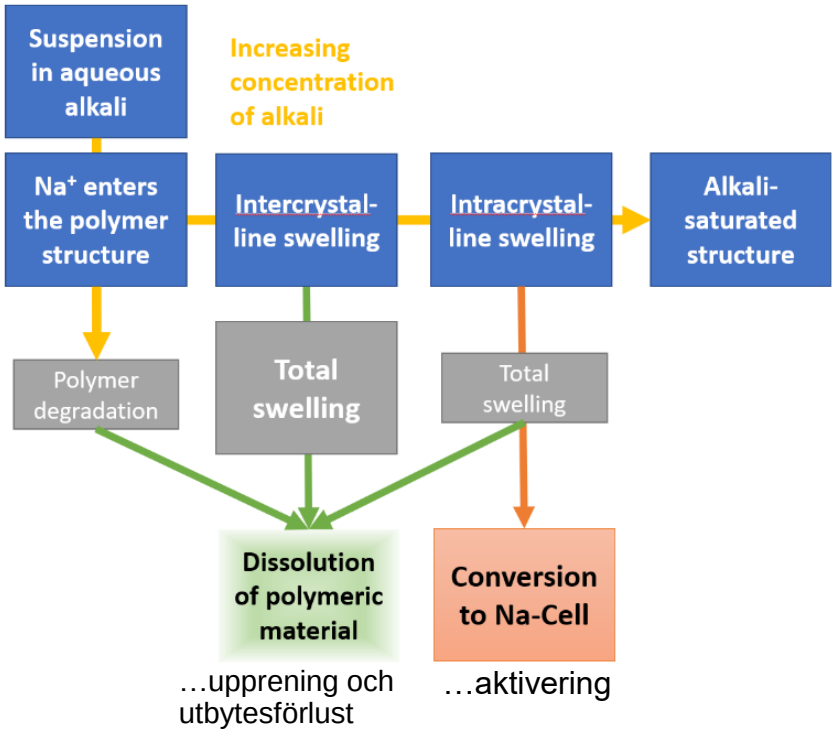
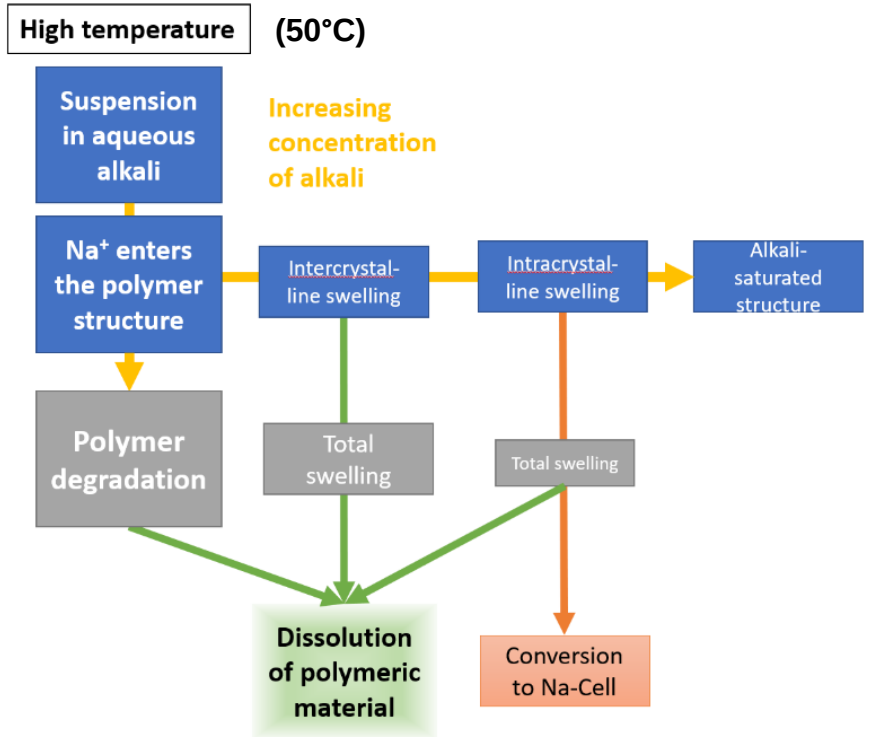


Figure: R18 at 20 C° versus intrinsic viscosity of a hardwood kraft dissolving pulp before alkalization.

Theory of alkalization





Schematics for alkali treatment of cellulosic material at increasing alkali concentration.

The size of the rectangles implies the extent of the phenomenon.
Left: Treatment at low temperature. Right: Treatment at high temperature

Götze 1967, Rydholm 1965, Wyatt 1966, Fengel und Wegener 1989, Woodings 2001, Sixta 2006a, Reyes et al. 2016

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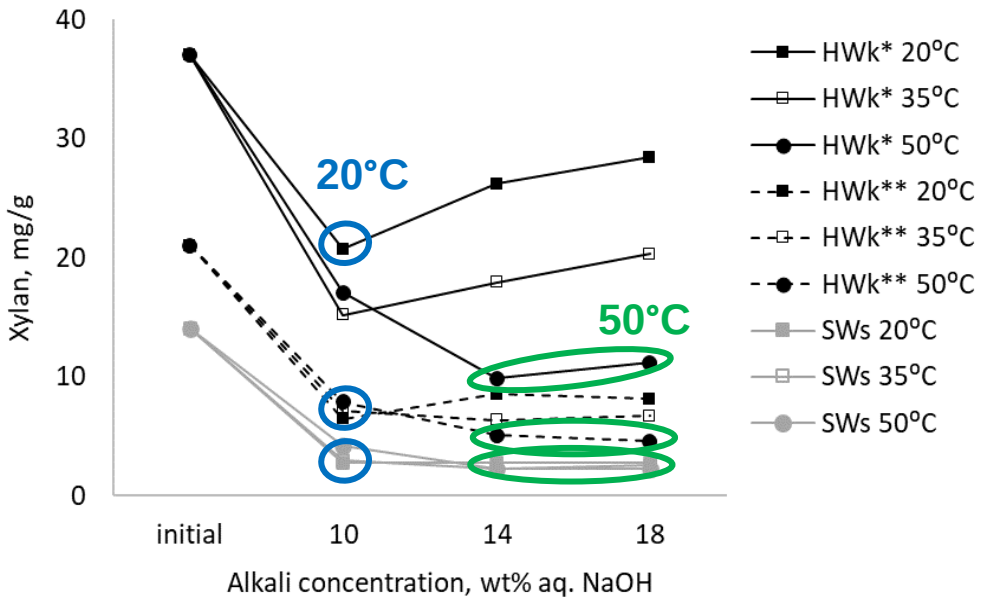
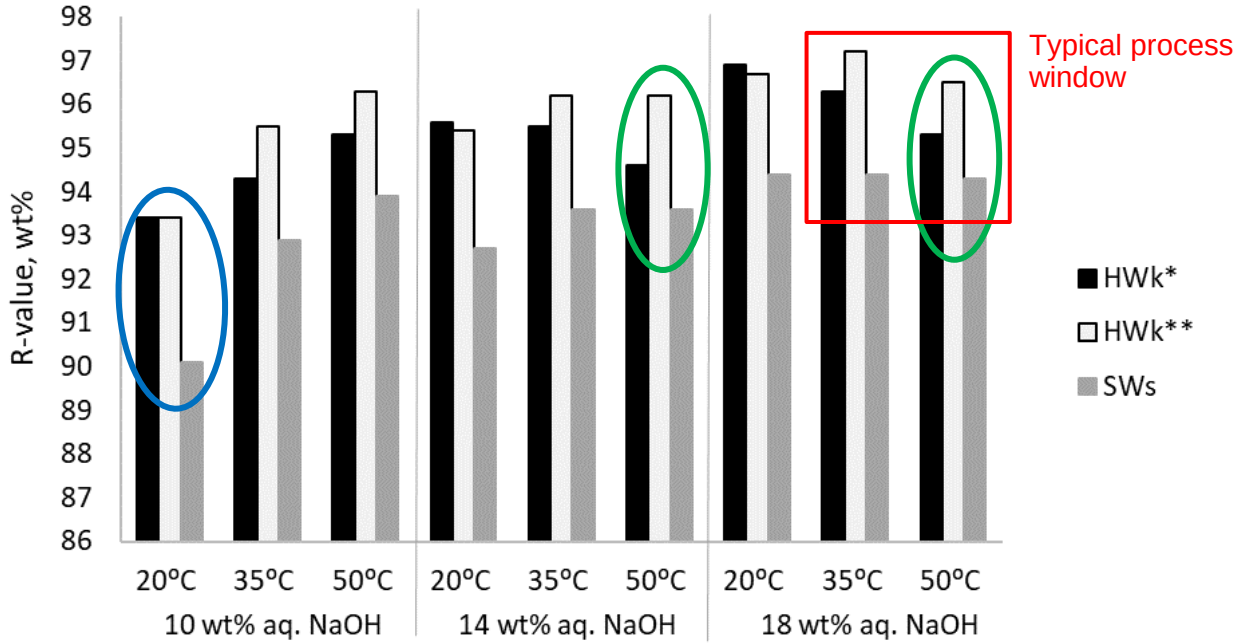
Purity and yield after alkalization

SWs Xylan content after extraction always low, yield max at 18%
HWk** Xylan content after extraction varies at high NaOH concentrations and can be balanced towards yield by adjusting T



Profiles of xylan content in the regenerated residue of three different pulps after alkaline extraction at different concentrations and temperatures (10, 14 and 18 wt% aq. alkali; 20, 35 and 50 °C)

(HWk*/** – hardwood kraft pulp, SWs – softwood sulfite pulp. 20, 35 resp. 50 – temperature in °C used for alkali extraction)



Residue, expressed as R-value upon extraction of pulp with aqueous NaOH at different concentrations and temperatures.

Most swelling
Effektive extraction

Fechter C, Fischer S, Reimann F, Brelid H, Heinze T (2020) Influence of pulp characteristics on the properties of alkali cellulose. Cellulose (London), Vol.27 (12), p.7227-7241)

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Alkalisation – crystalline phases and transformation

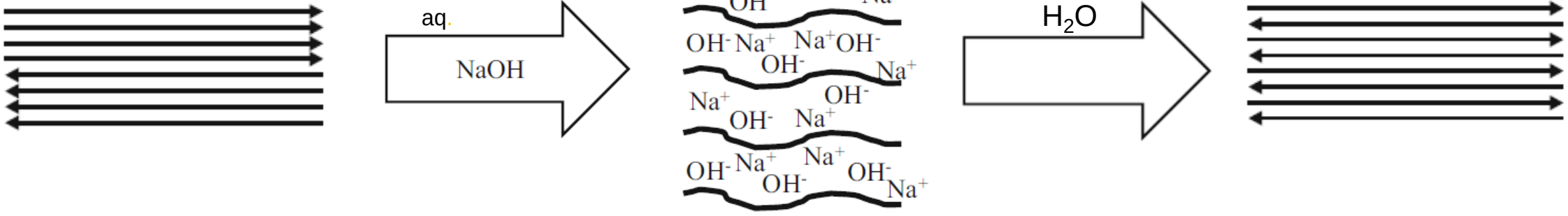
Cellulose I (Cell I)

Alkalisation (AC)

Sodium cellulose (Na-Cell)

Regeneration (rAC)

Cellulose II (Cell II)



Viscose process (derivatisation…)

According to Heinze et al. 2018

Cellulose II

initital contents similar in standard DWP

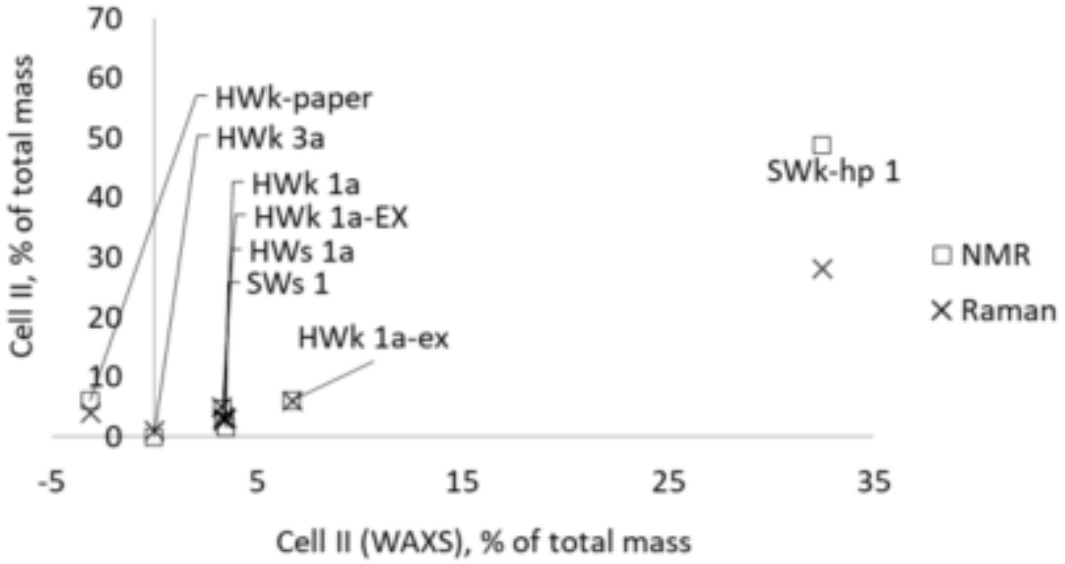


Figure 17: Cellulose II (Cell II) in different generic pulps measured with CP/MAS 13C-NMR spectroscopy, X-ray scattering (WAXS) and NIR FT Raman spectroscopy

Degree of transformation

$$D_T = \frac{100\ x\ (Cell\ II_{rAC} - Cell\ II_{initial})}{100 - Cell\ II_{initial}}$$

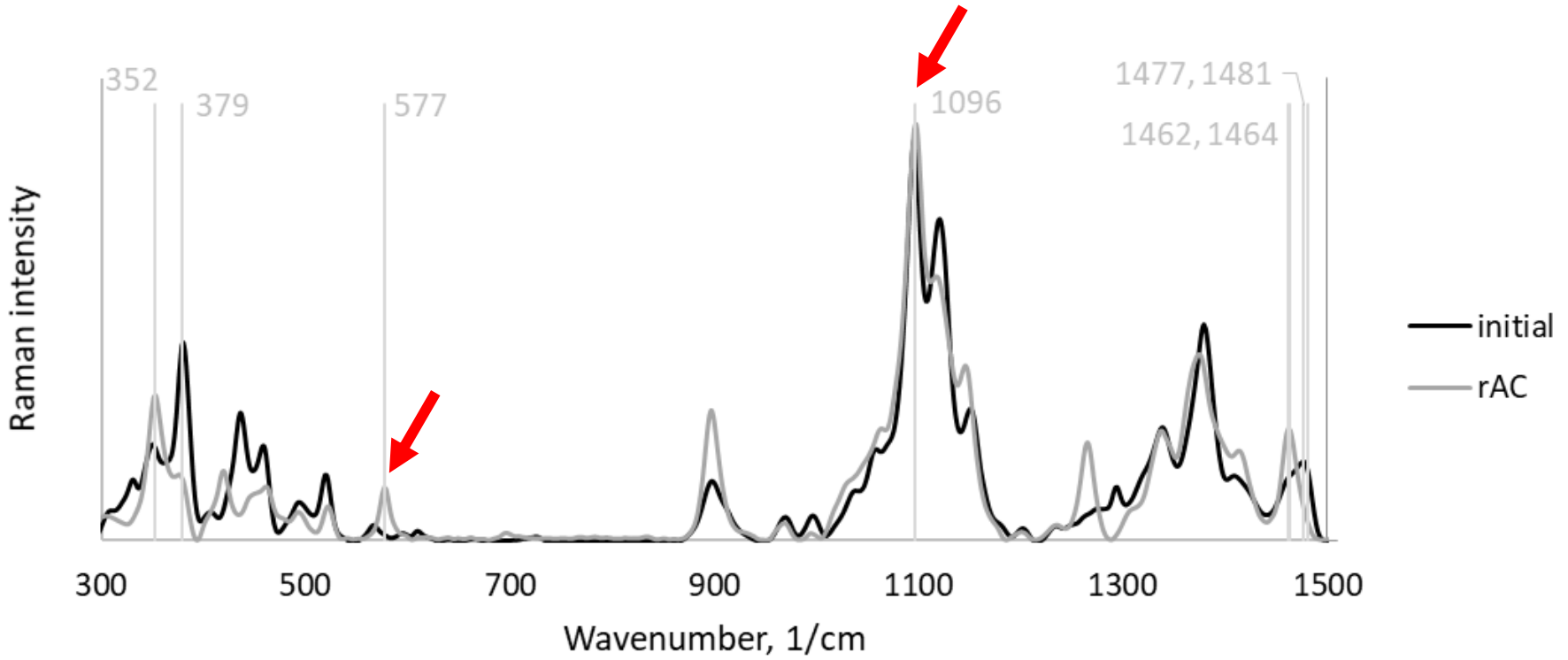


Figure: Raman spectrum of a pulp in native form and after alkaline extraction with 18 wt% aq. NaOH bei 50 °C (rAC). Bands of interest for evaluation of cellulose structure acc. to Agarwal 2017 are marked.

Fechter C, Fischer S, Reimann F, Brelid H, Heinze T (2020) Influence of pulp characteristics on the properties of alkali cellulose. Cellulose (London), Vol.27 (12), p.7227-7241)

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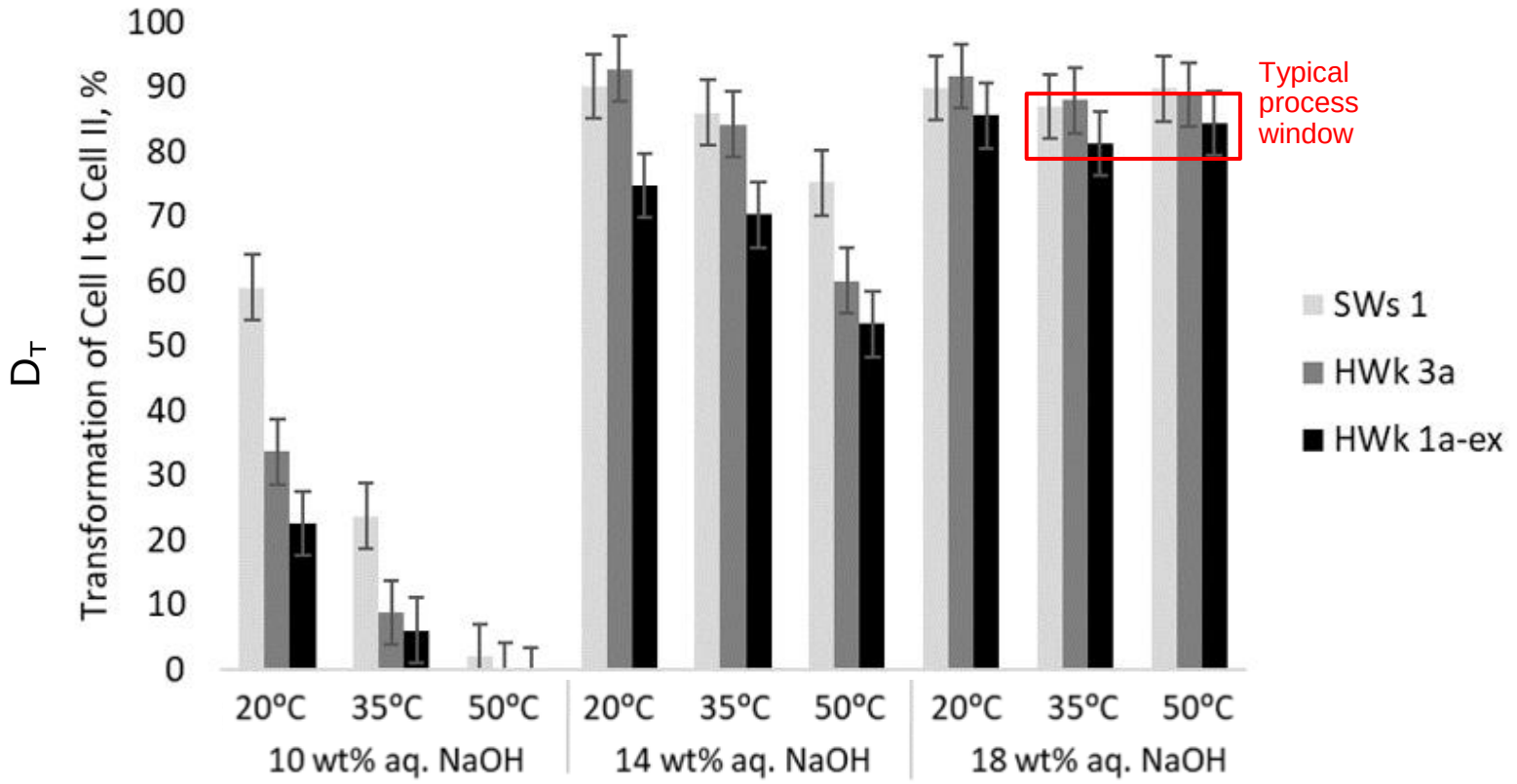
Degree of transformation after alkalization



All pulp are transformed to ca 90 % at 18 wt% aq. NaOH.

D_T at 10 och 14 wt% aq. NaOH differentiates pulp.
Differences could not be explained by supramolecular differences.

Transformation of Cell I to Cell II of different pulps (HWk 1a-ex – hardwood kraft pulp with high xylan, HWk 3a – hardwood kraft pulp, SWs 1 – softwood sulfite pulp) upon alkalization at different concentrations and temperatures; concentration of aqueous NaOH: 10, 14 or 18 wt%; temperature 20, 30, or 50 °C. The accuracy of the measurement is assumed to ±5 %-units.

Fechter C, Fischer S, Reimann F, Brelid H, Heinze T (2020) Influence of pulp characteristics on the properties of alkali cellulose. Cellulose (London), Vol.27 (12), p.7227-7241)

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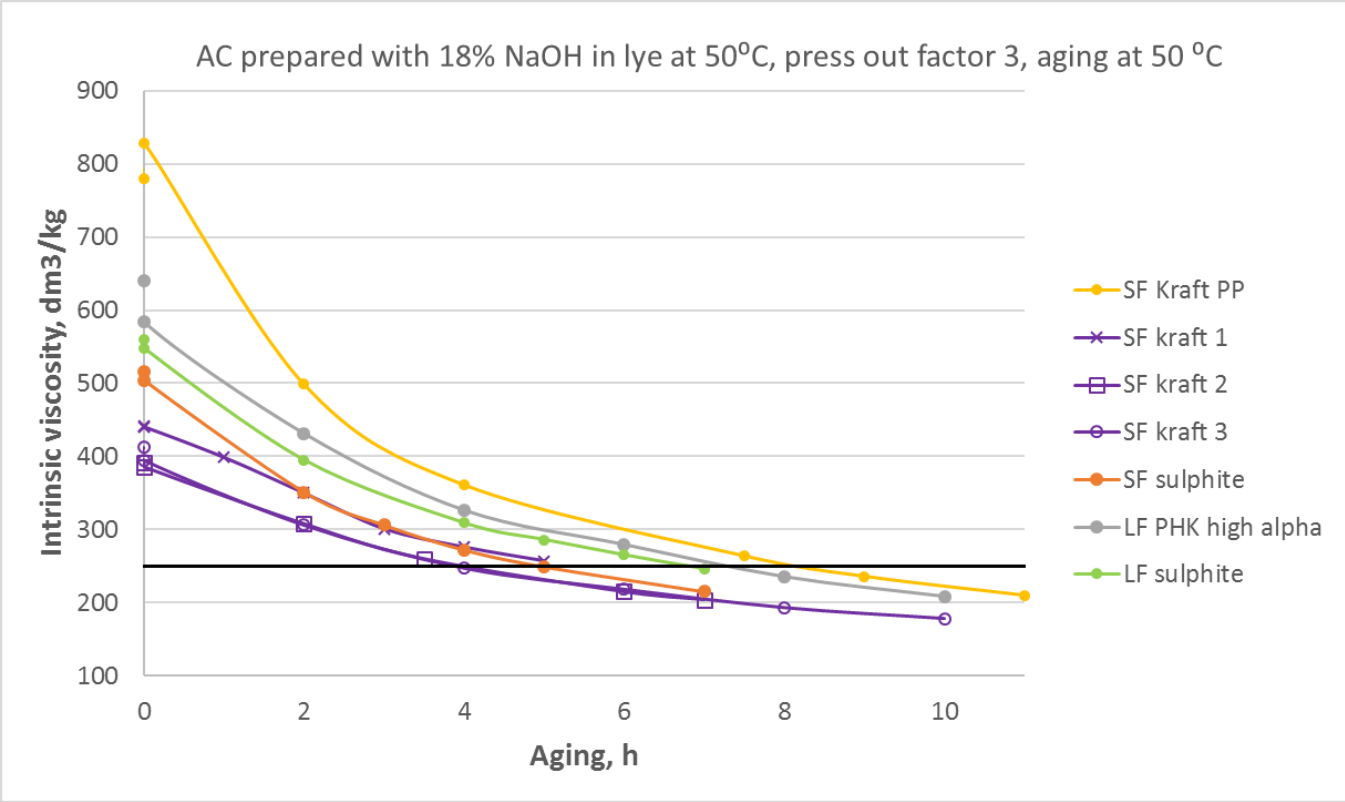
Preaging behavior of different pulps



Application support - What can we offer?

- Alkalization
- Fluffing
- Viscose lab
- Analysis

Pretreatment of pulp

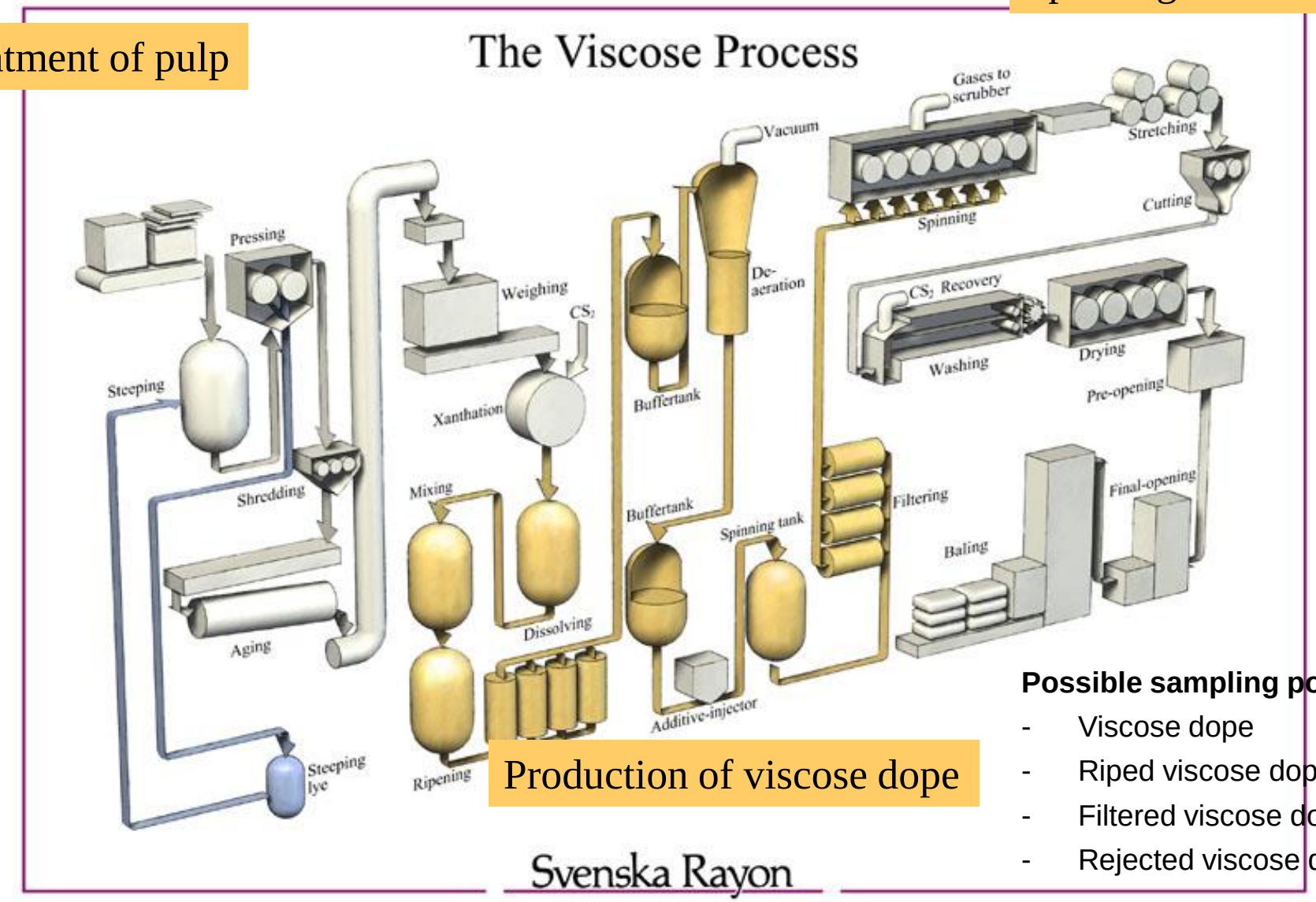
Possible sampling points

- Pulp feed
- Alkali cellulose
- Aged alkali cellulose
- Alkalization lye
- Press lye

Spinning of viscose dope

Possible sampling points

- Spinning bath
- Spun fiber
- Washing filtrates

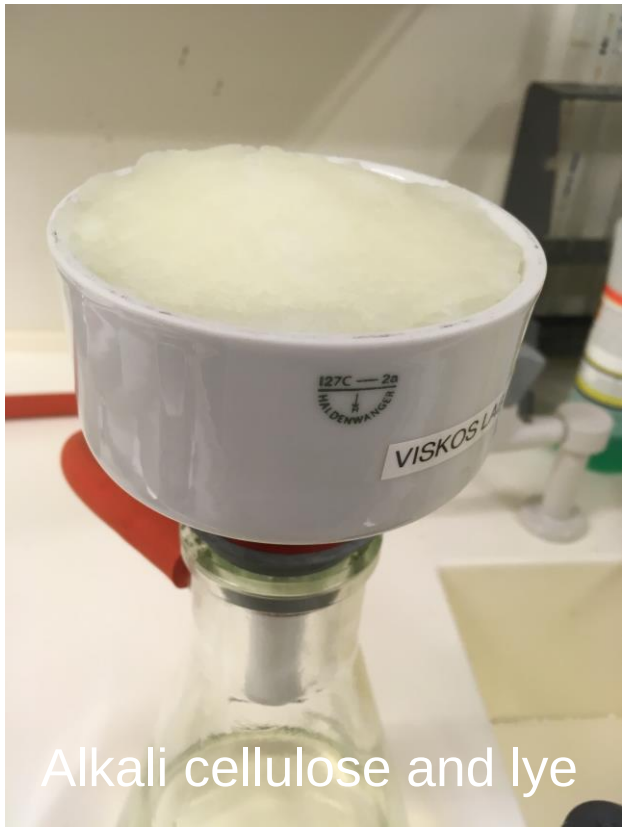


Production of viscose dope

Possible sampling points

- Viscose dope
- Riped viscose dope
- Filtered viscose dope
- Rejected viscose dope

Alkalisation lab (1)



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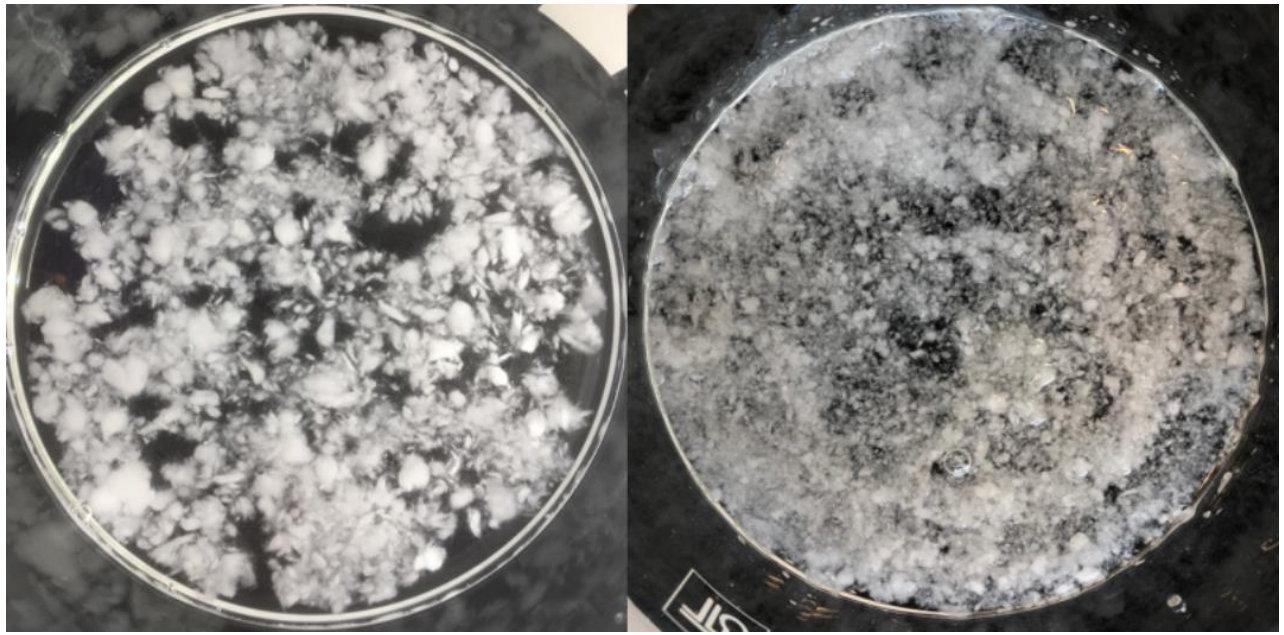
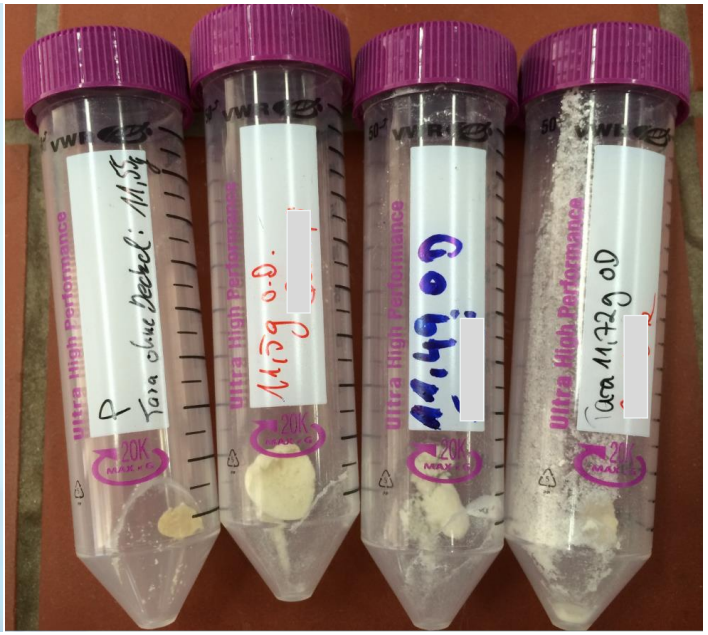
Alkalization lab (2)



Bloating trial – check of fluffing result

Aging



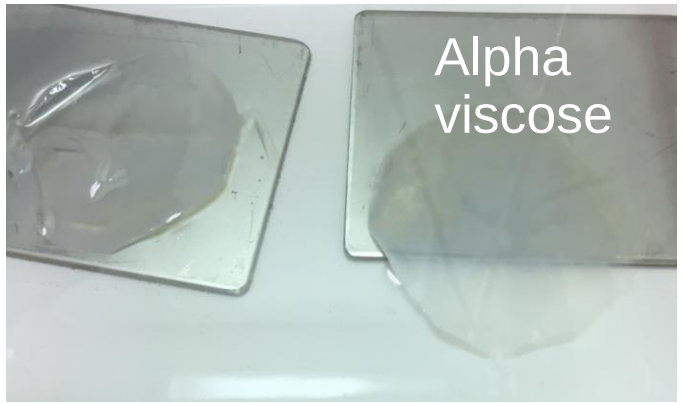
Precipitated lye

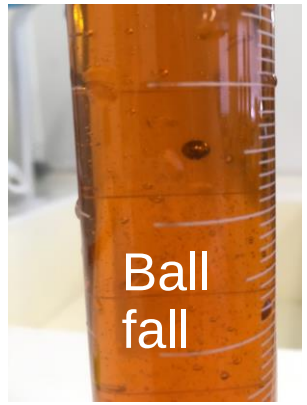
Viscose lab

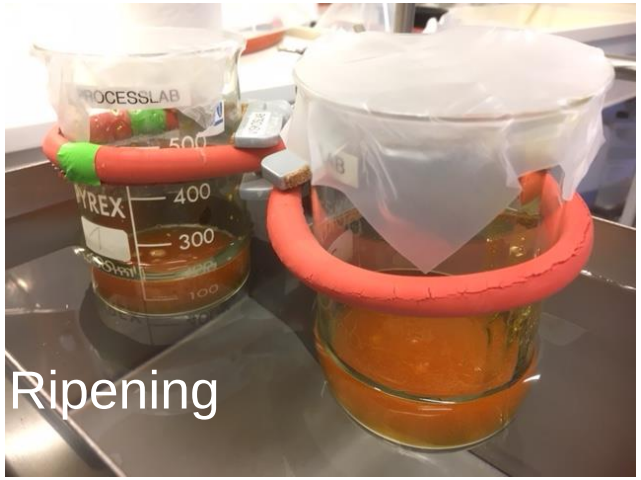

Xanthation

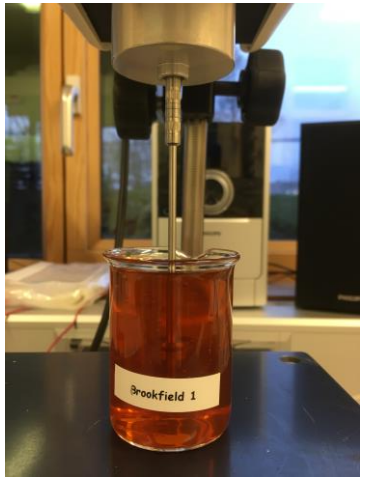

Xanthate

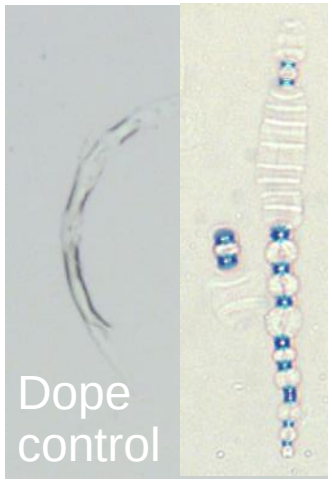

Dissolving

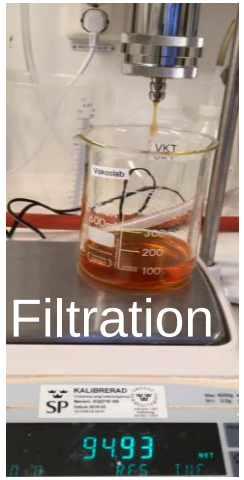

Alpha
viscose

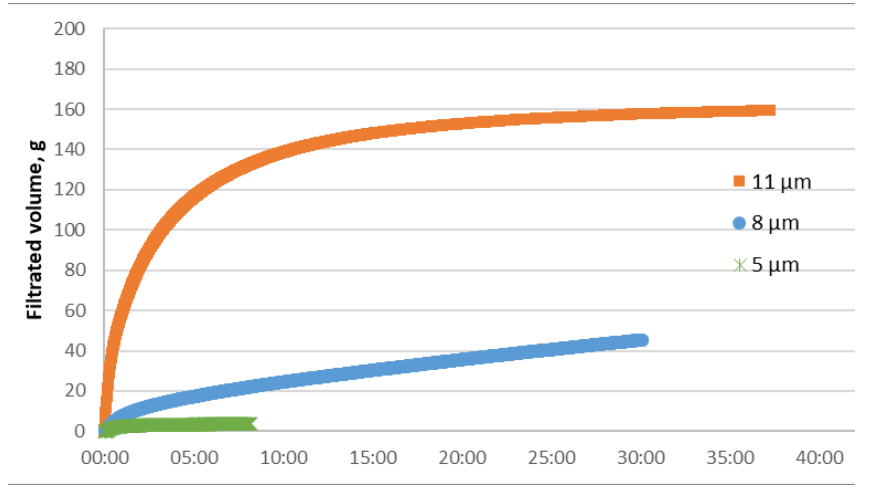

Ball
fall


Ripening



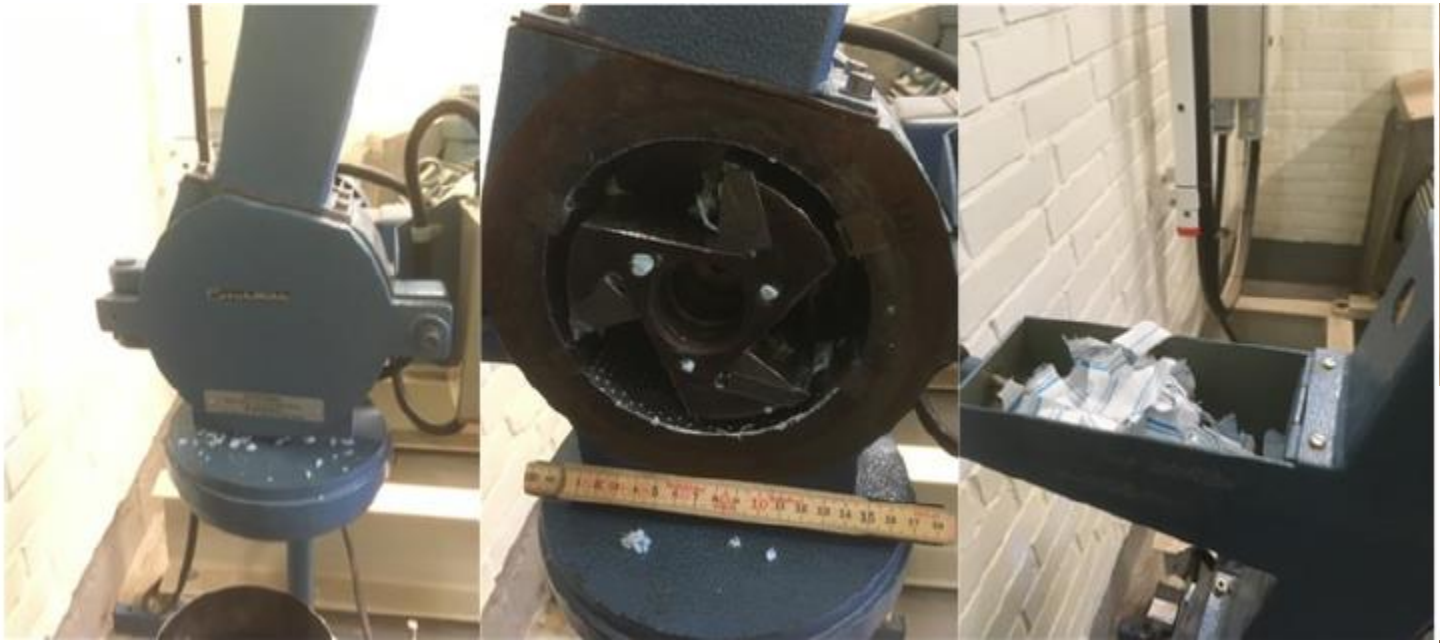

Dope
control

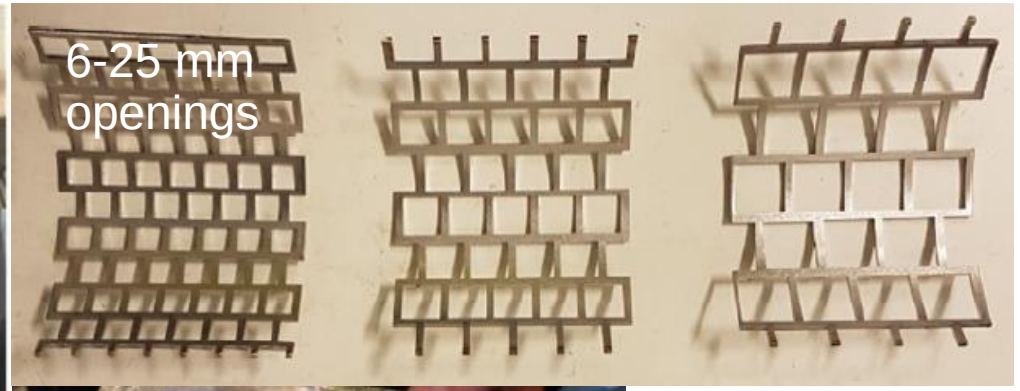

Filtration


Filtrated volume, g
200
180
160
140
120
100
80
60
40
20
0
00:00
05:00
10:00
15:00
20:00
25:00
30:00
35:00
40:00
11 µm
8 µm
5 µm

Fluffing

Opening of dry pulp





Analysis

- Wood fiber analysis (L&W Fibre Tester)
- Carbohydrate composition in pulp and lye (HPAE ICS)
- Extractives characterization (GC-FID and GC-MS)
- Metals (ICP)
- Molecular weight distribution (PGC-MALS)
- And many standard analysis and equipment

Possible Support Activities - Customer Projects

Process studies

- Use our viscose lab with focus on the alkalization step or other functions of our Innovation lab. Find out how pulp mix and process parameters interact.

Alkalization audits

- We help you to analyze the status of your pretreatment. Our focus is on the chemical composition of the fibers and the lyes.

Trouble shooting

- We will use our experience and modern equipment to try to help out
  - Analysis of intermediates and final product , deposit analysis etc

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