Investigating the Causes of Paper Strength Loss after Aqueous Treatments

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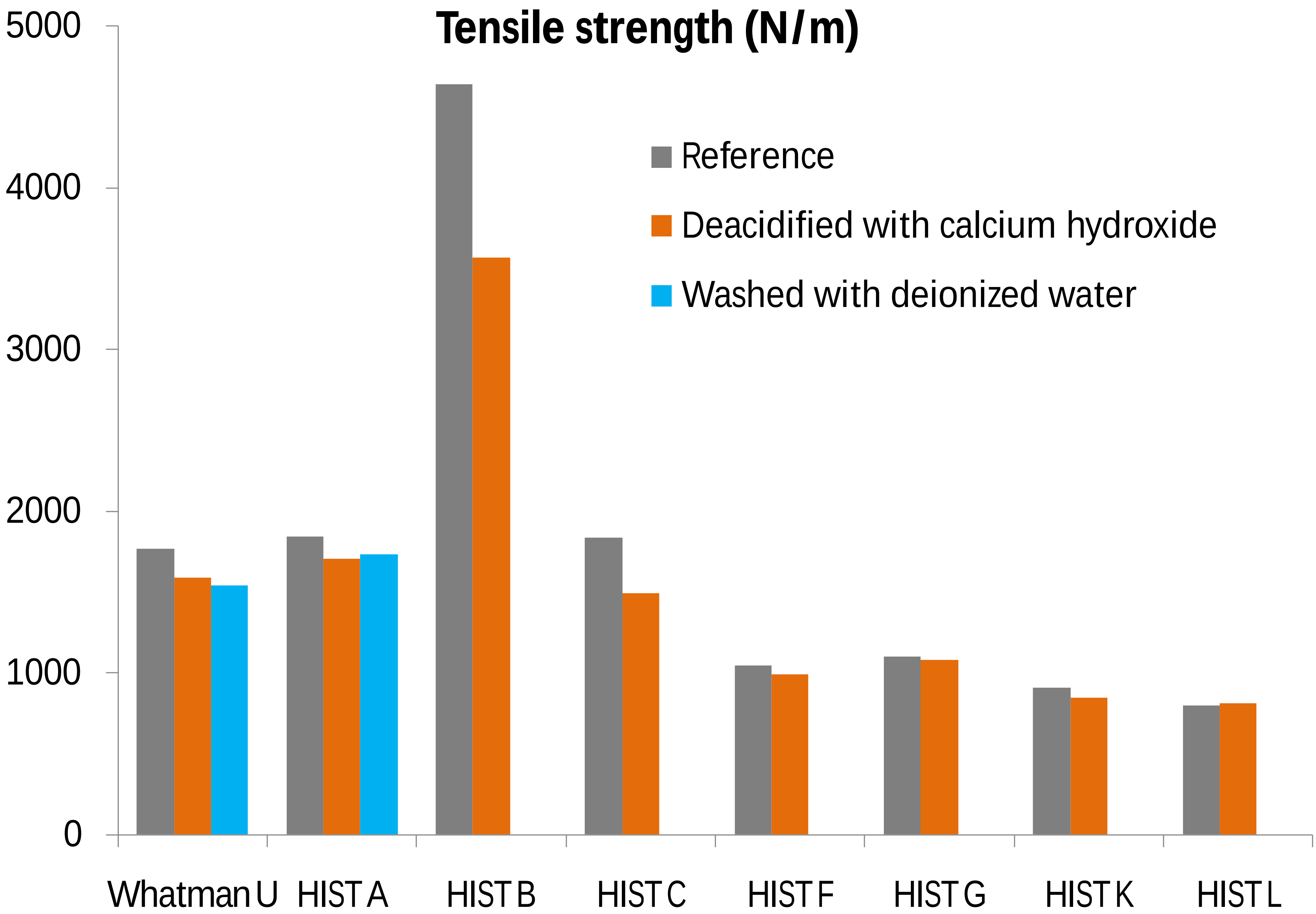
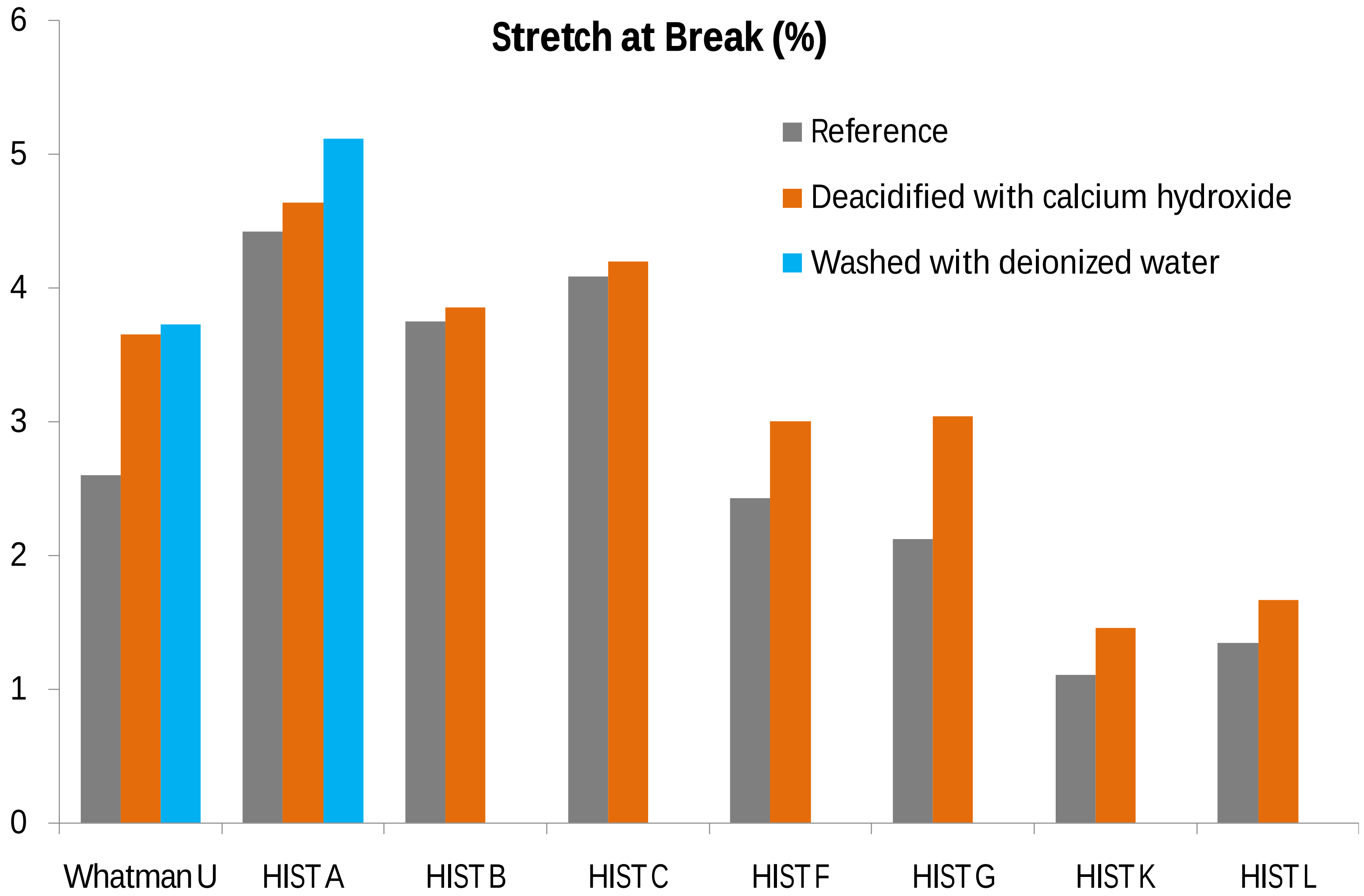
Introduction

Research incentive

- Previous unexpected and alarming results
- Aqueous treatments resulted in:
  - tensile strength loss
  - increase in stretch at break
- Sized and unsized samples
- Changes were statistically significant in most cases
- Similar scattered results in literature
- No plausible explanation


Tensile strength (N/m)
5000
4000
3000
2000
1000
0
Reference
Deacidified with calcium hydroxide
Washed with deionized water
Whatman U
HIST A
HIST B
HIST C
HIST F
HIST G
HIST K
HIST L


Stretch at Break (%)
Reference
Deacidified with calcium hydroxide
Washed with deionized water
0
1
2
3
4
5
6
Whatman U
HIST A
HIST B
HIST C
HIST F
HIST G
HIST K
HIST L

Aims of the research

- The investigation of the effects of aqueous treatments on various microstructural properties of pure cellulose paper
- The examination of the possible connection between the changes observed at the microscopic (microstructure) and the macroscopic level (strength properties)
- The investigation of any possible association with hornification

Hornification

- Irreversible changes that occur after the drying of cellulosic fibers, resulting in the reduction of water retention value and tensile strength
- Widely investigated by paper industry
- Very important in paper recycling

Methodology

Paper samples

- Whatman pure cellulose paper: Whatman U
- Historical rag paper samples: Hist A, B and C

Model conservation treatments

- Washing with deionized water
- Deacidification with semisaturated calcium hydroxide

Methods

- Air resistance (or air permeability) determination (Gurley method)
- Determination of the Specific Surface Area of cellulose by a water vapour sorption method (CIsorp|)
- Determination of volume changes, estimated by the changes of the dimensions of paper sheets
- Estimation of Crystallinity Index
- Mercury porosimetry for the evaluation of porosity changes

Results

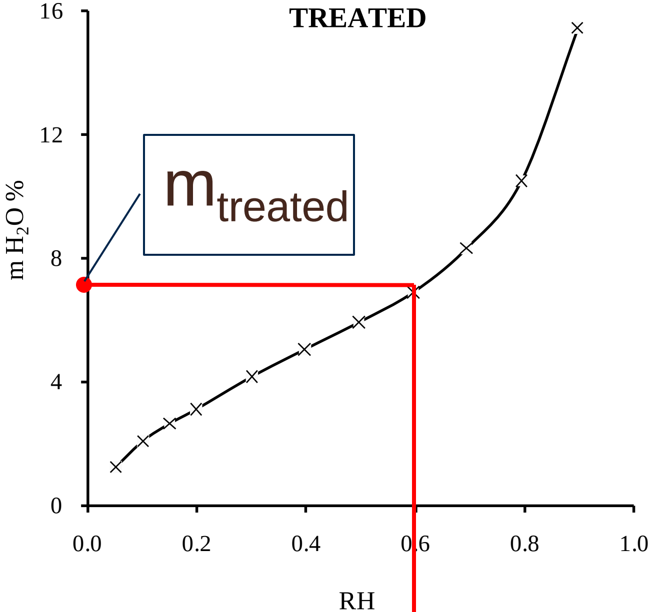
Changes (qualitative)

	TS	SAB	P % (MP)	Air Perm. (G)	S BET	V	CrI
After treatment	↓	↑	↑	↑	↑	↑	-

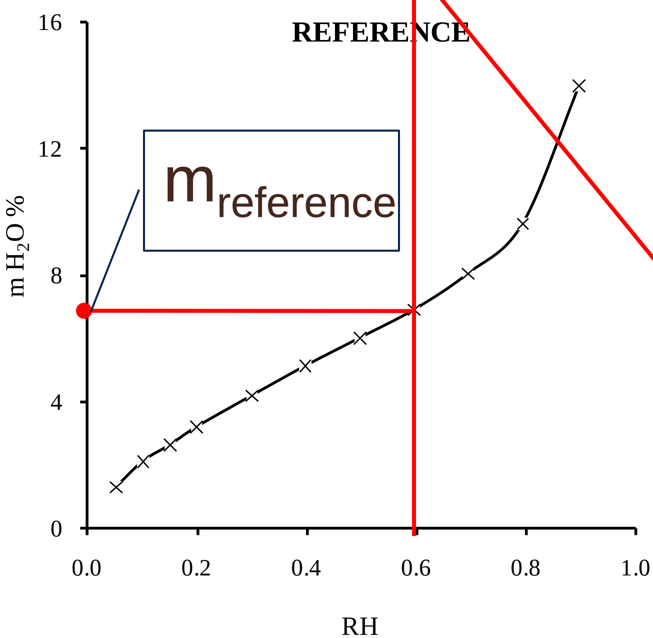
Changes in pore sizes

- No direct results from MP (inconsistent results)
- Deduced from the changes in the shape of the water vapour sorption isotherms with the aid of the f-plots
- f-plot: Plot of the ratio f of the moisture adsorbed at the same RH by the treated and the reference sample, against RH

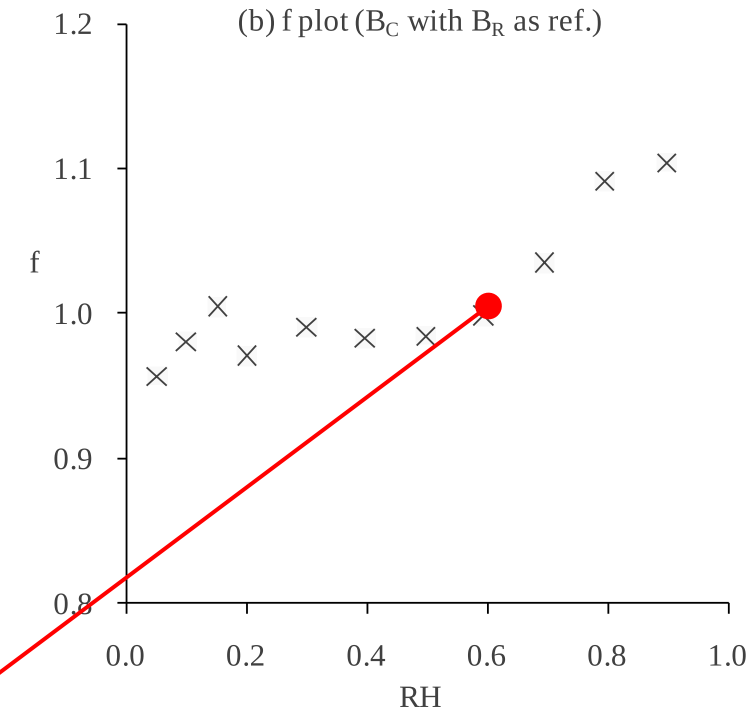
How an f-plot is constructed

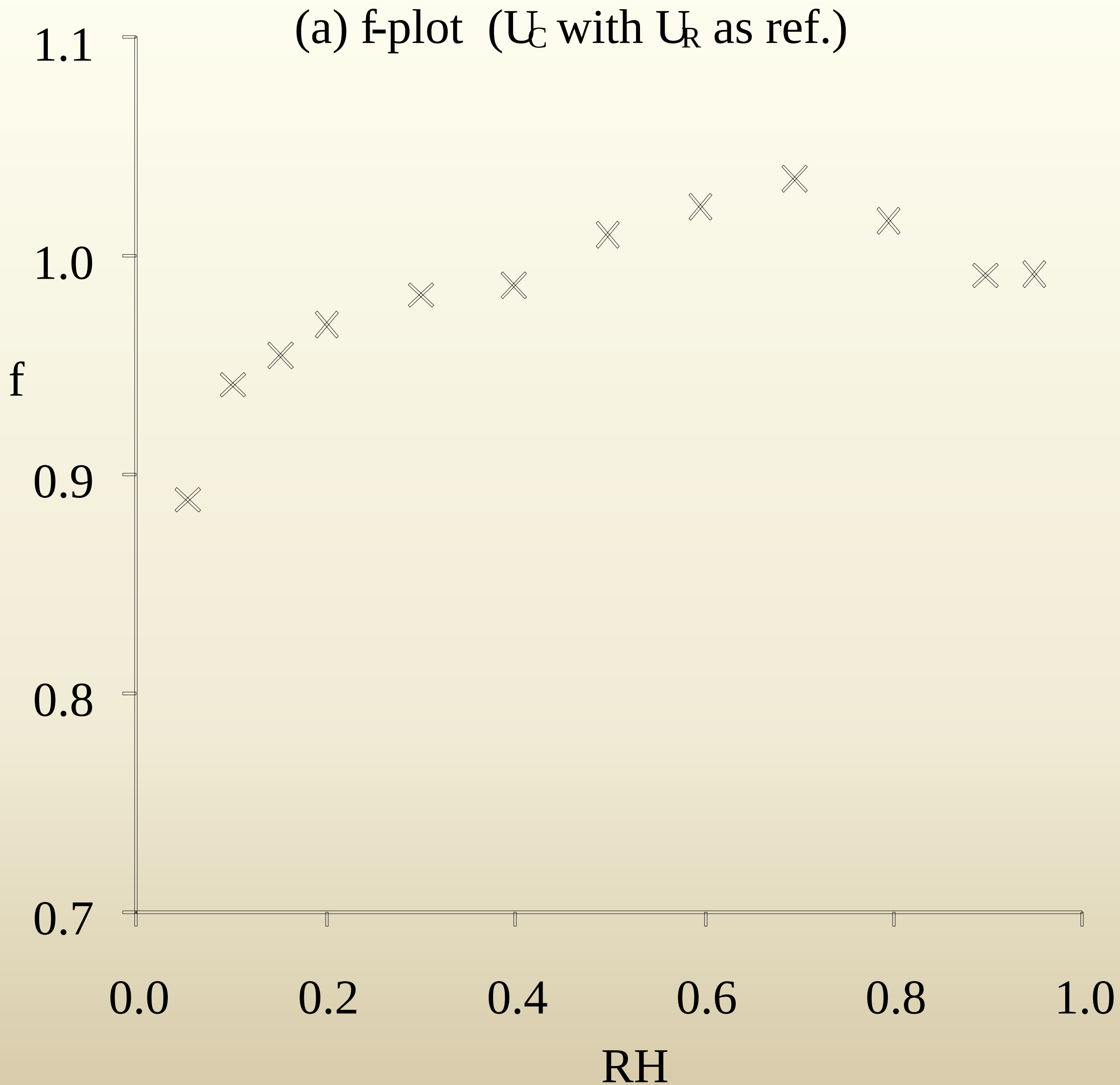


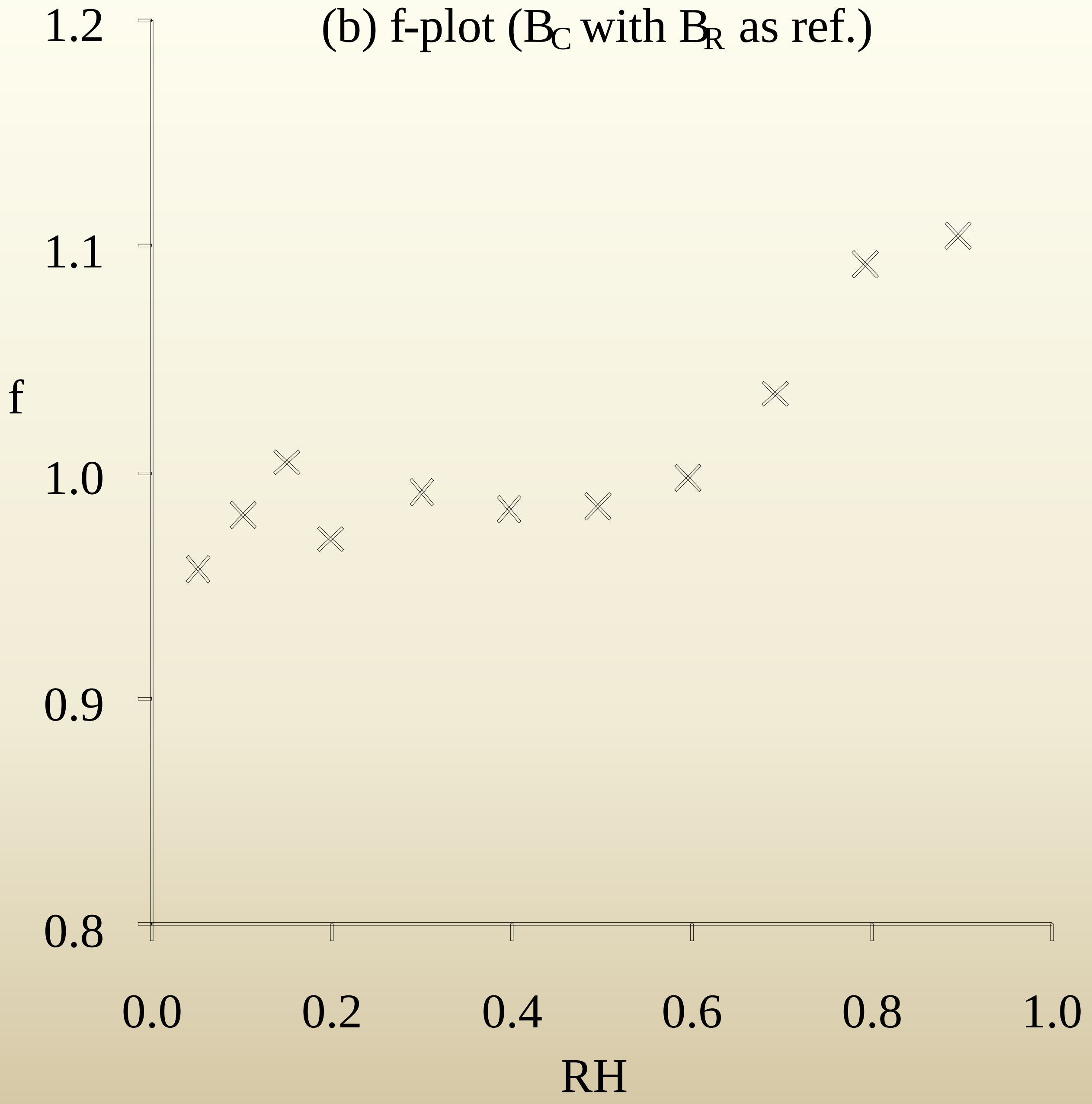
$$f = \frac{m_{treated}}{m_{reference}}$$



RH	f
0.052	0.957
0.101	0.981
0.150	1.004
0.199	0.970
0.300	0.991
0.397	0.983
0.496	0.985
0.595	**0.998**
0.693	1.035
0.793	1.092
0.896	1.104




(a) f-plot (UC with UR as ref.)
1.1
1.0
0.9
0.8
0.7
f
0.0
0.2
0.4
0.6
0.8
1.0
RH


(b) f-plot (B_C with B_R as ref.)
1.2
1.1
1.0
0.9
0.8
f
0.0
0.2
0.4
0.6
0.8
1.0
RH

Sorption capacity

- Decreases at low RH
- Increases at high RH

The size and/or the quantity:

- of the smaller pores (pores inside the cell wall) decreased
- of the larger pores (pores between the fibres and/or fibrils) increased

Discussion

- Aqueous treatments actually have an impact on the microstructure of paper
- Small but measurable increase of the specific surface area
- Substantial increase in air permeability
- No straightforward explanation of how the changes in the microstructure are related to the changes in mechanical properties
- Strength loss can be associated with hornification (from the literature)

Strength loss and hornification

- Creation of new irreversible hydrogen bonds between microfibrils inside the fibre wall
- The formation of new irreversible hydrogen bonds inside the fibre wall renders the cellulose fibres more compact, stiff and rigid
- Rigid fibers develop less bonded area and therefore lower tensile strength

- But, the increase in stretch at break cannot be explained
- Stretch at break **actually decreases** due to hornification after paper recycling

A tentative mechanism

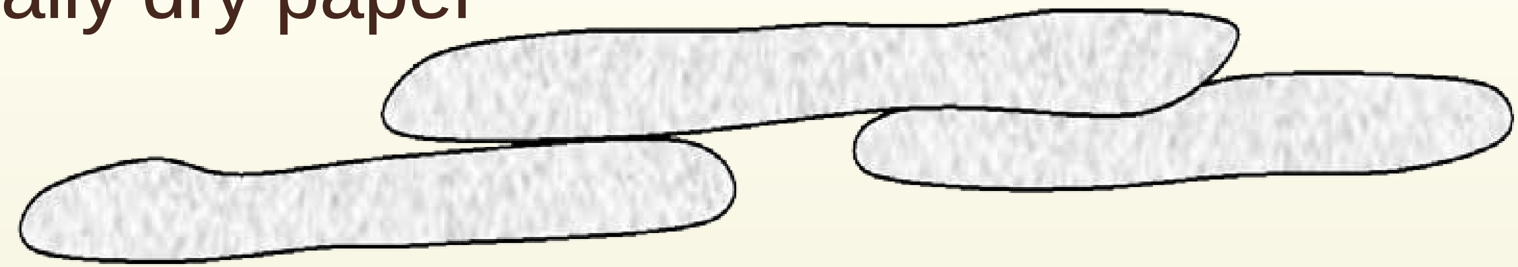
On wetting

- Immersion in water → uneven wetting
- Fronts of water are created and propagate
- Surface tension and swelling pulls fibres and fibrils partially out of the matrix
- Water breaks most of the hydrogen bonds and facilitates fibres shifting

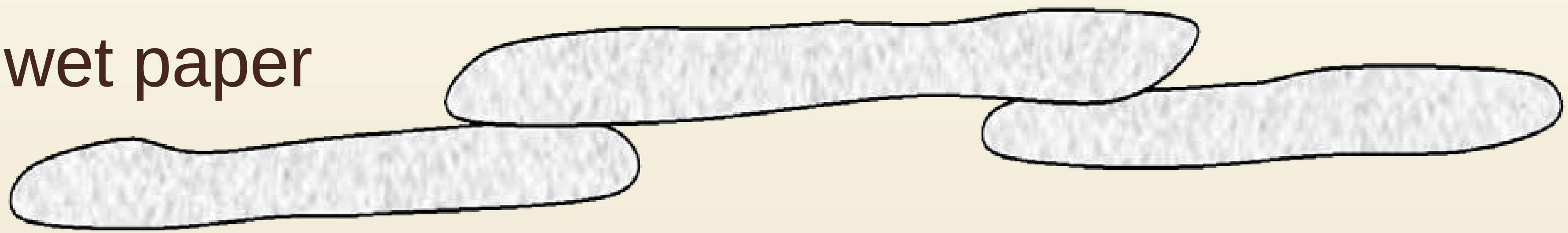
On drying

- The paper matrix contracts, bringing the fibres and fibrils closer to each other
- Hydrogen bonds start to form between them at the areas of contact
- Some fibres and fibrils end up bent and with less overlap with adjacent fibres
- The initial distance among fibres is not completely restored

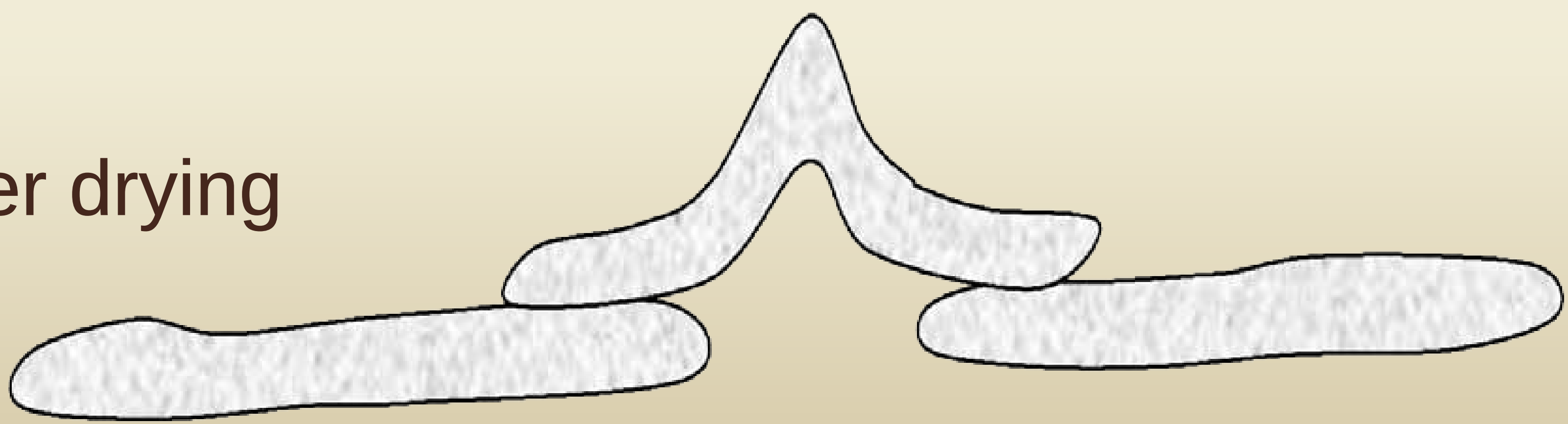
initially dry paper



wet paper



after drying



Consequences

- The voids among fibers and/or fibrils are enlarged
- Less fibre overlapping means less bonded area and therefore lower tensile strength
- Bent fibres and fibrils allow for more stretch before failure
- Inside the fibres and among microfibrils, irreversible hydrogen bonds are formed as expected because of hornification, resulting pore diminution and/or closure
- Between fibres and fibrils the bonding is attenuated and the voids are enlarged

Conclusions

- The porosity increases, as shown by the results of mercury porosimetry and volume measurements
- The water adsorption tests showed that the specific surface area of the samples also increases
- The Gurley tests showed that the air permeability is enhanced

- Changes in the microstructure of paper occur simultaneously and are related to the strength loss and the increase in stretch at break after aqueous treatments
- The details of the process remain obscure
- A tentative mechanism accounting for the observed changes is proposed that assumes the compaction of cellulose inside the fibres due to hornification, the increase of the size of the voids between fibres and/or fibrils, and the attenuation of bonding