Determining bulk density and coating porosity for coated paper samples

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Overview

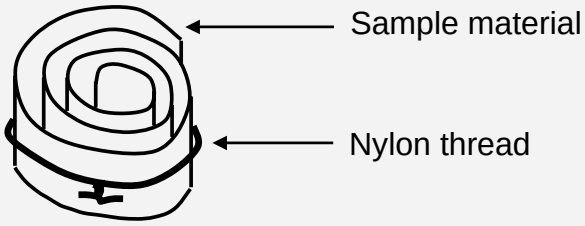
There are known to be limitations in the mercury porosimetry measurement of paper samples.

Improvements can be made via

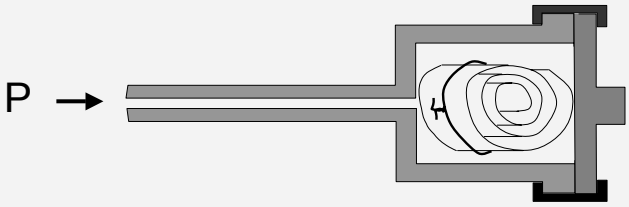
- sample preparation
- data corrections
  - to the mercury intrusion data itself
  - combining mercury intrusion data with independent fluid uptake measurement
- data interpretation
  - separating coating from basepaper
  - information about coating-basepaper interface pores

Sample Preparation

Minimise sample perimeter and sample folding



Sample in penetrometer



Three effects should be corrected for:

- mercury compression
- penetrometer expansion
- sample compression

Corrections - equation

Correction for mercury, penetrometer and skeletal compression effects using Pore-Comp*

Gane et al., Eng. Chem. Res. 35(5) 1996

$$V_{int} = V_{obs} - \delta V_{blank} + \left[0.175 (V^1_{bulk}) \log_{10} \left(1 + \frac{P}{1820} \right) \right] - V^1_{bulk} (1 - \Phi^1) \left(1 - \exp \left[\frac{(P^1 - P)}{M_{ss}} \right] \right)$$

Penetrometer

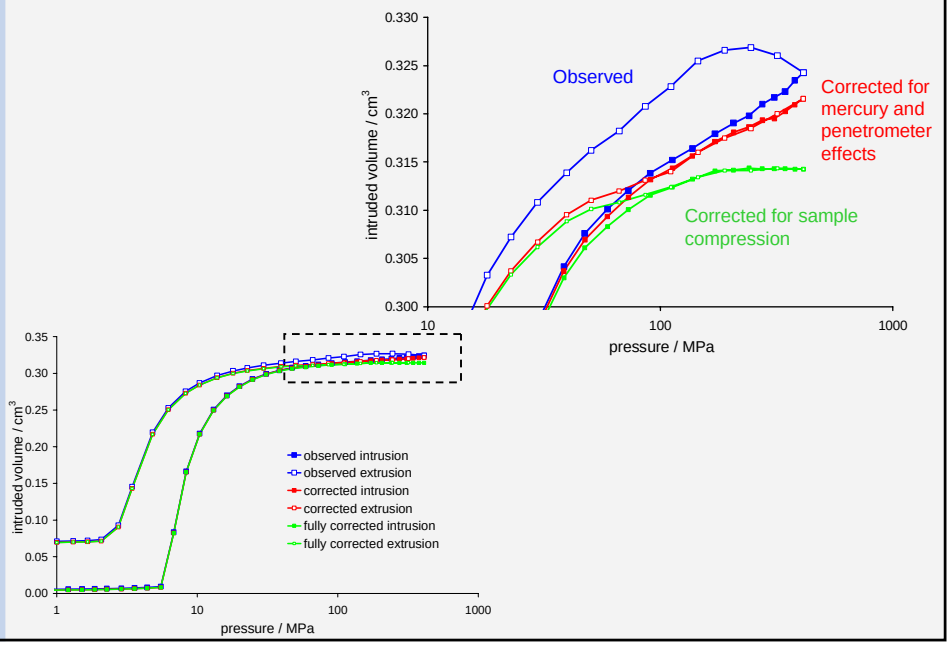
Mercury

Tait equation
(Cook and Hover, 1993)

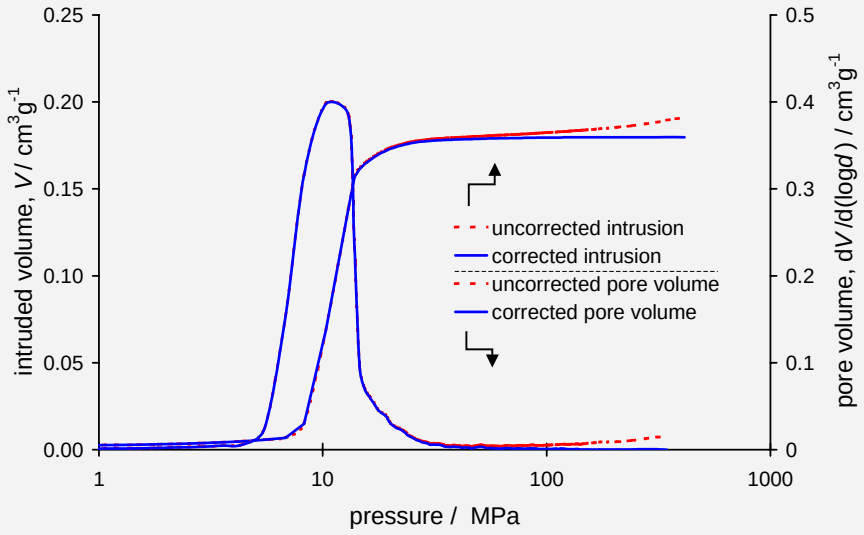
Sample compression

* Pore-Comp is a software name used by the Environmental and Fluid Modelling Group, University of Plymouth, Devon, PL4 8AA, U.K.

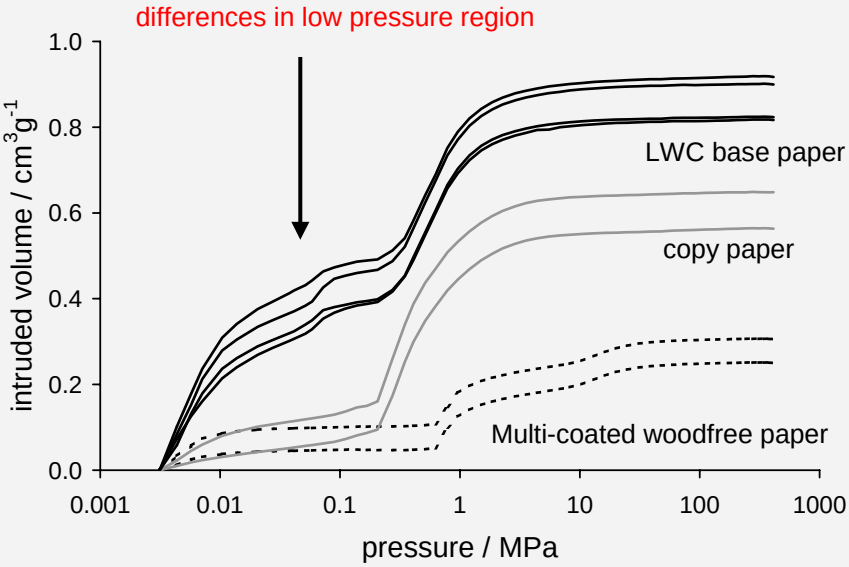
Corrections - graphical example



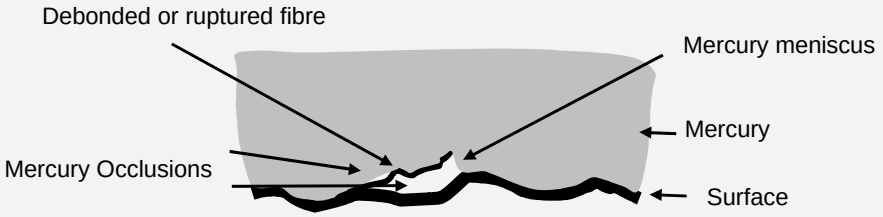
Difference seen at highest pressures



Paper samples



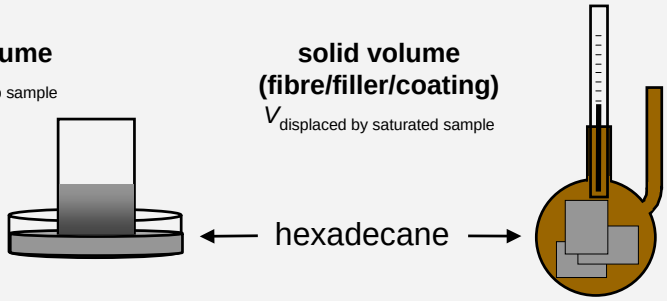
Occlusion



Measure pore volume

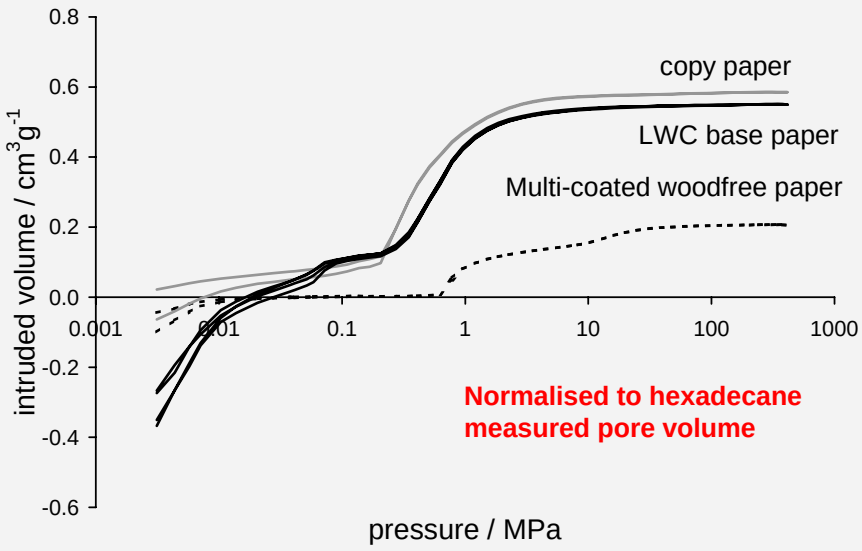
pore volume
$V_{\text{absorbed into sample}}$

solid volume (fibre/filler/coating)
$V_{\text{displaced by saturated sample}}$



$$\phi = \frac{V_{\text{absorbed into sample}}}{V_{\text{absorbed into sample}} + V_{\text{displaced by saturated sample}}}$$

Paper samples normalised to saturated volume



Summary so far ...

- use scrolled sample
- correct for mercury, penetrometer and sample compression effects
- correct for occlusion effects by normalising to hexadecane saturation volume
- determine the skeletal volume

→ porosity can be calculated

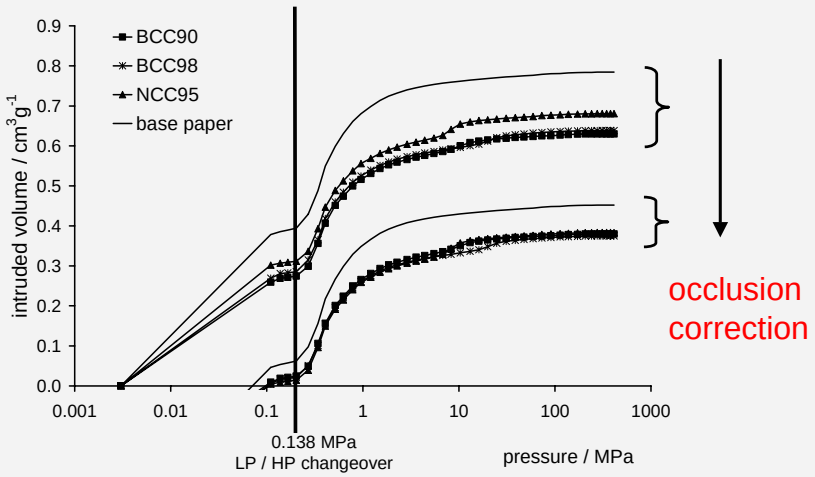
Coated paper samples

Pigment xxx**	Specific surface area / m^2g^{-1}	Particles < 2 µm / w/w%	Particles < 1 µm / w/w%	Median particle size by weight (d_{50}) / µm
BCC90	12.5	90	64	0.7
BCC98	19.2	98	90	0.38
NCC95	9.0	95	75	0.52

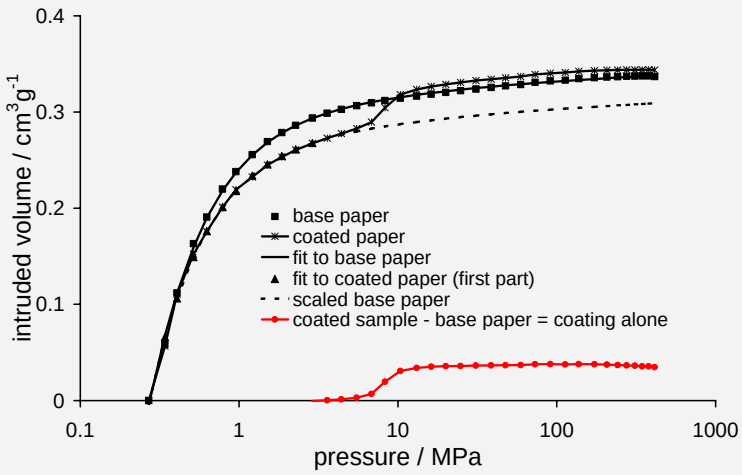
xxx B : broad N : narrow CC : $CaCO_3$

** w/w% < 2 µm

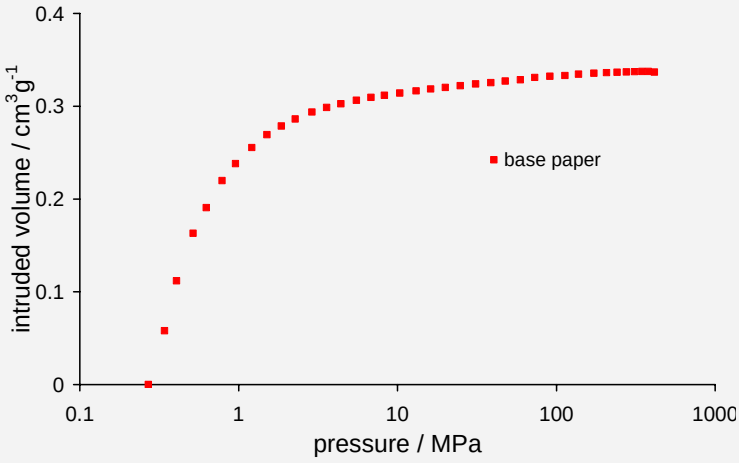
Porosimetry curves of coated samples



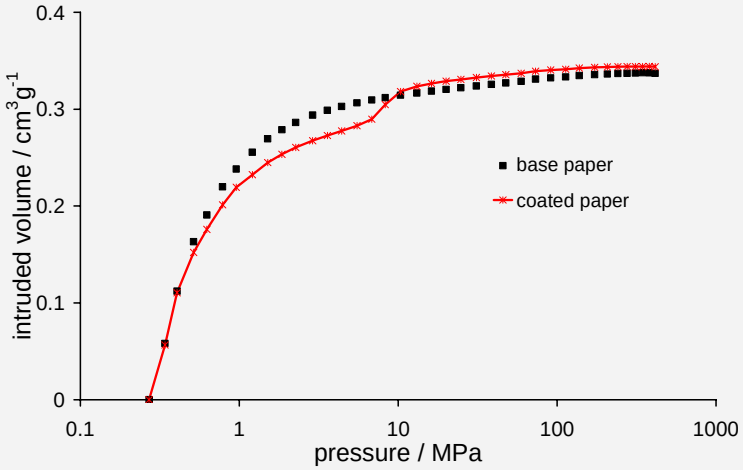
Want to calculate coating intrusion data only



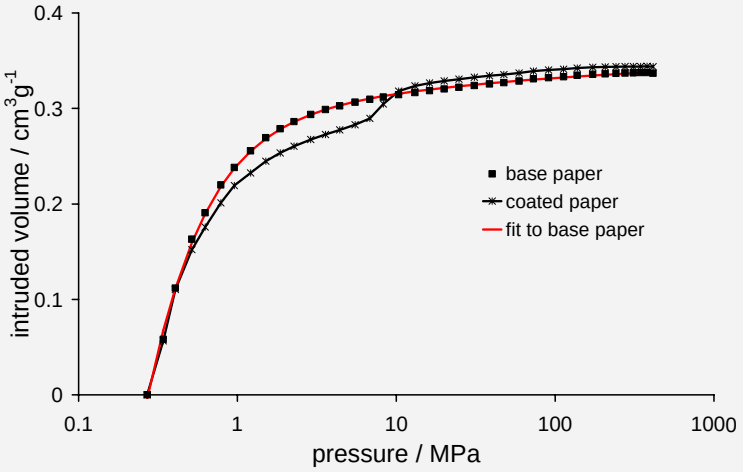
... measure the basepaper ...



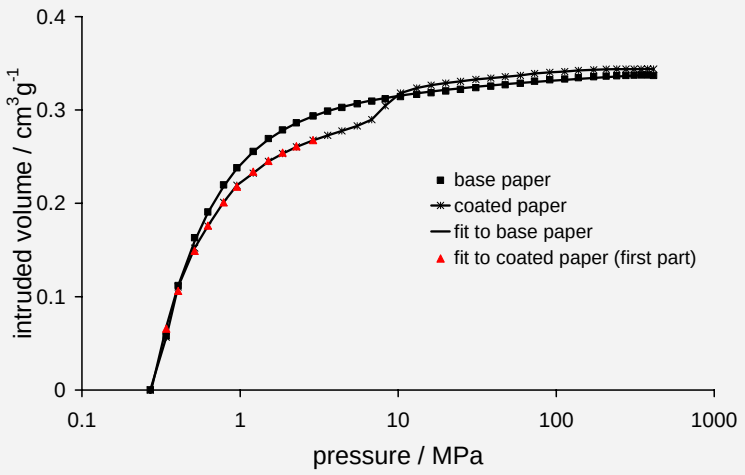
... measure the coated paper ...



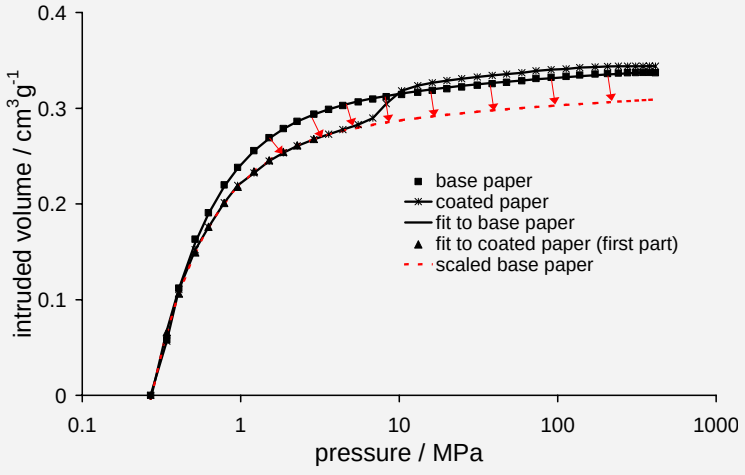
... fit curve to basepaper ...



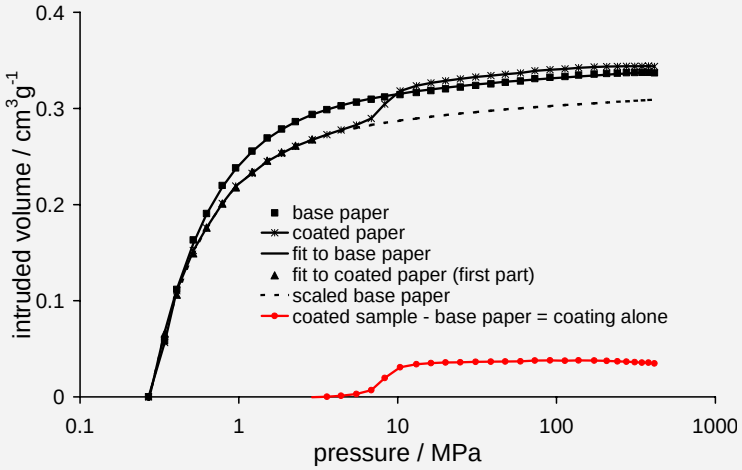
... fit curve to start of coated paper ...



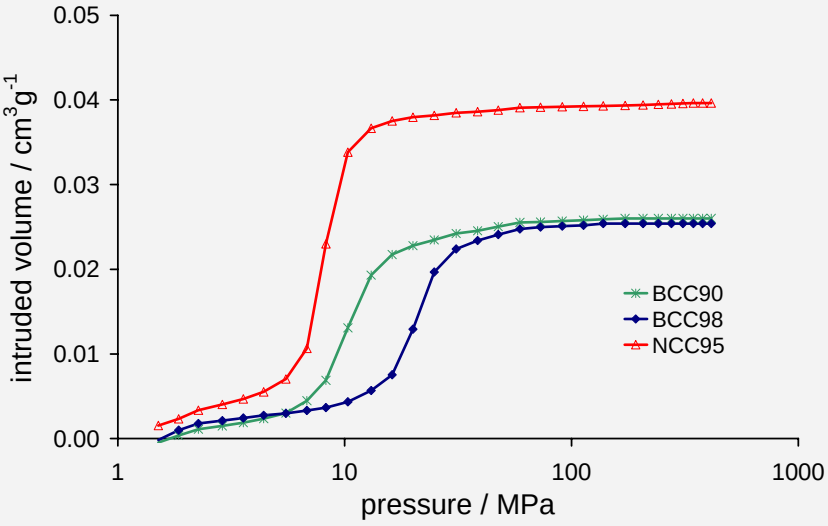
... scale basepaper to coated paper ...



... subtract from coated paper curve ➡ coating intrusion

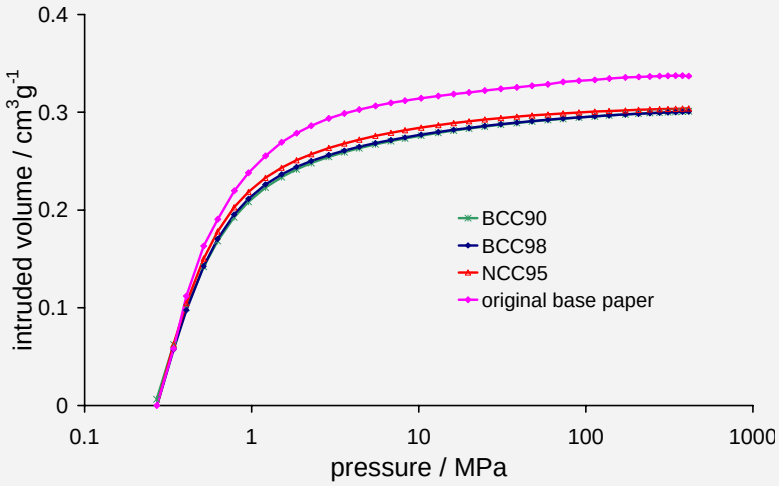


Paper coating intrusion curves



Basepaper intrusion curves

difference from original base paper is due to structural change of the substrate caused by the coating process



Coating porosity calculation

The pore volume and the skeletal volume of the base paper of the coated sample can be calculated ⇒ the bulk volume of the base paper

The bulk volume of the coated sample is calculated

subtraction ⇒ bulk volume of the coating alone

$$\phi = \frac{V_{\text{Hg intrusion into coating}}}{V_{\text{coating}}}$$

Summary of method for basepaper AND coated paper

- use scrolled basepaper and coated paper
- correct each for mercury, penetrometer and sample compression effects
- correct each for occlusion effects by normalising to hexadecane saturation volume

- fit basepaper curve gradient to initial gradient of coated paper curve and scale over whole curve
- subtract basepaper data from coated paper data
- difference = coating pore volume

- difference between basepaper curves before and after represents structural change of that substrate caused by the coating process

Summary of method for coated paper ONLY

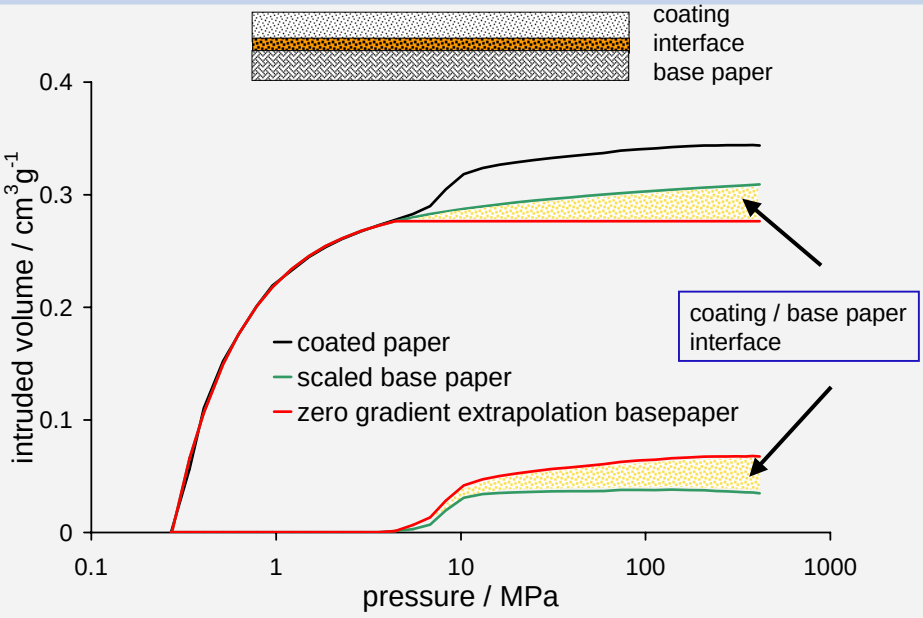
- use scrolled coated paper
- correct for mercury, penetrometer and sample compression effects
- correct for occlusion effects by normalising to hexadecane saturation volume

1
- extrapolate initial coated paper curve gradient to give basepaper curve
- subtract basepaper data from coated paper data
- coating pore volume

2
- from step in intrusion curve fit zero gradient extrapolation
- subtract basepaper data from coated paper data
- coating pore volume + substrate surface features

Difference related to coverage

Coating / base paper interface



Comparison of porosities

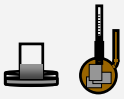
sample	coating on paper (held-out)	coating on paper (complete)	coating on foil
BCC90	14.2	22.3	
BCC98	15.0	23.6	26.0
NCC95	16.0	22.3	

- Porosity coating alone (held-out) => excluding interface region
- Porosity of the coating on foil is comparable to that of the coating on paper, which includes the penetrated interface region
- Difference between these values gives information regarding the grammage of the coating which has penetrated into the basepaper

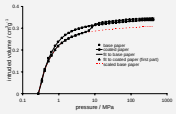
Conclusions ...

- **Correction strategy for occlusion proposed**
  - absorption volume of hexadecane into the structure is applied

- **Independent value for skeletal density measured by displacement of hexadecane volume by saturated sample shown**
  - porosity can be calculated

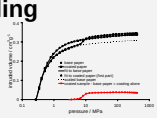


- **Matching the gradient correspondence of intrusion curves for uncoated basepaper and coated basepaper**
  - gives an extrapolated coated substrate intrusion curve lying under that of the coated sample. This curve removes interactional effect of coating on that substrate

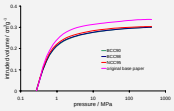


Conclusions

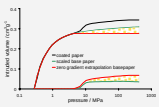
- **Difference between these curves gives the volume intruded into the coating that is not associated with any basepaper surface filling**



- **Comparison of the coated substrate intrusion with the uncoated substrate intrusion provides information on structural changes of the substrate caused by the coating/process**



- **Comparison of the coating void volume which is *un*associated with basepaper penetration, with that including the coating/basepaper interface, provides a novel evaluation of coating coverage**



Thank you !

Acknowledgement to Dr. Patrick Gane