# Mechanics and Physics of Porous Solids

Florian Osselin

Based on a lecture from O. Coussy and M. Vandamme





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- Basics of Mechanics
- The saturated porous solid
- 5 The unsaturated porous solid
- 6 Confined phase transitions
- Experimental considerations

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- pore size distribution
- specific surface area
- imaging of the porous medium

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- Measuring mechanical properties
  - bulk, shear, Young modulii
  - Biot coefficient and Biot modulus

Porosity

#### Porosity

Porosity is usually measured with a hydrostatic weighting. Indeed, usually the overall volume of the sample is not known.

with  $m_0$  the dry mass of the sample,  $m_1$  the saturated mass,  $m_H$  the hydrostatic mass (mass of the sample + Archimede's force), we have :

$$\phi = \frac{m_1 - m_0}{m_1 - m_H}$$



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Pore size distribution

#### Pore size distribution

To measure the pore size distribution, one uses the Mercury Intrusion porosimetry (see chapter on unsaturated porous media)

The results of MIP have to be carefully considered

- Interpretation strongly dependent on the pore model considered (don't forget the hysteresis)
- Bottleneck effect
- Drying temperature : one need to remove all the water to obtain a correct vacuum
  - drying shrinkage : crack for fragile materials
  - need a high temperature to empty the pores  $\rightarrow$  risk of dehydration especially for cement pastes

The confining stress and the pore pressure are equal in MIP:  $\epsilon = \frac{-p}{\kappa_{sk}}$ . Usually,  $K_{sk} \sim 10-100$  GPa. The maximum pressure for MIP is 200MPa leading to a deformation of 0.1 – 1%. This is fortunately usually not enough to damage the sample, however, the change in porosity induced by these high pressures might induce an error in the pore size distribution.

BET measurement of specific surface area

### Brunauer - Emett - Teller theory (1938)

Extends Langmuir theory of adsorption for multilayers.

- Homogeneous surface
- No lateral interaction between adsorbed molecules
- Uppermost layer in equilibrium with vapor
- First layer : heat of adsorption
- Other layers : heat of condensation
- At saturation, the number of layers become infinite

# BET equation : $\frac{1}{N\left(\frac{p}{p_0}-1\right)} = \frac{1}{CN_m} + \frac{C-1}{N_mC}\frac{p}{p_0}$

- N Number of adsorbed molecules per sample mass
- p Pressure of the gas
- Pressure at saturation
- C BET constant (linked the the heat of adsorption and the heat of condensation (between 3 and 1000, depends on the material)
- Nm Number of adsorbed molecules for one complete monolayer

### Measuring porous medium characteristics BET measurement of specific surface area

#### BET procedure

The sample to study is inserted in a chamber after being degassed in vacuum. Gas (usually N<sub>2</sub> at 77K (boiling point) is injected at different pressure and the adsorbed amount is measured (by mass or volume). The plot with  $p/p_0$  gives then  $N_m$  and :

Specific surface area =  $N_m imes \mathcal{N}_A imes \sigma$ 

with  $\mathcal{N}_A$  the Avogadro number and  $\sigma$  the area occupied by one molecule (0.162 nm<sup>2</sup> for N<sub>2</sub>).

#### Surface area depends strongly on the material

Usual values for specific surface area range from 0.1  $m^2/g$  to 1500  $m^2/g$  For cement, the value is usually 300  $m^2/kg$ 



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#### X-rays MicroTomography : imaging the porous solid

Similar to a medical scanner : use a Xray beam to obtain the density distribution of the sample : image matrix and pores Resolution usually of 1/10  $\mu m$  for samples of 10 cm size Allows to observe the main pores but not the small pores or in-pore crystals.





From Zandomeneghi et al. 2010

Intrinsic/relative permeabilities

Intrinsic and relative permeabilities can be measured with a steady-state method or a transient method

#### Steady-state method for intrinsic permeability

The idea is to use Darcy's law on a sample :  $\Delta P = \frac{Q\eta}{k}L$ . Intrinsic permeability is obtained by the slope of the curve  $\Delta P = f(Q)$ 



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pumps	injection of fluids at a constant flow rate (injection with controlled $\Delta P$ also possible.
confining pressure	Avoid any leakage between the sleeve and the rock. The sleeve usually in a chemical resistant rubber (VITON, NITRILE)
BPV	back pressure valve, used to control the pressure after the outlet. $% \left( {{{\boldsymbol{x}}_{i}}} \right)$
outlet flow	gazometer and flow weighting used to measure the outlet flow

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#### Relative permeabilities measurements

Relative permeabilities measurements are much harder do : injection of two fluids. Same procedure as for the intrinsic permeabilities : injection of the fluids and measure of  $\Delta P$ .

• usually start with a sample saturated with the wetting fluid



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- when the steady-state is achieved, record the pressure difference
- weight the sample to know the water saturation of calculate the difference between input and output (need to know the dead volumes)



Intrinsic/relative permeabilities

#### Issues with the steady-state measurements

- For both intrinsic and relative
  - not applicable for very low permeabilities (need very high pressure drop which might not be compatible with the current system)
  - for low permeability systems, the time to reach equilibrium is very long, sometimes not compatible with the volume of the pumps
  - it is important to know the reactivity of the injected fluid, some solids are chemically unstable and might dissolve if the wrong fluids is used
  - flow low permeability materials or for poorly consolidated systems, the pressure and stresses achieved during the measurements can damage the sample
- specific to relative permeabilities
  - saturations close to the residual saturations are difficult to achieve.
  - Capillary end effect : at the outlet the two fluids have the same pressure. Because of the continuity of pressure, it means that the saturation in the system is not homogeneous
  - weighting of the sample might cause the loss of fluid especially if the measurement was made at high pressure and some of the fluids are volatile or have a high compressibility
  - if the two fluids are partially miscible, need to reach the chemical equilibrium before injection
  - it is not possible to obtain a linear correlation. Only one point is obtained each time.

#### Permeability measurement by a transient method : the pulse decay

In a core at a defined wetting fluid saturation, a small pulse of pressure of the non-wetting fluid (5% of the outlet pressure) is created at the inlet. Measuring the evolution of the inlet and outlet pressure with time allows then to infer the value of the relative permeability of the non-wetting fluid

### Pro and cons for pulse decay method

- Pros
  - Quick and efficient method. Do not require to wait for the steady-state
  - Allows to measure the permeabilities for a low permeability core
- Cons
  - depends on the model used for the interpretation of the results. For accurate results needs a finite element simulation
  - does not measure the wetting phase relative permeability

Capillary pressure

#### Capillary pressure

To measure capillary pressure, one has to measure for every wetting fluid saturation the difference of pressure between the wetting and the non-wetting phase. Considering the hysteresis of the capillary pressure curve, it is important to set the condition of the experiment properly.

### Measuring the initial drainage curve

The measure can be done with a permeameter but some set-ups are dedicated to capillary pressure measurement

- Saturate the sample with the wetting fluid and insert it in the set-up
- Set the non-wetting injection pressure at a definite value. The percolation of the non-wetting fluid extracts the wetting fluid
- Calculate the wetting fluid saturation with the extracted volume (careful of dead volumes)
- Start over with a new non-wetting phase pressure

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An improvement can be made with a semi-permeable membrane only permeable to wetting fluid (Welge method)

A measurement of capillary pressure is also possible with a MIP experiment

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# Chemical and mineral determination X-ray diffraction (XRD)

### Principle of the measure

Only applicable on crystallized matter.

- the sample to characterize is crushed to powder
- a monochromatic X-ray beam is sent on the powder
- the detector turns around the sample and measures the intensity of the X-ray for every angle

The wavelength of X-rays is of the same order of magnitude as the interatomic distance : interaction with the atoms and reemission in all directions of electromagnetic rays. Because of the interferences between reemitted rays only defined angles will have a measurable signal : diffraction peaks

 $2d\sin\theta = n\lambda$  Bragg law

with d the distance between the crystallographic plans,  $\theta$  half of the angle of reemission, n the order of reflection (integer)  $\lambda$  the wavelength of the incident X-rays.

# Chemical and mineral determination X-ray diffraction (XRD)





XRD apparatus Center for Microscopy & Microanalysis

University of Queenland Australia

# Chemical and mineral determination X-ray diffraction (XRD)



XRD diagram of an Egyptian sandstone (El-Sherbiny and Amin 2012)

## Chemical and mineral determination X-ray diffraction (XRD)

### Identification of the crystalline phase

The diagram of diffraction is specific of the mineral studies. By comparing the experimental diagram with known diagrams (database *Powder diffraction file* with more than 150.000 files), one can identify the different crystalline phases in the studied sample. The method is semi-automatized. Because several mineral have a similar signature, the operator needs to choose which one is the most probable

#### Quantitative study

The area under the peaks is proportional to the quantity of the considered phase. Comparing the area allows then to have the proportion of each crystalline phase in the sample.