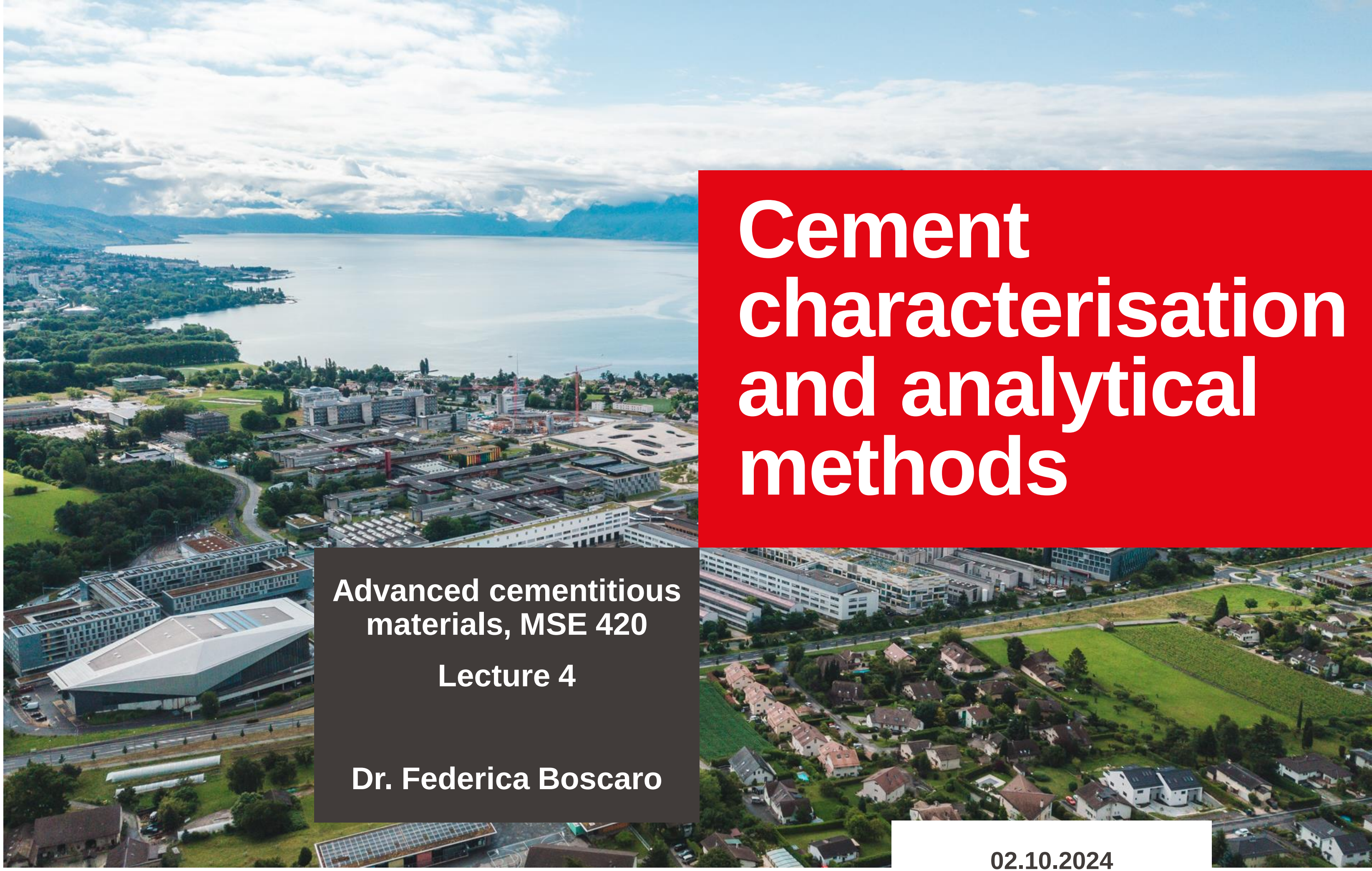
EPFL

LABORATORY OF CONSTRUCTION MATERIALS



Cement characterisation and analytical methods

Advanced cementitious materials, MSE 420

Lecture 4

Dr. Federica Boscaro

02.10.2024

Learning objectives

By the end of this class, you will be able to...

- **Identify** what characteristics of cement are important
- **Select** the correct analytical method(s) to measure a specific cement characteristic
- **Recognize** the limits of the available analytical methods

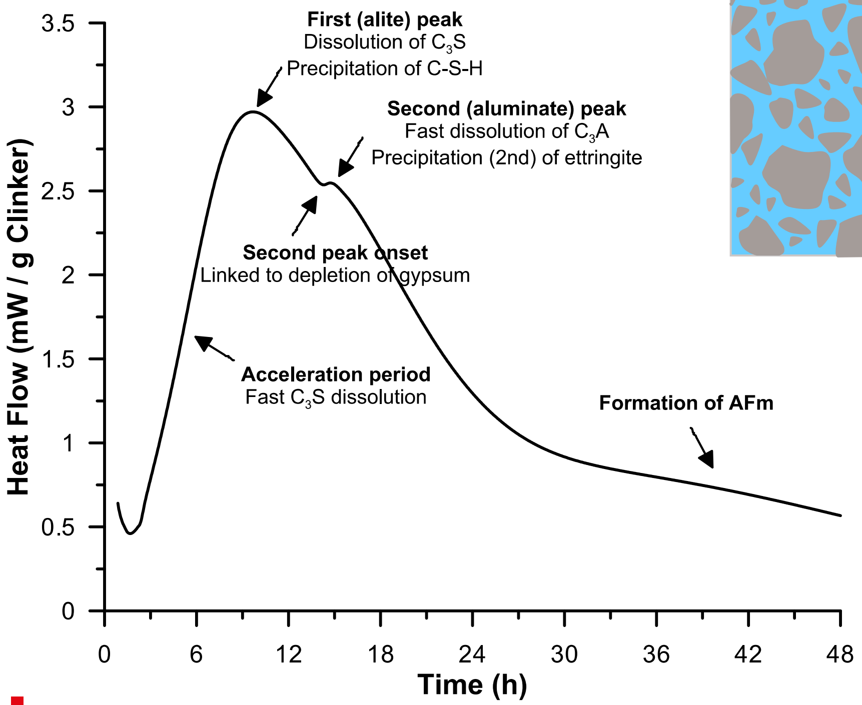
Why characterizing cementitious systems?

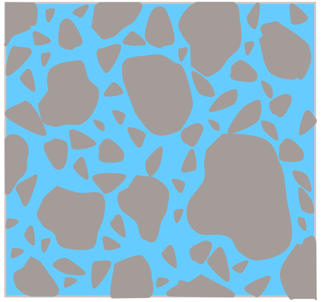
Characterization of anhydrous and hydrated systems is related to:

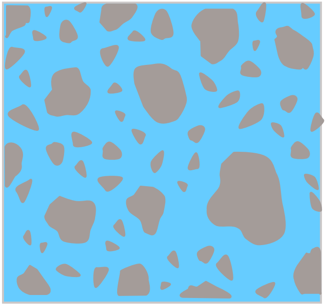
- Reactivity of anhydrous cement and SCMs
- Rheology
- Water demand
- Mechanical strength

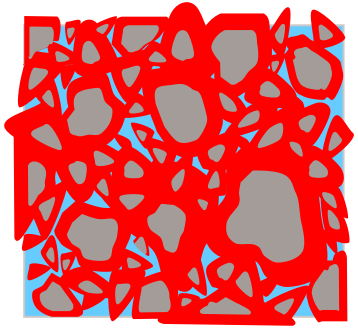
Prediction and understanding of durability issues

Calorimetry



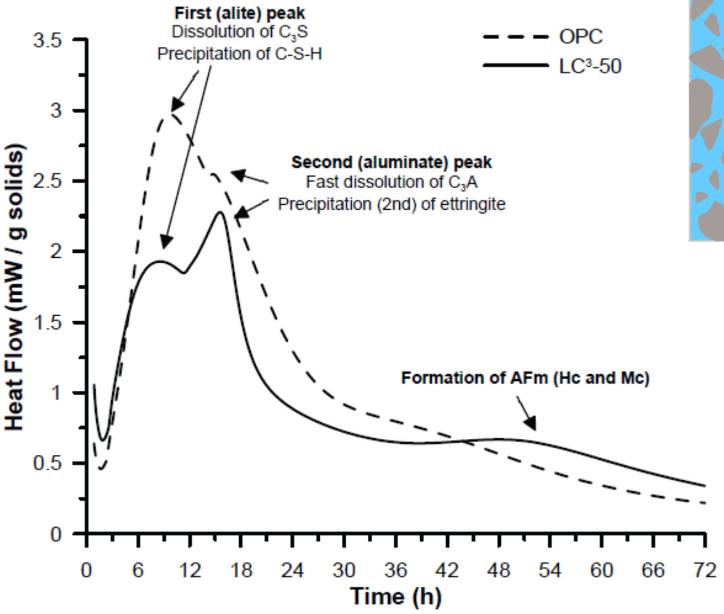


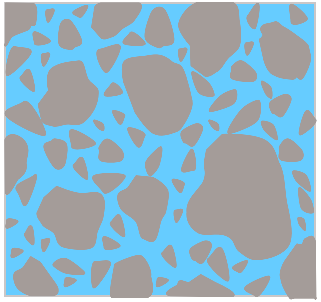


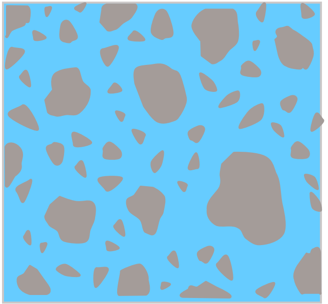


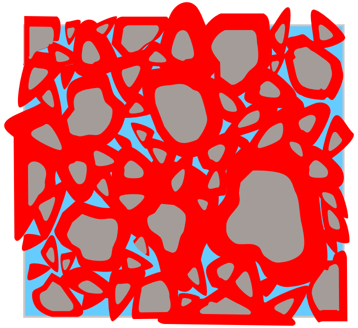
Zunino & Scrivener, 2019

Calorimetry









Zunino & Scrivener, 2019

Calorimetry

- It is the study of heat transfer during physical and chemical processes
- It is used to study the kinetics and the extent of the cement hydration by following the heat or the temperature increase
- Types of calorimeters:

Isothermal c.

tainstruments.com

Semi-adiabatic c.

calmetrix.com

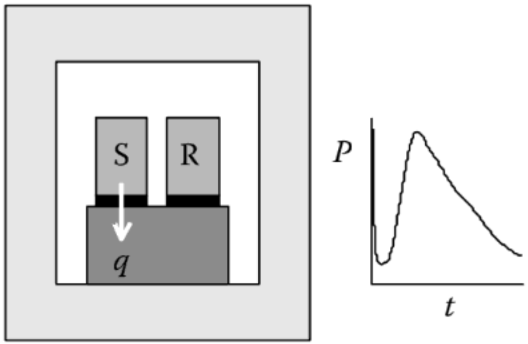
Adiabatic c.

controls-group.com

Calorimetry

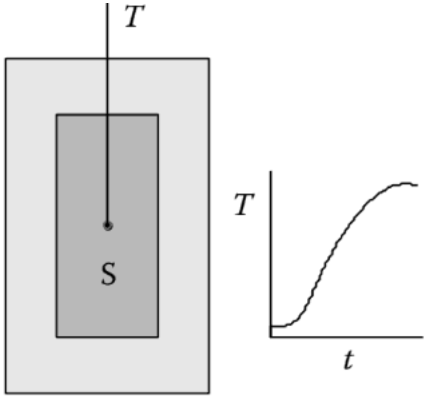
- Isothermal and semi-adiabatic are the most used calorimetric methods to study cement hydration
- They quantify the hydration kinetics in different ways

Isothermal c.



Sample: 1-100 g
Pastes, mortars, concrete (small aggregates)

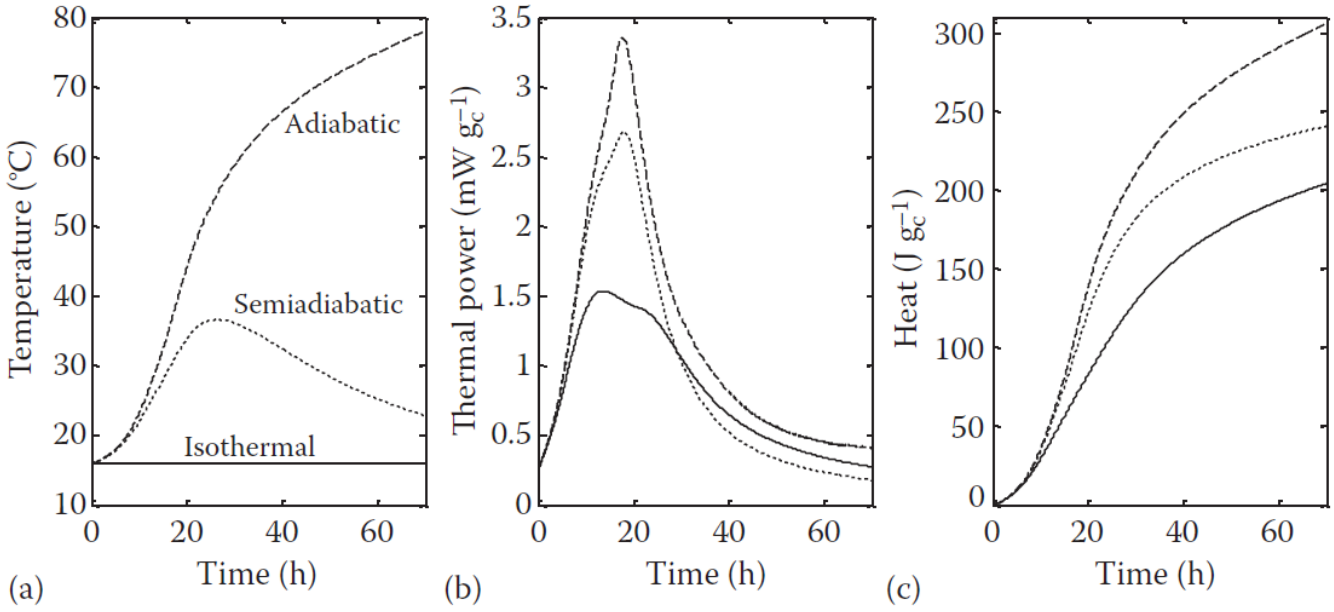
Semi-adiabatic c.



Sample: 0.5-1 kg to 10 kg
Mortars, concrete (up to 16 mm aggregates)

Wadsö et al, 2016

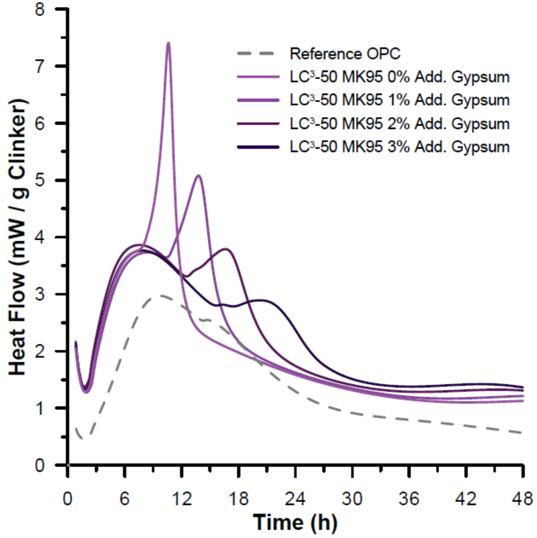
Calorimetry



Wadsö et al, 2016

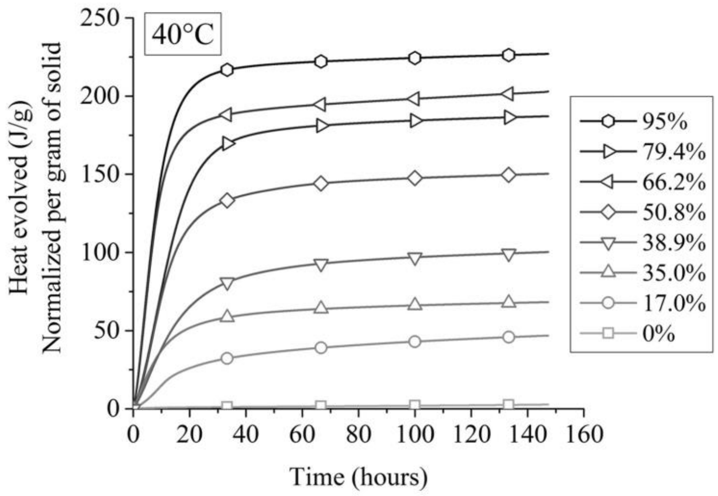
Calorimetry – Examples

Sulphate optimization



Zunino & Scrivener, 2019

R^3 test



Avet et al, 2016

Calorimetry – Summary

ADVANTAGES

- Quantitative study of hydration kinetics
- Hydration can be followed continuously
- Hydration does not need to be stopped
- Easy to test at different T
- Effect of SCMs, admixtures, correct sulphation, prediction of compressive strength
- All systems (pastes, mortars, concrete)
- Widely available

CAUTIONS

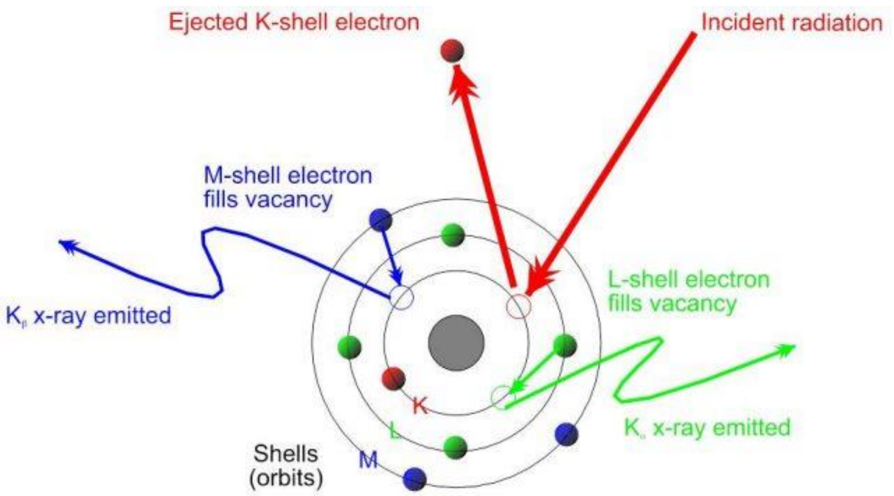
- Overall rate of reaction
- Reference samples are necessary for isothermal calorimetry
- Calibration
- Low signal at later ages

Chemical and Mineralogical characterization

- X-ray fluorescence (XRF)
- X-ray diffraction (XRD)
- Thermogravimetric analysis (TGA)
- Nuclear magnetic resonance (NMR) spectroscopy
- Fourier-transform infrared spectroscopy (FTIR)

X-ray fluorescence (XRF)

- It provides the elemental composition of anhydrous cement, SCMs and raw materials
- Performed on pellets or fused powders
- Widely used in the cement industry for quality control



- Primary X-ray radiation interacts with the atoms in the samples, displacing electrons from the inner shell -> formation of vacancies (atom is unstable)
- Electrons from higher orbits fill the vacancies
- A characteristic X-ray radiation is emitted (X-ray fluorescence). It has a specific energy that depends on the element

Composition and concentration of the element

bruker.com

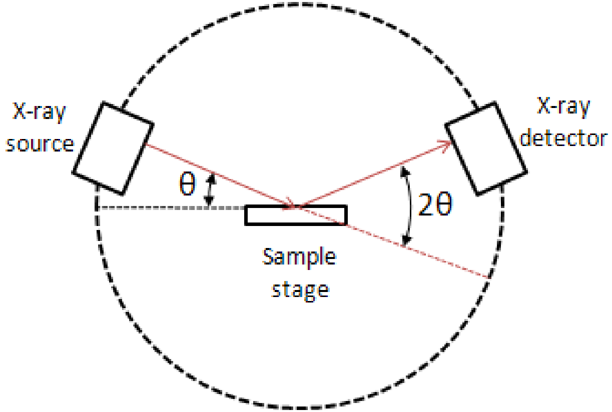
X-ray fluorescence (XRF)

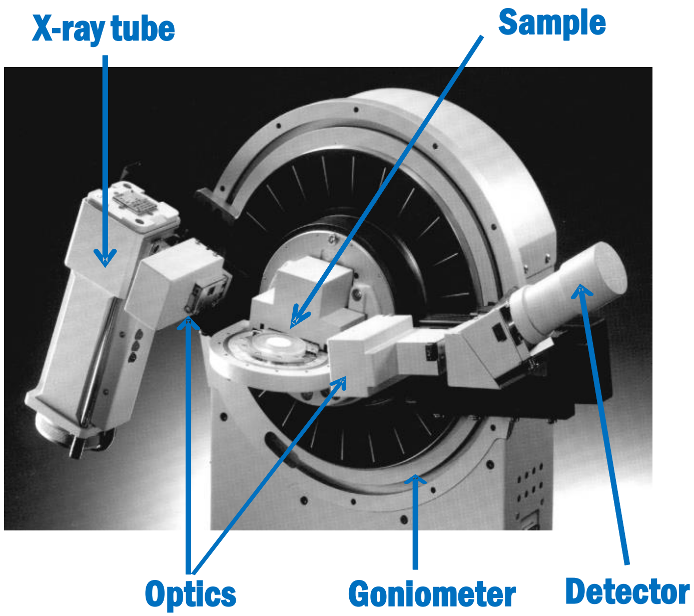
% (w/w)	CEM I 42.5 R	Limestone	Calcined clay (51 % kaolinite)
CaO	63.6	55.0	1.3
SiO_2	19.3	0.1	44.9
Al_2O_3	5.7	-	32.3
Fe_2O_3	3.6	-	15.4
MgO	0.2	0.2	0.8
SO_3	3.2	-	0.1
Na_2O	0.2	0.1	0.4
K_2O	1.2	-	0.2
TiO_2	0.3	-	2.4
P_2O_5	0.2	-	0.4
MnO	0.1	-	0.1
L.O.I.	0.8	42.6	1.7

Avet et al, 2016

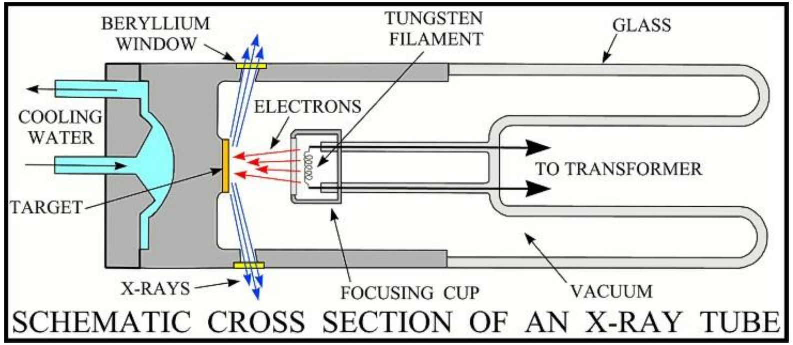
X-ray diffraction (XRD)

- It is used to determine the **mineralogical composition of anhydrous and hydrated cements**
- When primary X-rays from an X-ray tube strike a sample, they are **scattered** by the sample
- It provides information on the **crystal structure**

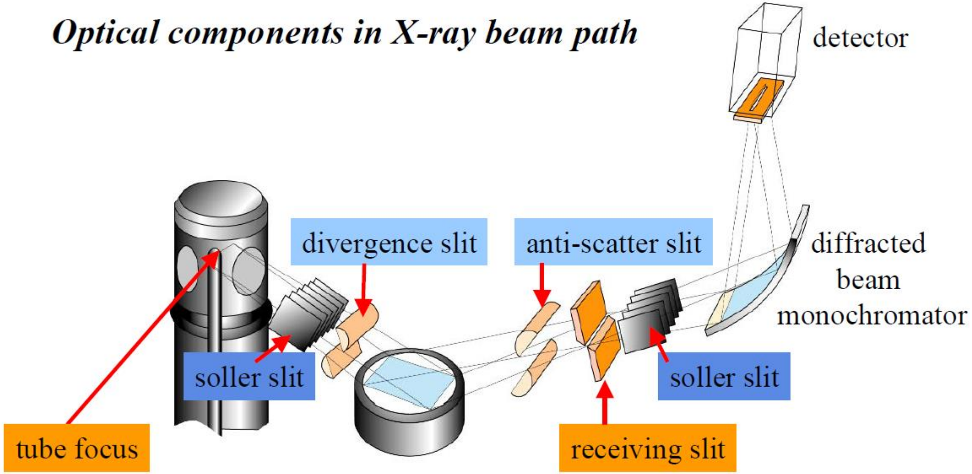




X-ray diffraction (XRD)

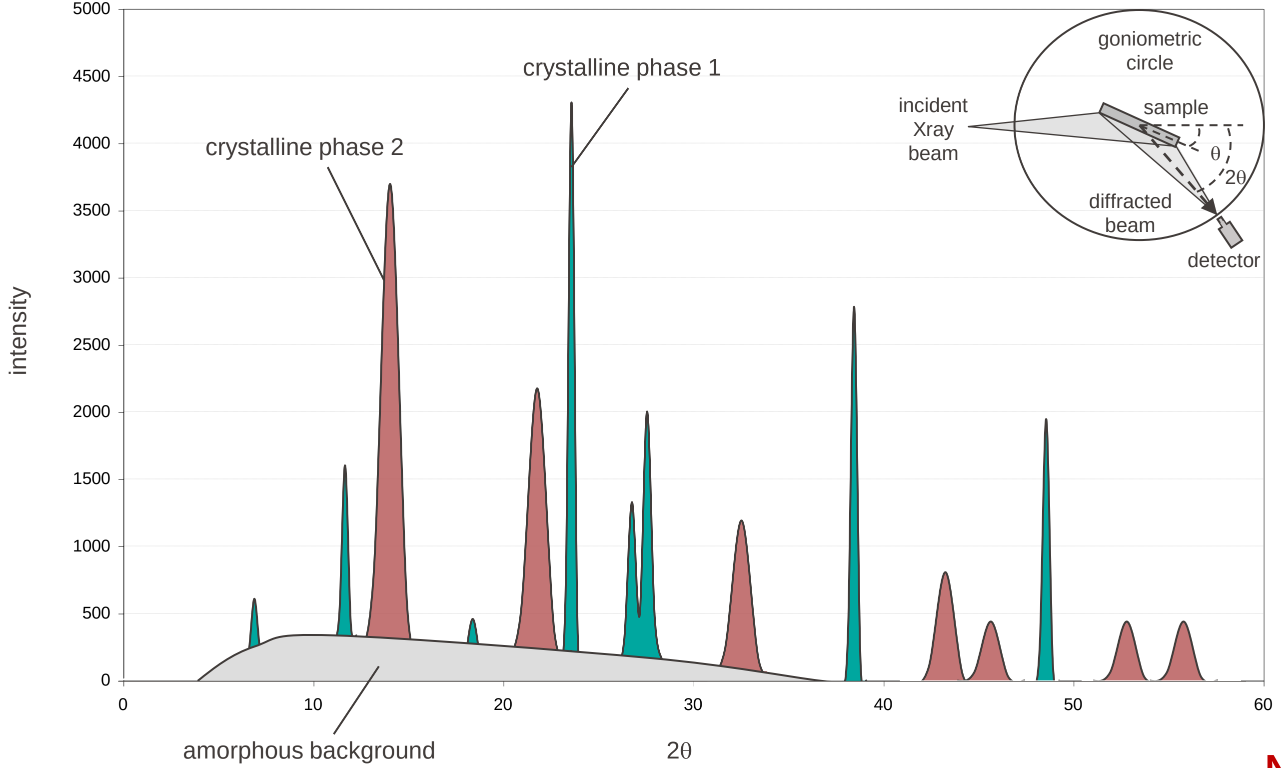


pubs.usgs.gov



Courtesy of Dr. Londono-Zuluaga

XRD – Diffractogram



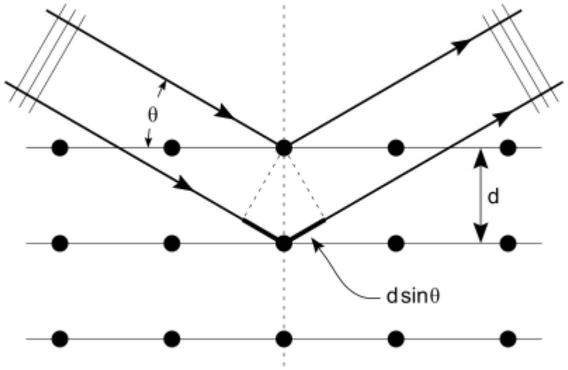
Courtesy of Dr. Gallucci and Prof. Scrivener (EPFL)

NB NOT a spectrum!

XRD – Bragg's law and structure factor

Bragg's law

Determines the position of the peaks



$$\boxed{2dsin\theta = n\lambda}$$

d = spacing between diffracting planes
θ = incident angle
n = an integer
λ = wavelength of the beam

Structure factor

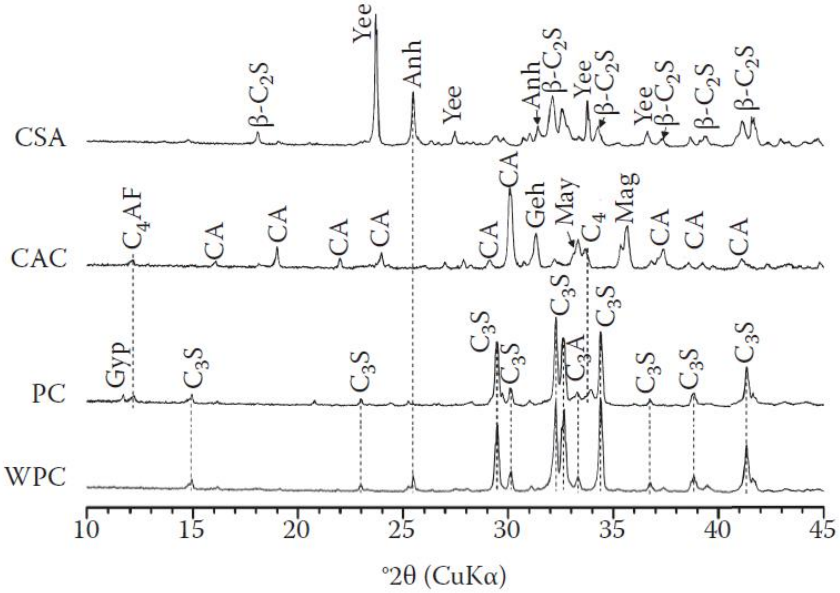
Determines the height of the peaks

$$F_K = \sum_j N_j f_j exp\left[2i\pi\left(hx_j + ky_j + lz_j\right)\right] exp\left(-B_j\right)$$

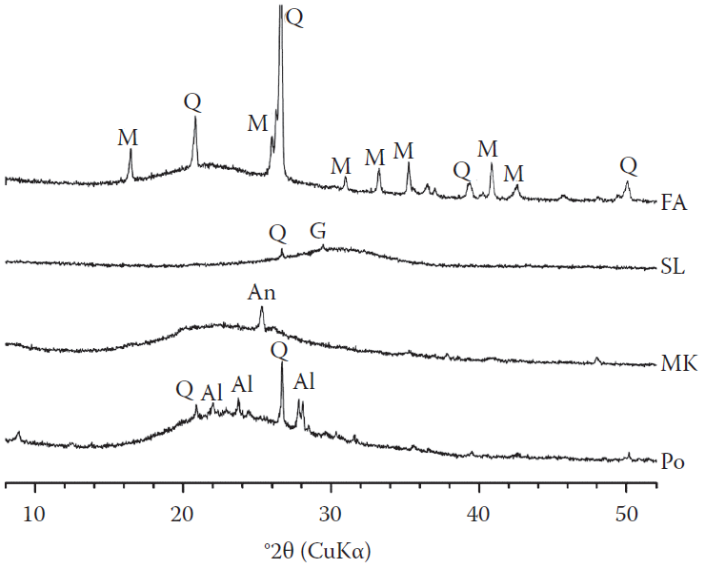
x_j, y_j, z_j = coordinates of the *j* atom in the unit cell
N_j = fractional occupancy for the *j* atomic site
f_j = atomic X-ray scattering factor
B_j = temperature factor

XRD – Examples

Anhydrous cements



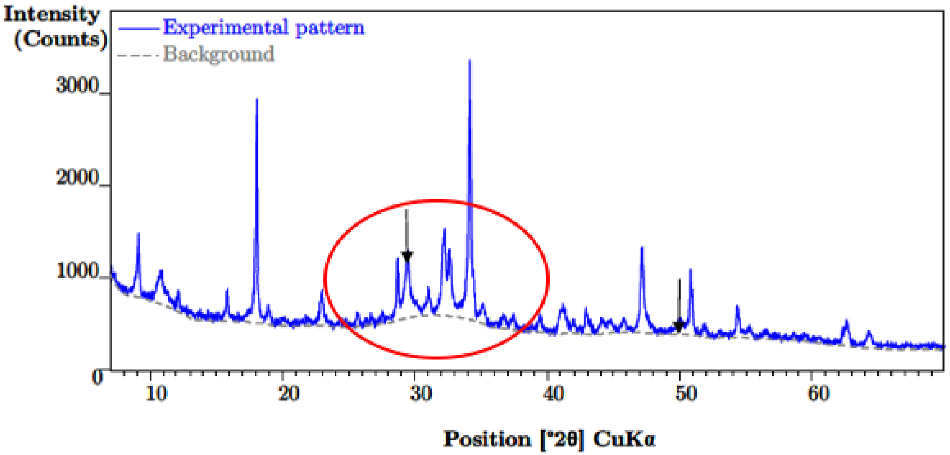
Supplementary cementitious materials (SCMs)



Snellings, 2016

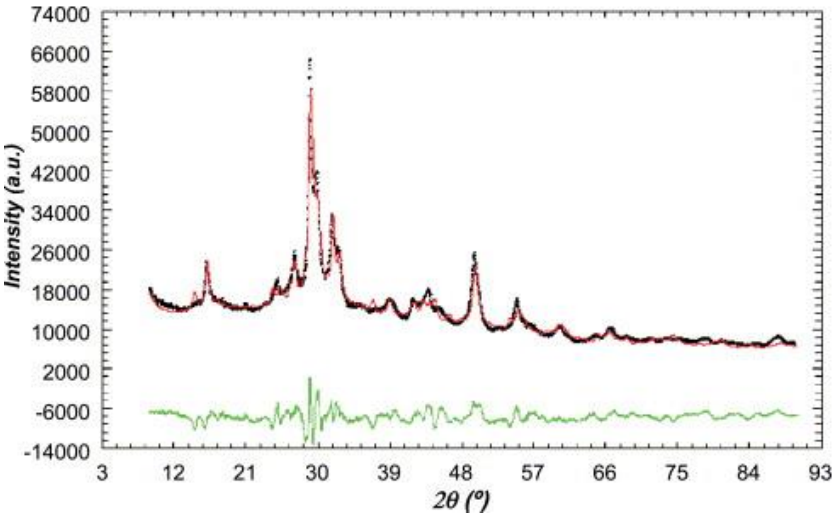
XRD – Examples

Hydrated cement pastes



Kocaba, EPFL 2009

C-S-H



Nonat, 2004

XRD – Phase quantification

The Rietveld method

It minimizes the differences between measured and calculated patterns at each data point *i* in the diffraction pattern using a least-squares approach

$$S_y = \sum_i w_i (y_i(obs) - y_i(calc))^2$$

$$y_i(calc) = \sum_{j=1}^{n} S_j \sum_{k=1}^{m} Lp_k m_k \left|F_{k,j}\right|^2 G_j(2\theta_i - 2\theta_{k,j}) A_j P_{k,j} + Bkg_i$$

$$W_\alpha = \frac{S_\alpha \left(ZMV\right)_\alpha}{\sum_{j=1}^{n} S_j \left(ZMV\right)_j}$$

XRD – Phase quantification

Quantification of non-diffracting materials

- **Internal standard**
  Addition of a crystalline material (of known crystallinity) in a known weight fraction

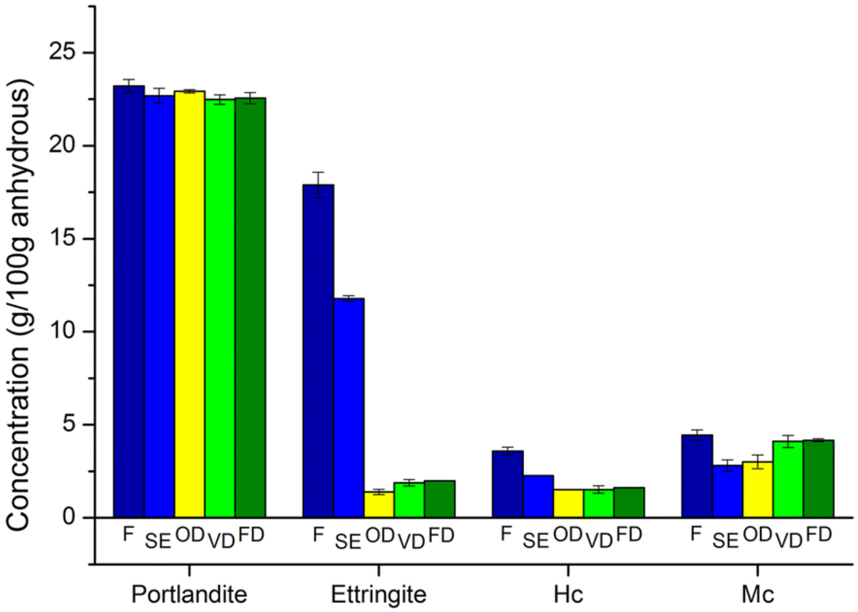
- **External standard**
  Comparison of the phase scale factors of a sample to the one of a standard material measured separately under identical conditions

Total amorphous content

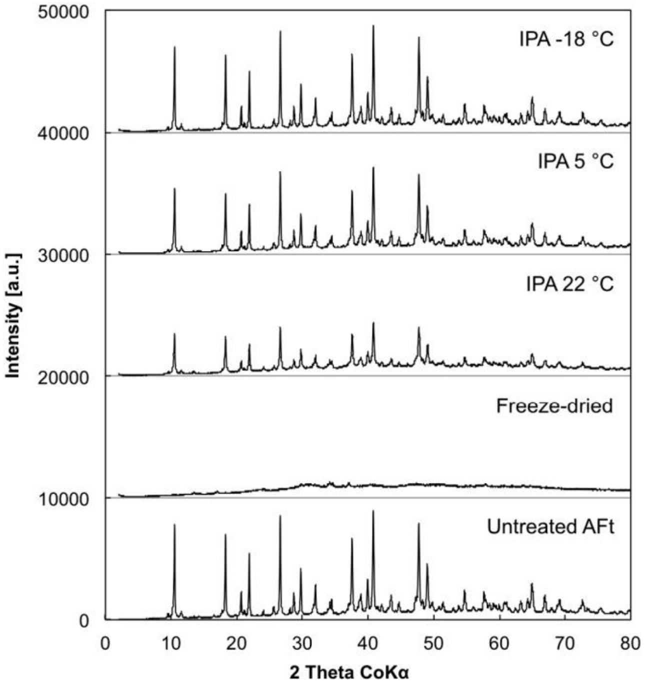
- **Partial Or No Known Crystal Structure (PONKCS) method**
  Calibration of the individual amorphous phases as a ‘standard phase’

Distinction of the different amorphous humps

XRD – Sample preparation for hydrated cements



Snellings et al, 2018



Mantellato et al, 2016

XRD – Summary

ADVANTAGES

- Quantitative analysis
- *In-situ* measurements are possible
- Simple and fast sample preparation
- Measurement time < 30 min
- Widely available

DISADVANTAGES

- High errors in the quantification of small quantities
- Amorphous phases not distinguished (but option of using PONKCS)
- Ettringite becomes X-ray amorphous on drying
- AFm phases are generally poorly crystalline
- Issue of preferred orientation

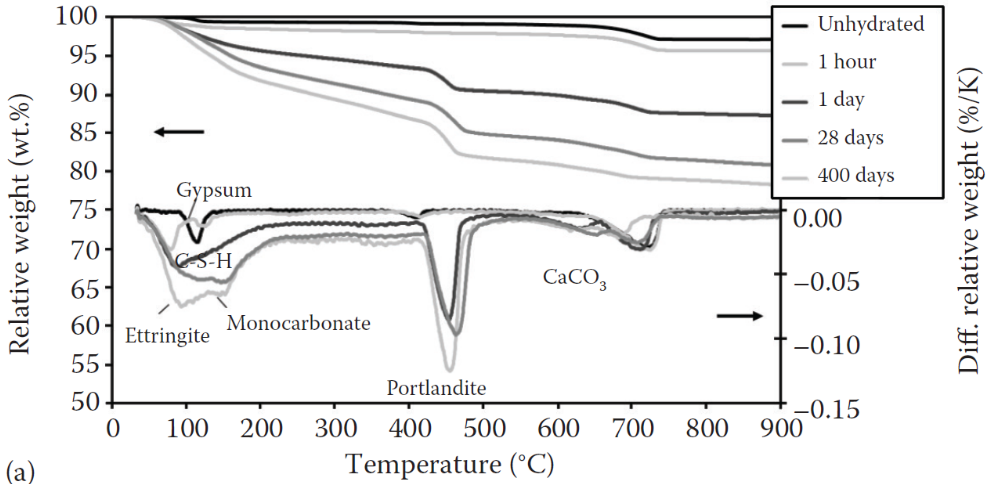
Thermogravimetric analysis (TGA)

- TGA is used to follow the hydration of cement or to evaluate the reactivity of SCMs
- Thermal reactions are generally associated with weight changes or release of heat: dehydration, dehydroxylation, decarbonation, oxidation, decomposition, phase transition, melting
- Temperature when these reactions occur are typical for each phase
- The sample is heated and the weight loss is measured
- Measurements of bound water, portlandite and calcium carbonate content
- It is able to identify X-ray amorphous phases
- Gas analysis (mass spectrometer)
- Complementary to other techniques (XRD, SEM, NMR)

tainstruments.com

Thermogravimetric analysis (TGA) - Examples

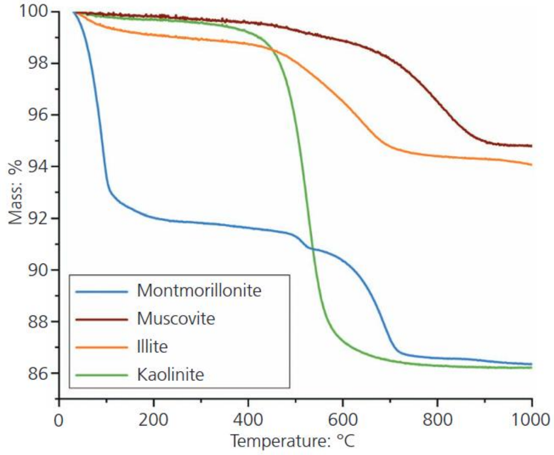
Hydrated cement (95% wt. PC + 4% wt. limestone)



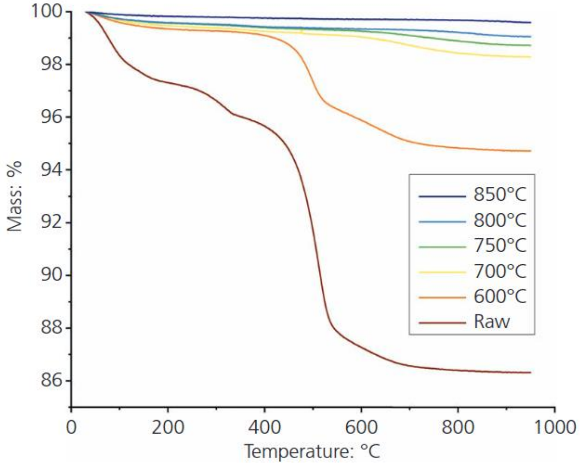
Lothenbach et al, 2008

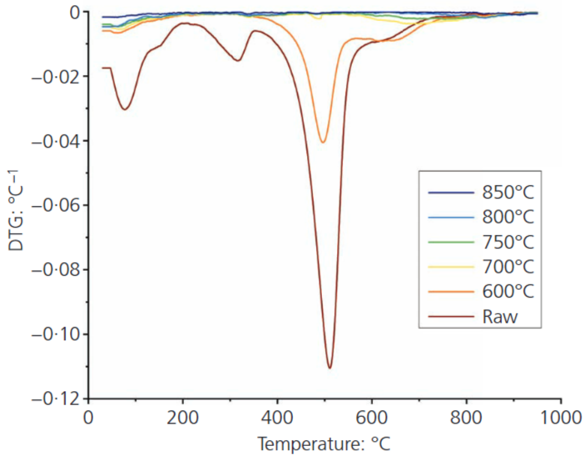
Thermogravimetric analysis (TGA) - Examples

Secondary phases



Calcination efficiency





Scrivener et al, 2019

TGA – Summary

ADVANTAGES

- Good technique to quantify portlandite
- Quantification of bound water
- Identification of amorphous phases
- Simple
- Measurement time of a few hours
- Widely available

CAUTIONS

- Exact positions are instrument dependent
- Effect of sample weight, type of vessel and gas used
- Risk of carbonation (ground sample)
- Hydration has to be stopped
  - C-S-H, AFt and AFm lose water below 100°C

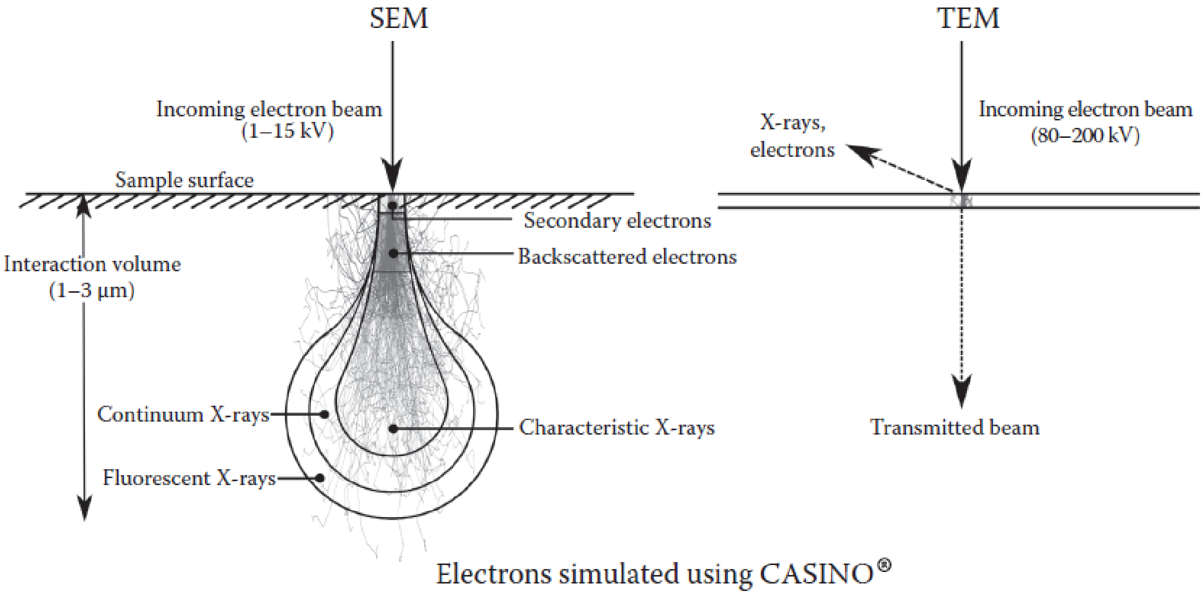
Microstructure

- Optical microscopy

- Electron microscopy
  - Scanning electron microscopy (SEM)
  - Transmission electron microscopy (TEM)

Electron microscopy

Interactions of electrons with matter



Scrivener et al, 2016

Scanning electron microscopy (SEM)

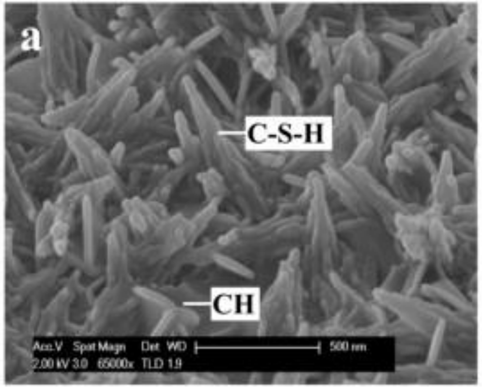
Secondary electrons (SE)

- From inelastic collisions
- Lower energy than the incident beam: near surface of the sample
- Highest resolution
- Intensity of SEs and brightness are determined by the inclination of the surface to the incident beam (edges, points)
- Image of the surface topography
- Qualitative

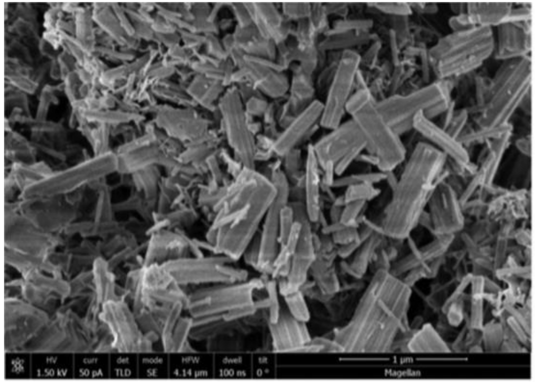
Backscattered electrons (BSE)

- From elastic collisions
- Similar energy to that of the incident beam: higher depth in the sample
- Lower resolution than SE images
- Intensity of BSEs and brightness are primarily a function of the atomic number of the atoms in the sample
- Good compositional contrast, avoid surface roughness
- Quantitative

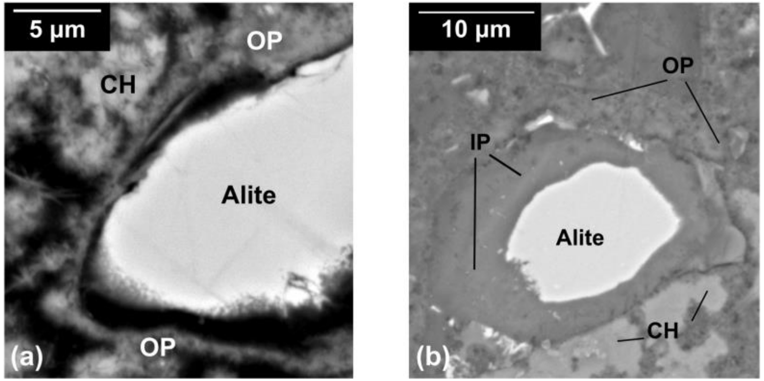
Scanning electron microscopy (SEM)



Mota et al, 2015



Das et al, 2022

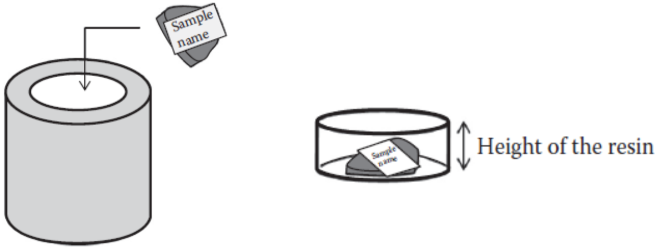


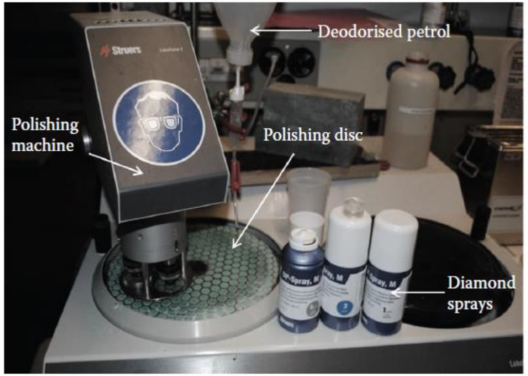
Rossen & Scrivener, 2017

Scanning electron microscopy (SEM)

Sample preparation

1. Hydration stoppage
2. Impregnation
3. Pre-polishing
4. Polishing with spray of diamond powders
5. Coating

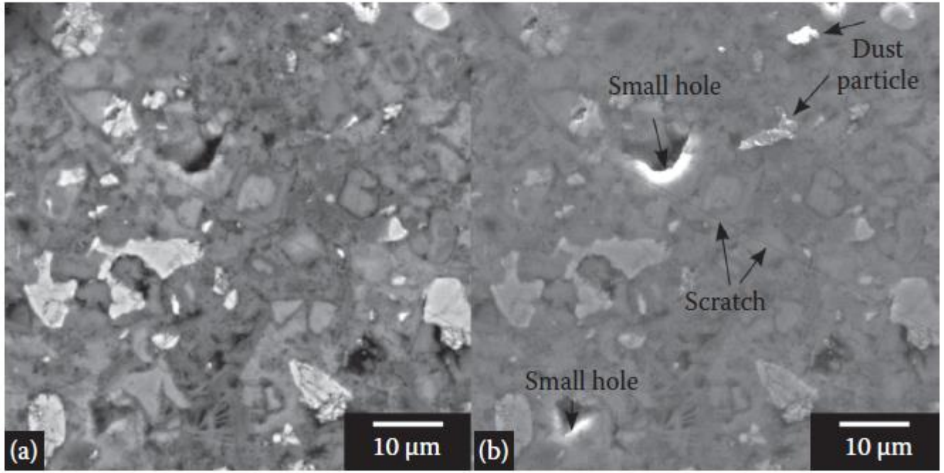




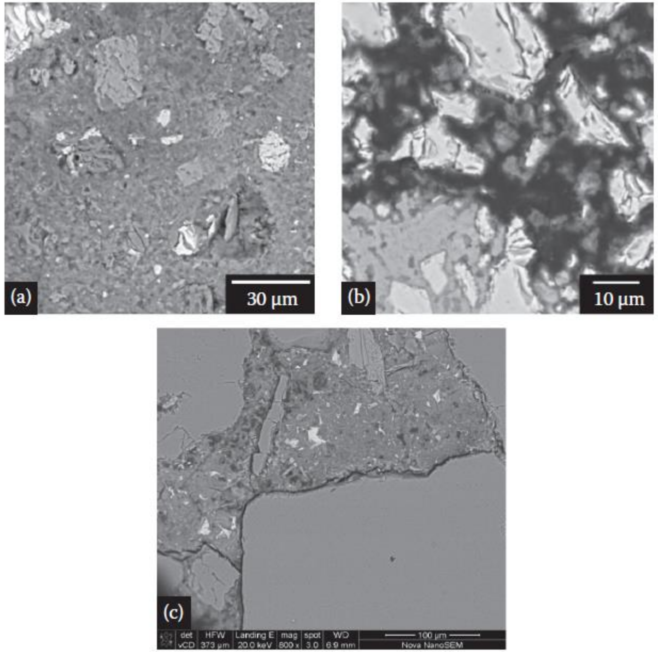
Scrivener et al, 2016

Scanning electron microscopy (SEM)

Sample preparation



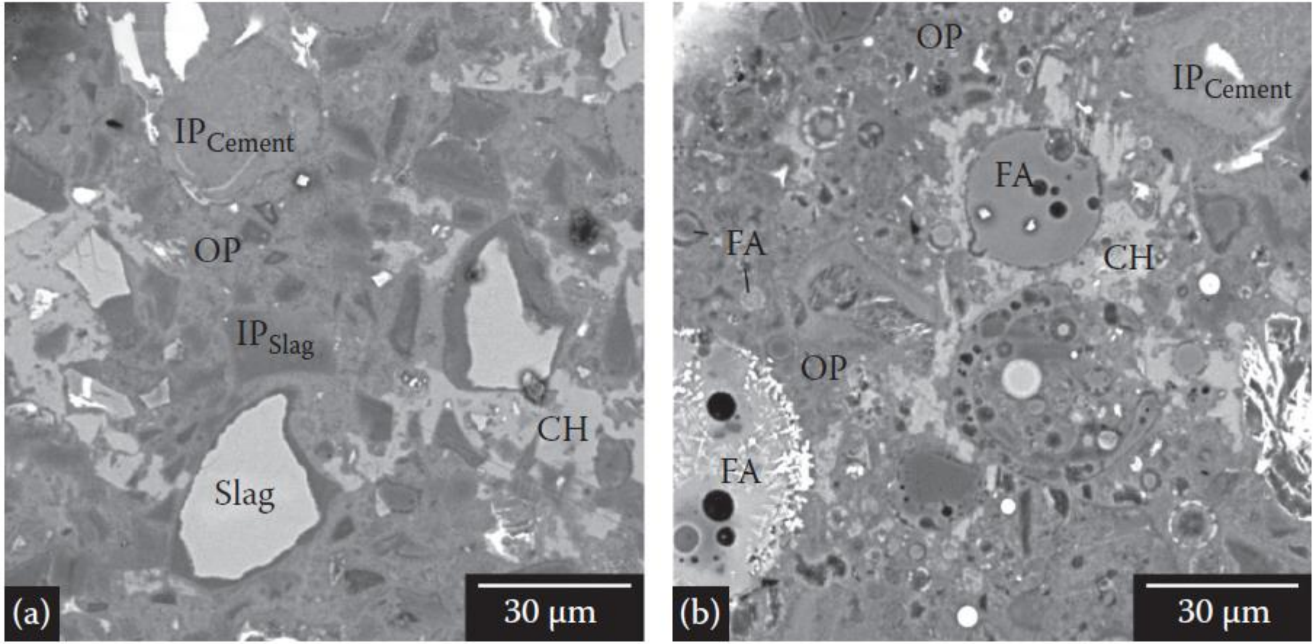
Scrivener et al, 2016



Courtesy of M. Kiliswa (University of Cape Town)

Scanning electron microscopy (SEM)

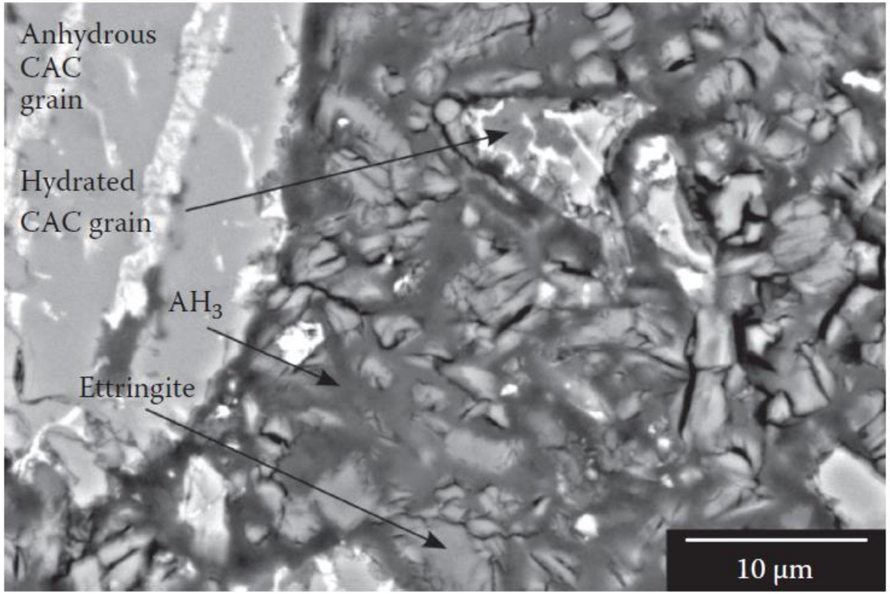
Hydrated OPC blended with slag or fly ash



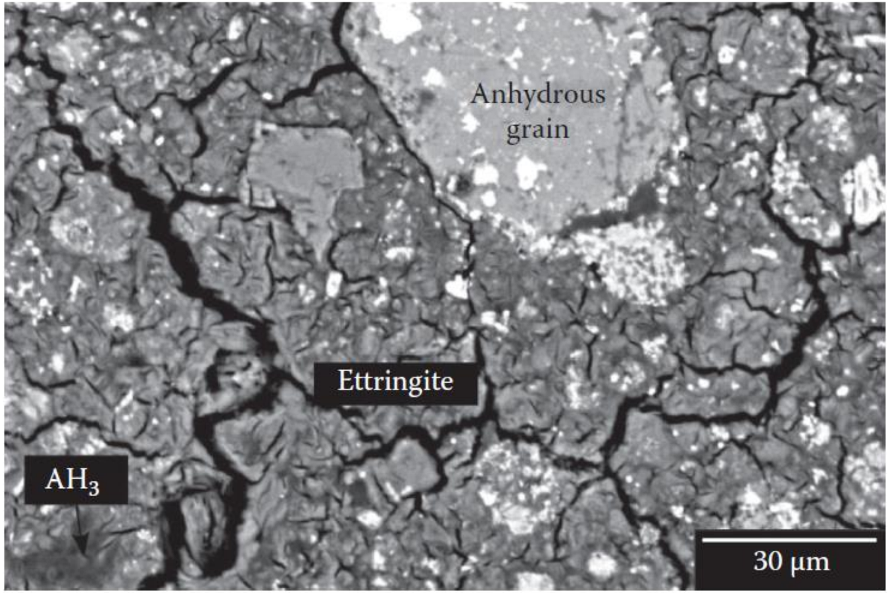
Scrivener et al, 2016

Scanning electron microscopy (SEM)

CAC + gypsum hydrated for 14 d



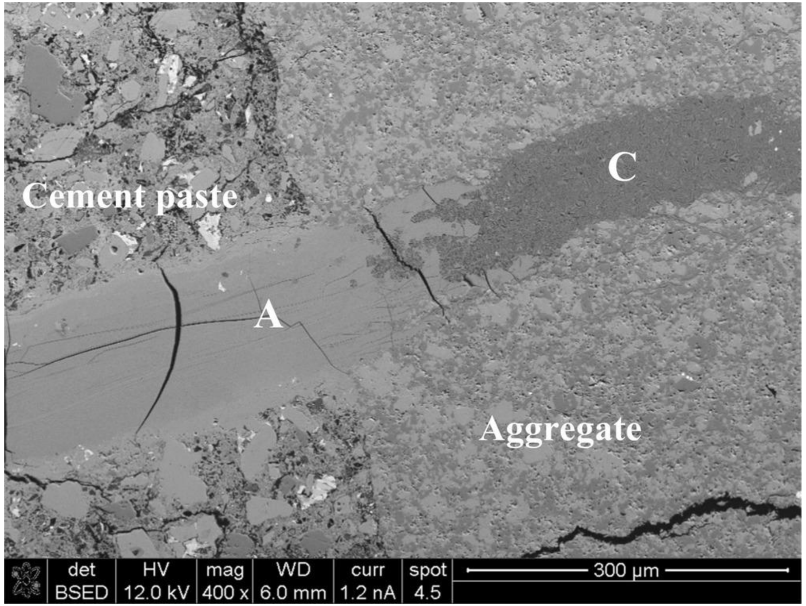
CSA + gypsum hydrated for 14 d



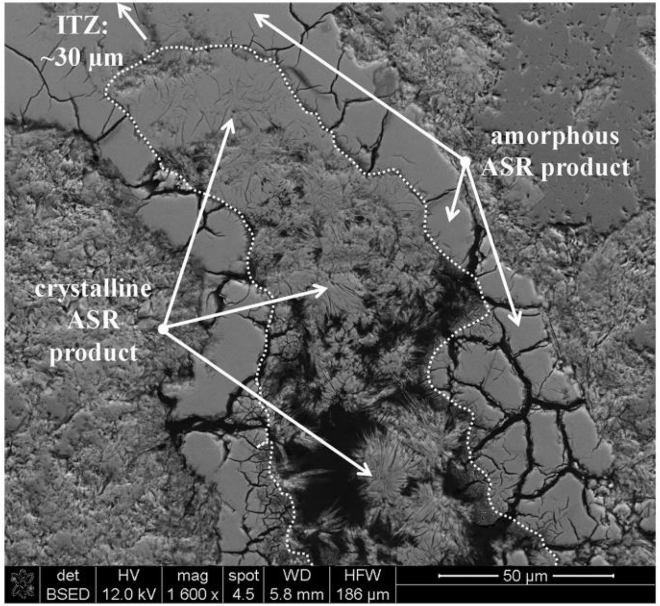
Courtesy of Dr. Bizzozero (EPFL)

Scanning electron microscopy (SEM)

Alkali-silica reaction (ASR)



Boehm-Courjault et al, 2020

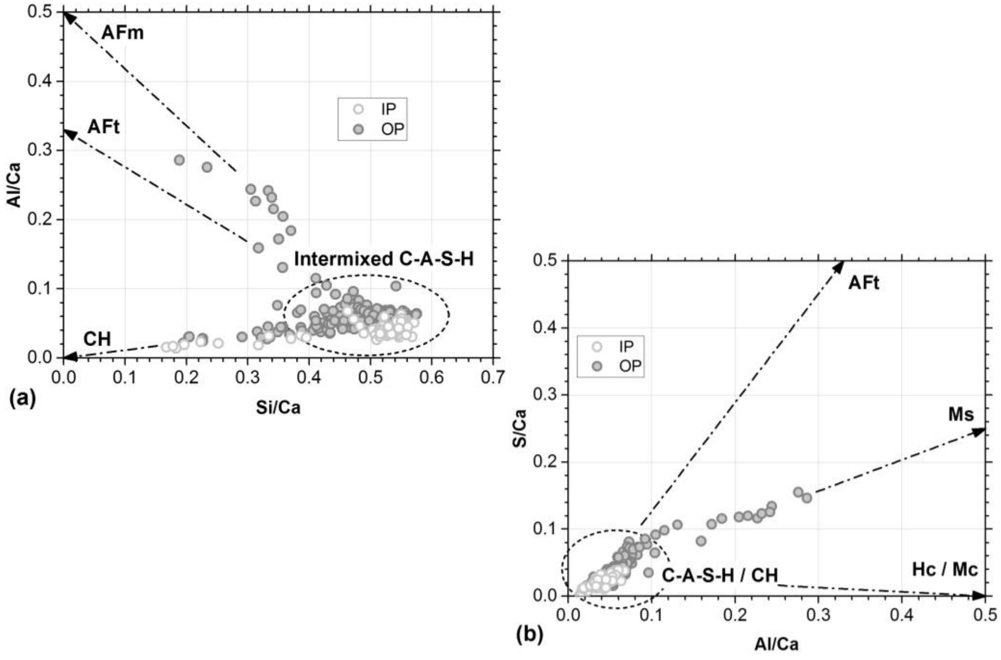


Leemann et al, 2020

Scanning electron microscopy (SEM)

Chemical analysis

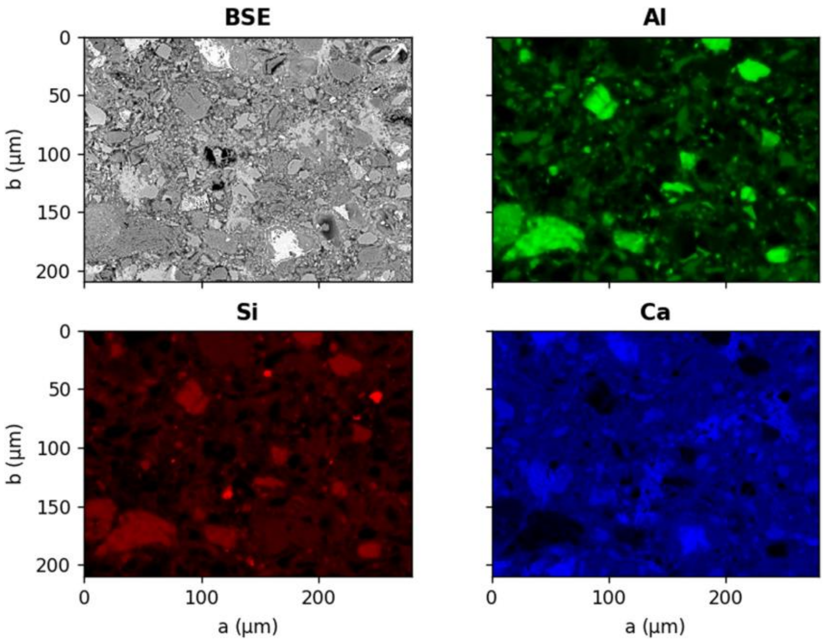
- O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe
- Energy-Dispersive Spectrometry (EDS) point analysis
- Limiting factors: intermixing of phases -> avoid interfaces
- Not enough for small particles (MK, SF diameter is less than 1 µm)
- Atomic ratios plotted on 2D-3D scatter plots



Rossen & Scrivener, 2017

Scanning electron microscopy (SEM)

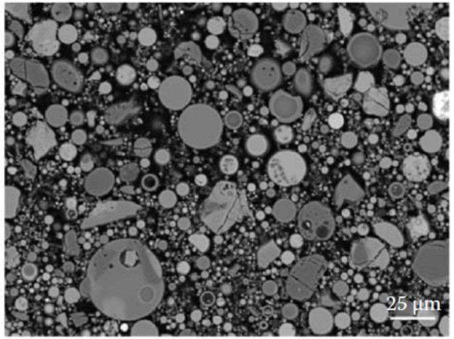
Elemental maps coupled with BSE images

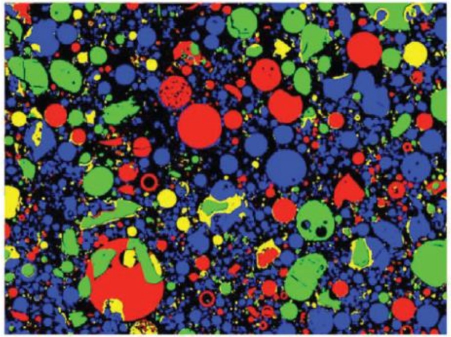


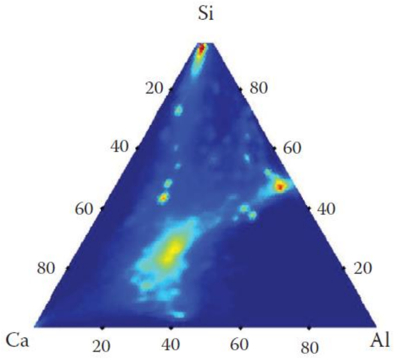
Georget et al, 2021

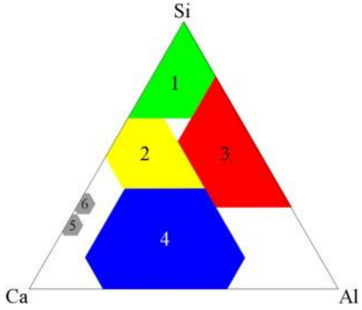
Scanning electron microscopy (SEM)

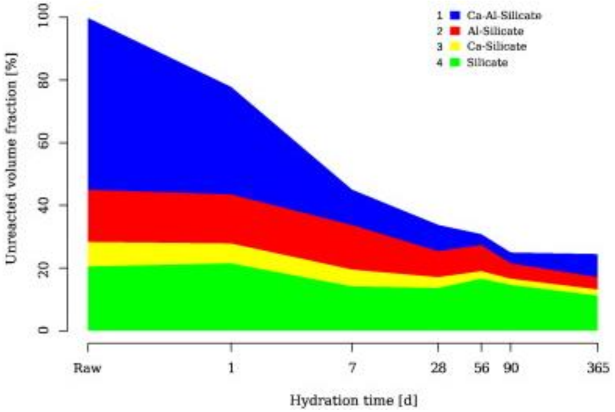
Elemental maps coupled with BSE images











Durdziński et al, 2015

SEM – Summary

ADVANTAGES

- Identification of phases
- Morphology
- Quantification
  - Pastes, mortars and concrete
  - Porosity
  - Reactivity of SCMs
- Distribution of phases, morphological analysis

CAUTIONS

- Long and not easy sample preparation
- Hydration needs to be stopped
- Interaction volume
- High number of images to have statistically representative results

Physical characterization

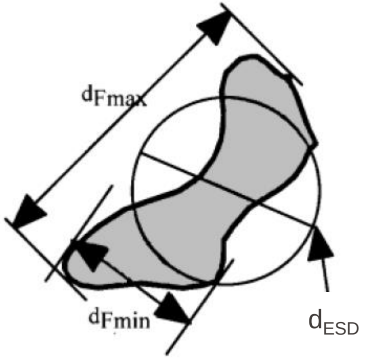
1. **Laser diffraction**
   - Particle size distribution (PSD)
2. **Blaine air permeability and N_2 adsorption**
   - Specific surface area (SSA)
3. **Mercury Intrusion Porosimetry (MIP)**
   - Porosity

Reactivity of cements
Rheology
Interactions with admixtures
Mechanical strength
Durability

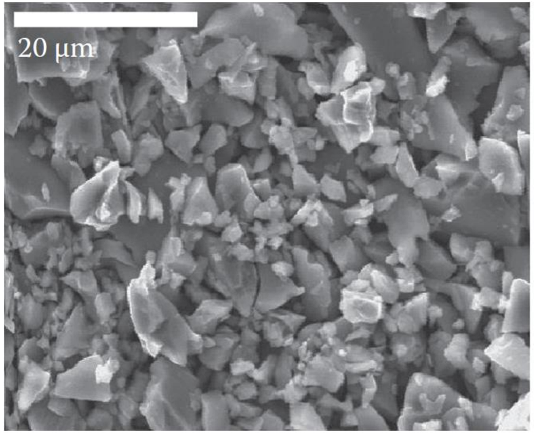
PSD – Laser diffraction

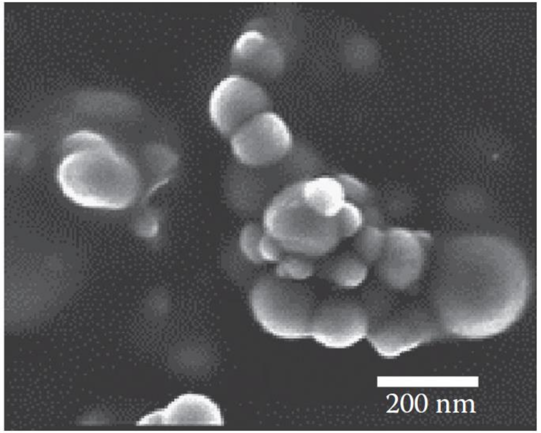
- PSD and SSA give information about the fineness of a powder
- Particle diameter is method dependent
- Equivalent spherical diameter (ESD) is reported
- Laser diffraction is the most used technique for measuring the PSD of cement

- Rapid (< 1 min)
- Best for particles 4 µm < x < 3000 µm (good down to 0.5 µm)



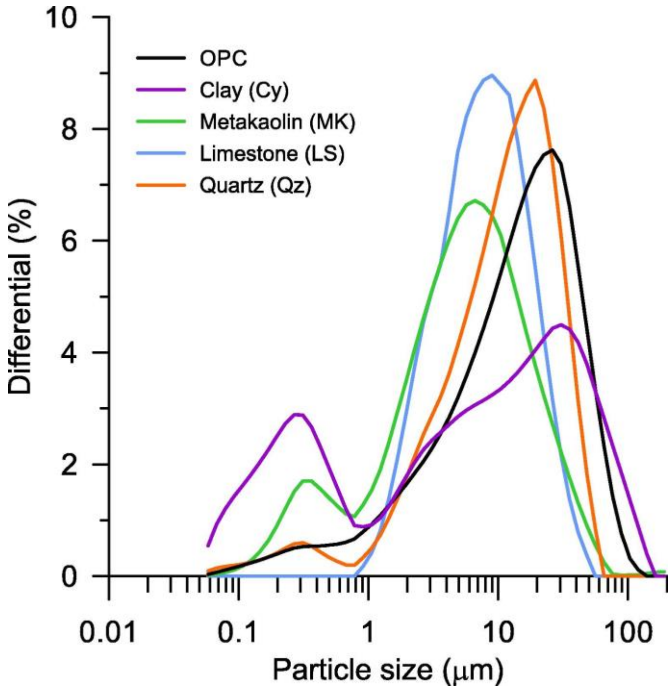
Bowen, 2002





Palacios et al, 2016

PSD – Laser diffraction

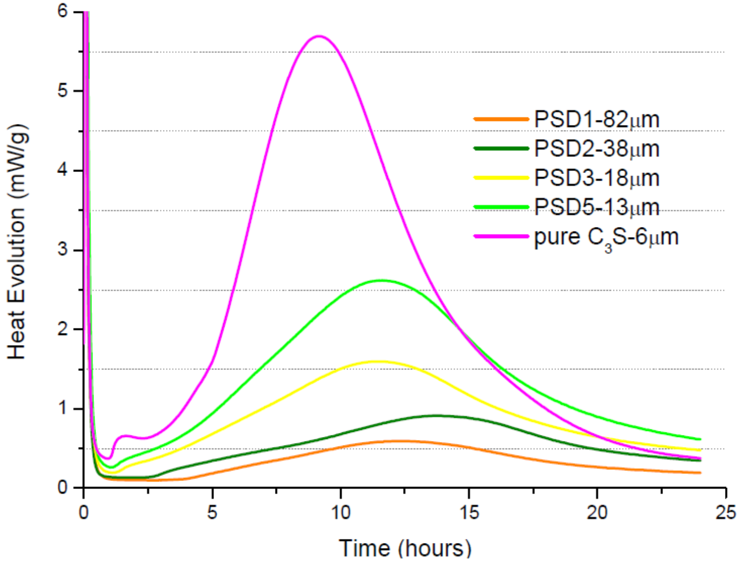


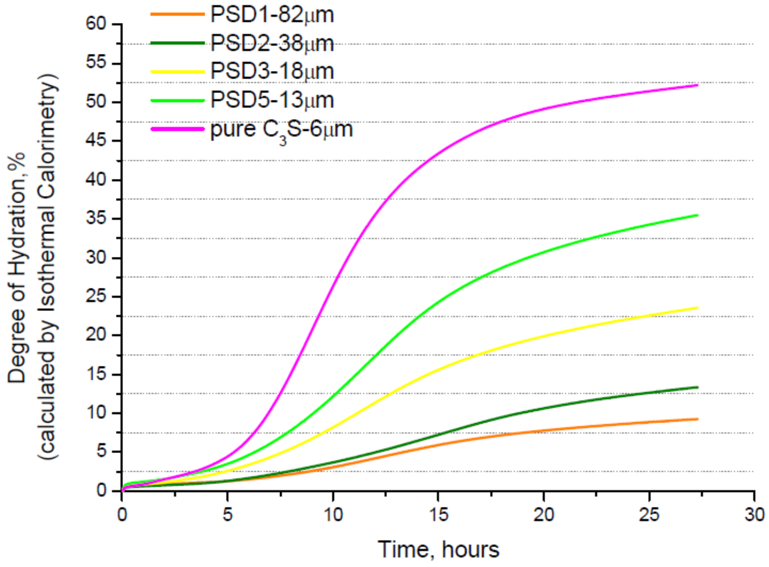
	OPC	LS	Qz	Cy	MK
D_{v90} (μm)	41.42	19.3	11.96	56.22	20.17
D_{v50} (μm)	14.22	7.71	4.56	7.72	5.13
D_{V10} (μm)	1.67	2.27	0.36	0.17	0.54

Zunino & Scrivener, 2021

PSD – Laser diffraction

Isothermal calorimetry of alite pastes with different PSD





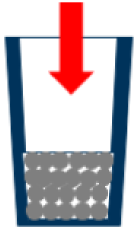
Costoya, EPFL 2008

Specific surface area (SSA)

Blaine air permeability

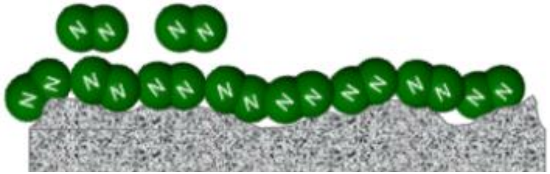
- Common in the cement industry
- No sample preparation
- Based on empirical calibration
- Assume mono-sized and spherical shape of particles (Kozeny-Carman theory)
- Poor reproducibility
- Not good for calcined clays

www.matest.com



Gas adsorption – SSA_{BET}

- Sample preparation required
- Gas access pores and cracks of the surface
- Does not assume particle shape
- Suitable for hydrated cements



Flatt & Marchon, CMS course (ETHZ)

www.micromeritics.com

Porosity

IUPAC* pores classification

- Macropores: d > 50 nm
- Mesopores: 2 nm < d < 50 nm
- Micropores: d< 2 nm

Mercury Intrusion Porosimetry (MIP)

N_2 adsorption

+ Electron microscopy, ^{1}H NMR relaxometry

Category of pores in hydrated cement materials

- Compacting / air voids: µm – mm, from imperfect placing
- Capillary pores: µm to a few nm, space not occupied by hydrates or unreacted cement grains
- Gel pores: nm, intrinsic porosity of C-S-H

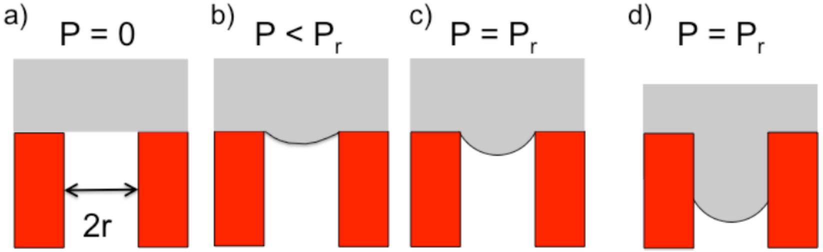
*International **U**nion of **P**ure & **A**pplied **C**hemistry

Porosity – MIP

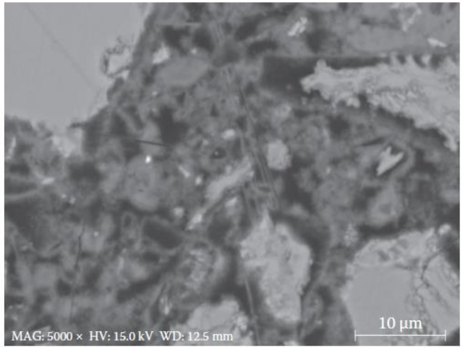
- Pore diameter range of 2 nm – 250 µm
- It is based on the intrusion of a nonwetting fluid (contact angle θ > 90º, Hg) into porous structures under increasing applied pressure (*P*). Hg can intrude only the interconnected porosity
- *P* is used to calculate the pore radius (*r*), assuming cylindrical pores, according to the Washburn eq.:

$$P = -\frac{2\gamma cos\theta}{r}$$

γ = 0.485 N/m at 25ºC (Hg)
θ = 140º



Courtesy of Prof. Flatt (ETHZ)



Berodier et al, 2016

Physical characterization – Summary

ADVANTAGES

LD

- Quick (< 5 min)
- Widely available

Blaine air permeability

- Quick and simple

SSA by gas adsorption

- Accurate
- Reproducible

CAUTIONS

LD

- Assume spherical particle shape
- Refractive index (care when the composition and purity vary)
- Use of proper dispersing liquid
- Avoid agglomeration

Blaine air permeability

- Narrow domain
- Poor reproducibility
- Not good for SCMs (fly ash, calcined clays)
- Assume mono-sized and spherical particles

SSA by gas adsorption

- Sample preparation (degassing conditions, method to stop the hydration, gas selection)

General remarks

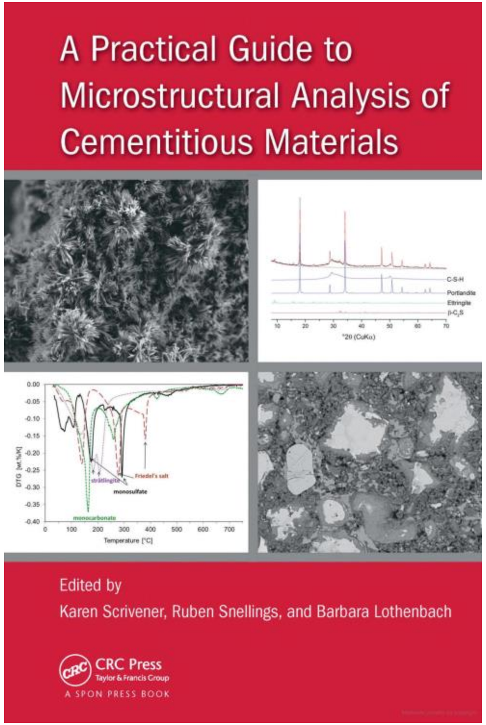
- All analytical techniques have an intrinsic error
- For most quantification methods, the relative error increases with the decrease in the absolute amounts
- Difficult to detect small quantities
- Calorimetry, XRD and SEM are the most important techniques for characterizing cement
- **Best is to combine several techniques**

Learning objectives

Now, at the end of this class, you are able to...

- **Identify** what characteristics of cement are important
- **Select** the correct analytical method(s) to measure a specific cement characteristic
- **Recognize** the limits of the available analytical methods

Recommended literature



Course schedule

Week #	Class date	Title	Lecturer
1	11/09/2024	Introduction and Literature Review	Prof. Karen Scrivener / Dr. Alastair Marsh
2	18/09/2024	Durability	Dr. Beatrice Malchiodi
3	25/09/2024	Cement hydration	Prof. Karen Scrivener
4	02/10/2024	Characterisation	Dr. Federica Boscaro
5	**09/10/2024**	**Presentation 1**	
6	16/10/2024	Admixtures	Dr. Federica Boscaro
7	**30/10/2024**	**Presentation 2**	
8	06/11/2024	Life cycle analysis for cementitious materials	Dr. Alastair Marsh
9	13/11/2024	Limestone calcined clay cements (LC^3)	Dr. Franco Zunino
10	20/11/2024	Concrete design	Dr. Beatrice Malchiodi
11	27/11/2024	Sustainability appraoches for construction	Dr. Alastair Marsh
12	04/12/2024	Concrete structures / Q&A on Presentation 3	Prof. David Ruggiero
13	**11/12/2024**	**Presentation 3**	
14	18/12/2024	Re-use & standardization	Prof. David Fernandez / Prof. Corentin Fivet

Questions?

Advanced cementitious materials, MSE 420

Lecture 4: Cement characterisation and analytical methods

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2nd October 2024