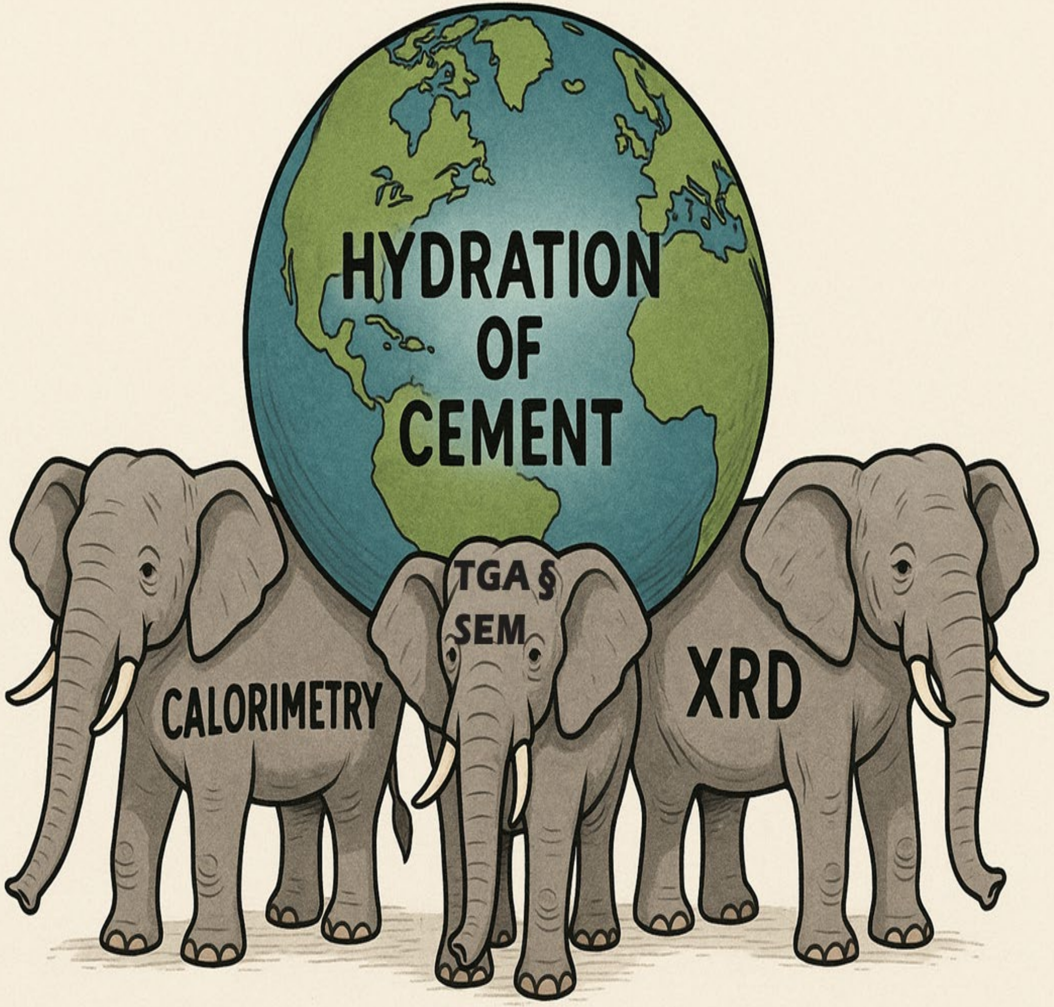


Analytical characterisation techniques for cementitious materials

Advanced cementitious materials, MSE 420

Lecture 7

Dr. Antonina Goncharov

Lecture Out line

1. Introduction and Motivation
2. Cement hydration
3. **Thermal methods: Calorimetry and TGA**
4. Chemical and **Mineralogical Characterization:** XRF**, XRD**
5. 10 – minutes break
6. Microstructure and Morphology: **SEM**, TEM
7. Physical Characterization: MIP, BET, PSD
8. Integration and Limitations
9. Discussion and Q&A
10. Summary

Learning objectives

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

- **Identify**
  Recognize which analytical techniques are best suited to study specific cement characteristics — chemical, physical, or microstructural — and why these properties matter for performance.
- **Interpret**
  Understand how each technique generates its signal (e.g., heat flow, mass loss, diffraction, imaging), what type of data it produces, and how to read that data to answer practical questions.
- **Select**
  Choose the most appropriate method — **Calorimetry, TGA, XRD, SEM, PSD, SSA, or MIP** — to address a defined practical or research objective.
- **Evaluate**
  Assess the strengths, limits, and complementarities of each technique to combine them effectively for a complete understanding of cementitious materials.

Why do we need characterization?

Characterization of anhydrous and hydrated systems is related to:

Cement/cement paste scale

- To **understand reactivity** — how cement reacts with water and supplementary materials (SCMs like fly ash or calcined clays).

Cement mortar/concrete scale

- To **control rheology and water demand** - key for workability.

Concrete scale

- To **predict strength and durability** — crucial for both structural engineers and architects concerned with long-term performance

Calorimetry

- **Signal mechanism**
- Measures **heat flow (mW/g)** — exothermic hydration reactions release heat.
- The calorimeter tracks heat over time → **hydration kinetics**.
- **Practical questions**
- When do the main hydration reactions occur?
- How do **SCMs or admixtures** affect **hydration kinetics**?
- How do **temperature** influence hydration behavior?
- **How to interpret the data**
- **Heat flow curve:** each peak = a distinct hydration stage (C_3S, C_3A, etc.).
- **Cumulative heat:** total hydration progress → **degree of hydration (α)**.
- Compare curves for **different binders, SCMs, admixtures.**
- **Applications in practice**
- Determine **rate and degree of hydration.**
- Evaluate **SCM reactivity (R^3 test)** and **sulfate optimization.**
- Correlate with **strength development.**

Calorimetry Types

When cement reacts with water, it releases heat — exothermic reaction.

By tracking this heat, we can follow the kinetics of hydration.

- **Isothermal calorimetry (1-100g)** measures heat flow at constant temperature – **ideal for lab research**.
- **Semi-adiabatic calorimetry (0.5-10 kg)** used by mortar and **concrete manufacturers** and in the field.
- **Adiabatic calorimetry** - Fully adiabatic calorimeters are suitable for studies of mass concrete – where the heat losses are negligible.
  - Types of calorimeters:

Isothermal c.

tainstruments.com

Semi-adiabatic c.

calmetrix.com

Adiabatic c.

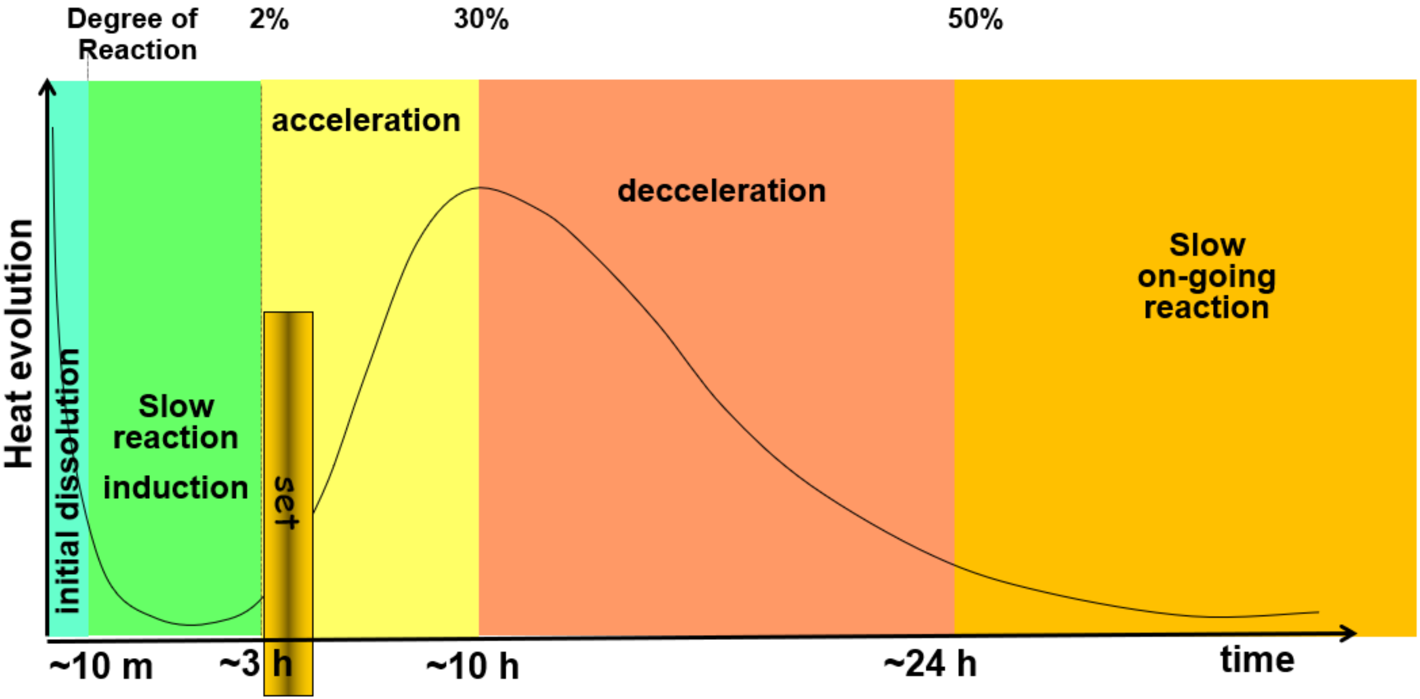
controls-group.com

Cement Hydration – Isotermal Calorimetry curve

This graph shows how cement reacts with water over time.

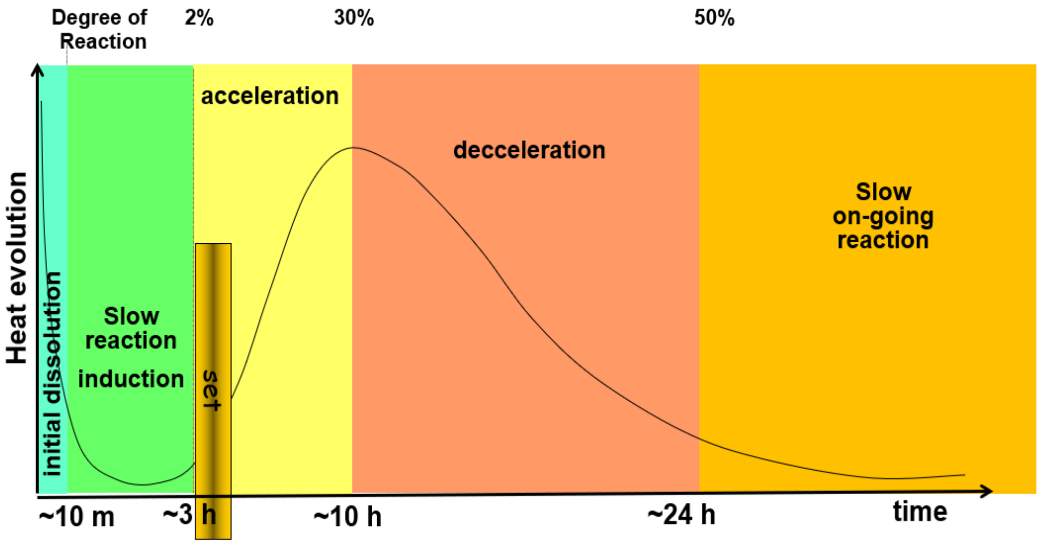
On the vertical axis - the <u>*heat flow*</u>
On the horizontal axis - <u>*time*</u>.

Each part of this curve represents a different stage in the life of cement paste - from liquid paste to a strong, solid material.



Based on slides by K. Scrivener

Cement Hydration – Early Stages

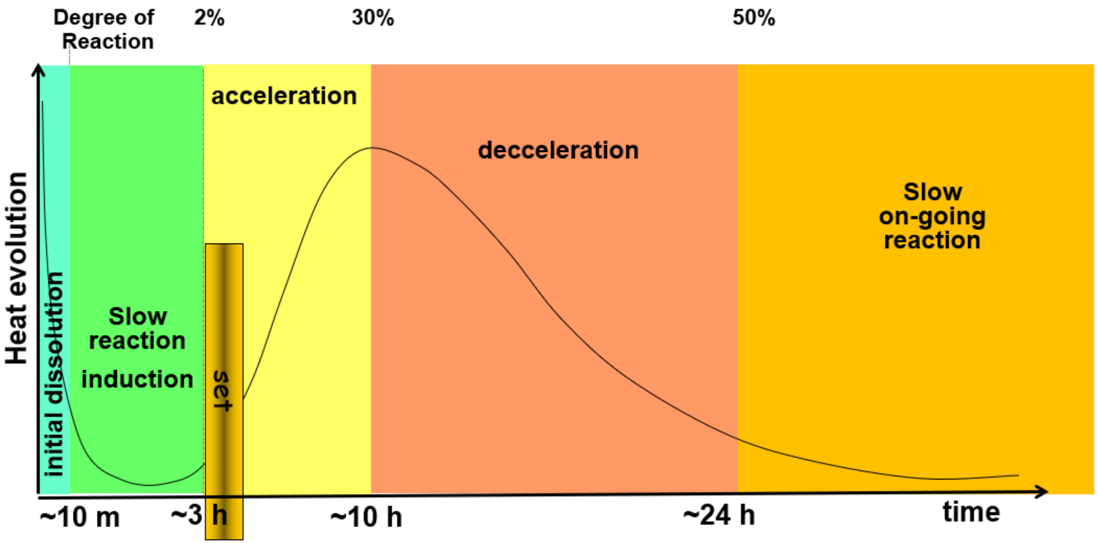


Based on slides by K. Scrivener

Hydration stages:

1. **Initial dissolution (0–10 min)**
   Cement grains dissolve → short heat peak.
   💡 *"Cement wakes up."*
2. **Induction period (10 min – 3 h)**
   Low heat; ions stabilize in solution.
   💡 *Paste stays plastic – concrete can be placed.*
3. **Acceleration (3 – 10 h)**
   Sharp rise in heat → C–S–H + CH form.
   💡 *Setting and hardening begin.*

Hydration Continues – Slower but Stronger



Hydration stages:

3. Deceleration (~10–24 h)
Reaction slows as hydration products coat grains.
💡 *Heat flow drops, paste densifies.*

4. Slow ongoing hydration (days–months)
Unreacted grains hydrate gradually.
💡 *Long-term strength and durability improve.*

Based on slides by K. Scrivener

Cement Hydration: Microstructure

Microstructure diagrams

These three images show how the microstructure evolves during hydration:

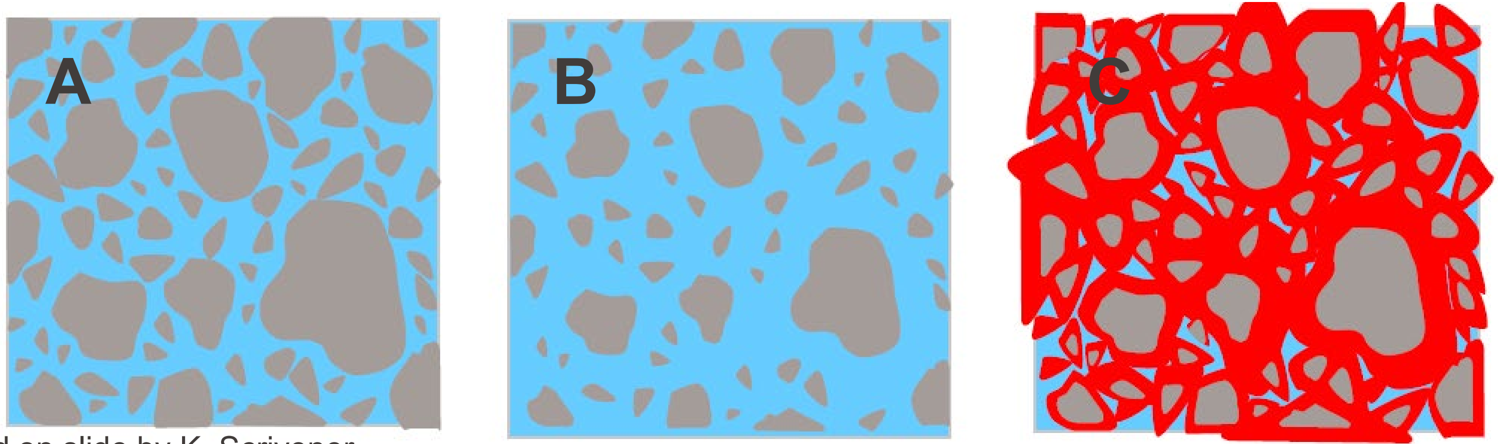
A: *We mix the grey cement powder with water. To start with the grains are just floating about in the water and we can cast the concrete into moulds.*

1. Large grey grains = unreacted clinker.
2. Blue phase = water.

B: *The cement grains dissolve in the water*

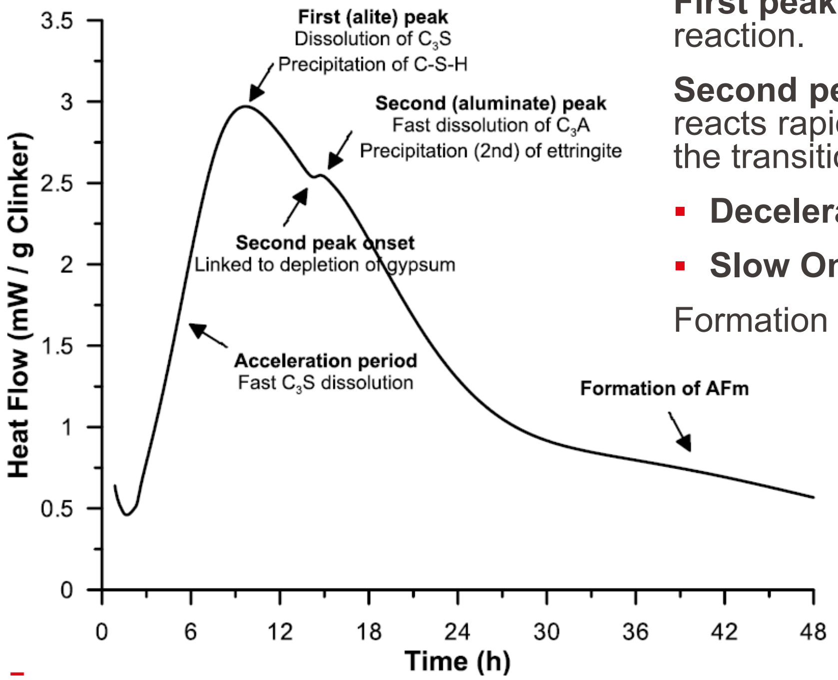
C: *The cement grains dissolve in the water. And then precipitate Hydrates – new solids which have higher volume and hold the grains together: creating a rigid solid*

1. Red network = Hydration Products (C–S–H,CH, AFt, AFm).



- Based on slide by K. Scrivener

Isothermal calorimetry



Zunino & Scrivener, 2019

The curve represents the rate of heat release (mW per gram of clinker) during cement hydration — how fast the chemical reactions are occurring.

- **Initial period + Induction period** .
- **Acceleration period:**

First peak - the alite peak, corresponding to the main strength-giving reaction.

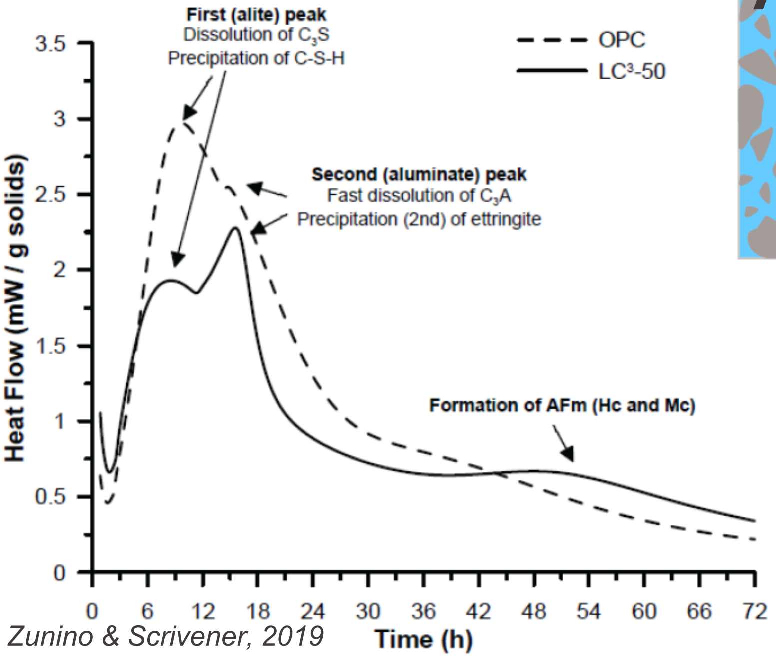
Second peak - aluminate peak Occurs when gypsum is depleted and C_3A reacts rapidly. Leads to the precipitation of ettringite (Aft). This peak reflects the transition from silicate to aluminate reactions.

- **Deceleration Period**
- **Slow On-Going Reaction**

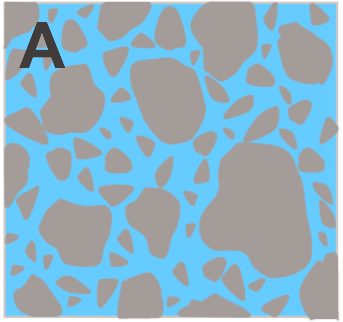
Formation of AFm (monosulfate)

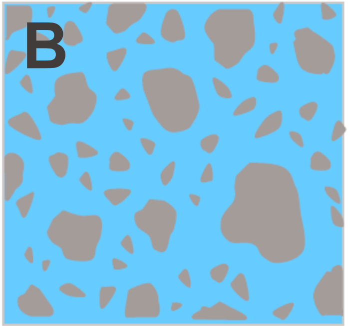
Isothermal calorimetry: OPC vs. LC3-50

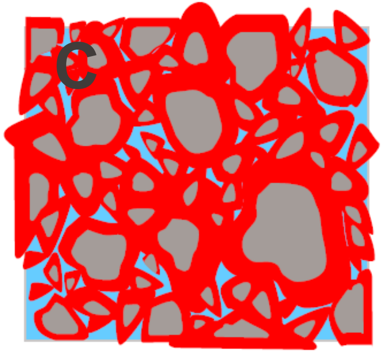
1. Which stage of the hydration curve corresponds to microstructure?
2. Why is the C_3A (aluminate) peak higher in LC^3-50 compared to OPC?



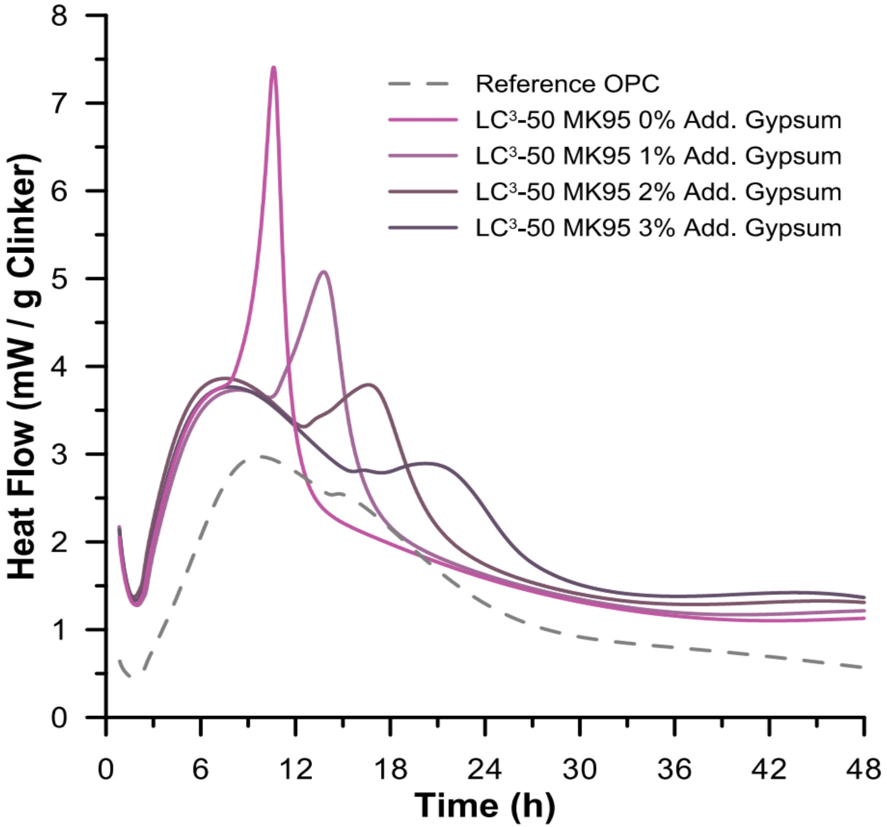
Zunino & Scrivener, 2019







Calorimetry - Examples



Heat flow of LC3 -50 MK95 systems with different amounts of gypsum addition.

Zunino & Scrivener, 2019

From Heat Flow to Degree of Hydration

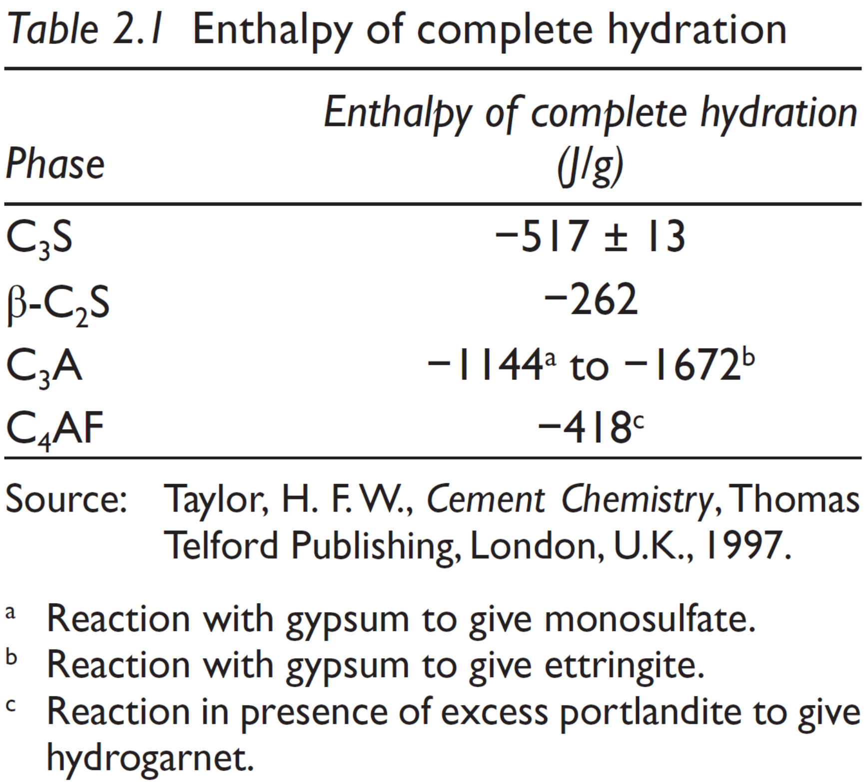


Table 2.1 Enthalpy of complete hydration

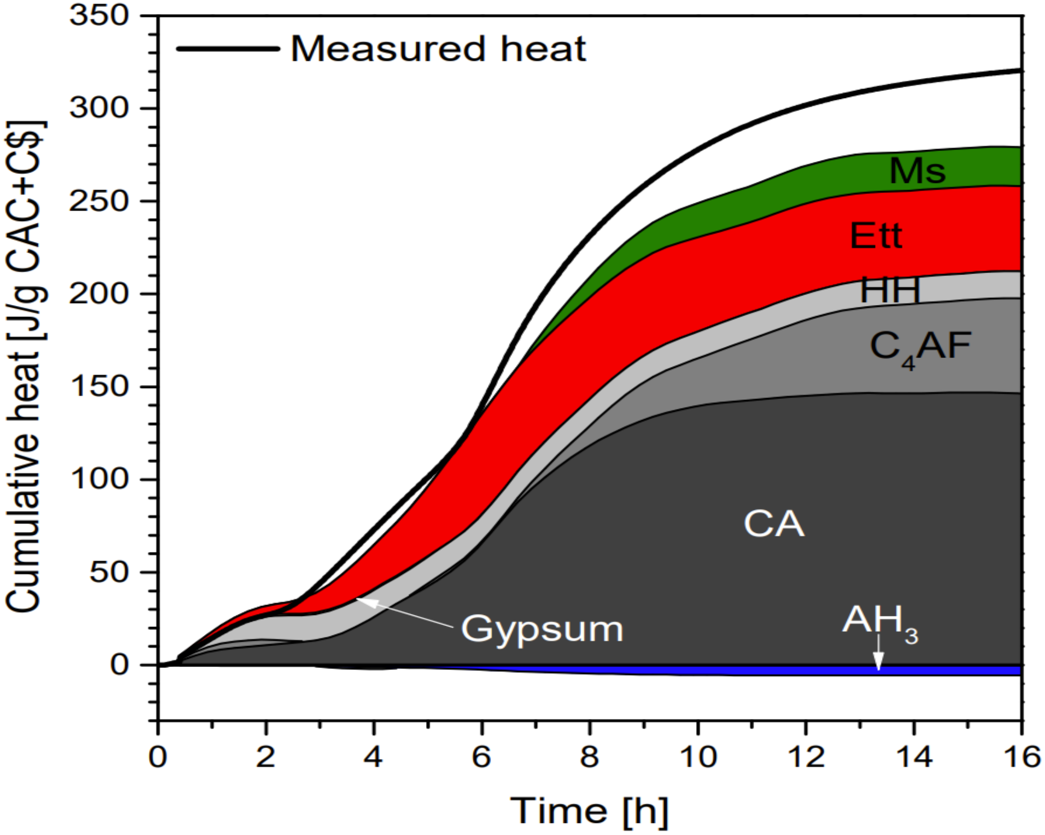
Phase	*Enthalpy of complete hydration (J/g)*
C_3S	−517 ± 13
β-C_2S	−262
C_3A	−1144[a] to −1672[b]
C_4AF	−418[c]

Source: Taylor, H. F. W., *Cement Chemistry*, Thomas Telford Publishing, London, U.K., 1997.

[a] Reaction with gypsum to give monosulfate.
[b] Reaction with gypsum to give ettringite.
[c] Reaction in presence of excess portlandite to give hydrogarnet.

- Numerical integration of the heat-flow curve gives the total heat of hydration (Q).
- If the hydration enthalpies of the clinker phases are known, the total heat can be converted approximately into a degree of hydration (α).
- The enthalpy of complete hydration (Q∞) can be estimated from the phase composition of Portland cement→ obtained from calculations or quantitative XRD.
- The ratio Q/Q∞ gives a practical estimate of the hydration degree from the cumulative heat release

Calorimetry - Examples

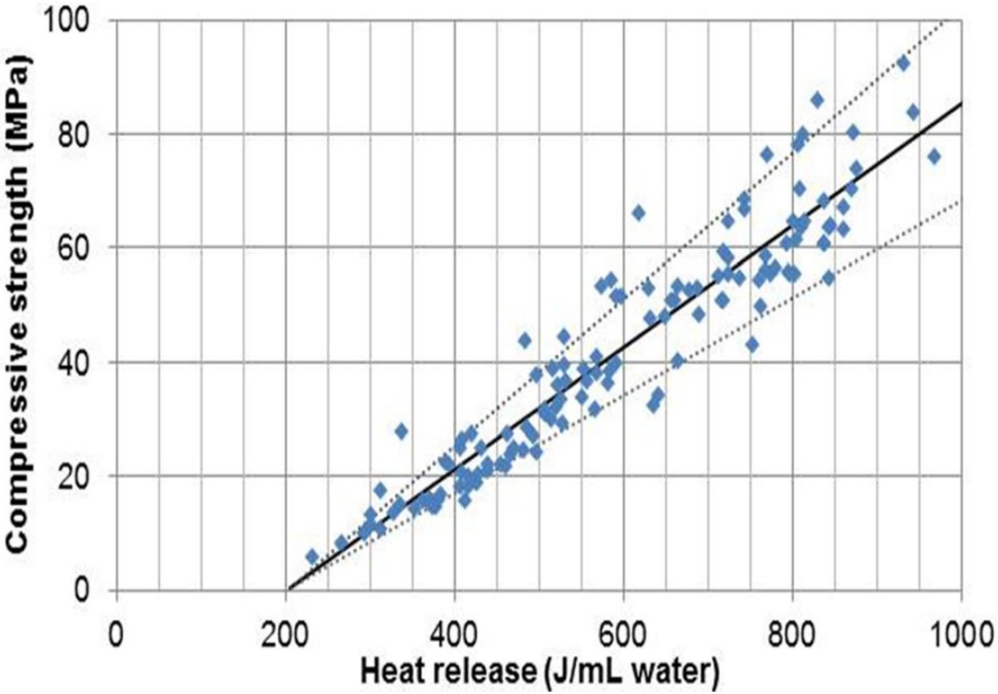


Comparison between measured and calculated heats of hydration of a calcium aluminate cement blended with hemihydrate
Bizzozero, J., PhD Thesis no. 6336, ÉPFL, 2014

Correlation with strength development

- **No universal rule:**
  Heat release and strength are not directly linked for all concretes — mix design (aggregate, w/c ratio, porosity) strongly influences strength.
- **But within one mix type (e.g., standard mortar):**
  Strength can be correlated with **cumulative heat** — more heat = more hydration = higher strength.
- **Why it matters:**
  Isothermal calorimetry gives a **fast, repeatable**, and **less labor-intensive** way to estimate early strength compared to compressive testing.

💡 *Cement producers use this relationship to predict early performance from heat measurements.*



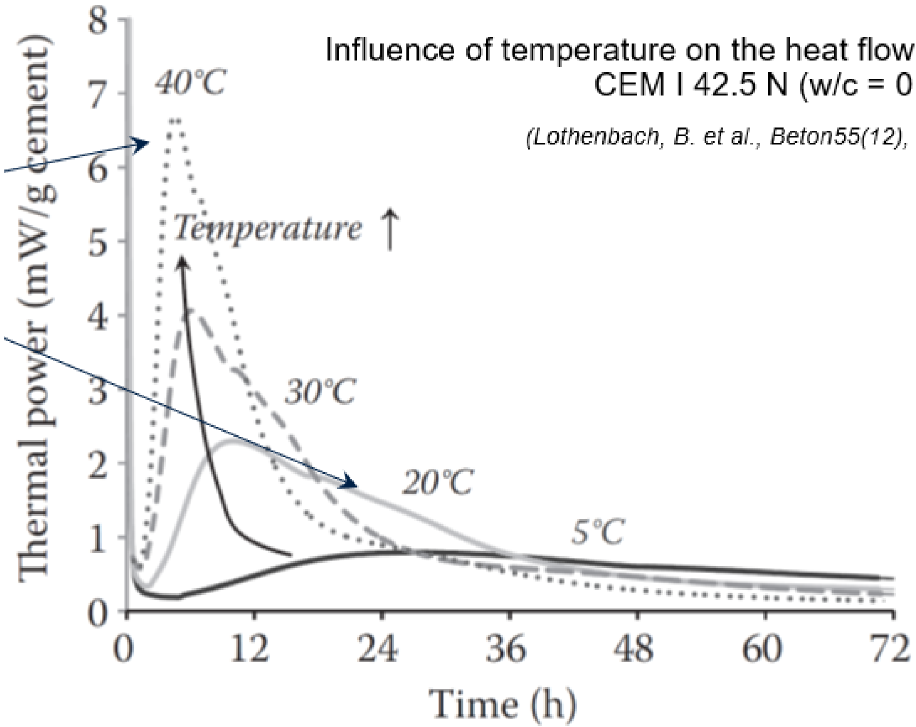
Compressive strength versus heat release per milliliter of water for mortars. The solid line indicates the best fit linear relationship, and the two dashed lines indicate 20% from the best fit values.

(Dale P. Bentz,1 Tim Barrett,2 Igor De la Varga,3 and W. Jason Weiss4, 2012)

Influence of temperature on hydration kinetics

WHY?

- **WHY? (Simplified Explanation)**
- The **total heat** released depends on **how much cement reacts**, not on the temperature itself.
- **Higher temperature** → **faster reactions** (both dissolution and hydrate formation).
- This means in calorimetry curves, the **peaks appear earlier and sharper** at higher temperatures.

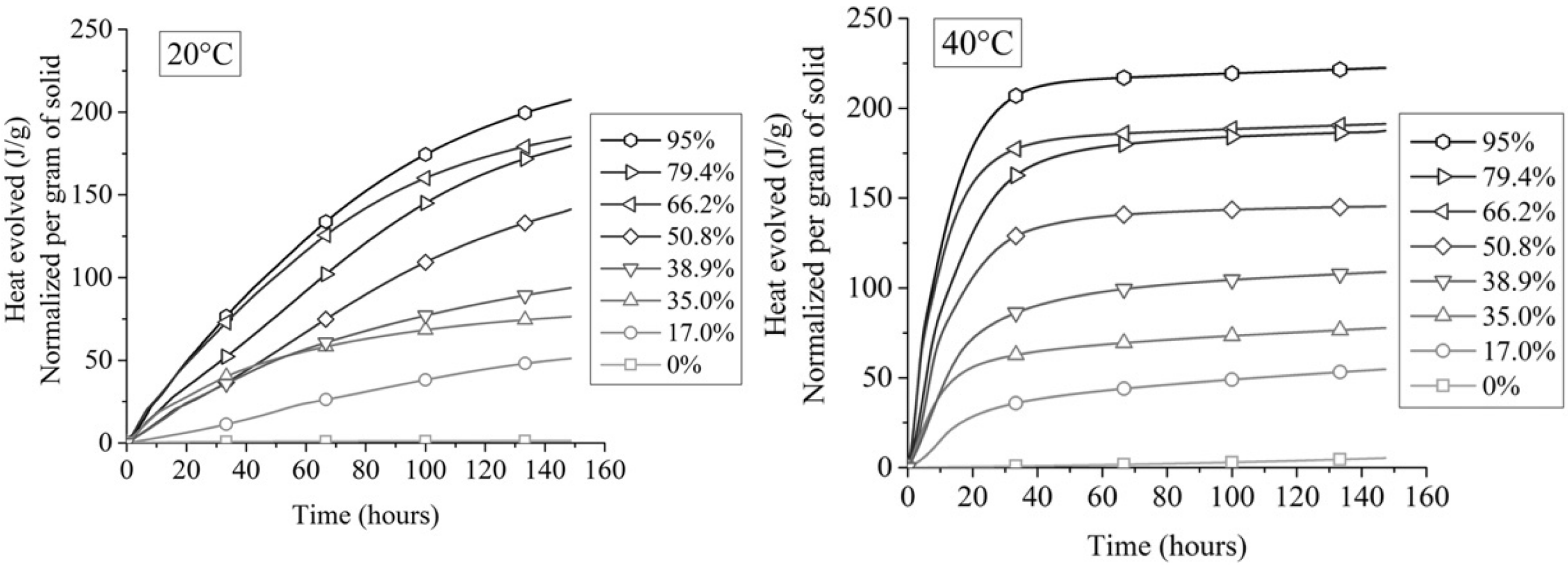


Influence of temperature on the heat flow of a CEM I 42.5 N (w/c = 0.40).

(Lothenbach, B. et al., Beton55(12), 2005)

Reactivity of SCM – R3 test in different temperatures

The R³ (Rapid, Relevant, Reliable) test measures the chemical reactivity of SCMs such as fly ash, slag, calcined clays, or silica fume. It is performed without cement, using a synthetic pore solution that simulates cement hydration conditions.



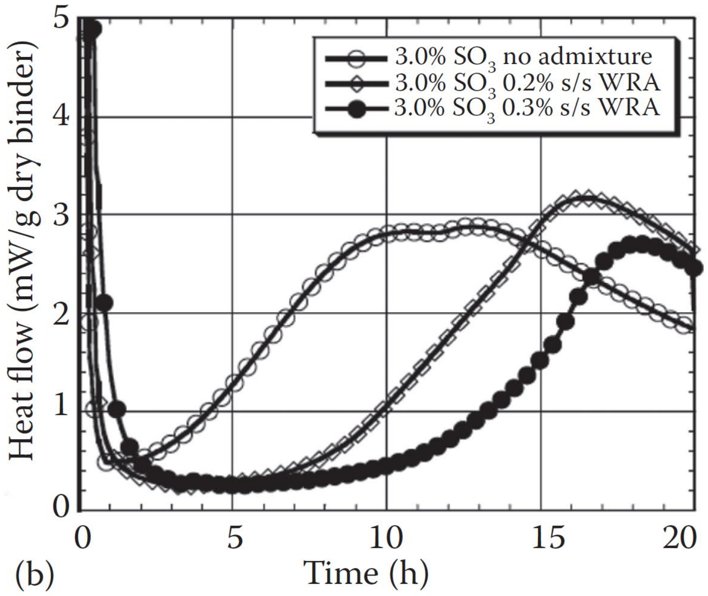
- Heat released for calcined clay-portlandite blends without limestone at 20 and 40 °C. *(François Avet and Karen Scrivener 2016)*

Interactions of cement & admixtures

- **Admixtures** are used to **control hydration kinetics** and improve concrete workability, setting, or strength.
- **Isothermal calorimetry** helps to **quantify how admixtures influence** the rate and mechanism of cement hydration.
- It is also a key tool to **detect incompatibilities** between binders and admixtures that can cause **delayed setting or abnormal strength development**.
- The effect of admixtures depends on:
  - **Type** of admixture (e.g., WRA, superplasticizer)
  - **Dosage** and **timing of addition**
  - **Mixing intensity** and **temperature**

Calorimetry provides a fast, reliable way to study and optimize these interactions.

Interactions of cement & admixtures: Example



Heat flow calorimetry of OPC without and with a **WRA** added that accelerates the aluminate reaction *(Sandberg, P. J. & L. R. Roberts, J. of ASTM Int. 2(6), 2005).*

WRA (Water-Reducing Admixture):

- Improves workability at lower water content
- Can delay early hydration, especially C_3A reaction
- Effect depends on **SO_3 content**, dosage, and timing

Calorimetry reveals:

- Delayed or abnormal hydration peaks
- Compatibility or imbalance between cement & admixture
- Need for sulfate adjustment

Calorimetry - Summary

- ☑ **Advantages**
- Quantifies **hydration kinetics** directly
- Tracks hydration **continuously and in real time**
- **No need to stop** hydration for measurements
- Easy testing at **different temperatures**
- Evaluates **SCMs, admixtures, and sulphate effects**
- Works for **pastes, mortars, and concretes**
- **Widely available** and simple to use

- ⚠ **Limitations / Cautions**
- Measures **overall reaction rate**, not phase-specific kinetics
- Requires **reference samples** for isothermal tests
- **Calibration** is essential for accuracy
- **Signal weakens** at later ages (low heat flow)

Thermogravimetric analysis -TGA

TGA — Mass Change with Temperature

- **Practical question:**
- How much portlandite, carbonate, or bound water is in the cement?
- What's the **degree of hydration** or carbonation level?
- **How can we normalize results by TGA?**
- **Signal mechanism:**
- Measures **mass loss** as temperature increases (up to 1000 °C).
- Different hydrates decompose at different temperatures.
- **How to interpret:**
- **Weight loss (%) vs. temperature (°C)** → thermal stability.
- **DTG curve**
- **Answers to practice:**
- Quantify **CH** → hydration degree.
- Quantify **CO_2 loss** → carbonation.
- Total mass loss → hydration evolution & SCM reactivity

https://cemlab.net.technion.ac.il/

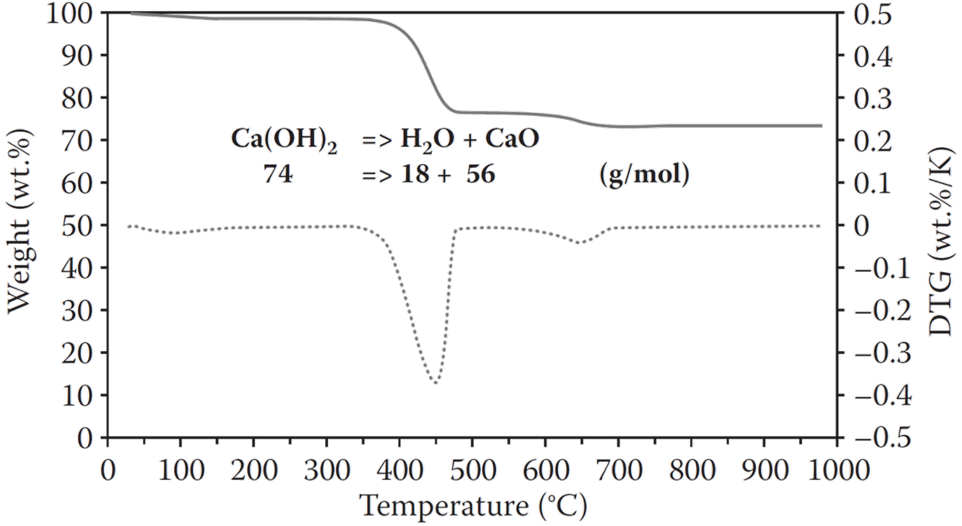
Important parameters in TGA:

- Heating rate
- Type of atmosphere (gas)
- Gas flow rate
- Materials of vessel
- Closed/open vessel
- Sample weight
- Method of stop hydration

Thermogravimetric analysis

- Minerals and hydrates can undergo several thermal reactions: dehydration, dehydroxylation, decarbonation, oxidation, decomposition, phase transition or melting.
- These reactions are generally associated with weight changes or release/consumption of heat.
- The temperature at which these processes occur are typical for the mineral.
- During TGA the sample is heated while the weight loss is recorded.
- Differentiation of the thermogravimetric **(TG)** data allows a better resolution and identification of consecutive weight losses: derivative thermogravimetry or differential thermogravimetry **(DTG).**

TG/DTG example



Between 400 °C and 500 °C, a sharp weight loss occurs due to decomposition of CH.

The sample loses about 24% of its weight, corresponding to the release of bound water.

The DTG curve shows a strong endothermic peak at ~450 °C — indicating the temperature of maximum decomposition rate.

$$Ca(OH)_{2,\text{measured}} = WL_{Ca(OH)_2} \times m_{Ca(OH)_2} / m_{(H_2O)} = WL_{Ca(OH)_2} \times \frac{74}{18}$$

- **X-axis:** Temperature (°C) — heating from room temperature up to about 1000 °C.

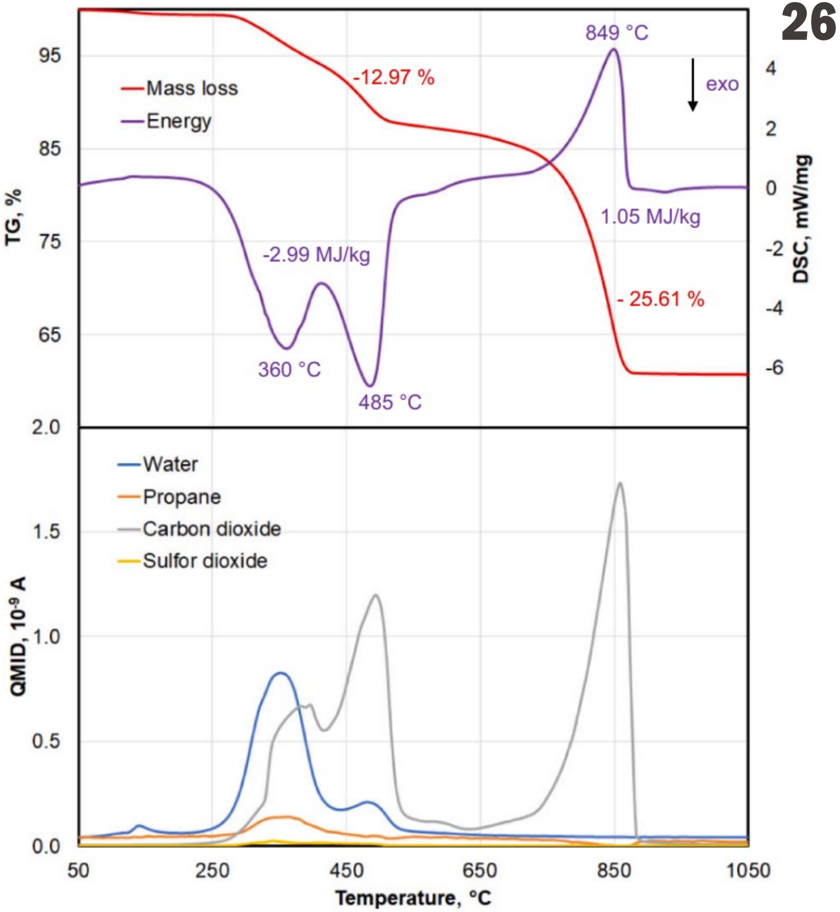
- **Left Y-axis (solid line):** Weight (%) — total mass of the sample as temperature increases

.

- **Right Y-axis (dotted line):** DTG (derivative weight loss, %/°C) — shows the rate of weight loss.

Differential Thermal Analysis

- In addition to TGA and DTG, differential scanning calorimetry (DSC) are also often used to analyze cements.
- DSC measures the difference in the heat needed to increase the temperature of a sample compared to a reference as a function of temperature.
- Some instruments allow to record simultaneously with the weight loss the type and the amount of gaseous reaction products.
- For this purpose the thermogravimeter is coupled directly to a mass spectrometer or an infrared spectrometer.

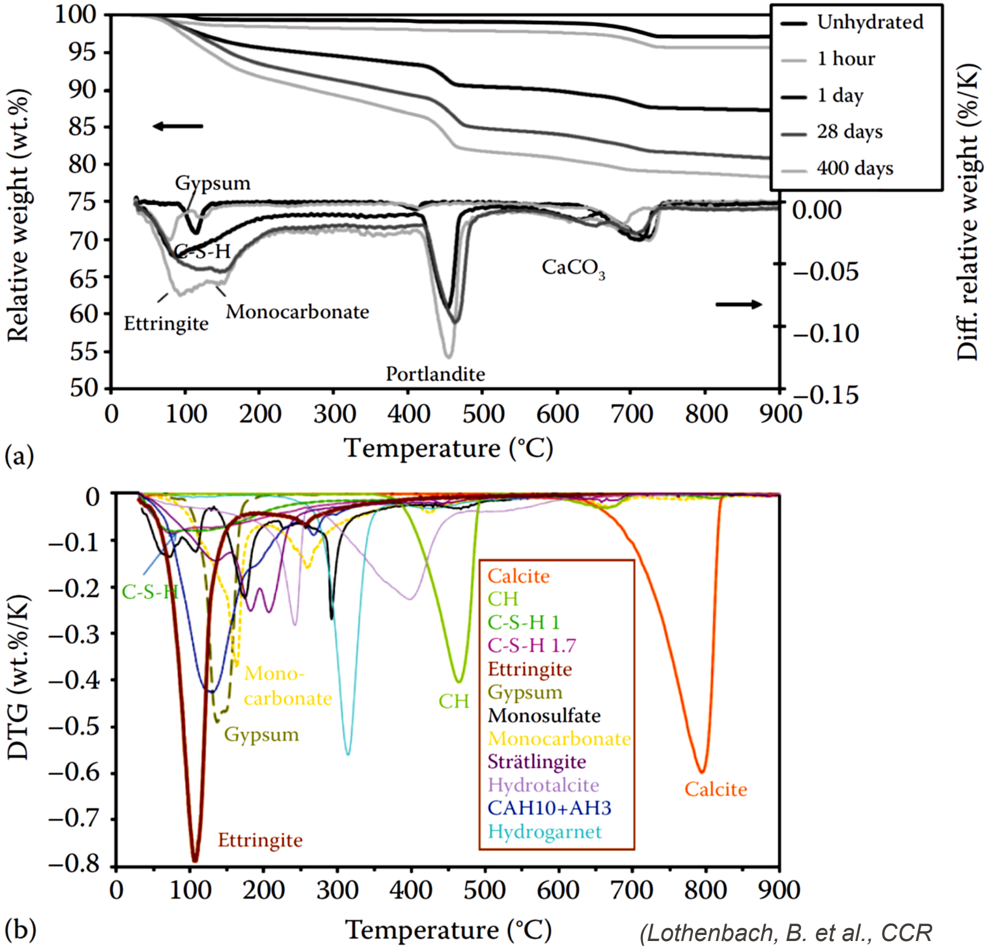


Mass loss and DSC curves for clinker with raw oil shale (top). Analysis of gases evaporated during the heating process (bottom) *(A. Goncharov, S. Zhutovsky 2022)*

Example: multimineral systems

Based on a TGA measurement, the amount of mineral or hydrate can be **easily** calculated in systems where **only one or two solids** are present.

However, in **multimineral systems**, such as hydrated cementitious materials, the **quantification is difficult** because the reactions often overlap.



(a) TGA/DTG of a hydrated OPC paste containing 4 wt.% of limestone
(b) DTG of solids typical for cementitious systems

(Lothenbach, B. et al., CCR 38(6), 848–860,2008.)

TGA - Summary

☑ Advantages

- Identifies and quantifies **hydration products** (e.g., portlandite, ettringite, carbonates, bound water).
- Measures **mass loss vs. temperature**, giving direct insight into **dehydration and decomposition** reactions.
- Allows estimation of:
  - **Portlandite content** → degree of hydration or pozzolanic reaction.
  - **CO_2 loss** → carbonation extent.
  - **Bound water** → total hydration progress.
- **Simple, fast, and widely available** technique.
- Can be combined with **DTG and DSC** for thermal and kinetic information.

⚠ Disadvantages / Limitations

- Only provides **indirect phase identification** (weight loss must be interpreted).
- **Overlapping reactions** make quantification difficult in complex (multi-phase) systems.
- **Sample preparation and heating rate** strongly affect results.
- **Amorphous and crystalline phases** with similar decomposition temperatures are hard to separate.
- Requires **careful calibration** and **expert interpretation**.

X-ray

The electromagnetic spectrum consists of different types of waves categorized by their wavelength (λ) and frequency (ν). X-rays fall between ultraviolet (UV) light and gamma rays, with short wavelengths and high energy.

Wavelength λ: 0.01 – 10 nm

Energy: 100 eV – 100 keV

Interatomic distance in crystals: typically 0.15 – 0.4 nm

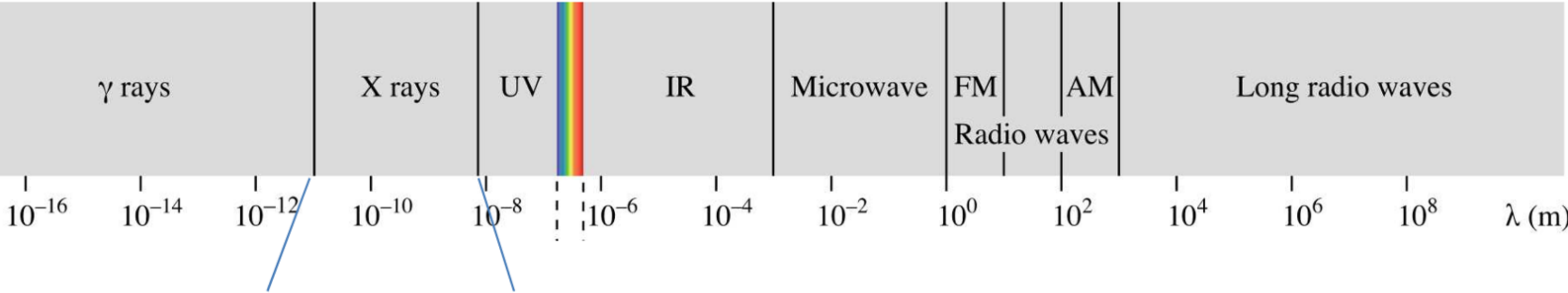


Figure from: Dr. Döbelin 2013

Interaction of X-rays with matter

Primary X-rays from an X-ray tube strike a sample

- can be **scattered** by the sample and produce scattered X-rays

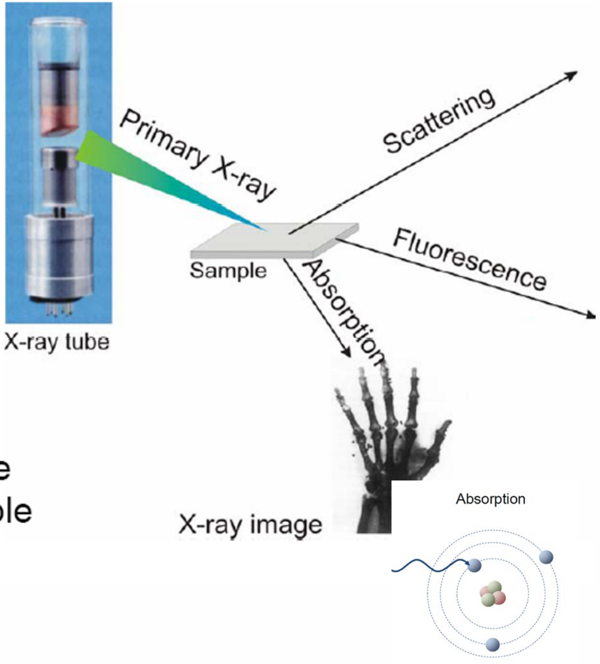
  ➔ X-ray diffractometry (XRD)

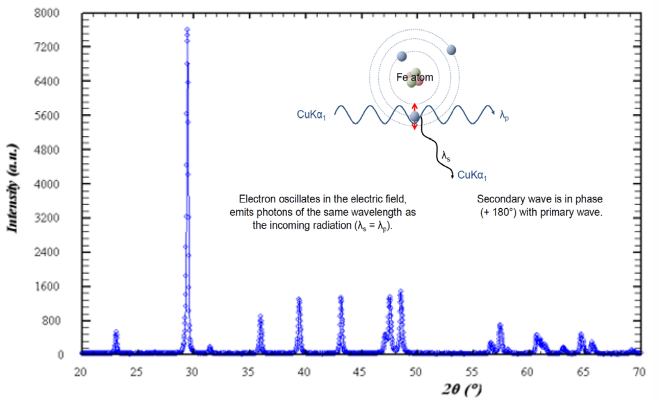
- can be **absorbed** and produce secondary X-rays

  ➔ X-ray spectrometry (XRF)

- can be **absorbed** according to the order of the elements of the sample

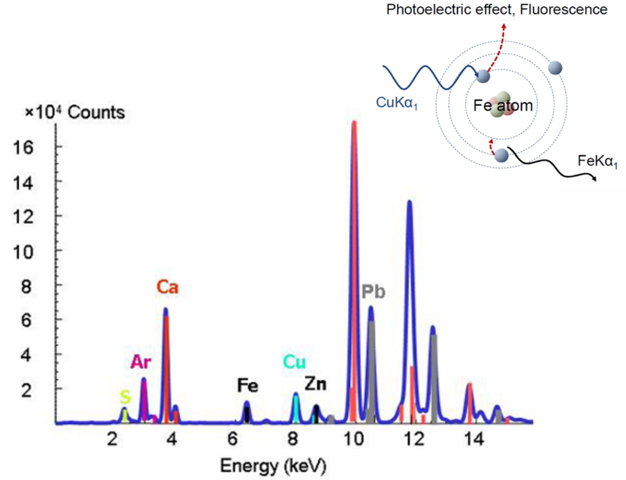
  ➔ X-ray imaging





Electron oscillates in the electric field, emits photons of the same wavelength as the incoming radiation ($\lambda_s = \lambda_p$).

Secondary wave is in phase (+ 180°) with primary wave.



Source: XRD 2016 “XRPD and Rietveld” course

X-ray for cement

XRF

Chemical composition

Widely used in the cement industry for quality control

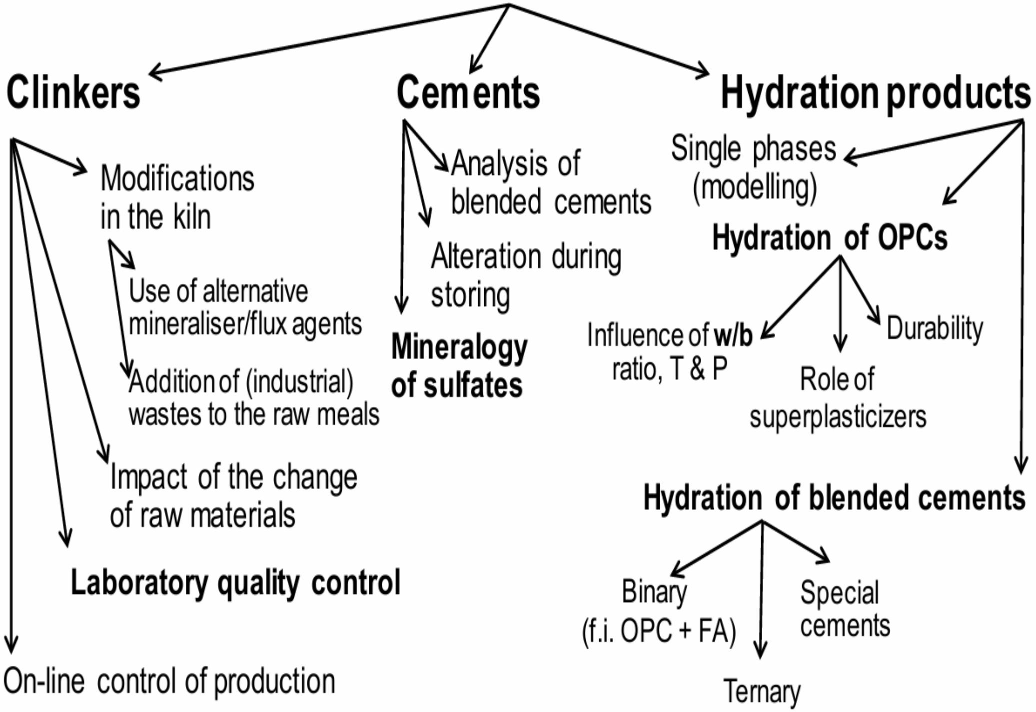
% (w/w)	CEM I 42.5 R	Limestone	Calcined clay (51 % kaolinite)
CaO	63.6	55.0	1.3
SiO_2	19.3	0.1	44.9
Al_2O_3	5.7	-	32.3
Fe_2O_3	3.6	-	15.4
MgO	0.2	0.2	0.8
SO_3	3.2	-	0.1
Na_2O	0.2	0.1	0.4
K_2O	1.2	-	0.2
TiO_2	0.3	-	2.4
P_2O_5	0.2	-	0.4
MnO	0.1	-	0.1
L.O.I.	0.8	42.6	1.7

Avet et al, 2016

XRD

Mineral composition

Qualitative and Quantitative Analysis



Clinkers
- Modifications in the kiln
  - Use of alternative mineraliser/flux agents
  - Addition of (industrial) wastes to the raw meals
- Impact of the change of raw materials
- **Laboratory quality control**
- On-line control of production

Cements
- Analysis of blended cements
- Alteration during storing
- **Mineralogy of sulfates**

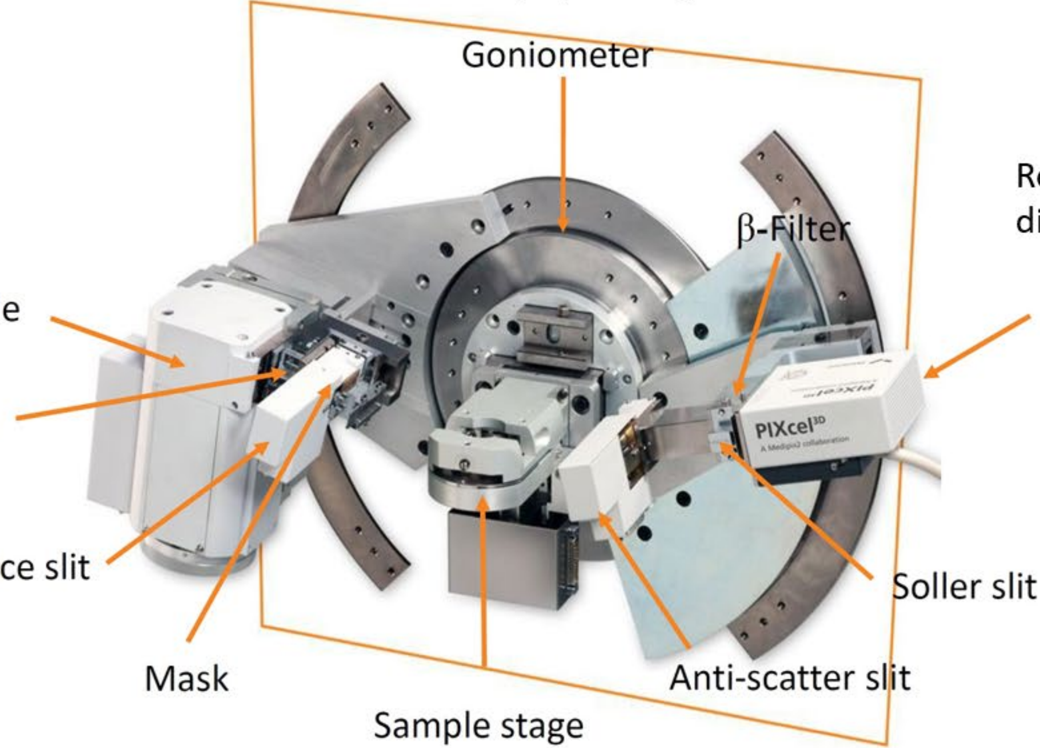
Hydration products
- Single phases (modelling)
- **Hydration of OPCs**
  - Influence of **w/b** ratio, T & P
  - Role of superplasticizers
  - Durability
- **Hydration of blended cements**
  - Binary (f.i. OPC + FA)
  - Ternary
  - Special cements

Modified from Aranda et al., 2012

XRD — Mineral Fingerprint

- **Practical question:**
- What crystalline phases are present?
- How much of each phase?
- **Signal mechanism:**
- X-rays diffract on crystal planes → each mineral gives a unique pattern.
- Intensity and position of peaks → qualitative and quantitative data.
- **How to interpret:**
- **2θ vs. intensity plot** = fingerprint of phases.
- Compare to databases (ICDD).
- Rietveld refinement → exact phase quantities.
- **Answers to practice:**
- Identify **what minerals form** during hydration.
- Quantify **clinker phases**, **portlandite**, **ettringite**, etc.
- Track **hydration progress** and **SCM contribution**.

Modern Powder Diffraction Setup Bragg-Brentano



Controls sample, source, and detector movement

Goniometer

Generates X-rays

X-ray tube

Soller slit

Divergence slit

focus X-rays

Mask

Sample stage

Holds the sample and rotated

β-Filter

Records diffracted X-rays at different angles (2θ)

Line Detectors

Soller slit

Anti-scatter slit

From course S .Zhutovsky: Advanced experimental methods for building materials, Technion

XRD software for qualitative - quantitative

Free software

MATCH!
Phase Identification from Powder Diffraction

GSAS-2

MAUD

Profex

Commercial

Malvern Panalytical
a spectris company

HighScore

Materials Data
JADE

BRUKER
DIFFRAC.SUITE EVA

BRUKER
DIFFRAC.SUITE TOPAS

Adopted from presentation Dr. Federica Boscaro 11th LC3 Doctoral School

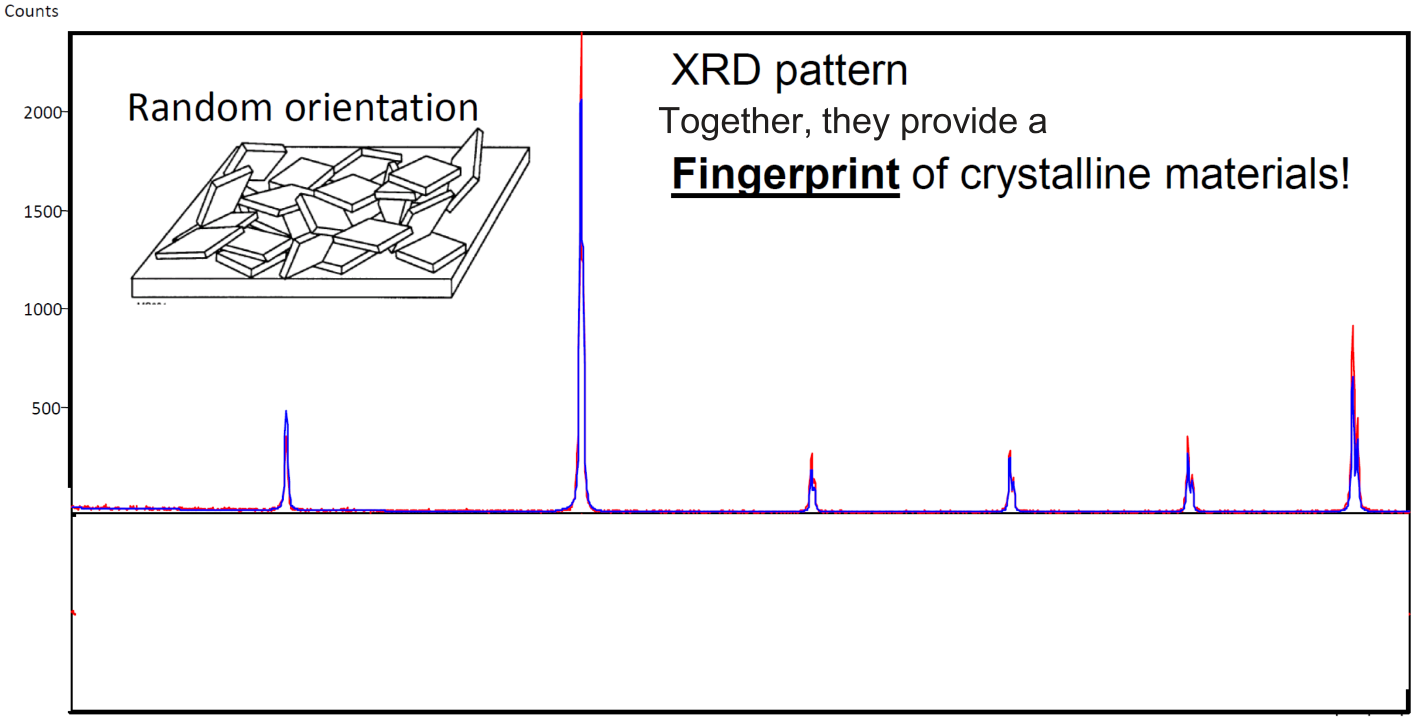
Reference Databases

- A reference database with known diffraction patterns of pure phases is mandatory for phase identification.
- There are several commercial or free possibilities:

1. Commercial ICDD reference databases
2. Commercial PAN-ICSD ref. database
3. The free COD reference database

XRD

- **Qualitative analysis**: Identifies which crystalline phases are present in the sample (e.g., alite, belite, gypsum, calcite).→ **"What minerals are there?"**
- **Quantitative analysis**: Determines how much of each phase is present using methods like Rietveld refinement.→ **"How much of each mineral?"**



XRD pattern

Together, they provide a **Fingerprint** of crystalline materials!

Crystalline and Amorphous Solids

Origin: κρυσταλλος (Greek - ice)

What is a Crystal?

A solid in which atoms occupy fixed positions and form a periodic arrangemen

Two key characteristics of a crystal:

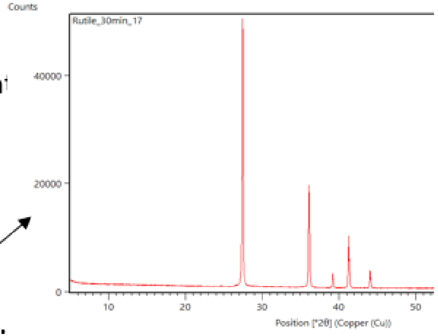
Periodicity – repeating atomic arrangement.

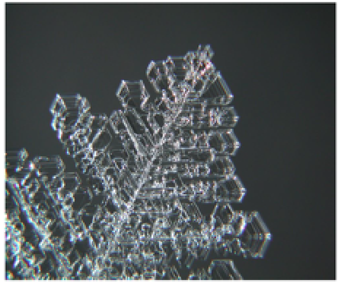
Symmetry – orderly and balanced structure.

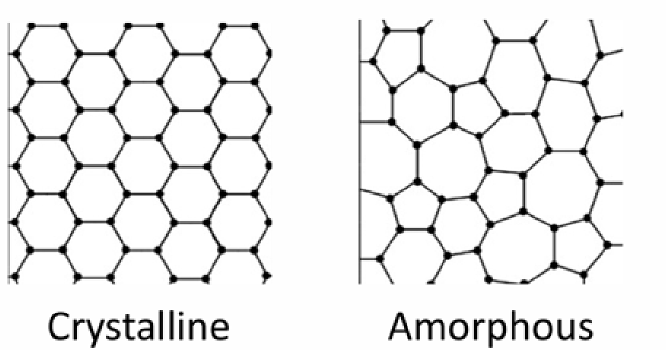
Crystalline vs. Amorphous Structures

Crystals have a regular internal structure and produce **sharp diffraction peaks.**

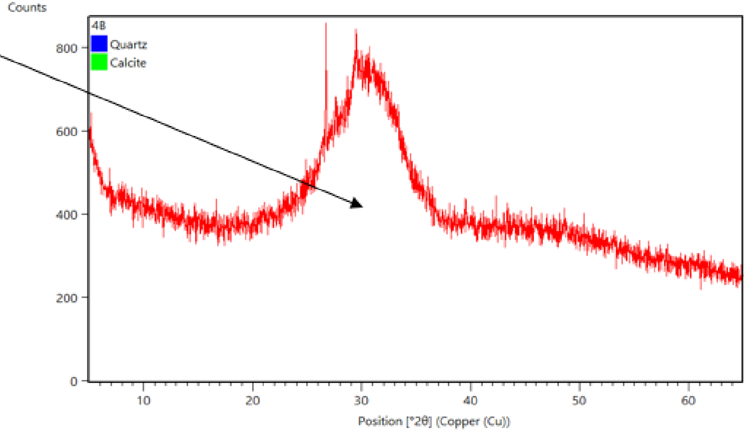
Amorphous materials lack long-range order, resulting in a **broad background signal** in diffraction patterns.







Figures from: Zallen, 1983



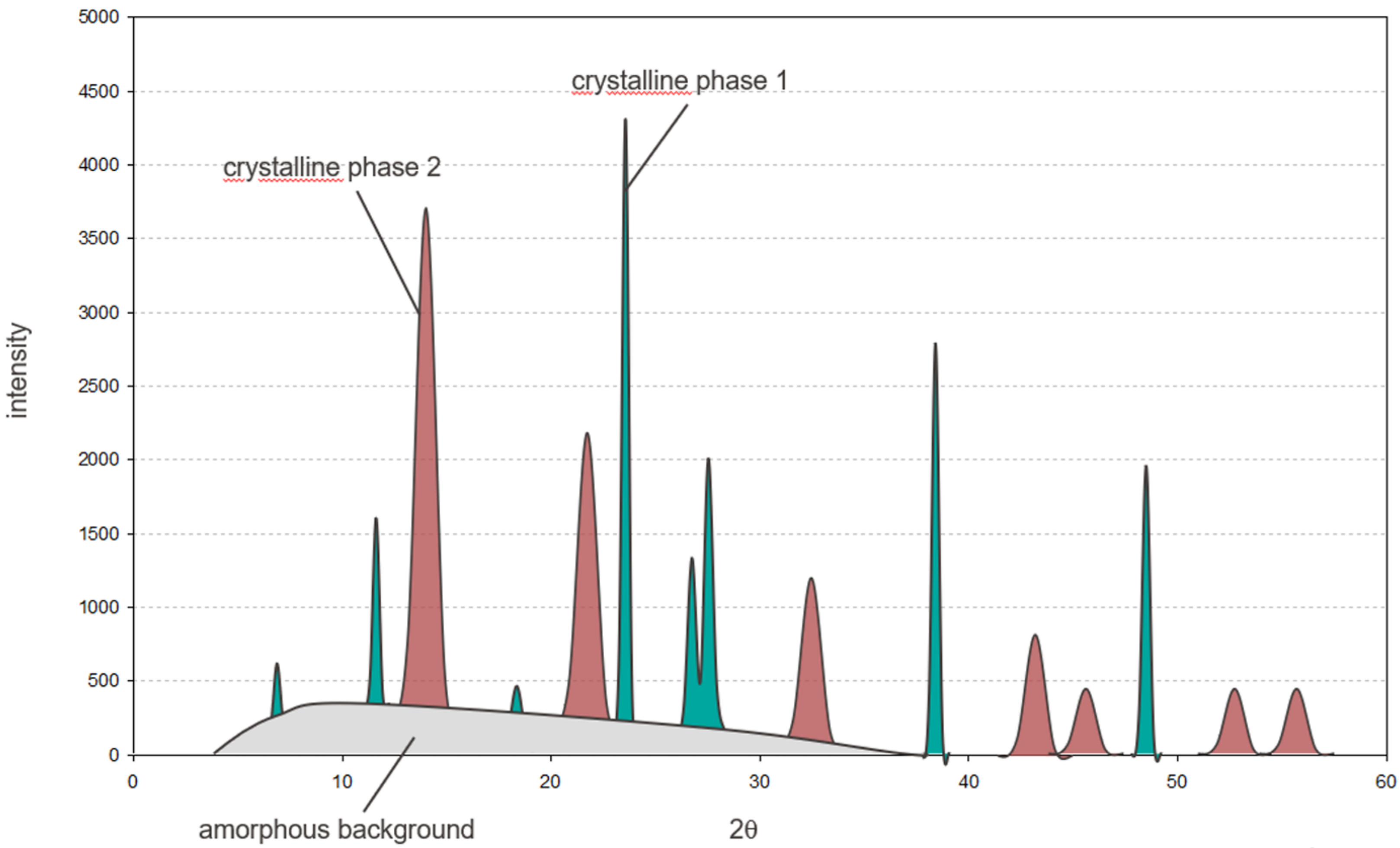
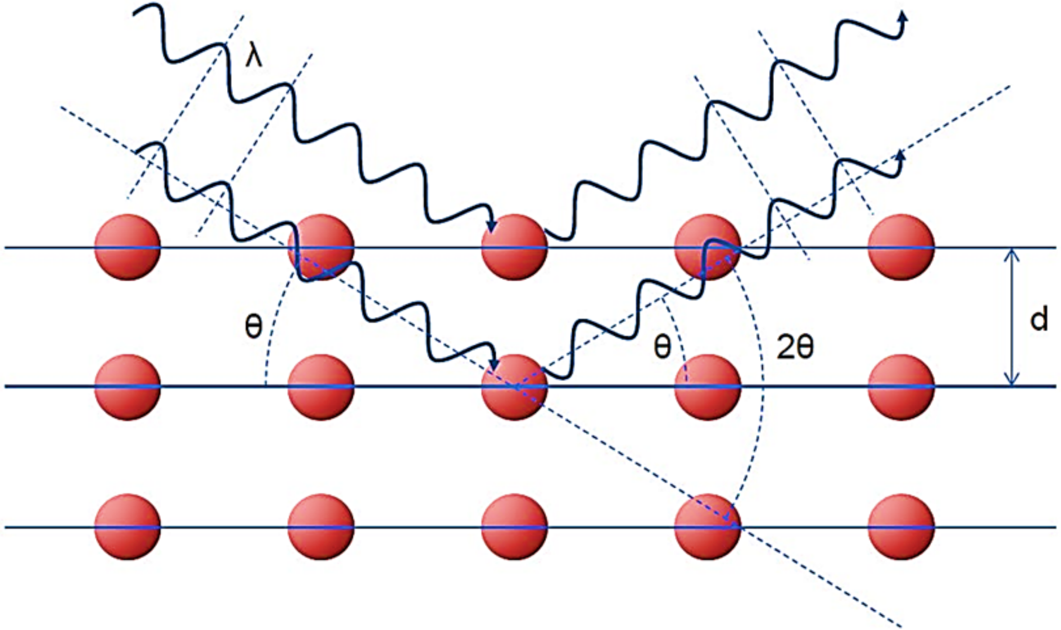


Figure from: Dr. Gallucci & Prof. Scrivener

Qualitative analysis

Bragg’s Law: $$n\lambda = 2d\sin\theta$$



Source: *XRD 2016 “XRPD and Rietveld” course*

λ = Wavelength of the incident X-ray
d = Interplanar spacing of the crystal lattice
θ = Diffraction angle (Bragg angle)
n = Order of reflection (usually 1 for most XRD applications)

Diffracted beam looks a reflection, but it is scattered radiation

Qualitative analysis

Diffraction pattern – Peak intensity

$$I_{p,hkl} = S_p \cdot (Lp) \cdot A \cdot \left[P_{p,hkl} \cdot \left|F_{p,hkl}\right|^{2}\right]$$

- Scale factor
- Lorentz-Polarization factor
- Absorption factor
- Texture Factor (PO)
- Structure Factor

Structure Factor

It contains the information about the crystal structure (i.e. the arrangement of the atoms in the unit cell)

$$F_p = \sum_n f_n o_n \ \exp\left(2\pi i\left\{hx_n + ky_n + lz_n\right\}\right)\exp(-B_n)$$

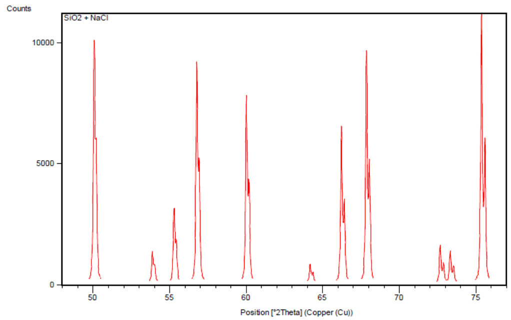
From presentation Dr. Federica Boscaro 11th LC3 Doctoral School

x_n, y_n, z_n = fractional coordinates of the atom n in the unit cell
f_n = atomic X-ray form factor (depends on the X-ray wavelength)
o_n = fractional site occupancy
B_n = atomic displacement parameter

Phase Identification - Qualitative analysis

A crystal structure will generate a characteristic XRD pattern

Collect the diffraction pattern for the unknown sample



Comparison with a **database** of known diffraction patterns

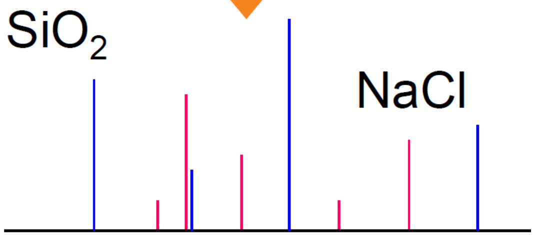
- ICDD – Int. Centre for Diffraction data
- PAN-ICSD, or free alternatives

100.000 – 500.000 possible patterns

Determination of peak positions and intensities

Phase = crystalline material with a typical 3D atomic arrangement

Phase identification:



Possibilities and limitations

- It is often possible to identify up to 10 phases in a phase mixture
- Typical detection limits are in the order of 0.1 to 1 % per phase

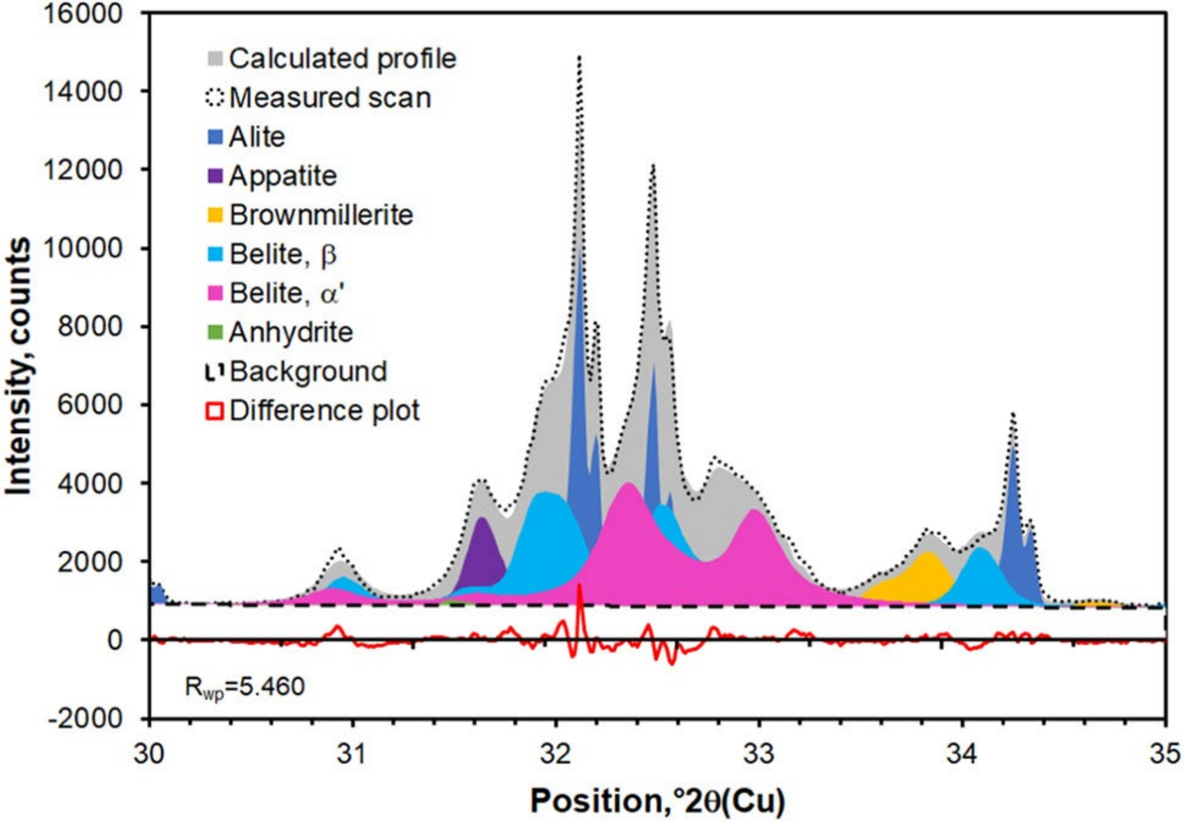
Other parameters can also be determined:

- Degree of crystallinity
- Crystallite size

From course S .Zhutovsky: Advanced experimental methods for building materials, Technion

Possibilities and limitations

- **Overlapping peaks in XRD patterns**—in complex materials like cement: phases C_3S and C_2S —are a common and challenging problem because these phases have similar crystal structures and often produce diffraction peaks at nearly the same 2θ positions.
-



(A. Goncharov, S. Zhutovsky 2022)

Question I: Polytypes

Is powder XRD the ideal tool to distinguish and identify the following phases?

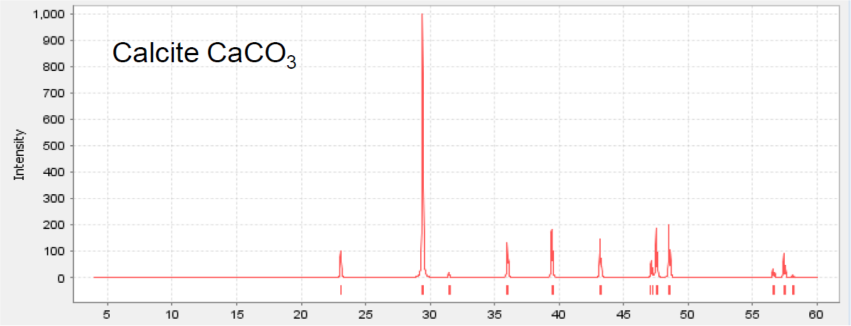
Phase	Composition	Space Group
Calcite	$CaCO_3$	R-3c
Magnesite	$MgCO_3$	R-3c
Siderite	$FeCO_3$	R-3c

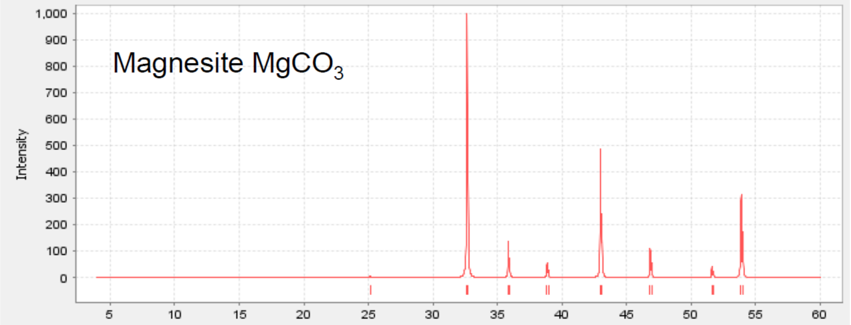
Structurally very similar (polytypes)

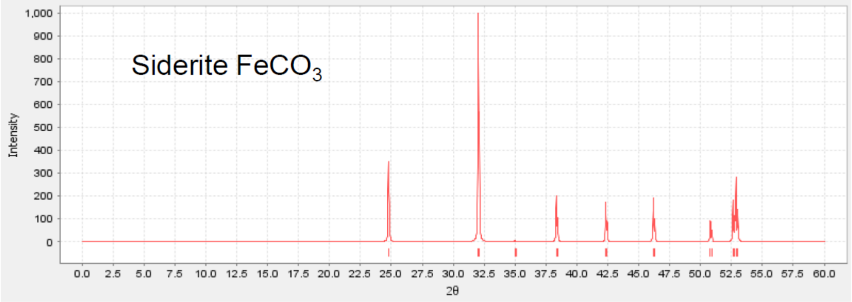
They generate similar diffraction patterns

XRD provides no direct information on Ca/Mg/Fe content

Only changes in unit cell dimensions.







- Similar diffraction patterns (mostly peak shifts)
- Some information on Mg/Ca/Fe contens from unit cell dimensions

Solution:
Combine XRD with chemical analysis (ICP, XRF, EDX, XPS…)

Question II: Polymorphs

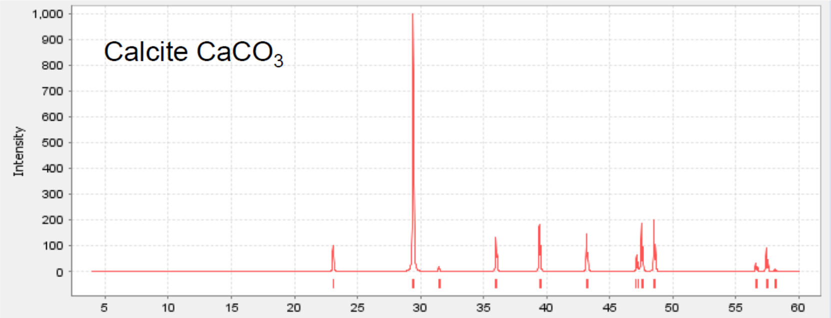
Is powder XRD the ideal tool to distinguish
and identify the following phases?

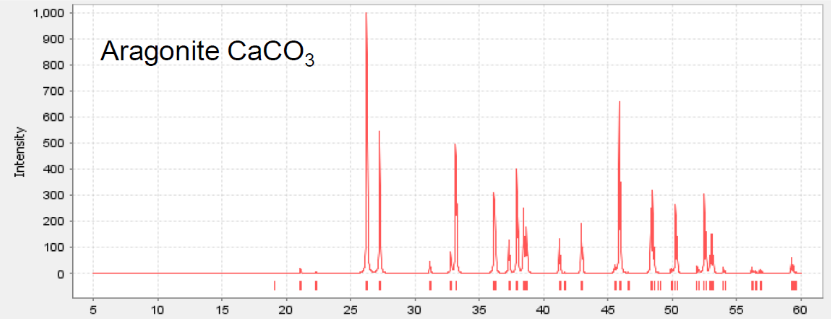
Phase	Composition	Space Group
Calcite	$CaCO_3$	R-3c
Vaterite	$CaCO_3$	P63/mmc
Aragonite	$CaCO_3$	Pnam

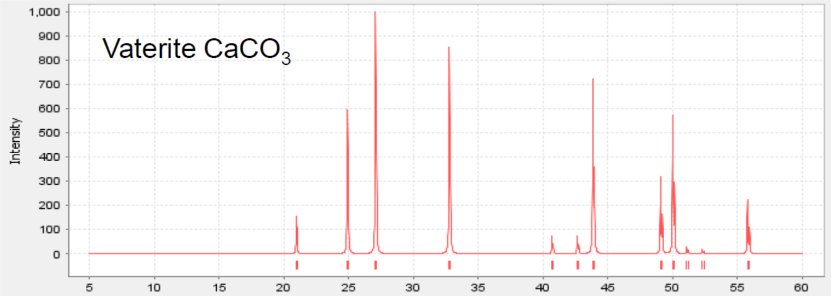
Structurally different (polymorphs)

Chemical analyses not able to distinguish (chem. identical)

XRD can easily distinguish







- Strongly different diffraction patterns.
- Easily identified by XRD

Quantitative analysis – The Rietveld method

Originally developed for the structure refinement of single crystal data from neutron diffraction

Extracts much more information from powder XRD data:

- Unit cell dimensions
- Phase quantities
- Crystallite sizes / shapes
- Atomic coordinates / Bond lengths
- Micro-strain in crystal lattice
- Texture effects
- Substitutions / Vacancies

No phase identification!

Identify your phases first
(unknown phase no Rietveld refinement)

No structure solution
(just structure refinement)

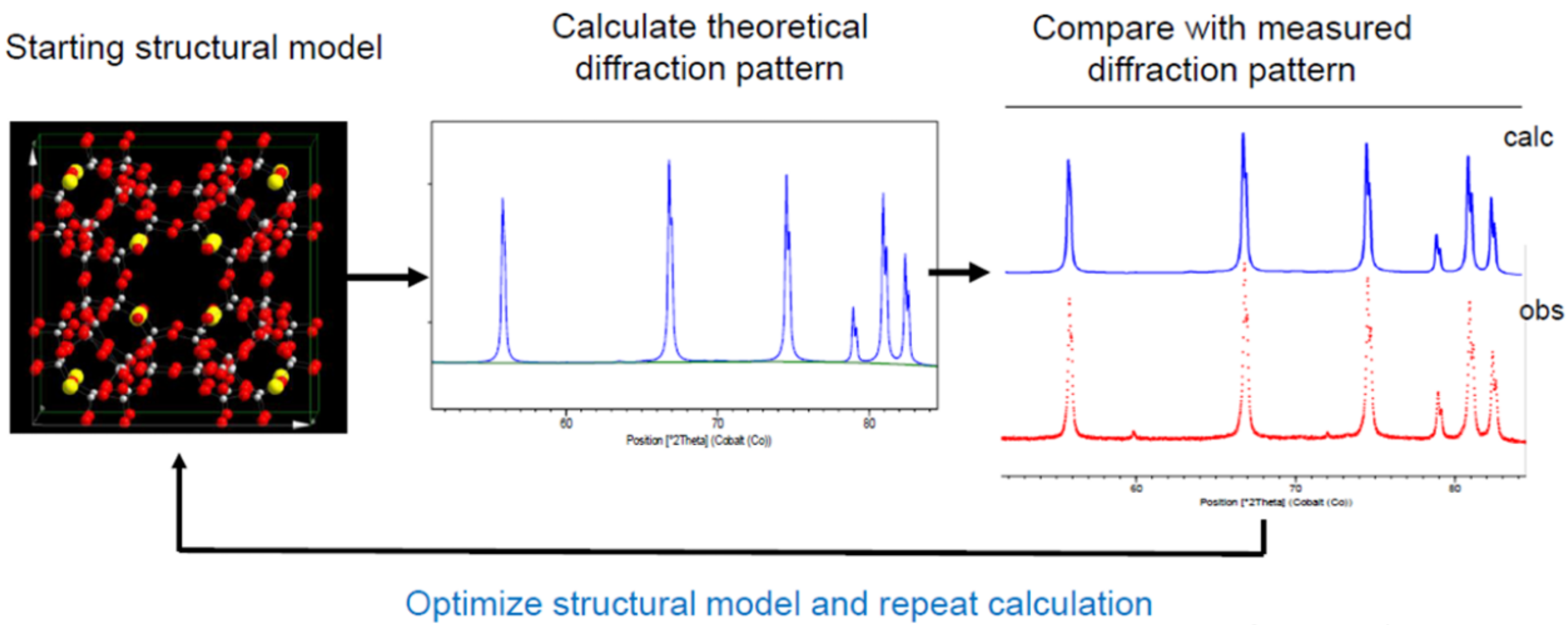
Needs excellent data quality!

Prof. Hugo Rietveld

Calculating the diffraction pattern

- With a crystal structure to solve Bragg's Law and F, you can calculate the diffraction pattern from an ideal crystal
- Ideal powder diffraction patterns can be simulated if you know ...
  - space group symmetry
  - unit cell dimensions
  - atom types
  - relative coordinates of atoms in unit cell
  - atomic site occupancies
  - atomic thermal displacement parameters
- ... for each and every phase in the sample

Rietveld Refinement



Starting structural model

Calculate theoretical diffraction pattern

Compare with measured diffraction pattern

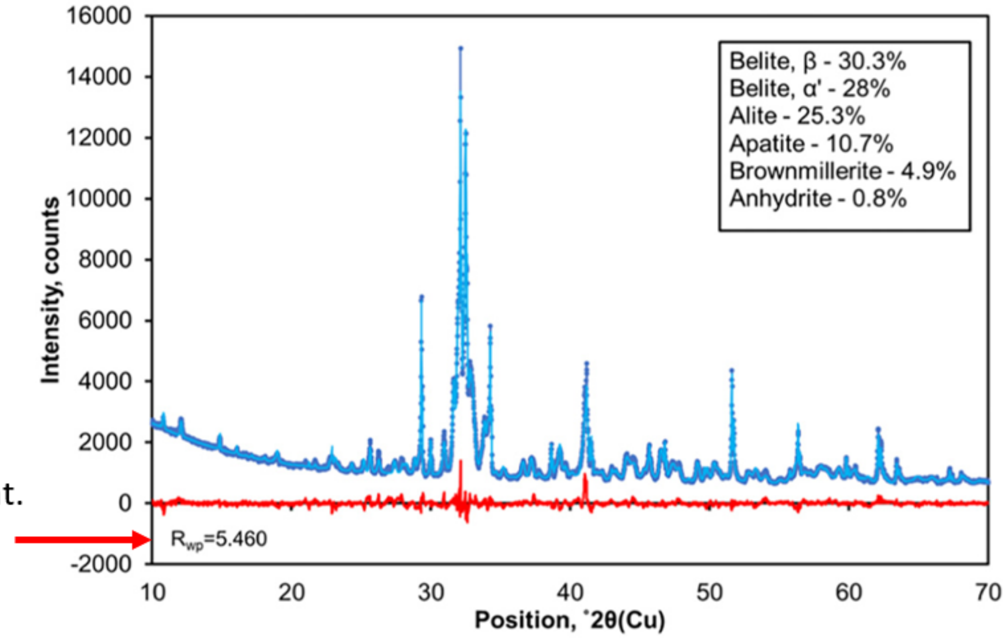
Optimize structural model and repeat calculation

Figure from: Dr. Dalconi, UNIPD 2022

Minimize differences between calculated and observed pattern by least-squares method = refinement

Rietveld Refinement

- Phase was identified correctly (peak sat the right position)
- But differences exist:
- Peak width
- Peak positions slightly shifted
- Intensities



- Rwp (Weighted Profile R-factor) is a statistical goodness-of-fit parameter used in Rietveld refinement.
- It measures the difference between observed and calculated XRD patterns.
- Lower Rwp values indicate better refinement quality

Antonina Goncharov, Semion Zhutovsky, 2022

Rietveld method: parameters

- Sample displacement
- Background (Polynomial, linear or Chebyshev model)
- Scale factor
- Unit cell (Lattice parameters)
- Profile (Peak shape, Strain, crystal size, ...)
- Preferred Orientation (PO), asymmetry, micro-absorption, atom position, occupancies...

Quantification of amorphous phase

1. Internal standard method

- Addition of a well known crystalline material in a specific amount

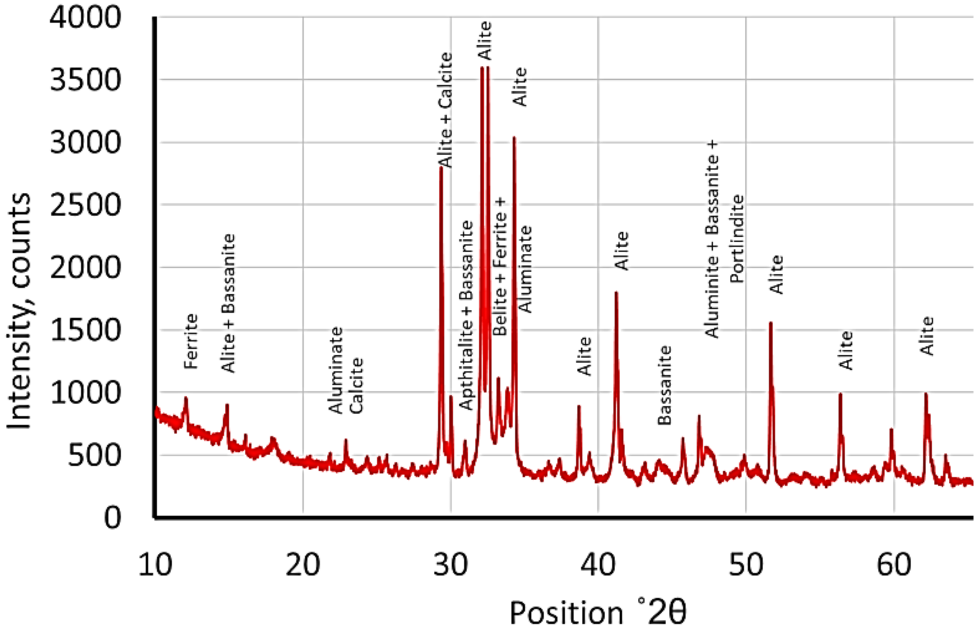
2. External standard method

- Comparison with a well known crystalline material measured separately at the same conditions of the sample

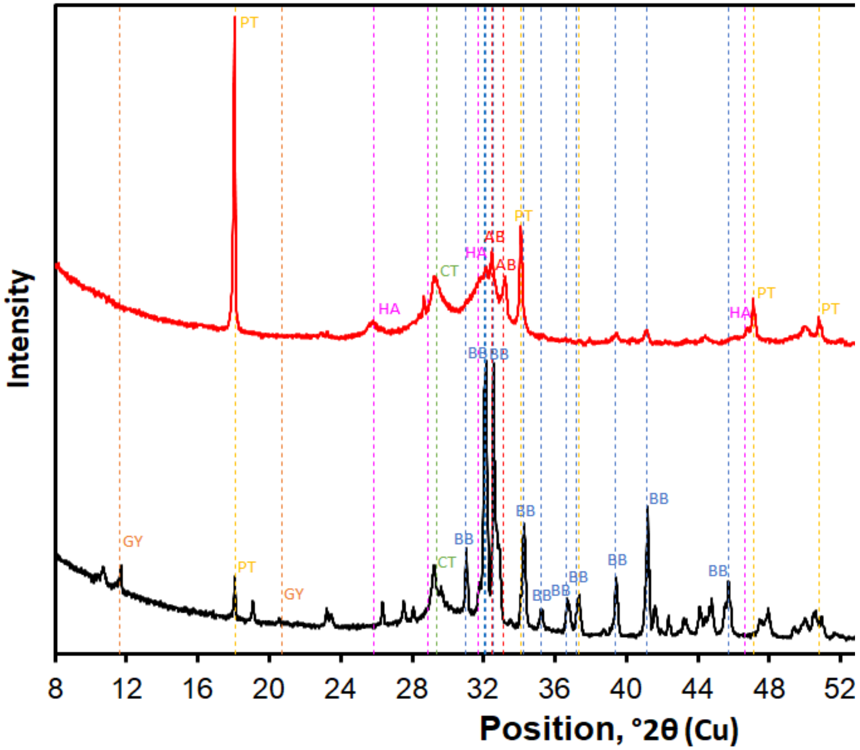
3. Partial Or No Known Crystal Structure (PONKCS) method-

- Previous individual amorphous phase calibration as a ‘standard phase’. Different amorphous phases can be quantified separately.

XRD – Examples



(Antonina Goncharov, Thesis, 2020)



(A. Goncharov, S. Zhutovsky,2026, not published)

XRD-Summary

☑ Advantages

- Identifies **crystalline phases** (e.g., C_3S, C_2S, C_3A, portlandite, ettringite, calcite, etc.)
- Enables **quantitative phase analysis** using **Rietveld refinement**
- Provides insight into **clinker quality**, **hydration progress**, and **SCM reactivity**
- **Non-destructive** and highly **reproducible** method
- Works for **raw materials, clinkers, pastes, mortars**, and **concretes**
- When combined with **XRF**, gives a **complete chemical–mineralogical picture**

⚠ Disadvantages / Limitations

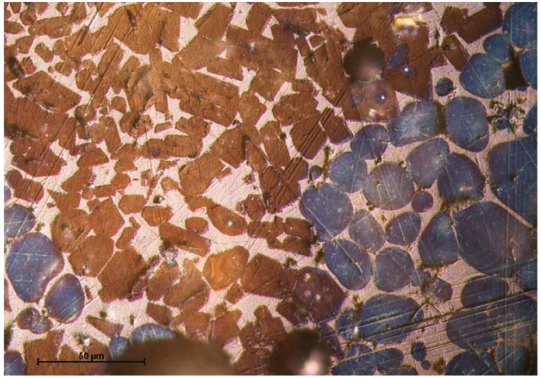
- Detects only **crystalline phases** — **amorphous materials** (e.g., C–S–H, glassy SCMs) are **not directly measured**
- **Quantification errors** can occur due to **preferred orientation** or **poor sample preparation**
- **Hydrated samples** may alter during drying or measurement
- Requires **expert interpretation** and **refinement software (e.g., Rietveld)**
- Time-consuming if multiple refinements or mixed systems are analyzed

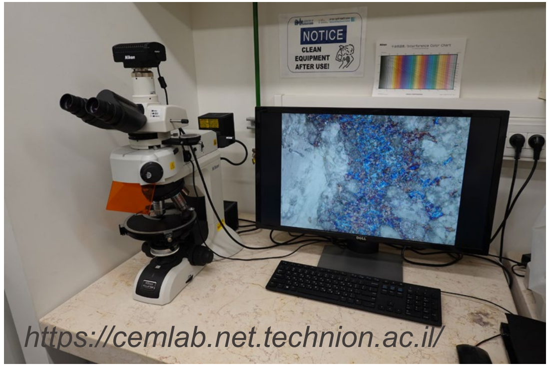
- **Polymorphs can be distinguished only by XRD!**

Microstructure

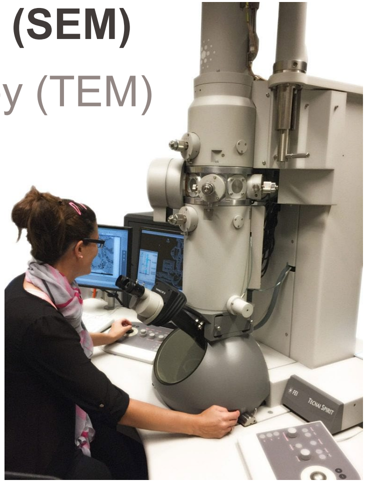
- Optical microscopy

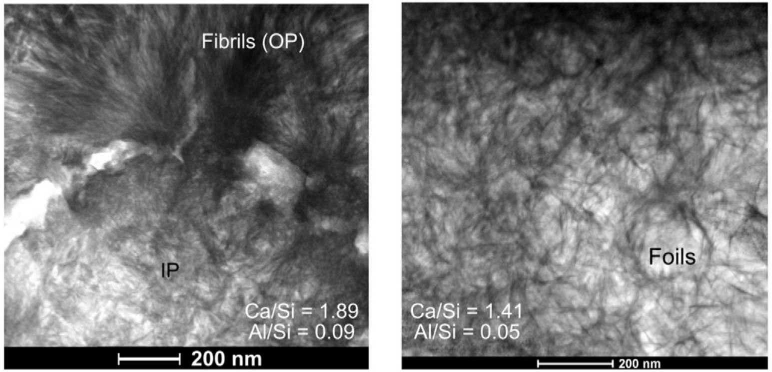
(A. Goncharov, S. Zhutovsky 2022)




https://cemlab.net.technion.ac.il/

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

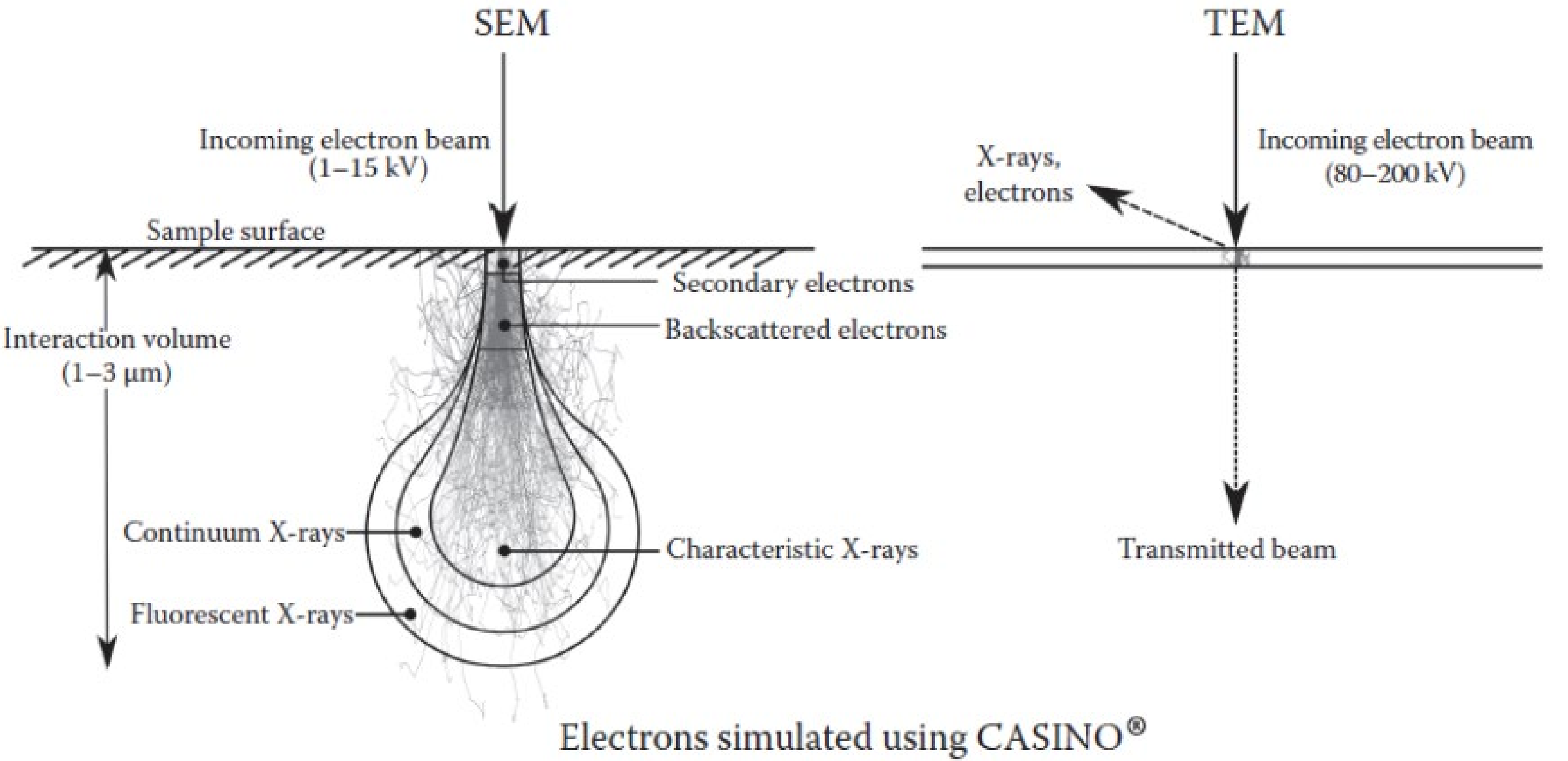

https://www.epfl.ch/research/facilities



(a) Plain cement (PC), 90 days, 20°C (b) PC 10SF, 90 days, 20°C

Rossen et al.(2015) CCR 75

Interactions of electrons with matter



Electrons simulated using CASINO®

Scrivener et al, 2016

Scanning Electron Microscopy

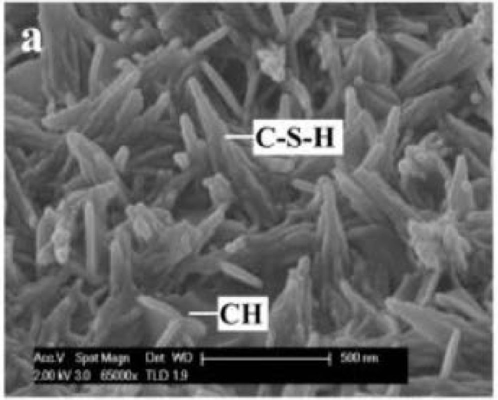
SEM — Microstructure in Real View

- **Practical question:**
- What does the hydrated microstructure look like?
- How are pores, hydrates, and unreacted grains distributed?
- **Signal mechanism:**
- Electron beam scans surface → reflected (BSE) and secondary electrons.
- Grey contrast = composition (heavy = bright, light = dark).
- **How to interpret:**
- **BSE images** show phase contrast and porosity.
- **EDS** provides local chemical composition.
- **Answers to practice:**
- Visualize **C–S–H morphology**, **porosity**, and **crack formation**.
- Evaluate **SCM reactivity** (residual particles).
- Validate findings from calorimetry and XRD.

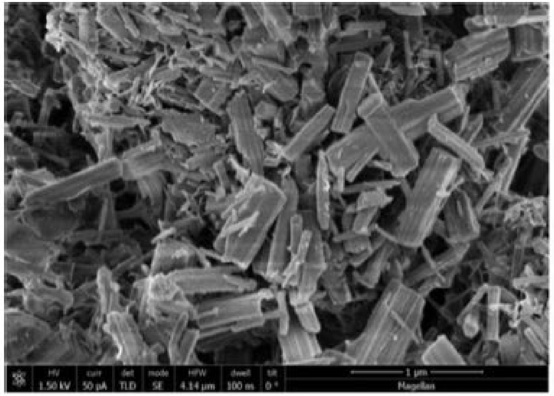
Scanning electron microscopy (SEM)

Secondary electrons (SE)	Backscattered electrons (BSE)
From inelastic collisions	From elastic collisions
Lower energy than the incident beam: near surface of the sample	Similar energy to that of the incident beam: higher depth in the sample
Highest resolution	Lower resolution than SE images
Intensity of SEs and brightness are determined by the inclination of the surface to the incident beam (edges, points)	Intensity of BSEs and brightness are primarily a function of the atomic number of the atoms in the sample
Image of the surface topography	Good compositional contrast, avoid surface roughness
Qualitative	Quantitative

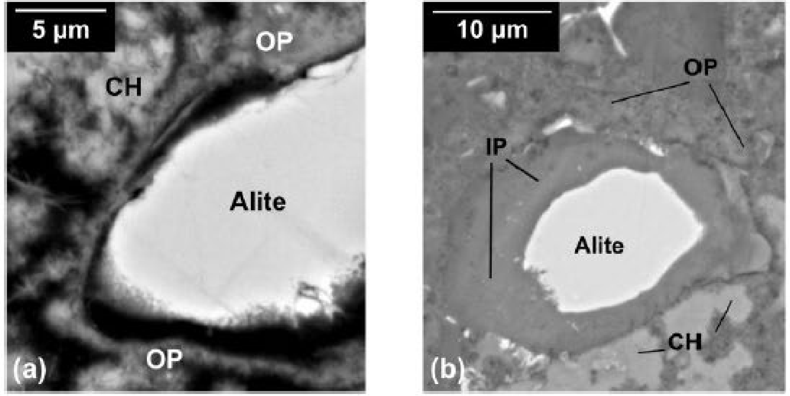
Scanning electron microscopy (SEM)



Mota et al, 2015



Das et al, 2022

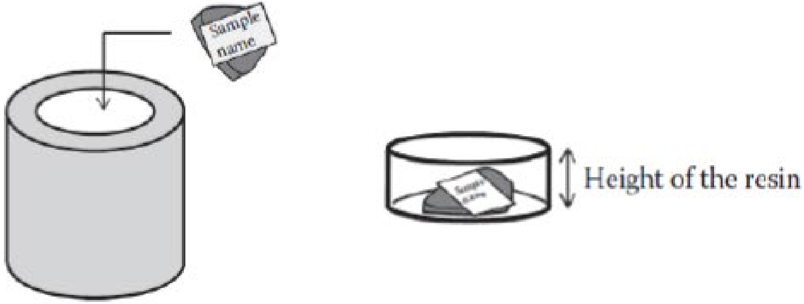


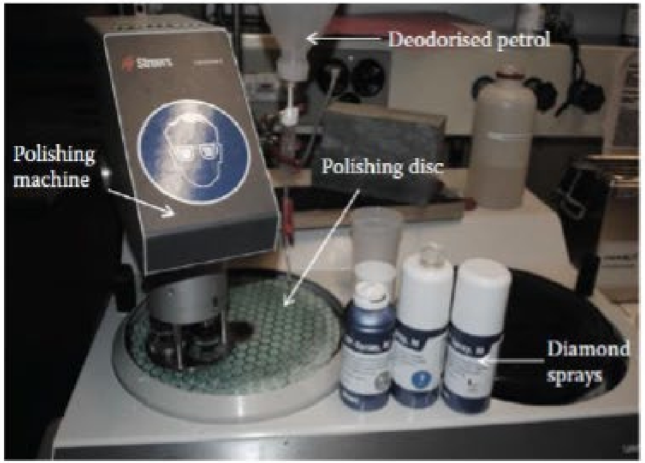
Rossen & Scrivener, 2017

Scanning electron microscopy (SEM)

Sample preparation

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

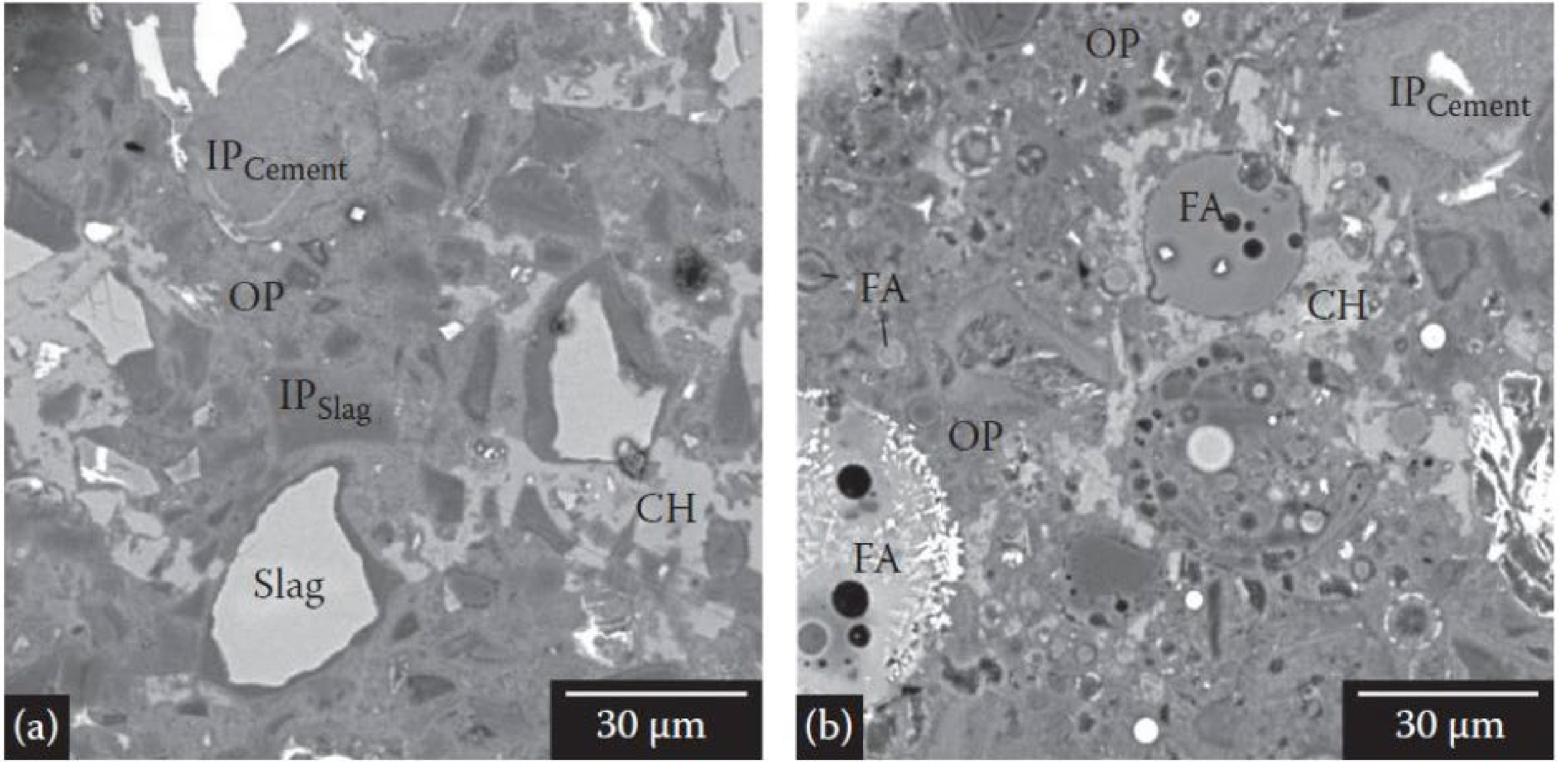




Scrivener et al, 2016

Scanning electron microscopy (SEM)

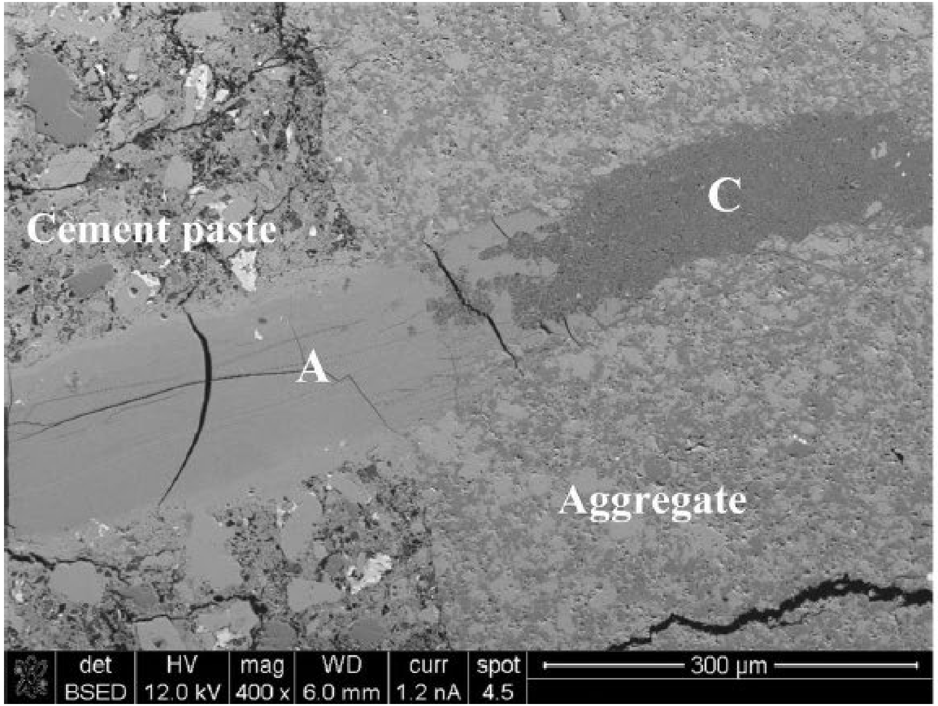
Hydrated OPC blended with slag or fly ash



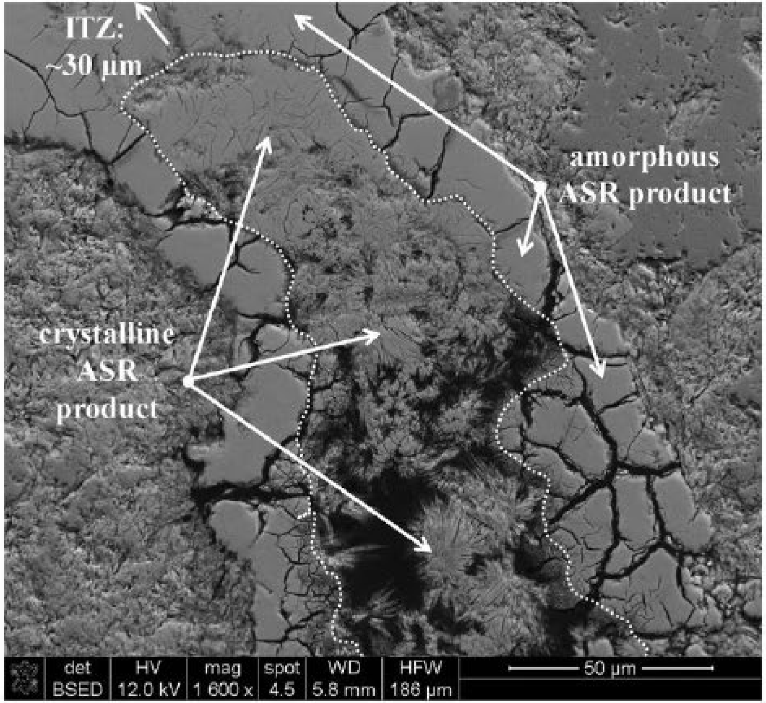
Scrivener et al, 2016

Scanning electron microscopy (SEM)

Alkali-silica reaction (ASR)



Boehm-Courjault et al, 2020

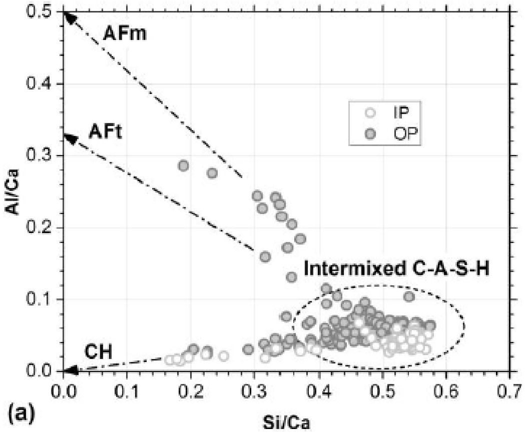


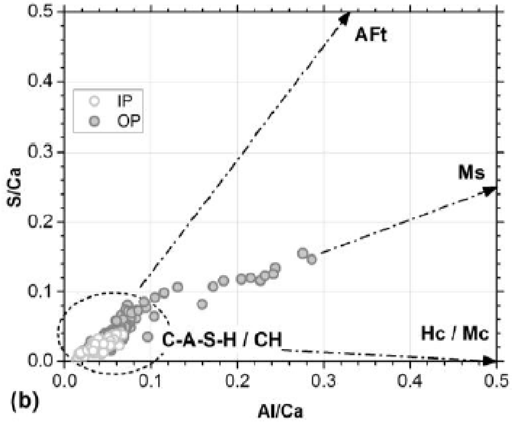
Leemann et al, 2020

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

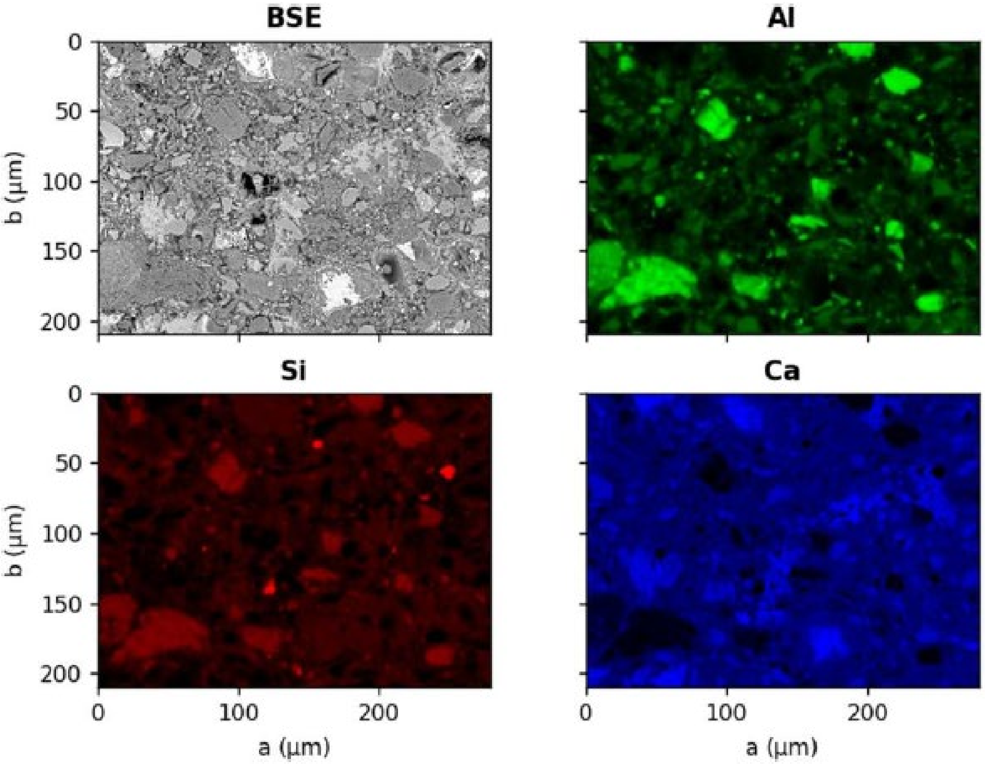




Rossen & Scrivener, 2017

Scanning electron microscopy (SEM)

Elemental maps coupled with BSE images



Georget et al, 2021

SEM - Summary

☑ Advantages

- Clear identification of hydration phases
- Direct observation of microstructure and morphology
- Quantitative analysis of:
  - Pastes, mortars, and concrete
  - Porosity and pore distribution
  - SCM reactivity and degree of hydration
- Mapping and distribution of phases for microstructural interpretation

⚠ Limitations

- Time-consuming and complex sample preparation
- Hydration must be stopped before imaging
- Limited information depth (interaction volume effects)
- Requires many images for statistically valid 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

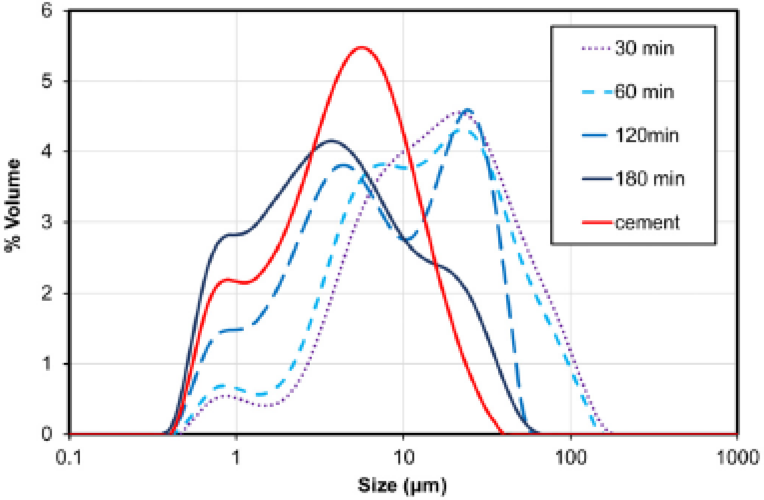
PSD – Laser diffraction

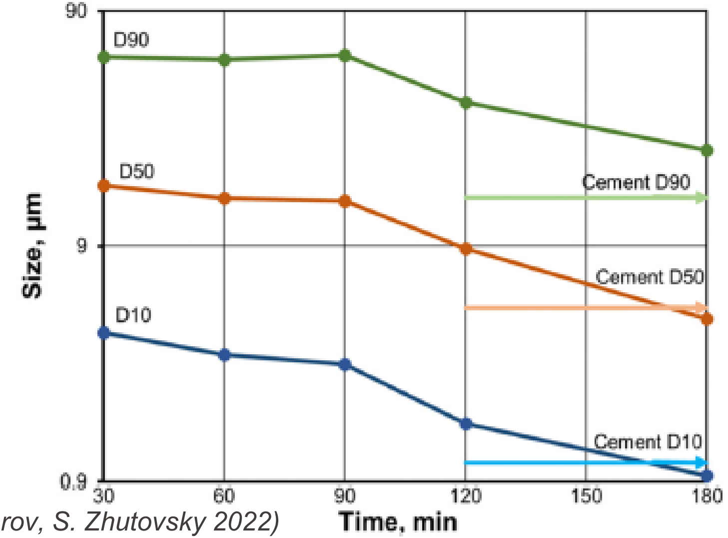
PSD – Particle Size Distribution

- **Practical questions**
- How to optimize grinding?
- How fine is the cement or SCM?
- How does particle size affect workability, hydration rate, and strength?
- **Signal mechanism**
- **Laser diffraction:** light scattering by particles → pattern intensity depends on size.
- Software converts scattering pattern to **volume or number distribution**.
- **How to interpret**
- Curve shows **% volume vs. particle diameter (µm)**.
- Key parameters:
  - *D10, D50, D90* → 10%, 50%, 90% passing sizes.
  - Narrow curve → uniform material; wide curve → mixed sizes.
- **Answers to practice**
- Fine particles → faster hydration, higher early strength.
- Coarse particles → lower water demand, slower reaction.
- Compare PSD of **cement vs SCMs** to predict blending effects.

PSD – Laser diffraction

https://cemlab.net.technion.ac.il/



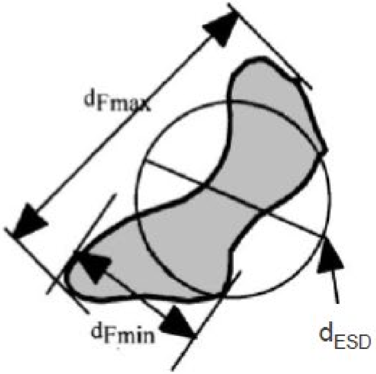


(A. Goncharov, S. Zhutovsky 2022)

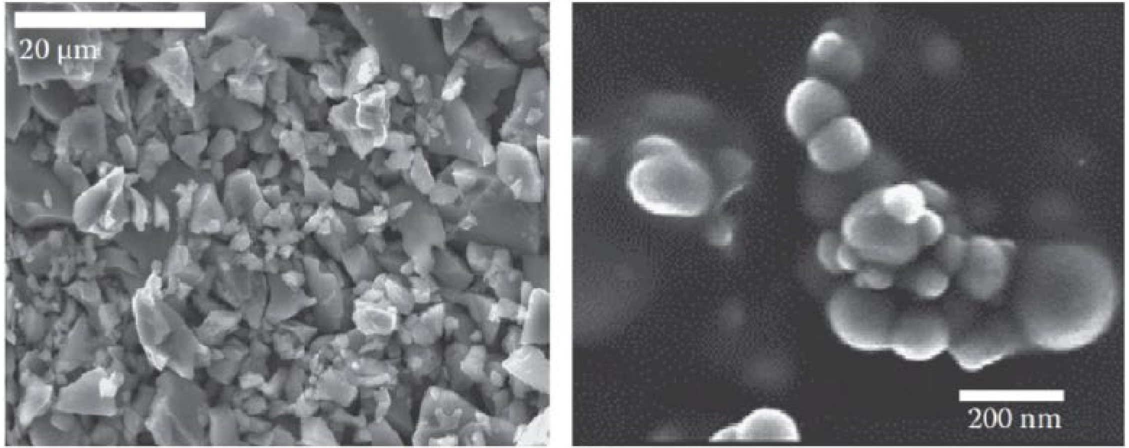
PSD – Laser diffraction

- 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)



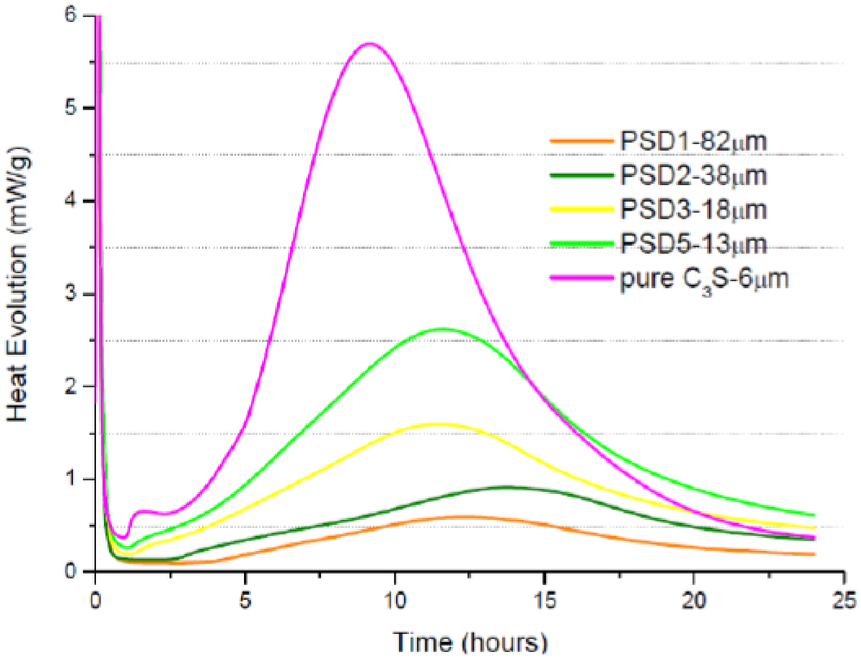
Bowen, 2002

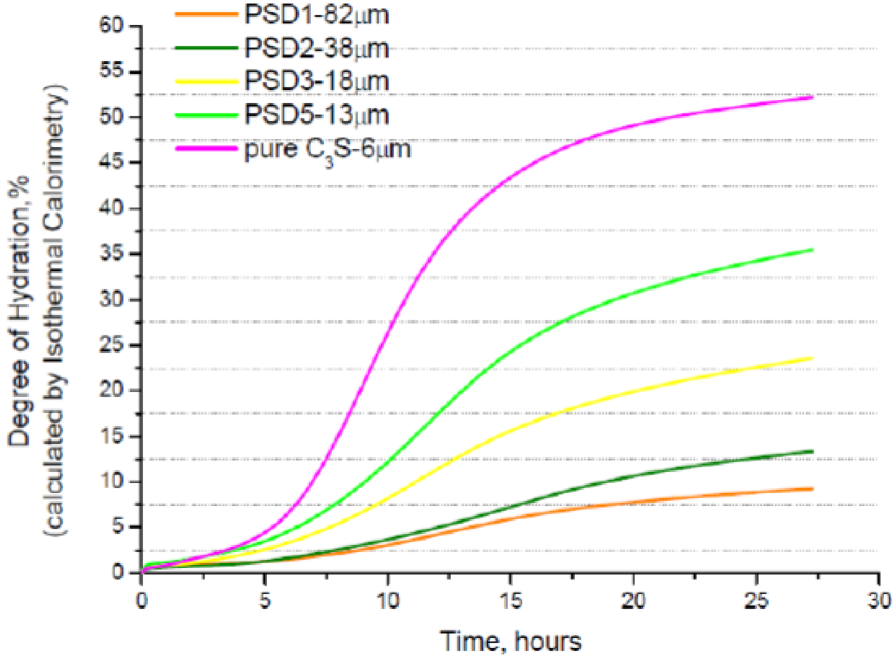


Palacios et al, 2016

PSD

Isothermal calorimetry of alite pastes with different PSD





Costoya, EPFL 2008

Specific surface area (SSA)

- **SSA – Specific Surface Area**
- **Practical questions**
- How much surface is available for reaction with water?
- Does fineness correlate with reactivity or water demand?
- **Signal mechanism**
- **Blaine Air Permeability:**
  - Measures **air flow resistance** through a compacted powder bed.
  - Reports surface area as “**cm²/g**”.
- **BET (Gas Adsorption):**
  - Adsorbs nitrogen on the surface of the powder at low temperature.
  - Calculates **true surface area (m²/g)** from adsorption isotherm.

Specific surface area (SSA)

- **How to interpret Answers to practice**

Method	Measures	Typical Range	Notes
Blaine	Air permeability (apparent area)	2000–6000 cm²/g	Fast, simple, routine cement control
BET	Gas adsorption (real surface)	1–20 m²/g	Sensitive to nano-scale roughness

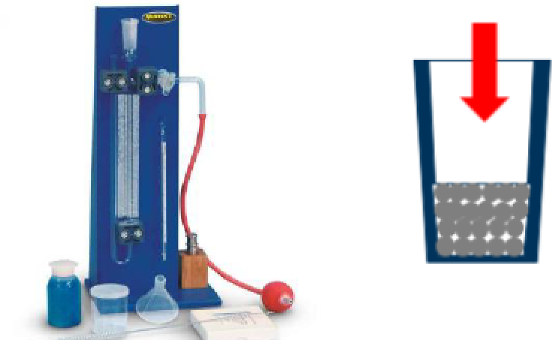
Answers to practice

- Higher SSA → faster hydration, higher early reactivity.
- Blaine is useful for **quality control**, BET for **research and SCMs**.
- Compare SSA to calorimetry data → **link fineness with reactivity**.

Specific surface area (SSA)

Blaine air permeability

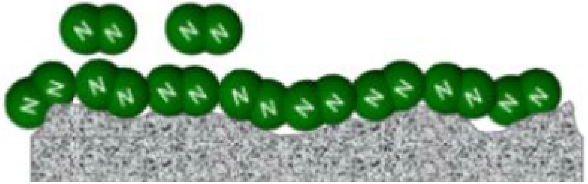
- Common in the cement industry
- No sample preparation
- Based on empirical calibration
- Assume mono-sized and spherical shape of particles (Kozeny-Carman theory)
- Poor reproducibility
- Not good for calcined clays



www.matest.com

Gas adsorption – SSA$_{BET}$

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



Flatt & Marchon, CMS course (ETHZ)

www.micromeritics.com

Physical characterization - Summary

☑ Advantages

Laser Diffraction (LD)
- Fast measurement (< 5 min)
- Widely available and easy to use

Blaine Air Permeability
- Simple and quick test for fineness

Specific Surface Area (SSA, Gas Adsorption)
- High accuracy and reproducibility
- Sensitive to fine particles and surface effects

⚠ Limitations

Laser Diffraction (LD)
- Assumes spherical particle shape
- Requires correct refractive index and dispersion liquid
- Sensitive to agglomeration

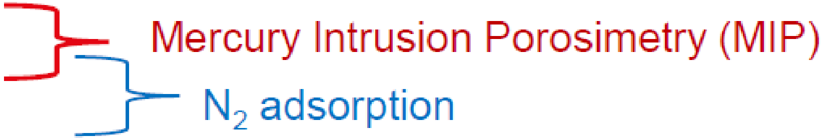
Blaine Air Permeability
- Limited particle size range
- Low reproducibility for SCMs (e.g. fly ash, calcined clays)
- Assumes mono-sized, spherical particles

Specific Surface Area (SSA)
- Sample preparation critical (degassing, hydration control)
- Results depend on gas type and method used

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 Union of Pure & Applied Chemistry

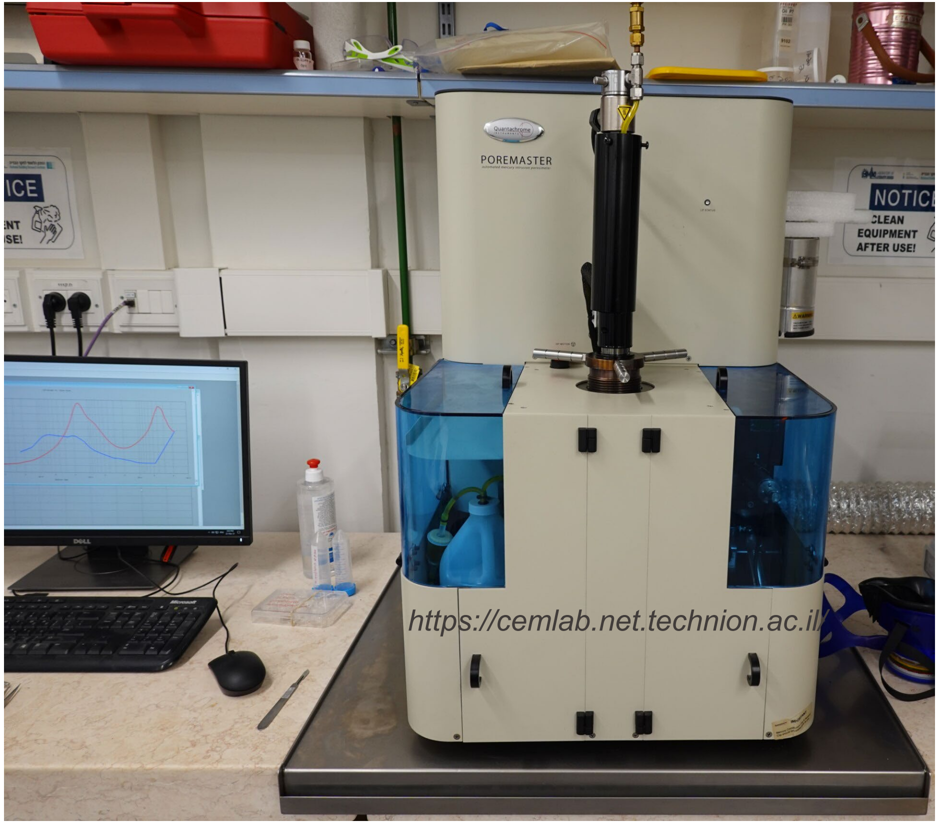
MIP

- **MIP – Mercury Intrusion Porosimetry**
- **Practical questions**
- What is the **pore size distribution** in hydrated cement or concrete?
- How do curing, SCMs, or w/c ratio affect **porosity and durability**?
- **Signal mechanism**
- **Mercury** is forced into pores under increasing pressure.
- Pressure ↔ pore size (Washburn equation):
- **How to interpret**
- Cumulative curve → total pore volume.
- Differential curve → pore size distribution.
- Typical ranges:
  - Gel pores: <10 nm
  - Capillary pores: 10–1000 nm
  - Entrained air: >1 µm
- **Answers to practice**
- Quantifies **total porosity**, **critical pore diameter**, and **pore refinement**.
- Helps assess **permeability, strength, and durability**.
- Compare MIP with SEM images or sorption data for microstructure validation.

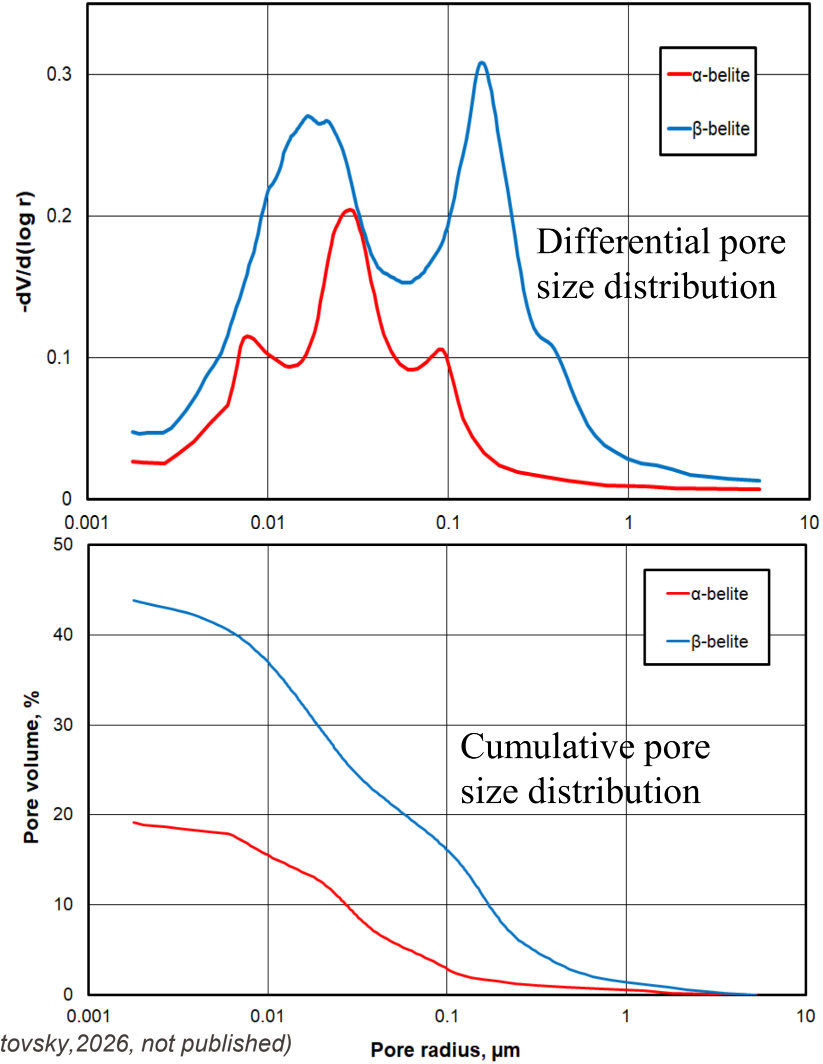
MIP only measures **connected pores** (those mercury can reach).
It's a powerful way to understand **pore structure, connectivity, and total porosity** of cement pastes or mortars.

MIP tells us how accessible and connected the pores are — but not exactly how they look.It's excellent for comparing porosity trends but must be combined with other methods (e.g., N_2 adsorption or SEM) for a full microstructural picture.

Porosity – MIP



https://cemlab.net.technion.ac.il/



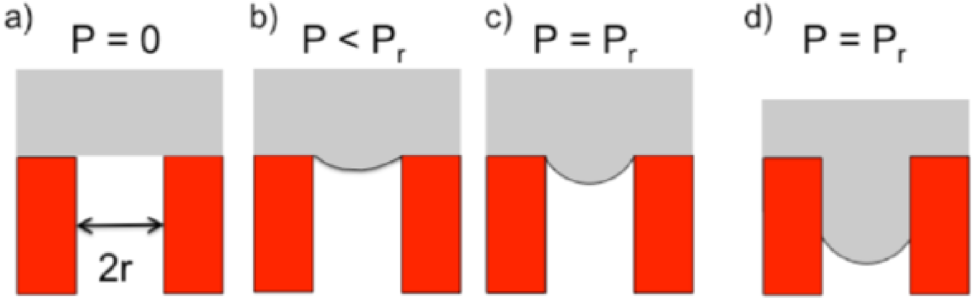
(A. Goncharov, S. Zhutovsky,2026, not published)

Porosity – MIP

- Pore diameter range of 2 nm – 250 µm
- It is based on the intrusion of a nonwetting fluid (contact angle $\theta > 90^o$, 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.:

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

$\gamma = 0.485$ N/m at 25ºC (Hg)
$\theta = 140^o$



Courtesy of Prof. Flatt (ETHZ)

What the diagram shows

•(a) At **P = 0**, mercury stays on the surface — no intrusion.
•(b) At **low pressure**, mercury starts to bend at the pore entrance.
•(c) When **P = Pr**, mercury just enters the pore.
•(d) As pressure increases, it fills smaller and smaller pores.

MIP - Summary

☑ Advantages

1. **Wide pore-size range** — can measure pores from **a few nanometers up to hundreds of micrometers.**
2. **Quantitative** — provides numerical data on **pore volume**, **porosity**, and **pore-throat size distribution.**
3. **Fast and repeatable** — one test gives the entire pore size spectrum.
4. **Useful for comparison** — can easily compare pore refinement due to **SCMs, curing, or mix changes.**
5. **Correlates with durability** — parameters such as **critical pore diameter** often link to permeability, drying shrinkage, and freeze–thaw resistance.

⚠ Disadvantages / Limitations

1. **Measures throats, not true pores** — due to the **ink-bottle effect**, it detects the *narrowest connection* (pore entry), not the full pore body.
2. **High pressures can damage microstructure** — may **collapse gel pores** or alter delicate hydrates (C–S–H).
3. **Non-representative for closed pores** — **only interconnected pores** are measured; isolated pores are ignored.
4. **Requires drying** — drying before testing can **alter the pore structure** (shrinkage, cracking, loss of water-filled pores).
5. **Toxic and complex** — **mercury is hazardous**, and the method needs strict safety procedures and specialized equipment.
6. **Assumptions** — assumes cylindrical pores, constant contact angle (≈140°), and fixed surface tension, which may not perfectly match cementitious materials.

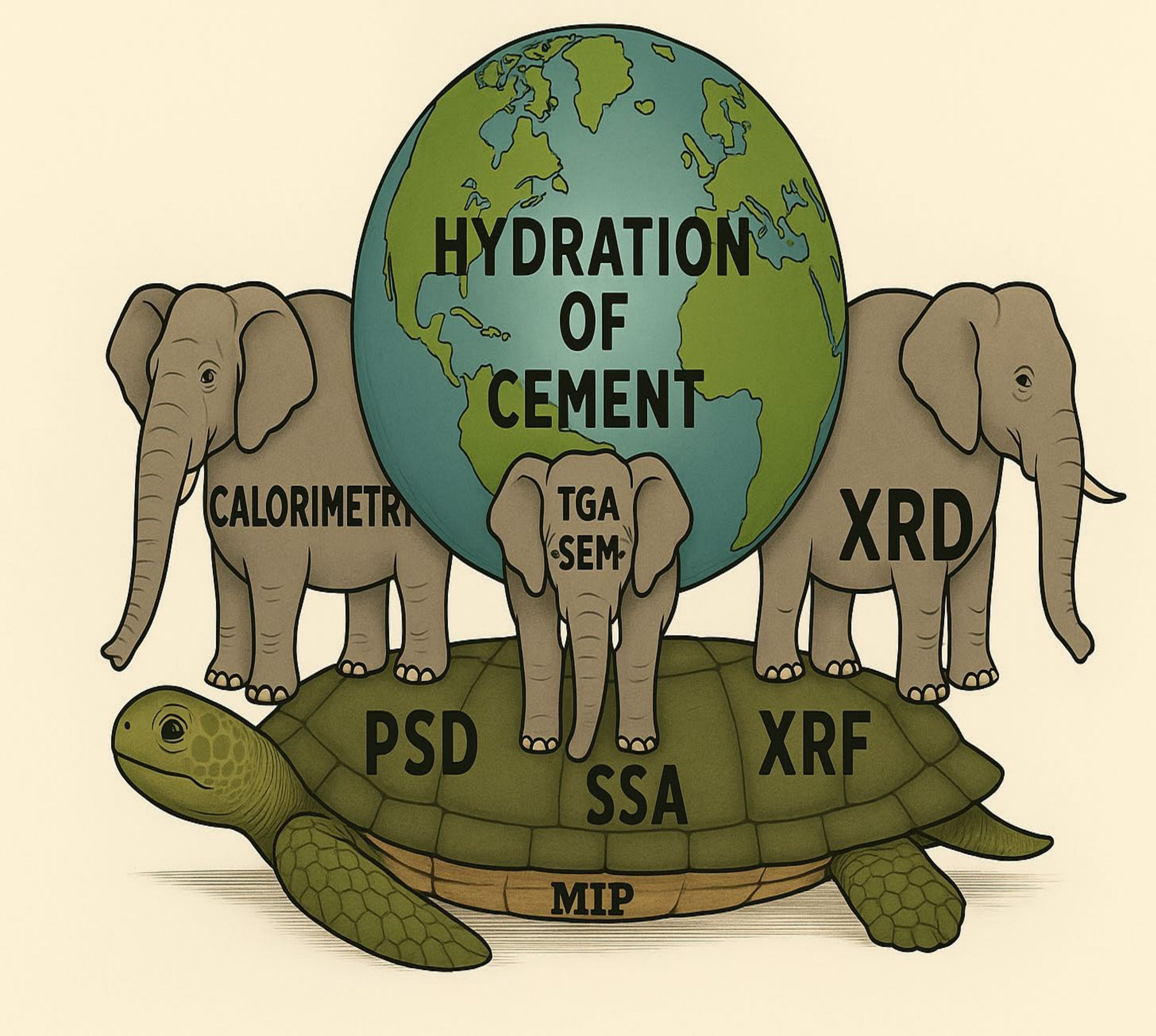
General remarks

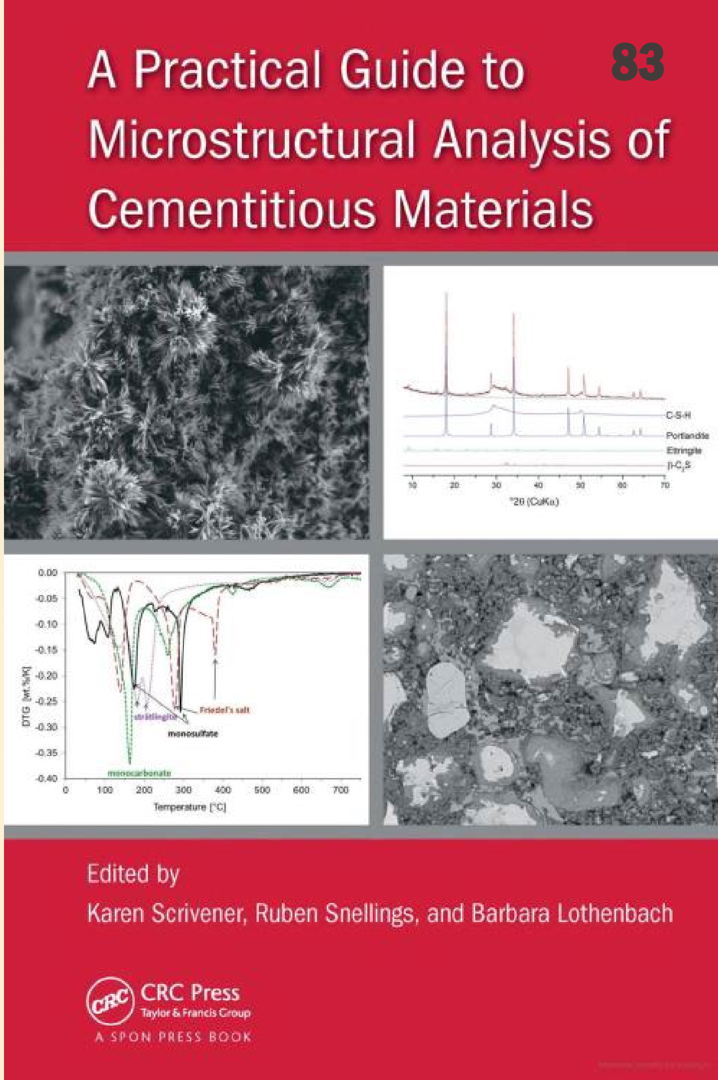
- All analytical techniques have an intrinsic error
- For most quantification methods, the relative error increases with the decrease in the absolute amounts
- Difficult to detect small quantities
- Calorimetry, TGA, XRD and SEM are the most important techniques for characterizing cement
- **Best is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





A Practical Guide to
Microstructural Analysis of
Cementitious Materials

Edited by
Karen Scrivener, Ruben Snellings, and Barbara Lothenbach

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