X-ray Powder Diffraction
Basics, Rietveld refinement and applications

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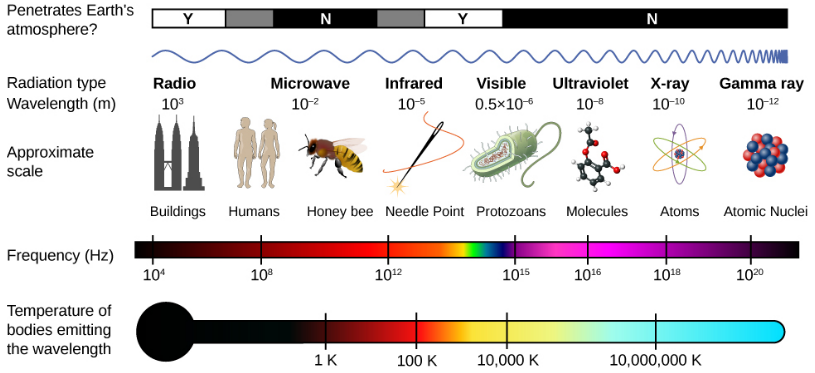
Time Line

- 1665: Diffraction effects observed by Francesco Maria Grimaldi
- 1868: X-rays Discovered by German Scientist Röntgen
- 1912: Discovery of X-ray Diffraction by Crystals: von Laue
- 1912: Bragg's Discovery
- 1928: 1st XRD studies on cement (Hansen & Brownmiller)
- 1969: Rietveld method for neutron diffraction (Hugo Rietveld)
- 1977: Rietveld method for XRD (Cox, Young & Thomas)
- 1987: 1st Rietveld quantification analysis (Hill & Howard)
- 1993: 1st Rietveld quantification analysis on cement (Taylor & Aldridge)
- 2006: Quantification of phases with PONKCS (Scarlett & Madsen)
- 2014: PONCKS method on cement (Ruben Snelling)

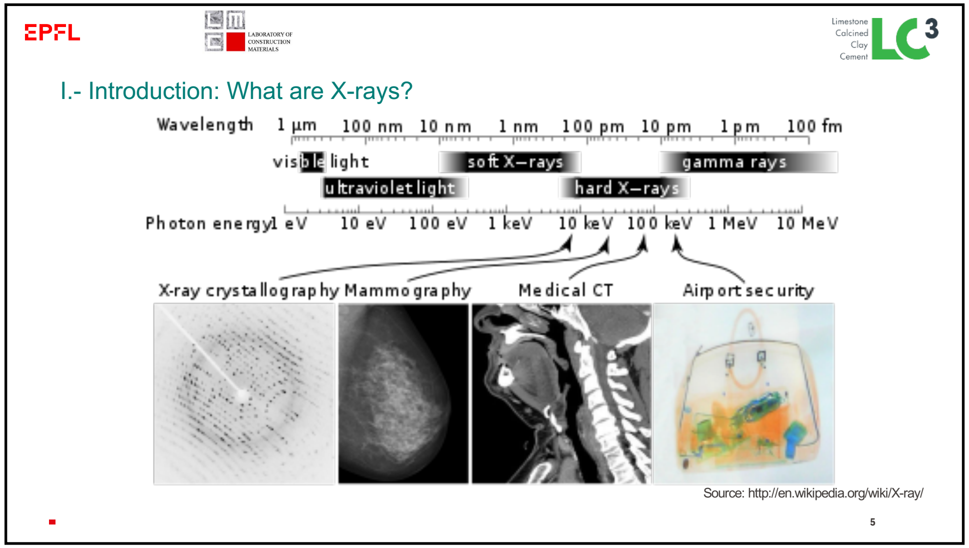
Outline

- What is powder diffraction? Basics of XRD
- Crystallographic review
- General uses
- Basic anatomy of the diffractometer
- What does the diffraction pattern really show?
- Sample preparation & data collection
- XRD softwares and databases
- General phase identification
- Rietveld refinement
- Practical examples

I.- Introduction: What are X-rays?

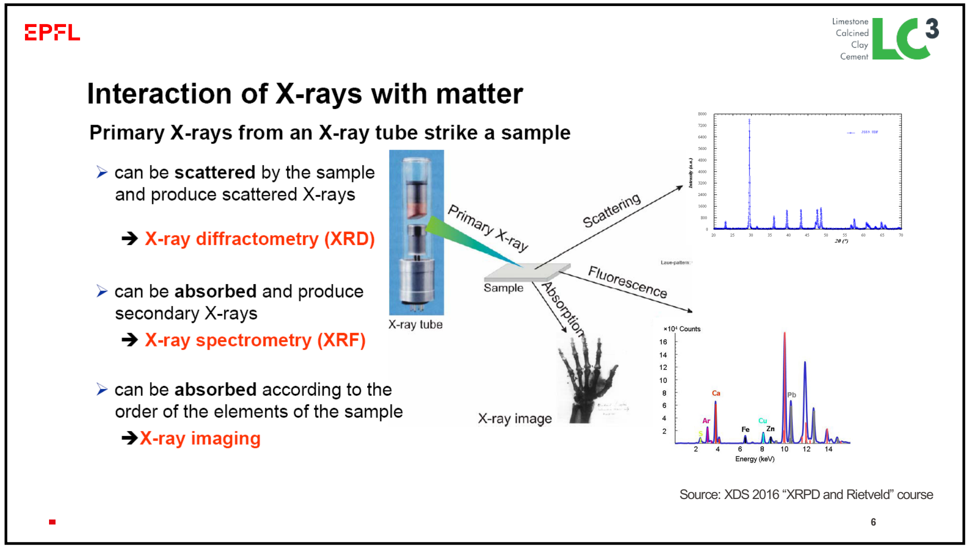


Source: XDS 2018 "XRPD and Rietveld" UNAL-Colombia course



I.- Introduction: What are X-rays?

Source: http://en.wikipedia.org/wiki/X-ray/

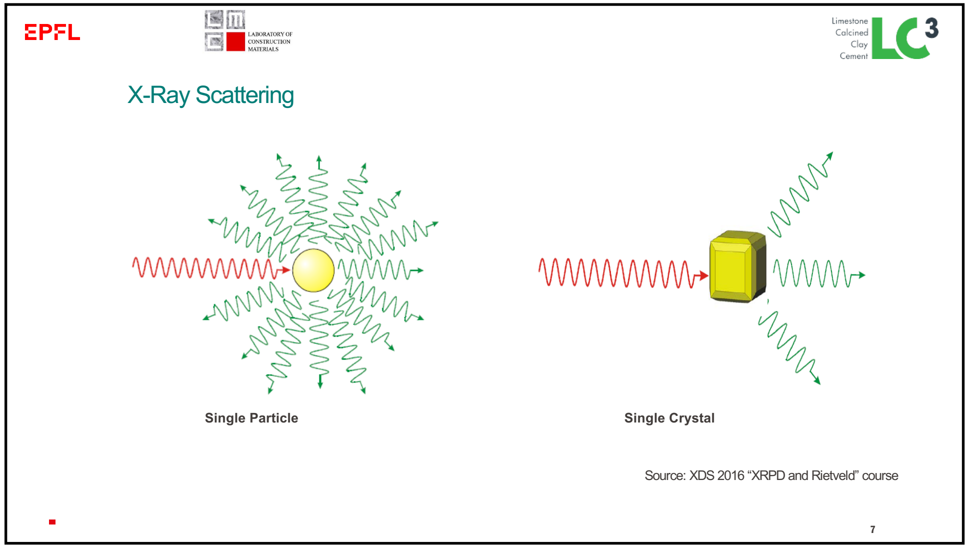


Interaction of X-rays with matter

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

Source: XDS 2016 “XRPD and Rietveld” course

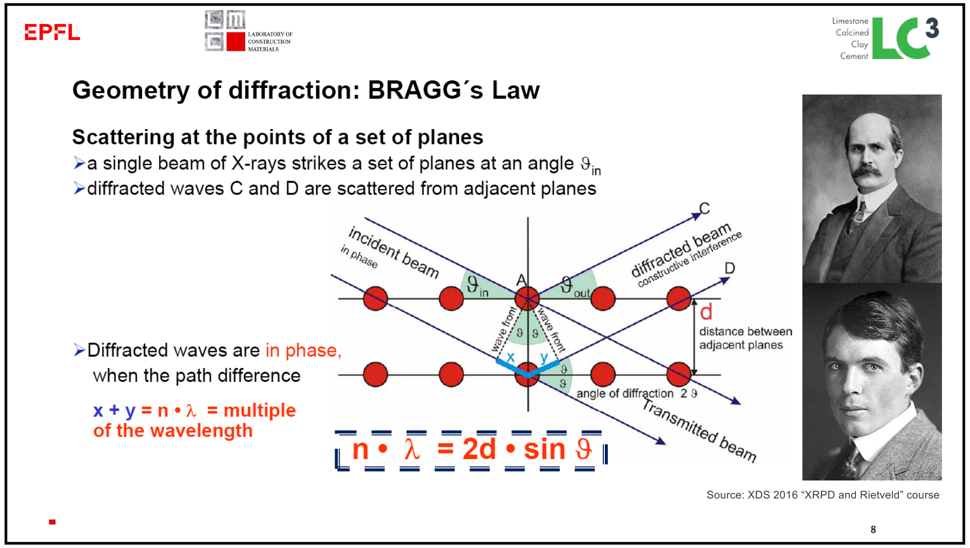


X-Ray Scattering

Single Particle

Single Crystal

Source: XDS 2016 “XRPD and Rietveld” course



Geometry of diffraction: BRAGG´s Law

Scattering at the points of a set of planes

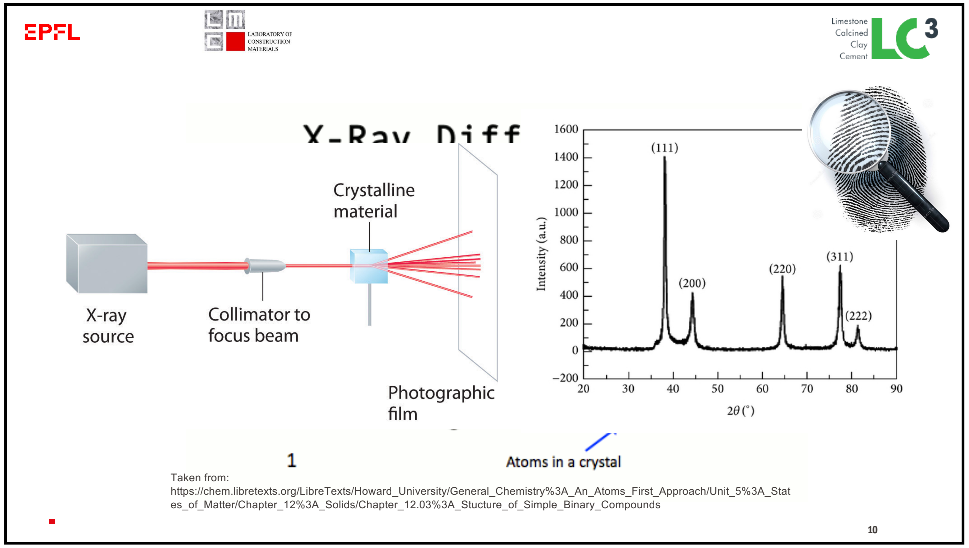
- a single beam of X-rays strikes a set of planes at an angle ϑ_{in}
- diffracted waves C and D are scattered from adjacent planes

- Diffracted waves are in phase, when the path difference

$x + y = n \cdot \lambda$ = multiple of the wavelength

$$\boxed{n \cdot \lambda = 2d \cdot \sin \vartheta}$$

Source: XDS 2016 “XRPD and Rietveld” course



Taken from:
https://chem.libretexts.org/LibreTexts/Howard_University/General_Chemistry%3A_An_Atoms_First_Approach/Unit_5%3A_States_of_Matter/Chapter_12%3A_Solids/Chapter_12.03%3A_Stucture_of_Simple_Binary_Compounds

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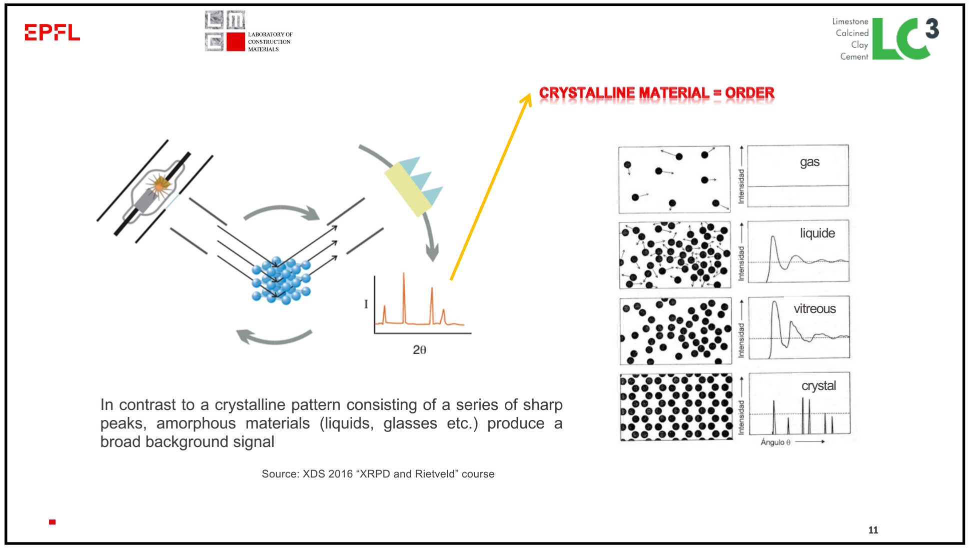

CRYSTALLINE MATERIAL = ORDER

In contrast to a crystalline pattern consisting of a series of sharp peaks, amorphous materials (liquids, glasses etc.) produce a broad background signal

Source: XDS 2016 “XRPD and Rietveld” course

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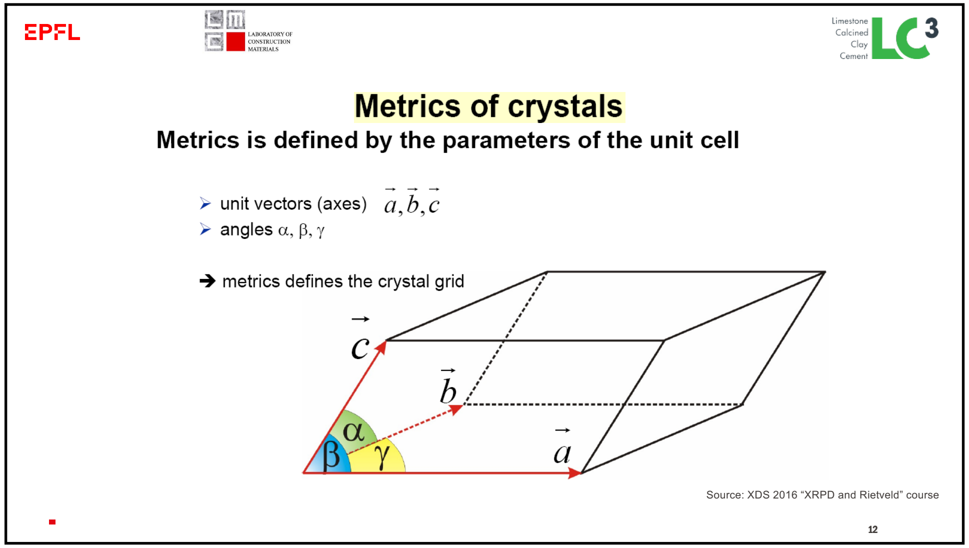

Metrics of crystals

Metrics is defined by the parameters of the unit cell

- unit vectors (axes) $\vec{a}, \vec{b}, \vec{c}$
- angles α, β, γ

➔ metrics defines the crystal grid

Source: XDS 2016 “XRPD and Rietveld” course

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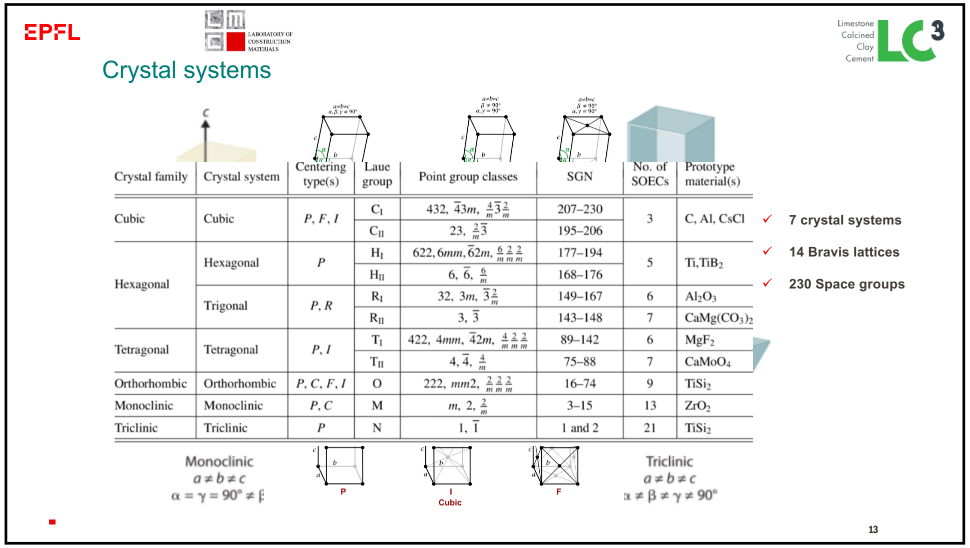

Crystal systems

Crystal family	Crystal system	Centering type(s)	Laue group	Point group classes	SGN	No. of SOECs	Prototype material(s)
Cubic	Cubic	*P, F, I*	C_I	$432,\ \bar{4}3m,\ \frac{4}{m}\bar{3}\frac{2}{m}$	207–230	3	C, Al, CsCl
			C_{II}	$23,\ \frac{2}{m}\bar{3}$	195–206		
Hexagonal	Hexagonal	*P*	H_I	$622, 6mm, \bar{6}2m, \frac{6}{m}\frac{2}{m}\frac{2}{m}$	177–194	5	Ti, TiB_2
			H_{II}	$6,\ \bar{6},\ \frac{6}{m}$	168–176		
	Trigonal	*P, R*	R_I	$32,\ 3m,\ \bar{3}\frac{2}{m}$	149–167	6	Al_2O_3
			R_{II}	$3,\ \bar{3}$	143–148	7	$CaMg(CO_3)_2$
Tetragonal	Tetragonal	*P, I*	T_I	$422,\ 4mm,\ \bar{4}2m,\ \frac{4}{m}\frac{2}{m}\frac{2}{m}$	89–142	6	MgF_2
			T_{II}	$4,\ \bar{4},\ \frac{4}{m}$	75–88	7	$CaMoO_4$
Orthorhombic	Orthorhombic	*P, C, F, I*	O	$222,\ mm2,\ \frac{2}{m}\frac{2}{m}\frac{2}{m}$	16–74	9	$TiSi_2$
Monoclinic	Monoclinic	*P, C*	M	$m,\ 2,\ \frac{2}{m}$	3–15	13	ZrO_2
Triclinic	Triclinic	*P*	N	$1,\ \bar{1}$	1 and 2	21	$TiSi_2$

- ✓ **7 crystal systems**
- ✓ **14 Bravis lattices**
- ✓ **230 Space groups**

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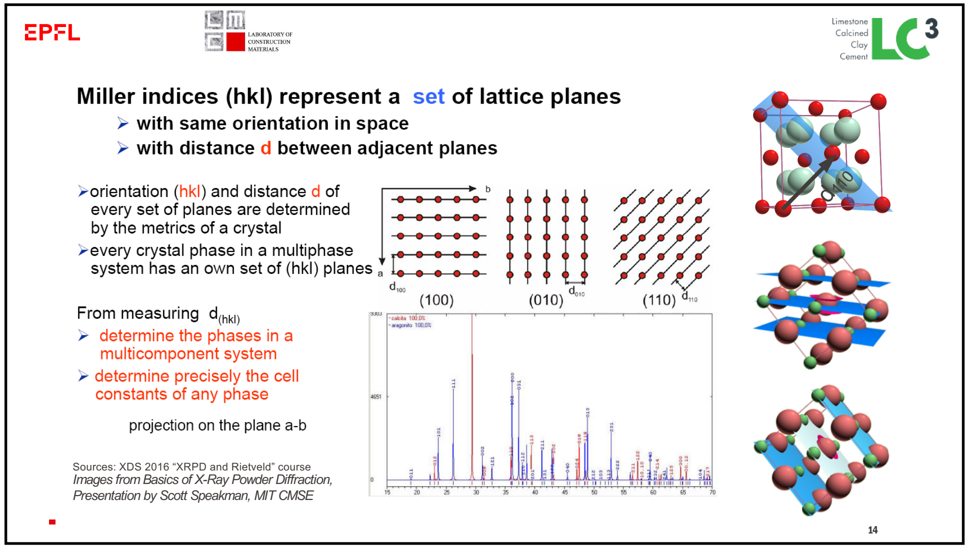


Miller indices (hkl) represent a set of lattice planes

- with same orientation in space
- with distance d between adjacent planes

- orientation (hkl) and distance d of every set of planes are determined by the metrics of a crystal
- every crystal phase in a multiphase system has an own set of (hkl) planes

From measuring $d_{(hkl)}$

- determine the phases in a multicomponent system
- determine precisely the cell constants of any phase

projection on the plane a-b

Sources: XDS 2016 "XRPD and Rietveld" course
Images from Basics of X-Ray Powder Diffraction, Presentation by Scott Speakman, MIT CMSE

Cubic:

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$$

Tetragonal:

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Rhombohedral:

$$\frac{1}{d^2} = \frac{(h^2+k^2+l^2)\sin^2\alpha + 2(hk+kl+hl)(\cos^2\alpha - \cos\alpha)}{a^2(1-3\cos^2\alpha + 2\cos^3\alpha)}$$

Orthorhombic:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Monoclinic:

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Triclinic:

$$\frac{1}{d^2} = \frac{1}{V^2}\left(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl\right)$$

where

$$S_{11} = b^2c^2\sin^2\alpha$$
$$S_{22} = a^2c^2\sin^2\beta$$
$$S_{33} = a^2b^2\sin^2\gamma$$
$$S_{12} = abc^2(\cos\alpha\cos\beta - \cos\gamma)$$
$$S_{23} = a^2bc(\cos\beta\cos\gamma - \cos\alpha)$$
$$S_{13} = ab^2c(\cos\gamma\cos\alpha - \cos\beta)$$

$$\boxed{n\lambda = 2d\,sin\theta}$$

$$\Downarrow$$

$$\boxed{2\theta \quad = 2\cdot\arcsin\left(\frac{\lambda}{2\cdot d_{hkl}}\right)}$$

General uses of X-ray powder diffraction

1 Identification of crystalline compounds (using known database). (Based on I_{hkl} and d_{hkl})

2 Determination of the unit cell parameters. (Based on d_{hkl})

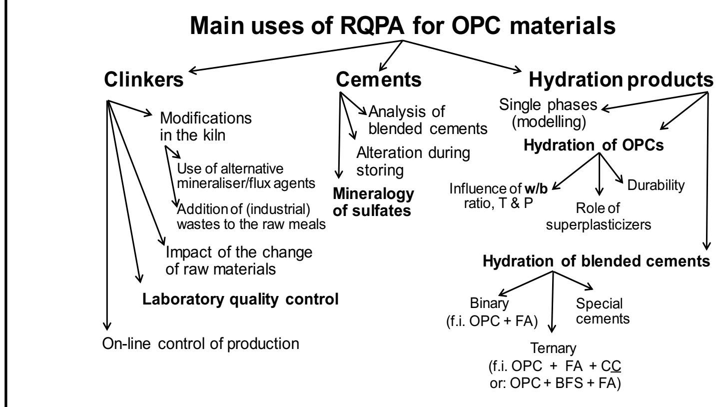
3 Determination of the crystal structure (atomic parameters). (Based on I_{hkl} and d_{hkl})

4 Quantitative phase analysis (sample purity). (Based on I_{hkl})

5 Determination of the microstructure of the phase. (Based on the shape-'FWHM' of the I_{hkl})
(average microparticle size and shape, microstrains, residual stress, etc.)

6 XRPD can be coupled to thermal variation (thermodiffractometry):
Uses for: phase transitions, chemical reactions, melting/crystallization, thermal expansion, …

7 XRPD can be coupled to pressure variation:
Uses for: phase transitions, equation of state determination, …



Main uses of RQPA for OPC materials

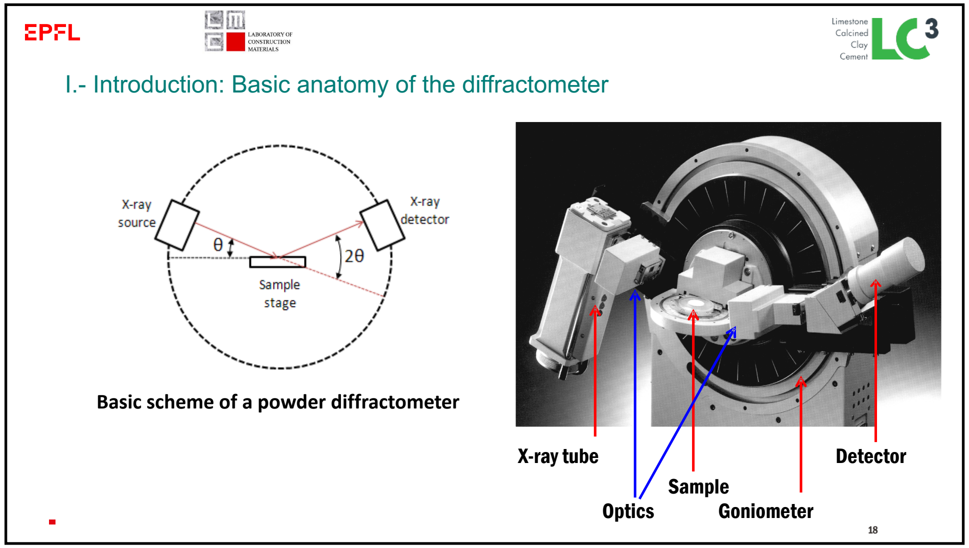
Clinkers
- Modifications in the kiln
  - Use of alternative mineraliser/flux agents
  - Addition of (industrial) wastes to the raw meals
- Impact of the change of raw materials
- **Laboratory quality control**
- On-line control of production

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 (f.i. OPC + FA + CC or: OPC + BFS + FA)
  - Special cements

RQPA gives useful information for cements (The answer will depend on the problem)

Modifed from: Aranda & De la Torre 2012. Rev. Min. Geo.



I.- Introduction: Basic anatomy of the diffractometer

Basic scheme of a powder diffractometer

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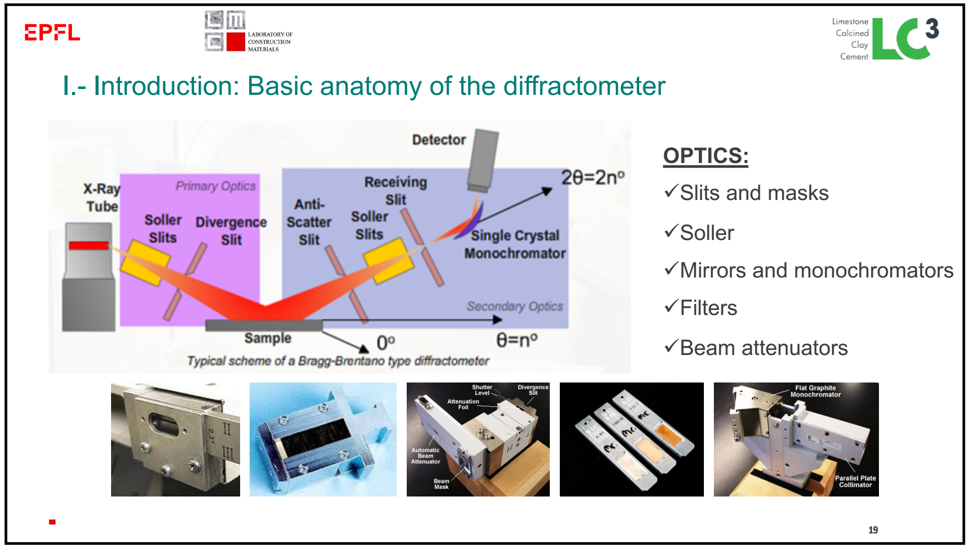

I.- Introduction: Basic anatomy of the diffractometer

Typical scheme of a Bragg-Brentano type diffractometer

OPTICS:

- ✓Slits and masks
- ✓Soller
- ✓Mirrors and monochromators
- ✓Filters
- ✓Beam attenuators

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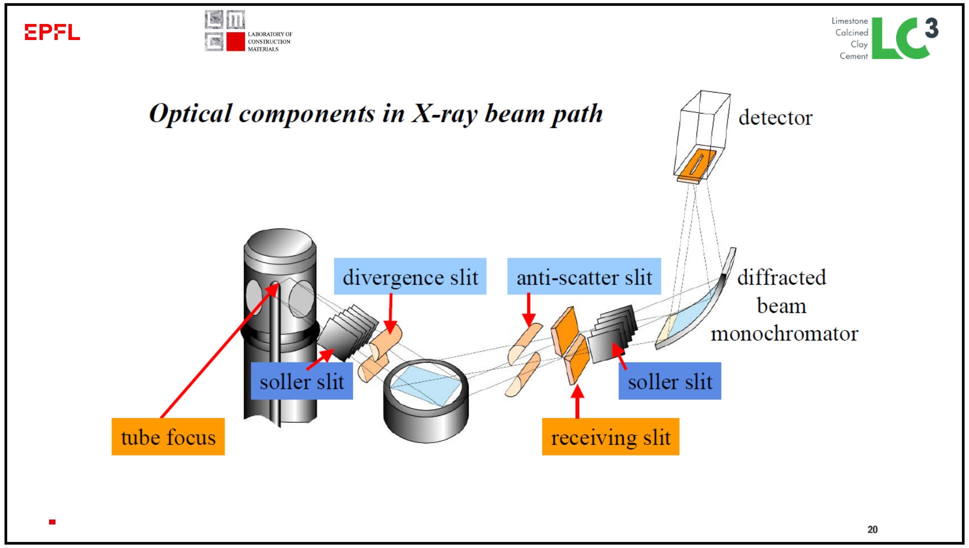

Optical components in X-ray beam path

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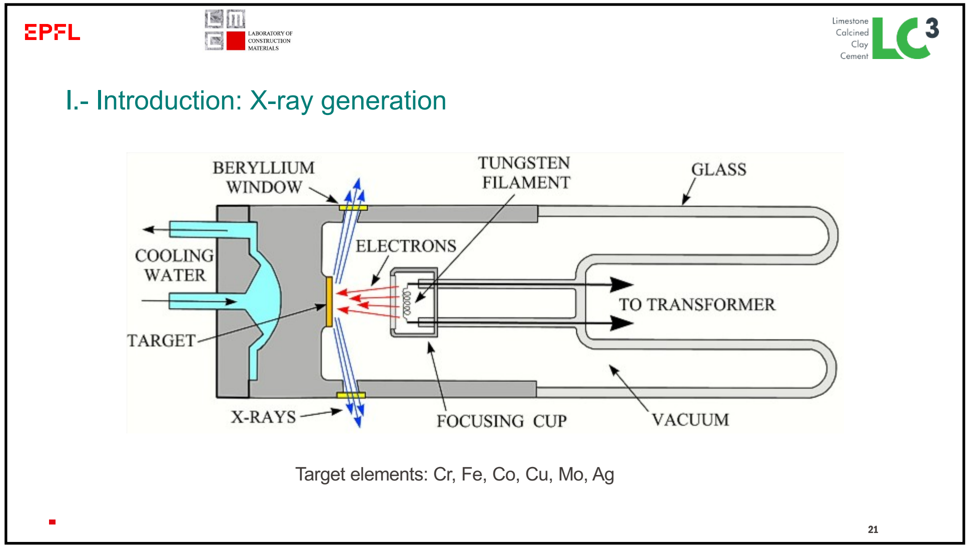

I.- Introduction: X-ray generation

Target elements: Cr, Fe, Co, Cu, Mo, Ag

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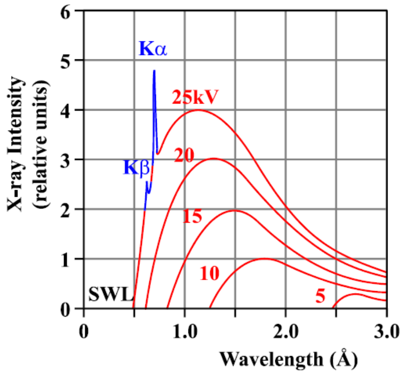
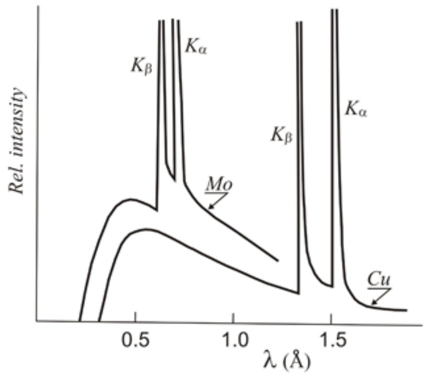
I.- Introduction: X-ray generation (Lab Sources)

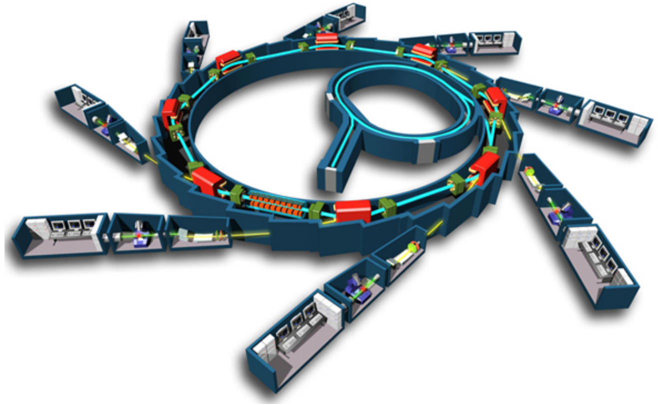




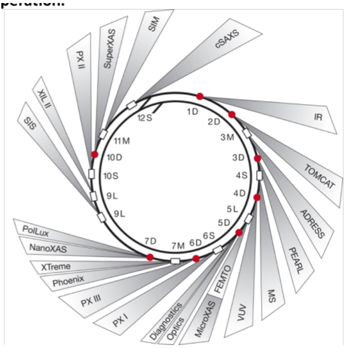
Moseley's Law

$$\sqrt{f} = k_1 \left(Z - k_2\right)$$

I.- Introduction: X-ray generation (Synchrotron)

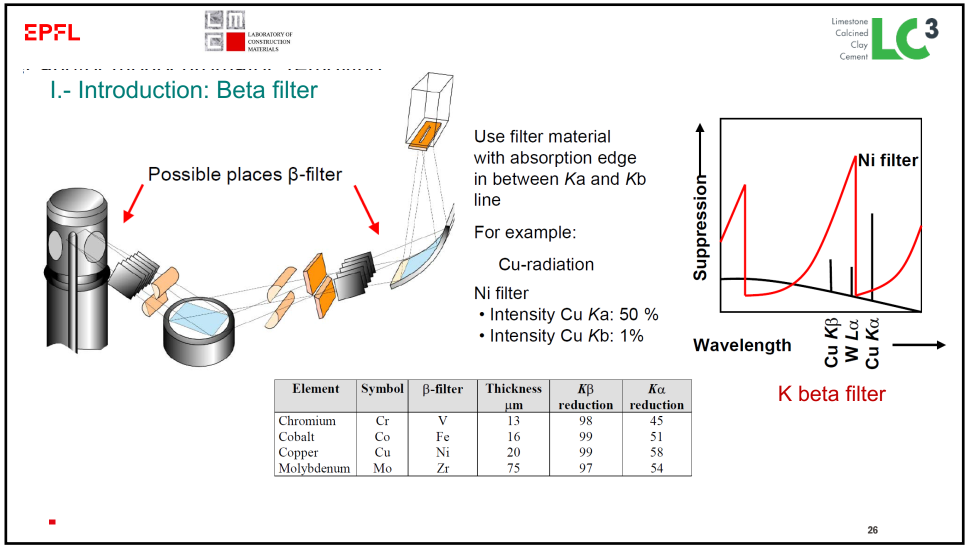


I.- Introduction: X-ray generation (Synchrotron)



LSL (Paul Scherrer Institute, Villigen - Switzerland)

I.- Introduction: X-ray generation (Synchrotron)



I.- Introduction: Beta filter

Use filter material with absorption edge in between *Ka* and *Kb* line

For example:

Cu-radiation

Ni filter

- Intensity Cu *Ka*: 50 %
- Intensity Cu *Kb*: 1%

K beta filter

Element	Symbol	β-filter	Thickness µm	*K*β reduction	*K*α reduction
Chromium	Cr	V	13	98	45
Cobalt	Co	Fe	16	99	51
Copper	Cu	Ni	20	99	58
Molybdenum	Mo	Zr	75	97	54

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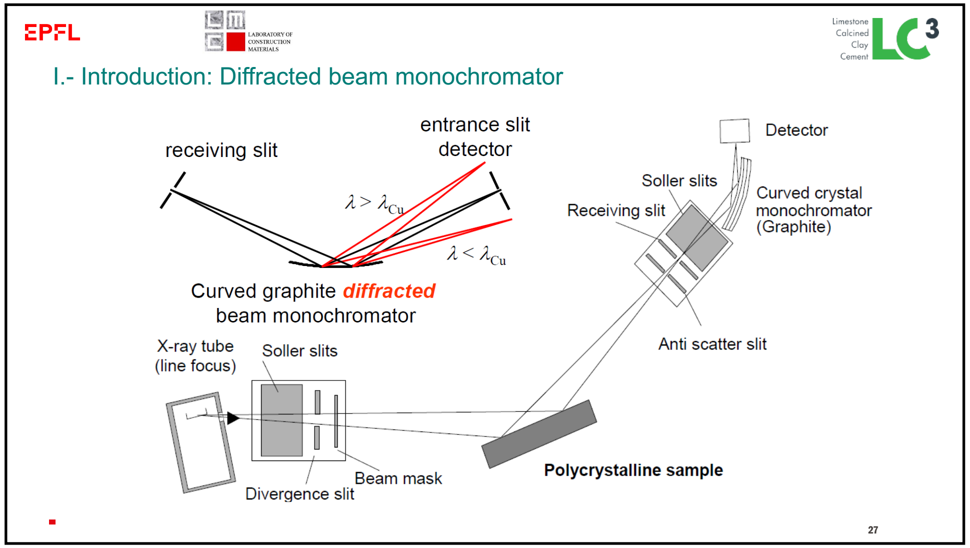

I.- Introduction: Diffracted beam monochromator

Curved graphite ***diffracted*** beam monochromator

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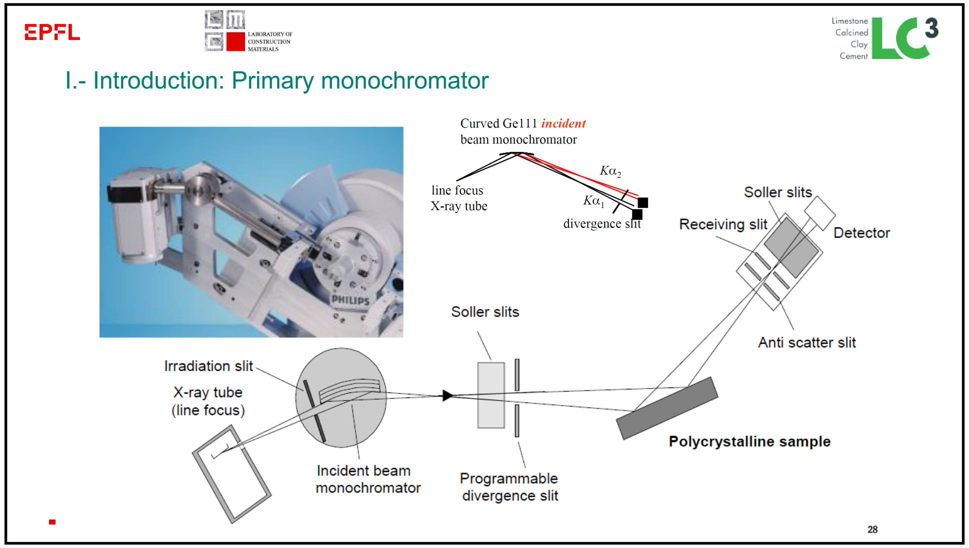

I.- Introduction: Primary monochromator

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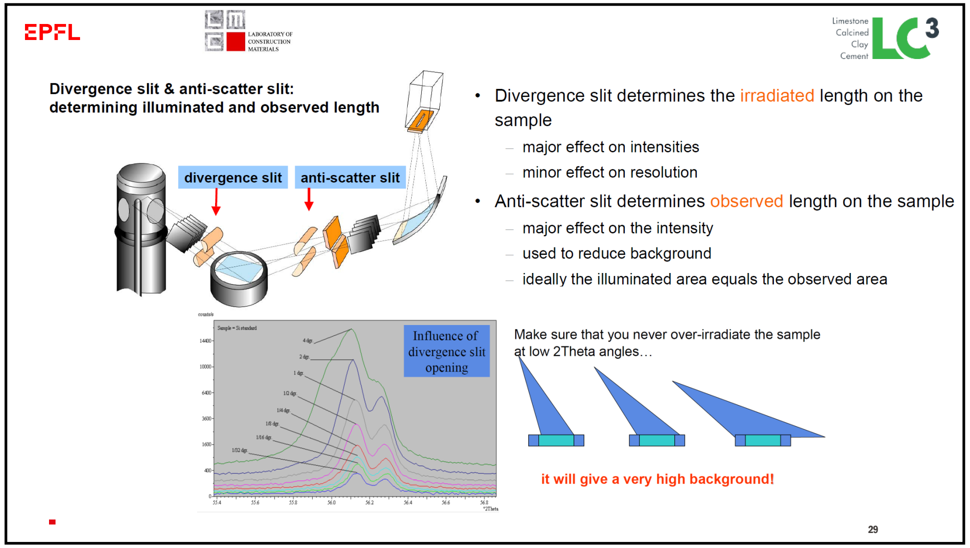

Divergence slit & anti-scatter slit: determining illuminated and observed length

- Divergence slit determines the irradiated length on the sample
  - major effect on intensities
  - minor effect on resolution
- Anti-scatter slit determines observed length on the sample
  - major effect on the intensity
  - used to reduce background
  - ideally the illuminated area equals the observed area

Make sure that you never over-irradiate the sample at low 2Theta angles…

it will give a very high background!

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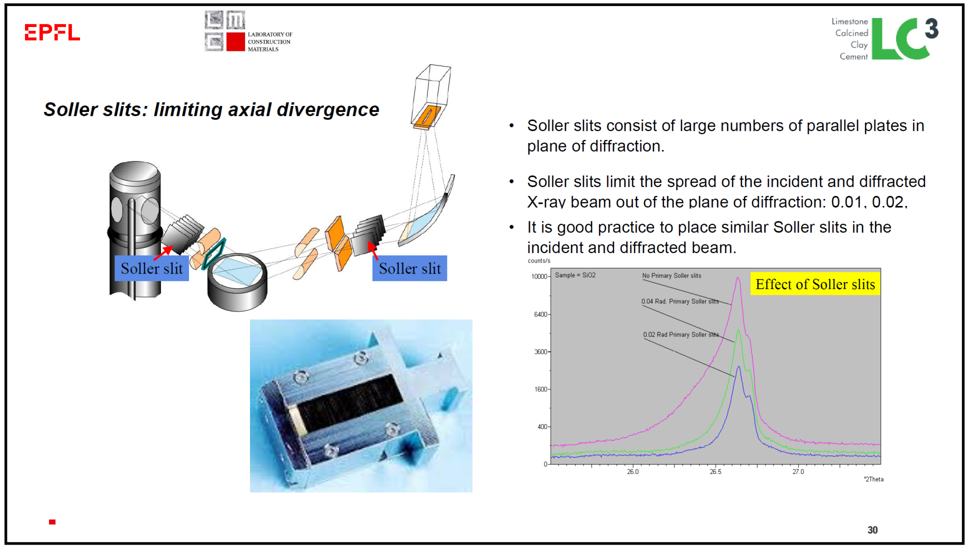

Soller slits: limiting axial divergence

- Soller slits consist of large numbers of parallel plates in plane of diffraction.
- Soller slits limit the spread of the incident and diffracted X-ray beam out of the plane of diffraction: 0.01, 0.02,
- It is good practice to place similar Soller slits in the incident and diffracted beam.

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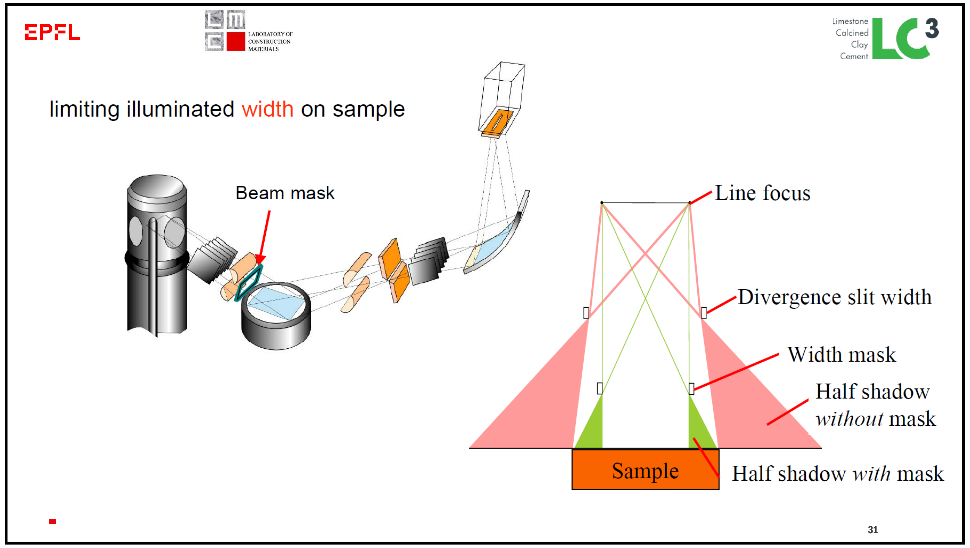

limiting illuminated width on sample

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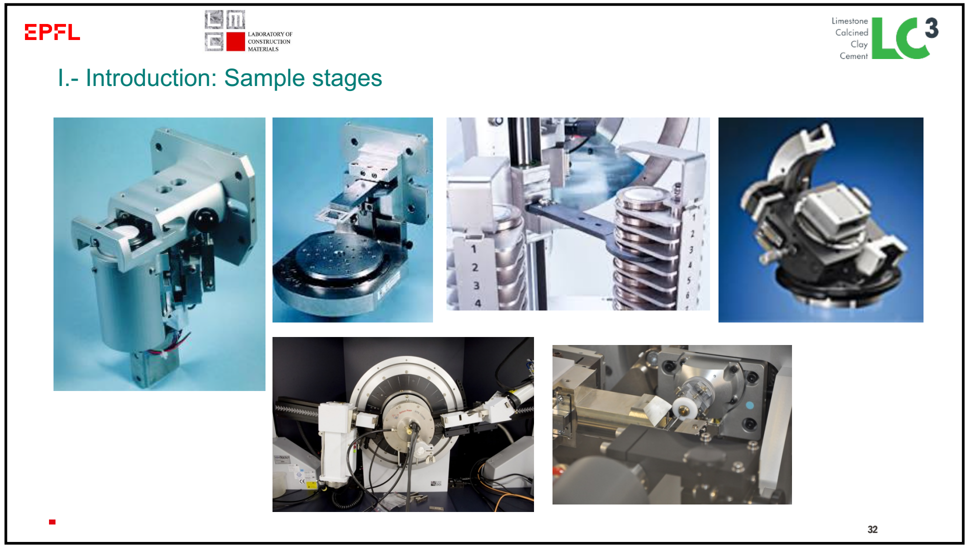

I.- Introduction: Sample stages

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Types of detectors

- Point Detector
  - Scintillation detectors
  - Gas filled detectors
- Linear detector

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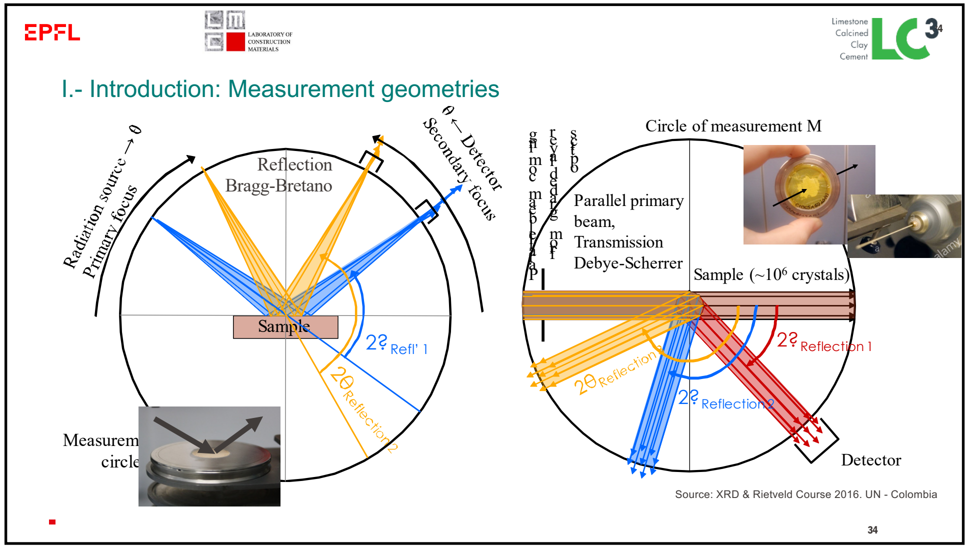
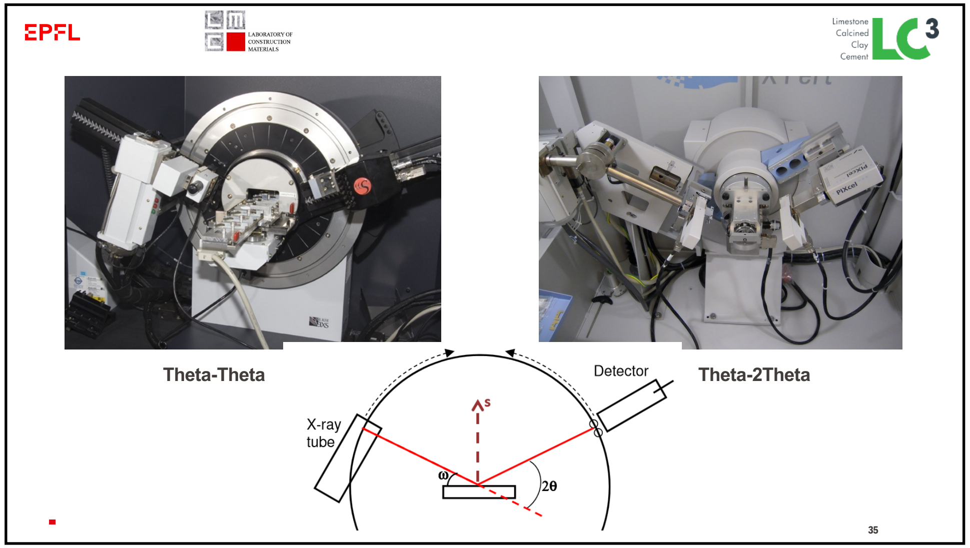
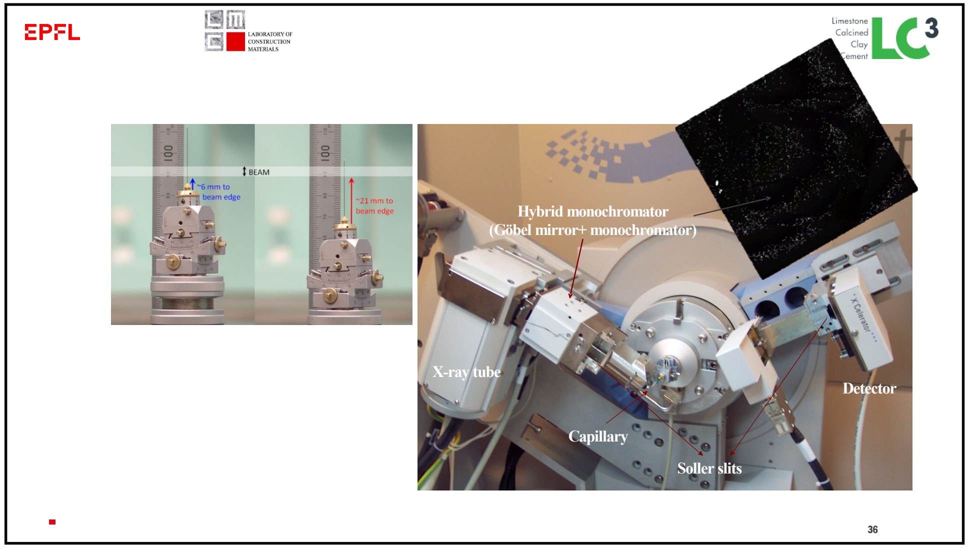
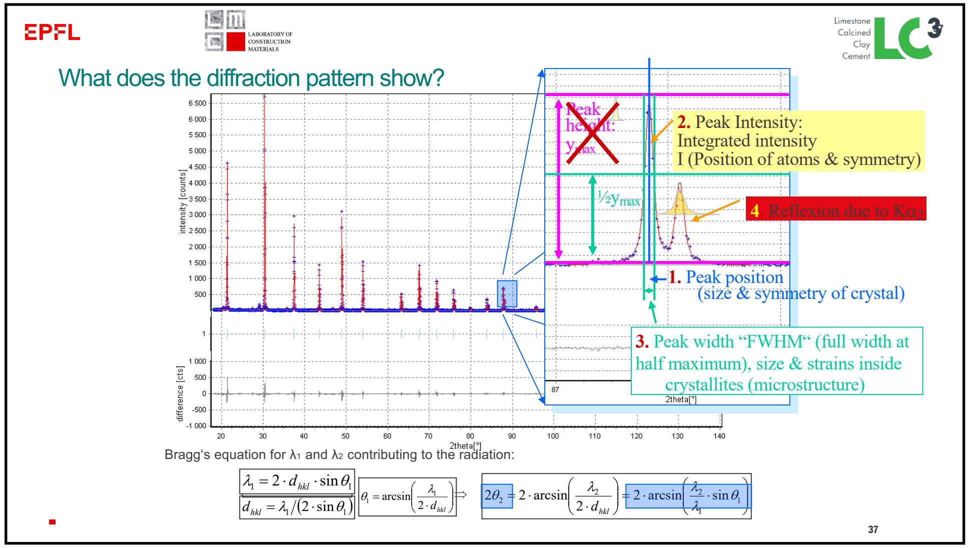


I.- Introduction: Measurement geometries

Source: XRD & Rietveld Course 2016. UN - Colombia







What does the diffraction pattern show?

1. Peak position (size & symmetry of crystal)

2. Peak Intensity: Integrated intensity I (Position of atoms & symmetry)

3. Peak width "FWHM" (full width at half maximum), size & strains inside crystallites (microstructure)

4. Reflexion due to Kα₂

Bragg's equation for λ₁ and λ₂ contributing to the radiation:

$$\lambda_1 = 2 \cdot d_{hkl} \cdot \sin\theta_1$$

$$d_{hkl} = \lambda_1 / (2 \cdot \sin\theta_1)$$

$$\theta_1 = \arcsin\left(\frac{\lambda_1}{2 \cdot d_{hkl}}\right) \Rightarrow 2\theta_2 = 2 \cdot \arcsin\left(\frac{\lambda_2}{2 \cdot d_{hkl}}\right) = 2 \cdot \arcsin\left(\frac{\lambda_2}{\lambda_1} \cdot \sin\theta_1\right)$$

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

Absorsion factor

Texture Factor (PO)

Structure Factor

Peak intensity

- F_{hkl} = structure factor. Sum over all atoms j of the unit cell
  - Per atom: Coordinates x_j, y_j, z_j and isotropic displacement parameter B_j

$$F_{hkl} = \sum_{j=1}^{N_{EZ}} f_j \cdot e^{i\phi_j} \cdot T_j$$

Scattering factor· Phase factor· displacem‘ factor

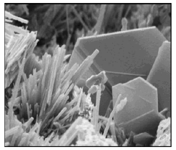
$$= \sum_{j=1}^{N_{EZ}} \left(c + \sum_{m=1}^{4} a_m \cdot e^{-b_m \cdot \frac{\sin^2\theta}{\lambda^2}} \right)_j \cdot e^{2\pi i (hx_j + ky_j + \ell z_j)} \cdot e^{-B_j \frac{\sin^2\theta_{hkl}}{\lambda^2}}$$

$$P_{hkl} = \left(PO_p^2 \cdot \cos^2 \alpha_{hkl} + \frac{\sin^2 \alpha_{hkl}}{PO_p} \right)^{-3/2}$$

Platy/Sheets crystallite:
$PO_p < 1$

Needle shaped crystallite:
$PO_p > 1$

No texture:
$PO_p = 1$, all $P_{hkl} = 1$
→ fig. spherical



Source: https://www.fhwa.dot.gov/publications/research/infrastructure/pavements/pccp/04150/chapt14.cfm

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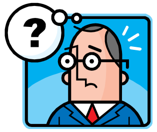


Early Decisions

Sample

Instrument

Data Collection

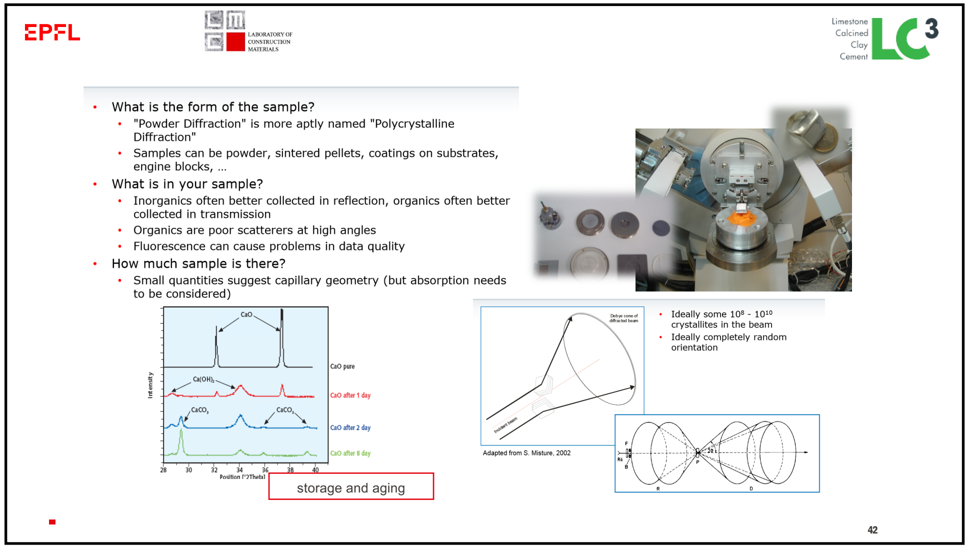
- Early decisions:
  - What are the sample properties?
  - What data quality is necessary?
  - What instrument and measurement parameters to use?

> "Although the physical nature of a specimen from which the X-ray powder-diffraction data are collected is seemingly simple, sample preparation and data collection are generally the source of most of the serious problems with accurate X-ray diffraction analysis"

Minimize systematic sample related effects!
This is as important as the optimization minimization of the instrument configuration!

- Avoid persisting with poor data (if possible)
  - Find a better sample
    - Re-prepare or remake the sample
  - Change instrument or instrument setup
  - Improve data collection parameters

- Don't rely on any software corrections!
  - Variable slits conversion
  - Preferred orientation corrections
  - Microabsorption corrections (worst!)
  - ...



- What is the form of the sample?
  - "Powder Diffraction" is more aptly named "Polycrystalline Diffraction"
  - Samples can be powder, sintered pellets, coatings on substrates, engine blocks, …
- What is in your sample?
  - Inorganics often better collected in reflection, organics often better collected in transmission
  - Organics are poor scatterers at high angles
  - Fluorescence can cause problems in data quality
- How much sample is there?
  - Small quantities suggest capillary geometry (but absorption needs to be considered)

storage and aging

Adapted from S. Misture, 2002

- Ideally some 10^8 - 10^{10} crystallites in the beam
- Ideally completely random orientation

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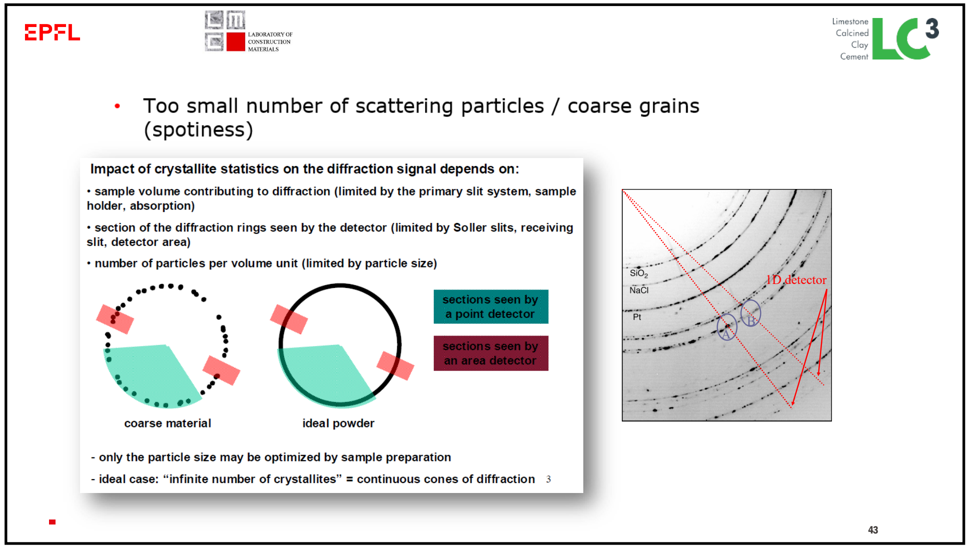


- Too small number of scattering particles / coarse grains (spotiness)

Impact of crystallite statistics on the diffraction signal depends on:

- sample volume contributing to diffraction (limited by the primary slit system, sample holder, absorption)
- section of the diffraction rings seen by the detector (limited by Soller slits, receiving slit, detector area)
- number of particles per volume unit (limited by particle size)

coarse material

ideal powder

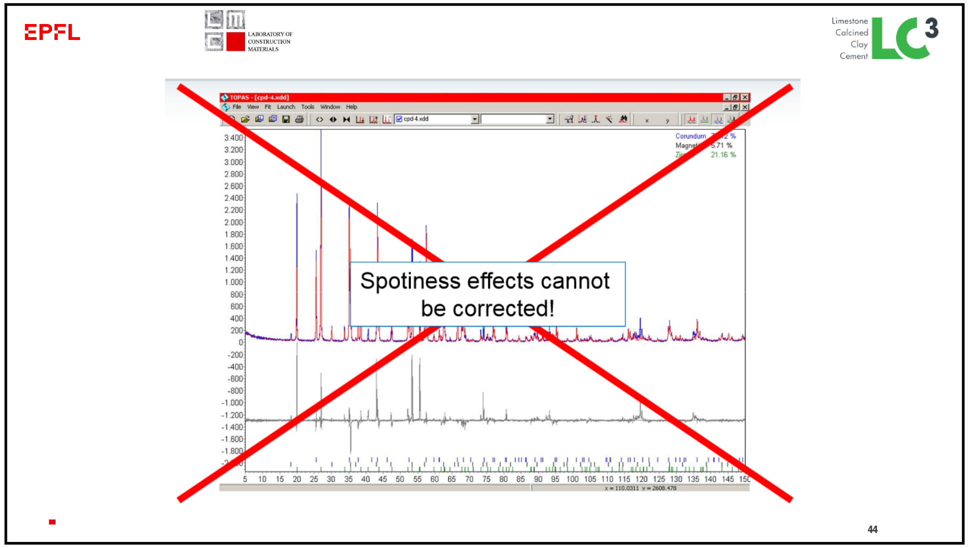
sections seen by a point detector

sections seen by an area detector

- only the particle size may be optimized by sample preparation

- ideal case: "infinite number of crystallites" = continuous cones of diffraction 3

43



Spotiness effects cannot be corrected!

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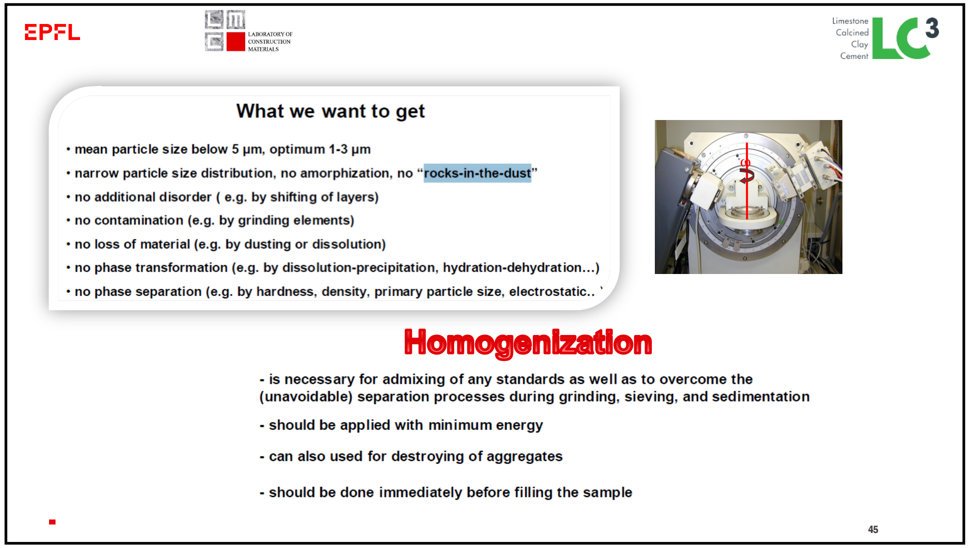

What we want to get

- mean particle size below 5 µm, optimum 1-3 µm
- narrow particle size distribution, no amorphization, no "rocks-in-the-dust"
- no additional disorder (e.g. by shifting of layers)
- no contamination (e.g. by grinding elements)
- no loss of material (e.g. by dusting or dissolution)
- no phase transformation (e.g. by dissolution-precipitation, hydration-dehydration…)
- no phase separation (e.g. by hardness, density, primary particle size, electrostatic..

Homogenization

- is necessary for admixing of any standards as well as to overcome the (unavoidable) separation processes during grinding, sieving, and sedimentation

- should be applied with minimum energy

- can also used for destroying of aggregates

- should be done immediately before filling the sample

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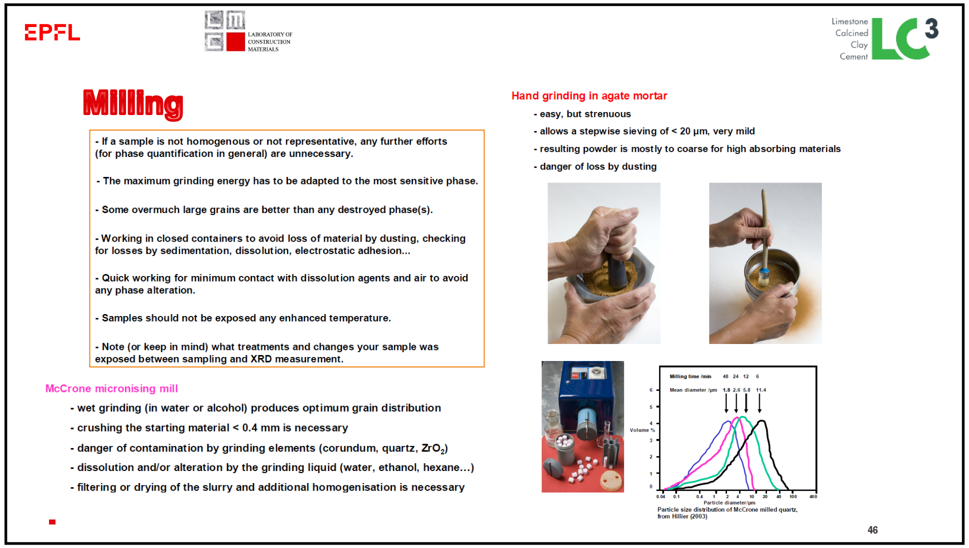

Milling

- If a sample is not homogenous or not representative, any further efforts (for phase quantification in general) are unnecessary.
- The maximum grinding energy has to be adapted to the most sensitive phase.
- Some overmuch large grains are better than any destroyed phase(s).
- Working in closed containers to avoid loss of material by dusting, checking for losses by sedimentation, dissolution, electrostatic adhesion...
- Quick working for minimum contact with dissolution agents and air to avoid any phase alteration.
- Samples should not be exposed any enhanced temperature.
- Note (or keep in mind) what treatments and changes your sample was exposed between sampling and XRD measurement.

Hand grinding in agate mortar

- easy, but strenuous
- allows a stepwise sieving of < 20 µm, very mild
- resulting powder is mostly to coarse for high absorbing materials
- danger of loss by dusting

McCrone micronising mill

- wet grinding (in water or alcohol) produces optimum grain distribution
- crushing the starting material < 0.4 mm is necessary
- danger of contamination by grinding elements (corundum, quartz, ZrO_2)
- dissolution and/or alteration by the grinding liquid (water, ethanol, hexane…)
- filtering or drying of the slurry and additional homogenisation is necessary

Particle size distribution of McCrone milled quartz, from Hillier (2003)

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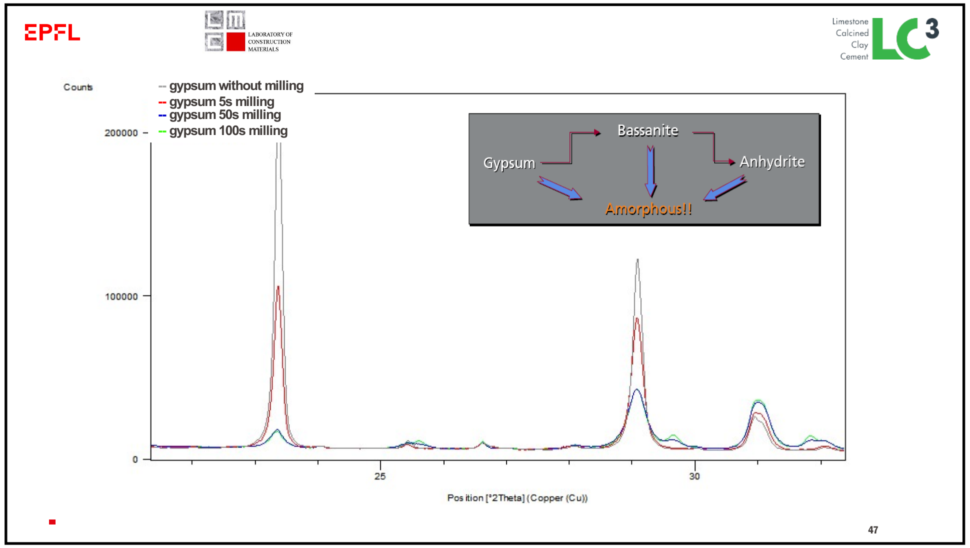
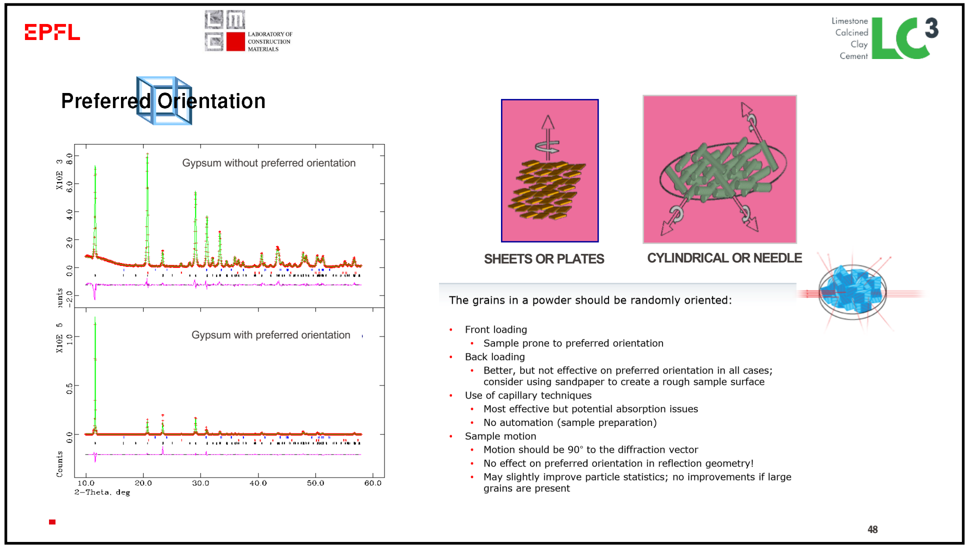


47



Preferred Orientation

The grains in a powder should be randomly oriented:

- Front loading
  - Sample prone to preferred orientation
- Back loading
  - Better, but not effective on preferred orientation in all cases; consider using sandpaper to create a rough sample surface
- Use of capillary techniques
  - Most effective but potential absorption issues
  - No automation (sample preparation)
- Sample motion
  - Motion should be 90° to the diffraction vector
  - No effect on preferred orientation in reflection geometry!
  - May slightly improve particle statistics; no improvements if large grains are present

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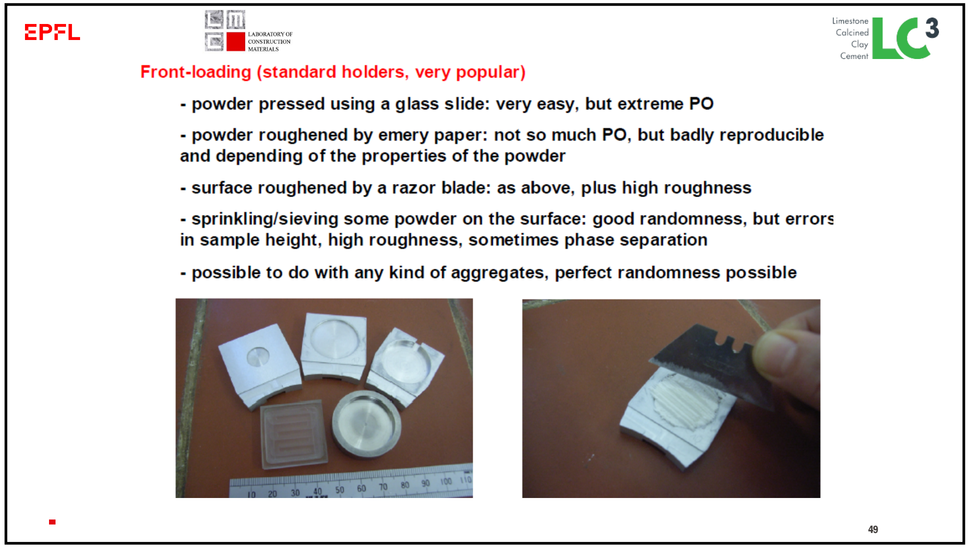

Front-loading (standard holders, very popular)

- powder pressed using a glass slide: very easy, but extreme PO
- powder roughened by emery paper: not so much PO, but badly reproducible and depending of the properties of the powder
- surface roughened by a razor blade: as above, plus high roughness
- sprinkling/sieving some powder on the surface: good randomness, but errors in sample height, high roughness, sometimes phase separation
- possible to do with any kind of aggregates, perfect randomness possible

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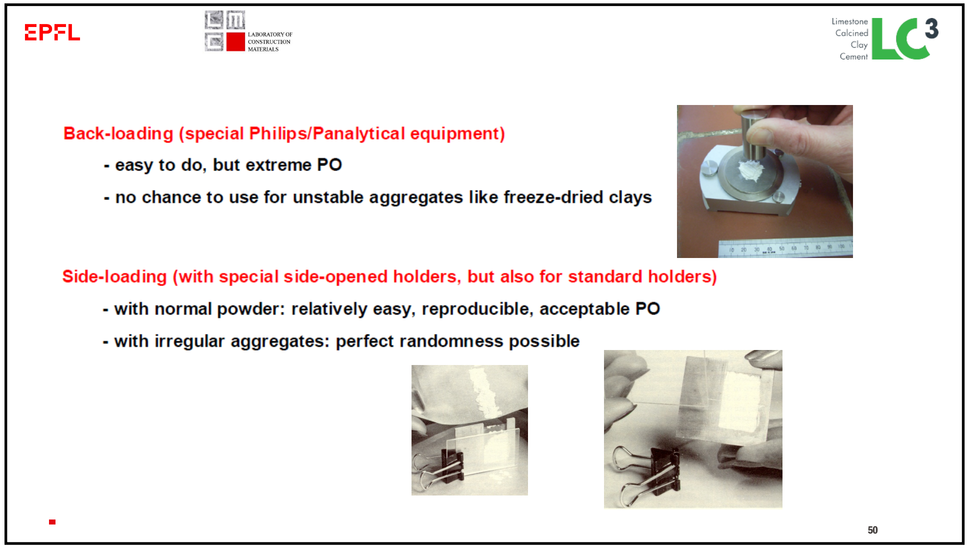

Back-loading (special Philips/Panalytical equipment)

- **easy to do, but extreme PO**
- **no chance to use for unstable aggregates like freeze-dried clays**

Side-loading (with special side-opened holders, but also for standard holders)

- **with normal powder: relatively easy, reproducible, acceptable PO**
- **with irregular aggregates: perfect randomness possible**

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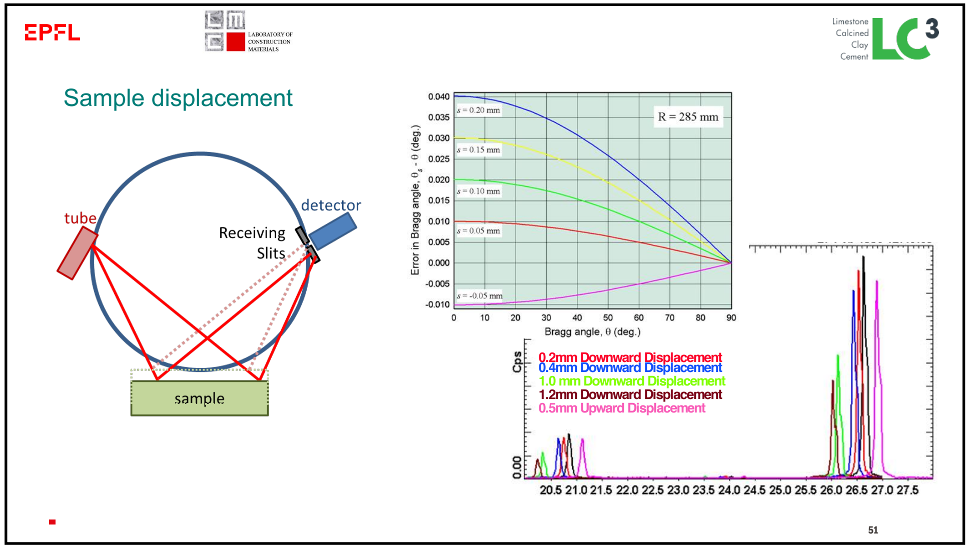

Sample displacement

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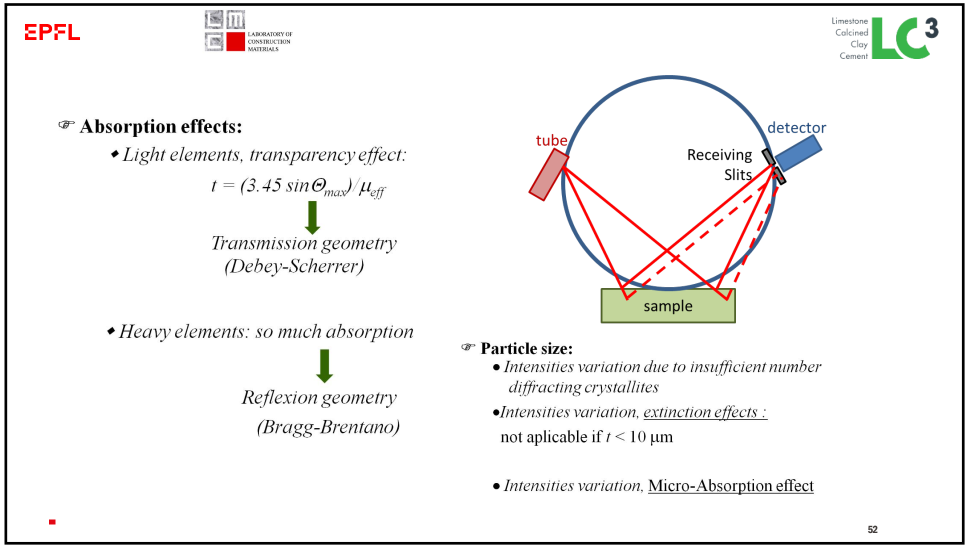

☞ **Absorption effects:**

- *Light elements, transparency effect:*

  $t = (3.45 \sin\Theta_{max})/\mu_{eff}$

  ⬇

  Transmission geometry (Debey-Scherrer)

- *Heavy elements: so much absorption*

  ⬇

  Reflexion geometry (Bragg-Brentano)

☞ **Particle size:**

- *Intensities variation due to insufficient number diffracting crystallites*
- *Intensities variation, extinction effects :* not aplicable if $t < 10$ µm
- *Intensities variation,* Micro-Absorption effect

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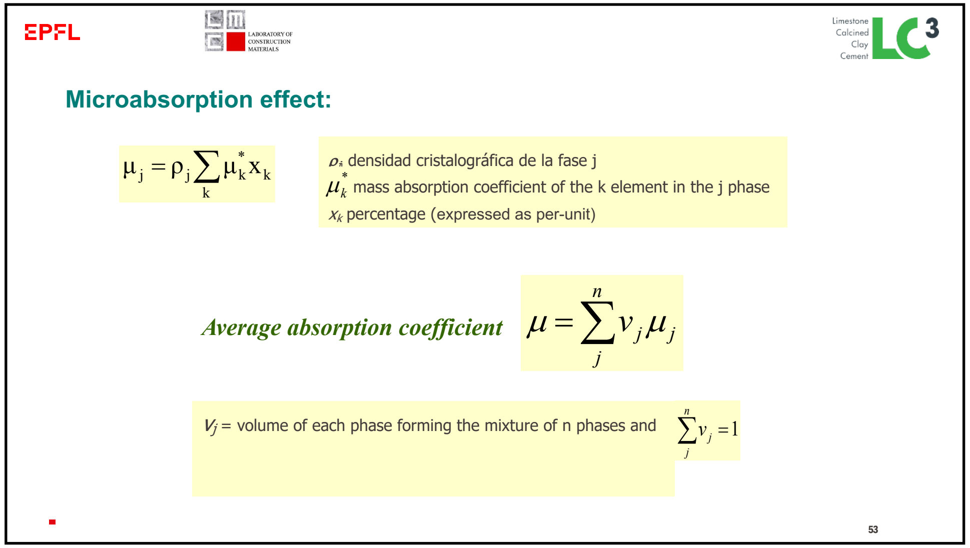

Microabsorption effect:

$$\mu_j = \rho_j \sum_k \mu_k^* x_k$$

ρ_j densidad cristalográfica de la fase j
μ_k^* mass absorption coefficient of the k element in the j phase
x_k percentage (expressed as per-unit)

Average absorption coefficient $$\mu = \sum_j^n v_j \mu_j$$

V_j = volume of each phase forming the mixture of n phases and $\sum_j^n v_j = 1$

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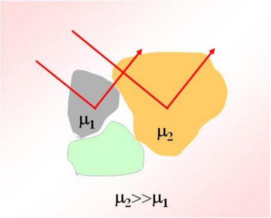
Micro-Absorption takes place in those samples with phases with different absorption coefficients between them and between the average absorption coefficient of the mixture

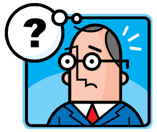
➢Overestimation of the compound with small μ and particle size

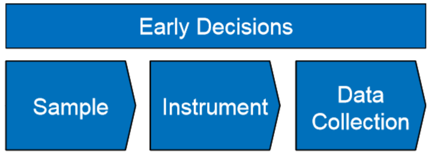
➢Underestimation of the compound with large μ and particle size



BRINDLEY CORRECTION

MILLING LOOK { contamination
amorphisation





- Early decisions:
  - What are the sample properties?
  - What data quality is necessary?
  - What instrument and measurement parameters to use?

The choice of the optimum instrument configuration must consider the aim of the experiment as well as specific sample properties

optimization:

- ☐ **low diffraction background**
- ☐ **maximum resolution of peaks**

{
- ❑Slits, mask
- ❑Soller
- ❑Mirrors and monochromators
- ❑Filter

compromise between measurement time and data quality

Data collection for an appropriate pattern

PARAMETERS TO CONSIDER (check list):

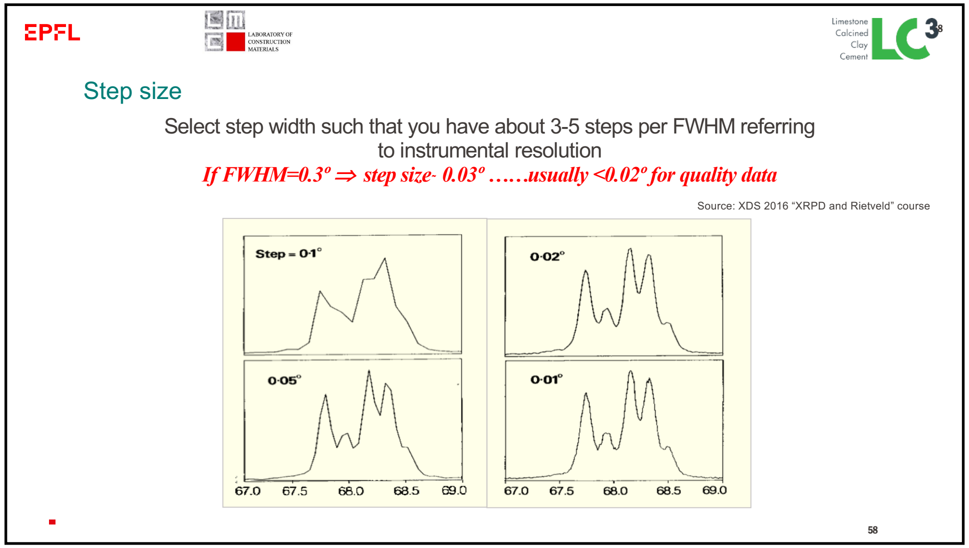
1.- Radiation source and geometry (Start and end angle)

2.- Step size

3.- Counting time

4.- Sample preparation

"Although the physical nature of a specimen from which the X-ray powder-diffraction data are collected is seemingly simple, sample preparation and data collection are generally the source of most of the serious problems with accurate X-ray diffraction analysis"



Step size

Select step width such that you have about 3-5 steps per FWHM referring to instrumental resolution

If FWHM=0.3° ⇒ step size- 0.03° ……usually <0.02° for quality data

Source: XDS 2016 “XRPD and Rietveld” course

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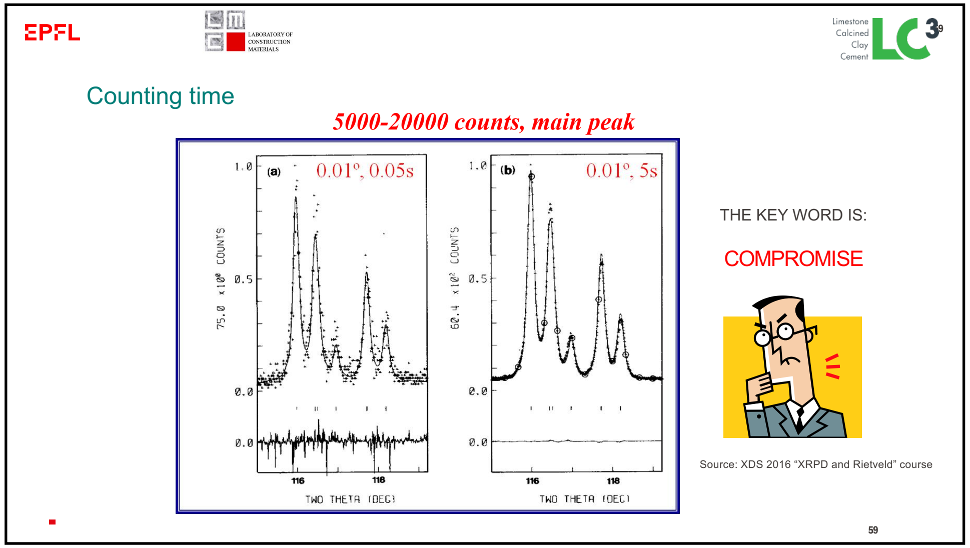

Counting time

5000-20000 counts, main peak

THE KEY WORD IS:

COMPROMISE

Source: XDS 2016 “XRPD and Rietveld” course

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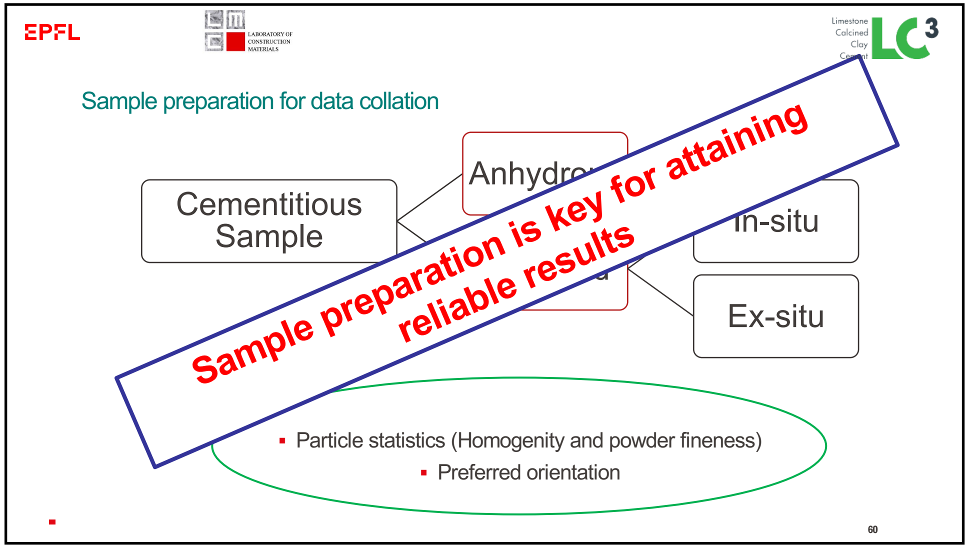

Sample preparation for data collation

Sample preparation is key for attaining reliable results

- Particle statistics (Homogenity and powder fineness)
- Preferred orientation

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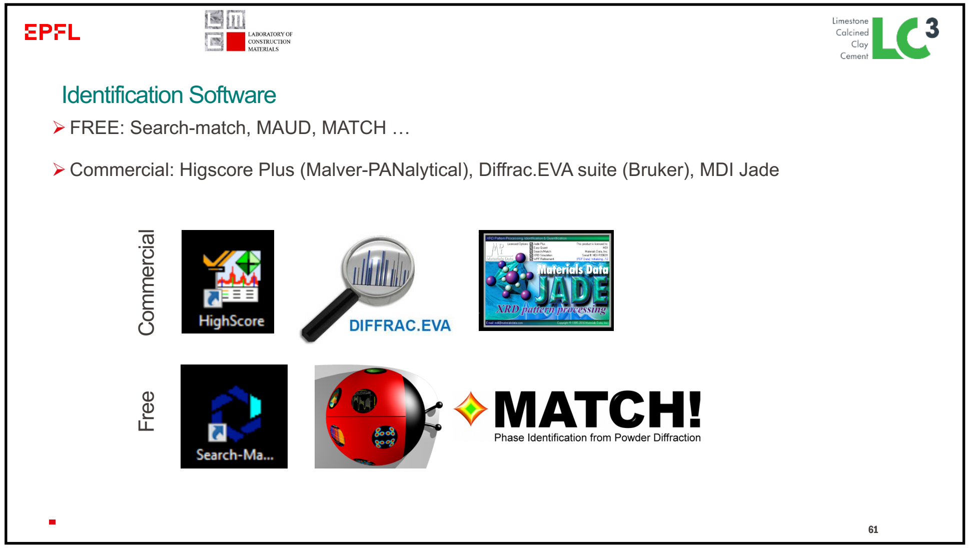

Identification Software

- FREE: Search-match, MAUD, MATCH …
- Commercial: Higscore Plus (Malver-PANalytical), Diffrac.EVA suite (Bruker), MDI Jade

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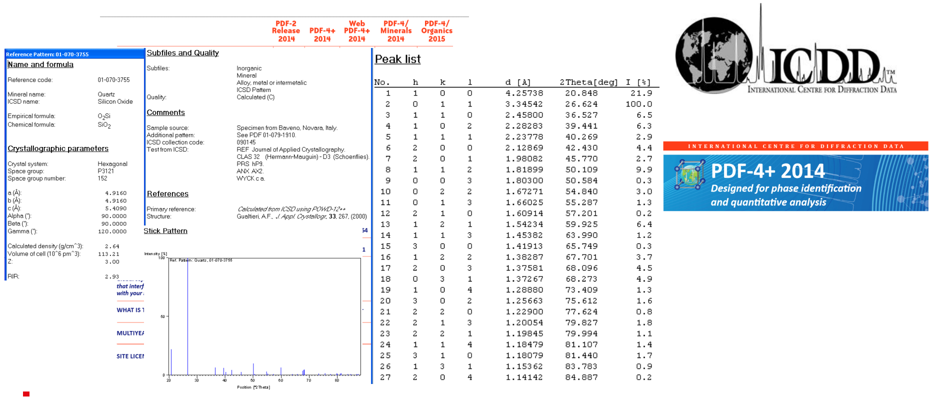
Crystallographic pattern databases



PDF-2 Release 2014 | PDF-4+ 2014 | Web PDF-4+ 2014 | PDF-4/ Minerals 2014 | PDF-4/ Organics 2015

Reference Pattern: 01-070-3755

Name and formula

Reference code: 01-070-3755

Mineral name: Quartz
ICSD name: Silicon Oxide

Empirical formula: O_2Si
Chemical formula: SiO_2

Crystallographic parameters

Crystal system: Hexagonal
Space group: P3121
Space group number: 152

a (Å): 4.9160
b (Å): 4.9160
c (Å): 5.4090
Alpha (°): 90.0000
Beta (°): 90.0000
Gamma (°): 120.0000

Calculated density (g/cm^3): 2.64
Volume of cell (10^6 pm^3): 113.21
Z: 3.00

RIR: 2.93

Subfiles and Quality

Subfiles: Inorganic
Mineral
Alloy, metal or intermetalic
ICSD Pattern
Quality: Calculated (C)

Comments

Sample source: Specimen from Baveno, Novara, Italy.
Additional pattern: See PDF 01-079-1910.
ICSD collection code: 090145
Test from ICSD: REF Journal of Applied Crystallography.
CLAS 32 (Hermann-Mauguin) - D3 (Schoenflies).
PRS hP9.
ANX AX2.
WYCK c a.

References

Primary reference: *Calculated from ICSD using POWD-12++*
Structure: Gualtieri, A.F., *J. Appl. Crystallogr.*, **33**, 267, (2000)

Stick Pattern

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	0	0	4.25738	20.848	21.9
2	0	1	1	3.34542	26.624	100.0
3	1	1	0	2.45800	36.527	6.5
4	1	0	2	2.28283	39.441	6.3
5	1	1	1	2.23778	40.269	2.9
6	2	0	0	2.12869	42.430	4.4
7	2	0	1	1.98082	45.770	2.7
8	1	1	2	1.81899	50.109	9.9
9	0	0	3	1.80300	50.584	0.3
10	0	2	2	1.67271	54.840	3.0
11	0	1	3	1.66025	55.287	1.3
12	2	1	0	1.60914	57.201	0.2
13	1	2	1	1.54234	59.925	6.4
14	1	1	3	1.45382	63.990	1.2
15	3	0	0	1.41913	65.749	0.3
16	1	2	2	1.38287	67.701	3.7
17	2	0	3	1.37581	68.096	4.5
18	0	3	1	1.37267	68.273	4.9
19	1	0	4	1.28880	73.409	1.3
20	3	0	2	1.25663	75.612	1.6
21	2	2	0	1.22900	77.624	0.8
22	2	1	3	1.20054	79.827	1.8
23	2	2	1	1.19845	79.994	1.1
24	1	1	4	1.18479	81.107	1.4
25	3	1	0	1.18079	81.440	1.7
26	1	3	1	1.15362	83.783	0.9
27	2	0	4	1.14142	84.887	0.2

INTERNATIONAL CENTRE FOR DIFFRACTION DATA

PDF-4+ 2014

Designed for phase identification and quantitative analysis

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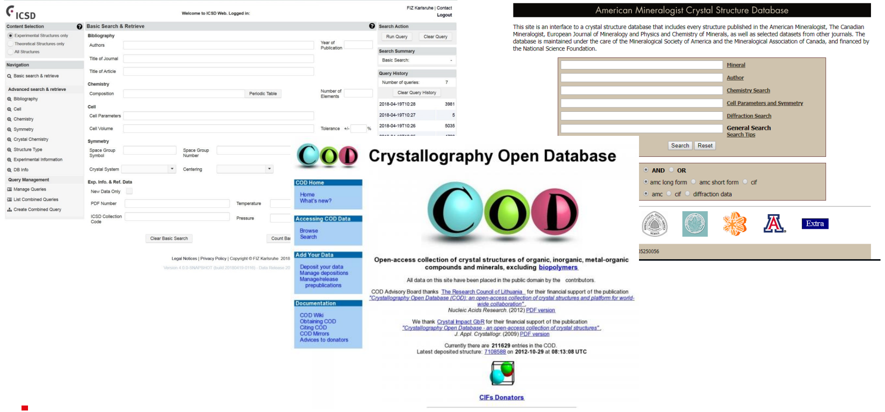
Crystallographic pattern databases



2018-04-19T10:28	3981
2018-04-19T10:27	5
2018-04-19T10:26	5035

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Version 4.0.0-SNAPSHOT (build 20180419-0116) - Data Release 20

American Mineralogist Crystal Structure Database

This site is an interface to a crystal structure database that includes every structure published in the American Mineralogist, The Canadian Mineralogist, European Journal of Mineralogy and Physics and Chemistry of Minerals, as well as selected datasets from other journals. The database is maintained under the care of the Mineralogical Society of America and the Mineralogical Association of Canada, and financed by the National Science Foundation.

)5250056

Crystallography Open Database

Open-access collection of crystal structures of organic, inorganic, metal-organic compounds and minerals, excluding biopolymers

All data on this site have been placed in the public domain by the contributors.

COD Advisory Board thanks The Research Council of Lithuania for their financial support of the publication *"Crystallography Open Database (COD): an open-access collection of crystal structures and platform for world-wide collaboration"*, *Nucleic Acids Research*. (2012) PDF version

We thank Crystal Impact GbR for their financial support of the publication *"Crystallography Open Database - an open-access collection of crystal structures"*, *J. Appl. Crystallogr.* (2009) PDF version

Currently there are **211629** entries in the COD.
Latest deposited structure: 7108588 on **2012-10-29** at **08:13:08 UTC**

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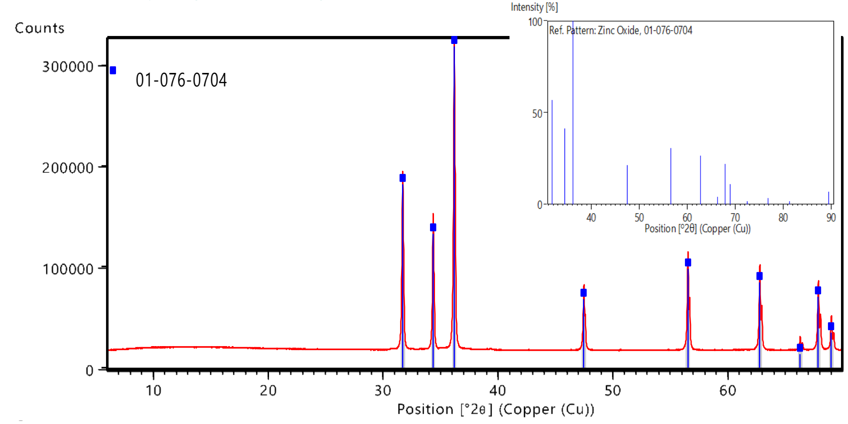
Qualitative analysis (Identification)



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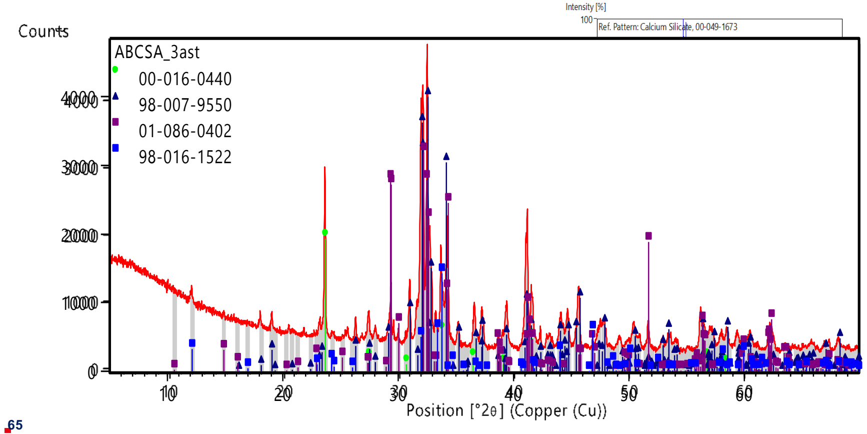
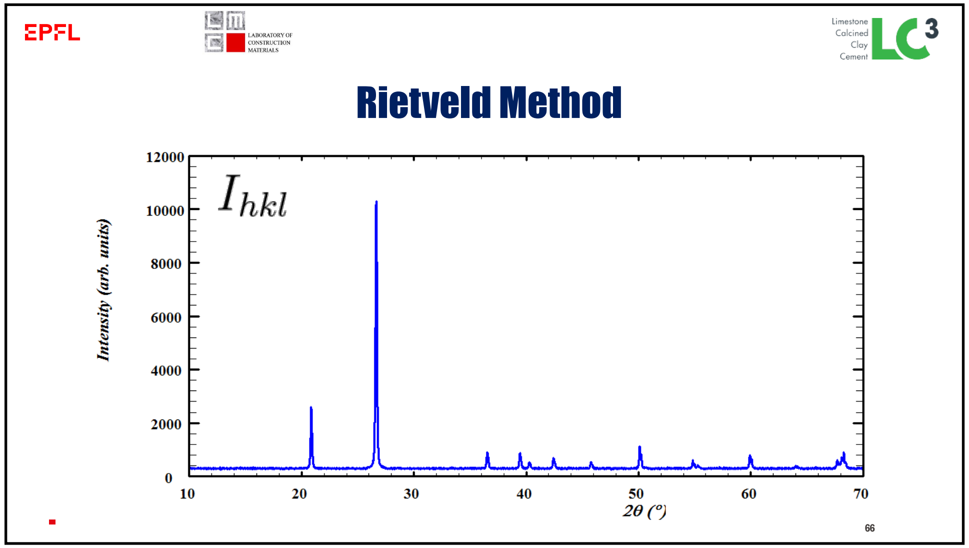
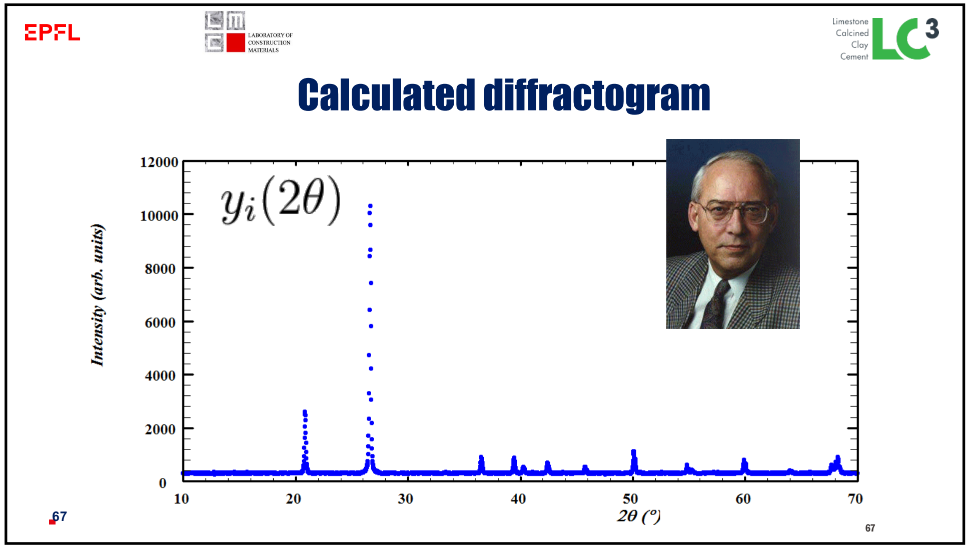
Qualitative analysis (Identification)



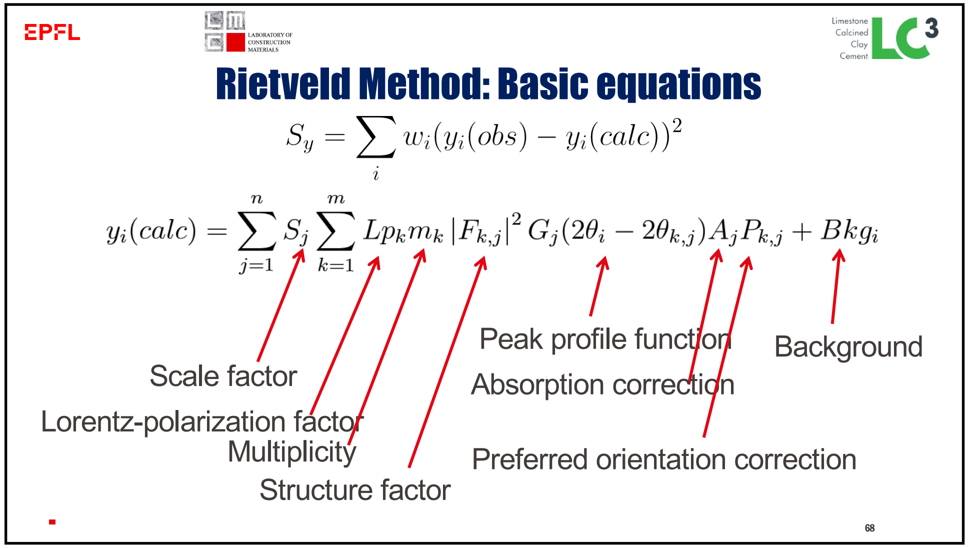
65



Rietveld Method



Calculated diffractogram



Rietveld Method: Basic equations

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

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

Scale factor

Lorentz-polarization factor

Multiplicity

Structure factor

Peak profile function

Absorption correction

Preferred orientation correction

Background

Scale factor

$$S_\alpha = K_e \frac{W_\alpha}{\rho_\alpha V_\alpha^2 \mu_m} = K_e \frac{W_\alpha}{(ZMV)_\alpha \mu_m}$$

To eliminate K_e, it is necessary a restriction:
The sum of W's must be 100%

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

The Rietveld method has to be regarded as SEMI-QUANTITATIVE

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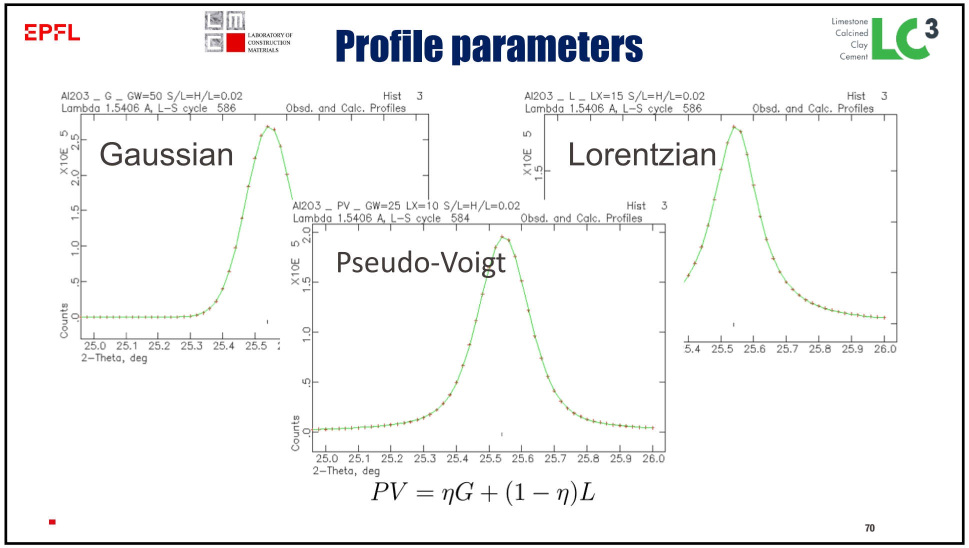

Profile parameters

$$PV = \eta G + (1-\eta)L$$

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Profile parameters

Gaussian (Cagliotti equation):

$$FWHM^2 = Utan^2\theta + Vtan\theta + W + \frac{P}{cos^2\theta}$$

Lorentzian:

$$FWHM^2 = Xtan\theta + \frac{Y}{cos\theta}$$

NOTE: Some programs use the same FWHM for both profile functions!

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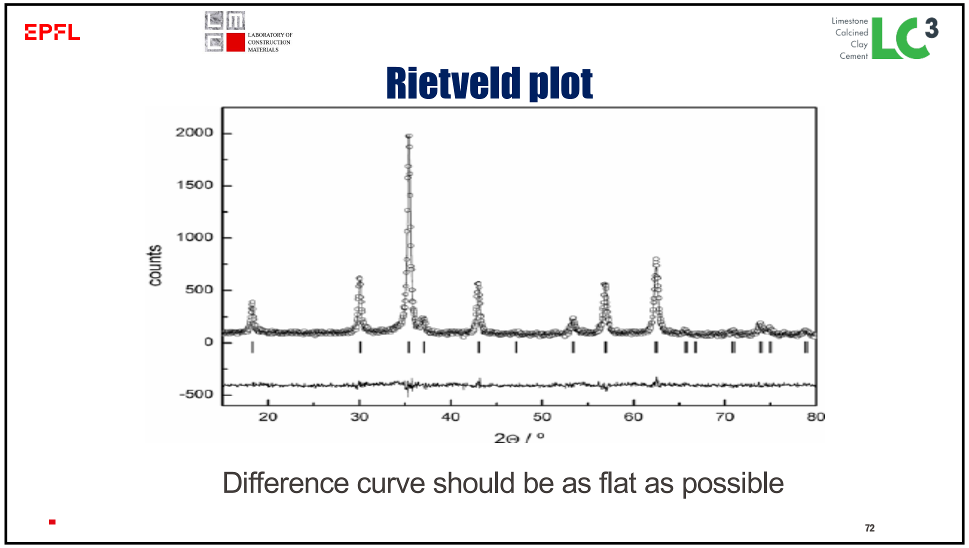

Rietveld plot

Difference curve should be as flat as possible

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Agreement indices

$$R_{wp} = 100\sqrt{\frac{\sum_{i=1}^{n} w_i\,(y_i(obs) - y_i(calc))^2}{\sum_{i=1}^{n} w_i y_i^2(obs)}}$$

$$R_{exp} = 100\sqrt{\frac{N-P+C}{\sum_{i=1}^{n} w_i y_i^2(obs)}}$$

$$R_P = 100\frac{\sum_{i=1}^{n} |y_i(obs) - y_i(calc)|}{\sum_{i=1}^{n} |y_i(obs)|}$$

$$R_F = 100\frac{\sum_{khl} |F_{hkl}(obs) - F_{hkl}(calc)|}{\sum_{hkl} |F_{hkl}(obs)|}$$

$$R_B = 100\frac{\sum_{khl} |I_{hkl}(obs) - I_{hkl}(calc)|}{\sum_{hkl} |I_{hkl}(obs)|}$$

$$GoF = \chi^2 = \left(\frac{R_{wp}}{R_{exp}}\right)^2$$

These values should be as low as possible, but...
...this is **NOT** the aim of the method!!

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Usual refiment parameters

- *Zero Shift or Sample displacement*
  - Sample displacement
- *Background*
  - Using a polynomial, lineal or chebyshev model
- *Scaling*
  - Phase fraction
- *Unit cell - ρV^2*
  - Adjust of the lattice parameters
- *Profile*
  - Modify the peak shape to model your sample
  - Strain, crystal size, etc
- *Preferred Orientation (PO), asymmetry, microabsorption, atom position, occupancies, etc…*

Quantification of Non-diffracting materials (ACn)

➢Internal Standard

By the addition of a well known crystalline material in a specific amount.

➢External Standard

By a comparison between a well known crystalline material measured (separately) at the same conditions of the sample.

➢ Partial Or No Known Crystal Structure (PONKCS) Method

By previous individual amorphous phase calibration as an "standard phase". Different amorphous phases can be quantified separately.

Internal standard

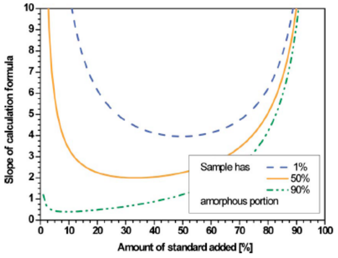
$$\text{ACn, \%} = \frac{1 - W_S / R_S}{100 - W_S} \times 10^4$$

Select a standard

- ✓ Similar particle size of the test sample
- ✓ Mass absorption coefficient (MAC) similar to the test sample

Amount of standard

Depends on the amorphous amount that it can be theoretically determined (Westphal et al 2009)



External standard

#.- **Avoid complications** from mixing an internal standard with the sample.

#.- Useful for reflection geometry diffractometer (Bragg-Brentano).

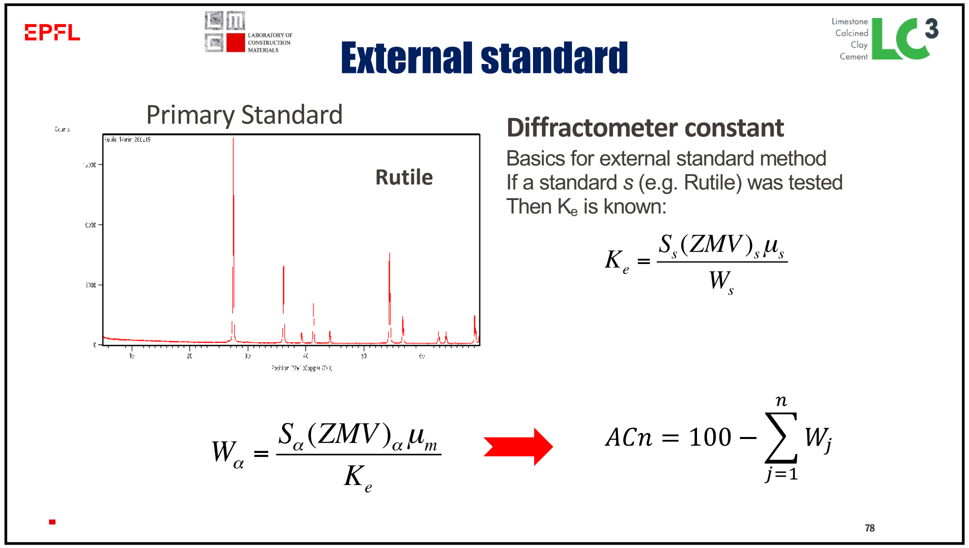
#.- Consists in determine the diffractometer constant, Ke (=G), with an appropriate standard.

#.- The mass attenuation coefficient of the sample is needed, μs. This must be independently determined, for example by X-ray fluorescence spectrometry.

DRAWBACK

#.- Any change on diffractometer configuration/conditions, force you check again the set-up.

#.- All the time, requires the **recording of two patterns** in identical diffractometer configuration/condition.



External standard

Diffractometer constant

Basics for external standard method
If a standard *s* (e.g. Rutile) was tested
Then K_e is known:

$$K_e = \frac{S_s (ZMV)_s \mu_s}{W_s}$$

$$W_\alpha = \frac{S_\alpha (ZMV)_\alpha \mu_m}{K_e} \quad \rightarrow \quad ACn = 100 - \sum_{j=1}^{n} W_j$$

PONCKS Method

- Calibration of a phase of unknown structure:

Mix of the amorphous phase α and a standard (weight fractions known)

$$W_\alpha = W_s \frac{S_\alpha \rho_\alpha V_\alpha^2}{S_s \rho_s V_s^2}$$

$$\Downarrow$$

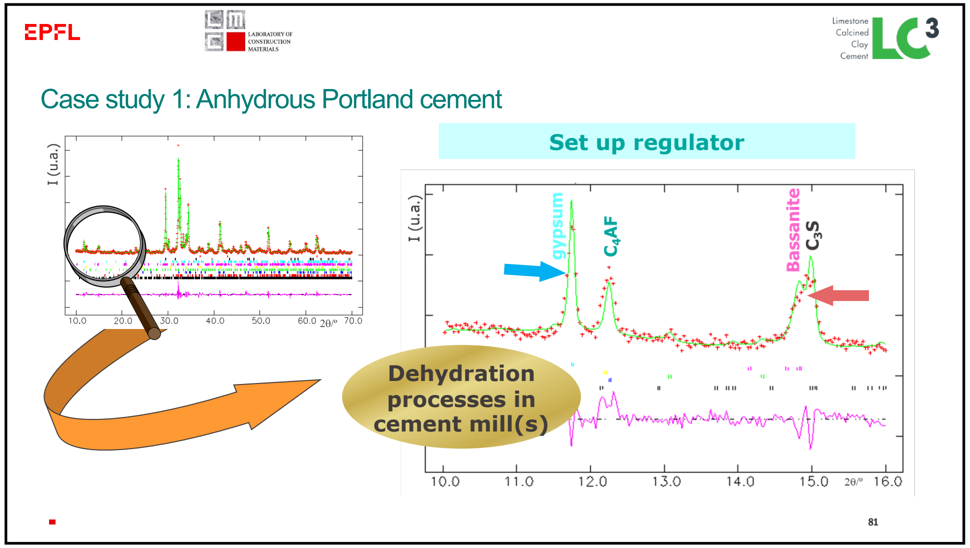
Peak phase calibration factor

$$\boxed{\rho_\alpha V_\alpha^2} = \frac{W_\alpha}{W_s} \frac{S_s \rho_s V_s^2}{S_\alpha}$$

In unknown mixes the refined amorphous phase scale factor can then be recalculated into a weight fraction

Practical examples

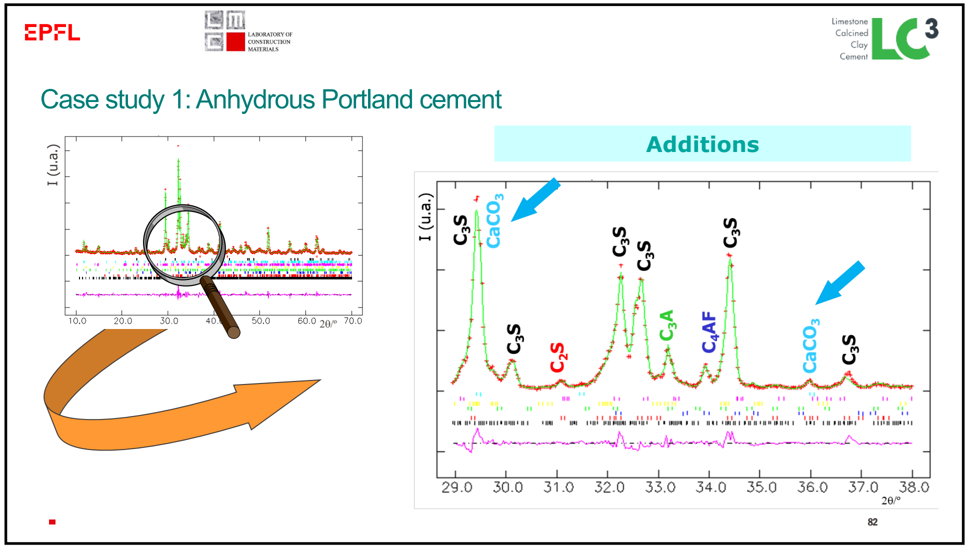
- 1. Ordinary Portland cement (anhydrous)
- 2. Hydrated cement paste
  - General refinement approach
  - Renormalization of results
- 3. Hydrated blended cement pastes
  - 3a: Anhydrous blended cements
  - 3b: Hydrated LC^3 cement paste
  - 3c: Hydrated slag cement paste
- 4. In-situ hydration studies
  - 4a: Dopant effect on C_3S hydration
  - 4b: PSD on hydration of C_3S/C_3A
- Summary



Case study 1: Anhydrous Portland cement

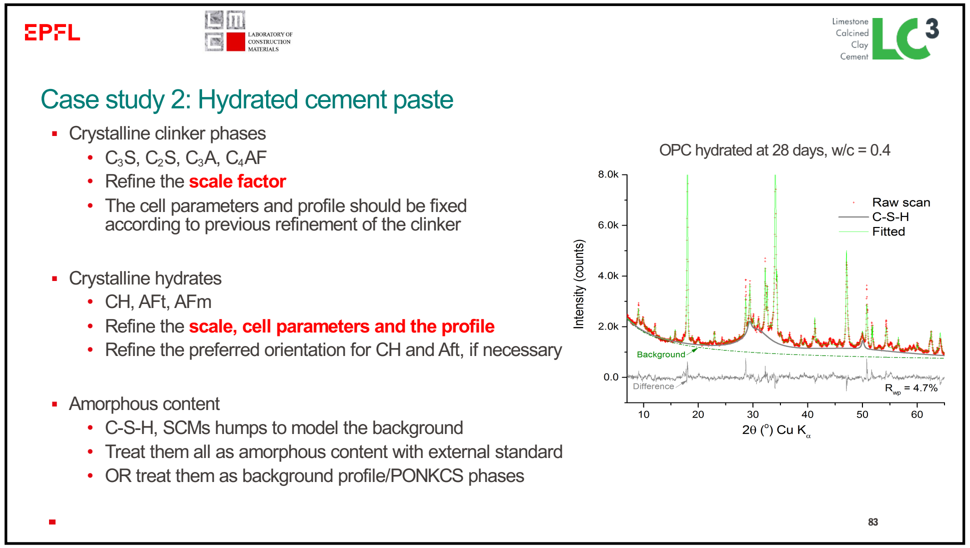
Set up regulator

Dehydration processes in cement mill(s)



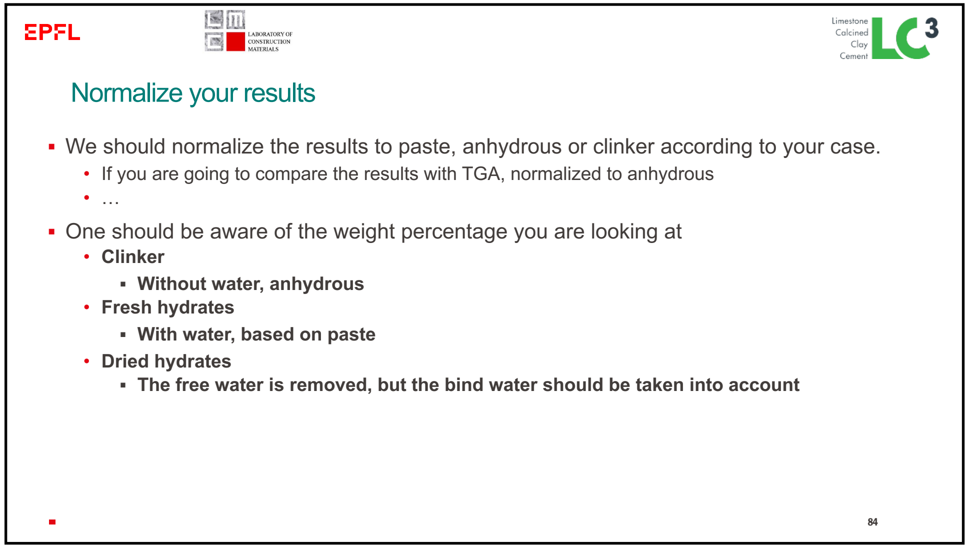
Case study 1: Anhydrous Portland cement

Additions



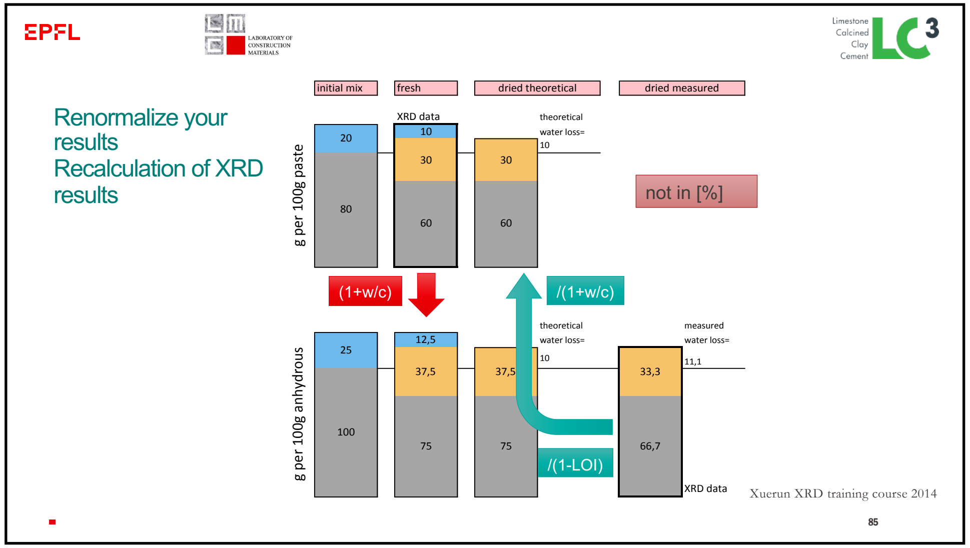
Case study 2: Hydrated cement paste

- Crystalline clinker phases
  - C_3S, C_2S, C_3A, C_4AF
  - Refine the **scale factor**
  - The cell parameters and profile should be fixed according to previous refinement of the clinker
- Crystalline hydrates
  - CH, AFt, AFm
  - Refine the **scale, cell parameters and the profile**
  - Refine the preferred orientation for CH and Aft, if necessary
- Amorphous content
  - C-S-H, SCMs humps to model the background
  - Treat them all as amorphous content with external standard
  - OR treat them as background profile/PONKCS phases



Normalize your results

- We should normalize the results to paste, anhydrous or clinker according to your case.
  - If you are going to compare the results with TGA, normalized to anhydrous
  - …
- One should be aware of the weight percentage you are looking at
  - **Clinker**
    - **Without water, anhydrous**
  - **Fresh hydrates**
    - **With water, based on paste**
  - **Dried hydrates**
    - **The free water is removed, but the bind water should be taken into account**



Renormalize your results
Recalculation of XRD results

Xuerun XRD training course 2014

Renormalize your results
Recalculation formulas

- fresh specimen (disc):
  - per 100g paste m=mXRD
  - per 100g anhydrous m=mXRD·(1+w/c)
- dried specimen (powder):
  - per 100g paste m=mXRD*(1+ H_2O_{bound})/(1+w/c)
  - per 100g anhydrous m=mXRD*(1+ H_2O_{bound})

H_2O_{bound} on ignited basis

- dried specimen (powder):
  - per 100g paste m=mXRD/[(1-H_2O_{bound})/(1+w/c)]
  - per 100g anhydrous m=mXRD/(1- H_2O_{bound})

H_2O_{bound} on dried basis

PC hydrates	Content (g/ 100g fresh paste)						DoH (%)
Ages (d)	Clinker	CH		AFt	Free water(TG)	Total Am.	Clinker
0	62.5	0	TG	0	28.6	0	0
1	29.2	8.4	10.7	7.7	17.4	52.7	53.3
3	23.7	10.9	12.3	10.2	15.7	53.2	62.1
28	16.3	13.5	14.3	6.8	13.3	61.3	73.9

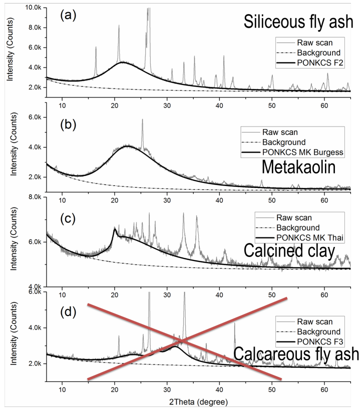
- Portlandite (CH) and ettringite (AFt) content
- Degree of hydration (DoH) for clinker
  - Hydration of the clinker phases
  - Thermodynamic modeling (GEMS)
  - Mass balance calculations using BSE-EDS
  - Other modeling

Case 3: Hydrated blended cement pastes

- Characteristic humps of amorphous materials
  - E.g.,Siliceous fly ash, metakaolin, calcined clay, C-S-H
  - Raw materials needed to characterize the amorphous humps
    - The calibration and the treatment of the background is the key
    - The fitted amorphous humps from raw materials can be employed to model the humps as background in unknow samples
- PONKCS method
  (Partial Or No Known Crystal Structure)
  - For quantification of specific amorphous phases
  - For amorphous phases with characteristic 'hump', $\rho_\alpha V_\alpha^2$ is unknown (no cell, no crystal structure), but it can be calibrated experimentally and then used for quantification:

$$\rho_{ponkcs} V_{ponkcs}^2 = (K_e w_{ponkcs})/(\mu_m S_{ponkcs})$$

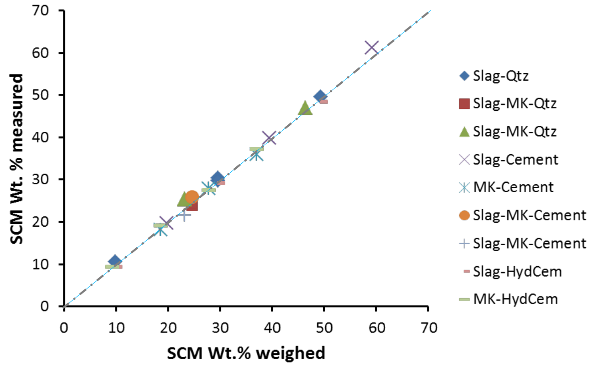
$$W_\alpha = \frac{S_\alpha (\rho V^2)_\alpha \mu_m}{K_e}$$

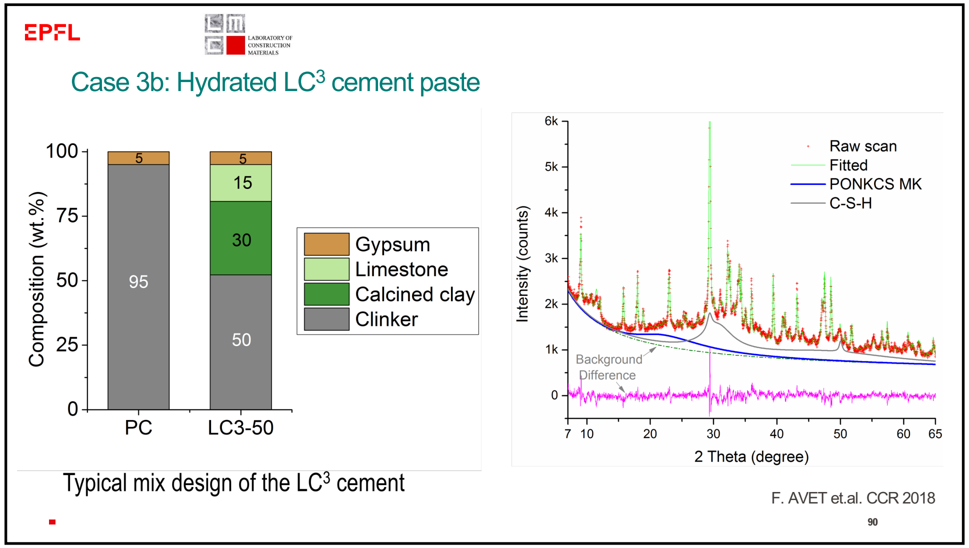


(Scarlett & Madsen, 2006)

Case 3a: Anhydrous blended cements

- **PONKCS applied to blended cements – model mixes (Snellings et al., 2014)**





EPFL

LABORATORY OF CONSTRUCTION MATERIALS

Case 3b: Hydrated LC^3 cement paste

Typical mix design of the LC^3 cement

F. AVET et.al. CCR 2018

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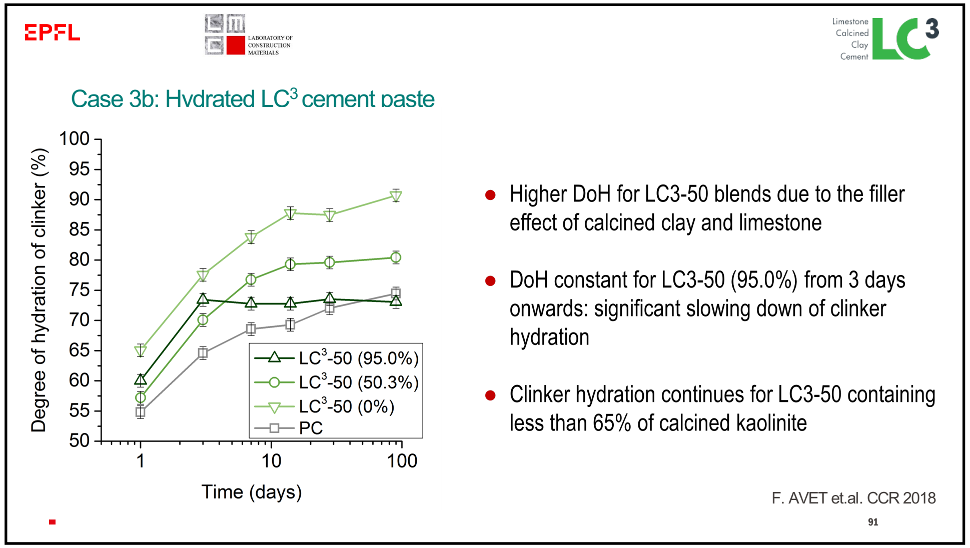

EPFL

LABORATORY OF CONSTRUCTION MATERIALS

Limestone Calcined Clay Cement LC^3

Case 3b: Hydrated LC^3 cement paste

- Higher DoH for LC3-50 blends due to the filler effect of calcined clay and limestone
- DoH constant for LC3-50 (95.0%) from 3 days onwards: significant slowing down of clinker hydration
- Clinker hydration continues for LC3-50 containing less than 65% of calcined kaolinite

F. AVET et.al. CCR 2018

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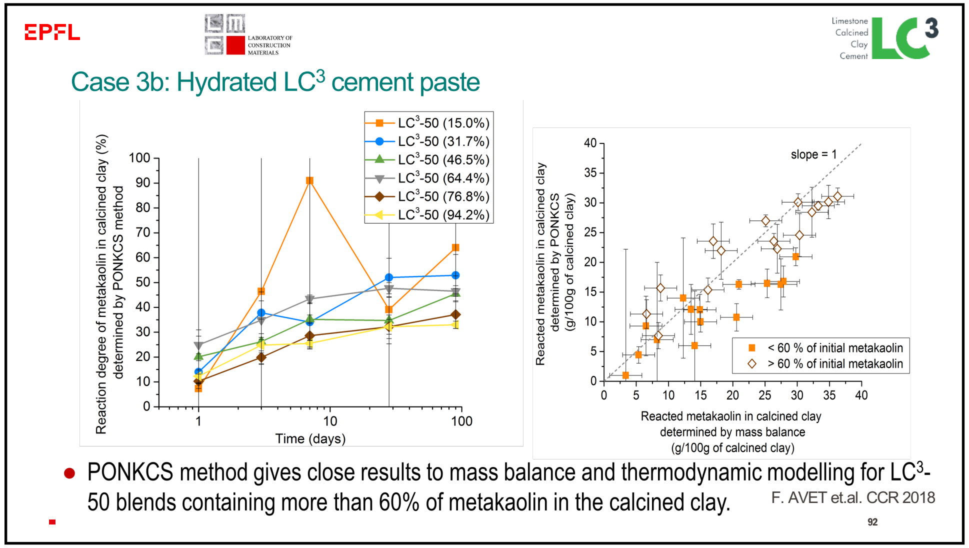

EPFL

LABORATORY OF CONSTRUCTION MATERIALS

Limestone Calcined Clay Cement LC^3

Case 3b: Hydrated LC^3 cement paste

- PONKCS method gives close results to mass balance and thermodynamic modelling for LC^3-50 blends containing more than 60% of metakaolin in the calcined clay.

F. AVET et.al. CCR 2018

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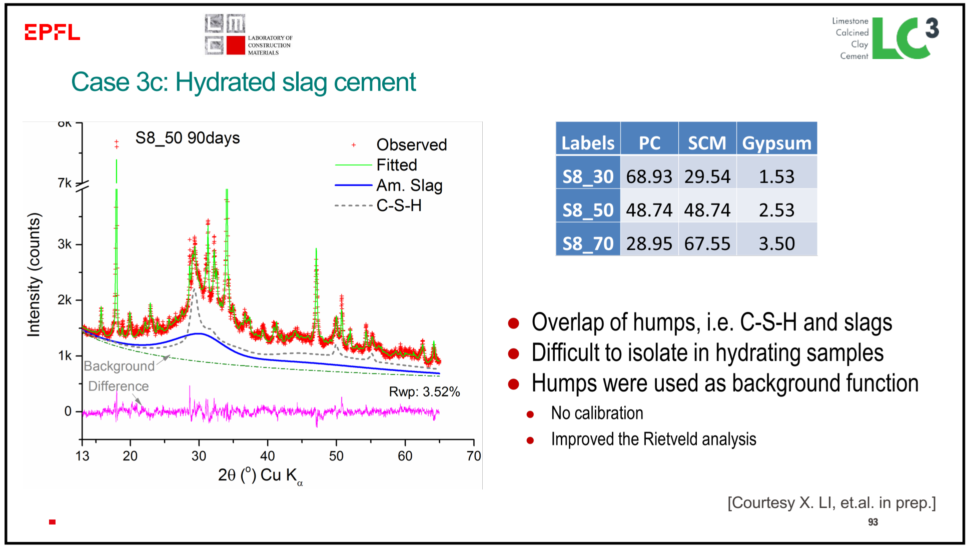

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LABORATORY OF CONSTRUCTION MATERIALS

Limestone Calcined Clay Cement LC^3

Case 3c: Hydrated slag cement

Labels	PC	SCM	Gypsum
S8_30	68.93	29.54	1.53
S8_50	48.74	48.74	2.53
S8_70	28.95	67.55	3.50

- Overlap of humps, i.e. C-S-H and slags
- Difficult to isolate in hydrating samples
- Humps were used as background function
  - No calibration
  - Improved the Rietveld analysis

[Courtesy X. LI, et.al. in prep.]

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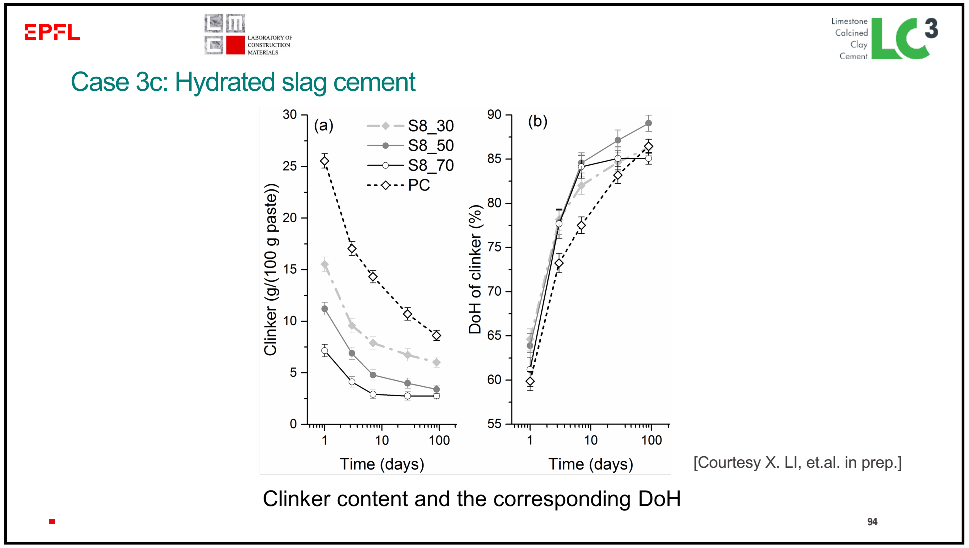

Case 3c: Hydrated slag cement

[Courtesy X. LI, et.al. in prep.]

Clinker content and the corresponding DoH

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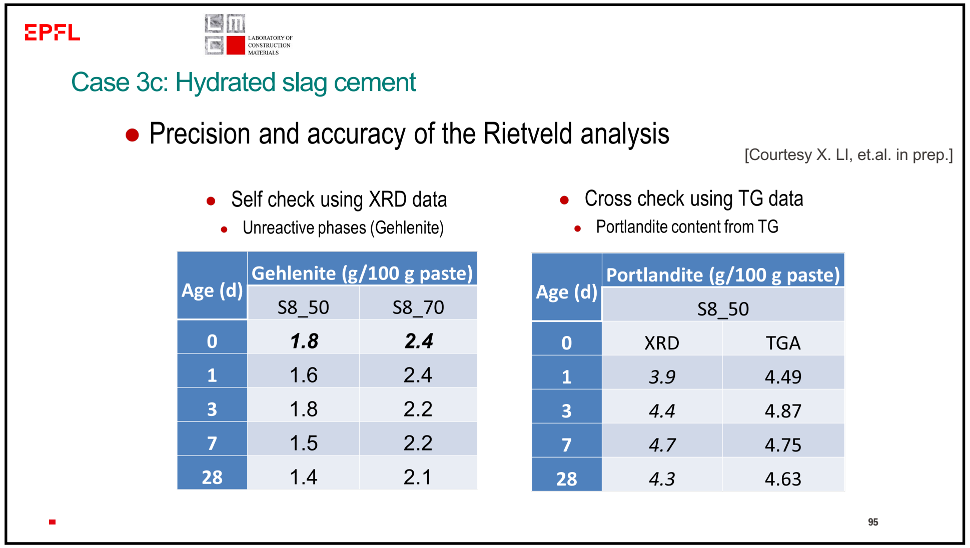

Case 3c: Hydrated slag cement

- Precision and accuracy of the Rietveld analysis

[Courtesy X. LI, et.al. in prep.]

- Self check using XRD data
  - Unreactive phases (Gehlenite)

Age (d)	Gehlenite (g/100 g paste)	
	S8_50	S8_70
0	***1.8***	***2.4***
1	1.6	2.4
3	1.8	2.2
7	1.5	2.2
28	1.4	2.1

- Cross check using TG data
  - Portlandite content from TG

Age (d)	Portlandite (g/100 g paste)	
	S8_50	
0	XRD	TGA
1	*3.9*	4.49
3	*4.4*	4.87
7	*4.7*	4.75
28	*4.3*	4.63

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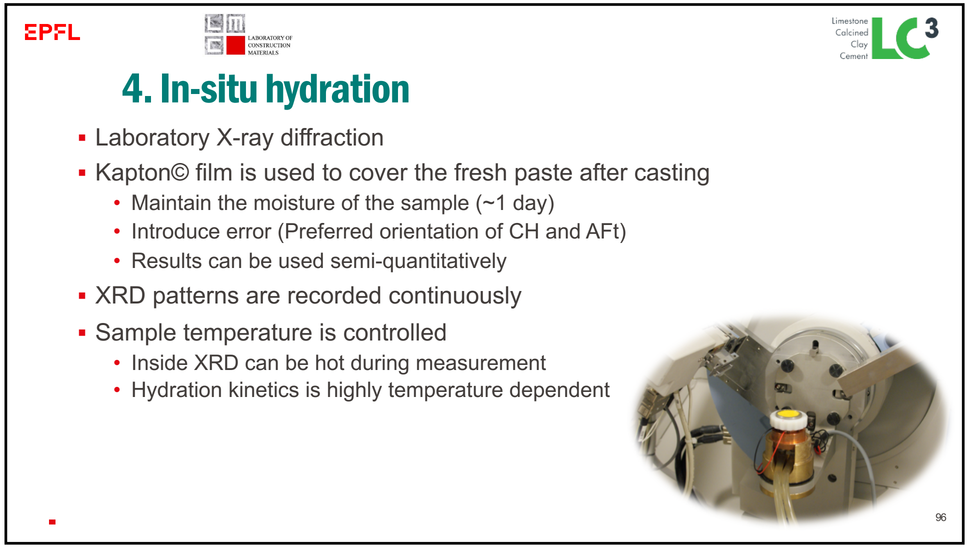

4. In-situ hydration

- Laboratory X-ray diffraction
- Kapton© film is used to cover the fresh paste after casting
  - Maintain the moisture of the sample (~1 day)
  - Introduce error (Preferred orientation of CH and AFt)
  - Results can be used semi-quantitatively
- XRD patterns are recorded continuously
- Sample temperature is controlled
  - Inside XRD can be hot during measurement
  - Hydration kinetics is highly temperature dependent

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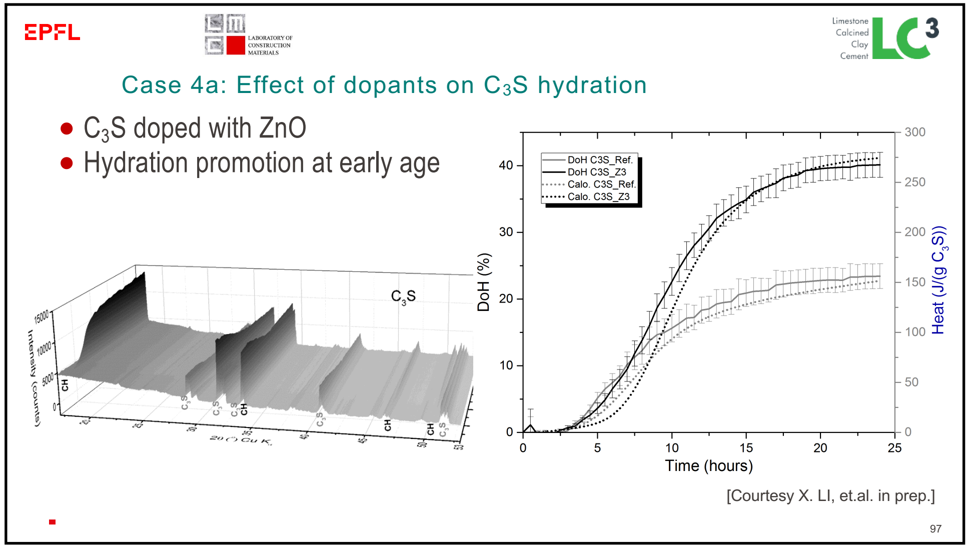

Case 4a: Effect of dopants on C_3S hydration

- C_3S doped with ZnO
- Hydration promotion at early age

[Courtesy X. LI, et.al. in prep.]

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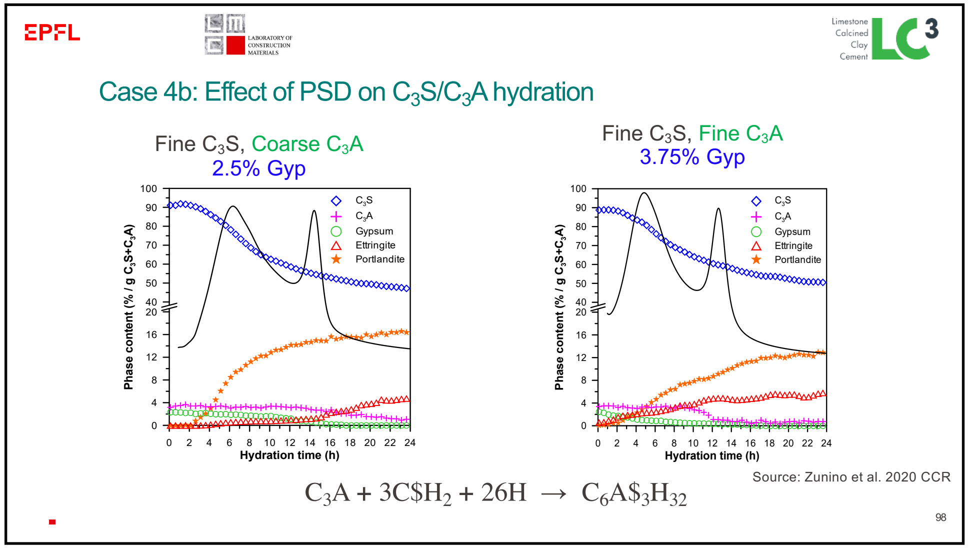


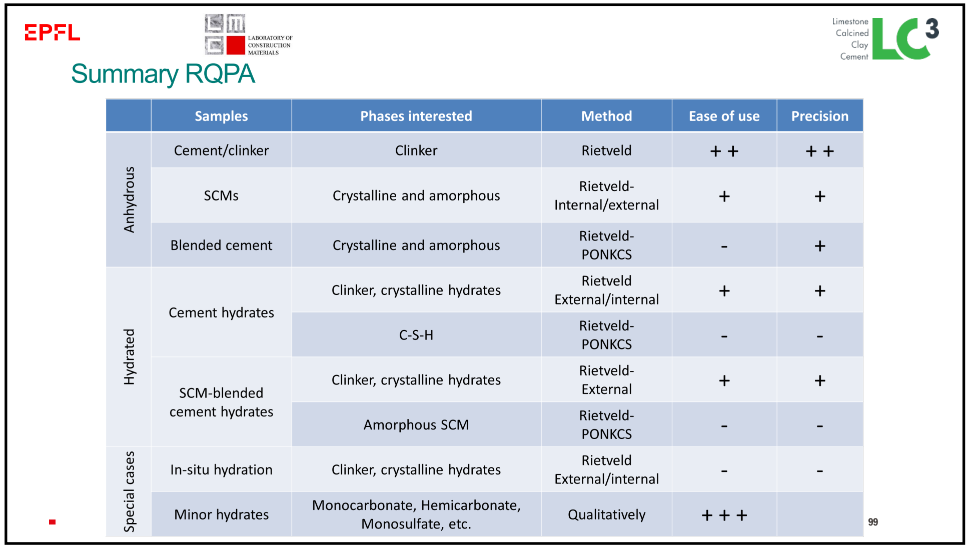
Case 4b: Effect of PSD on C_3S/C_3A hydration

Fine C_3S, Coarse C_3A
2.5% Gyp

Fine C_3S, Fine C_3A
3.75% Gyp

Source: Zunino et al. 2020 CCR

$$C_3A + 3C\$H_2 + 26H \rightarrow C_6A\$_3H_{32}$$



Summary RQPA

	Samples	Phases interested	Method	Ease of use	Precision
Anhydrous	Cement/clinker	Clinker	Rietveld	+ +	+ +
	SCMs	Crystalline and amorphous	Rietveld-Internal/external	+	+
	Blended cement	Crystalline and amorphous	Rietveld-PONKCS	-	+
Hydrated	Cement hydrates	Clinker, crystalline hydrates	Rietveld External/internal	+	+
		C-S-H	Rietveld-PONKCS	-	-
	SCM-blended cement hydrates	Clinker, crystalline hydrates	Rietveld-External	+	+
		Amorphous SCM	Rietveld-PONKCS	-	-
Special cases	In-situ hydration	Clinker, crystalline hydrates	Rietveld External/internal	-	-
	Minor hydrates	Monocarbonate, Hemicarbonate, Monosulfate, etc.	Qualitatively	+ + +