Advanced Topics in the Science and Technology of Concrete
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Microstructural Characterisation of Cementitious Materials Part 1

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So these lectures will be about microstructure. They are really based on this book, couple of years ago and the main intention here was to really provide a practical guide. So this is, students who are the people doing the experiments and so really it is very much focused on what to do and particularly what not to do in carrying out microstructural characterisation.

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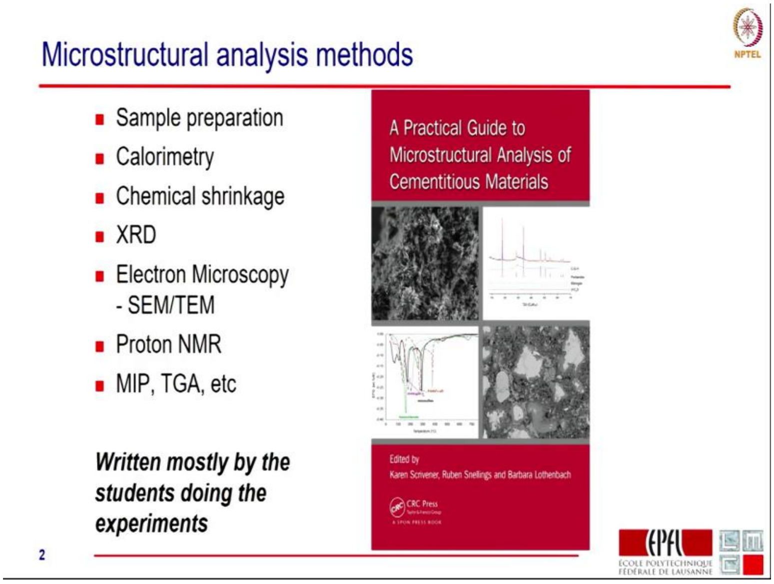

Microstructural analysis methods

- Sample preparation
- Calorimetry
- Chemical shrinkage
- XRD
- Electron Microscopy - SEM/TEM
- Proton NMR
- MIP, TGA, etc

Written mostly by the students doing the experiments

A Practical Guide to Microstructural Analysis of Cementitious Materials

Edited by
Karen Scrivener, Ruben Snellings and Barbara Lothenbach

CRC Press

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So I really strongly advise you to look in this book because it is much, much more there than I can possibly cover in these short lectures today.

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MOOC launching 18th September

- Includes lectures and practical demonstrations:
- SEM
- XRD
- Etc

And also we have another course which covers not only the structural characterisation but also lots of aspects of cement chemistry and you may also be interested to follow this from EPFL.

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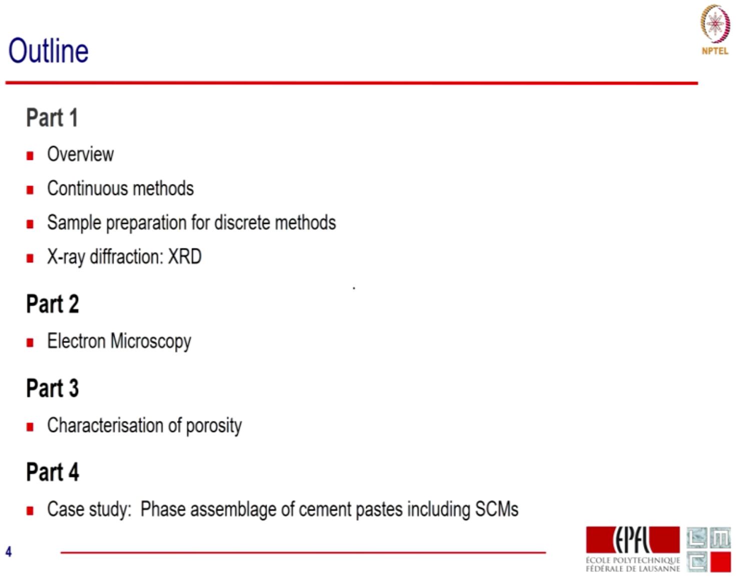

Outline

Part 1

- Overview
- Continuous methods
- Sample preparation for discrete methods
- X-ray diffraction: XRD

Part 2

- Electron Microscopy

Part 3

- Characterisation of porosity

Part 4

- Case study: Phase assemblage of cement pastes including SCMs

So microstructural characterisation I will have four parts in this. In this first part we will make an overview of what we are trying to do, talk about continuous methods, sample preparation and X-ray diffraction. In the second part I will talk about Electron Microscopy.

In the third part porosity and the fourth part which is very short will be a case study to show how we can bring all these techniques together to look at phase assemblages in cement paste.

So what are we trying to do? Well, the idea is that what is happening in cements and concrete is you have this hydration reaction. And during this hydration reaction the water reacts with the cement to give you hydrates.

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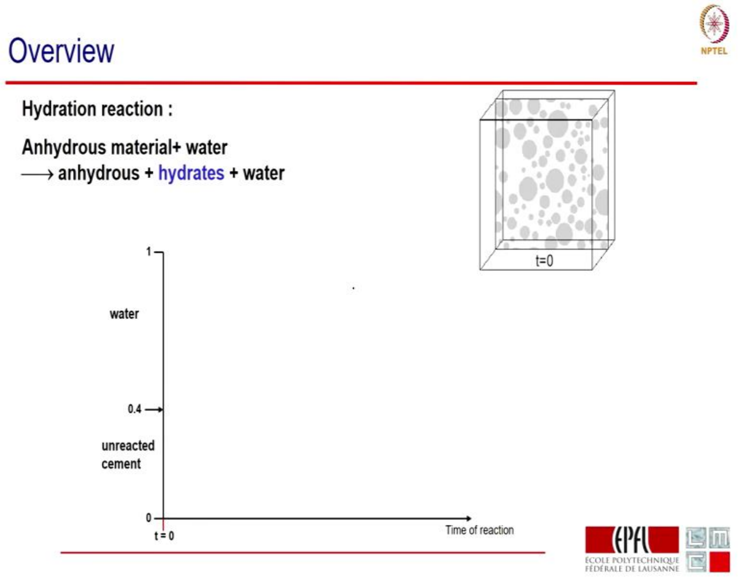

Overview

Hydration reaction :

Anhydrous material+ water

⟶ anhydrous + hydrates + water

So in a simple case of just C_3S or alite this could be the anhydrous phase reacting here and the hydrates forming calcium hydroxide and CSH. In the more complicated case where we have all the different phases in cement and then we have some other hydrate phases.

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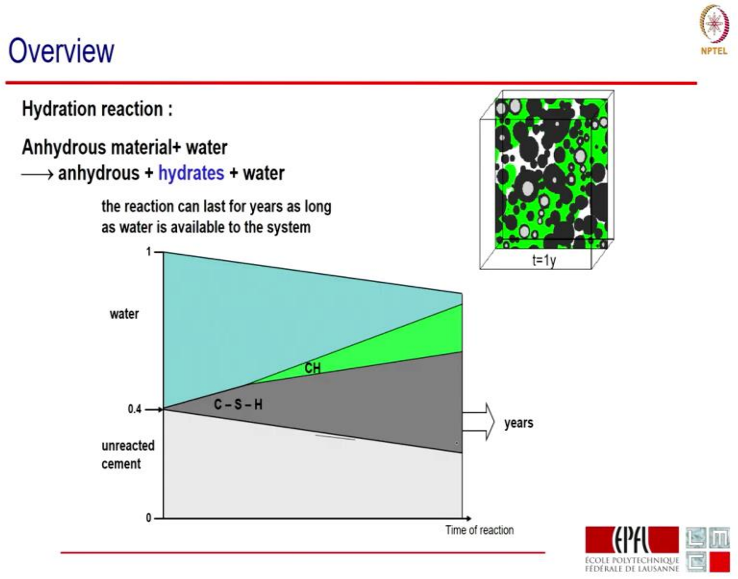

Overview

Hydration reaction :

Anhydrous material+ water

⟶ anhydrous + hydrates + water

the reaction can last for years as long as water is available to the system

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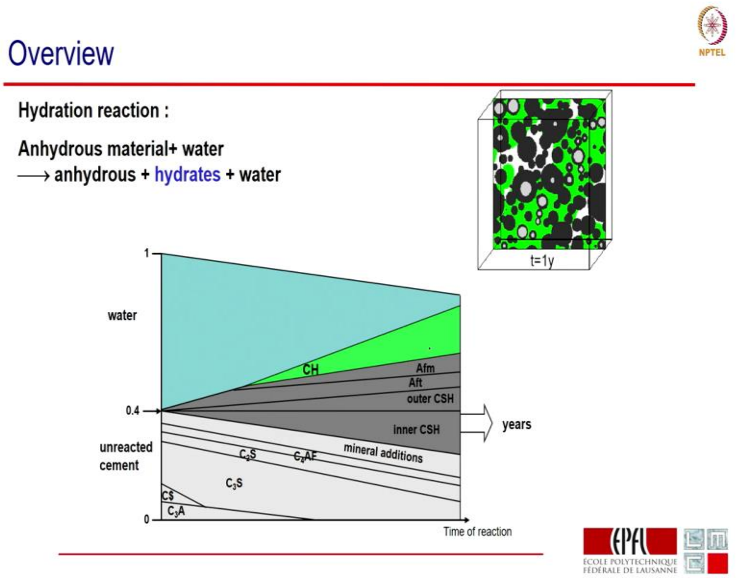

Overview

Hydration reaction :

Anhydrous material+ water

⟶ anhydrous + hydrates + water

And if you want to know more about these different hydrate phases then I advise you to look at the other course I mentioned earlier. They are all described in quite a lot of detail. During the reaction, in fact we have an overall decrease in volume, that’s to say the volume of the water plus the unreacted material is slightly larger than that of the hydrates that form. And for that reason if we have a sealed system then we will also form voids which are also pores. And this hydration reaction can really go on for many years although it is probably like 80 percent complete within the first 28 days. So that’s the hydration reaction.

Well, what were we interested in is the phase content and distribution, how the phase is formed, this kinetics etc, and then also microstructural characterisation can be used for looking at durability aspects, how is the microstructure affected by the environment, what are the mechanisms responsible for degradation?

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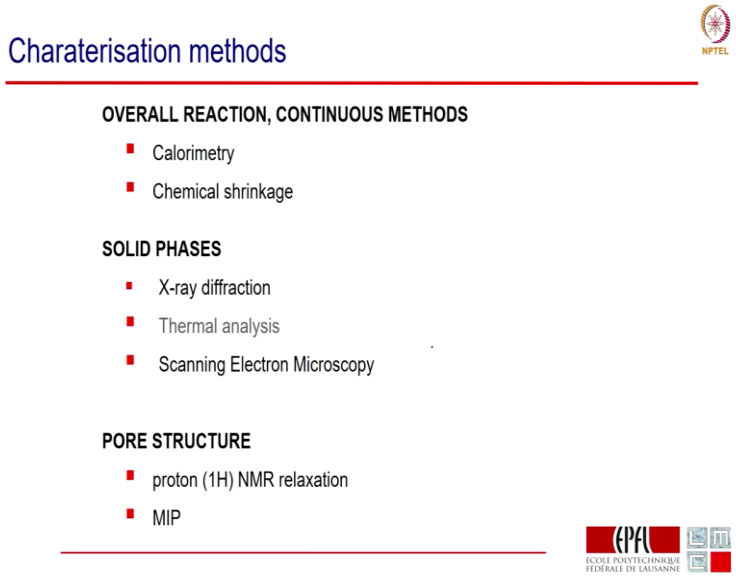

Charaterisation methods

OVERALL REACTION, CONTINUOUS METHODS

- Calorimetry
- Chemical shrinkage

SOLID PHASES

- X-ray diffraction
- Thermal analysis
- Scanning Electron Microscopy

PORE STRUCTURE

- proton (1H) NMR relaxation
- MIP

So in terms of characterisation methods we can take it in three parts. First of all we have methods that follow the overall reaction which I call continuous methods. Then we have methods which we can use to look at the solid phases, X-ray diffraction, thermal analysis, the scanning electron microscopy are the most common.

Unfortunately we only have time to talk about X-ray diffraction and scanning electron microscopy here. And then lastly we have techniques to look at the pore structure.

Now before going into the methods in more detail, a few general remarks. And first and foremost, you have to be aware that there is no such thing as a perfect measurement, not even in the most theoretical physics or the most practical physics can you have absolutely accurate measurements. Every measurement has an intrinsic error and you have to be aware of these.

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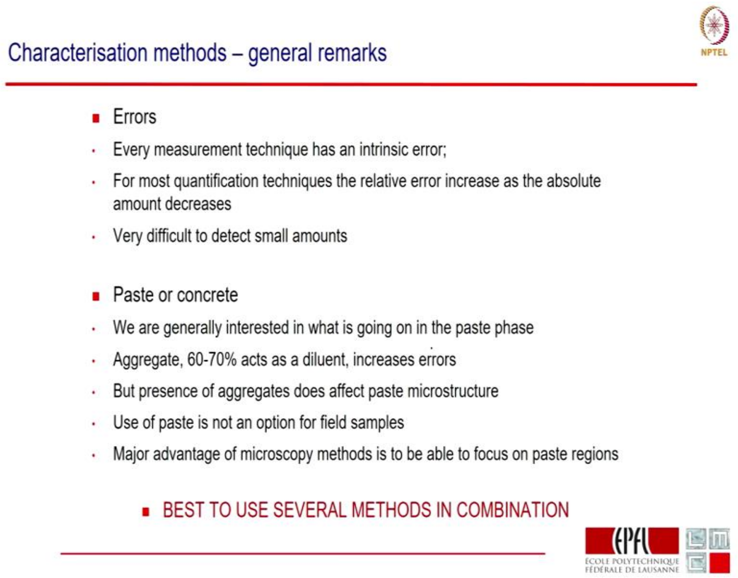

Characterisation methods – general remarks

- Errors
  - Every measurement technique has an intrinsic error;
  - For most quantification techniques the relative error increase as the absolute amount decreases
  - Very difficult to detect small amounts
- Paste or concrete
  - We are generally interested in what is going on in the paste phase
  - Aggregate, 60-70% acts as a diluent, increases errors
  - But presence of aggregates does affect paste microstructure
  - Use of paste is not an option for field samples
  - Major advantage of microscopy methods is to be able to focus on paste regions
- BEST TO USE SEVERAL METHODS IN COMBINATION

And for most techniques the relative error increases as the absolute amount decreases. So for example, in the early age it will be quite difficult to quantify the very small amounts of hydrates that form. Later on if you get larger amounts then the quantification becomes more accurate.

The second thing is to consider where we want to look at paste or concrete. Now of course concrete is the material we use in the real world but the changes that are taking place are generally going on in the paste phase.

And the problem we have that if we are looking in concrete then we can have about 60 to 70 percent of aggregate and that’s just the diluting effect.

So we already have this challenge of trying to determine small amounts of phases. If we then only have, dilute that by 3 or, 3 times or so then of course we make the situation worse.

So generally for microstructural characterisation we tend to focus on paste samples but we have to be careful that we can make the paste in the same way that is going to be similar to what you have in a concrete. And there the mixing is especially important as I will say later.

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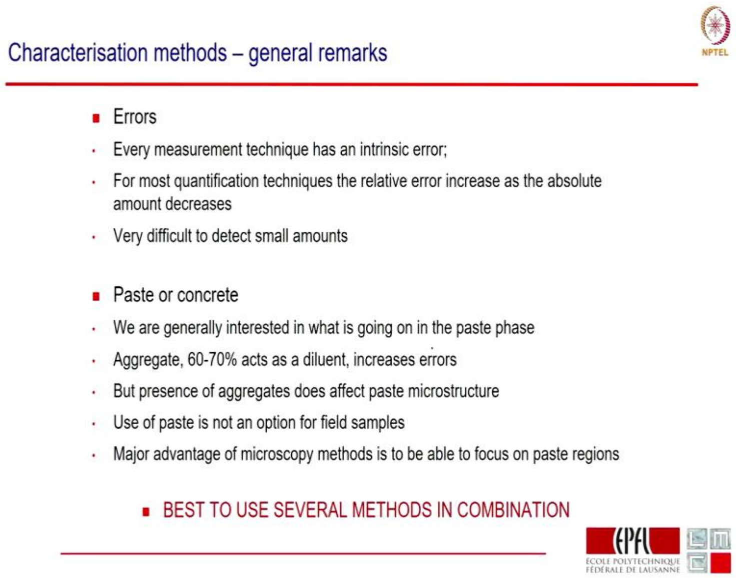

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- BEST TO USE SEVERAL METHODS IN COMBINATION

And one of the main advantages of the microscopy techniques is really we can focus on the paste regions. And lastly as we will see in the case study there you really need to use several methods in combination. You can use one method to check the validity of another method.

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Continuous measurements

In outline:
Many operational details
See book

So continuous methods we are going to look at very, very briefly. There are many details where you need to be careful in terms of experimentation and for those I refer you to the book.

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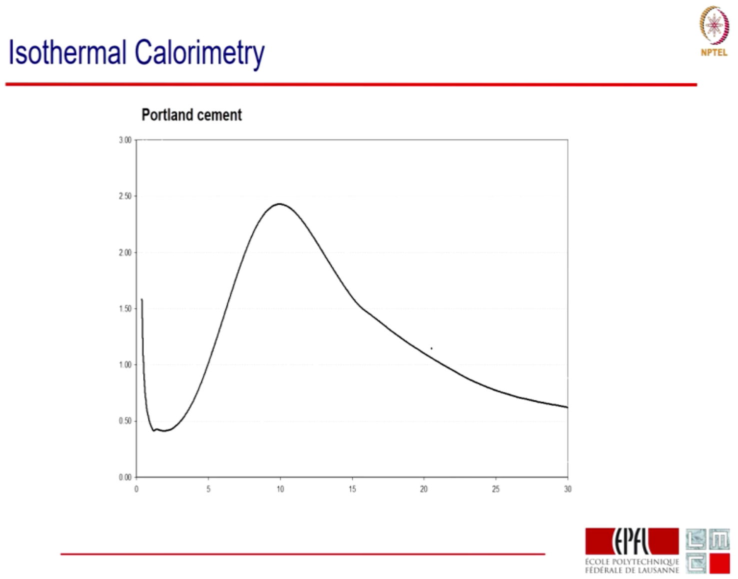

Isothermal Calorimetry

So perhaps the foremost technique for following the hydration reaction is isothermal calorimetry. An isothermal calorimetry looks at the heat evolution from a hydrating sample. And this heat evolution is a signature the reaction is going on. So the higher the heat evolution, the more reaction we have going on. And here we see the curve which is typical for Portland cements.

We see at the beginning we have this very high rate of heat evolution, then this falls away quickly and remains at a low level for several hours and that’s very important for a practical point of view because this gives you the time to mix your concrete, to move it to the side and to put it in the forms.

And then after 2 or 3 hours the rate of heat evolution starts to increase again to a maximum at about 10 hours and then it decreases. So this is a very powerful technique to follow the overhydration particularly for the first day or so. Just the few points which are important, first of all this calorimetric condition is really equivalent to a sealed sample, generally if you are not adding any water. And if you have very low water cement ratio then this can make quite an important difference.

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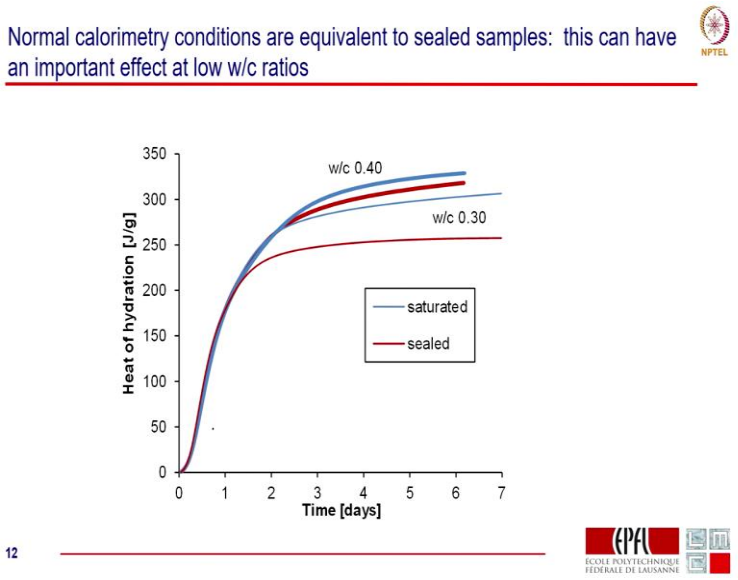

Normal calorimetry conditions are equivalent to sealed samples: this can have an important effect at low w/c ratios

So, see here the curve for paste at 0.3 with no added water and after only 1 or 2 days, the hydration is slowing down. Whereas if we put a small amount of water on top of that sample then you can see the hydration is going forward more, more strongly.

By the time we get to a water cement ratio of 0.4 then you can see this extra amount of water does not really make much difference.

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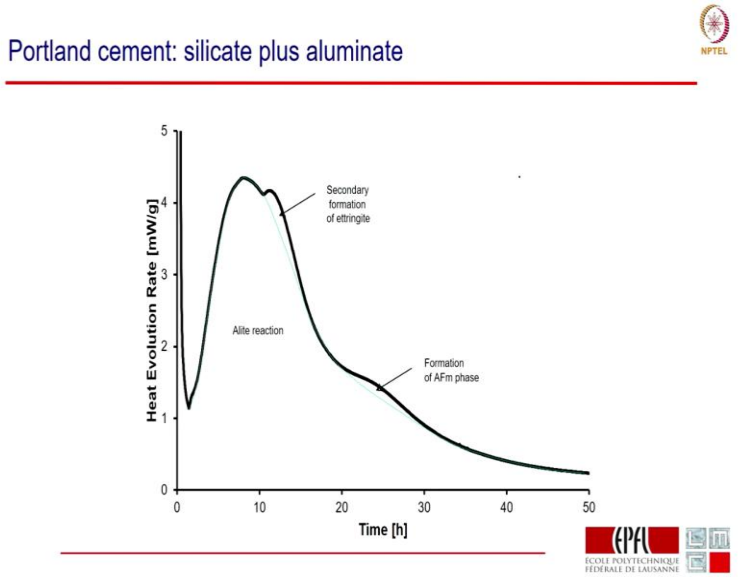

Portland cement: silicate plus aluminate

Very generally and as I said, you need to look at other things to see the more details we have this superposition of this alite reaction and the aluminate reaction in the first day. This big broad peak here is the alite reaction and then we may have peaks on the decelerating part of the curve due to the different reactions of the aluminate phase.

And it is very important that from the point of view of having a proper addition of sulphate in the material that those aluminate peaks occur after the main silicate peak.

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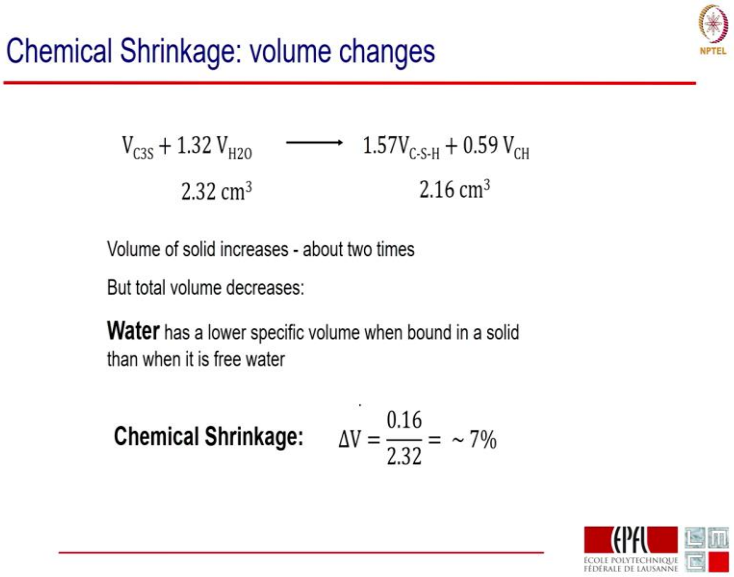

Chemical Shrinkage: volume changes

$$V_{C3S} + 1.32\, V_{H2O} \longrightarrow 1.57 V_{C\text{-}S\text{-}H} + 0.59\, V_{CH}$$

$$2.32 \text{ cm}^3 \qquad\qquad 2.16 \text{ cm}^3$$

Volume of solid increases - about two times

But total volume decreases:

Water has a lower specific volume when bound in a solid than when it is free water

Chemical Shrinkage: $\Delta V = \frac{0.16}{2.32} = \sim 7\%$

Second technique we have to look at continuous changes is what is called chemical shrinkage and this measures the volume changes.

$$V_{C3S} + 1.32\, V_{H2O} \rightarrow 1.57 V_{C\text{-}S\text{-}H} + 0.59 V_{CH}$$

$$2.32 \text{ cm}^3 \qquad\qquad 2.16 \text{ cm}^3$$

So if we look at the stoichiometry of the reaction of C_3S for example, as we see here, we can see that one volume of C_3S reacts with 1.32 volumes of water, and then it produces 1.57 volumes of CSH and 0.59 of calcium hydroxide.

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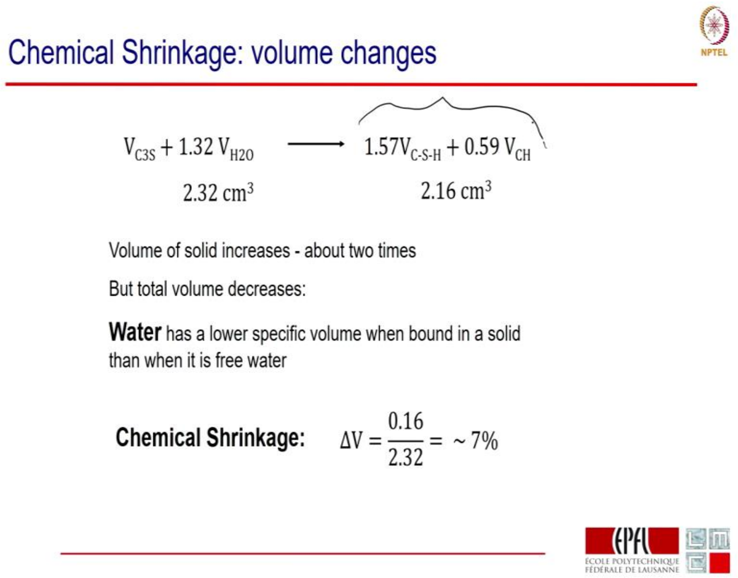

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So we see that the total solid volume that is to say this part plus this part is now roughly double the original solid volume we had at the beginning.

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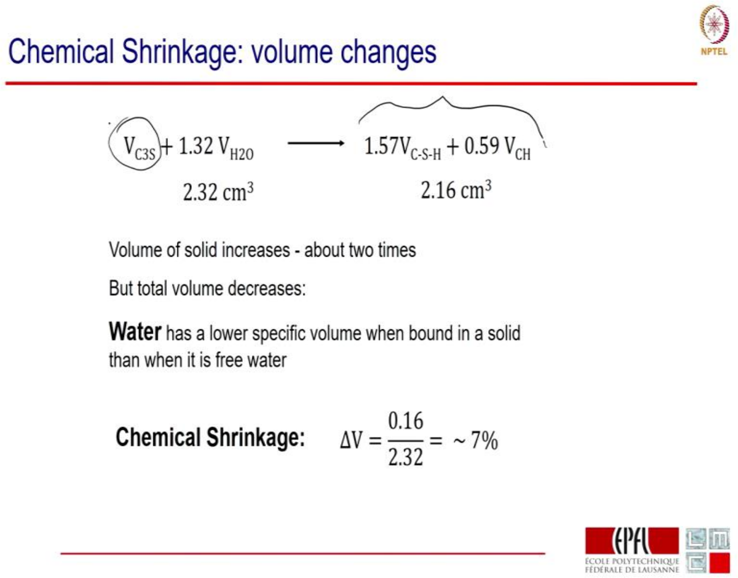

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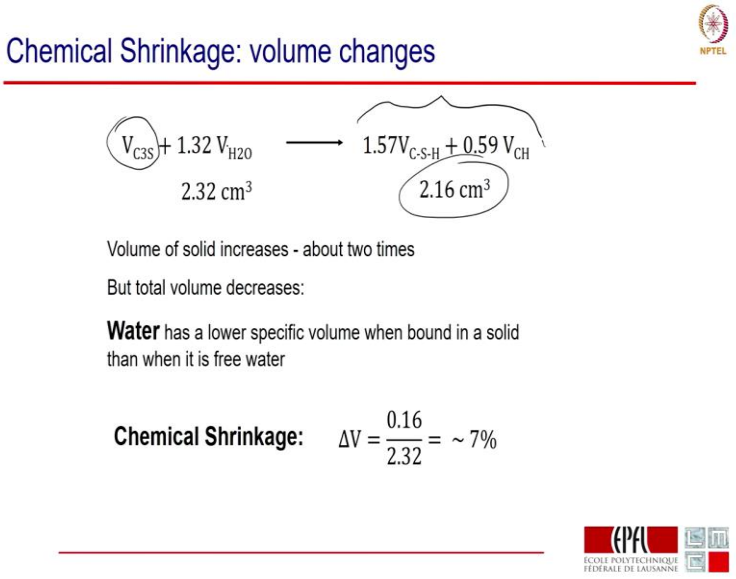

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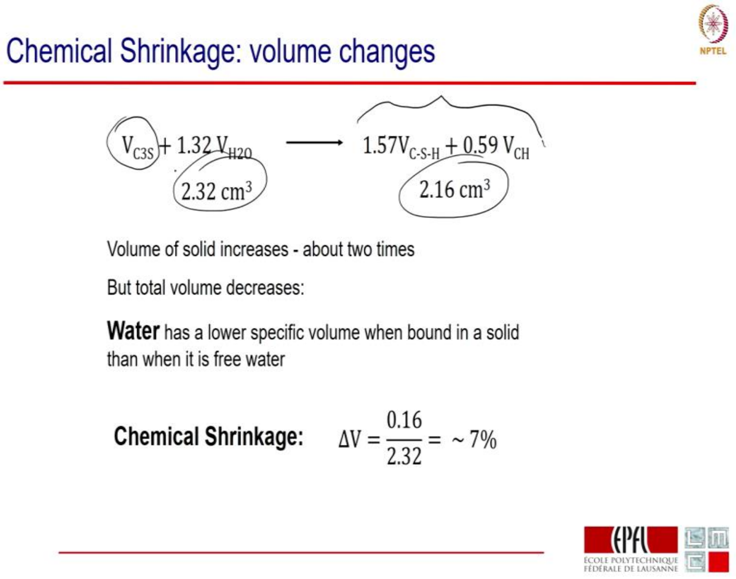

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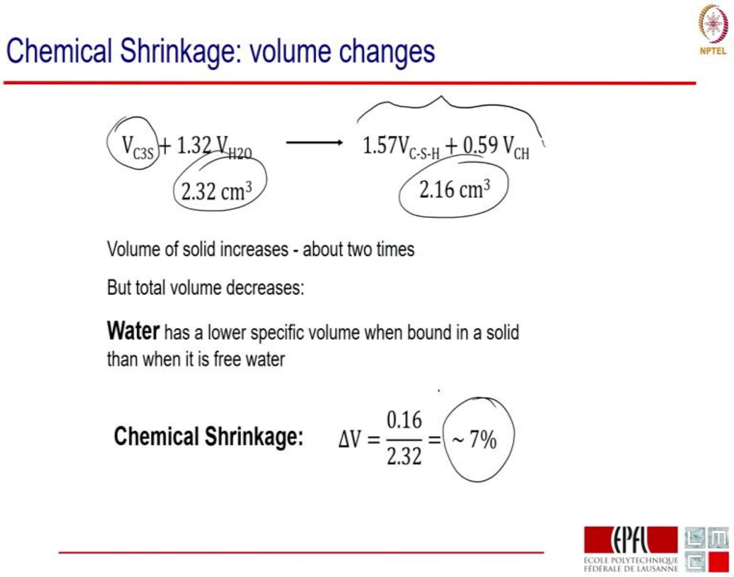

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However if we compare the totals of both sides, these two figures here, we see that we have a small decrease in volume of about roughly 7 percent. And depending on the different anhydrous material that decrease in volume will be in the range from 5 to 10 percent.

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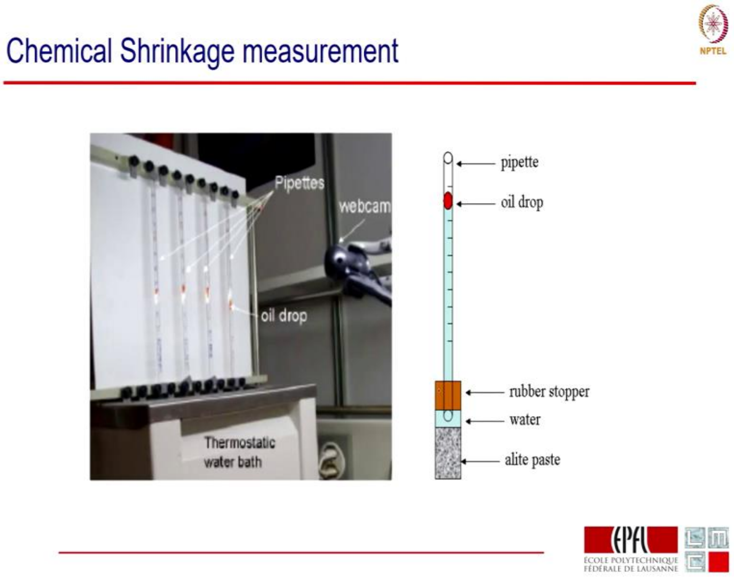

Chemical Shrinkage measurement

Now this is very useful thing because it gives us a very, very simple method by which we can follow the hydration in this chemical shrinkage measurement. So here we see the setup that we have built at EPFL. It is really very simple and can be done really cheaply because the only equipment that is really very consequence is this water bath and even that is quite cheap.

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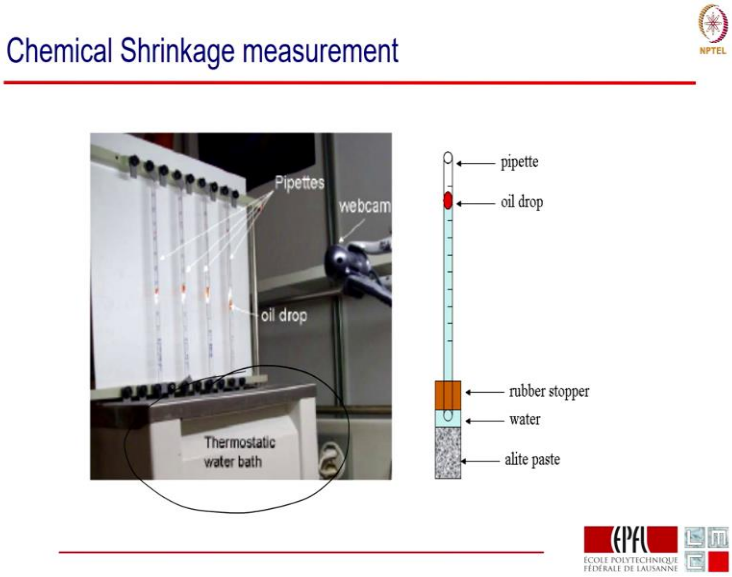

Chemical Shrinkage measurement

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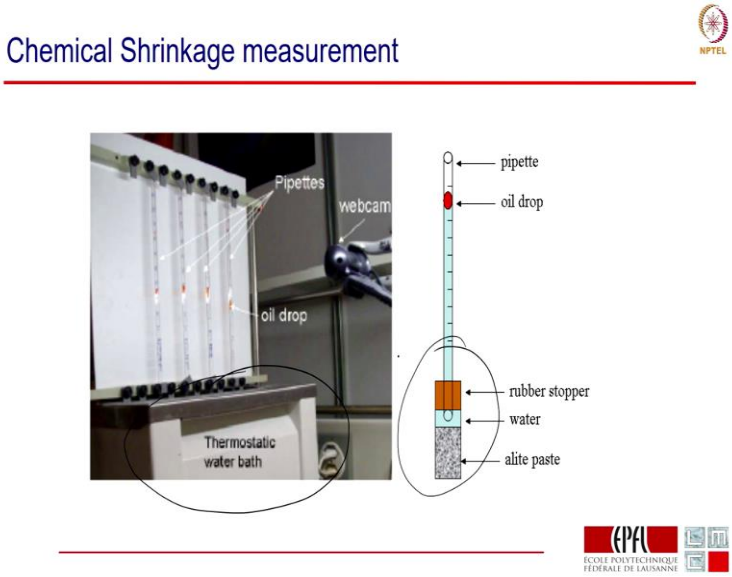

Chemical Shrinkage measurement

In this water bath, you have these small samples. You put a little bit of cement paste at the bottom of your sample. You fill it up with water and then the water goes up continuously and at the top you have this oil drop.

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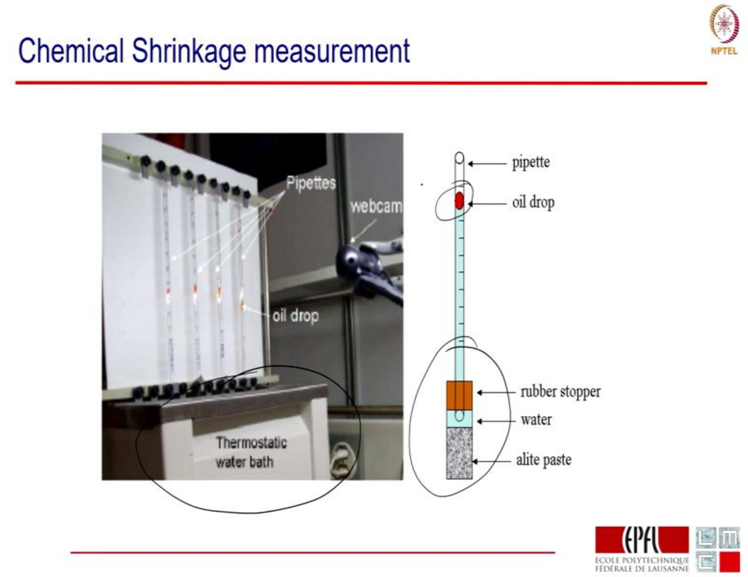

Chemical Shrinkage measurement

And this oil drop presents evaporation and the fact that you have some color onto this oil drop gives you a means to follow the reaction by this simple webcam here.

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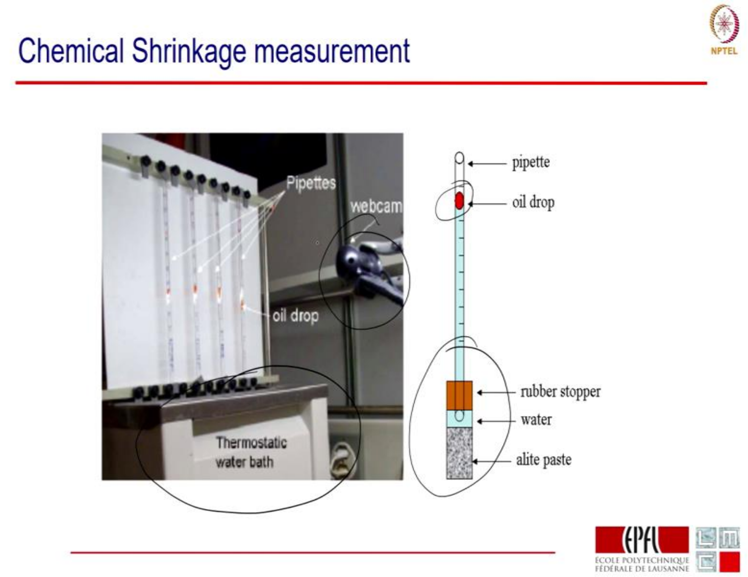

Chemical Shrinkage measurement

So here we see the oil drops, these will move over time and these can then be detected by the webcam and analyzed automatically. If you do not have a webcam then you can have a student who comes in and measures the position of the drop at regular intervals, but that is not quite so convenient.

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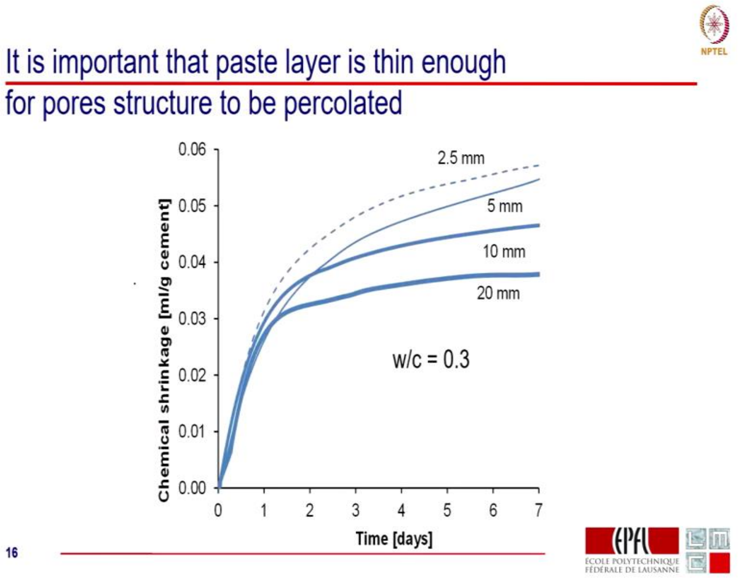

It is important that paste layer is thin enough for pores structure to be percolated

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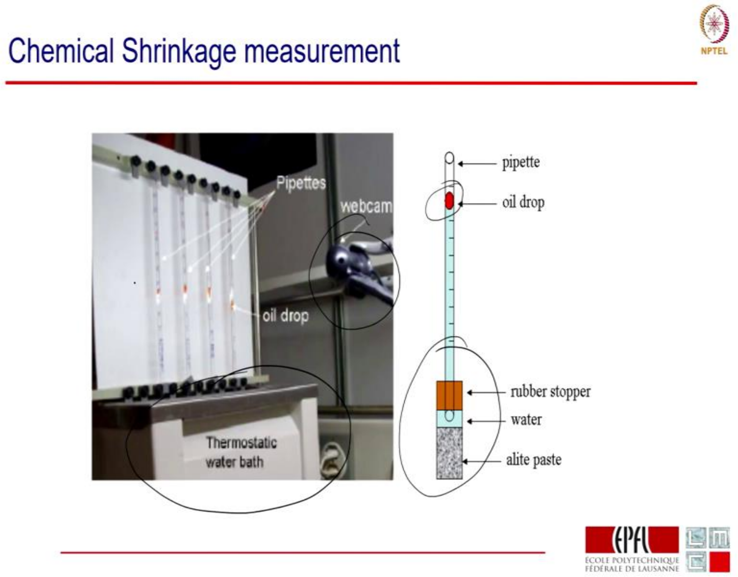

Chemical Shrinkage measurement

Now in this experiment the main aspect to look at is the thickness of the sample is too thick here, then the water cannot continuously penetrate all the pores in the sample. And of course again this becomes more important as we go to low water cement ratios.

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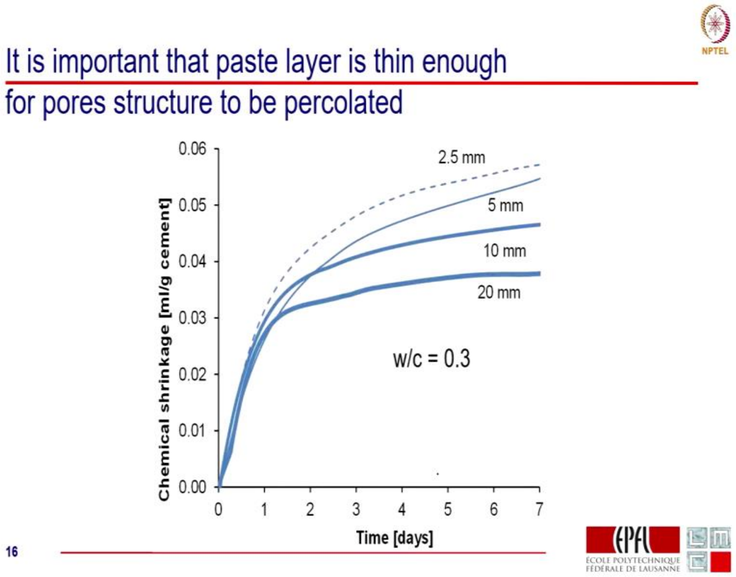

It is important that paste layer is thin enough for pores structure to be percolated

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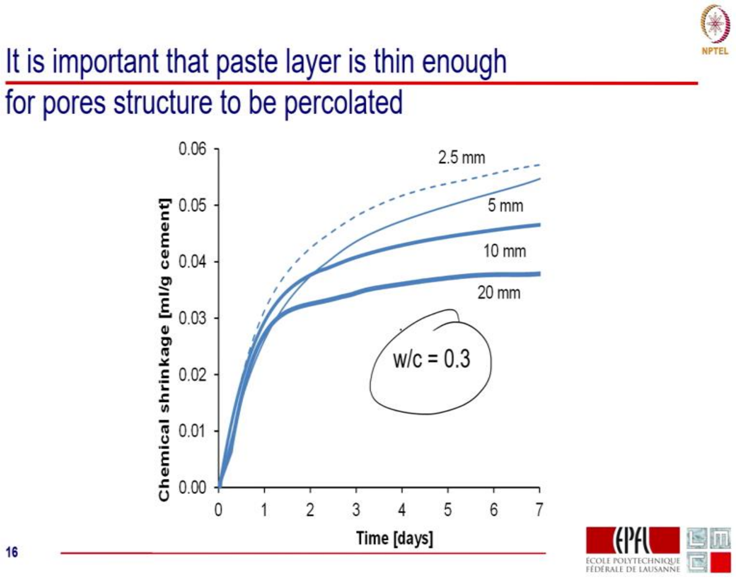

It is important that paste layer is thin enough for pores structure to be percolated

So here we see a very low water cement ratio 0.3 and clearly this thick specimen at 20 millimeters, after only you get about one day, water is not really penetrating the sample. And we have to go down to very thin layer to really get continuous hydration.

Now the problem with having a thin layer is then you have a higher error. Now when you go back to the water cement ratio of 0.4 then it is quite reasonable to have a layer in the range to 5 to 10 millimeters. This is roughly the level you want.

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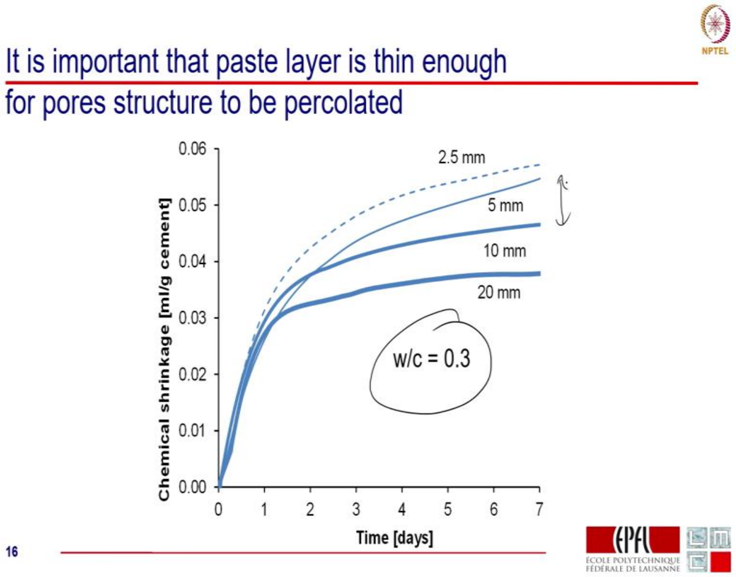

It is important that paste layer is thin enough for pores structure to be percolated

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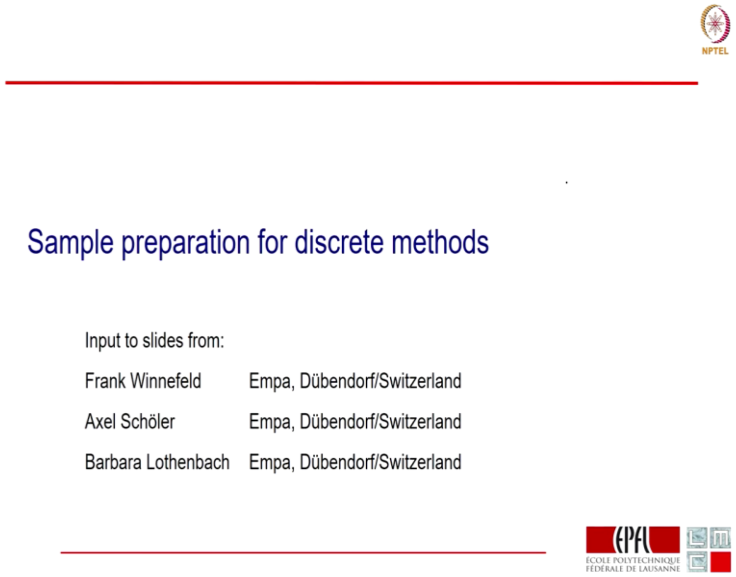

Sample preparation for discrete methods

Input to slides from:

Frank Winnefeld	Empa, Dübendorf/Switzerland
Axel Schöler	Empa, Dübendorf/Switzerland
Barbara Lothenbach	Empa, Dübendorf/Switzerland

So those two are the continuous methods. Now when we look at discrete methods, discrete means that we have to make a sample and then at individual times we have to stop the hydration and do the complete analysis. And here sample preparation is very important. There is whole chapter on this in the book and I would like to thank some of the authors of the book who helped prepare these slides in this part here.

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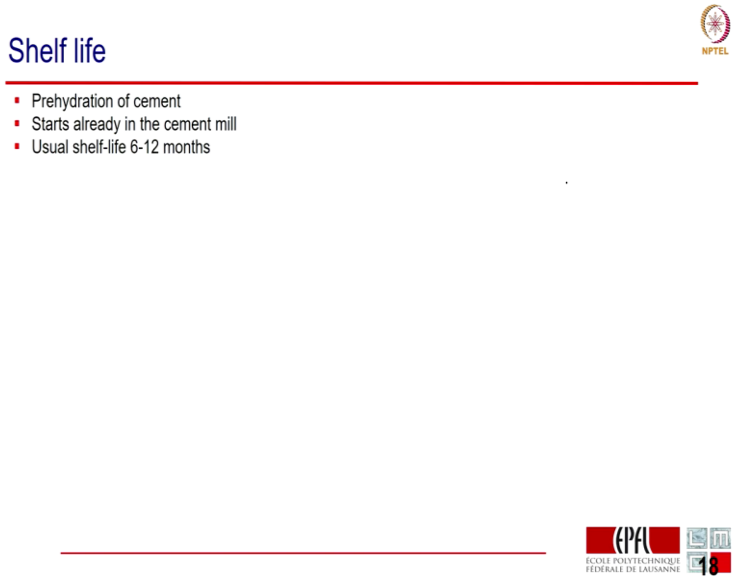

Shelf life

- Prehydration of cement
- Starts already in the cement mill
- Usual shelf-life 6-12 months

Now what you really have to be aware about is of course the shelf life of cement. You can have prehydration of cement and this may start already as soon as you ground the cement. In typical conditions the shelf life will be only about 6 to 12 months and in hot humid conditions such as you have here in Chennai it will probably be quite a lot shorter than that.

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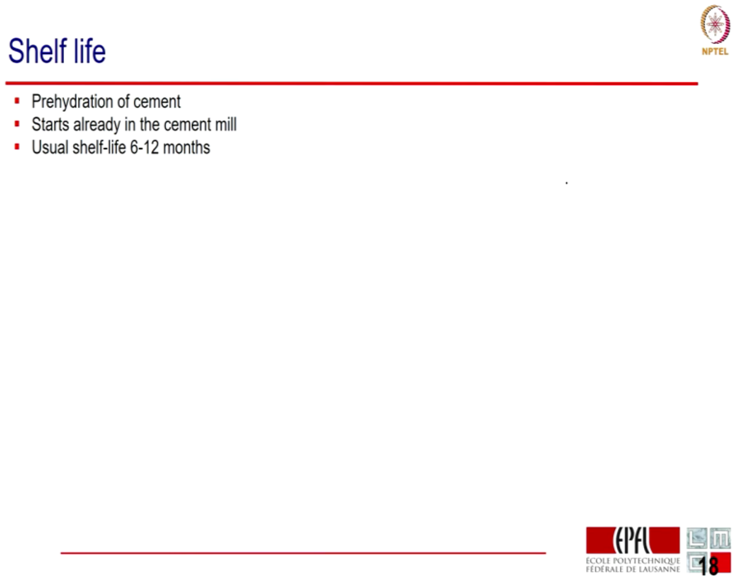

Shelf life

- Prehydration of cement
- Starts already in the cement mill
- Usual shelf-life 6-12 months

And this can have quite a dramatic effect on the hydration.

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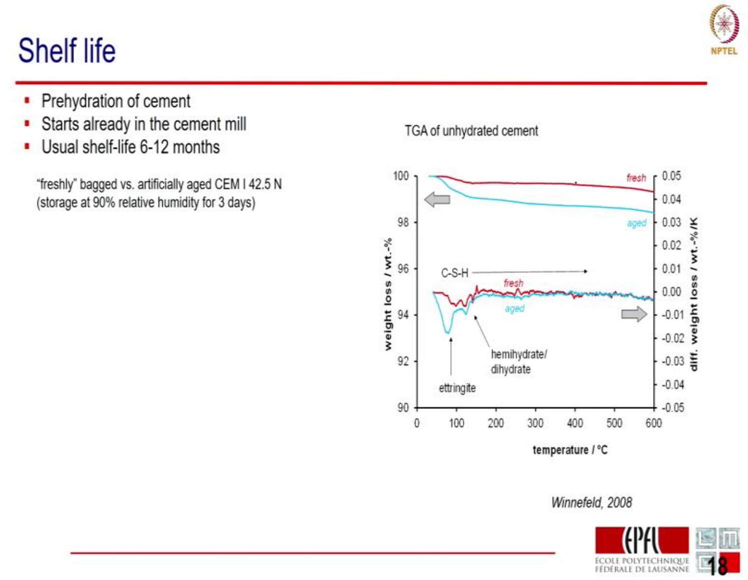

Shelf life

- Prehydration of cement
- Starts already in the cement mill
- Usual shelf-life 6-12 months

"freshly" bagged vs. artificially aged CEM I 42.5 N
(storage at 90% relative humidity for 3 days)

TGA of unhydrated cement

Winnefeld, 2008

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Prolonging the storage time

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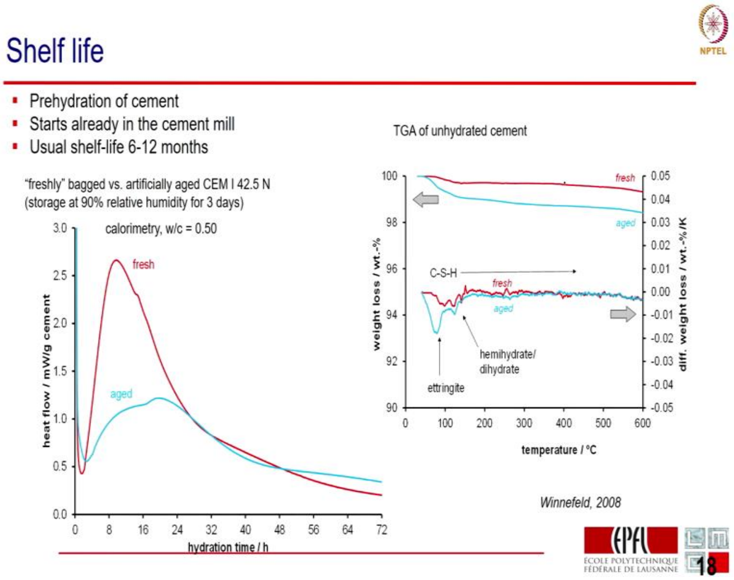

Shelf life

- Prehydration of cement
- Starts already in the cement mill
- Usual shelf-life 6-12 months

"freshly" bagged vs. artificially aged CEM I 42.5 N
(storage at 90% relative humidity for 3 days)

TGA of unhydrated cement

Winnefeld, 2008

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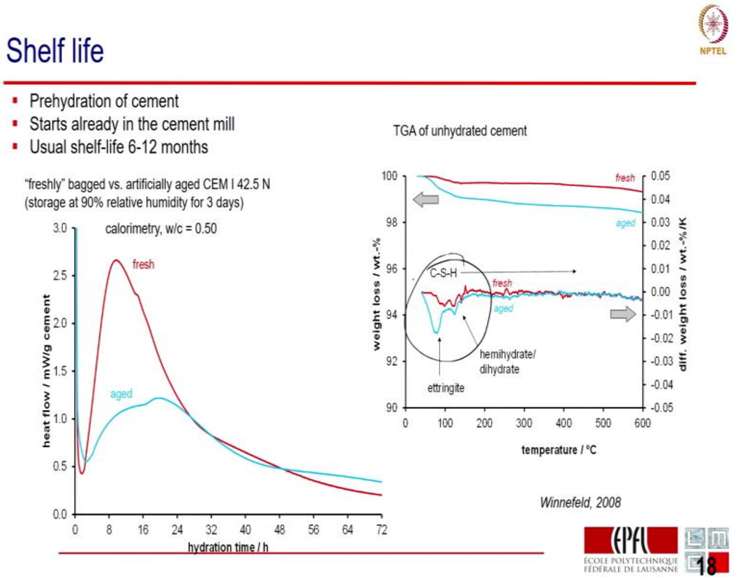

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(storage at 90% relative humidity for 3 days)

TGA of unhydrated cement

Winnefeld, 2008

So here on the red we see a thermogravimetric analysis and you can see in this region here how water has been absorbed by the cement paste particularly by the aluminate phases and we have a small formation already of ettringite.

So this shows you the aging and then here on the left we can see the dramatic effect this will have on the reaction kinetics that you can see the heat evolution here in the aged sample is really very much reduced compared to the fresh sample.

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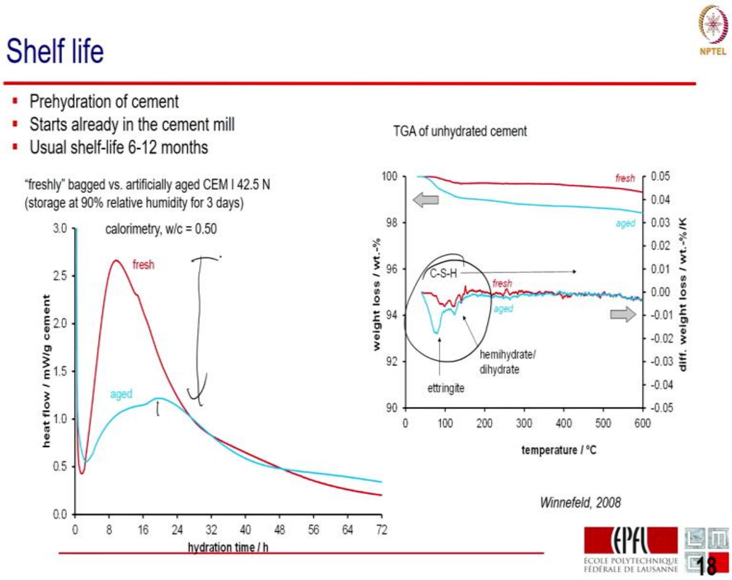

Shelf life

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- Usual shelf-life 6-12 months

"freshly" bagged vs. artificially aged CEM I 42.5 N
(storage at 90% relative humidity for 3 days)

TGA of unhydrated cement

Winnefeld, 2008

So you have to be very careful about this and plan your experiments to hopefully and mix everything at the same time so you have the similar sample.

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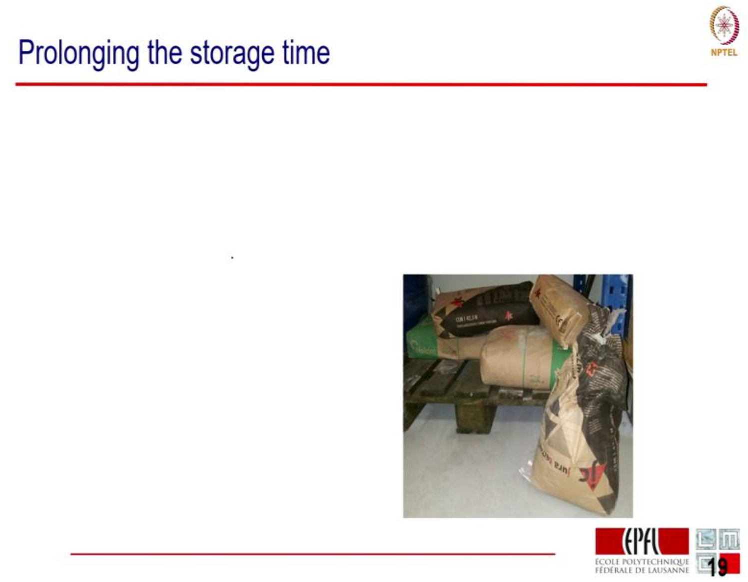

Prolonging the storage time

If you store your sample carefully, so not in banks like this and really the recommendation is do not buy your cement in a shop, really get it direct from the manufacturer.

(Refer Slide Time: 13:59)

Prolonging the storage time

- Do not buy your cement in a shop. Ask the manufacturer.
- Store your unhydrated binders in small portions sealed under low rH conditions.

Rather funny story, we have collaboration with colleagues in the Department of Physics, University of Surrey, so you know very good scientists but one day they said we have these very funny results.

And when we explored what was the situation, we worked out that they had just gone to the local shop and bought a bag of cement which would may be been lying around in the shop for, who knows, how long.

So be very careful about this. When you do get your cement, what you want to do is to break it up into smaller batches and put each of these smaller batches in sealed containers. Plastic bucket is quite good and store these under low relative humidity conditions.

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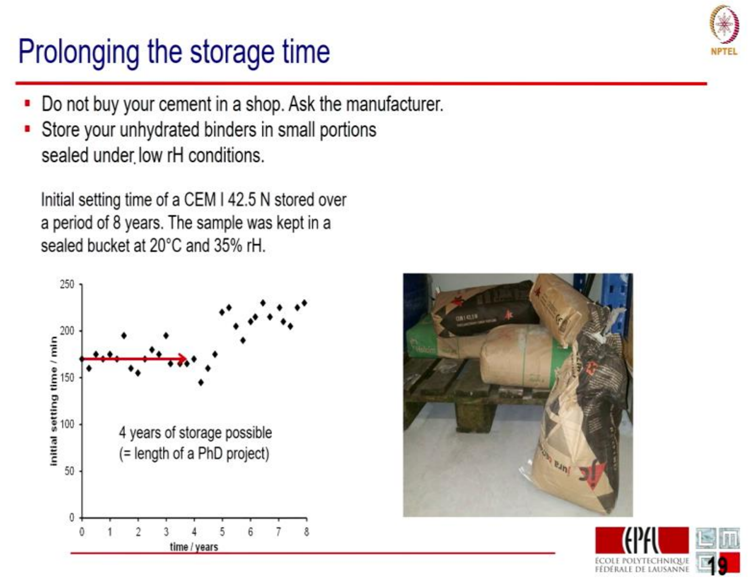

Prolonging the storage time

- Do not buy your cement in a shop. Ask the manufacturer.
- Store your unhydrated binders in small portions sealed under low rH conditions.

Initial setting time of a CEM I 42.5 N stored over a period of 8 years. The sample was kept in a sealed bucket at 20°C and 35% rH.

If you take those precautions, you can see here that the setting time was monitored for this cement during 8 years and for 4 years it is not really too bad, not typically the length of a PhD study. So do be careful with your cement.

As soon as you get it,break it up into smaller batches, work for one container at a time and try to minimize the amount of times you are opening or closing the container.

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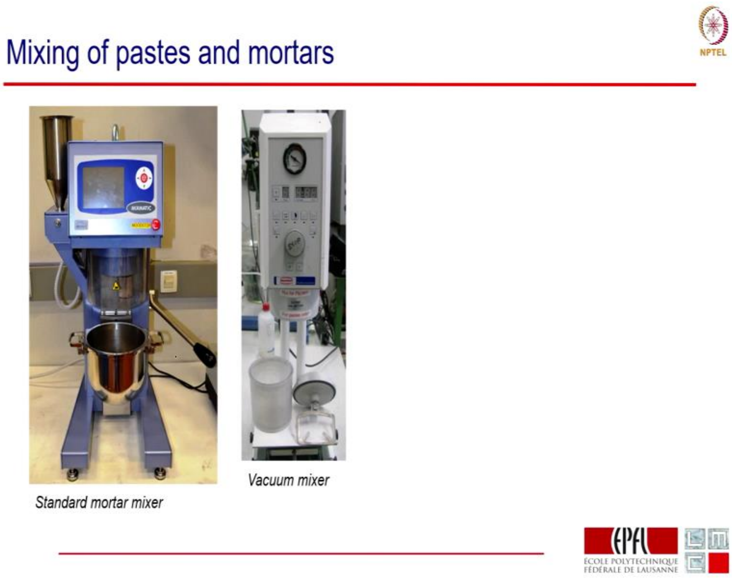

Mixing of pastes and mortars

Standard mortar mixer

Vacuum mixer

Then for mixing this shows a typical kind of mortar mixer or vacuum mixer. Now as I said for microstructural characterization we really want to look more at paste.

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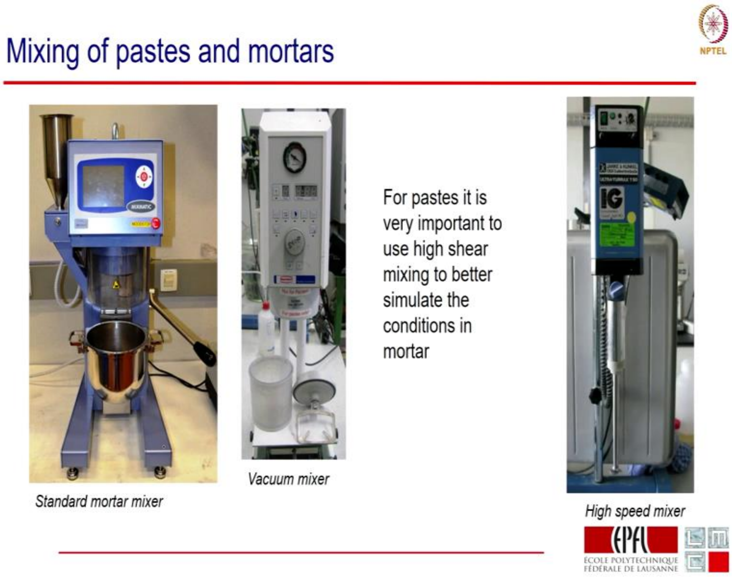

Mixing of pastes and mortars

Standard mortar mixer

Vacuum mixer

For pastes it is very important to use high shear mixing to better simulate the conditions in mortar

High speed mixer

And for paste we had very important that you really use a kind of high shear mixing with some kind of impeller which will impart shear to the paste such as down here to simulate the conditions in the mortar.

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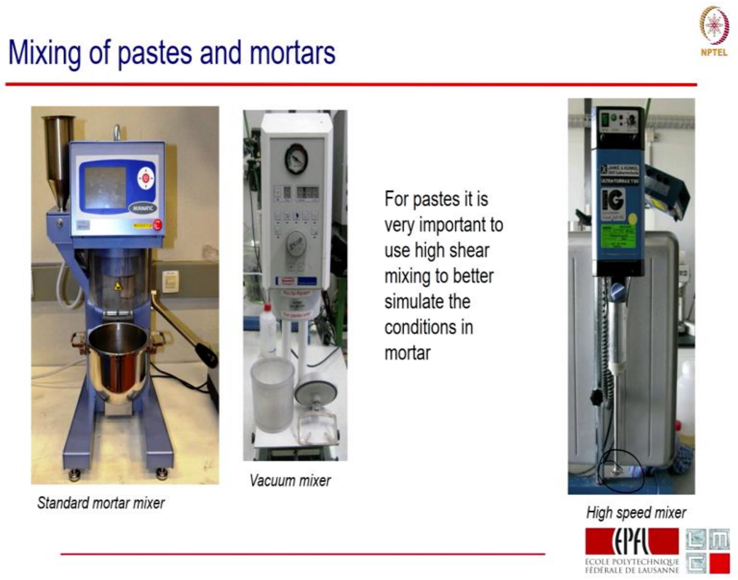

Mixing of pastes and mortars

For pastes it is very important to use high shear mixing to better simulate the conditions in mortar

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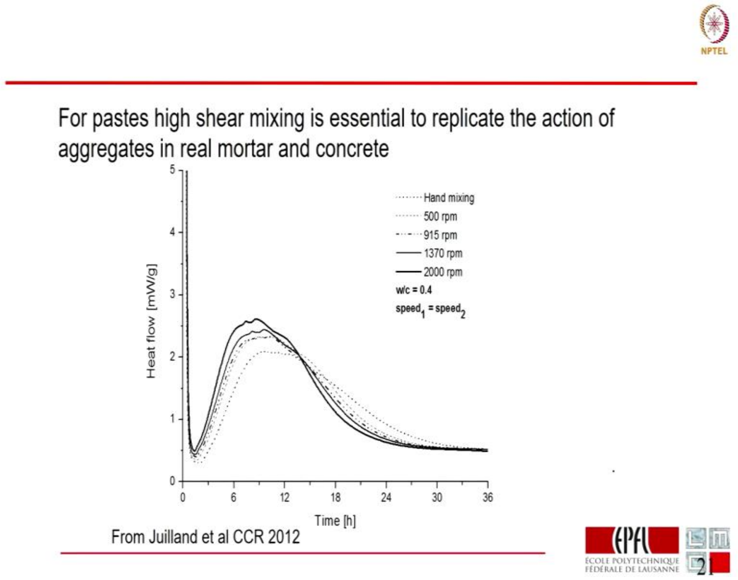

For pastes high shear mixing is essential to replicate the action of aggregates in real mortar and concrete

From Juilland et al CCR 2012

And in this slide we can see how dramatic that effect is. That this is the hand mix sample here and then when we go to a situation which is more like the curing, we have in mortar then we very much accelerate the hydration reactions, so if you are not doing that then you really will get a false idea of the hydration kinetics.

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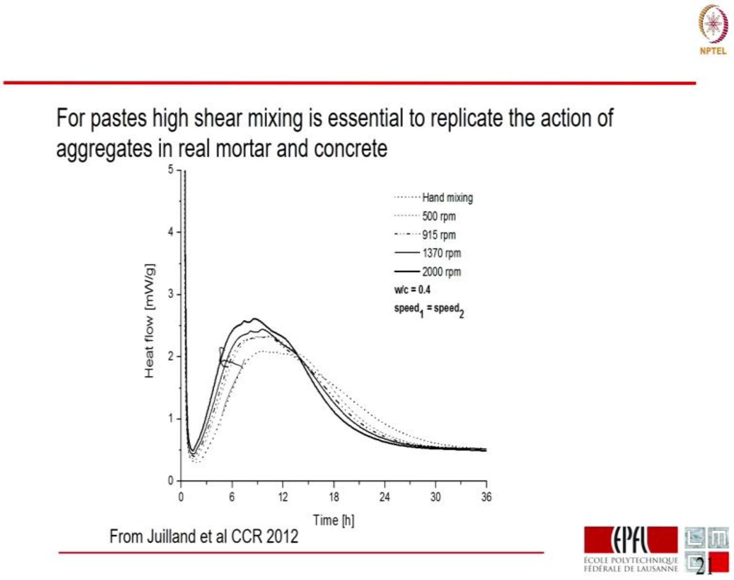

For pastes high shear mixing is essential to replicate the action of aggregates in real mortar and concrete

From Juilland et al CCR 2012

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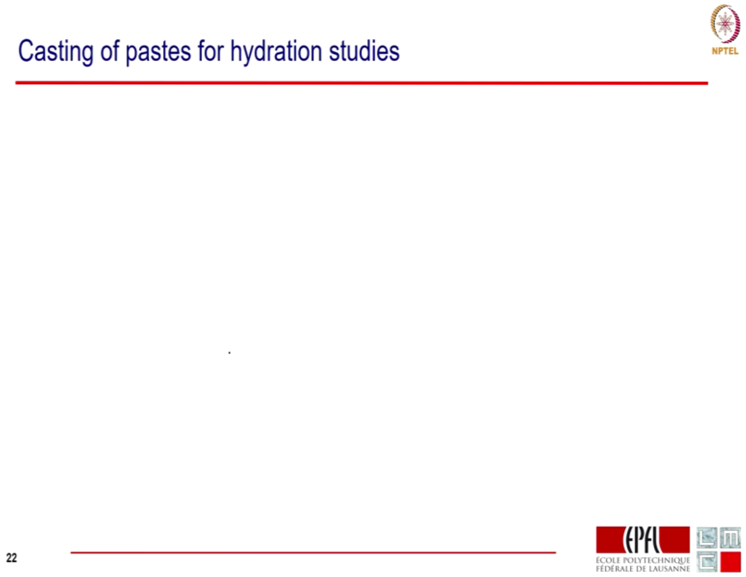
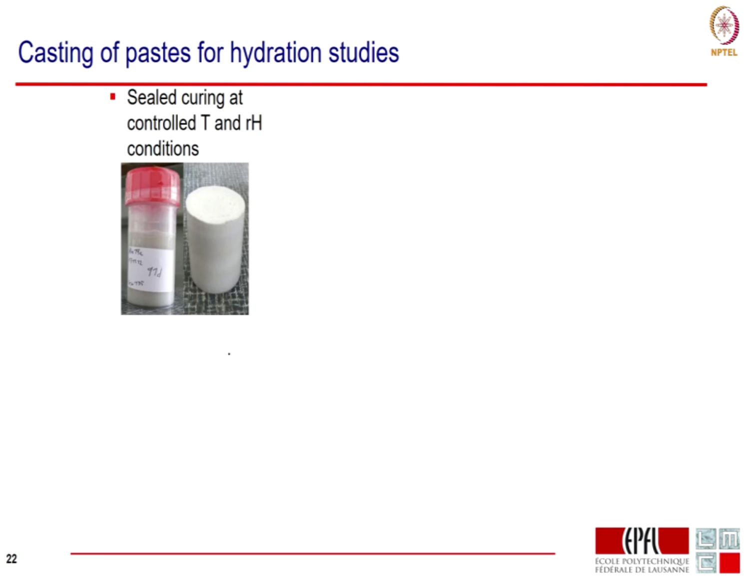


Casting of pastes for hydration studies

(Refer Slide Time: 16:11)



Casting of pastes for hydration studies

- Sealed curing at controlled T and rH conditions

Cast paste, this is the kind of typical method you can use. You can either make individual samples in small containers like this and store them in sealed conditions and then at individual time, you take these slices and each of these slices can be analyzed by the methods we are going to talk about later.

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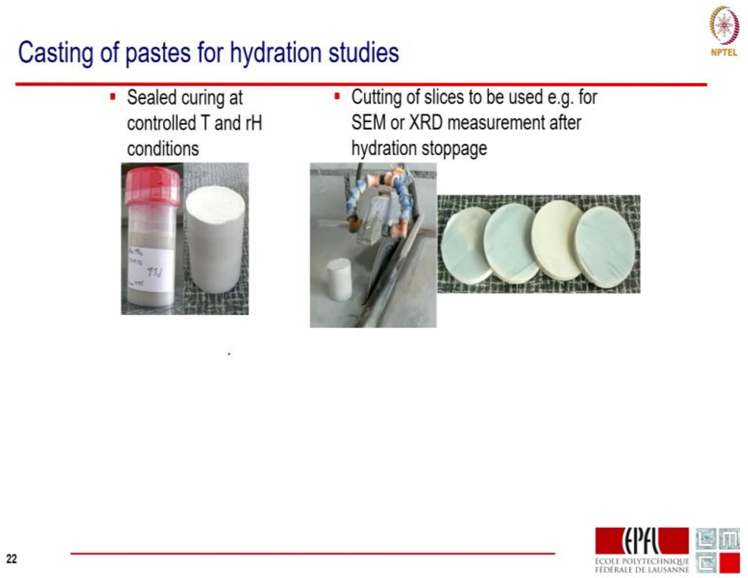

Casting of pastes for hydration studies

- Sealed curing at controlled T and rH conditions
- Cutting of slices to be used e.g. for SEM or XRD measurement after hydration stoppage

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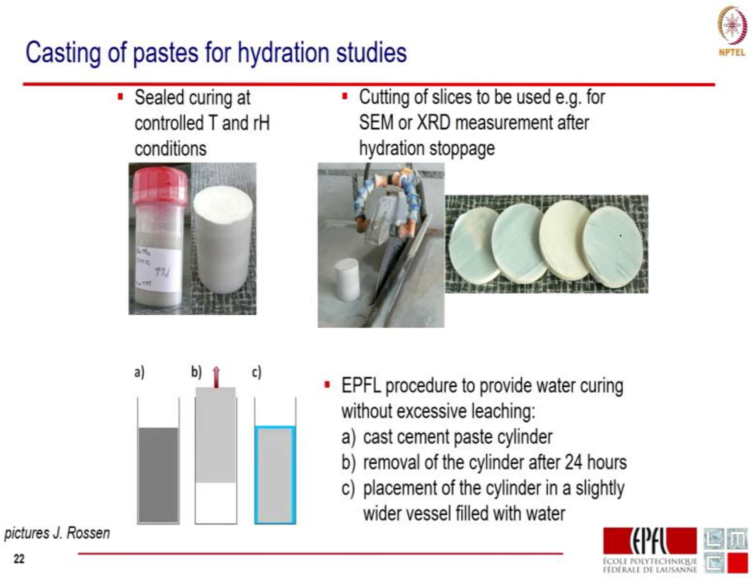

Casting of pastes for hydration studies

- Sealed curing at controlled T and rH conditions
- Cutting of slices to be used e.g. for SEM or XRD measurement after hydration stoppage

- EPFL procedure to provide water curing without excessive leaching:
  a) cast cement paste cylinder
  b) removal of the cylinder after 24 hours
  c) placement of the cylinder in a slightly wider vessel filled with water

pictures J. Rossen

If you want to simulate water curing then what we recommend is you have a small container like this. After 24 hours you take the sample out of the container and then put in another container which is just a little bit bigger.

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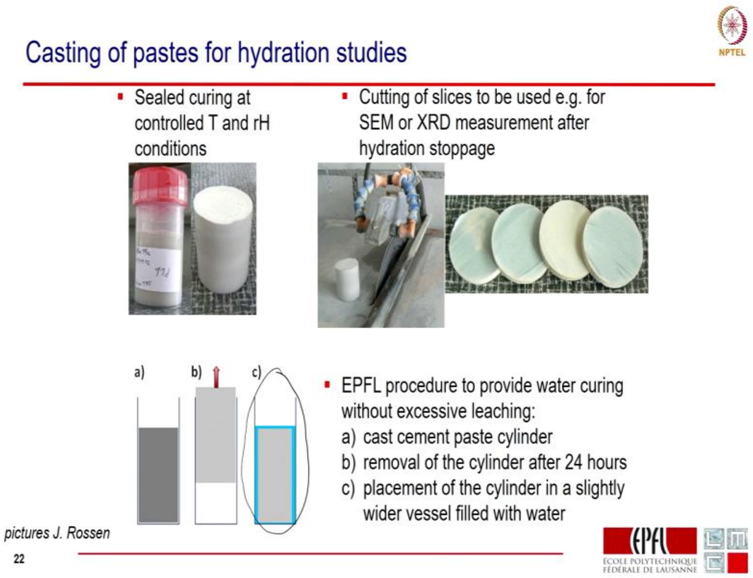


Casting of pastes for hydration studies

- Sealed curing at controlled T and rH conditions
- Cutting of slices to be used e.g. for SEM or XRD measurement after hydration stoppage

a)
b)
c)

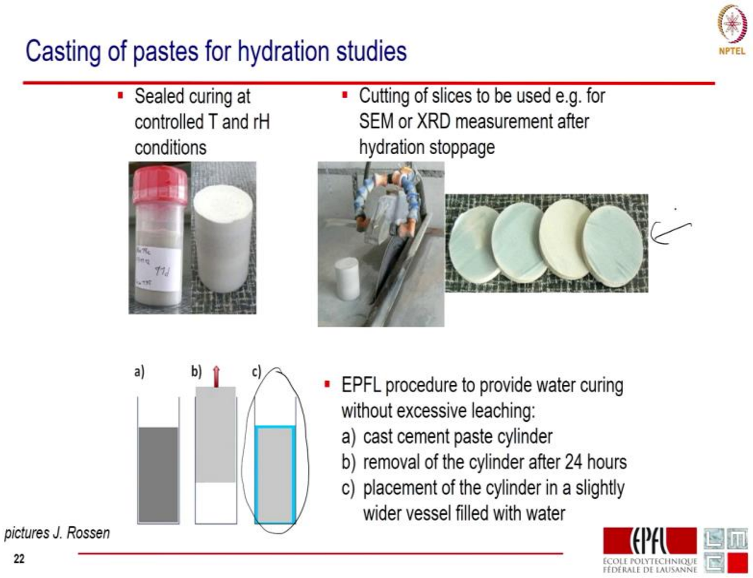
- EPFL procedure to provide water curing without excessive leaching:
  a) cast cement paste cylinder
  b) removal of the cylinder after 24 hours
  c) placement of the cylinder in a slightly wider vessel filled with water

pictures J. Rossen

So the amount of water you have is really very small amount and will minimize the amount of leaching you have from your sample.

Don’t store your samples in calcium hydroxide solution which is what many people recommend in literature because it is not really calcium that is leaching out, it is actually the alkalides that leach out. And if you leach out the alkalides you have very much changed the reaction kinetics particularly of your supplementary cementitious materials. So the best way to supply extra water is just by having a very small amount of water which won't change the situation inside the sample.

(Refer Slide Time: 17:29)



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  a) cast cement paste cylinder
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  c) placement of the cylinder in a slightly wider vessel filled with water

pictures J. Rossen

And then similarly you can cut slices as is shown here but when you are making the analysis you should always avoid the edges and really look central part because this is likely to be the most homogenous and the most well-cured.

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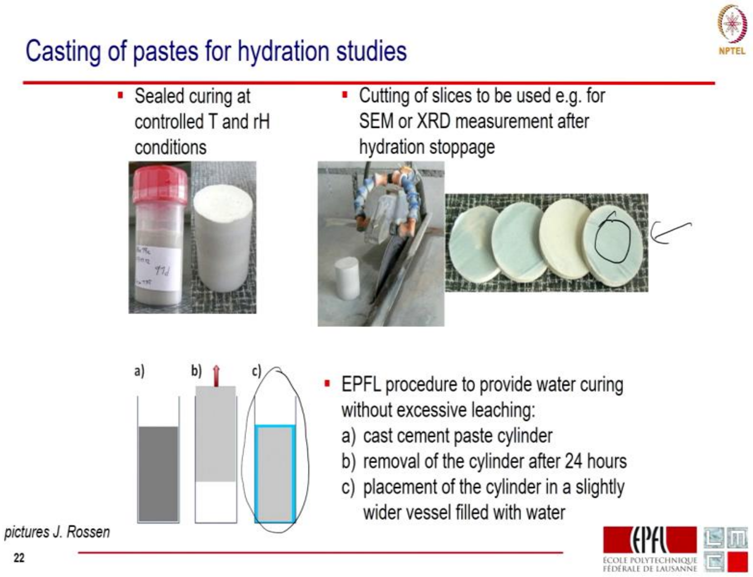

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pictures J. Rossen

(Refer Slide Time: 17:40)

Hydration stoppage – why?

Now why do we need to stop hydration?

(Refer Slide Time: 17:43)

Hydration stoppage – why?

- Target: removal of free water, preservation of microstructure

Well, the real idea of this is to remove the free water while preserving the microstructure.

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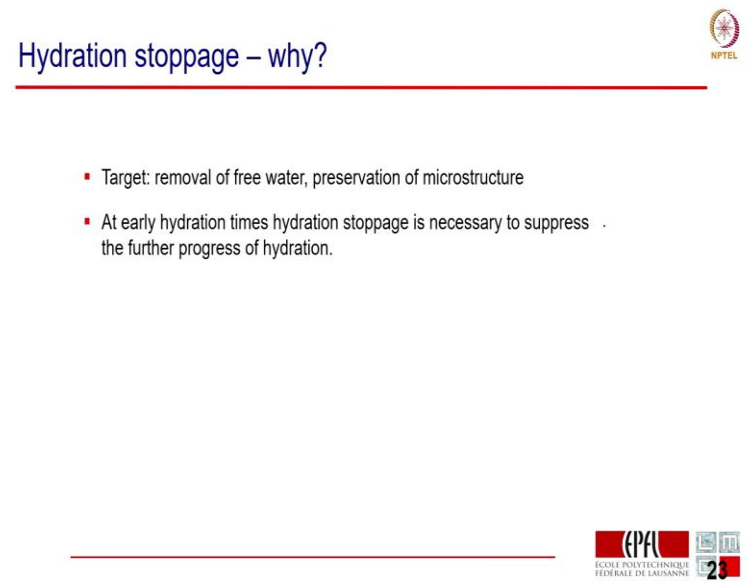

Hydration stoppage – why?

- Target: removal of free water, preservation of microstructure
- At early hydration times hydration stoppage is necessary to suppress the further progress of hydration.

And of course, at early hydration times for example if you want to look in what is going on through that main heat evolution peak you need it to stop the further progress of hydration.

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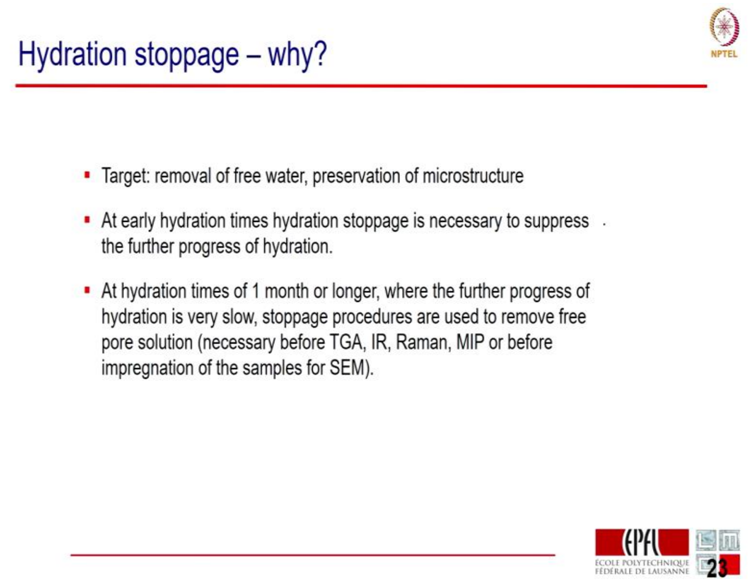

Hydration stoppage – why?

- Target: removal of free water, preservation of microstructure
- At early hydration times hydration stoppage is necessary to suppress the further progress of hydration.
- At hydration times of 1 month or longer, where the further progress of hydration is very slow, stoppage procedures are used to remove free pore solution (necessary before TGA, IR, Raman, MIP or before impregnation of the samples for SEM).

When you have longer times, say for example one month, it is not really necessary but some techniques you may need to remove free water such as SEM.

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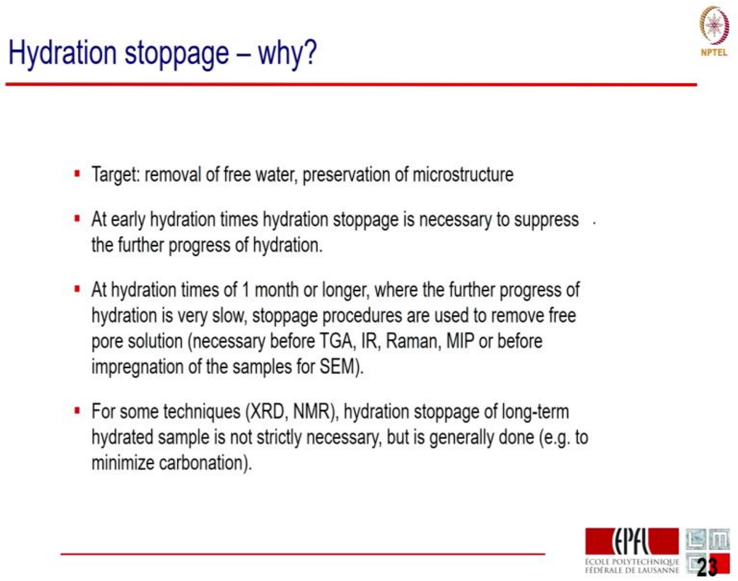

Hydration stoppage – why?

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- At hydration times of 1 month or longer, where the further progress of hydration is very slow, stoppage procedures are used to remove free pore solution (necessary before TGA, IR, Raman, MIP or before impregnation of the samples for SEM).
- For some techniques (XRD, NMR), hydration stoppage of long-term hydrated sample is not strictly necessary, but is generally done (e.g. to minimize carbonation).

And in other cases where even though you do not need to remove the water it may be good way of minimizing the amount of carbonation.

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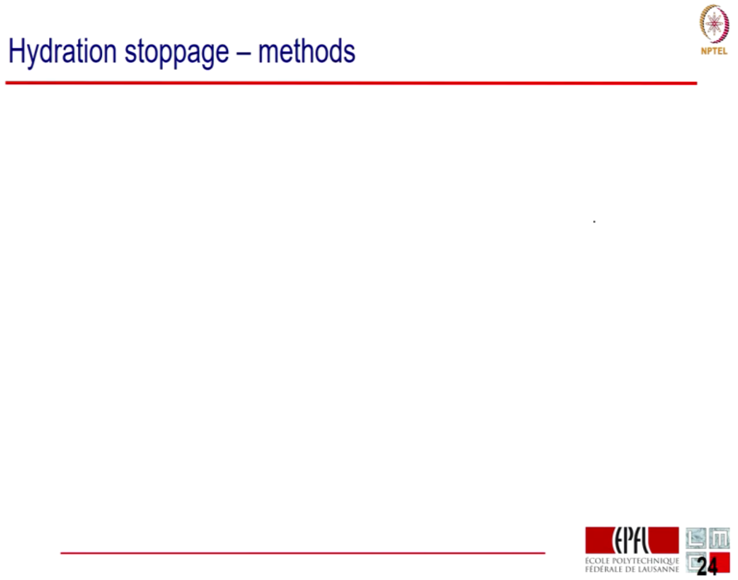
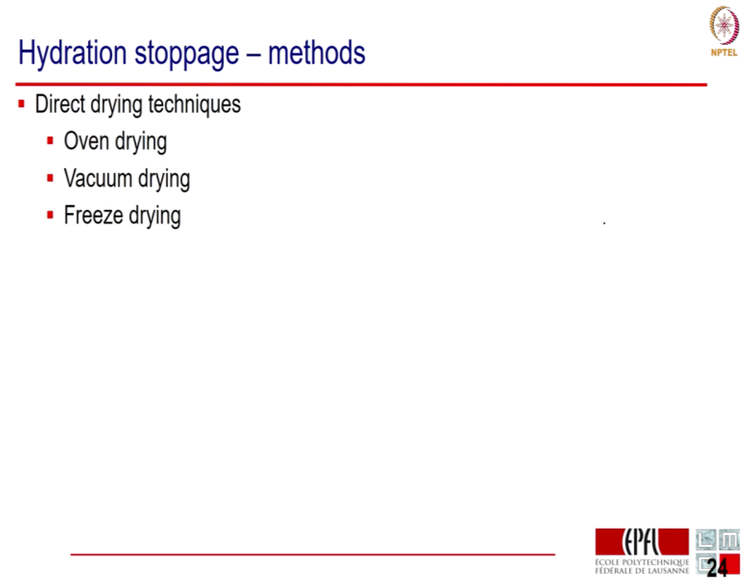


Hydration stoppage – methods

(Refer Slide Time: 18:23)



Hydration stoppage – methods

- Direct drying techniques
  - Oven drying
  - Vacuum drying
  - Freeze drying

So these many, many methods which have been discussed in the literature, the most popular and actually the worse and it was one thing you really retained from these lectures, it is really do not prepare your samples by drying in oven. It is worst technique to use. But for these direct drying techniques there are lots of different conditions that can be varied.

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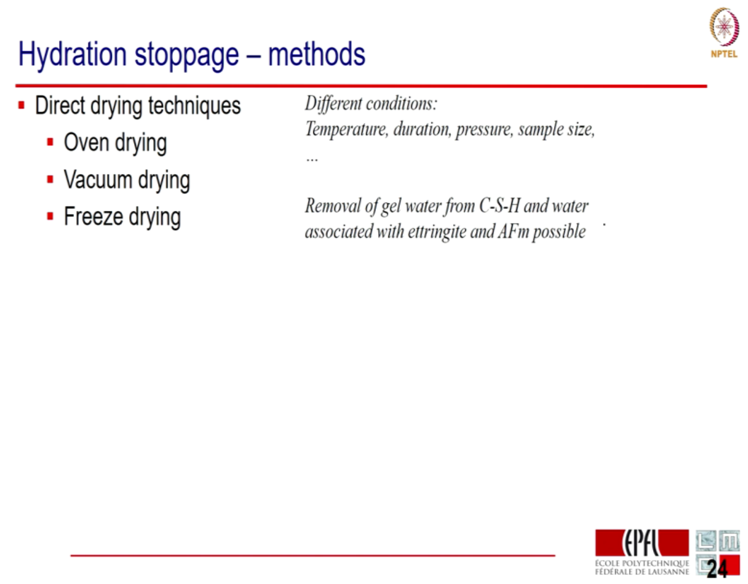

Hydration stoppage – methods

- Direct drying techniques
  - Oven drying
  - Vacuum drying
  - Freeze drying

Different conditions:
Temperature, duration, pressure, sample size, …

Removal of gel water from C-S-H and water associated with ettringite and AFm possible

The temperature, duration etc, most of all the sample size, and the sample size is very important.

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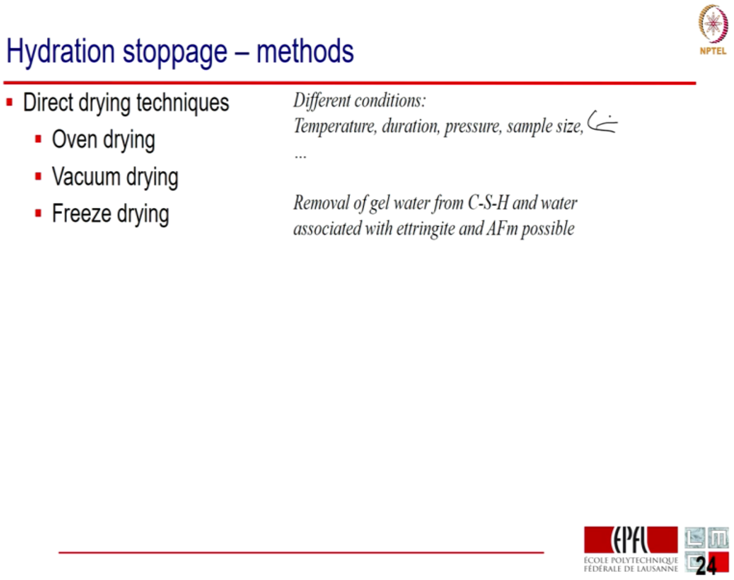

Hydration stoppage – methods

- Direct drying techniques
  - Oven drying
  - Vacuum drying
  - Freeze drying

Different conditions:
Temperature, duration, pressure, sample size,
...

Removal of gel water from C-S-H and water associated with ettringite and AFm possible

And this is why we tend to focus on these quite thin slices here because then the thin slices we can quite rapidly stop the hydration by either one of these direct drying techniques or by solvent exchange techniques.

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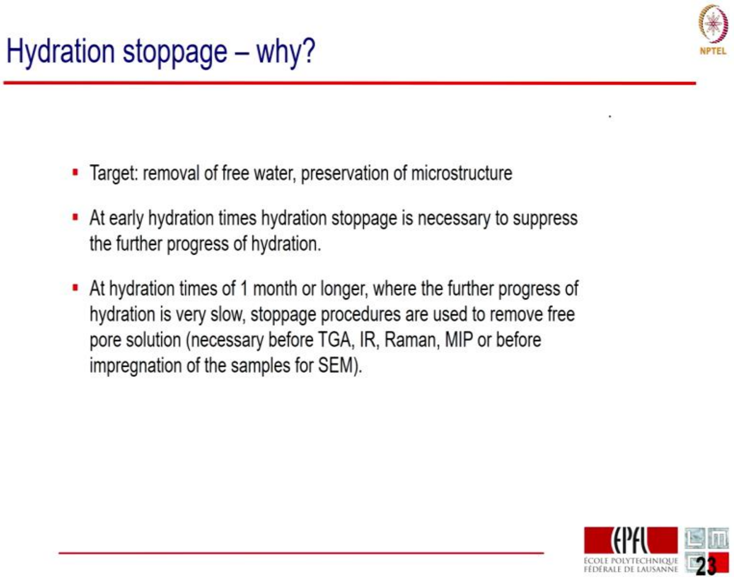

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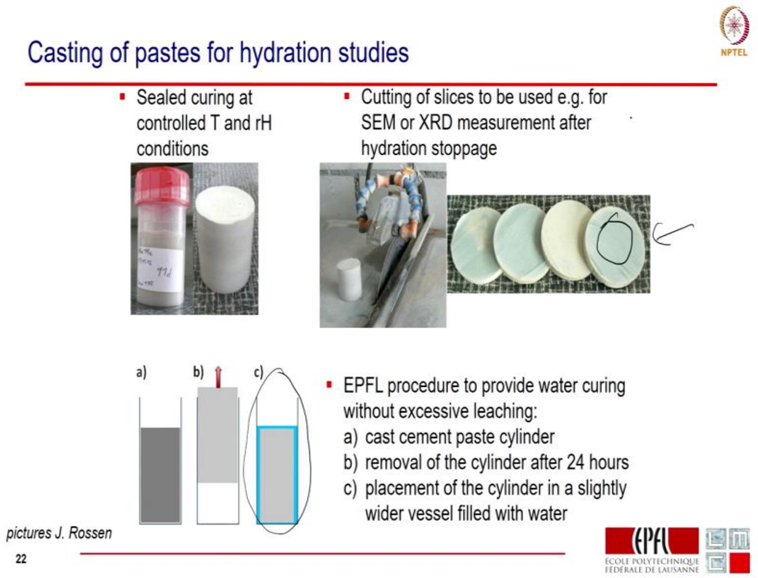

Casting of pastes for hydration studies

- Sealed curing at controlled T and rH conditions
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pictures J. Rossen

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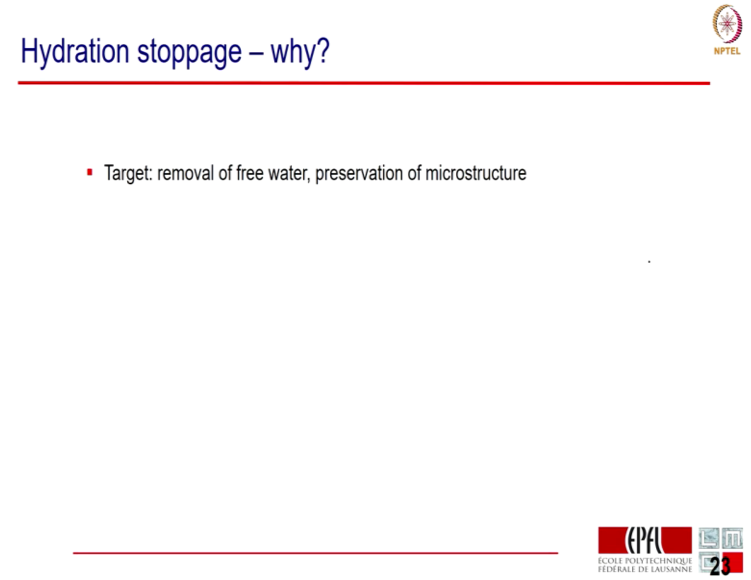

Hydration stoppage – why?

- Target: removal of free water, preservation of microstructure

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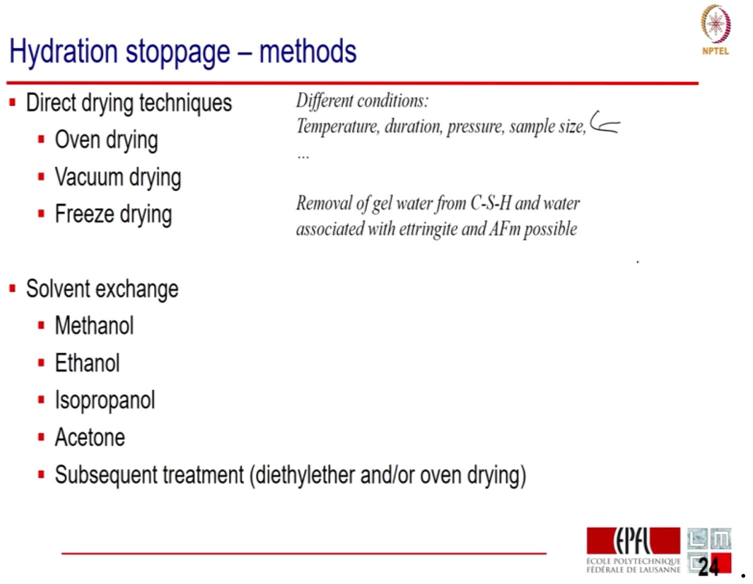

Hydration stoppage – methods

- Direct drying techniques
  - Oven drying
  - Vacuum drying
  - Freeze drying
- Solvent exchange
  - Methanol
  - Ethanol
  - Isopropanol
  - Acetone
  - Subsequent treatment (diethylether and/or oven drying)

Different conditions:
Temperature, duration, pressure, sample size,
...

Removal of gel water from C-S-H and water associated with ettringite and AFm possible

And these are the methods really I would tend to recommend from practicality and particularly isopropanol is probably the more strongly recommended although acetone also is very good technique.

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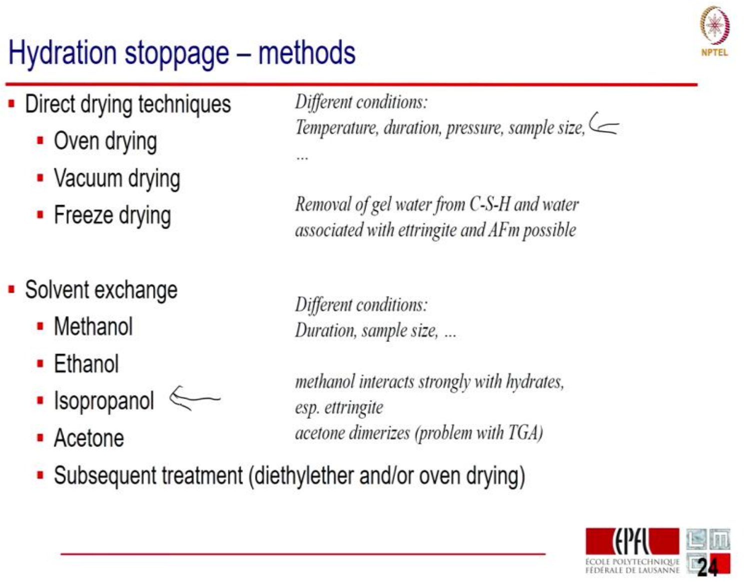

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Different conditions:
Temperature, duration, pressure, sample size,
...

Removal of gel water from C-S-H and water associated with ettringite and AFm possible

Different conditions:
Duration, sample size, ...

methanol interacts strongly with hydrates, esp. ettringite
acetone dimerizes (problem with TGA)

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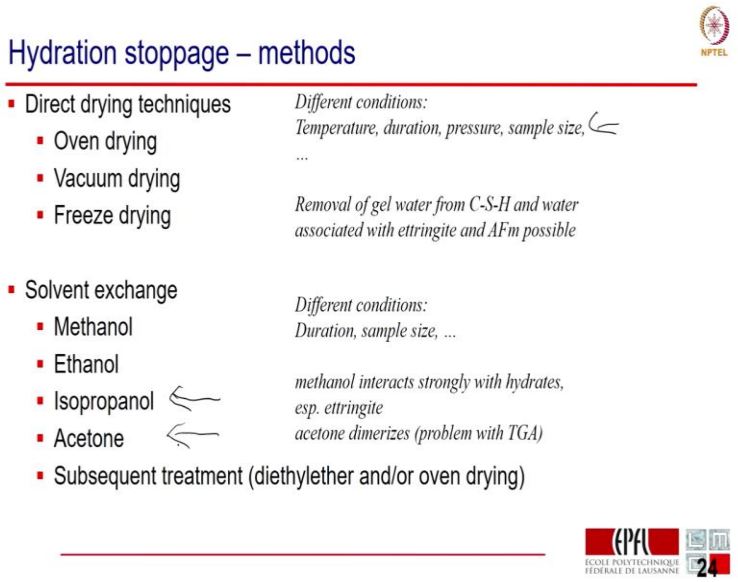

Hydration stoppage – methods

- Direct drying techniques
  - Oven drying
  - Vacuum drying
  - Freeze drying

Different conditions:
Temperature, duration, pressure, sample size, …

Removal of gel water from C-S-H and water associated with ettringite and AFm possible

- Solvent exchange
  - Methanol
  - Ethanol
  - Isopropanol
  - Acetone
  - Subsequent treatment (diethylether and/or oven drying)

Different conditions:
Duration, sample size, …

methanol interacts strongly with hydrates, esp. ettringite
acetone dimerizes (problem with TGA)

Methanol we tend not to use because it is being claimed to have cause health problems. And the problem of ethanol is that ethanol often picks up a lot of water.

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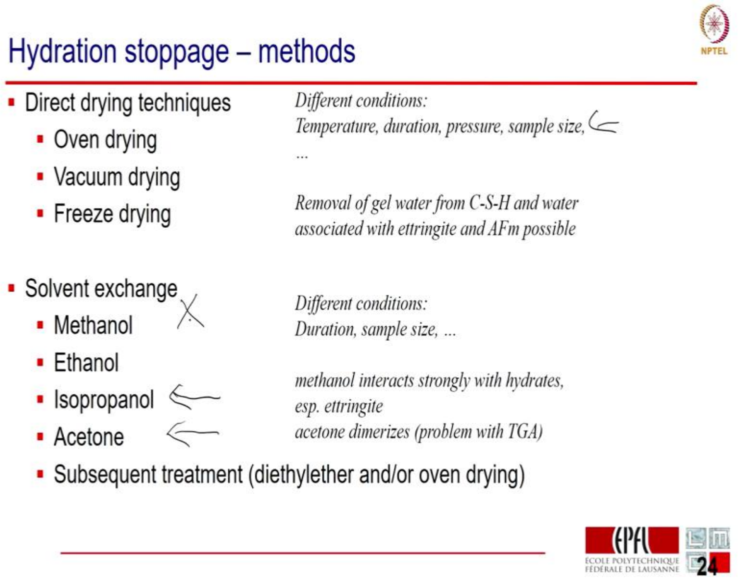

Hydration stoppage – methods

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  - Acetone
  - Subsequent treatment (diethylether and/or oven drying)

Different conditions:
Duration, sample size, …

methanol interacts strongly with hydrates, esp. ettringite
acetone dimerizes (problem with TGA)

So it is not really effective in stopping the hydration.

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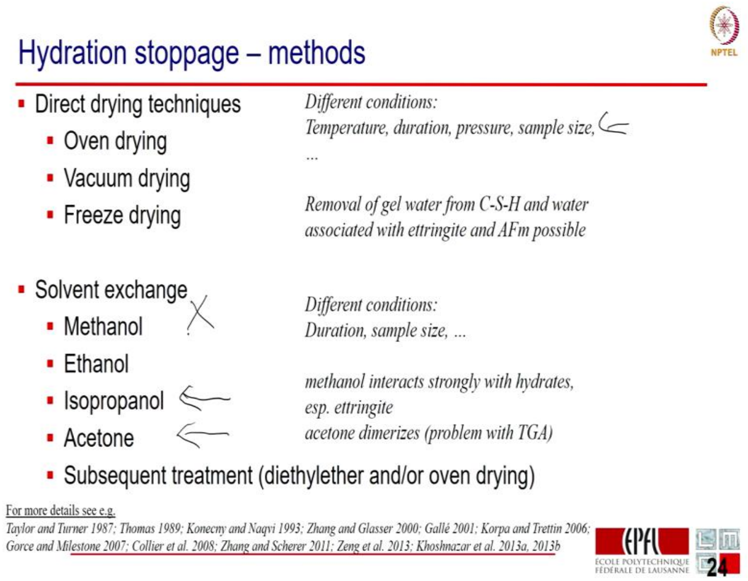

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  - Subsequent treatment (diethylether and/or oven drying)

Different conditions:
Duration, sample size, …

methanol interacts strongly with hydrates, esp. ettringite
acetone dimerizes (problem with TGA)

For more details see e.g.
Taylor and Turner 1987; Thomas 1989; Konecny and Naqvi 1993; Zhang and Glasser 2000; Gallé 2001; Korpa and Trettin 2006; Gorce and Milestone 2007; Collier et al. 2008; Zhang and Scherer 2011; Zeng et al. 2013; Khoshnazar et al. 2013a, 2013b

And you can look in the literature, many, many details of these studies.

Now the problem is that nearly all these methods do produce something to be aware of what these changes can be.

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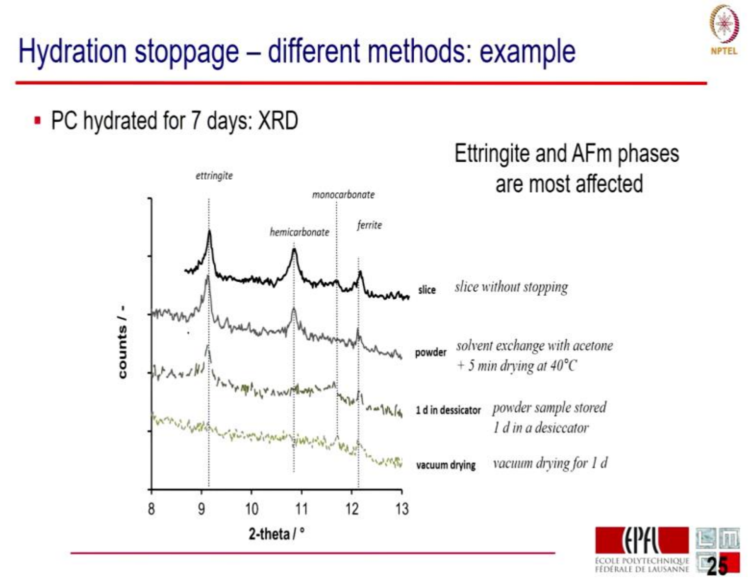

Hydration stoppage – different methods: example

- PC hydrated for 7 days: XRD

Ettringite and AFm phases are most affected

And here I just showed examples, there are many more you can look at in the book and this shows with the X-ray diffraction pattern and it is really mostly the ettringite and the AFm phases that are most effective.

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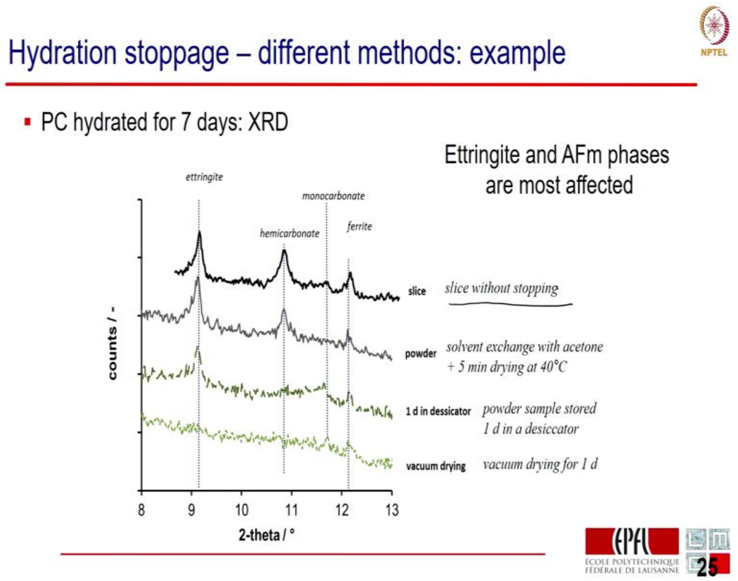

Hydration stoppage – different methods: example

- PC hydrated for 7 days: XRD

Ettringite and AFm phases are most affected

slice without stopping

solvent exchange with acetone + 5 min drying at 40°C

powder sample stored 1 d in a desiccator

vacuum drying for 1 d

So here we see a slice without any stopping and we can see this very nice ettringite peak here.

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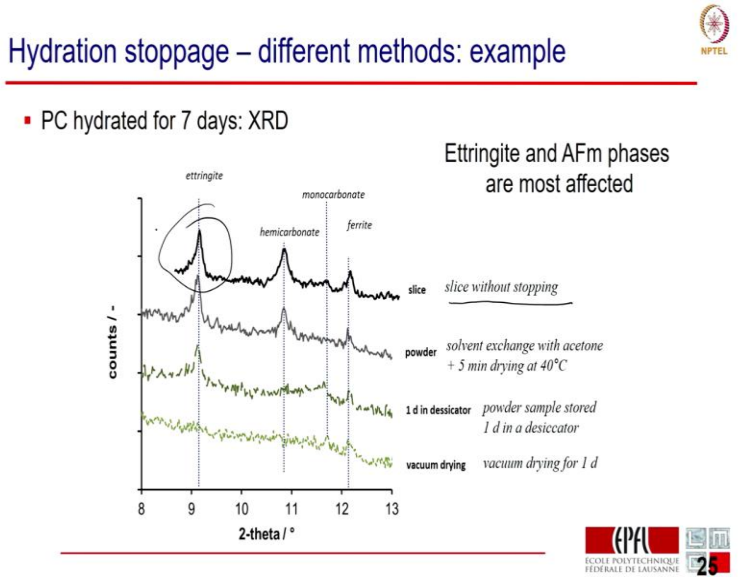

Hydration stoppage – different methods: example

- PC hydrated for 7 days: XRD

Ettringite and AFm phases are most affected

slice without stopping

solvent exchange with acetone + 5 min drying at 40°C

powder sample stored 1 d in a desiccator

vacuum drying for 1 d

This is generally much lower and for example here we have got vacuum drying only for one day but you see the ettringite has been completely destroyed.

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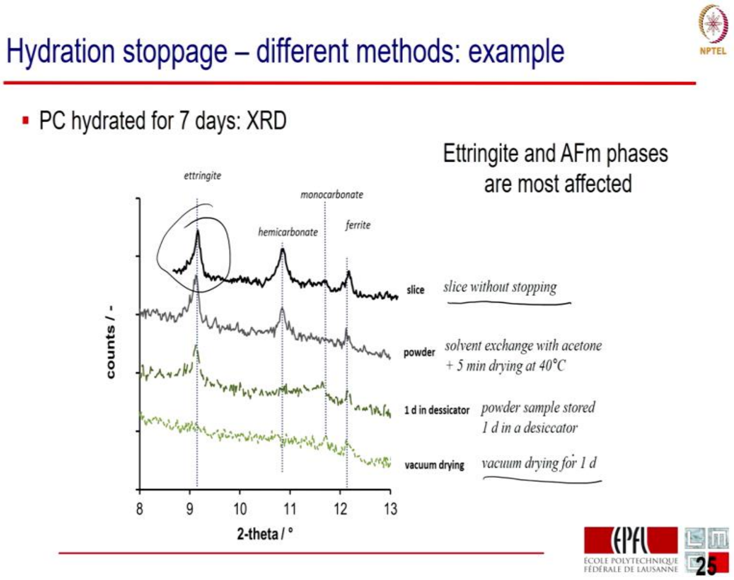
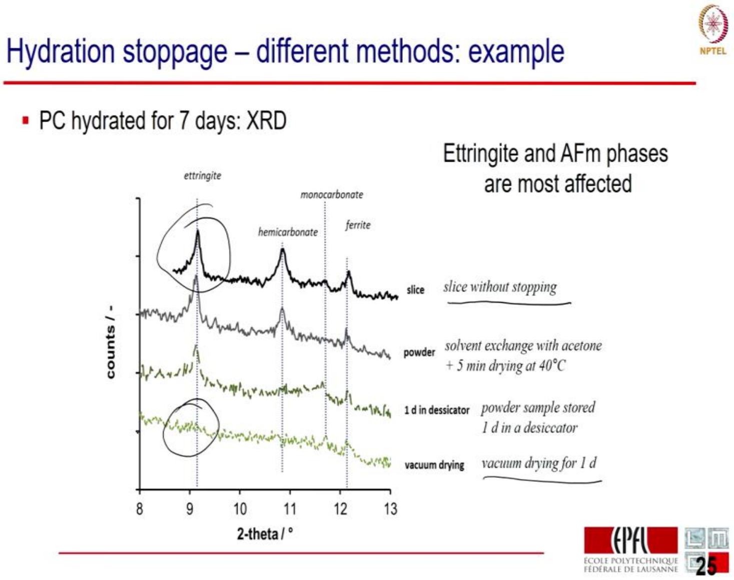


Hydration stoppage – different methods: example

- PC hydrated for 7 days: XRD

Ettringite and AFm phases are most affected

(Refer Slide Time: 20:19)

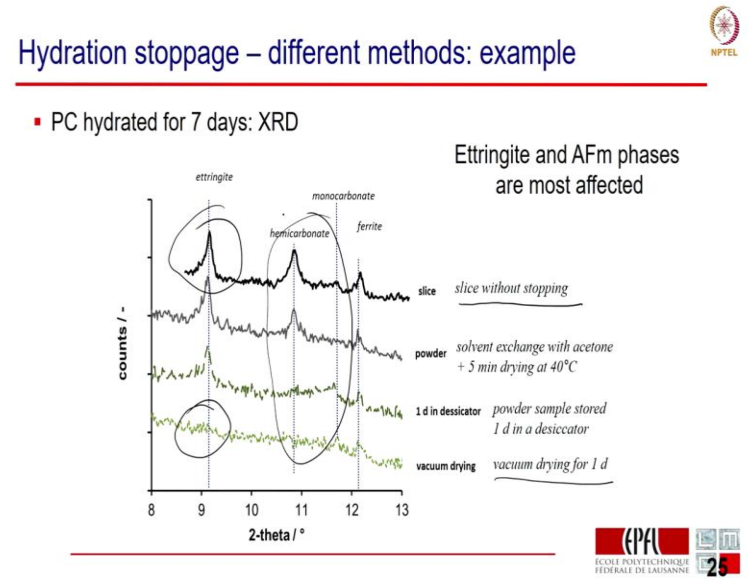


Hydration stoppage – different methods: example

- PC hydrated for 7 days: XRD

Ettringite and AFm phases are most affected

(Refer Slide Time: 20:26)



Hydration stoppage – different methods: example

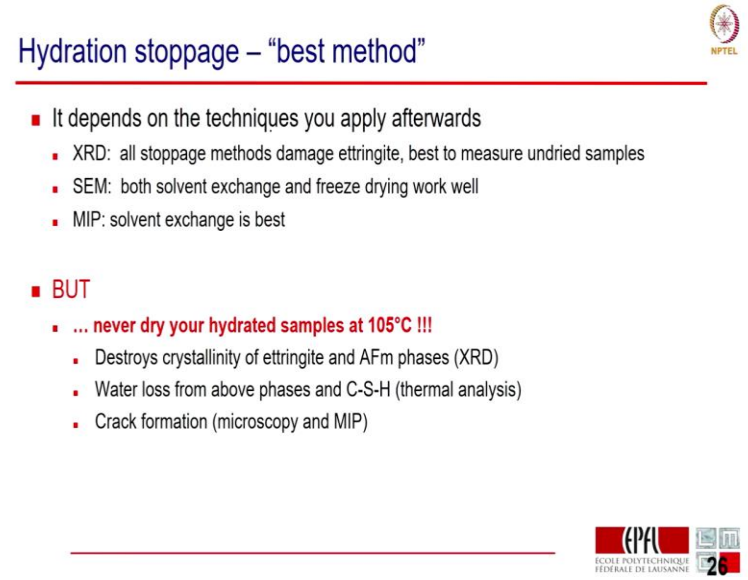
- PC hydrated for 7 days: XRD

Ettringite and AFm phases are most affected

We will also have changes in the spaces, the hemi and mono carbo-aluminate, this of course can also be affected by small quantities of CO_2 in the air and that is another important thing. Really try to protect your samples as much as possible from CO_2; storing in a desiccator with a client, with a product that absorbs CO_2 is the best way to do that.

So for X-ray diffraction as we will talk about later, then the best method is not to stop at all but of course this does depend on having machine available so you can cut your slice, take it straight to the diffractometer and make your measurement really without any delay.

(Refer Slide Time: 21:03)



Hydration stoppage – "best method"

- It depends on the techniques you apply afterwards
  - XRD: all stoppage methods damage ettringite, best to measure undried samples
  - SEM: both solvent exchange and freeze drying work well
  - MIP: solvent exchange is best
- BUT
  - **... never dry your hydrated samples at 105°C !!!**
    - Destroys crystallinity of ettringite and AFm phases (XRD)
    - Water loss from above phases and C-S-H (thermal analysis)
    - Crack formation (microscopy and MIP)

So the best method for stopping really depends on what you want to do afterwards. If you want to do X-ray diffraction it is best to measure undried samples.

If you are more interested in SEM, as we will see later, both solvent exchange and freeze drying work well, interested in mercury intrusion porosimetry then solvent exchange is by far the best as we will see later.

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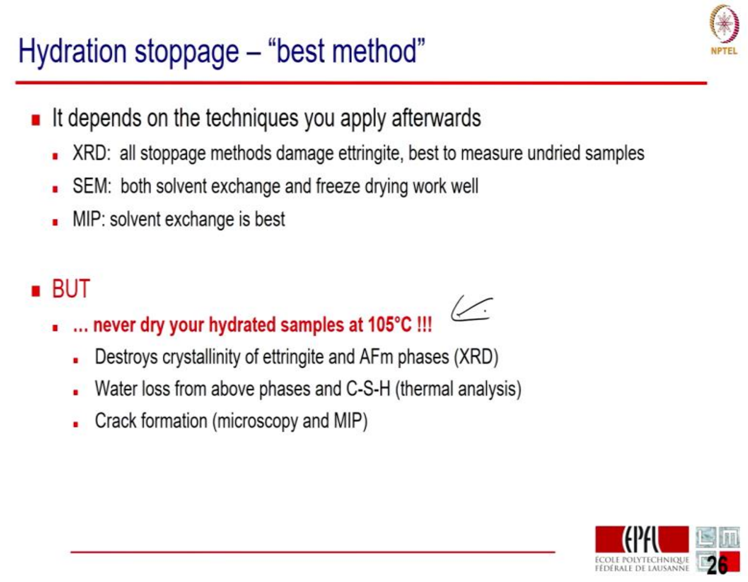

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But and I stress again, please do not dry your samples at a 105 degrees C. Your complete microstructure, you completely change the porosity. It is really a bad method.

(Refer Slide Time: 21:47)

X-ray diffraction - XRD

Thanks to Rietveld analysis this is now the pre-eminent technique to quantify crystalline phases

Slides from Ruben Snellings

So to finish this first part we are going to look briefly at X-ray diffraction and again I stress what the material I can cover here is really only very small, everything you need to, but hopefully you can get some idea.

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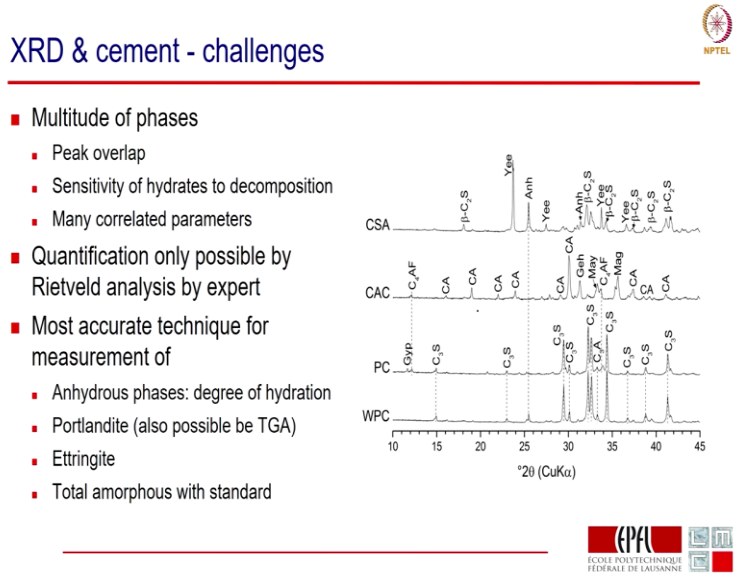

XRD & cement - challenges

- Multitude of phases
  - Peak overlap
  - Sensitivity of hydrates to decomposition
  - Many correlated parameters
- Quantification only possible by Rietveld analysis by expert
- Most accurate technique for measurement of
  - Anhydrous phases: degree of hydration
  - Portlandite (also possible be TGA)
  - Ettringite
  - Total amorphous with standard

Now X-ray diffraction is where the preheat technique for looking at the crystalline phases, the challenge we have with cement is we have a huge amount of peak overlap.

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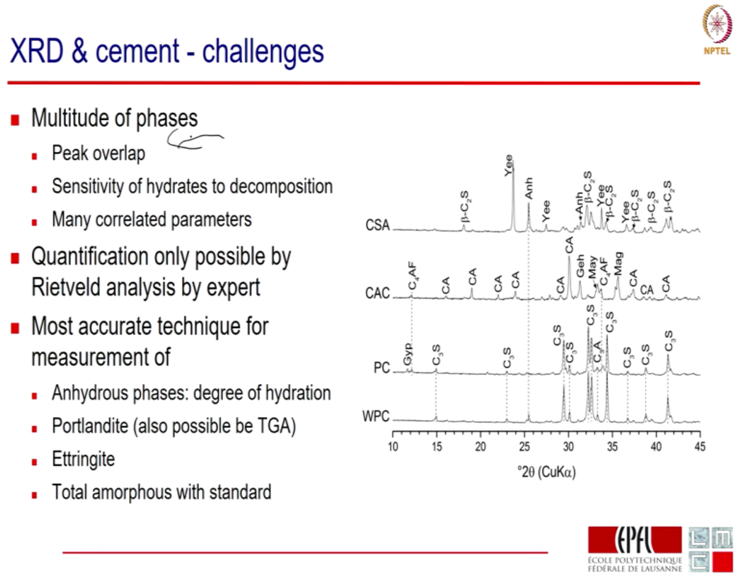

XRD & cement - challenges

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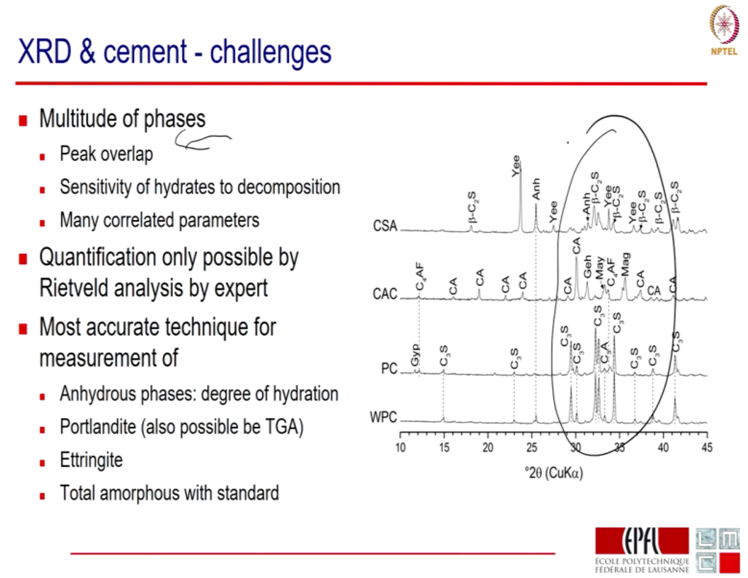
  - Anhydrous phases: degree of hydration
  - Portlandite (also possible be TGA)
  - Ettringite
  - Total amorphous with standard

And this is not really surprising, because in cement, we were dealing with a quite small number of elements, always things like calcium and silicon and aluminum with oxygen so the bond distances will always be the same and this means that the lattice vacant spacings also tend to be very similar.

(Refer Slide Time: 22:33)



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- Most accurate technique for measurement of
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  - Portlandite (also possible be TGA)
  - Ettringite
  - Total amorphous with standard

And this is why we get this incredible amount of peak overlap, from particularly in this area here for the anhydrous phases, everything is coming in very, very similar positions. So the detailed quantification really has been a breakthrough in recent years, this development of this Rietveld analysis but it really has to be applied by an expert to get the best results.

Nevertheless if you do this properly, X-ray diffraction is by far away the most accurate technique for looking at the amount of anhydrous phases and from that you can calculate the degree of hydration. It is also very good for looking at Portlandlite if you are careful to avoid preferential orientation but TGA is also good for that.

And ettringite, and of course we can look at the total amorphous if you use a standard.

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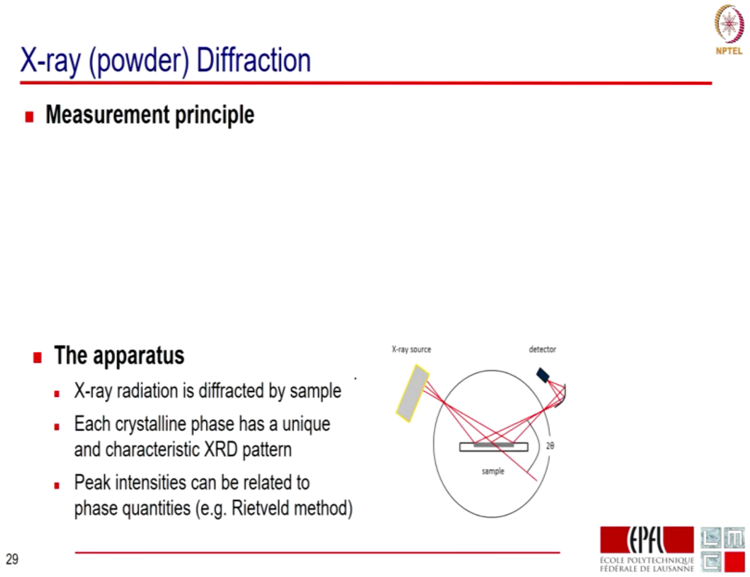


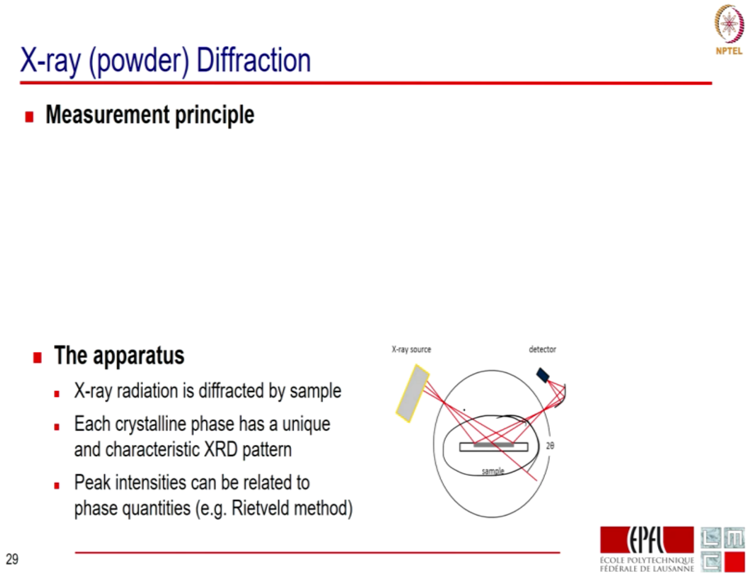
X-ray (powder) Diffraction

- **Measurement principle**

- **The apparatus**
  - X-ray radiation is diffracted by sample
  - Each crystalline phase has a unique and characteristic XRD pattern
  - Peak intensities can be related to phase quantities (e.g. Rietveld method)

So the apparatus in X-ray diffraction is nowadays almost universally the diffractometer which replaced all other techniques which are based on photos etc and the idea of this diffractometer is we have a disk of cement paste which is usually spinning and then X-ray source and the detector move at the same angle, so we get, the X-rays which are diffracted at a given angle can be captured by the detector.

(Refer Slide Time: 23:42)



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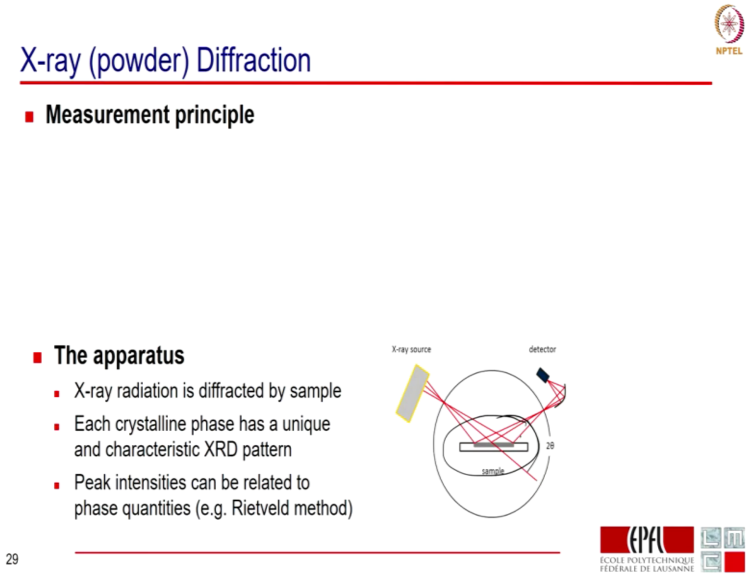

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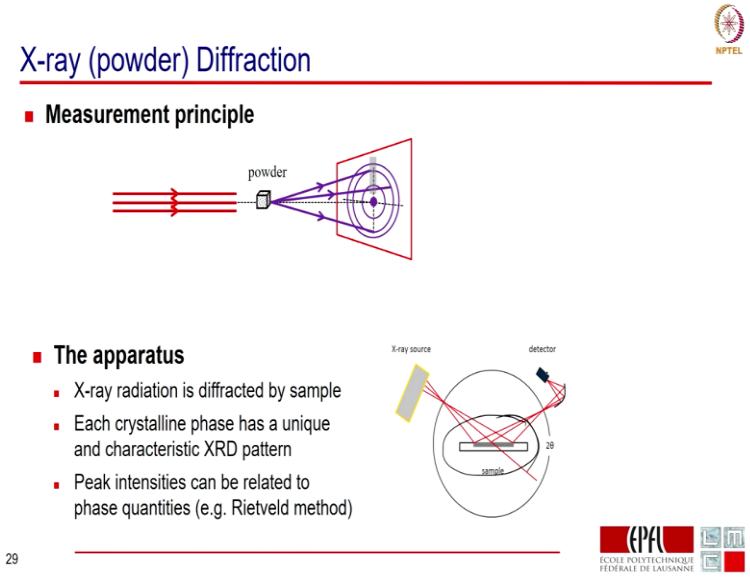

X-ray (powder) Diffraction

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- **The apparatus**
  - X-ray radiation is diffracted by sample
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And the idea of this technique is that we have a powder, a powder has lots of different crystals in different orientations and this would give, on a sort of photograph, this would give rings. But by this diffractometer setup we compress this data into one dimension.

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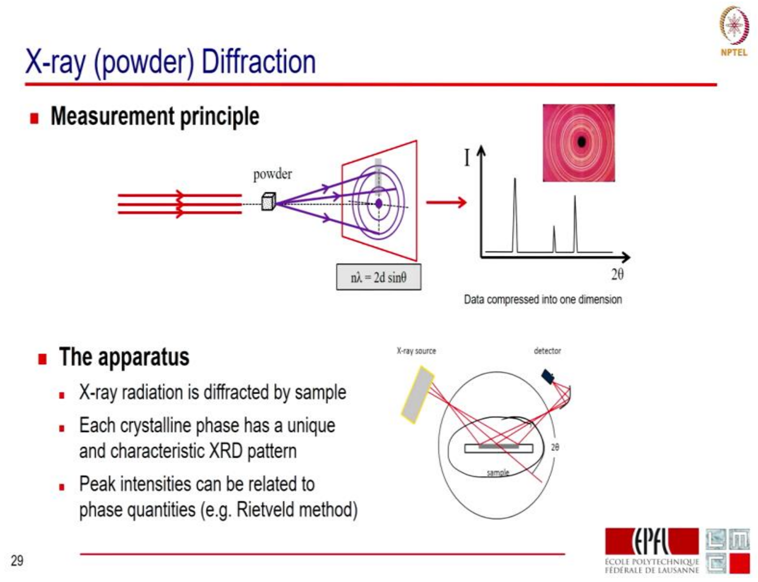

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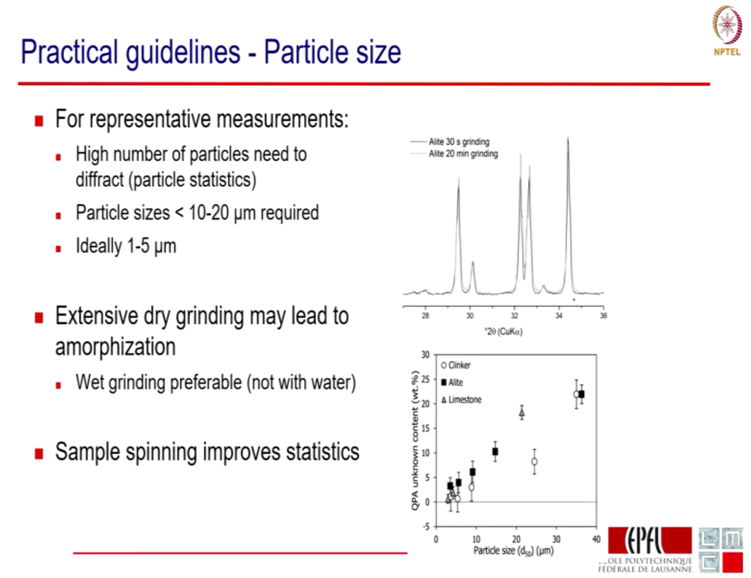


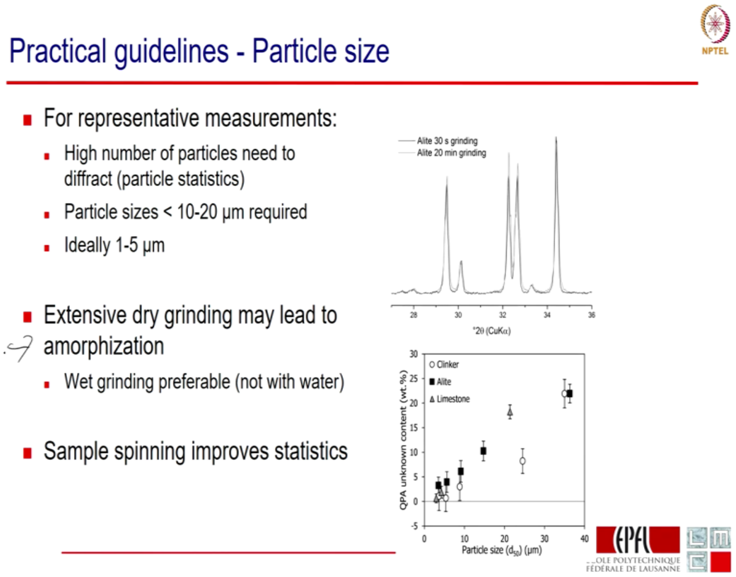
Practical guidelines - Particle size

- For representative measurements:
  - High number of particles need to diffract (particle statistics)
  - Particle sizes < 10-20 µm required
  - Ideally 1-5 µm
- Extensive dry grinding may lead to amorphization
  - Wet grinding preferable (not with water)
- Sample spinning improves statistics

So some practical guidelines. First of all, it is important to minimize the particle size and it is particularly can be important if you want to quantify the amorphous phase.

So it has been a lot of debate about whether we have amorphous phases in unhydrated cement and here we can see some results by a paper by Snellingx and myself that if you reduce the particle size enough then you see really there is no amorphous phase.

(Refer Slide Time: 25:03)



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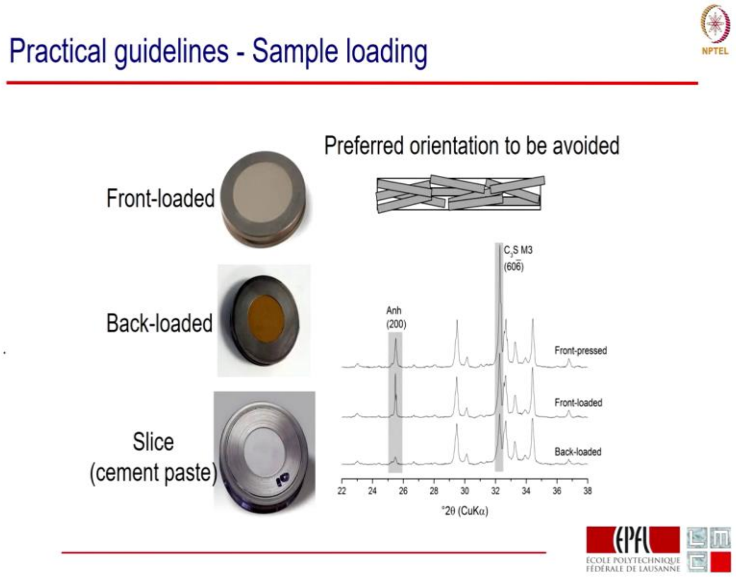
  - Particle sizes < 10-20 μm required
  - Ideally 1-5 μm
- Extensive dry grinding may lead to amorphization
  - Wet grinding preferable (not with water)
- Sample spinning improves statistics

But be careful, because if you are going to dry your sample, grind your sample dry, then you can actually produce amorphous phases. So you have to do wet grinding but of course not with water. Again use something like isopropanol. So this is the kind of sample.

(Refer Slide Time: 25:11)



Practical guidelines - Sample loading

Front-loaded

Back-loaded

Slice (cement paste)

Preferred orientation to be avoided

Traditionally people used what is called a front loading technique. That is to say you put your powder into the sample holder and then you smooth it off, the problem is that this really tends to produce preferential orientation.

If you have crystals which are platy or long phases like this, they tend to be oriented and this can make a very, very strong impact on the intensity of the peak. So the recommendation is either to use what is called backloading which is where you put your sample holder on a flat plate and then to load the powder from the back, or to use slices as we talked about before.

And in the slices when you are hydrating, you have not ground that maybe to the ideal particle size but most of the crystals are formed in very small crystallized anhydrite, so you can get quite good results.

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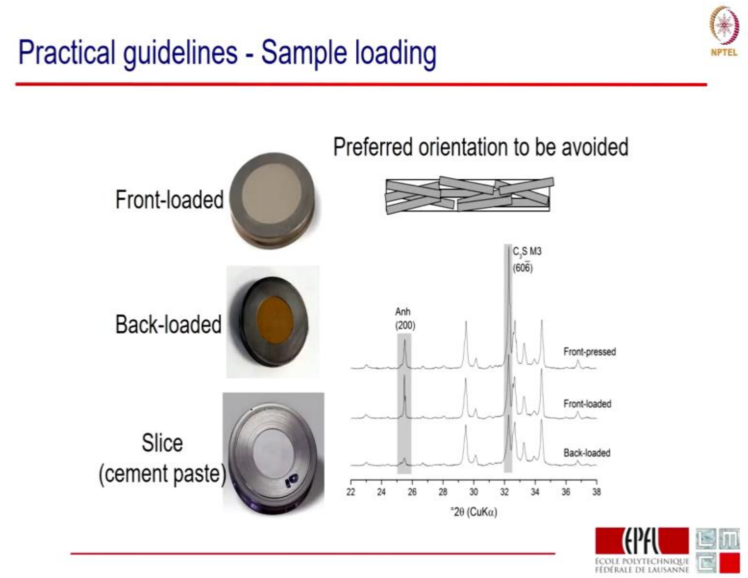

Practical guidelines - Sample loading

Front-loaded

Back-loaded

Slice
(cement paste)

Preferred orientation to be avoided

And here we can see the impact of the different loading techniques in terms of this preferential orientation. You see the backloading, we have the best situation here.

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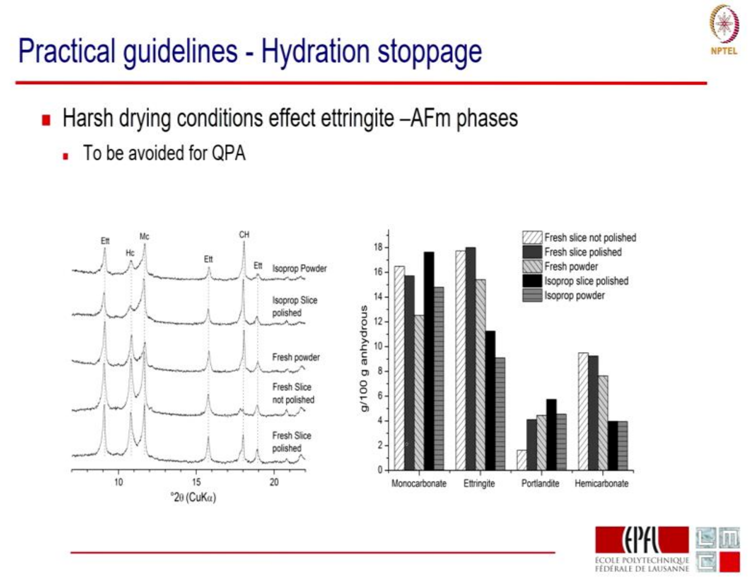

Practical guidelines - Hydration stoppage

- Harsh drying conditions effect ettringite –AFm phases
  - To be avoided for QPA

The second point as we already mentioned is the stoppage of hydration, ettringite is the most effective phase.

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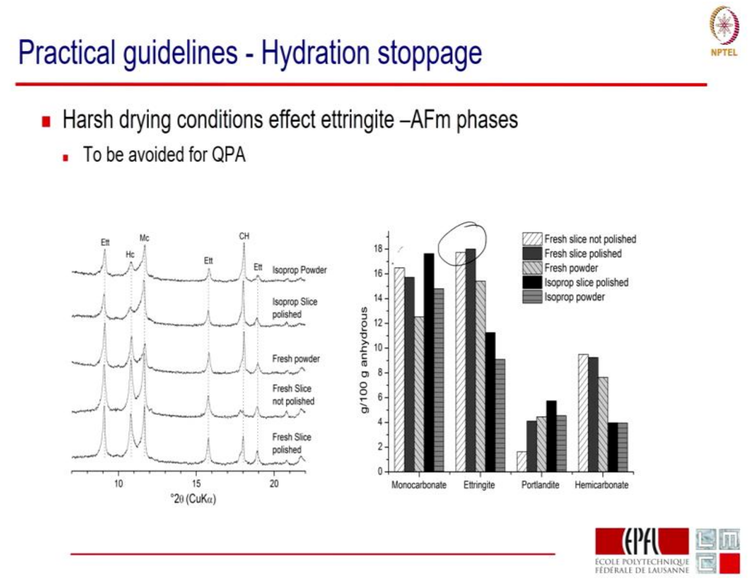

Practical guidelines - Hydration stoppage

- Harsh drying conditions effect ettringite –AFm phases
  - To be avoided for QPA

We can see over here a series of different techniques generally for preserving the monocarbonate and the ettringite, these first two of the slice of the best but if you have a slice and you do not do any sort of rough polishing then you can have a bad impact on your Portlandite.

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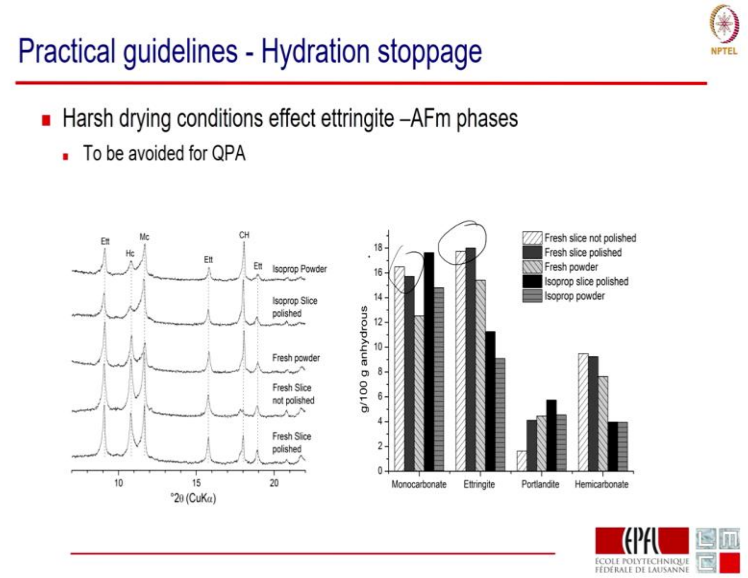

Practical guidelines - Hydration stoppage

- Harsh drying conditions effect ettringite –AFm phases
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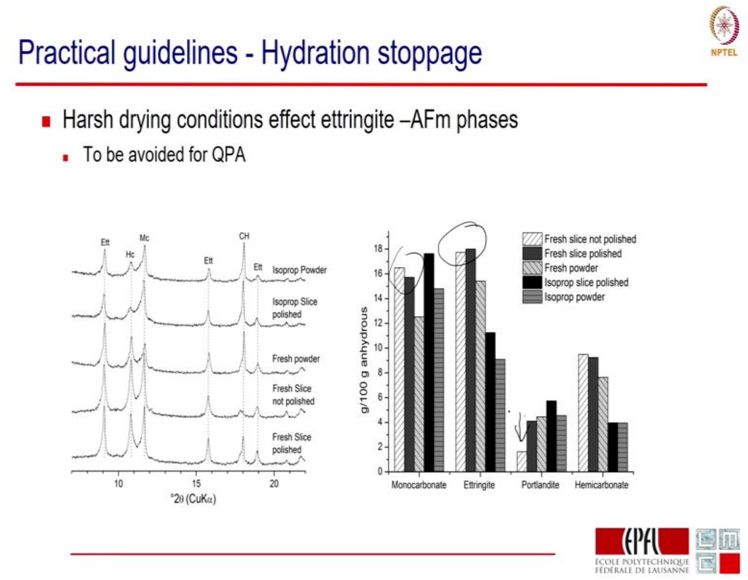

Practical guidelines - Hydration stoppage

- Harsh drying conditions effect ettringite –AFm phases
  - To be avoided for QPA

So the technique we really recommend is these fresh slices with just the light amount of polishing on an emery paper.

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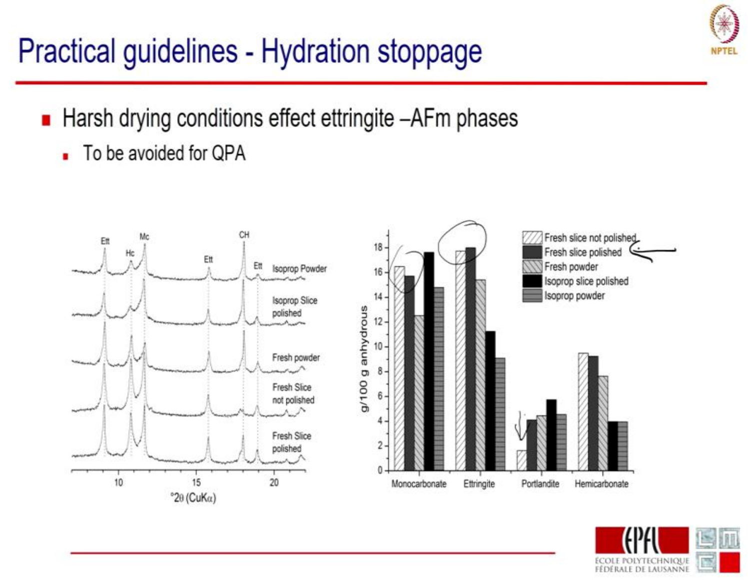

Practical guidelines - Hydration stoppage

- Harsh drying conditions effect ettringite –AFm phases
  - To be avoided for QPA

And this slide here just summarizes the most popular preparation techniques of fresh mix where you can look at the hydration in-situ of a slice or a powder.

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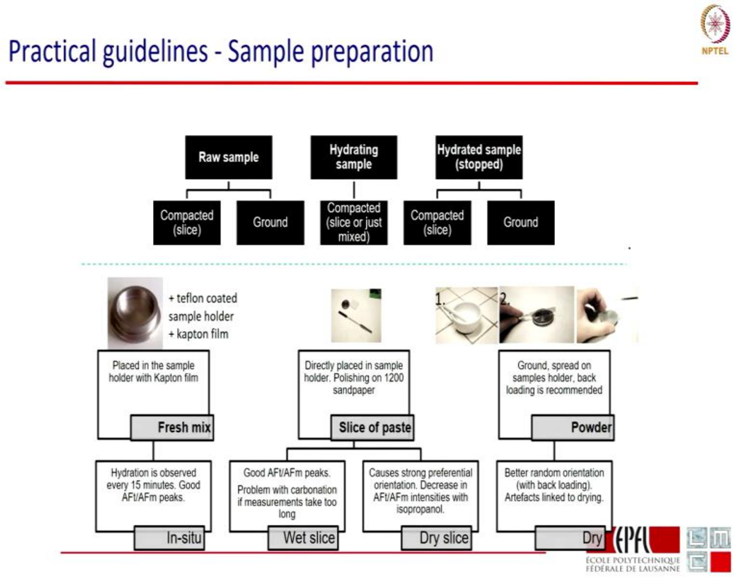

Practical guidelines - Sample preparation

Raw sample
- Compacted (slice)
- Ground

Hydrating sample
- Compacted (slice or just mixed)

Hydrated sample (stopped)
- Compacted (slice)
- Ground

+ teflon coated sample holder
+ kapton film

Fresh mix: Placed in the sample holder with Kapton film
- **In-situ**: Hydration is observed every 15 minutes. Good AFt/AFm peaks.

Slice of paste: Directly placed in sample holder. Polishing on 1200 sandpaper
- **Wet slice**: Good AFt/AFm peaks. Problem with carbonation if measurements take too long
- **Dry slice**: Causes strong preferential orientation. Decrease in AFt/AFm intensities with isopropanol.

Powder: Ground, spread on samples holder, back loading is recommended
- **Dry**: Better random orientation (with back loading). Artefacts linked to drying.

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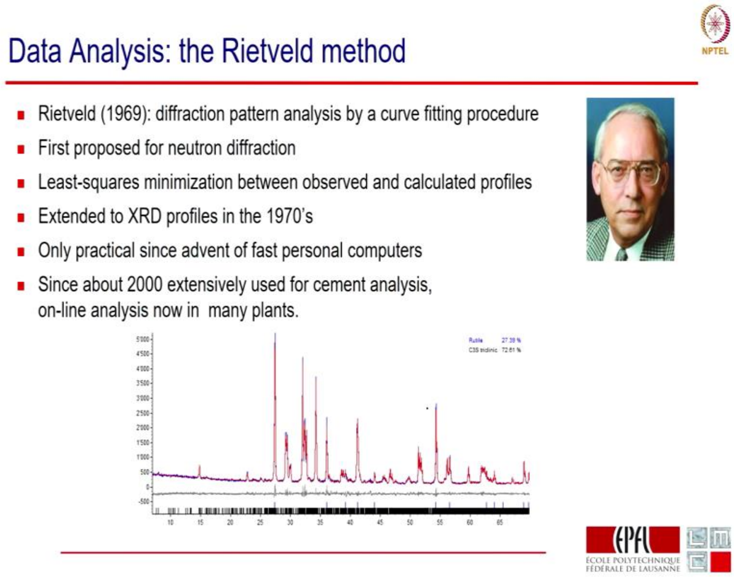


Data Analysis: the Rietveld method

- Rietveld (1969): diffraction pattern analysis by a curve fitting procedure
- First proposed for neutron diffraction
- Least-squares minimization between observed and calculated profiles
- Extended to XRD profiles in the 1970's
- Only practical since advent of fast personal computers
- Since about 2000 extensively used for cement analysis, on-line analysis now in many plants.

Now this method of the Rietveld analysis is extremely powerful and really has made a revolution in the past two decades in the analysis of cements because of this problem of peak overlap.

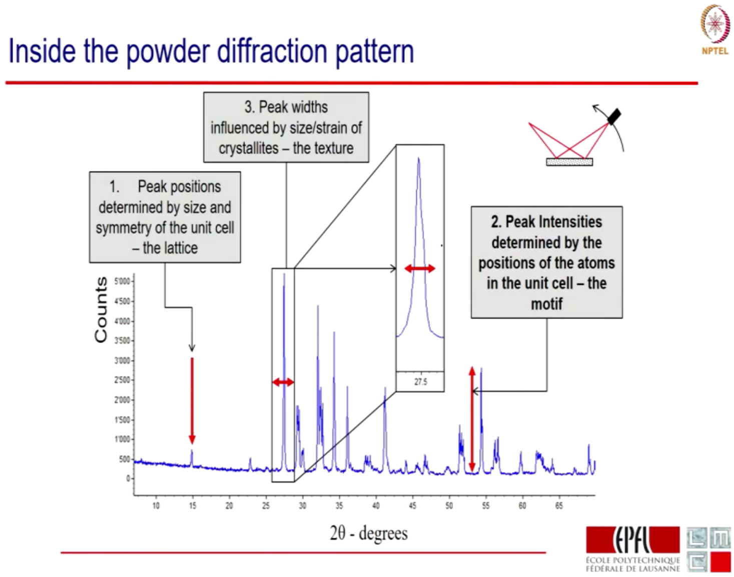
Now the idea for this analysis was, Professor Rietveld came up with this in 1969 for neutron diffraction and the idea is you have a calculated pattern, you have an observed pattern and you minimize the difference by least squares method.

So this is quite easy in terms of the principle but in terms of the application, because you have many, many techniques and you have to minimize individually for each of these peaks, then it is really only become practical since the advent of fast personal computers.

And this has really made a revolution and since the turn of the century this is now more and more implanted in cement plants.

And really has started to completely replace the Bogue calculation for the phases in cement phase which is really, completely inaccurate.

(Refer Slide Time: 28:28)



Inside the powder diffraction pattern

3. Peak widths influenced by size/strain of crystallites – the texture

1. Peak positions determined by size and symmetry of the unit cell – the lattice

2. Peak Intensities determined by the positions of the atoms in the unit cell – the motif

Now if we look in more detail at these peaks, there are many, many different things that can impact the height of the peaks. And of course these would have to be calculated in these Rietveld analysis. So the peak positions first of all is determined by the size and symmetry of the unit cell.

The intensities is determined by the position of the atoms, the motif and then the width can also be affected by many different aspects, the size of the crystallites, the configuration of the equipment etc.

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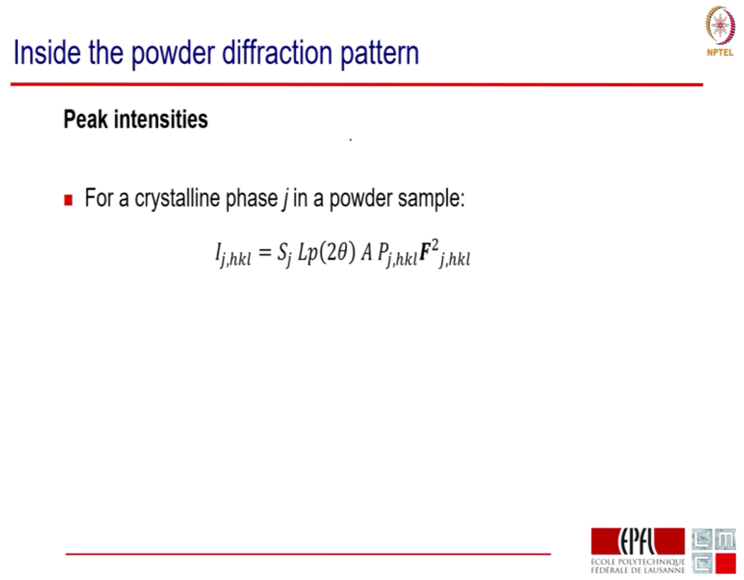

Inside the powder diffraction pattern

Peak intensities

- For a crystalline phase *j* in a powder sample:

$$I_{j,hkl} = S_j \, Lp(2\theta) \, A \, P_{j,hkl} \boldsymbol{F}^2{}_{j,hkl}$$

And this would lead to this very complicated equation with many, many different variables and all these variables can be refined.

$$I\, j, hkl = Sj \, Lp \, (2\theta) \, A \, Pj, hkl \, F^2 \, j, hkl$$

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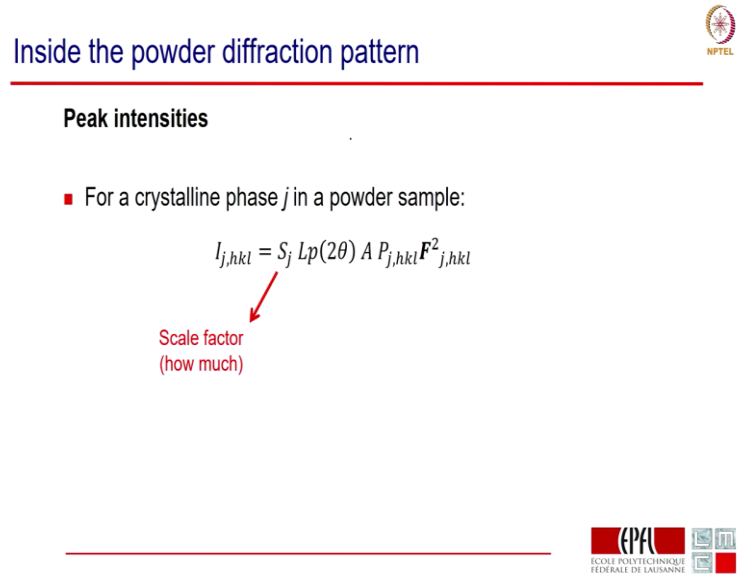


Inside the powder diffraction pattern

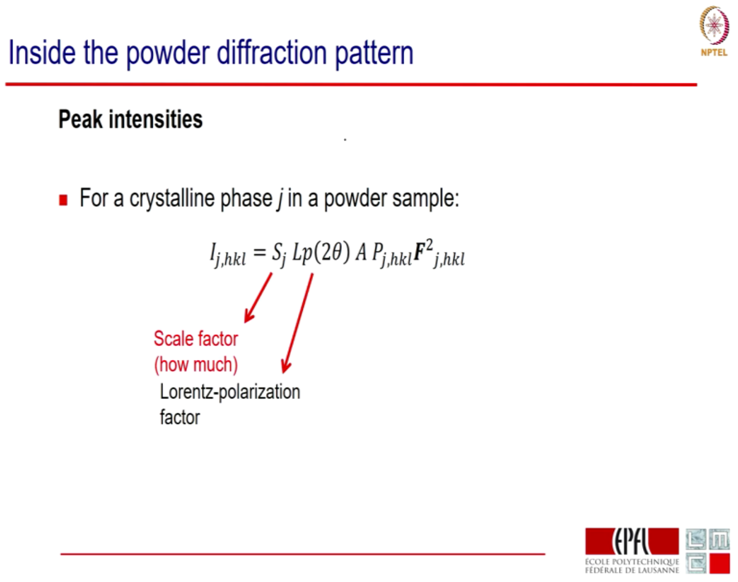
Peak intensities

- For a crystalline phase *j* in a powder sample:

$$I_{j,hkl} = S_j \, Lp(2\theta) \, A \, P_{j,hkl} \boldsymbol{F}^2{}_{j,hkl}$$

Scale factor
(how much)

(Refer Slide Time: 29:02)



Inside the powder diffraction pattern

Peak intensities

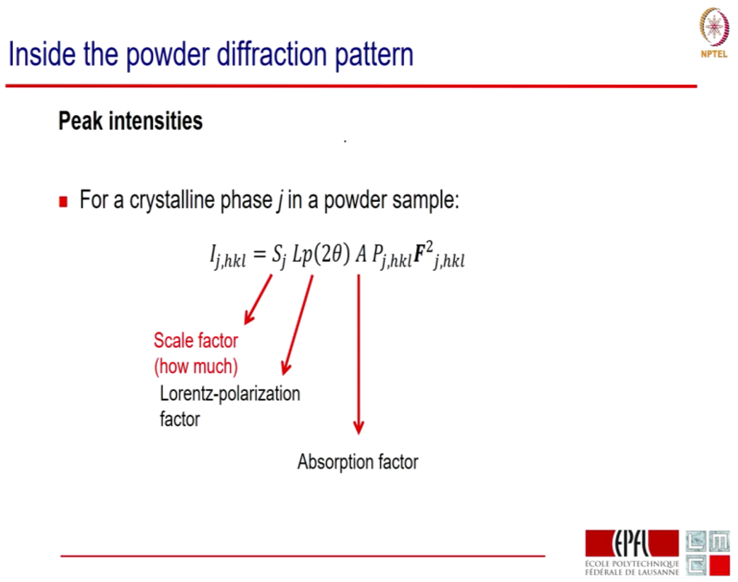
- For a crystalline phase *j* in a powder sample:

$$I_{j,hkl} = S_j\, Lp(2\theta)\, A\, P_{j,hkl}\boldsymbol{F}^2{}_{j,hkl}$$

Scale factor (how much)

Lorentz-polarization factor

(Refer Slide Time: 29:03)



Inside the powder diffraction pattern

Peak intensities

- For a crystalline phase *j* in a powder sample:

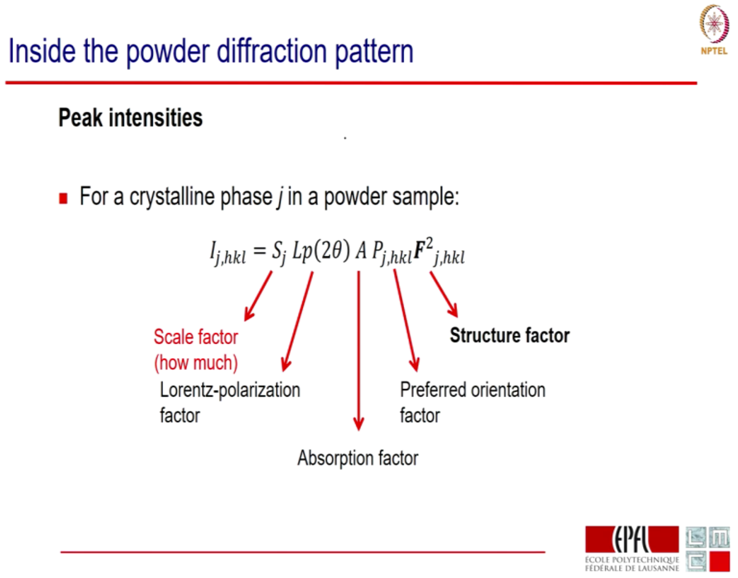
$$I_{j,hkl} = S_j\, Lp(2\theta)\, A\, P_{j,hkl}\boldsymbol{F}^2{}_{j,hkl}$$

Scale factor (how much)

Lorentz-polarization factor

Absorption factor

(Refer Slide Time: 29:04)



Inside the powder diffraction pattern

Peak intensities

- For a crystalline phase *j* in a powder sample:

$$I_{j,hkl} = S_j \, Lp(2\theta) \, A \, P_{j,hkl} \boldsymbol{F}^2{}_{j,hkl}$$

Scale factor (how much)

Lorentz-polarization factor

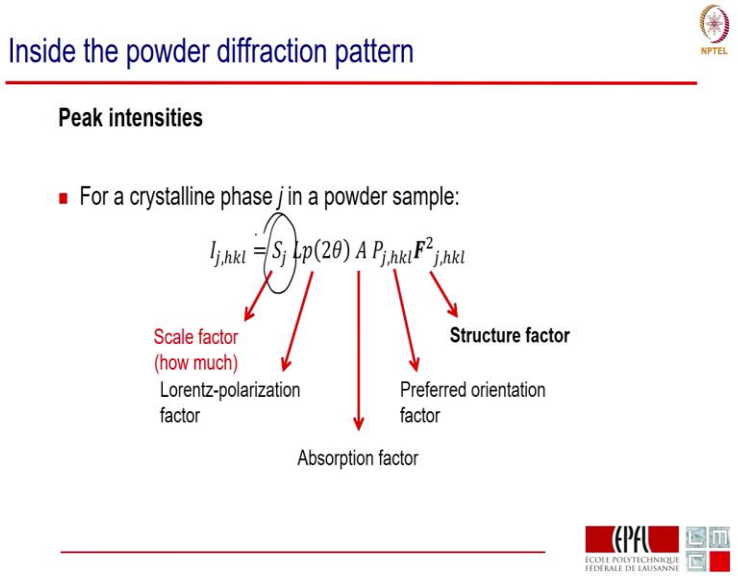
Absorption factor

Preferred orientation factor

Structure factor

And this is the problem and this is why you need a certain amount of expertise to apply the technique because if you let all these variables vary at will, then you can end up with any old rubbish.

(Refer Slide Time: 29:24)



Inside the powder diffraction pattern

Peak intensities

- For a crystalline phase *j* in a powder sample:

$$I_{j,hkl} = S_j \, Lp(2\theta) \, A \, P_{j,hkl} \boldsymbol{F}^2{}_{j,hkl}$$

Scale factor (how much)

Lorentz-polarization factor

Absorption factor

Preferred orientation factor

Structure factor

Well, we are trying to find here is what is called the scale factor which is basically how much of the phase we have in the mixture.

And all of these parameters here, either we know or we can let them vary within well-defined limit.

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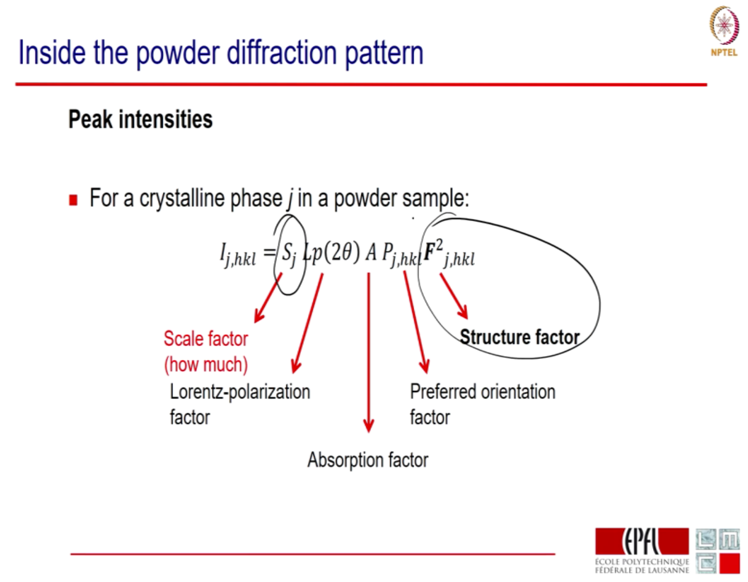

Inside the powder diffraction pattern

Peak intensities

- For a crystalline phase *j* in a powder sample:

$$I_{j,hkl} = S_j\, Lp(2\theta)\, A\, P_{j,hkl}\, \boldsymbol{F}^2_{j,hkl}$$

Scale factor (how much)

Lorentz-polarization factor

Absorption factor

Preferred orientation factor

Structure factor

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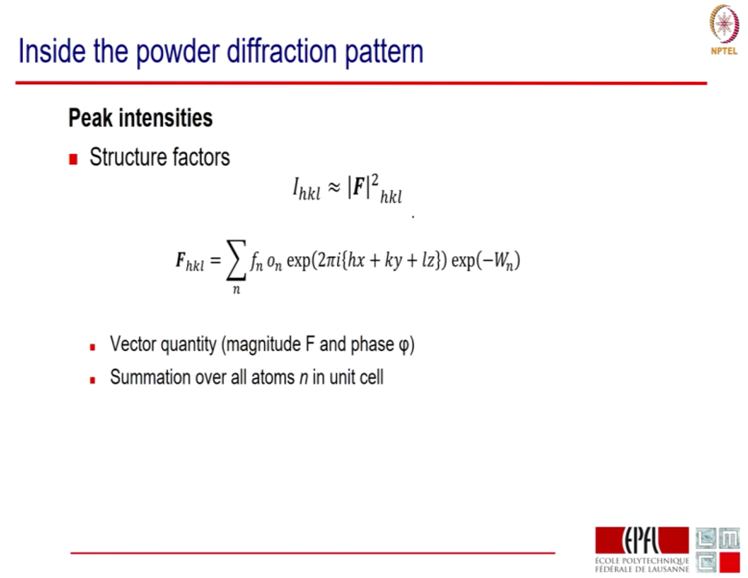

Inside the powder diffraction pattern

Peak intensities

- Structure factors

$$I_{hkl} \approx |\boldsymbol{F}|^2_{hkl}$$

$$\boldsymbol{F}_{hkl} = \sum_n f_n\, o_n \exp(2\pi i\{hx + ky + lz\}) \exp(-W_n)$$

  - Vector quantity (magnitude F and phase φ)
  - Summation over all atoms *n* in unit cell

$$I\ hkl \approx |F|^2 hkl$$

$$Fhkl = \sum_n fn\ on \exp(2\pi i\{hx + \ ky + iz\}) \exp(-Wn)$$

So just one of these, the structure factor here for example, this is not the end of the story because this structure factor itself is then the sum of the atomistic scattering factors and then the positions in the unit cell.

So this, you can see, adds even more variables to the equation.

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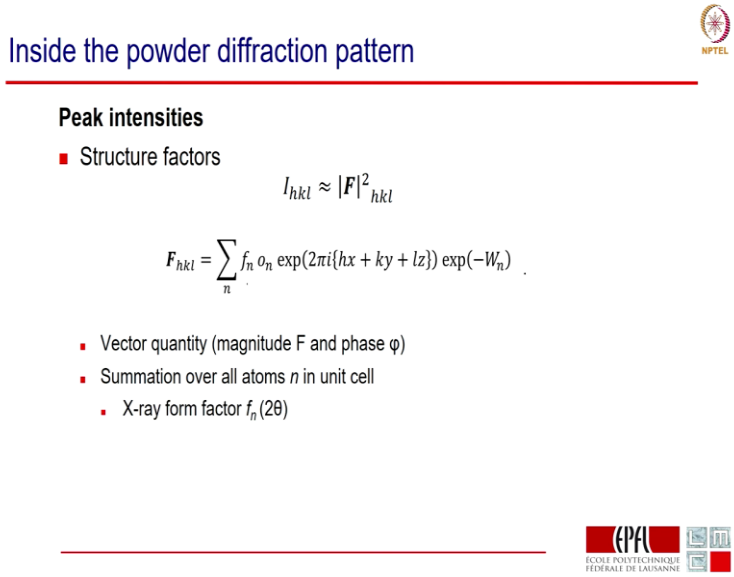

Inside the powder diffraction pattern

Peak intensities

- Structure factors

$$I_{hkl} \approx |\boldsymbol{F}|^2{}_{hkl}$$

$$\boldsymbol{F}_{hkl} = \sum_n f_n \, o_n \exp(2\pi i\{hx + ky + lz\}) \exp(-W_n)$$

  - Vector quantity (magnitude F and phase φ)
  - Summation over all atoms *n* in unit cell
    - X-ray form factor $f_n(2\theta)$

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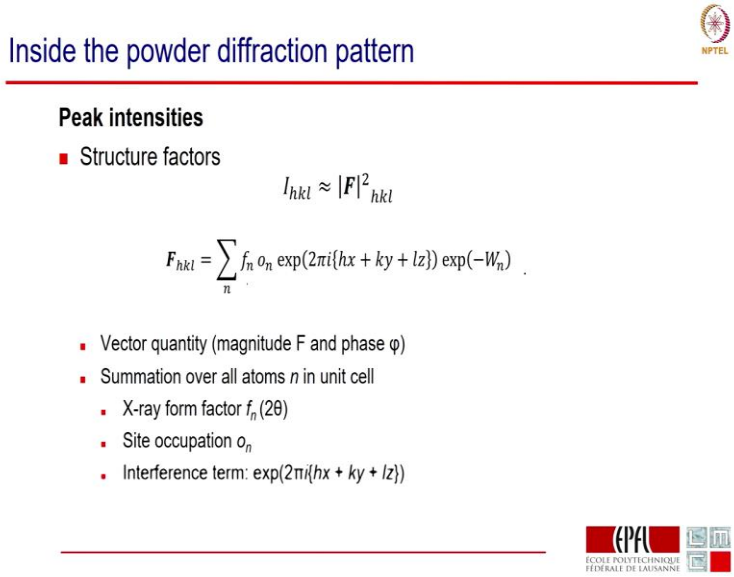

Inside the powder diffraction pattern

Peak intensities

- Structure factors

$$I_{hkl} \approx |\boldsymbol{F}|^2{}_{hkl}$$

$$\boldsymbol{F}_{hkl} = \sum_n f_n \, o_n \exp(2\pi i\{hx + ky + lz\}) \exp(-W_n)$$

  - Vector quantity (magnitude F and phase φ)
  - Summation over all atoms *n* in unit cell
    - X-ray form factor $f_n(2\theta)$
    - Site occupation o_n
    - Interference term: $\exp(2\pi i\{hx + ky + lz\})$

So we have not got time to really go into the full detail of how you can do refinement.

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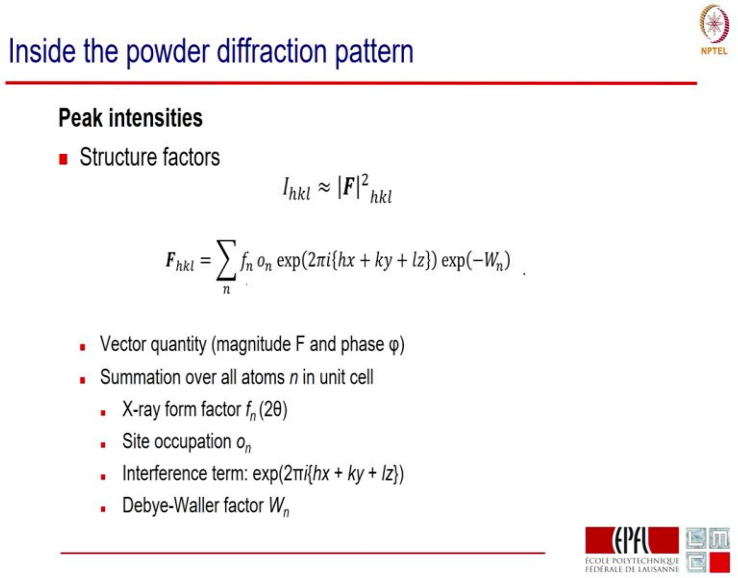

Inside the powder diffraction pattern

Peak intensities

- Structure factors

$$I_{hkl} \approx |\boldsymbol{F}|^2{}_{hkl}$$

$$\boldsymbol{F}_{hkl} = \sum_n f_n\, o_n \exp(2\pi i\{hx + ky + lz\}) \exp(-W_n)$$

- Vector quantity (magnitude F and phase φ)
- Summation over all atoms *n* in unit cell
  - X-ray form factor $f_n(2\theta)$
  - Site occupation o_n
  - Interference term: $\exp(2\pi i\{hx + ky + lz\})$
  - Debye-Waller factor W_n

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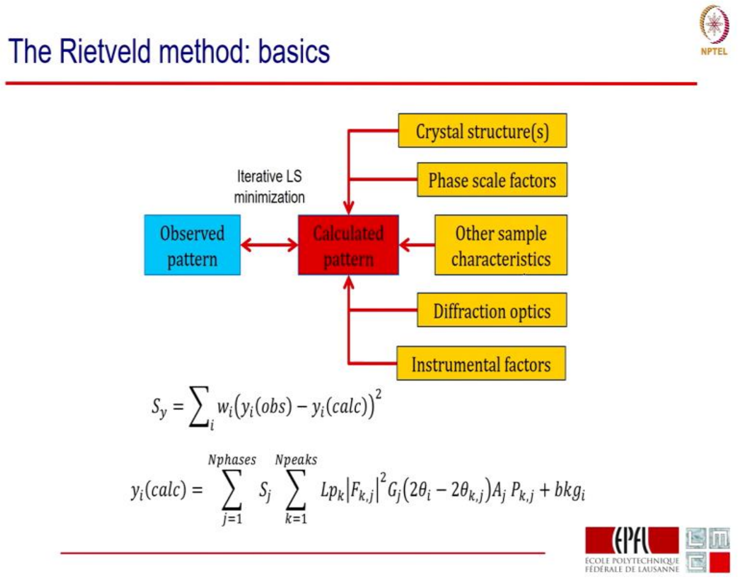

The Rietveld method: basics

Iterative LS minimization

Observed pattern

Calculated pattern

Crystal structure(s)

Phase scale factors

Other sample characteristics

Diffraction optics

Instrumental factors

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

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

$$Sy = \sum_i wi(yi(obs) - yi(calc))^2$$

$$yi\ (calc) = \sum_{j=1}^{Nphases} Sj \sum_{k=1}^{Npeaks} Lpk|Fk.j|^2 Gj(2\theta i - 2\theta k, j) Aj\, Pk, j + bkgi$$

It is summarized here in this very, very simple equation that you are trying to minimize the least squares between these two patterns but you have to do that over all the different peaks with all the different variables.

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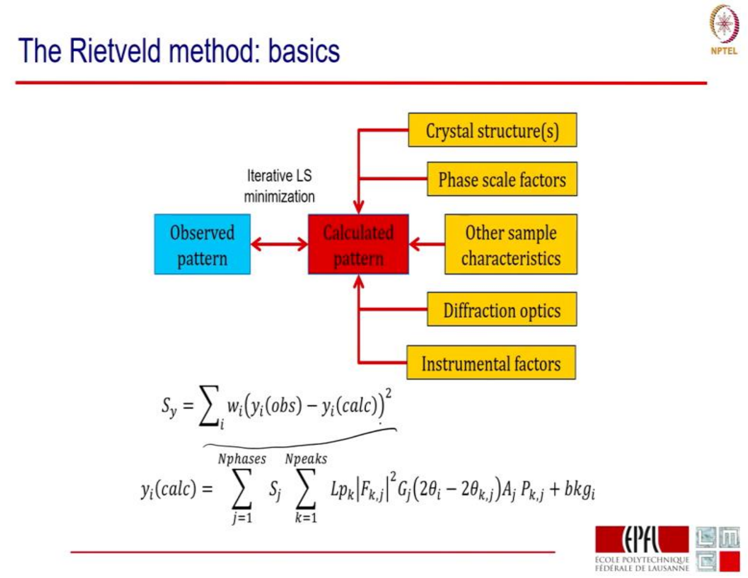
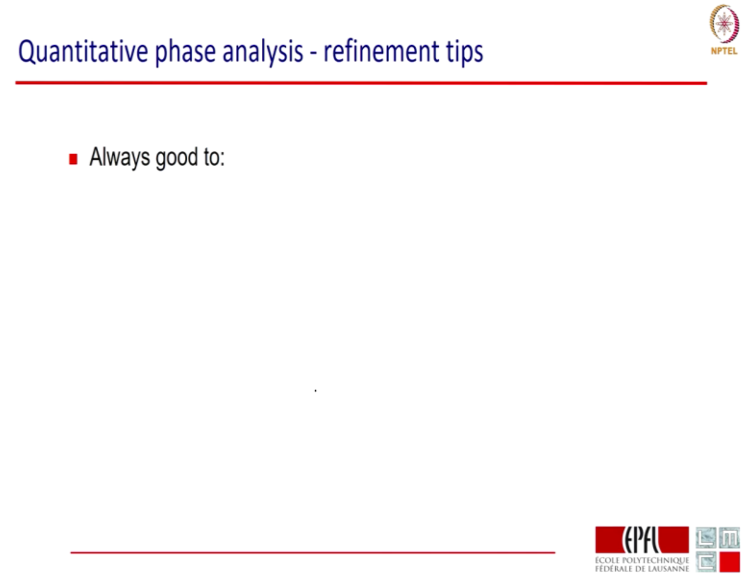


The Rietveld method: basics

$$S_y = \sum_i \underbrace{w_i\left(y_i(obs) - y_i(calc)\right)^2}$$

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

(Refer Slide Time: 30:20)



Quantitative phase analysis - refinement tips

- Always good to:

So just some small tips but of course, you have to really look at this in more detail if you want to do it yourself.

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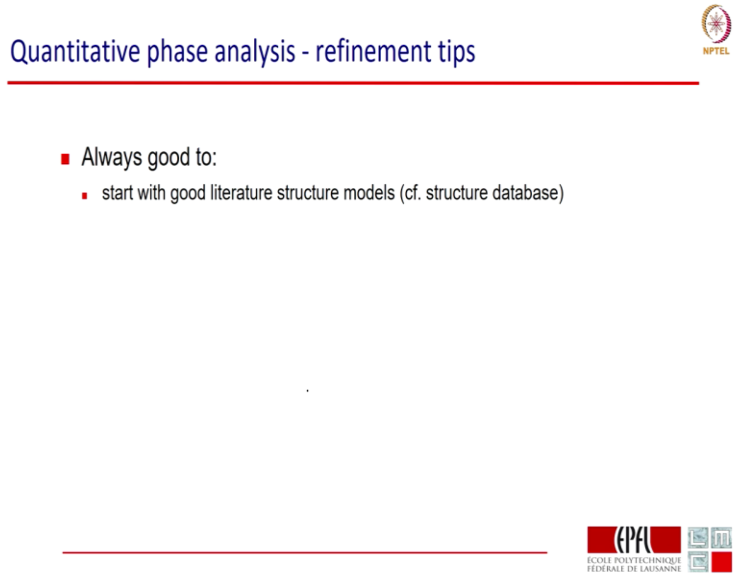

Quantitative phase analysis - refinement tips

- Always good to:
  - start with good literature structure models (cf. structure database)

It is really important to start with good literature structure models, a good database.

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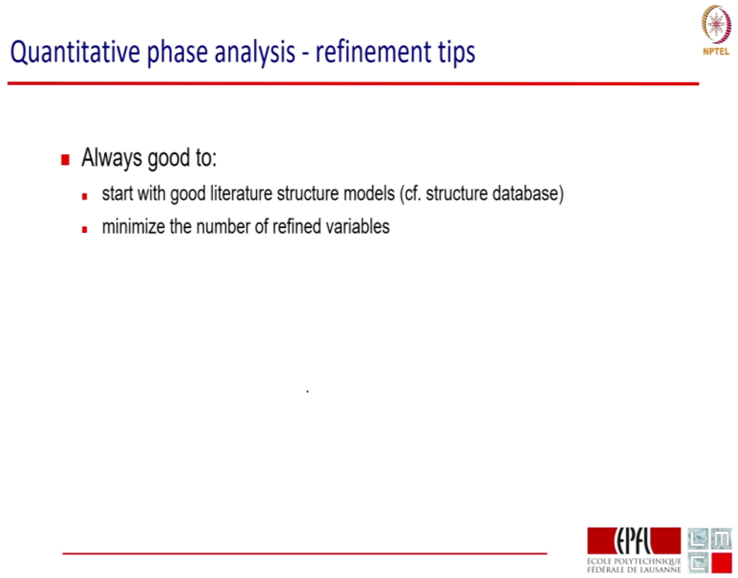

Quantitative phase analysis - refinement tips

- Always good to:
  - start with good literature structure models (cf. structure database)
  - minimize the number of refined variables

It is really important about to minimize the number of refined variables because if you let everything vary, you can end up with any old rubbish.

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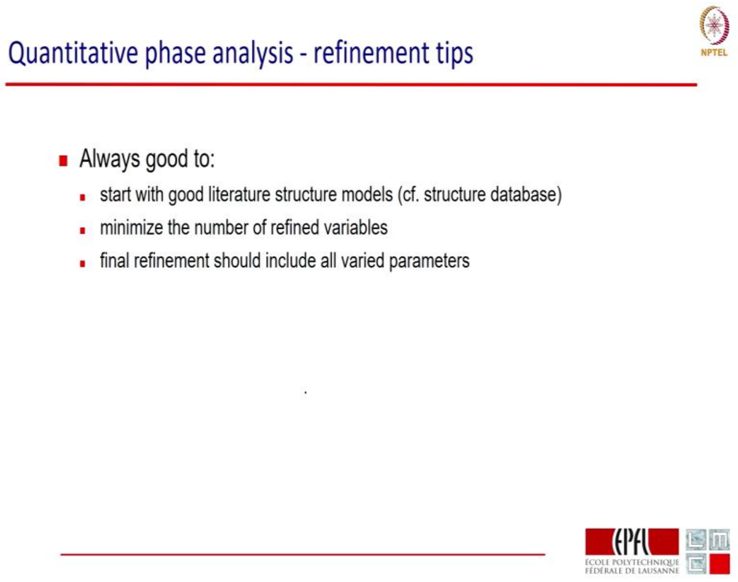
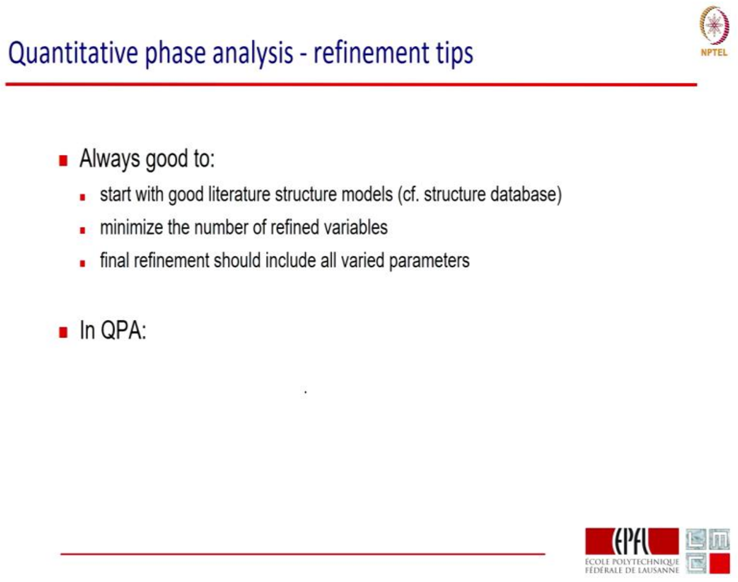


Quantitative phase analysis - refinement tips

- Always good to:
  - start with good literature structure models (cf. structure database)
  - minimize the number of refined variables
  - final refinement should include all varied parameters

The final refinement should include, or you should really say, all the parameters of this has been varied and in quantitative phase analysis usually what we do, we refine only the scale factors in the lattice parameter.

(Refer Slide Time: 30:49)



Quantitative phase analysis - refinement tips

- Always good to:
  - start with good literature structure models (cf. structure database)
  - minimize the number of refined variables
  - final refinement should include all varied parameters
- In QPA:

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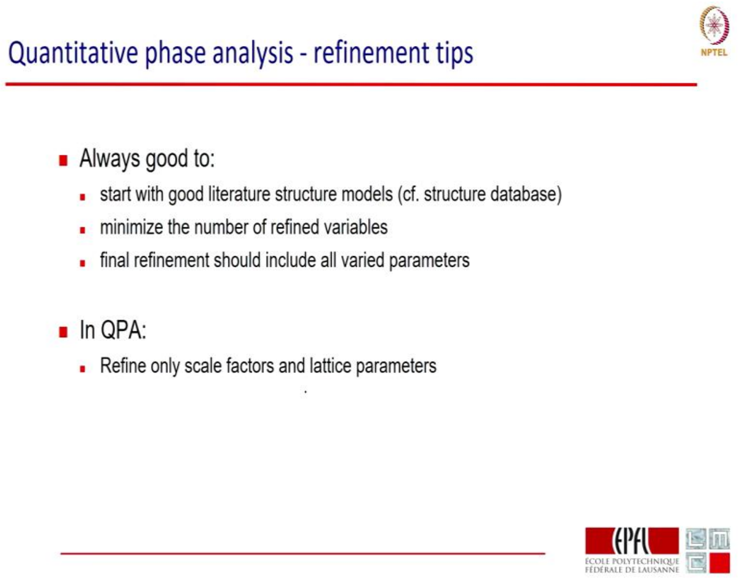

Quantitative phase analysis - refinement tips

- Always good to:
  - start with good literature structure models (cf. structure database)
  - minimize the number of refined variables
  - final refinement should include all varied parameters
- In QPA:
  - Refine only scale factors and lattice parameters

So we allow the lattice parameters to adjust a bit, in case there has been a slight shift in the peaks due to the solid solution or something like that.

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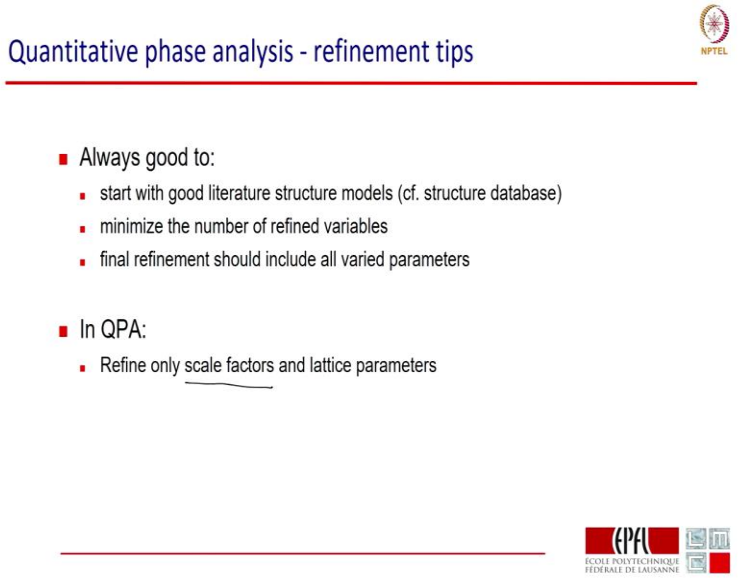

Quantitative phase analysis - refinement tips

- Always good to:
  - start with good literature structure models (cf. structure database)
  - minimize the number of refined variables
  - final refinement should include all varied parameters
- In QPA:
  - Refine only scale factors and lattice parameters

And of course, the scale factor we have to vary because that is the thing we are trying to find.

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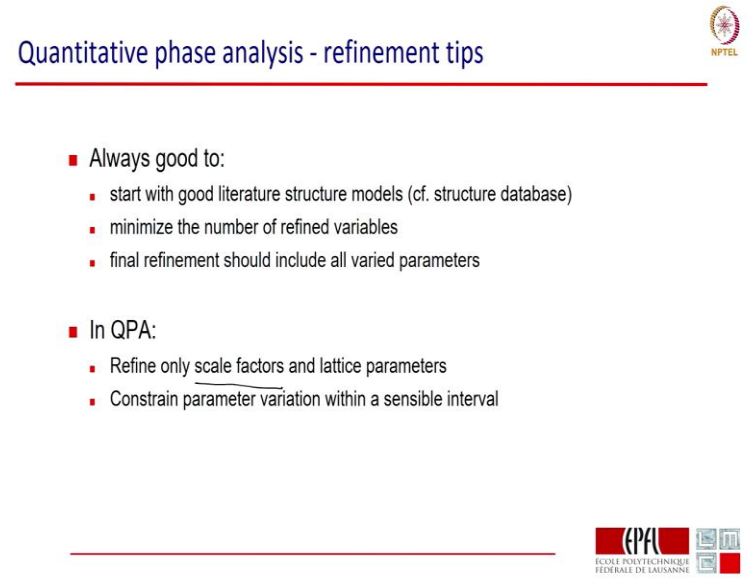

Quantitative phase analysis - refinement tips

- Always good to:
  - start with good literature structure models (cf. structure database)
  - minimize the number of refined variables
  - final refinement should include all varied parameters
- In QPA:
  - Refine only scale factors and lattice parameters
  - Constrain parameter variation within a sensible interval

But even these lattice parameters, we have to constrain the variation within a sensible interval.

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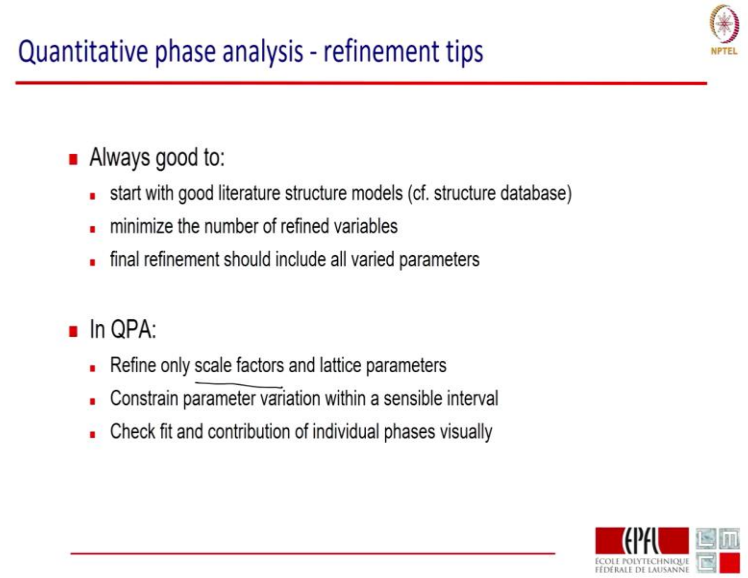

Quantitative phase analysis - refinement tips

- Always good to:
  - start with good literature structure models (cf. structure database)
  - minimize the number of refined variables
  - final refinement should include all varied parameters
- In QPA:
  - Refine only scale factors and lattice parameters
  - Constrain parameter variation within a sensible interval
  - Check fit and contribution of individual phases visually

And then it is important to check the fit and to check that fit visually. Don’t just rely on numerical parameters. Have a look at the pattern. Have a look at the peaks are in the right place and things like that.

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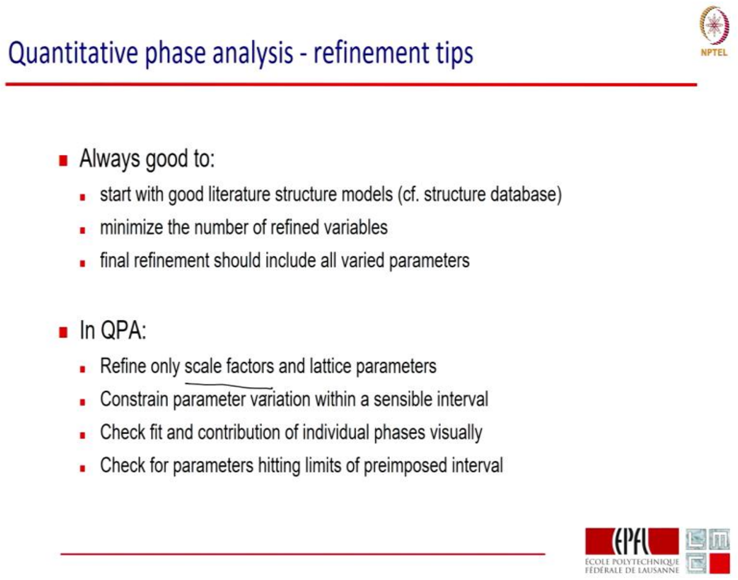

Quantitative phase analysis - refinement tips

- Always good to:
  - start with good literature structure models (cf. structure database)
  - minimize the number of refined variables
  - final refinement should include all varied parameters
- In QPA:
  - Refine only scale factors and lattice parameters
  - Constrain parameter variation within a sensible interval
  - Check fit and contribution of individual phases visually
  - Check for parameters hitting limits of preimposed interval

And check these limits of the variation.

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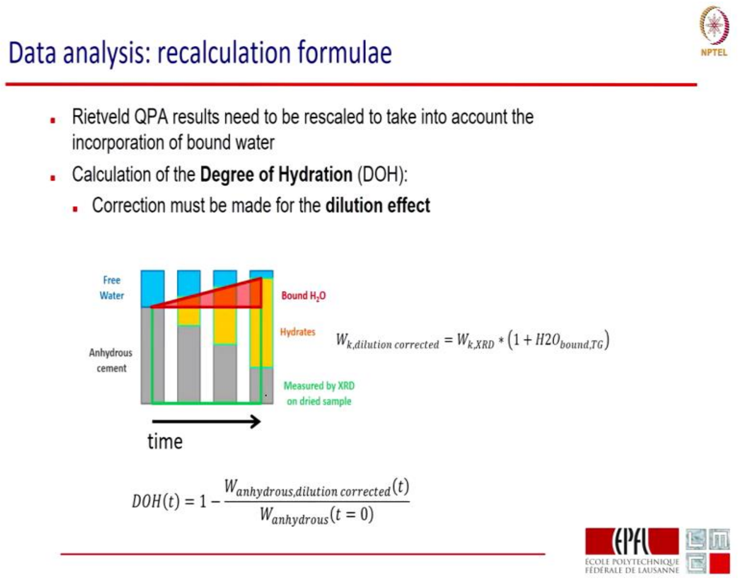

Data analysis: recalculation formulae

- Rietveld QPA results need to be rescaled to take into account the incorporation of bound water
- Calculation of the **Degree of Hydration** (DOH):
  - Correction must be made for the **dilution effect**

$$W_{k,dilution\ corrected} = W_{k,XRD} * \left(1 + H2O_{bound,TG}\right)$$

$$DOH(t) = 1 - \frac{W_{anhydrous,dilution\ corrected}(t)}{W_{anhydrous}(t=0)}$$

$$DOH(t) = 1 - \frac{W\ anhydrous, dilution\ corrected\ (t)}{W\ anhydrous\ (t=0)}$$

The other aspect that is important to mention is the, the reference weight.

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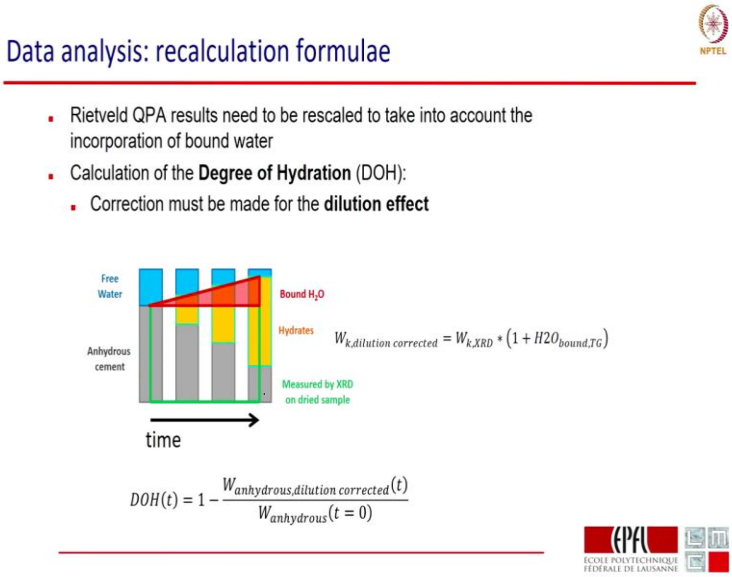

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$$DOH(t) = 1 - \frac{W_{anhydrous,dilution\ corrected}(t)}{W_{anhydrous}(t=0)}$$

So when we are trying to calculate something like degree of hydration, we have to be aware that at the beginning we have a sample with free water which is usually removed.

And then the anhydrous cement but as the hydration is going on, more and more of that free water is combined in the hydrate which means the analysis, the weight of stuff we are analyzing has increased here to here (as shown in the following slides).

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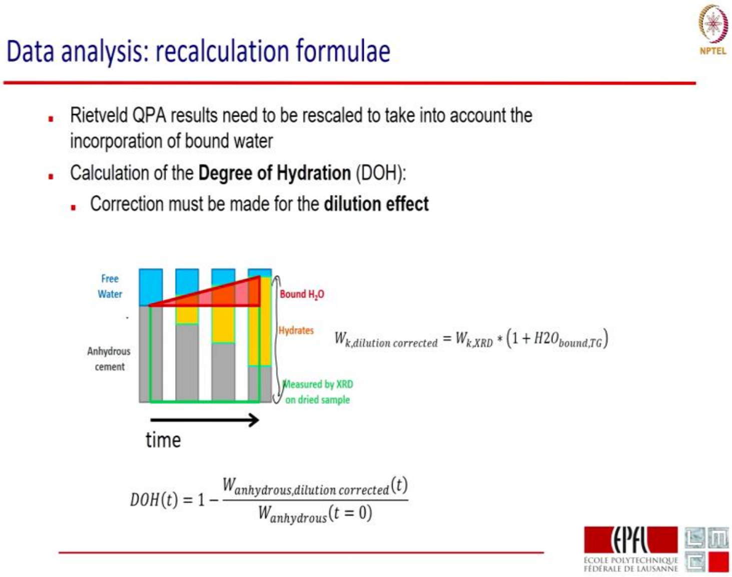

Data analysis: recalculation formulae

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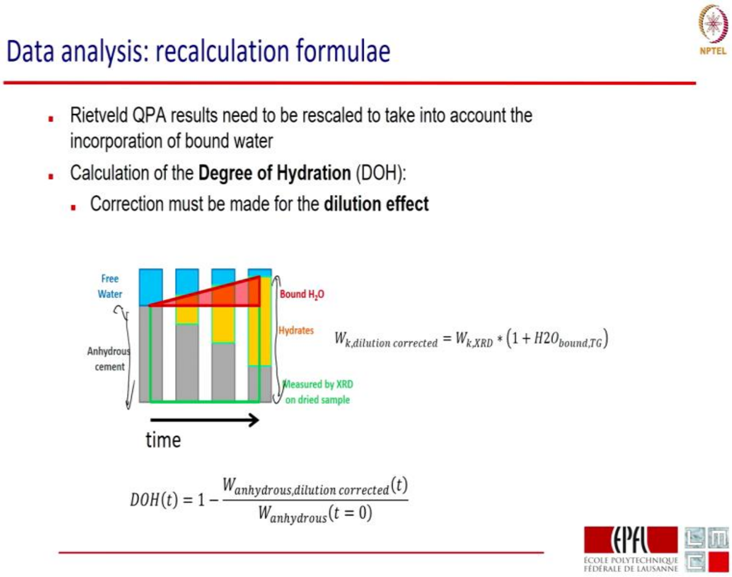

Data analysis: recalculation formulae

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$$DOH(t) = 1 - \frac{W_{anhydrous,dilution\ corrected}(t)}{W_{anhydrous}(t=0)}$$

And we have to take this into account otherwise without having everything normalized to the same amount, and we generally do that by making in parallel a thermogravimetric analysis to analyze the amount of bound water.

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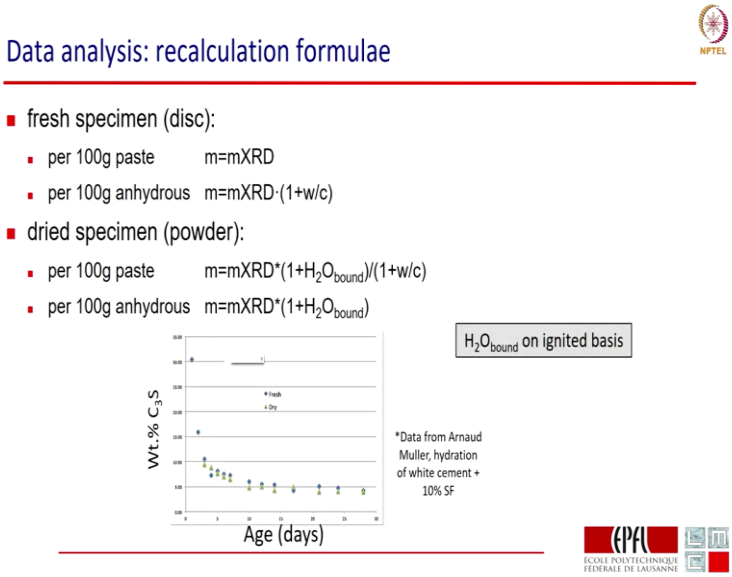

Data analysis: recalculation formulae

- 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

*Data from Arnaud Muller, hydration of white cement + 10% SF

- 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 * ($1+H_2O_{bound}$)

And if we do that we can have equations which can convert everything to the ignited basis and if we do that, whether we do fresh samples or dried samples we can get very similar values.

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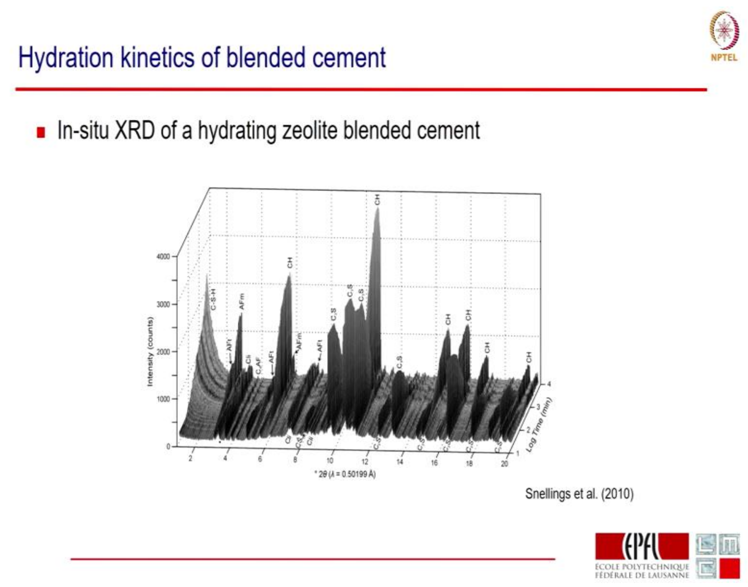

Hydration kinetics of blended cement

- In-situ XRD of a hydrating zeolite blended cement

Snellings et al. (2010)

So here we just see how we can look at the hydration reaction by stacking up lots of therefore patterns. You can see here for example, here how the calcium hydroxide is evolving

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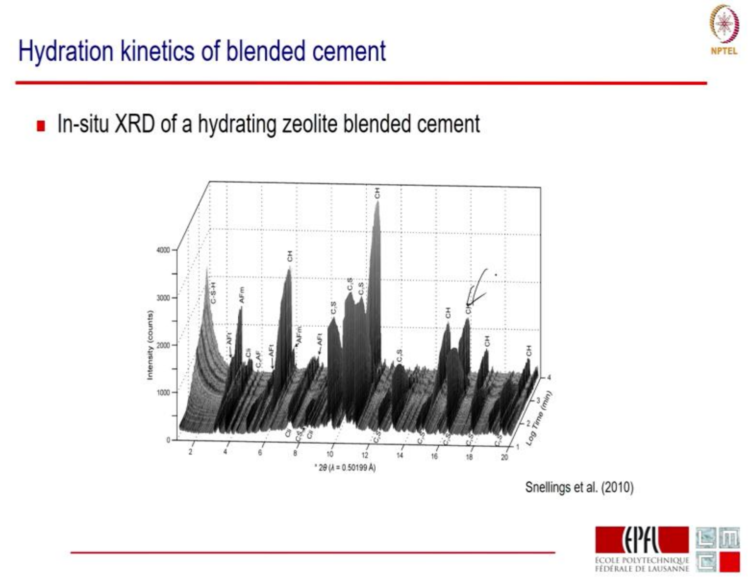

Hydration kinetics of blended cement

- In-situ XRD of a hydrating zeolite blended cement

Snellings et al. (2010)

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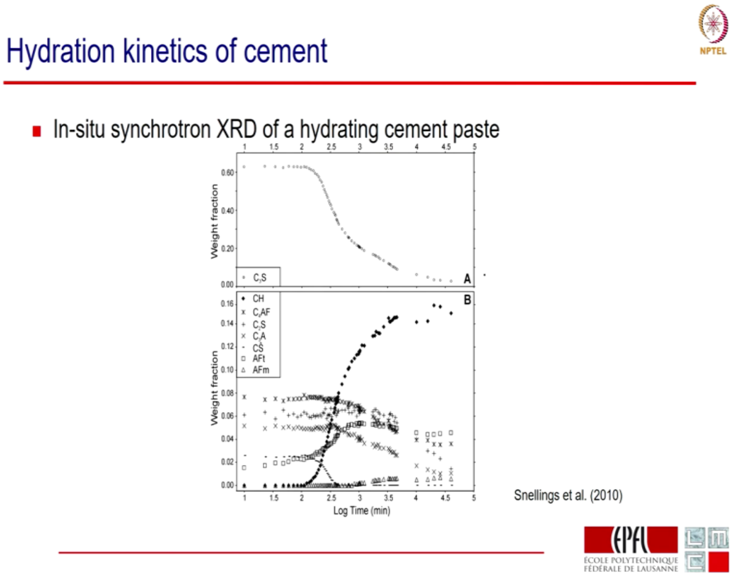

Hydration kinetics of cement

- In-situ synchrotron XRD of a hydrating cement paste

Snellings et al. (2010)

usually it is more useful to look in this kind of format where we compress this data into the evolution of certain phases with time.

And this can really be very, very powerful technique for looking at the hydration kinetics.

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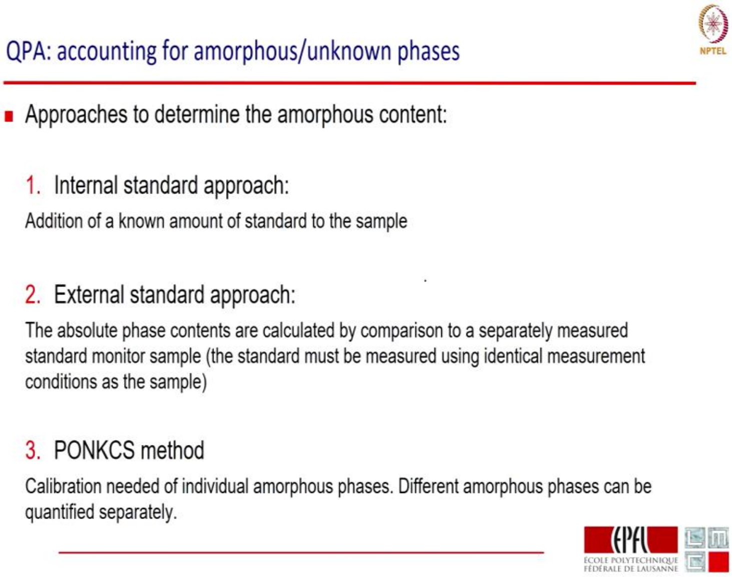

QPA: accounting for amorphous/unknown phases

- Approaches to determine the amorphous content:

1. Internal standard approach:
   Addition of a known amount of standard to the sample
2. External standard approach:
   The absolute phase contents are calculated by comparison to a separately measured standard monitor sample (the standard must be measured using identical measurement conditions as the sample)
3. PONKCS method
   Calibration needed of individual amorphous phases. Different amorphous phases can be quantified separately.

If we want to look at amorphous phase we have various approaches. The most important are the standard techniques, either internal standard or external standard. Internal standard has the advantage that the standard pattern and the unknown pattern are correct, collected under exactly the same conditions.

The problem is if you want to look at the hydrated sample you must not put your standard in when you are doing your mixing because your standard can through the filler effect we talk about tomorrow can impact the hydration itself.

And for this reason when you want to look at fresh slices which is

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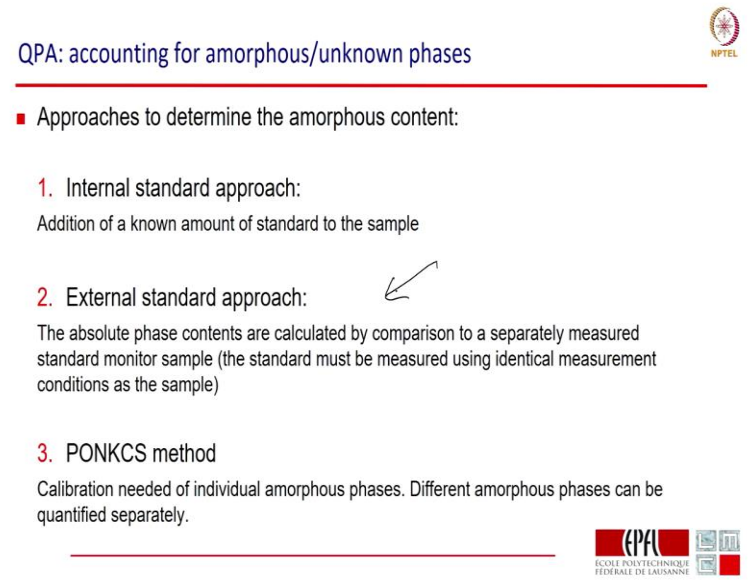

QPA: accounting for amorphous/unknown phases

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   The absolute phase contents are calculated by comparison to a separately measured standard monitor sample (the standard must be measured using identical measurement conditions as the sample)
3. PONKCS method
   Calibration needed of individual amorphous phases. Different amorphous phases can be quantified separately.

the most practical way of doing things, then this external standard approach is much better. But the important thing here, you have to really measure your external standard and your reference sample under the same conditions at more or less the same time.

If you are doing a batch of measurements of say 10 samples, therefore for every 10 samples you measure your standard sample because the X-ray intensity from the standard diffractometer is continuously decreasing over time.

Now there is a lot of discussion about this technique called the PONKCS method. This means pattern of no known crystal structure and this can work quite well for anhydrous phases to discover the amount of slag in an anhydrous cement, or the amount of fly ash but when you have hydration it is not always good for differentiating for example between calcium silicate hydrate and slag.

(Refer Slide Time: 34:54)

End Part 1

So that was, you know overview of the techniques and also rapid introduction to X-ray diffraction.

(Refer Slide Time: 35:05)

End Part 1