Advanced Topics in the Science and Technology of Concrete
Professor Karen Scrivener
Laboratory of Construction Materials
Ecole Polytechnique Federal De Lausanne
Microstructural Characterisation of Cementitious Materials Part 3

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So in this third part let us talk about techniques to measure porosity. Porosity is probably the most important aspect of the microstructure because it is the pores that determine the strength and the ingress of all the things that control problems with durability.

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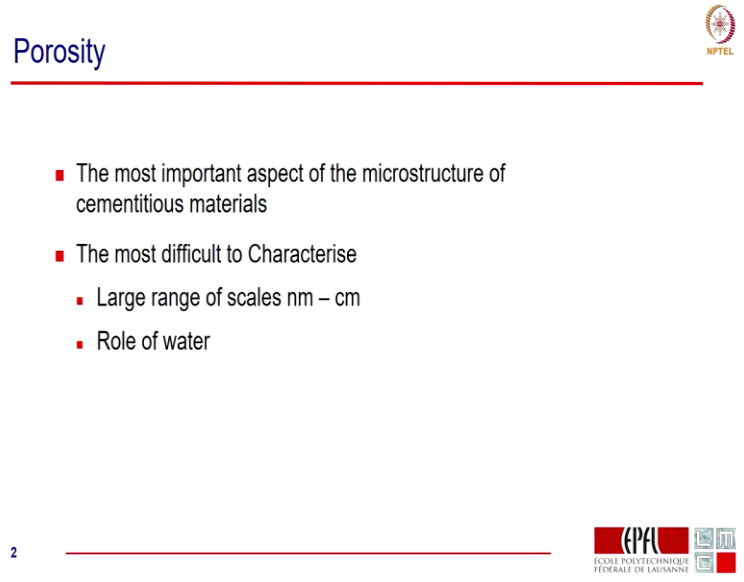

Porosity

- The most important aspect of the microstructure of cementitious materials
- The most difficult to Characterise
  - Large range of scales nm – cm
  - Role of water

It is probably the most difficult to characterize and it is the most difficult to characterize for two reasons. First of all we have this very large range of scales. We want to look at things from nanometer scale to centimeter scale, and secondly the role of water. So we mix the cement with water. Water is an integral part of the structure and therefore for most characterization techniques, we need to remove the water. And this really gives the problem with the fine pores.

Now today I am going to talk about three techniques to study porosity.

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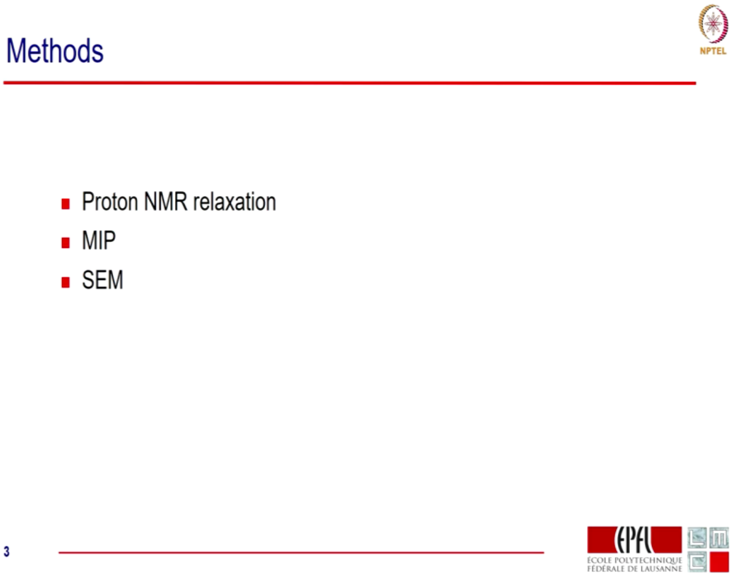

Methods

- Proton NMR relaxation
- MIP
- SEM

I am going to talk a lot about proton NMR relaxation. Now although this is not a common technique and it is not so widely available, the reason I am going to talk about it is, it is a unique technique where you can locate the pore structure without drying. So what we can learn from proton NMR is that it best represents the reality. And then it can help us understand what really we were saying by more common techniques, particularly by mercury intrusion porosimetry. And when we do that, we actually see that mercury intrusion porosimetry is actually very good technique. I mean lot of literature says it is rubbish and does not measure anything useful but I really think that is not true.

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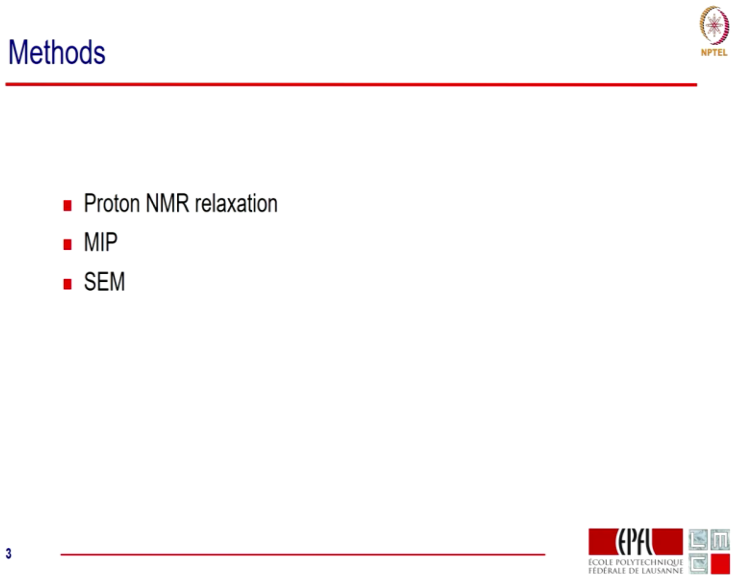

Methods

- Proton NMR relaxation
- MIP
- SEM

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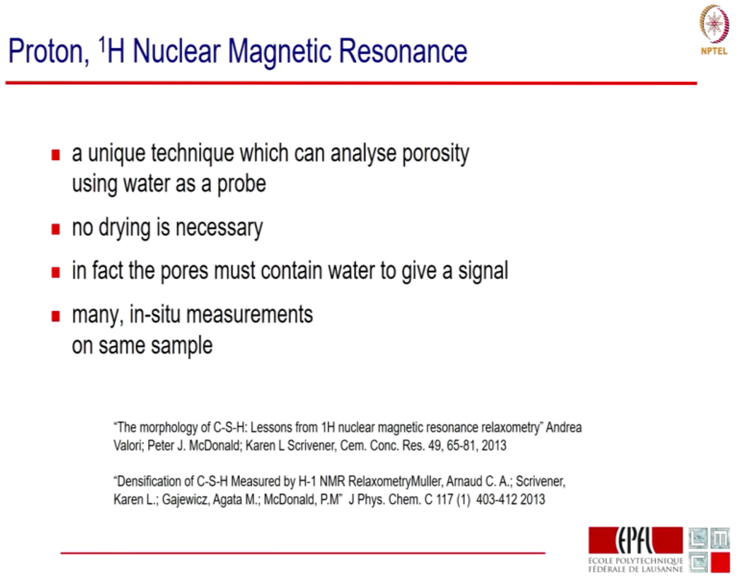

Proton, ^{1}H Nuclear Magnetic Resonance

- a unique technique which can analyse porosity using water as a probe
- no drying is necessary
- in fact the pores must contain water to give a signal
- many, in-situ measurements on same sample

"The morphology of C-S-H: Lessons from 1H nuclear magnetic resonance relaxometry" Andrea Valori; Peter J. McDonald; Karen L Scrivener, Cem. Conc. Res. 49, 65-81, 2013

"Densification of C-S-H Measured by H-1 NMR RelaxometryMuller, Arnaud C. A.; Scrivener, Karen L.; Gajewicz, Agata M.; McDonald, P.M" J Phys. Chem. C 117 (1) 403-412 2013

And SEM is really not all that useful on a quantitative basis. So proton or 1 H, that is the nucleus of the hydrogen atom is a proton, nuclear magnetic resonance is a unique technique which can analyze porosity using the water as a probe.

So you do not need to dry the sample at all and in fact, just the opposite. You can only interrogate pores that have water in them. And the big advantage, because you do not have to dry, and because it is a non-destructive technique, you can have the same sample and you really look at how (()) over time. And we have got a number of publications about this where you can go and look at to see the details of this technique.

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Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

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Use of bench-top NMR to measure the density, composition and desorption isotherm of C–S–H in cement paste

A.C.A. Muller[a], K.L. Scrivener[a], A.M. Gajewicz[b], P.J. McDonald[b,*]

ARTICLE INFO

ABSTRACT

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Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

The morphology of C–S–H: Lessons from ^{1}H nuclear magnetic resonance relaxometry

A. Valori[a], P.J. McDonald[a,*], K.L. Scrivener[b]

ARTICLE INFO

ABSTRACT

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

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Densification of C–S–H Measured by ^{1}H NMR Relaxometry

Arnaud C. A. Muller,[†] Karen L. Scrivener,[†] Agata M. Gajewicz,[‡] and Peter J. McDonald[*,‡]

[†]Laboratory of Construction Materials, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

[‡]Department of Physics, University of Surrey, Guildford, Surrey, GU2 7XH, U.K.

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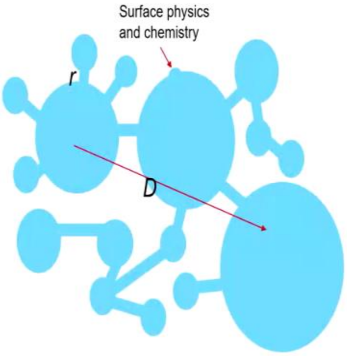
Proton, ^{1}H Nuclear Magnetic Resonance



Now the basic idea of this Nuclear Magnetic Resonance is nuclear magnetic relaxation. If you think about the water molecules in this bottle of water here, the magnetic spins of those protons are very randomly oriented. There will be slight alignment with the earth's magnetic field but that will be fairly random.

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If you put it in the machine and apply magnetic field, all the spins of those protons gets aligned either up or down, compared to the magnetic field. And then you remove the magnetic field and you see how long it takes for the random orientation to come back. That is very simplistic definition but it is good enough for our purposes here. Now if I have got this water in this bottle, it takes roughly 4 seconds for the protons to go back to the normal random orientation. I can measure that.

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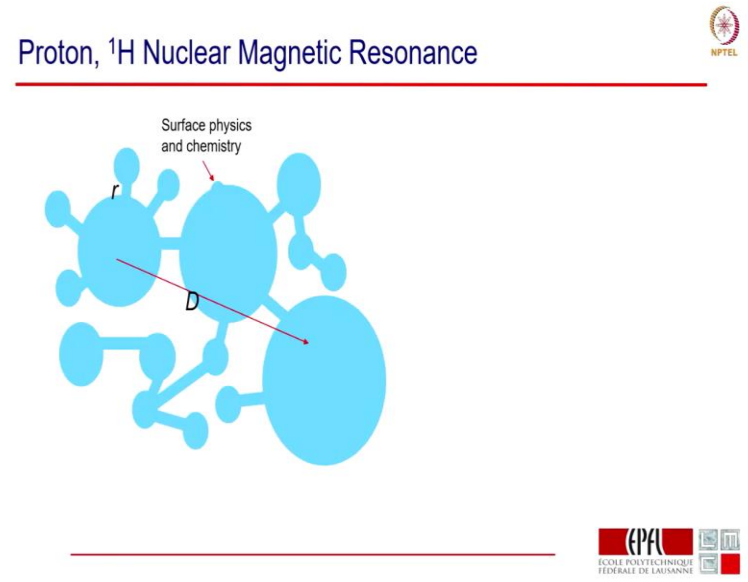

Proton, ^{1}H Nuclear Magnetic Resonance

If I now add water in a pore here, this water molecule moves around at random in the pore and if it hits the surface, it immediately relaxes. So the smaller the pore is, the faster on average it is going to hit the surface. And shorter is going to be the relaxation time. So that is the basic idea.

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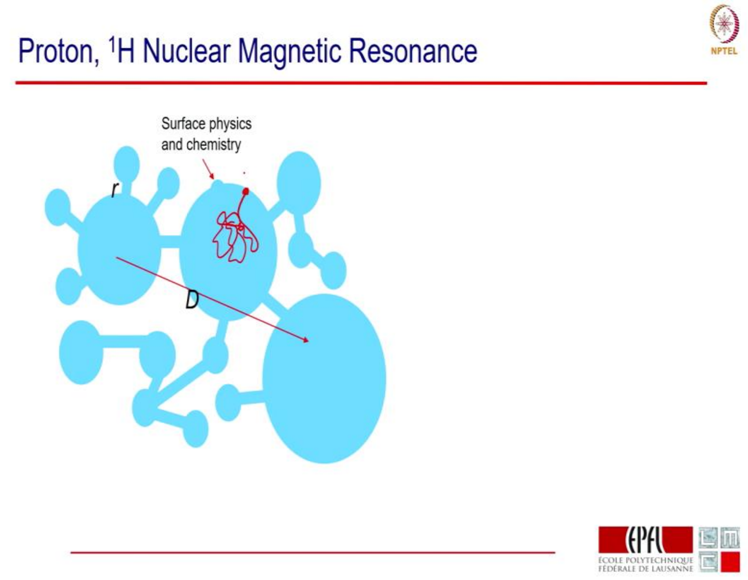

Proton, ^{1}H Nuclear Magnetic Resonance

If you want to know more about physics you can read more about it, but that is all we need to know to understand it. That is, as the water goes into smaller and smaller pores, the relaxation time goes down.

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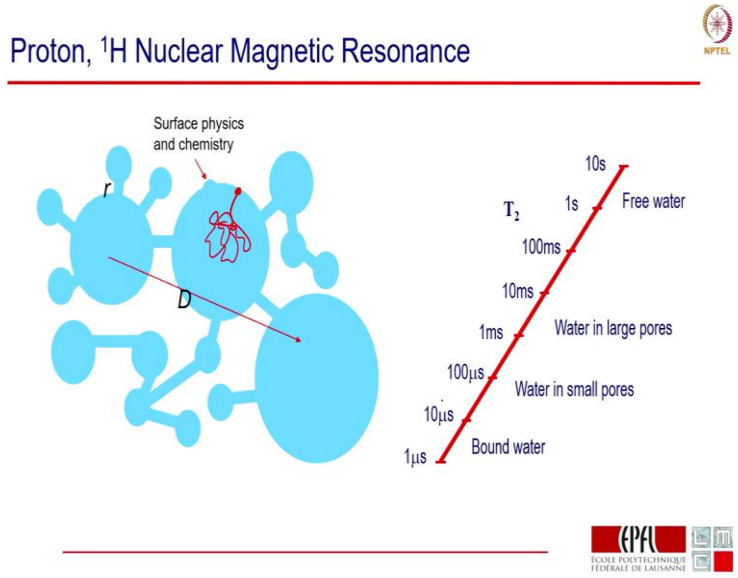

Proton, ^{1}H Nuclear Magnetic Resonance

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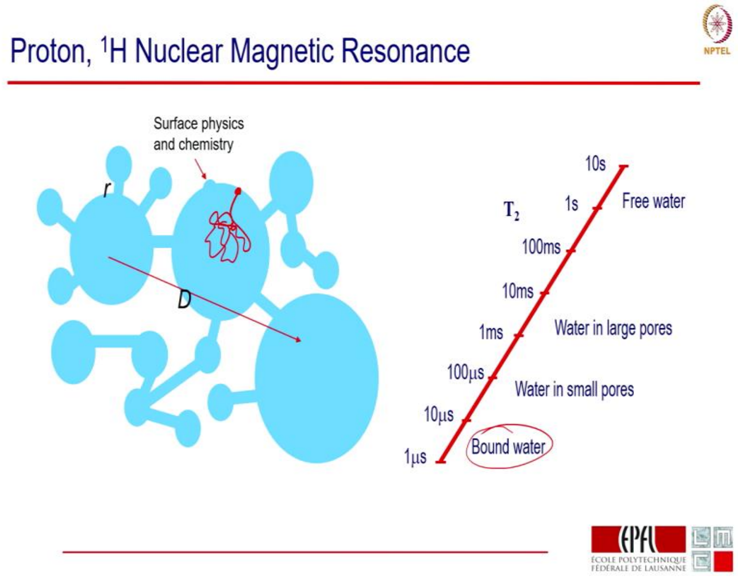

Proton, ^{1}H Nuclear Magnetic Resonance

Bound water has a very short relaxation time. Now you will also see this is labeled T 2.

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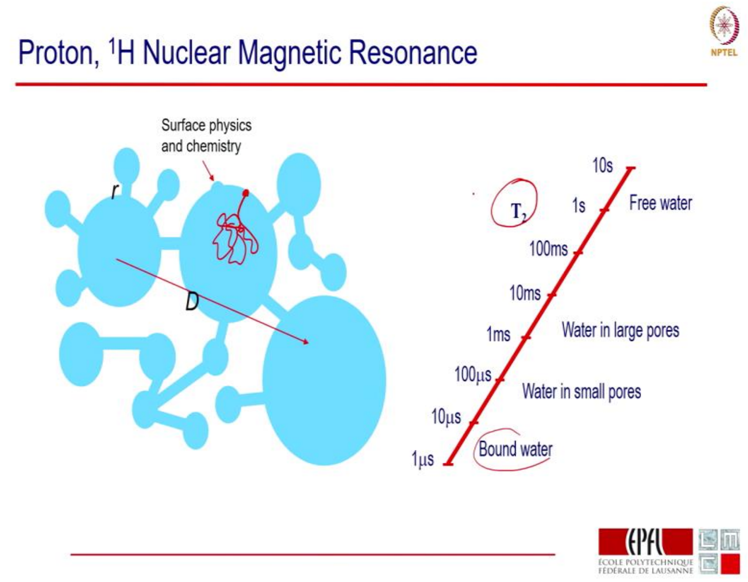

Proton, ^{1}H Nuclear Magnetic Resonance

It is actually different relaxation times T 1, T 2. You can go and read about the details of that, but we are going to be focusing on this T 2

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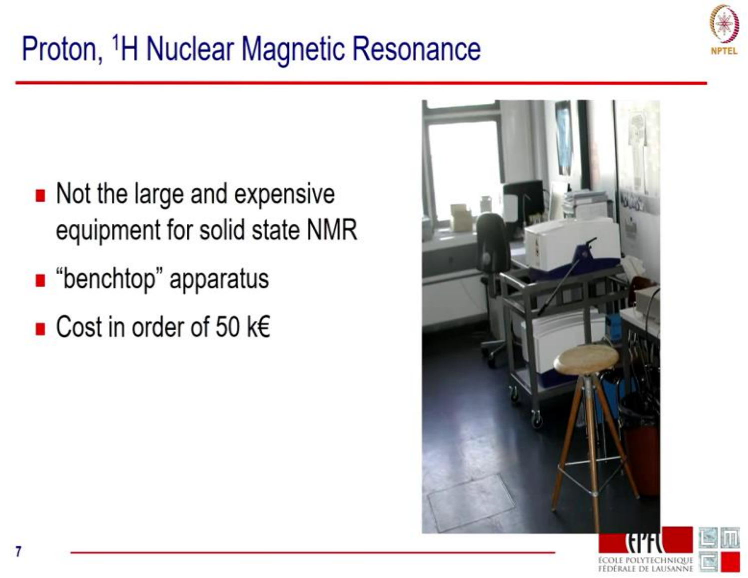

Proton, ^{1}H Nuclear Magnetic Resonance

- Not the large and expensive equipment for solid state NMR
- "benchtop" apparatus
- Cost in order of 50 k€

Now equipment you need for this proton NMR is very big magnet. You may have seen all these shiny, steel huge magnets for solid state NMR like silicon NMR, aluminum NMR. It is not the same as that. It is really a benchtop apparatus. You can see it here in our lab. You see it is not very big.

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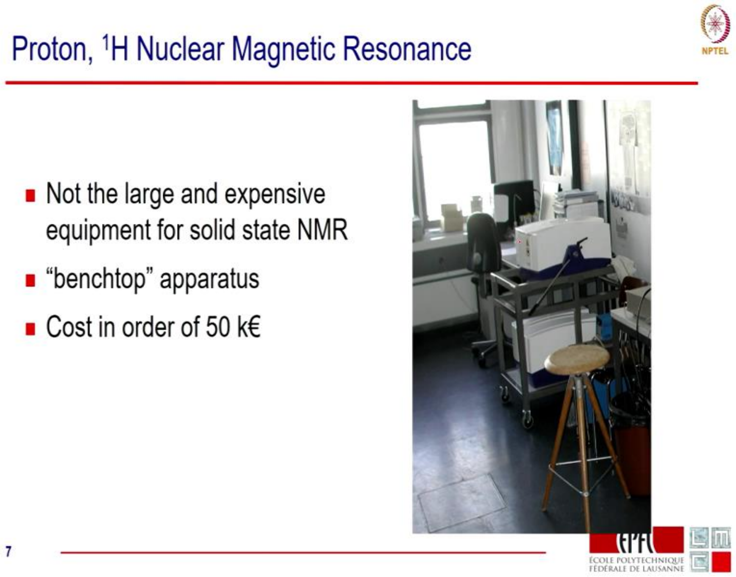

Proton, ^1H Nuclear Magnetic Resonance

- Not the large and expensive equipment for solid state NMR
- “benchtop” apparatus
- Cost in order of 50 k€

It is also not too expensive. It is of the order of 50 thousand Euros, which is fairly low. I mean it is much less than an SEM, it is much less than X-ray diffraction.

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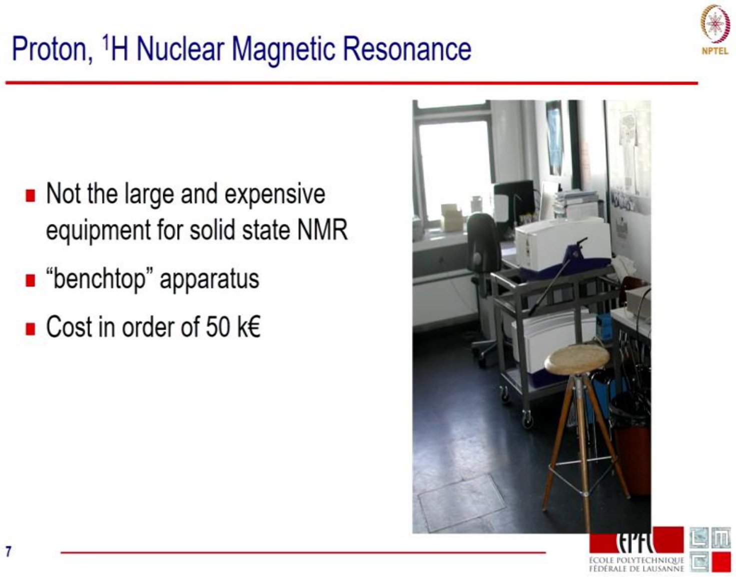

Proton, ^1H Nuclear Magnetic Resonance

- Not the large and expensive equipment for solid state NMR
- “benchtop” apparatus
- Cost in order of 50 k€

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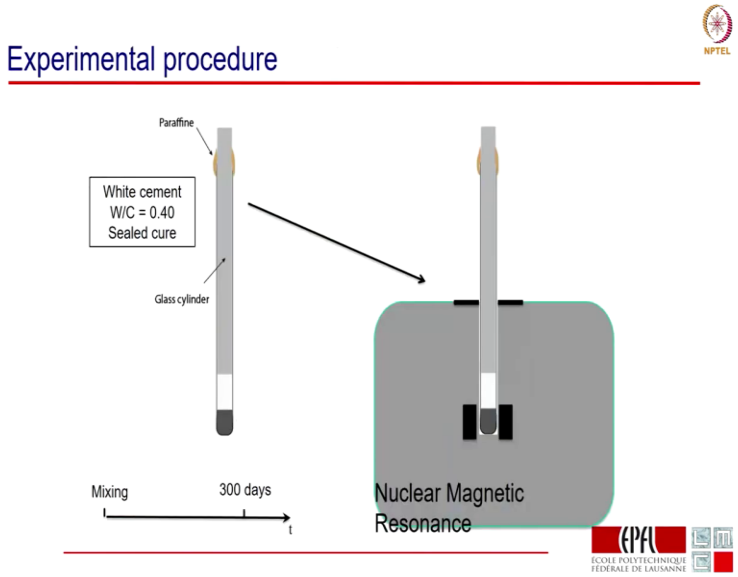

Experimental procedure

And so we see that there is a kind of hole here. We can make up our cement paste, we have these sample holders. This is a little bit of cement paste down here.

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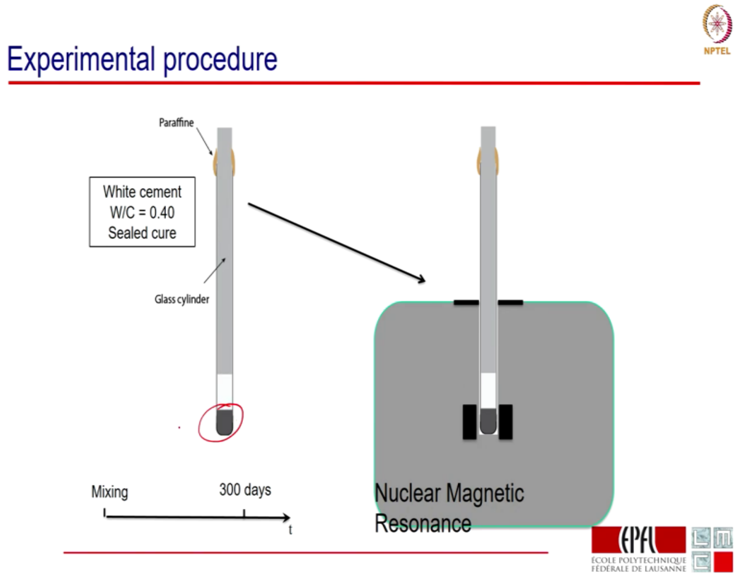

Experimental procedure

And then we very carefully seal this. We have to have only this little bit of paste because only the bit between the magnets down here is measured. We can then have this sample in tube. We can put in them. We can measure it, we can take it out, we can keep it on the control temperature, we can put it back in the next day, and put it back in the next week and so on and so forth. And we have done these following samples up to at least one year.

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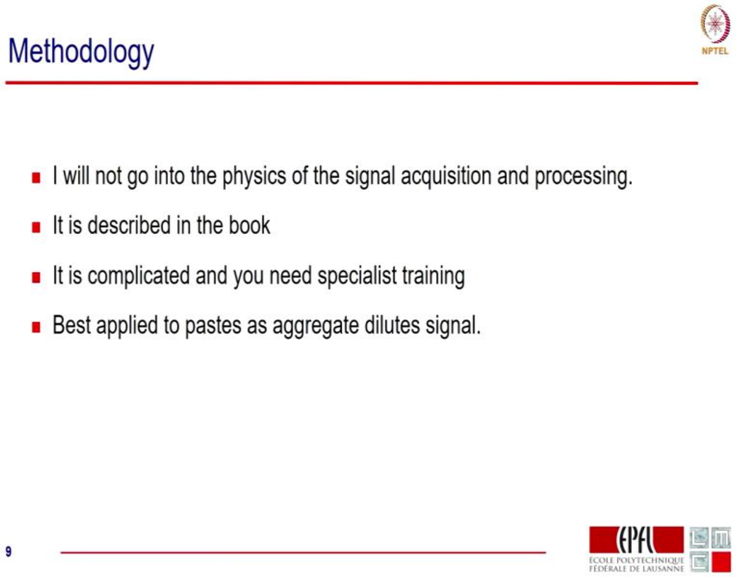

Methodology

- I will not go into the physics of the signal acquisition and processing.
- It is described in the book
- It is complicated and you need specialist training
- Best applied to pastes as aggregate dilutes signal.

So I am not going to go into the details about the physics. It is described in the book. It is a little bit complicated and you need to really understand it with a specialist. Again like most of the microstructural characterization techniques is best applied to paste because aggregates dilute the signal.

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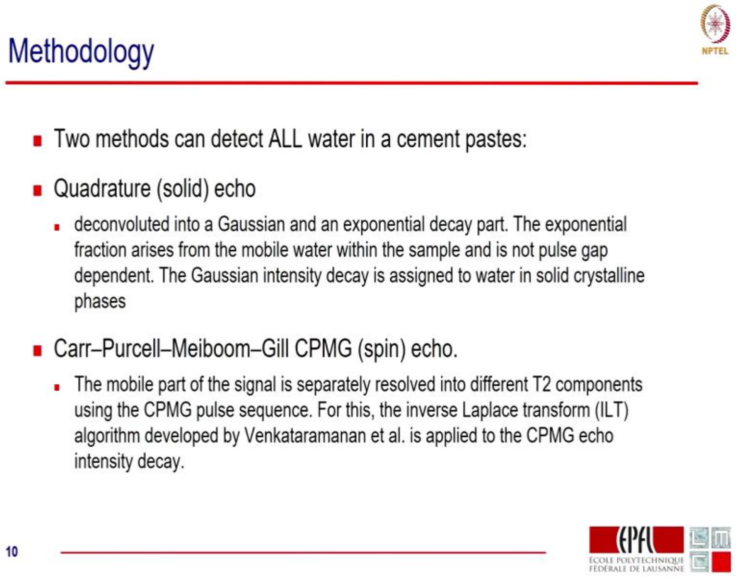

Methodology

- Two methods can detect ALL water in a cement pastes:
- Quadrature (solid) echo
  - deconvoluted into a Gaussian and an exponential decay part. The exponential fraction arises from the mobile water within the sample and is not pulse gap dependent. The Gaussian intensity decay is assigned to water in solid crystalline phases
- Carr–Purcell–Meiboom–Gill CPMG (spin) echo.
  - The mobile part of the signal is separately resolved into different T2 components using the CPMG pulse sequence. For this, the inverse Laplace transform (ILT) algorithm developed by Venkataramanan et al. is applied to the CPMG echo intensity decay.

So I said I am not going to go into it but just to mention it, the real breakthrough it had in the last two years is really to know that we are detecting all water in cement paste.

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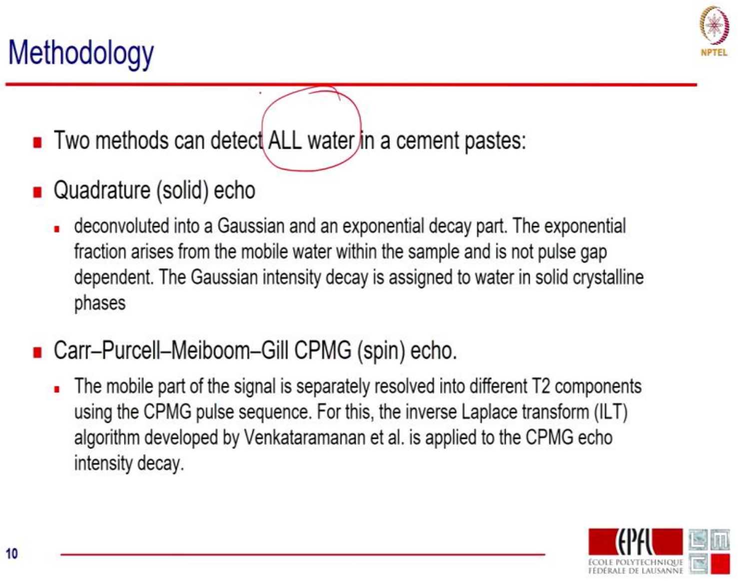

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So people have used this technique for 40 or 50 years. The problem is that if they were using different machines and different techniques they would may be only seeing part of the spectra. And to really understand that spectra, we need to make sure we can see all of it. So we use these two techniques, Quadrature solid echo and the C P M G signal, and we with putting these two techniques together, we know we can look at all the water in the cement paste. And we know that because we can do experiments like this.

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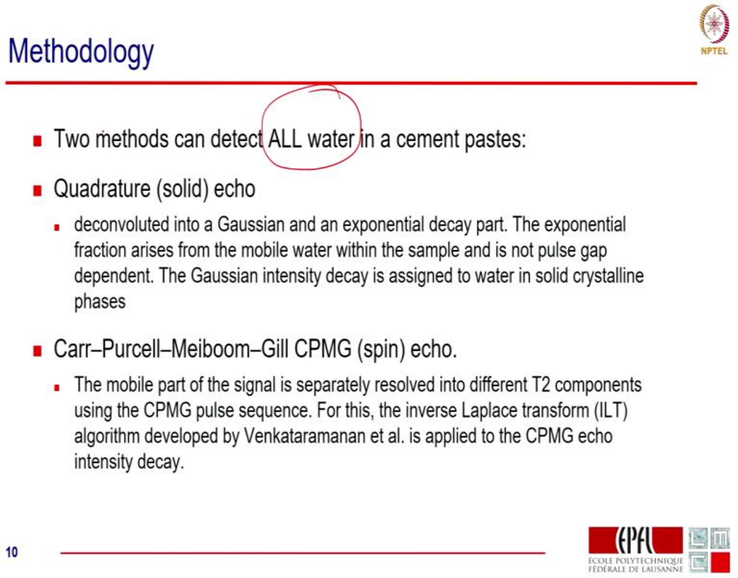

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10

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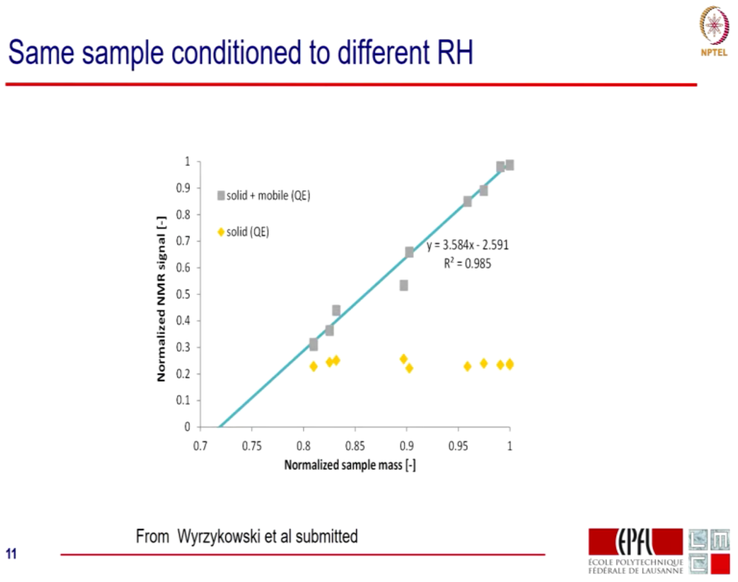

Same sample conditioned to different RH

From Wyrzykowski et al submitted

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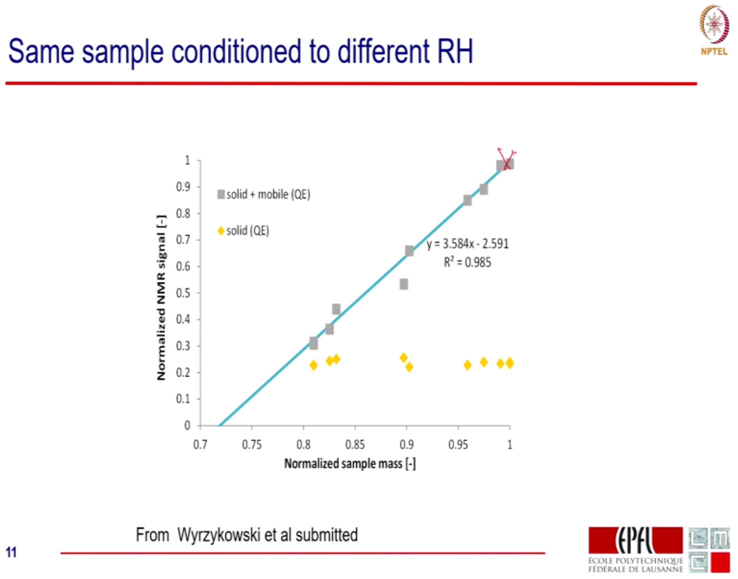

Same sample conditioned to different RH

From Wyrzykowski et al submitted

So here is an experiment where we take the cement. We then dry it under different relative humidity and you see that as this sample dries, as it loses mass, then the NMR signal goes down in direct proportion. So we know that the signal corresponds exactly to the water. We can see the signal from what we call the solid part remains more or less constant over time. And we can calculate this means in terms of the water here.

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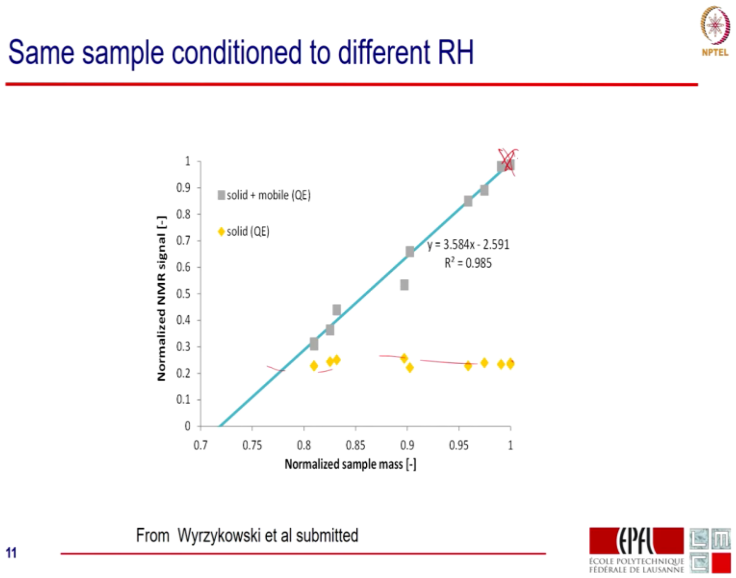

Same sample conditioned to different RH

From Wyrzykowski et al submitted

We can see how it matches up with the original water we put in this sample. So we have done all that and we know we look at all the water. And then what do we get, in terms of spectra?

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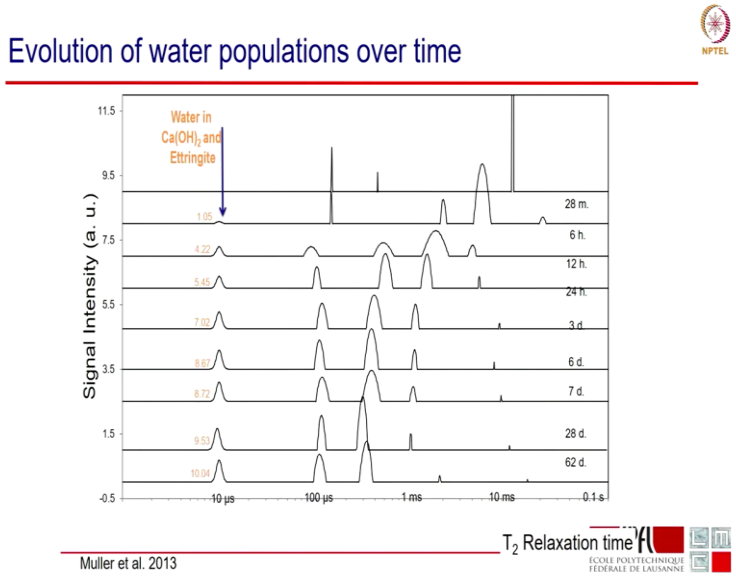

Evolution of water populations over time

Muller et al. 2013

So we get this kind of spectra and first of all we have that part which we get from the quadrature solid echo. So this is what we call the solid water. And this actually corresponds to the water in the crystalline phases. We can make a very careful calculation of the amount of water here. We can double check with techniques like X-ray diffraction how much calcium hydroxide we have got and how much ettringite we got. We can calculate the amount of water in those phases.

We can see it corresponds very, very closely. So we can be really confident that this signal here is the water in the crystalline hydrates, in this example Calcium hydroxide and ettringite, we may also have AFm phases in some other cases. And then we can see the different other populations that are evolved over time.

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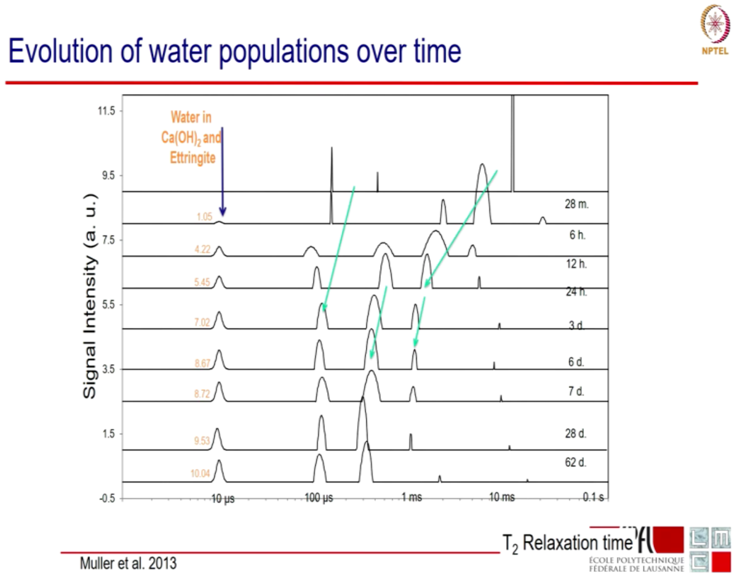

Evolution of water populations over time

Muller et al. 2013

So this is the short time and as we go longer and longer time, the positions and the heights of these signals are moving. Now, because we know that the signal here is only water in crystalline hydrates, by deduction we can see that this signal here is actually now the interlayer water. So this is the water in the CSH interlayer.

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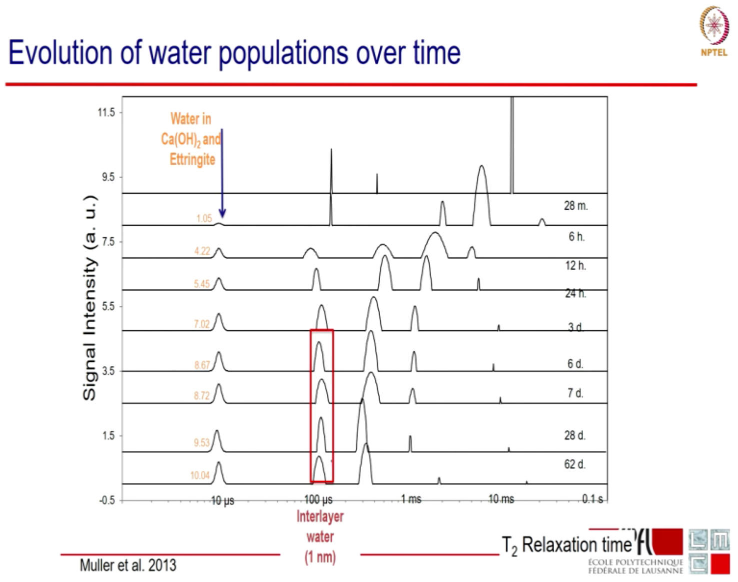

Evolution of water populations over time

Muller et al. 2013

CSH is a layer structure. We have layers of calcium oxygen sheets and between these sheets then we have water molecules. And this interlayer water comes with an equivalent size of roughly 1 nanometer. And then the next population here is the gel water and this has a characteristic size about 3 to 4 nanometers.

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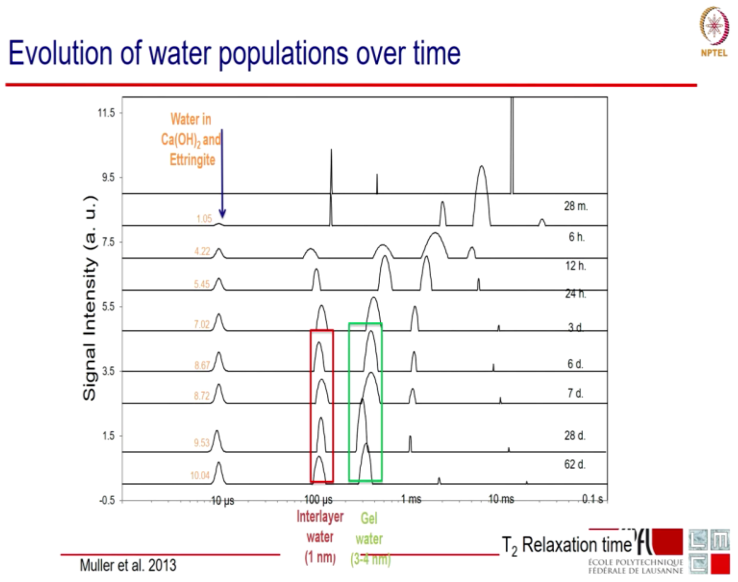

Evolution of water populations over time

Muller et al. 2013

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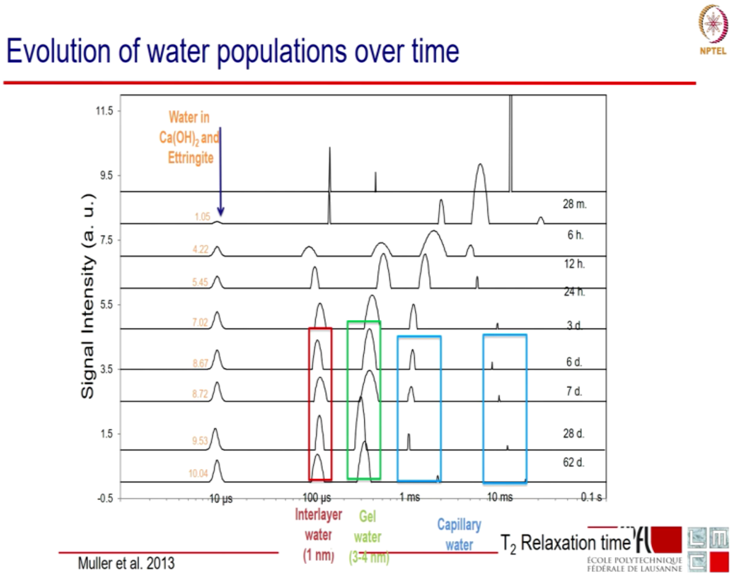
Evolution of water populations over time



Muller et al. 2013

And then finally we have the capillary porosity here. Now what is important to observe is that, in this sample which is a sealed sample, we get a very low amount of capillary pores which still contain water. Now remember this is a sealed sample. This means after setting, because of the chemical shrinkage we start to create voids. So one also have empty capillary pores which you cannot measure with this technique.

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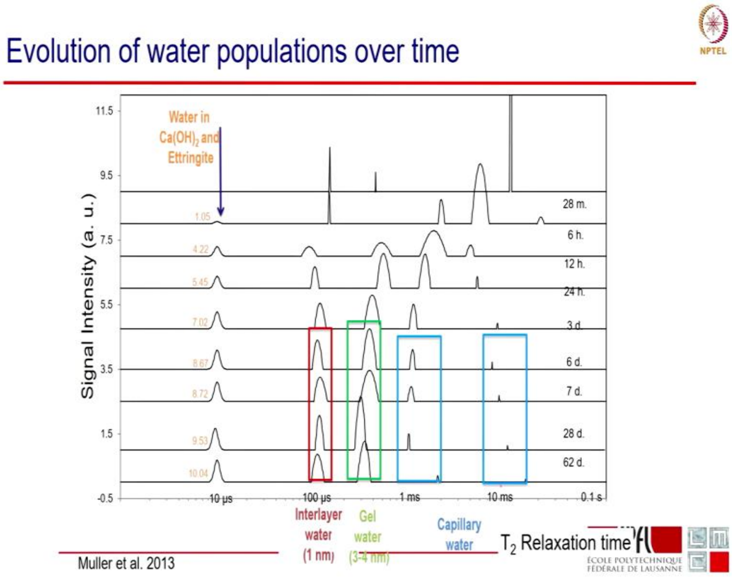
Evolution of water populations over time



Muller et al. 2013

But what we see is that generally 2 or more populations and the finest population quite quickly after few days settles down to this constant size of about 10 nanometers or so.

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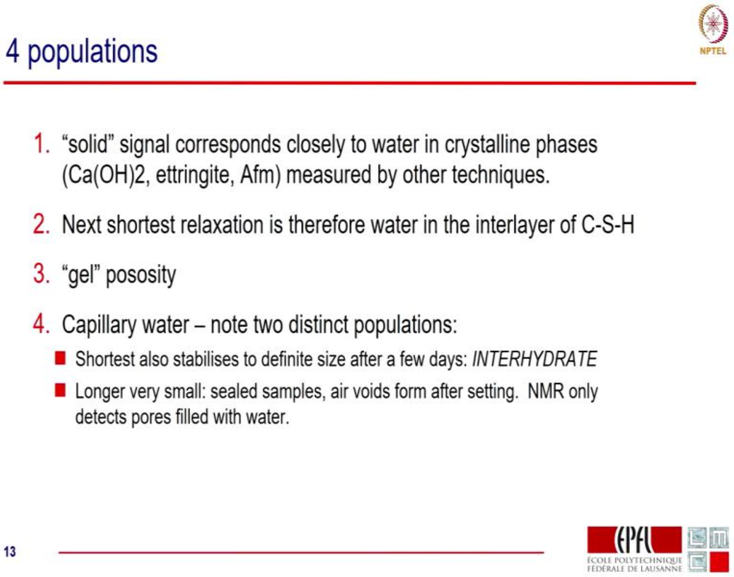

4 populations

1. “solid” signal corresponds closely to water in crystalline phases (Ca(OH)2, ettringite, Afm) measured by other techniques.
2. Next shortest relaxation is therefore water in the interlayer of C-S-H
3. “gel” pososity
4. Capillary water – note two distinct populations:
   - Shortest also stabilises to definite size after a few days: *INTERHYDRATE*
   - Longer very small: sealed samples, air voids form after setting. NMR only detects pores filled with water.

So all of what I have just said is summarized here. We have these 4 populations, the solid signal, the interlayer water, gel porosity and then capillary water.

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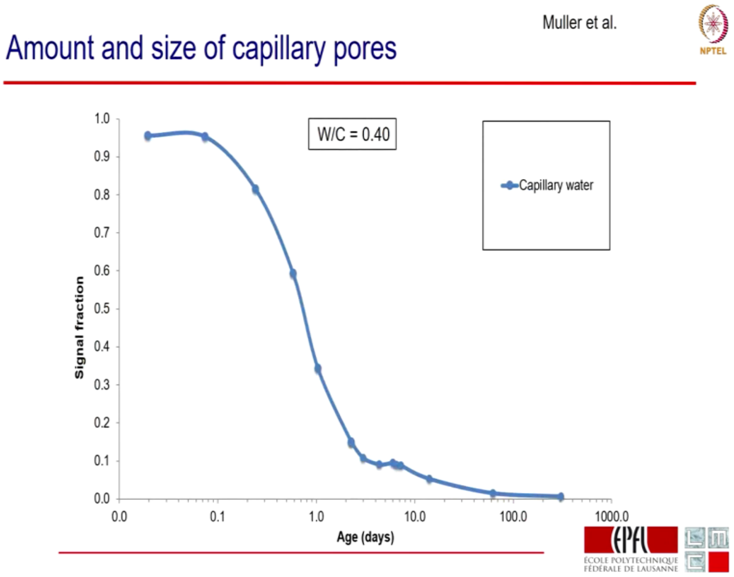

Amount and size of capillary pores

Muller et al.

Now if we then process this spectra we can see how these different populations are evolving over time. So here we see how the capillary pores evolve. The capillary pores are decreasing very rapidly during the main heat evolution peak. So this is the kind of inverse of what you can see by calorimetry. As the reaction goes on, it consumes the water, the capillary water is going down and the average size of that capillary water is going down.

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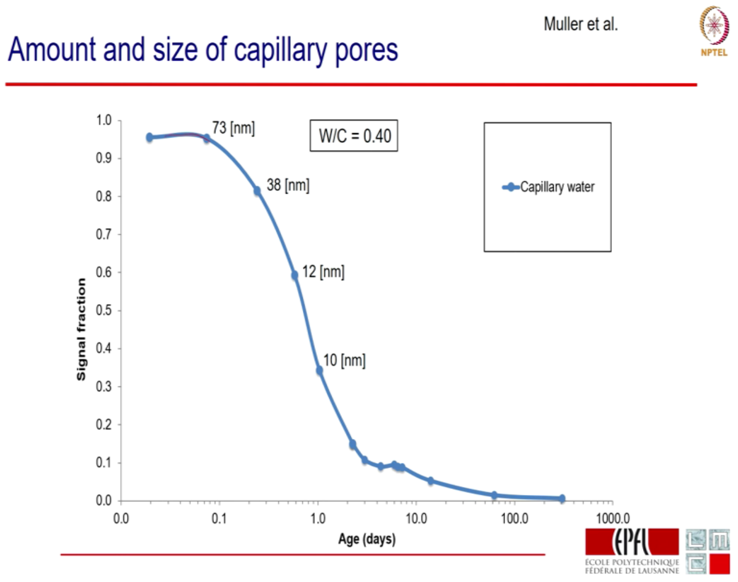

Amount and size of capillary pores

Muller et al.

Now look how small are the sizes, and that is really where we come back to scanning electron microscopy. We realize the scanning electron microscopy is not telling anything about the most important porosity. Because already after 1 day the computer reports that contain water 12 nanometers in size. We cannot resolve that at all in SEM.

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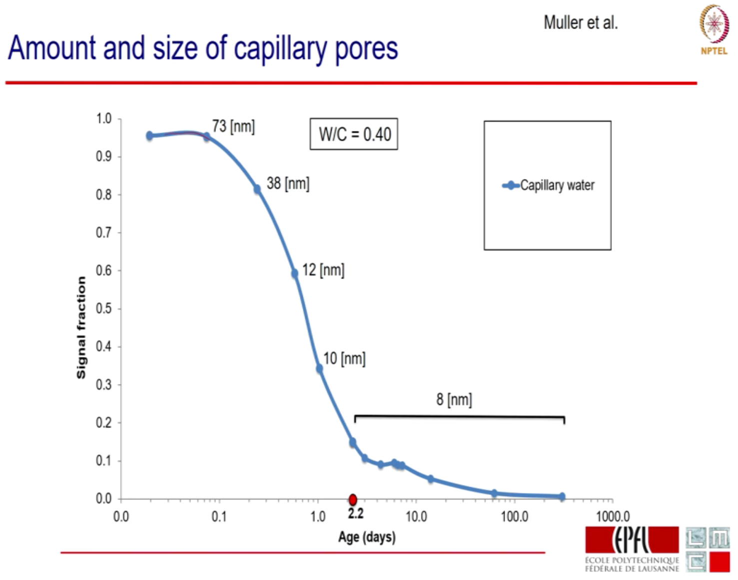

Amount and size of capillary pores

Muller et al.

And what is quite interesting is, after certain points in this case of a white cement, this is just about 2.2 days, the size does not seem to change any more even though the amount gets less. And when the size tends to stay fixed, this value of 8 nanometers, we call these inter-hydrate pores.

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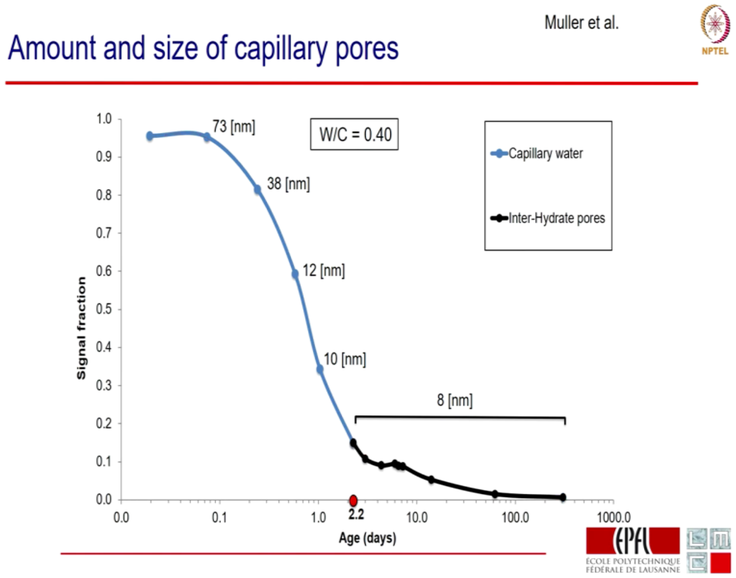

Muller et al.

Amount and size of capillary pores

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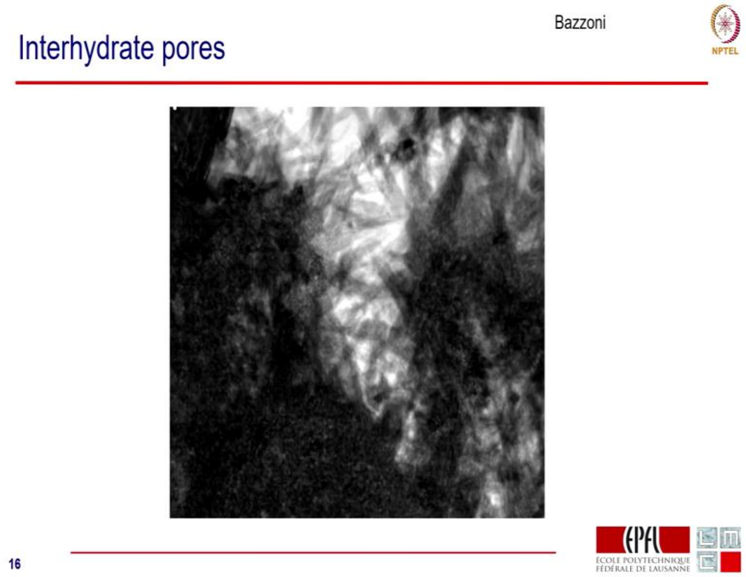

Bazzoni

Interhydrate pores

Because what we think is, that after this point most of the porosity, certainly all of that that contains water are these very fine spaces between the CSH needles. See they are more like slits. They are not like sort of little round pores that you may be used to thinking about.

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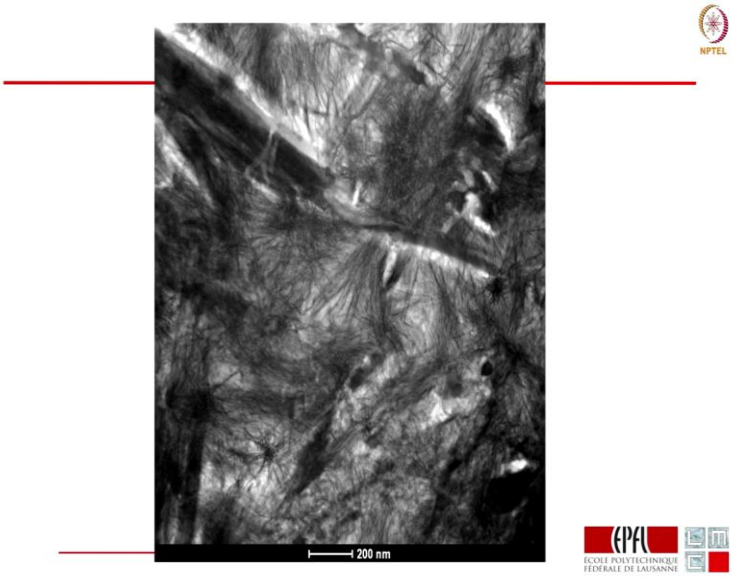

And there is the picture I showed you earlier again, so this is what we mean by these inter-hydrate pores.

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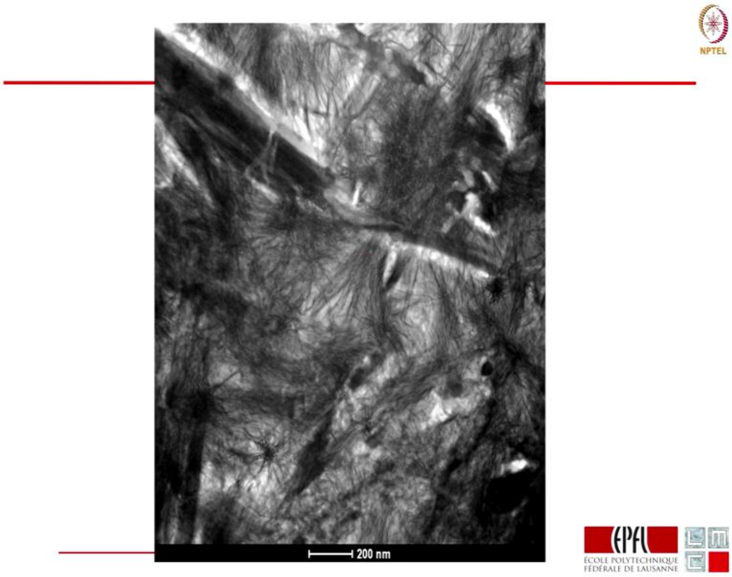

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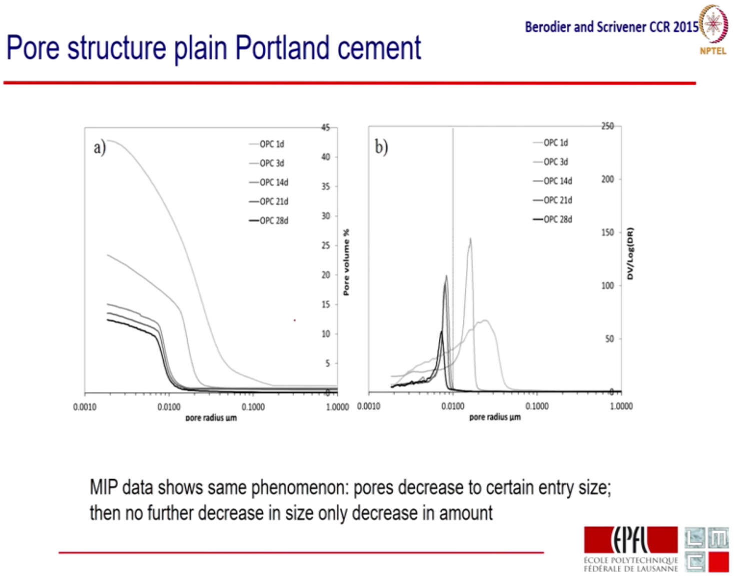
Pore structure plain Portland cement

Berodier and Scrivener CCR 2015

MIP data shows same phenomenon: pores decrease to certain entry size; then no further decrease in size only decrease in amount

We can see the same phenomenon by mercury intrusion porosimetry. We can see that we get no mercury intrusion and then we get a very strong intrusion and the size of this first pore entry after certain time does not get any smaller. It goes down to a certain size and it does not get smaller. So we are really seeing the same phenomenon that after quite short time, the only way of getting in to this sample is through these fine inter-hydrate pores.

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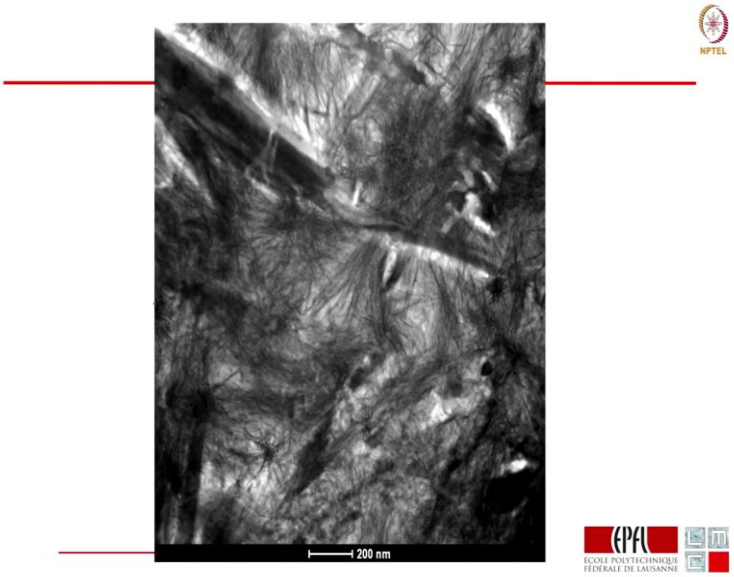

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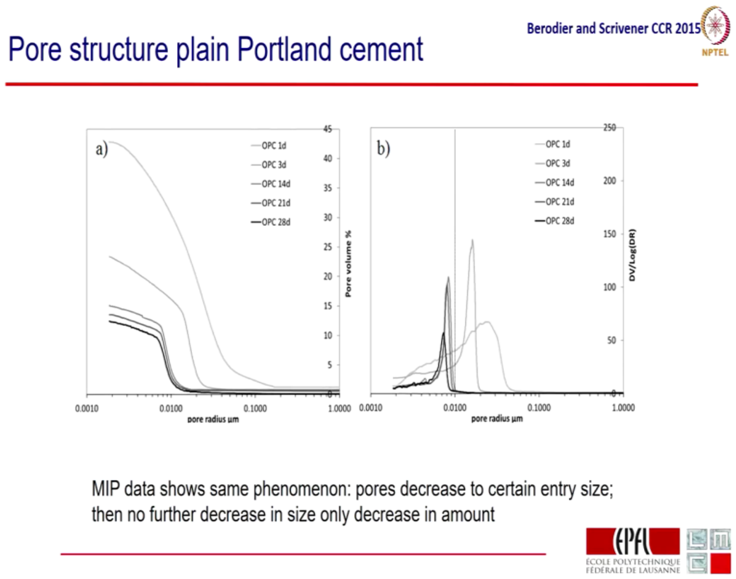

Pore structure plain Portland cement

Berodier and Scrivener CCR 2015

MIP data shows same phenomenon: pores decrease to certain entry size; then no further decrease in size only decrease in amount

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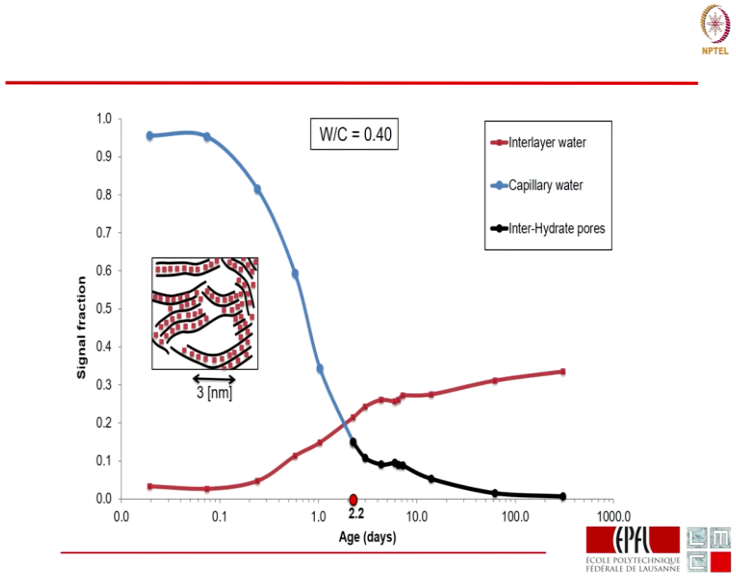

So if we look at the other signals, here we see this signal for the interlayer water. So this is showing as the growth of CSH and this is a little model here of the CSH. You can see this material represent these calcium, oxygen, silicon layers and then the water between them, this red water. And you see this evolves quite fast, during the main heat evolution peak and then more slowly afterwards.

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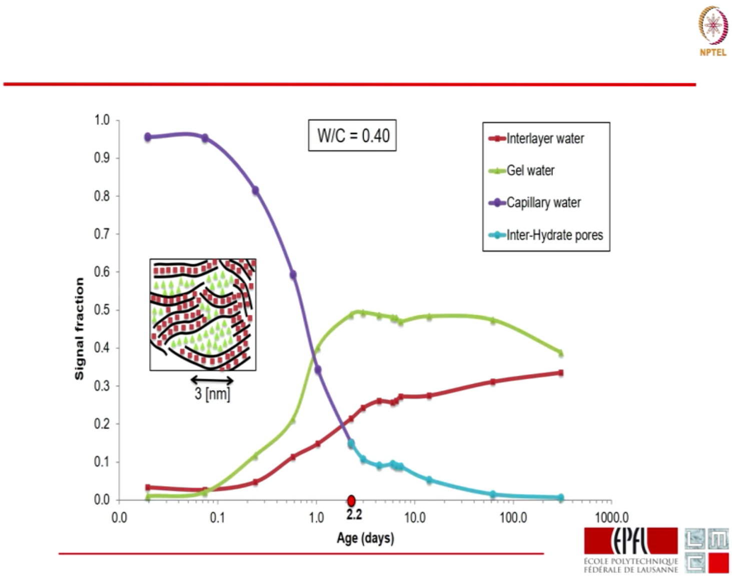

If we now look at gel porosity, at the beginning during the main heat evolution peak, when we are growing those needles of CSH, we are also forming gel pores. But when we get to this point at which all the capillary pores left are these inter-hydrate pores, you see the gel pores are just stabilizing. We are not forming any more gel pores. So we only actually form gel pores in cement paste during the early rapid hydration. And then we form a much denser CSH which seems not to contain gel pores.

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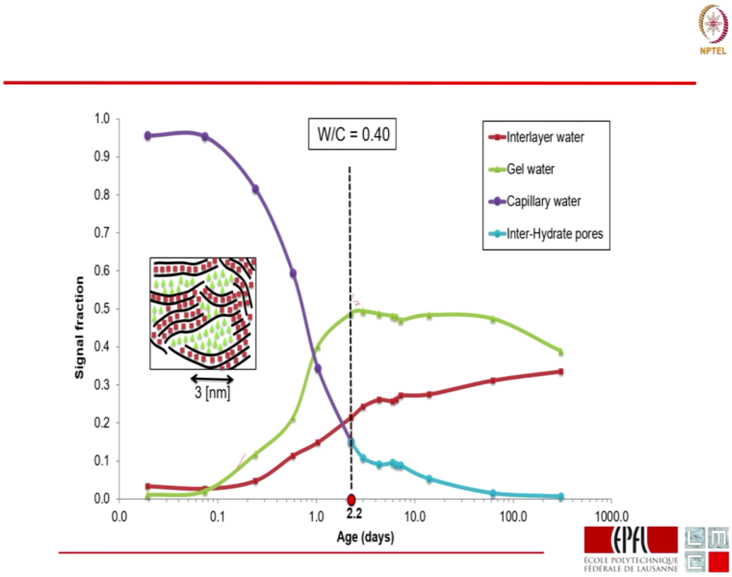

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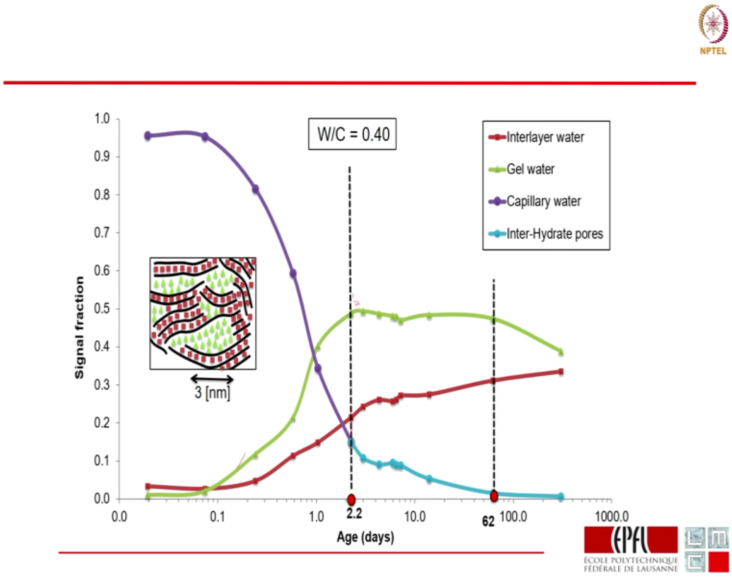

Even at very long ages, we may find that either the gel pores are disappearing or the water in them is disappearing. Probably the former that these gel pores are actually getting filled in by more C S H.

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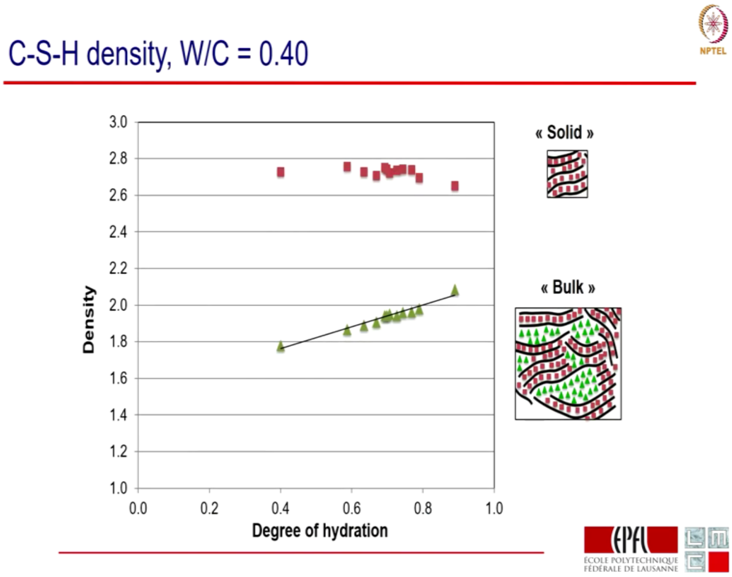
C-S-H density, W/C = 0.40

And we can actually make other calculations; so for example we can put all this information together and make very detailed mass and volume balances to calculate the density of CSH. And this is actually the only technique you can use to calculate the density of CSH. It is very, very interesting from that point of view because you can do it routinely on different samples.

So it was done before with small angle neutron scattering but that is not a very accessible technique. You have to go to a kind of a special facility. Here we can see that, if we are considering just the solid part which is the kind of nano-crystalline regions where we just have sheets of C S H with the interlayer water between them, then the density of these regions is pretty constant through time at about 2.71.

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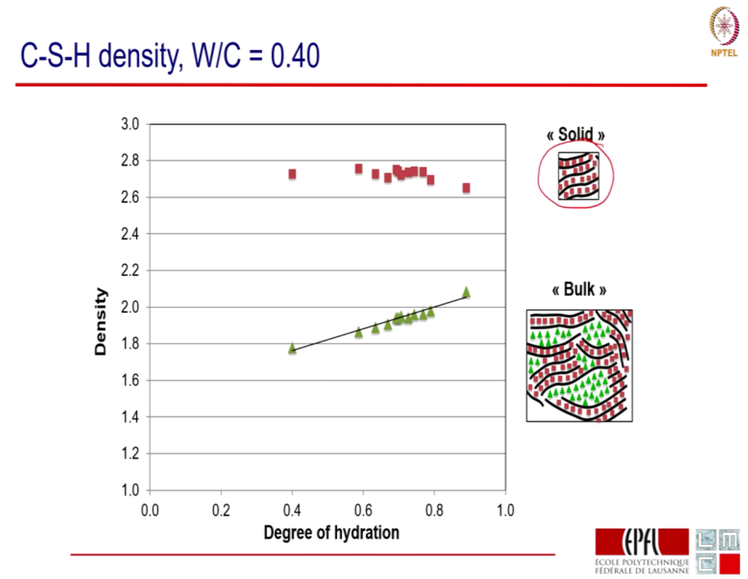
C-S-H density, W/C = 0.40

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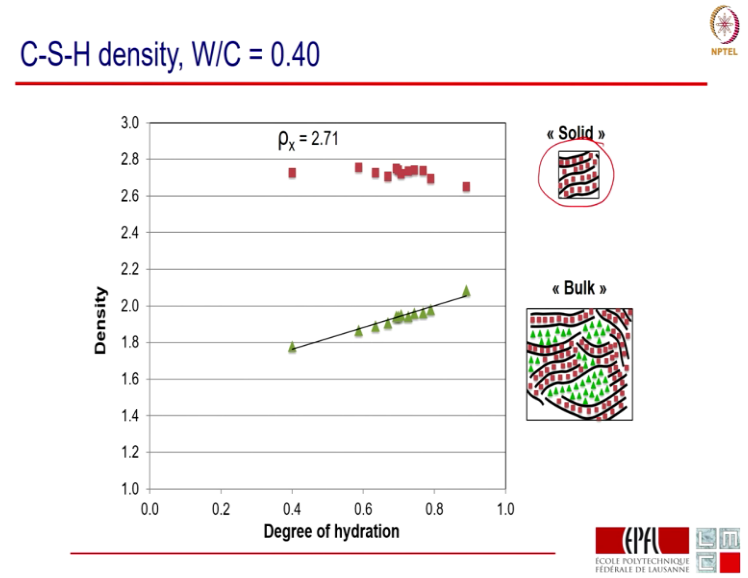
C-S-H density, W/C = 0.40

On the other hand if we would consider the bulk density where we are considering the CSH plus the gel pores which is more important from a structural point of view of how the material is behaving, then we can see that because we only form gel pores during the early phases the average pore density increases and it stabilizes at this value of about 2 which quite interestingly is very, very similar to what people have calculated by other techniques.

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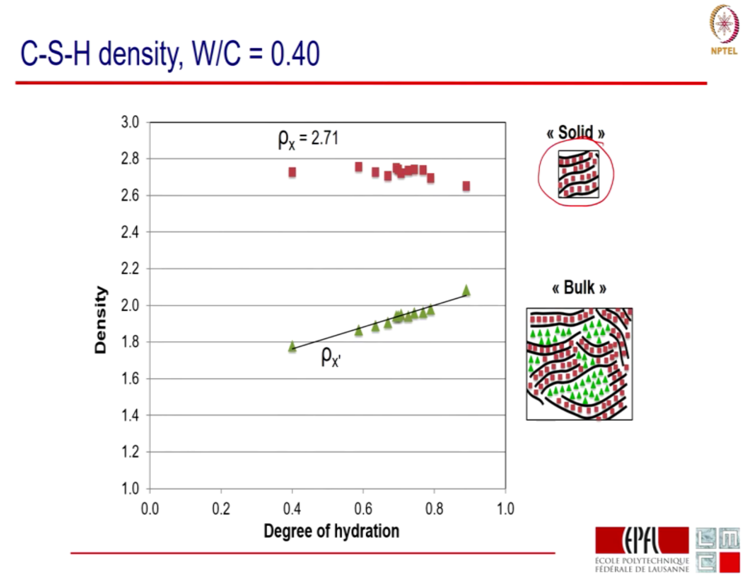

C-S-H density, W/C = 0.40

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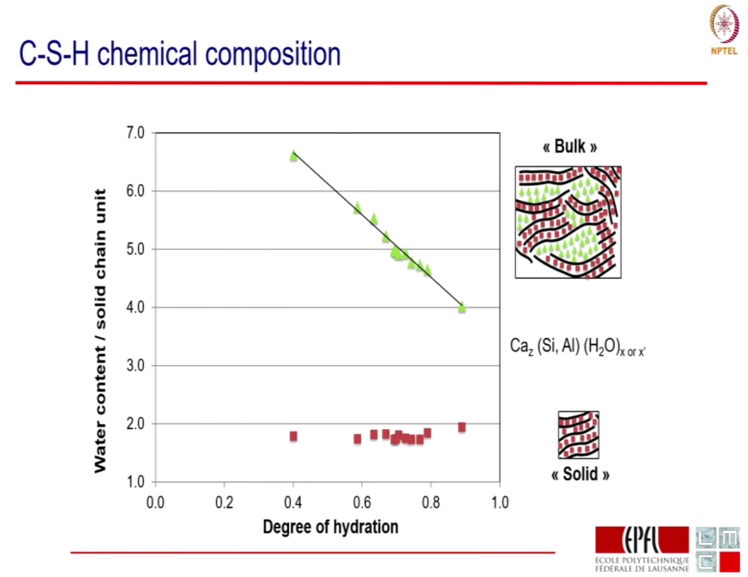
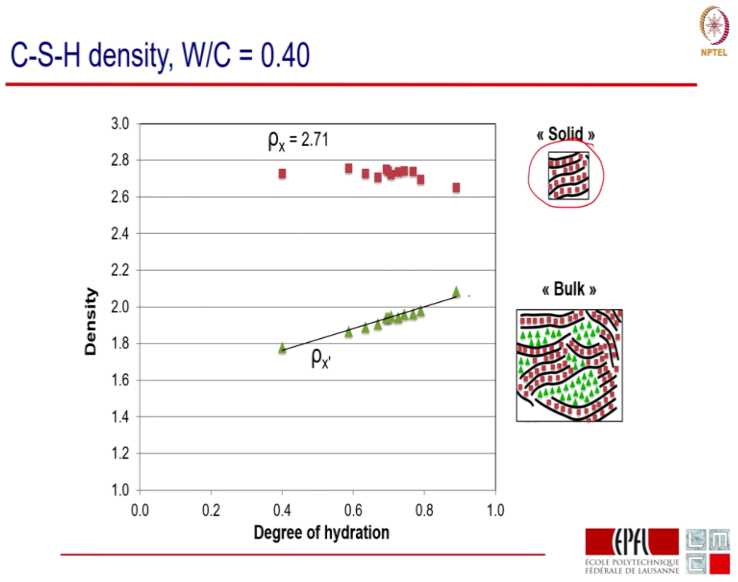


C-S-H chemical composition

(Refer Slide Time: 15:51)



C-S-H density, W/C = 0.40

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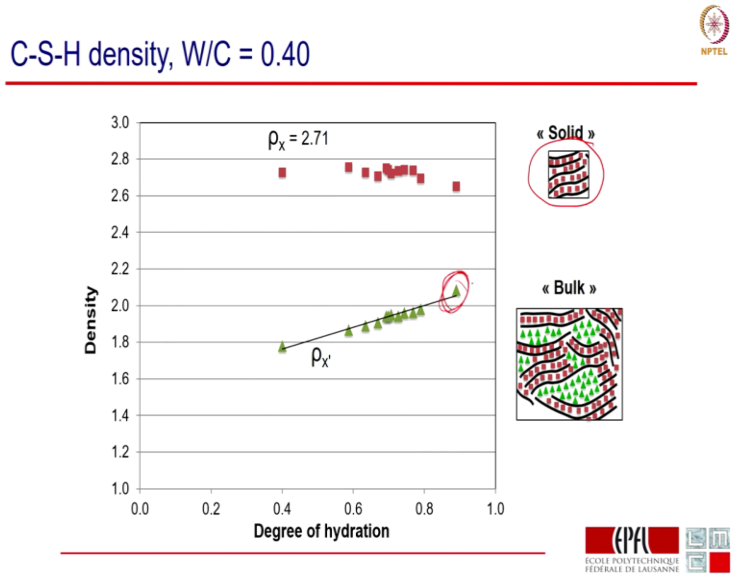

C-S-H density, W/C = 0.40

So it is very, very coherent with everything we can see from other techniques.

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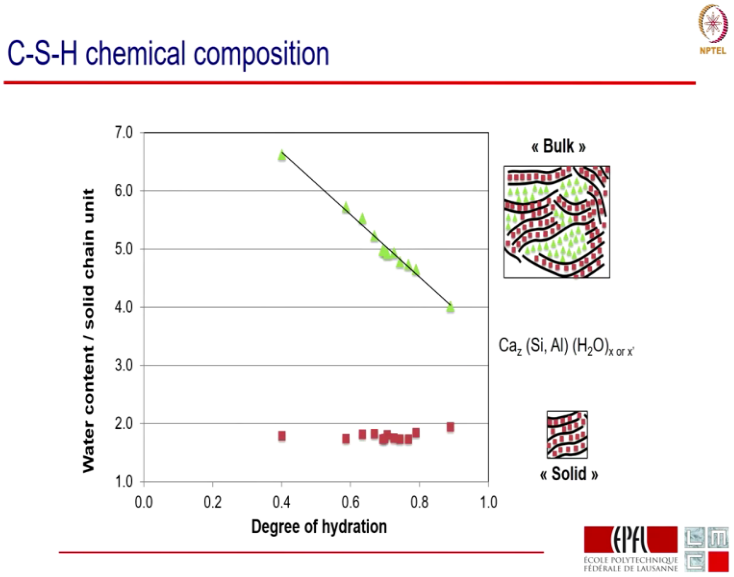

C-S-H chemical composition

We can also calculate the amount of water in the C S H. The water in the solid part is quite stable at about 2 molecules of water per silicon whereas in the bulk one, the average amount of water tends to go down but ends up at the value of about 4 which again is very, very similar to what is calculated by other techniques.

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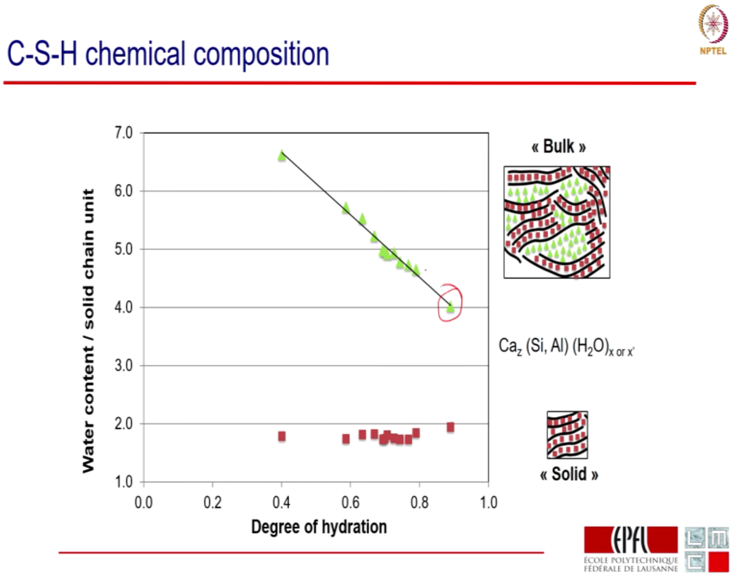

C-S-H chemical composition

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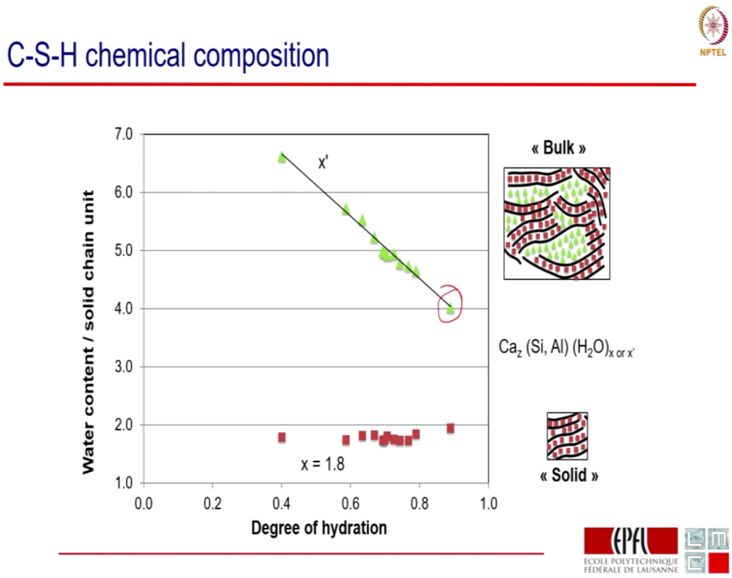

C-S-H chemical composition

Ca_z (Si, Al) $(H_2O)_{x \text{ or } x'}$

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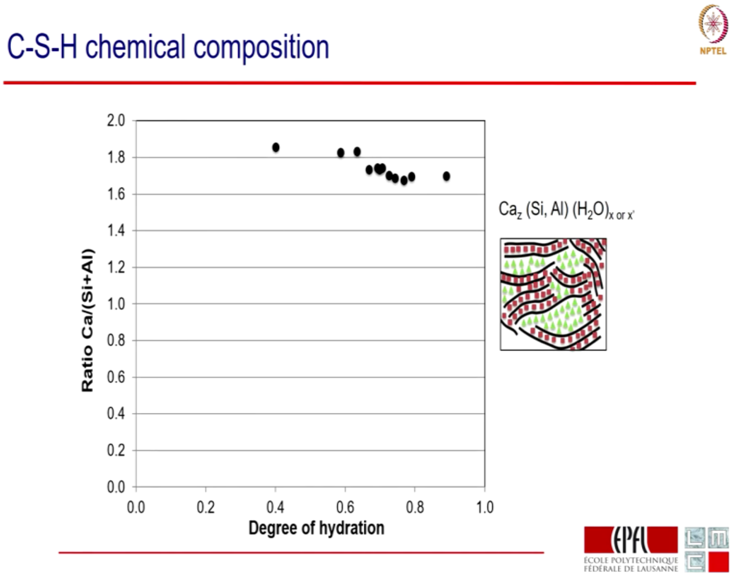

C-S-H chemical composition

Ca_z (Si, Al) $(H_2O)_{x \text{ or } x'}$

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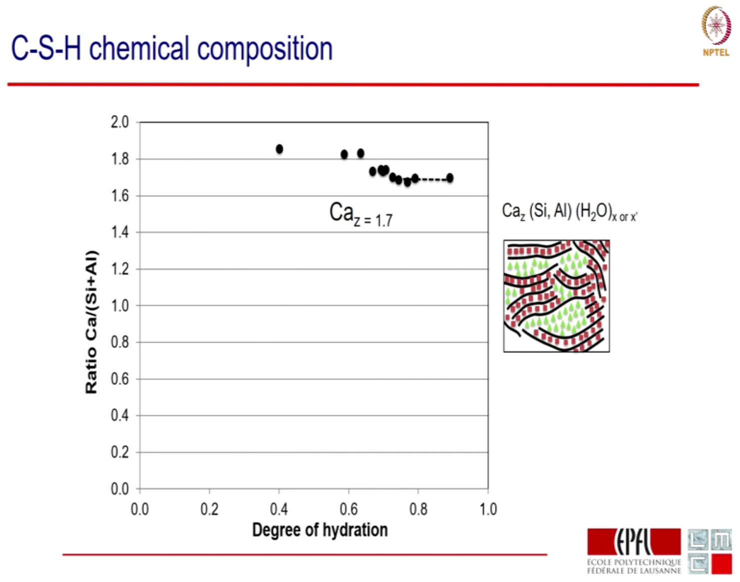
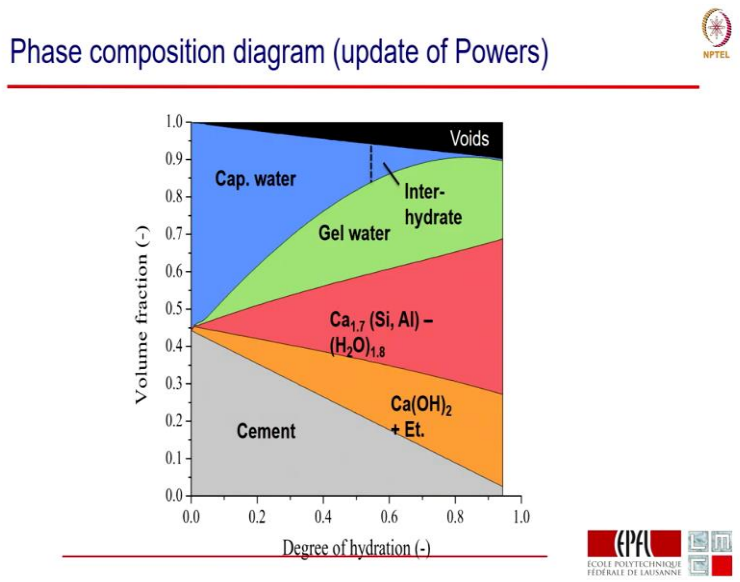

C-S-H chemical composition

(Refer Slide Time: 16:33)


Phase composition diagram (update of Powers)

So we can put all this information together to update this Powers diagram. So Powers made a diagram of the volume ratios of all the different materials as a function of degree of hydration. And he made very precise measurements on very mature samples which actually agree extremely well with these final volumes we see here. Except that, in Powers' case he lumped together all these hydrates, he did not distinguish between the different hydrates which now we can do with these, with NMR or with X-ray diffraction.

And in the case of Powers' diagram we have these kind of straight line relationships. He also drew a straight line relationship for the gel pores. He drew it like that so I am not drawing very well too.

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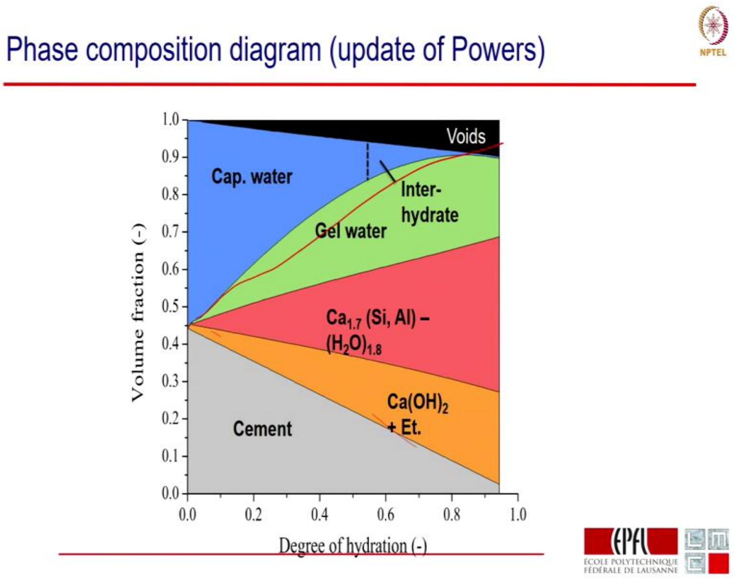

Phase composition diagram (update of Powers)

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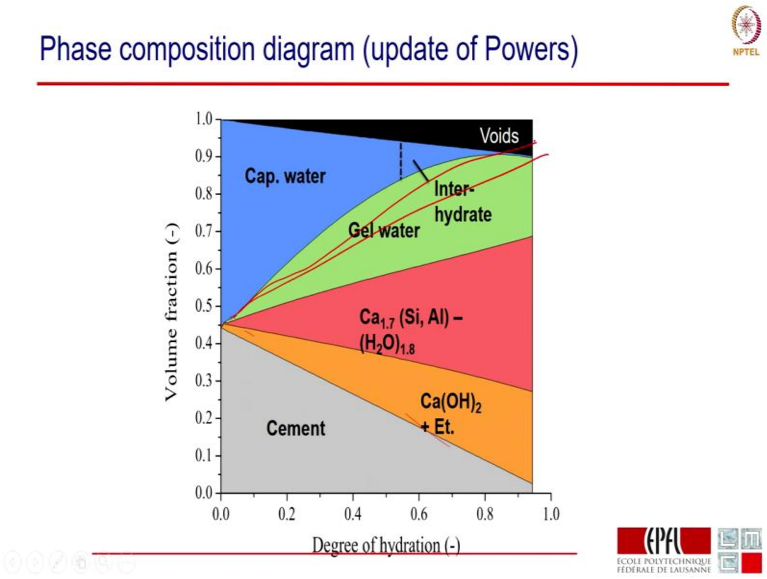

Phase composition diagram (update of Powers)

Since the gel pores are forming earlier, the boundary here between the gel and the capillary porosity is actually curved.

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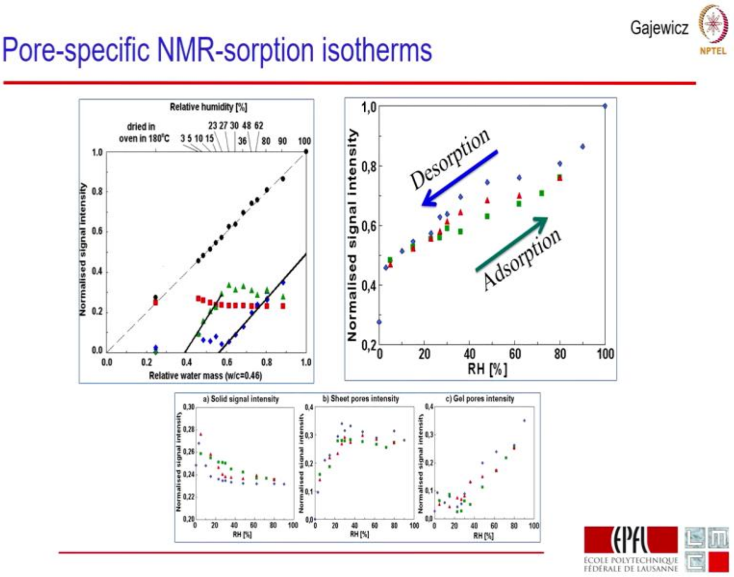

Pore-specific NMR-sorption isotherms

Gajewicz

We can also see how the water in different population oppose changes with relative humidity. So these are some very careful experiments which have been done over several absorption desorption cycles. We see that the large capillary pores almost never contain water. Already when you are down to, relative humidity is in the high 90s you have emptied what were really the capillary pores. Then the, vis-à-vis the gel pores, this is the interlayer and this is the solid.

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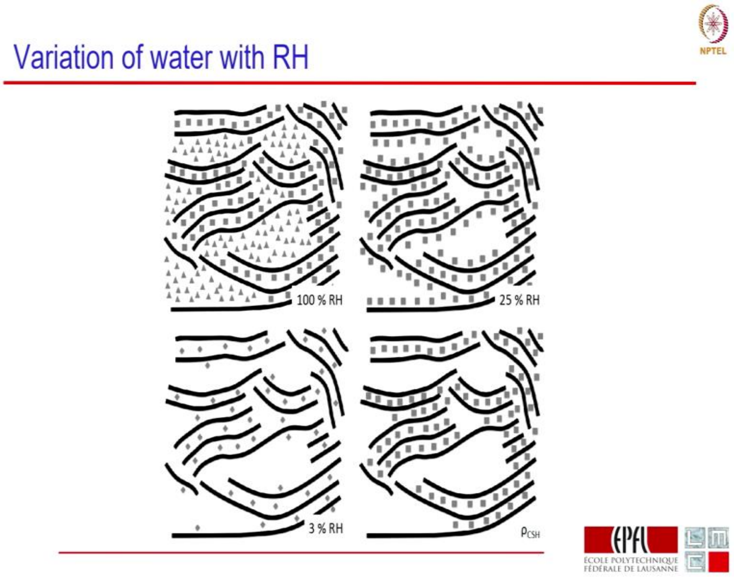

Variation of water with RH

And this gives you different diagram of how you can imagine the state of water in the C S H at different relative humidity. So at 100 percent we have the interlayer and gel pores filled, when we dry it out say 25 percent then the gel pores will all be empty and then if we dry more than that, it will even take water out of the interlayer of the C S H.

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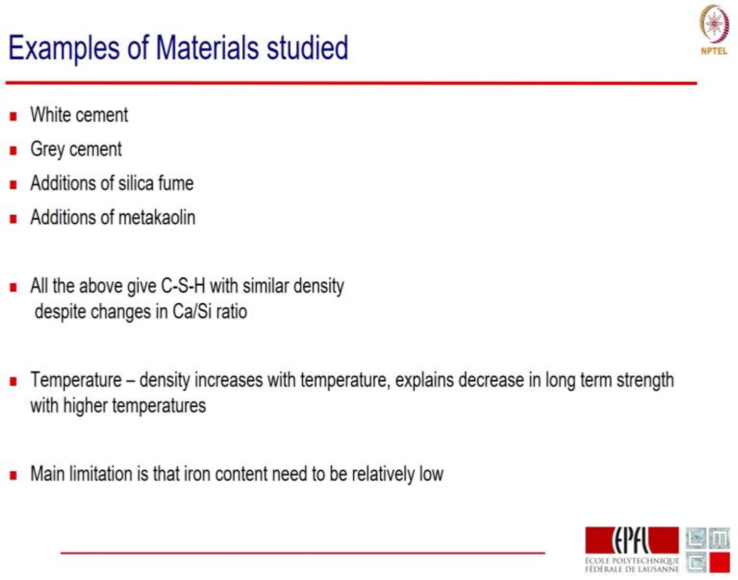

Examples of Materials studied

- White cement
- Grey cement
- Additions of silica fume
- Additions of metakaolin

- All the above give C-S-H with similar density despite changes in Ca/Si ratio

- Temperature – density increases with temperature, explains decrease in long term strength with higher temperatures

- Main limitation is that iron content need to be relatively low

So we now studied a lot of materials by this technique, with the most of the stuff on white cement, because the main limitation of this technique is that the iron content needs to be quite low.

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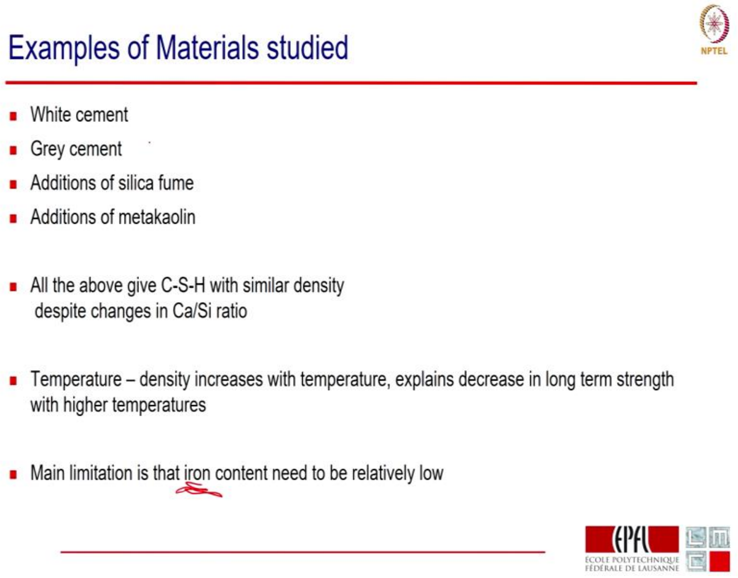

Examples of Materials studied

- White cement
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- All the above give C-S-H with similar density despite changes in Ca/Si ratio

- Temperature – density increases with temperature, explains decrease in long term strength with higher temperatures

- Main limitation is that iron content need to be relatively low

But you can still do grey cement and with the experiments of addition of silica fume, with additions of metakaolin. Interestingly, we see that the density of the C S H tends to stay very similar despite changes in calcium silicon ratio. The one thing that really does affect the density very much is the temperature. As you increase the temperature, even quite modestly to say 40 or 60 degrees, you have increased the density of the C S H and this is the reason why if you have materials that are cured at higher temperatures, their long term strength will generally be lower than the materials cured at lower temperatures.

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Mercury intrusion porosimetry

So that is the picture we see from N M R and then how does this help us to understand what we see by mercury intrusion porosimetry.

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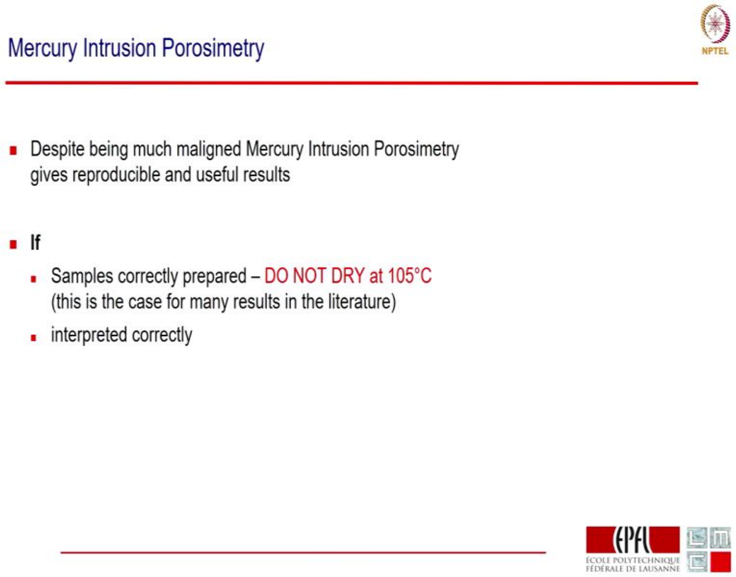

Mercury Intrusion Porosimetry

- Despite being much maligned Mercury Intrusion Porosimetry gives reproducible and useful results
- If
  - Samples correctly prepared – DO NOT DRY at 105°C (this is the case for many results in the literature)
  - interpreted correctly

Now as I said, mercury intrusion porosimetry has been very heavily criticized and many people say we do not use that anymore. And yeah we tend to say. But I hope that I can convince you that it can give reproducible and useful results if your samples are prepared correctly. And this is where the drying is absolutely critical. Unfortunately most people who have done mercury intrusion porosimetry in the past stick their sample in oven at a 105 and then do the experiment. And then you get nonsense. Because you form cracks. These cracks are like highways, the mercury can go down these highways and you cannot understand anything. And secondly you have to interpret it correctly. And that we can now do thanks to this picture we have from the N M R.

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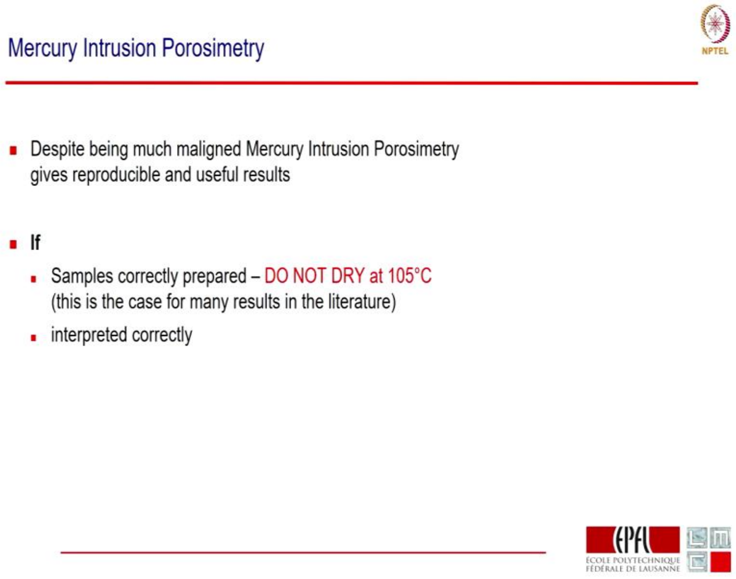

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- Despite being much maligned Mercury Intrusion Porosimetry gives reproducible and useful results
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  - interpreted correctly

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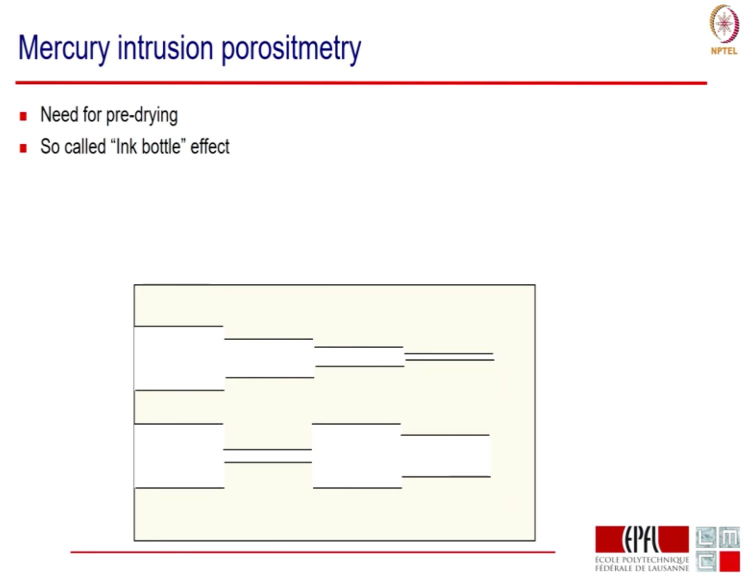

Mercury intrusion porositmetry

- Need for pre-drying
- So called “Ink bottle” effect

So the main problem is we need to predry and the second problem is this so called ink bottle effect. So the idea of this is that if you have a pore structure, where you have the bigger pores leading to smaller pores and so on and so forth, then everything is fine. But more normally, you have larger pores which can only be accessed through smaller pores.

So what we see is this, you see that in the top case everything is fine, but in the bottom case all of the sudden this huge volume gets intruded when we force the mercury through this very small pore size.

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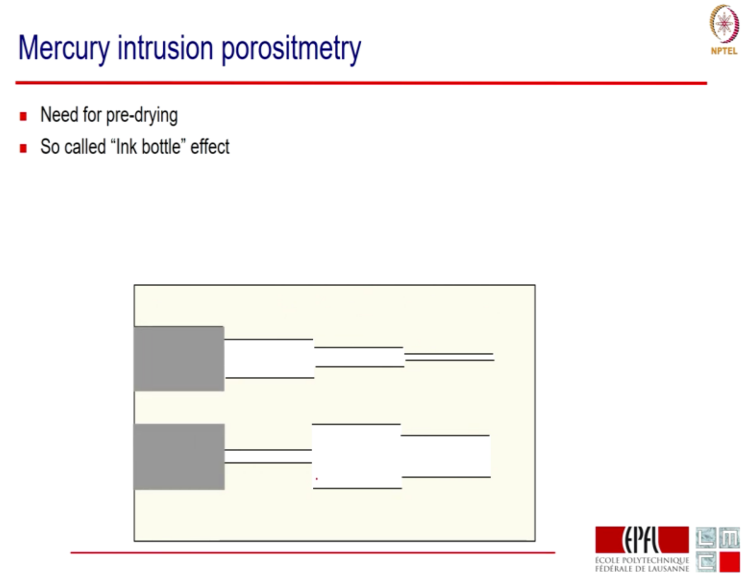

Mercury intrusion porositmetry

- Need for pre-drying
- So called “Ink bottle” effect

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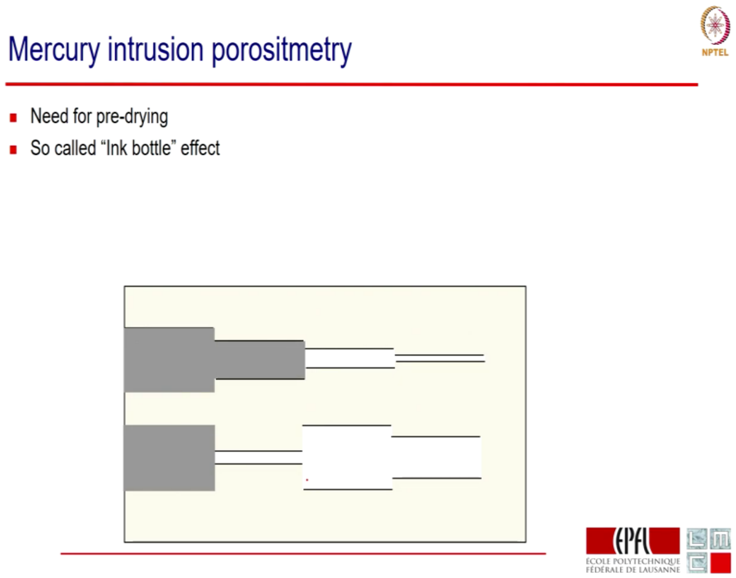

Mercury intrusion porositmetry

- Need for pre-drying
- So called “Ink bottle” effect

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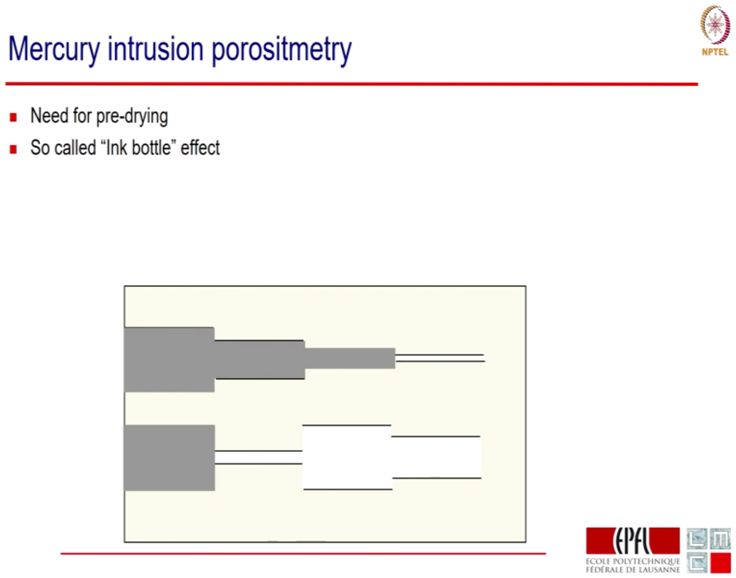

Mercury intrusion porositmetry

- Need for pre-drying
- So called “Ink bottle” effect

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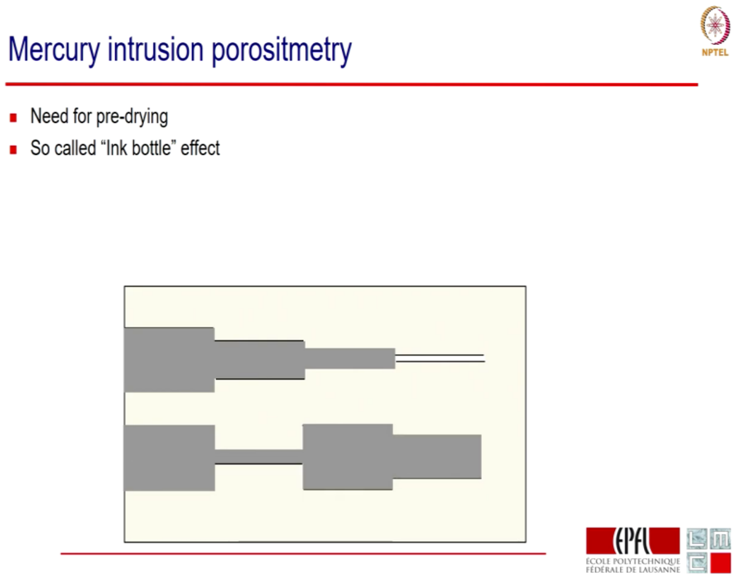

Mercury intrusion porositmetry

- Need for pre-drying
- So called “Ink bottle” effect

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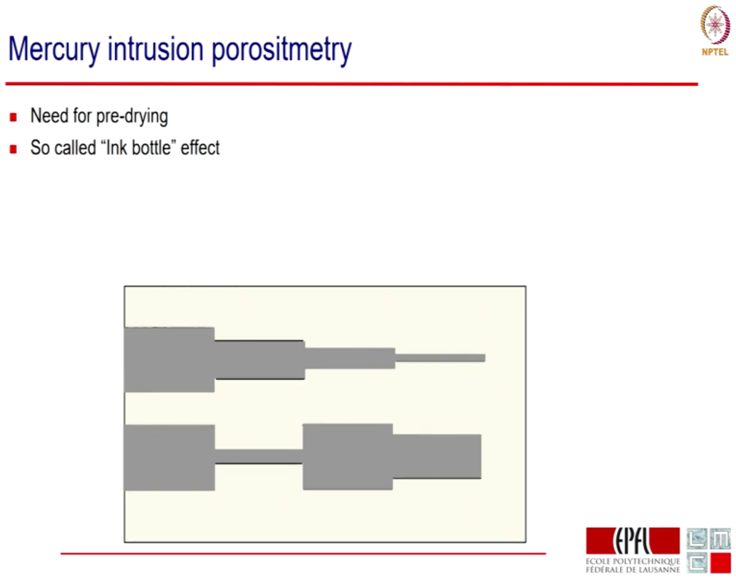

Mercury intrusion porositmetry

- Need for pre-drying
- So called “Ink bottle” effect

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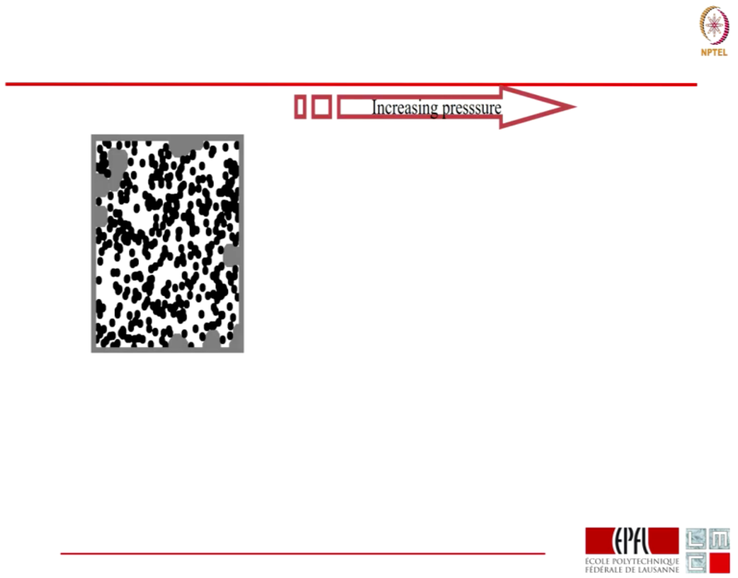

Increasing presssure

And in reality, if you imagine a sort of simplified microstructure like this, this is ideal microstructure. White represents the pores and the black is the solid. Now we are pushing mercury in from the side and you see that even though the pore in the middle may be quite large, they do not get access until we have high enough pressure that we can access through this small entry. So this is what it means in terms of a pore entry diameter.

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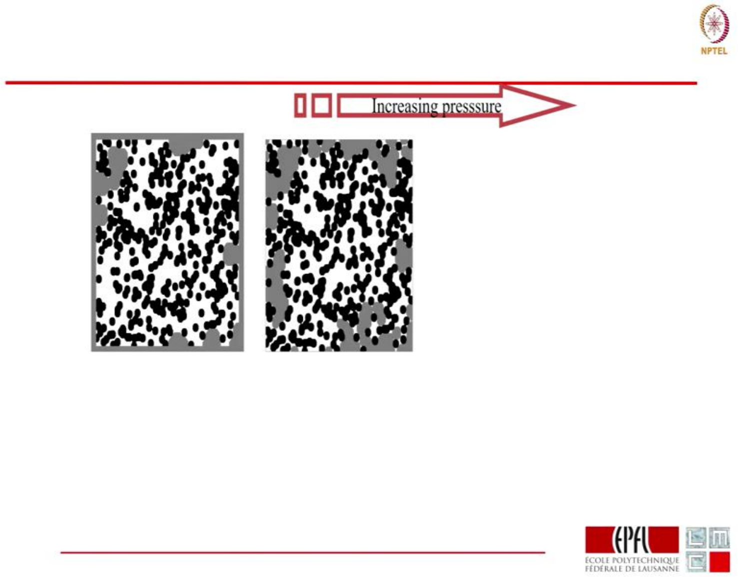

Increasing presssure

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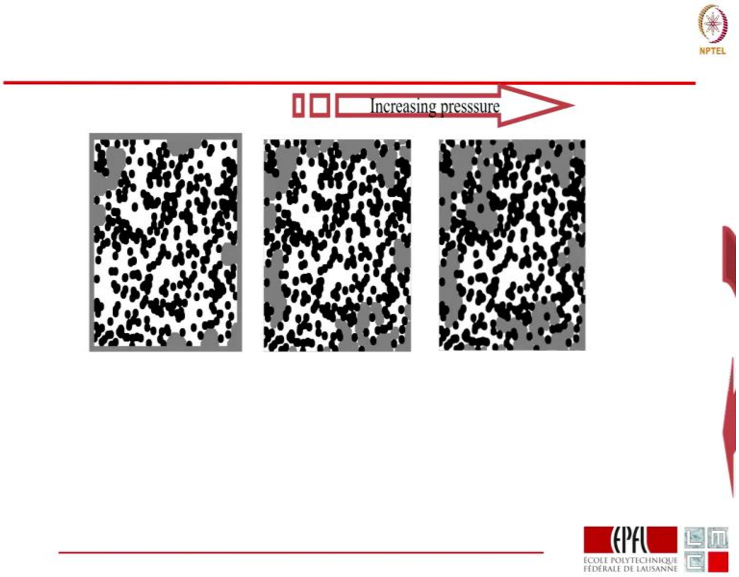

Increasing presssure

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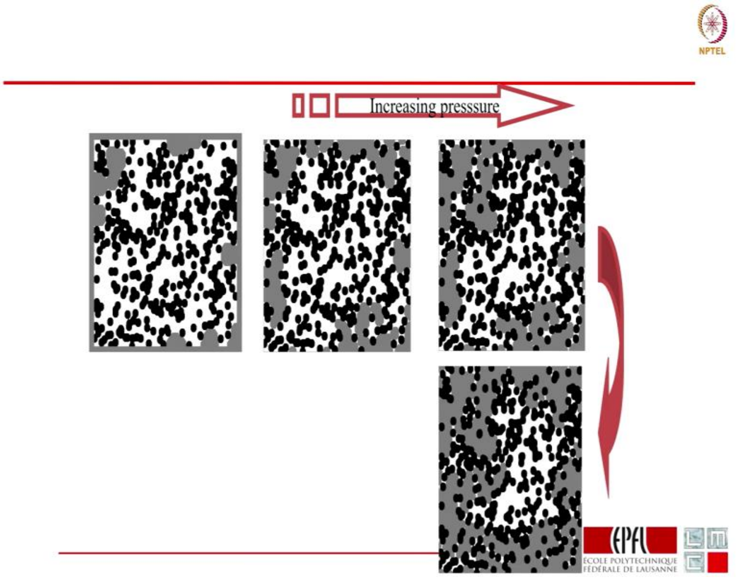

Increasing presssure

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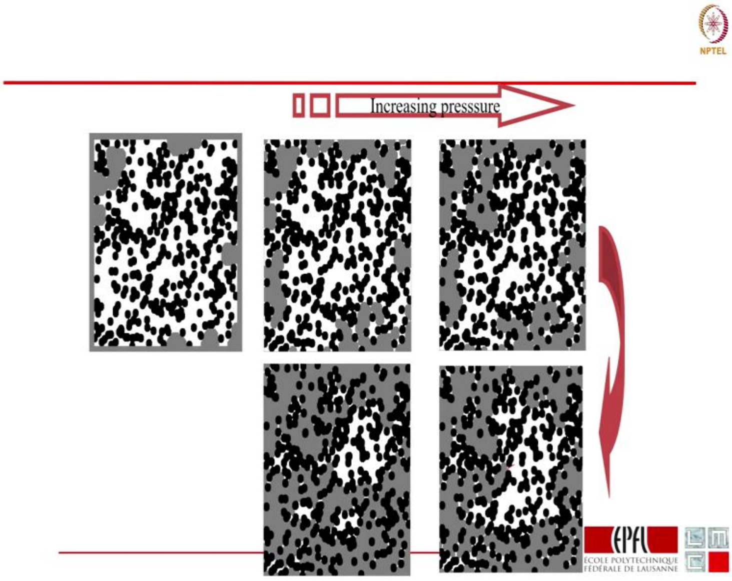

Increasing presssure

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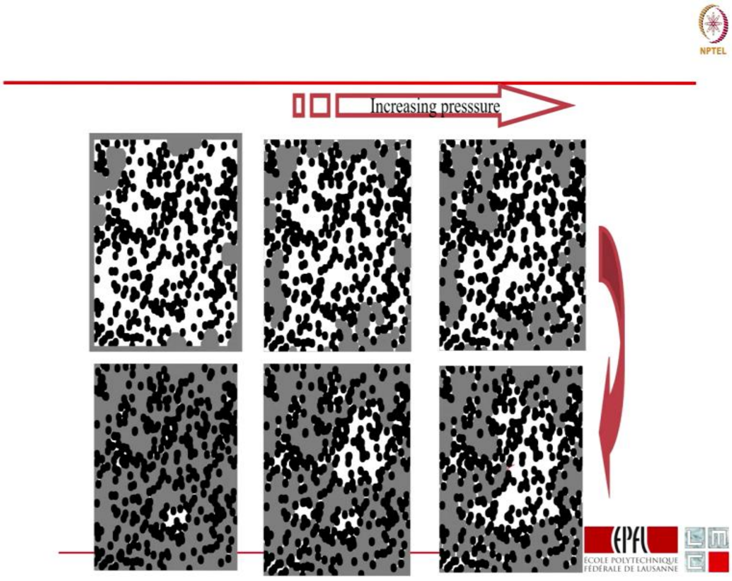

Increasing presssure

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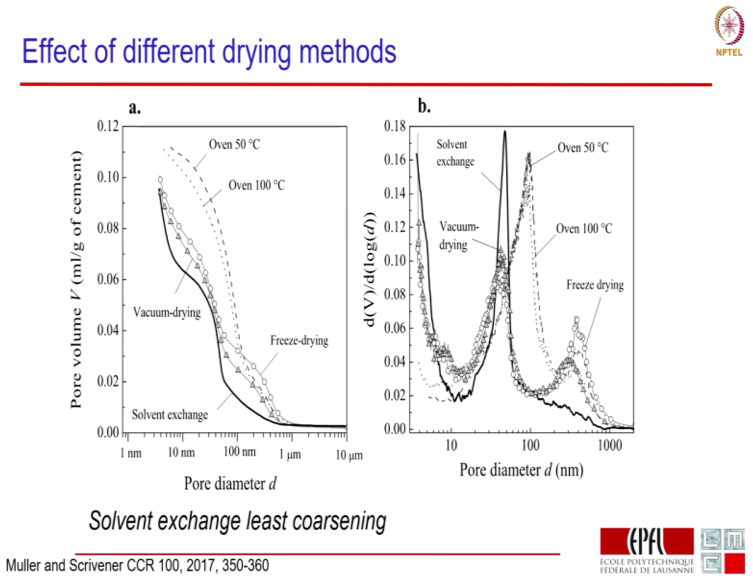

Effect of different drying methods

Solvent exchange least coarsening

Muller and Scrivener CCR 100, 2017, 350-360

So first, the most important is the effect of different drying methods. So here we see the results with drying methods, with solvent exchange, freeze drying, vacuum drying and then oven drying. Now the solvent exchange is what we think is the best technique. You see that we get very little intrusion into the sample until we get down to this quite fine pore size of the few 10s of nanometers. When we oven dry we increase this by, like an order of magnitude. So you make the pore seems 10 times bigger which is just completely wrong.

And freeze drying, vacuum drying is not too bad but not as good as solvent exchange. So solvent exchange is really the technique you want to look at here and all results I am showing here are just recently published in this paper in Cement and Concrete Research.

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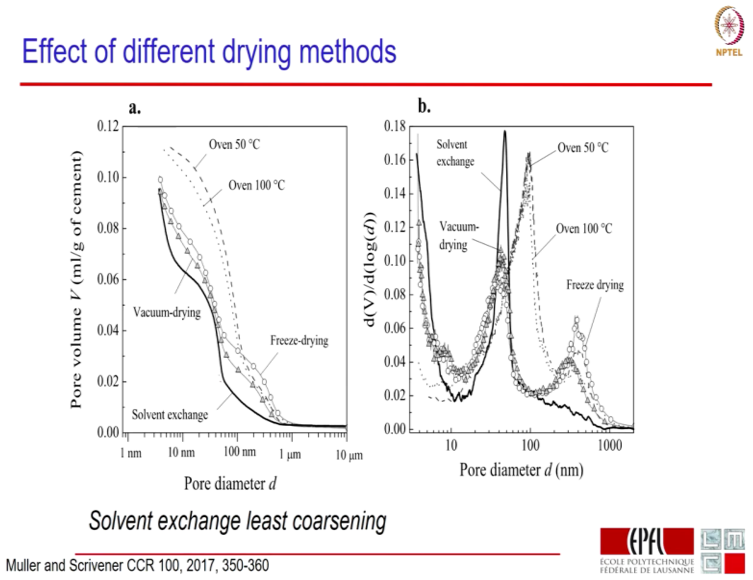

Effect of different drying methods

Solvent exchange least coarsening

Muller and Scrivener CCR 100, 2017, 350-360

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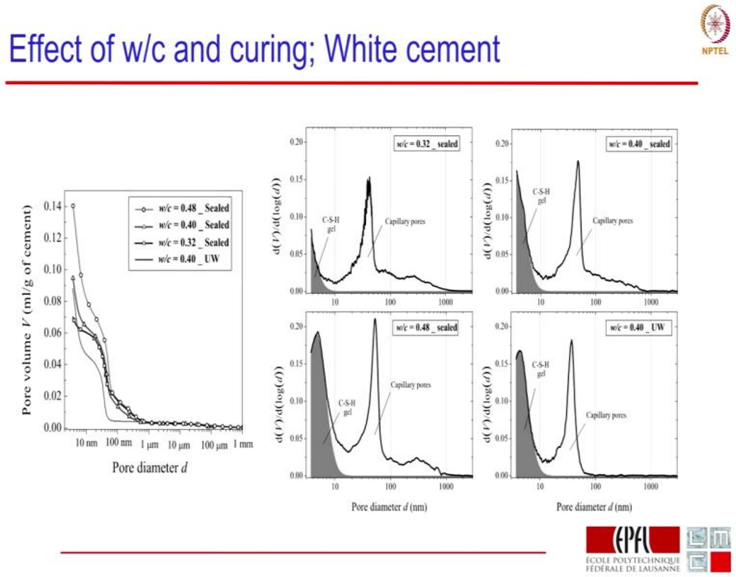

Effect of w/c and curing; White cement

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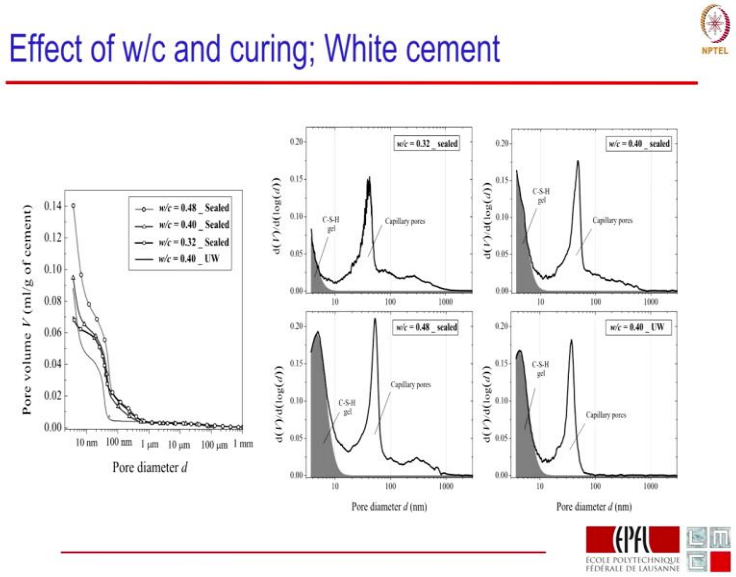

Effect of w/c and curing; White cement

So for white cement, we see that the mercury intrudes in and then right on the very fine pore size we also seem to see another intrusion. And we think the second part here where the curves goes up again is when we start to go into some of the gel pores. And we do not really know why we seem to get mercury in some gel pores in white cement but not in other cement. But anyway we can separate out this effect. So in this treatment here we removed this fine peak here because this is part of the gel pores.

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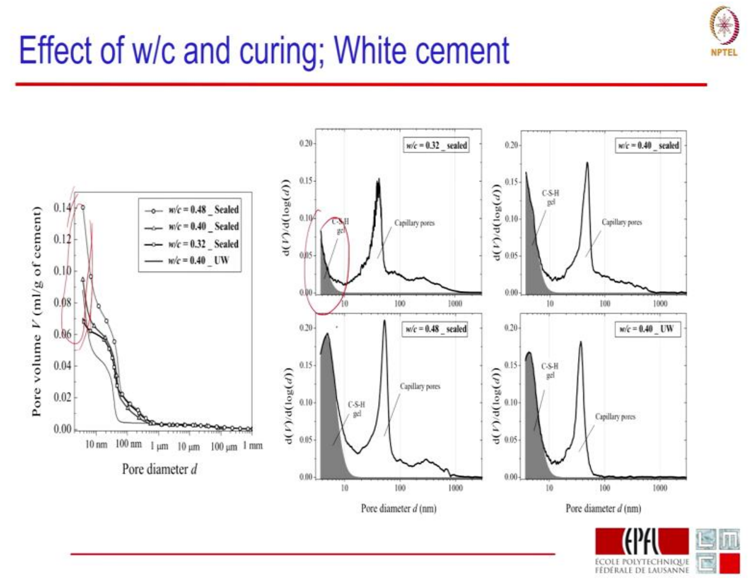

Effect of w/c and curing; White cement

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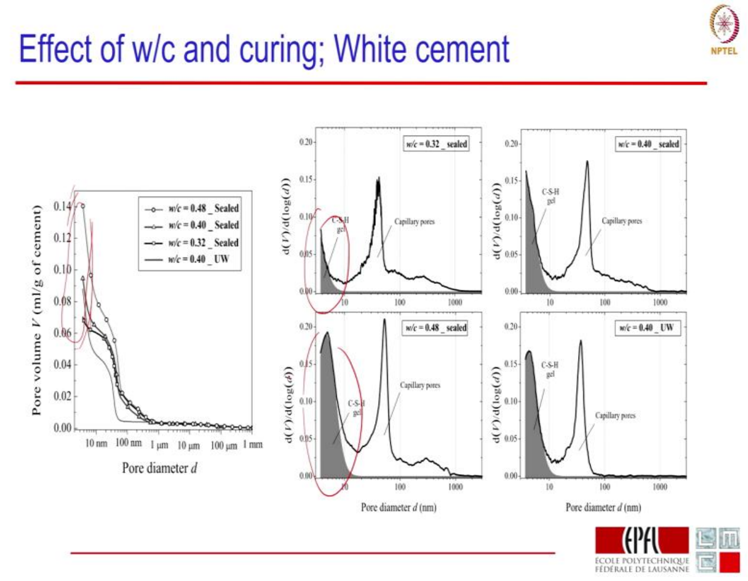

Effect of w/c and curing; White cement

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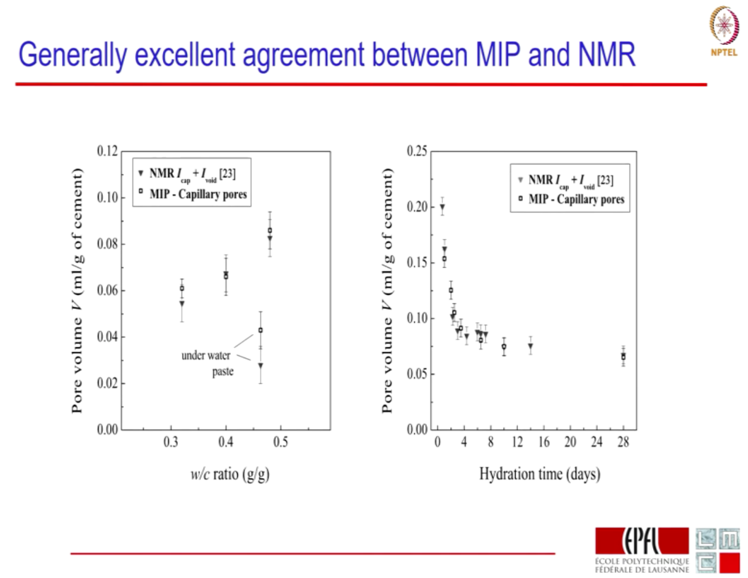

Generally excellent agreement between MIP and NMR

And then when we compare these two measurements, so we have mercury, we have the capillary pores

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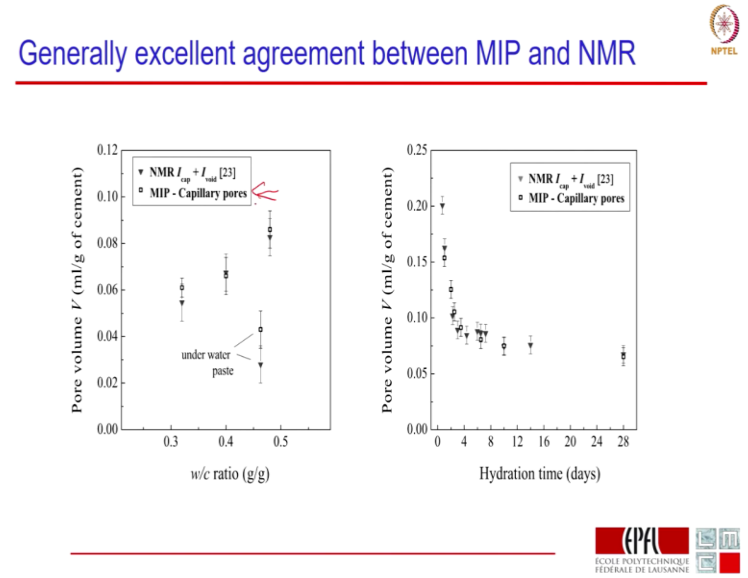

Generally excellent agreement between MIP and NMR

and N M R we have the capillary pores that I told you about earlier but of course we have to add in the voids, because many of the pores are not containing water. We have to take those into account.

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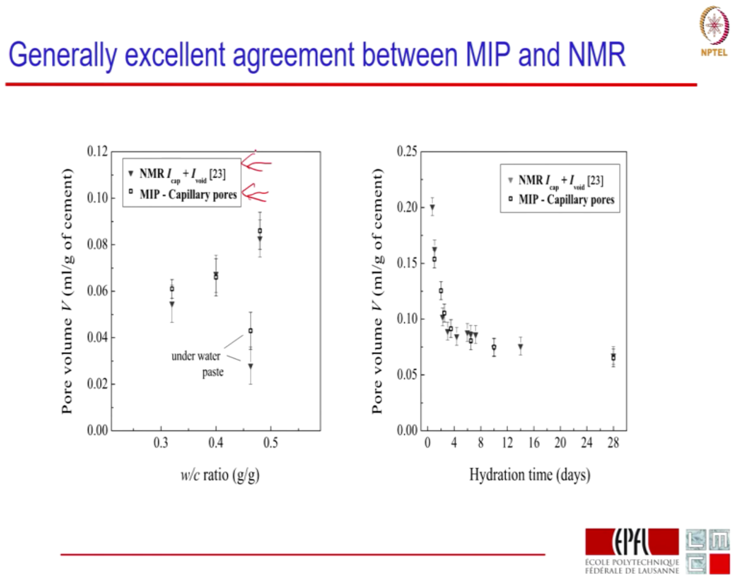

Generally excellent agreement between MIP and NMR

So we have N M R capillary plus the voids compared to M I P capillary. And what you see is incredibly good agreement. We have a slight disagreement here for the sample cured under water. But we think the problem here was that the size of the samples we used in the two cases was not really the same. So we had the problem of, you know and as I said with chemical shrinkage, when you have a large sample, water may not well get into all the pores.

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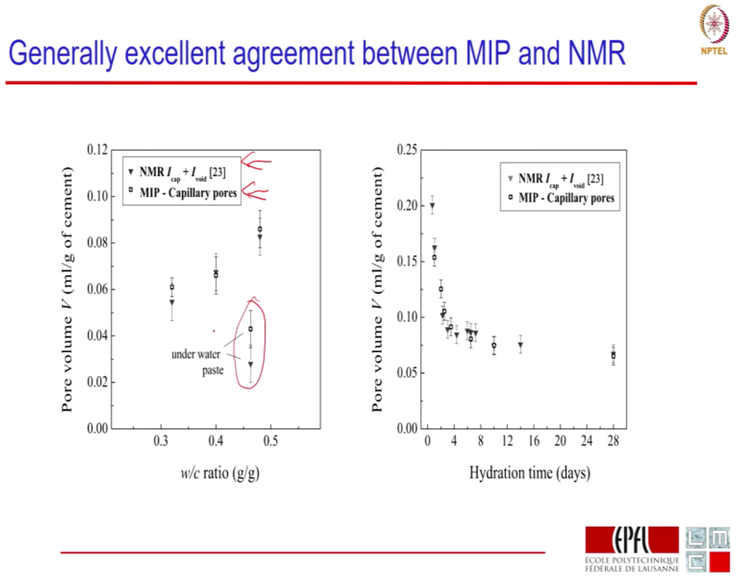

Generally excellent agreement between MIP and NMR

So the hugely and very important results here is if you do your M I P carefully you can measure the same porosity as you know by N M R which is on undried sample. So here we compare the two different techniques for the different sample ages and you can see the M I P is measuring the voids, the voids which are created by the chemical shrinkage, it is measuring the blue part which is the capillary pores that is measured by N M R and for some reason a little bit of this gel pores. It is very, very smooth part of this gel pores so it is better to ignore that.

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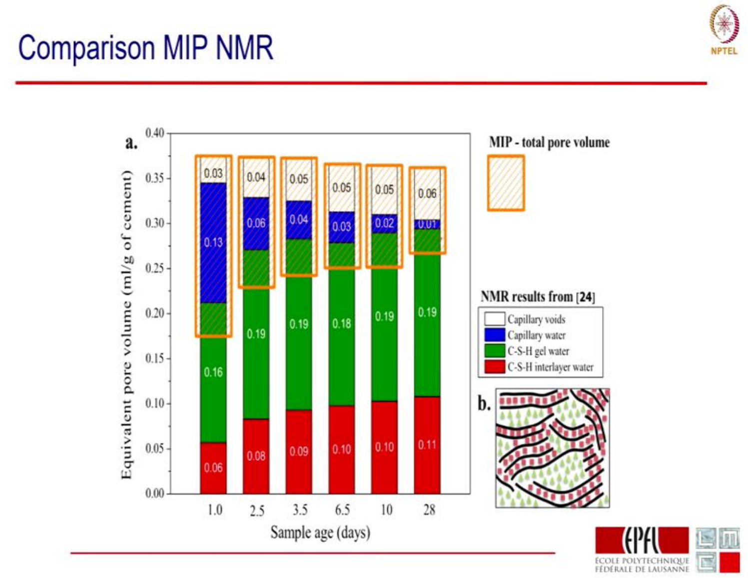

Comparison MIP NMR

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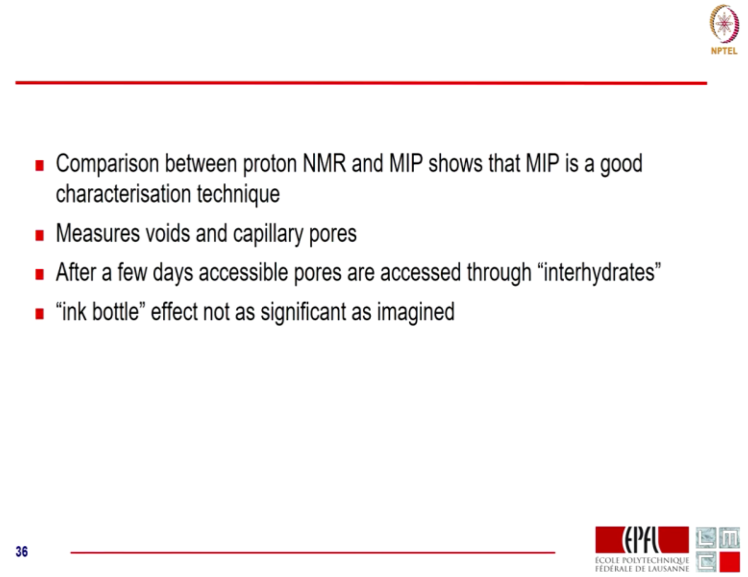

- Comparison between proton NMR and MIP shows that MIP is a good characterisation technique
- Measures voids and capillary pores
- After a few days accessible pores are accessed through “interhydrates”
- “ink bottle” effect not as significant as imagined

The fact that we have this good agreement also really tells us that the ink bottle effect is not really as significant as people would have imagined. Because, after few days all the accessible porosity is really dominated by this stuff we call interhydrates.

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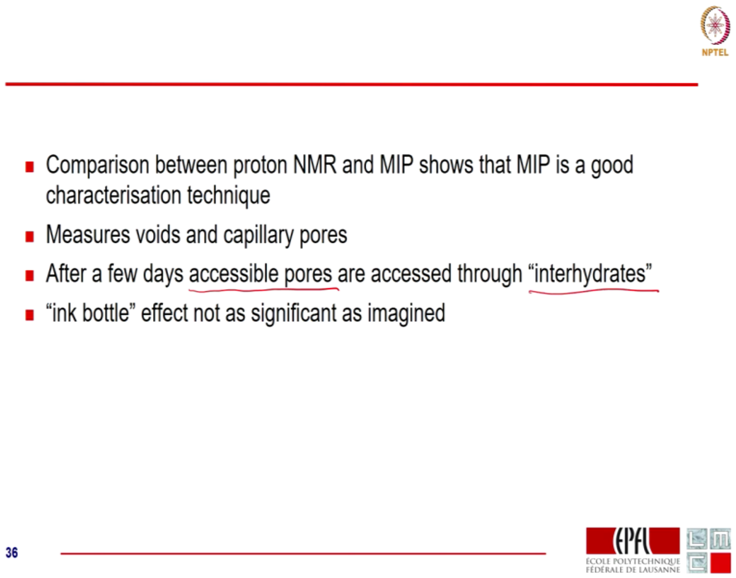

- Comparison between proton NMR and MIP shows that MIP is a good characterisation technique
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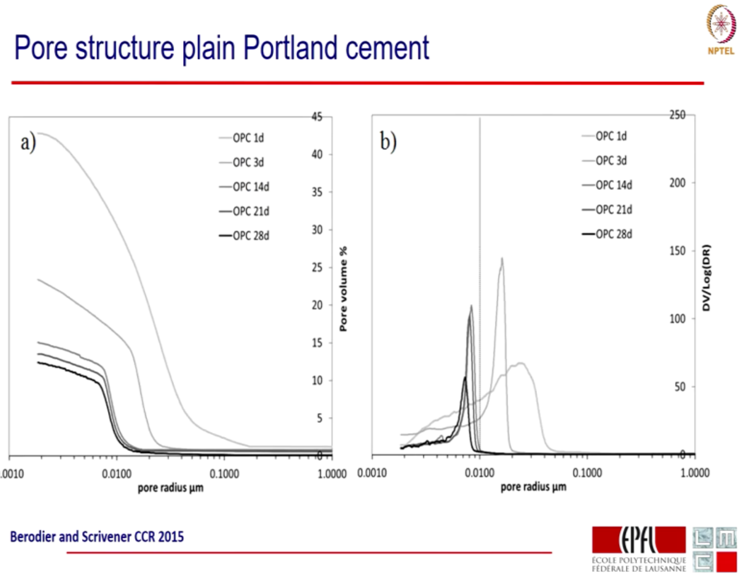

Pore structure plain Portland cement

Berodier and Scrivener CCR 2015

So this is what we see in Portland cement paste. We see that this pore entry after few days is not going down anymore. We can see the same thing with fly ash and with the slag.

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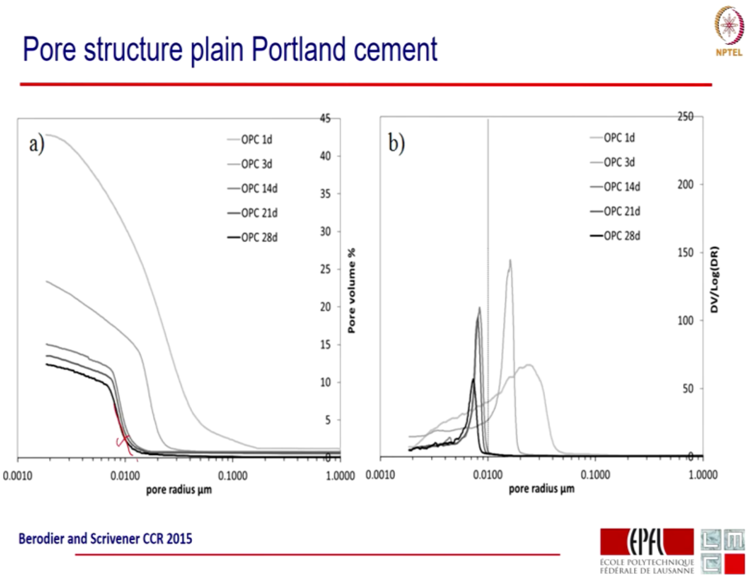

Pore structure plain Portland cement

Berodier and Scrivener CCR 2015

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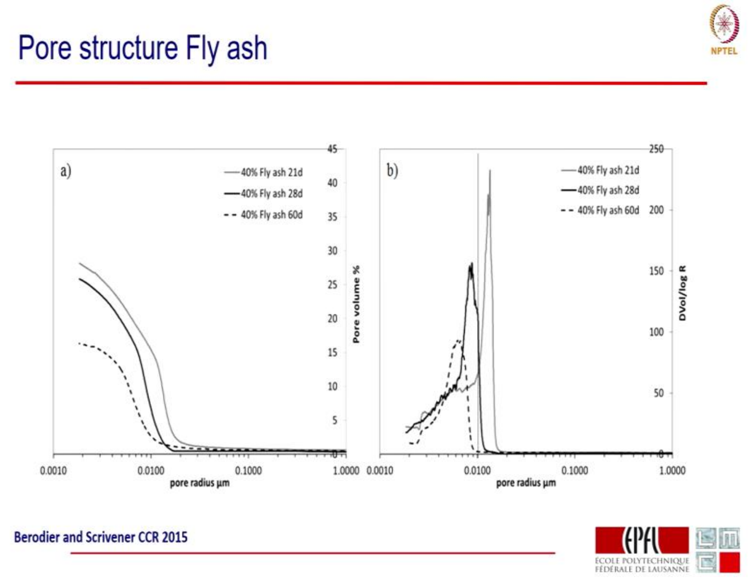

Pore structure Fly ash

Berodier and Scrivener CCR 2015

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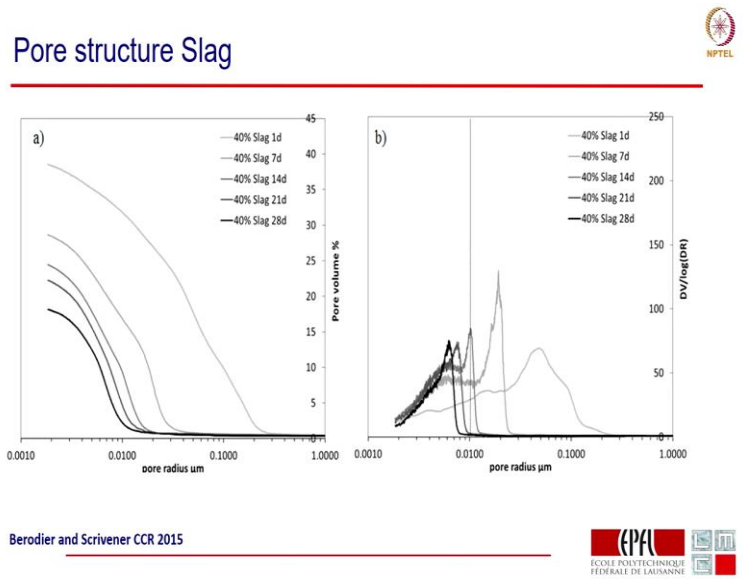

Pore structure Slag

Berodier and Scrivener CCR 2015

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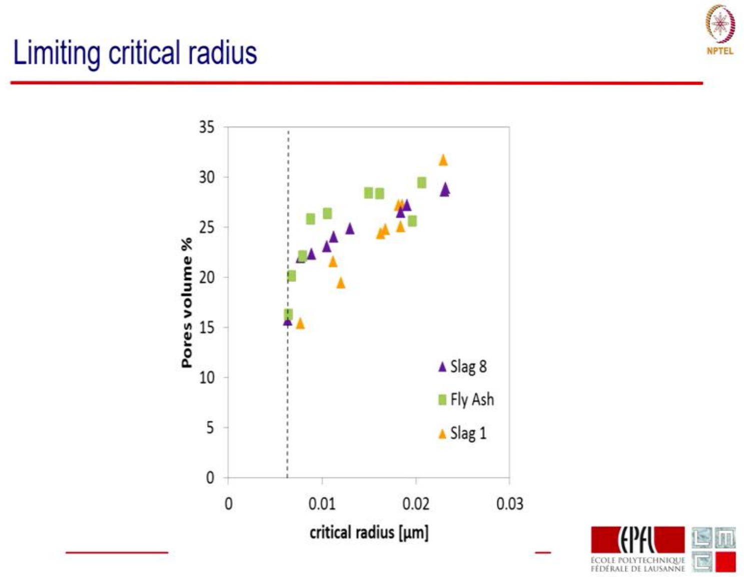

Limiting critical radius

When we put all these together, we see that over time all of these materials can eventually come down to this limiting critical radius which is in the range of about 8 nanometers or so. So this is the radius. Before when we were talking of the N M R we were talking about slit. so the size of the pores we measure by M I P is about somewhat bigger than by N M R, by twice as big and so we still have some effect in drying but in terms of the total porosity we think it is Ok.

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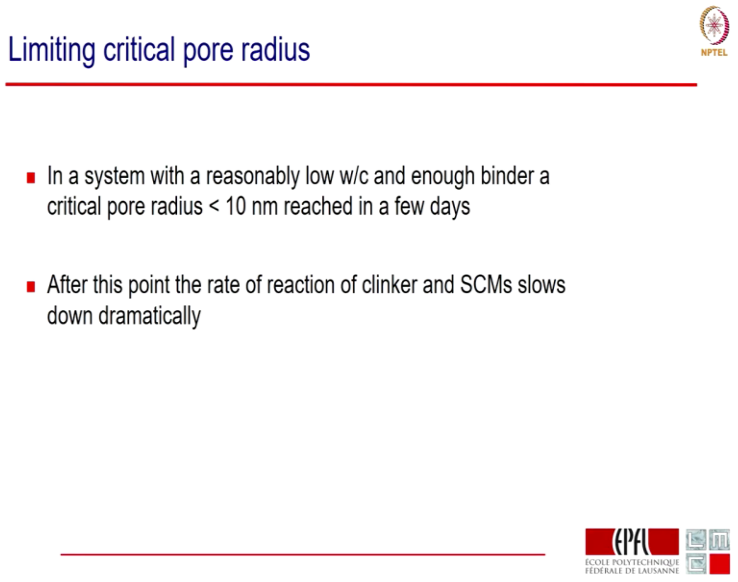

Limiting critical pore radius

- In a system with a reasonably low w/c and enough binder a critical pore radius < 10 nm reached in a few days
- After this point the rate of reaction of clinker and SCMs slows down dramatically

And what is interesting about this limiting critical pore radius is that, after this point the rate of reaction of the clinker and S E M phases really slows down dramatically. So this is a point which really has a big impact on the kinetics of hydration. We think the reason for this is that, if you think in terms of classical crystal growth, when the crystal wants to grow into this pore, the curvature has to increase. If the curvature increases then the supersaturation has to increase. Therefore, once the pores get down to a certain pore size the saturation of the pore solution is not high enough to allow any further growth.

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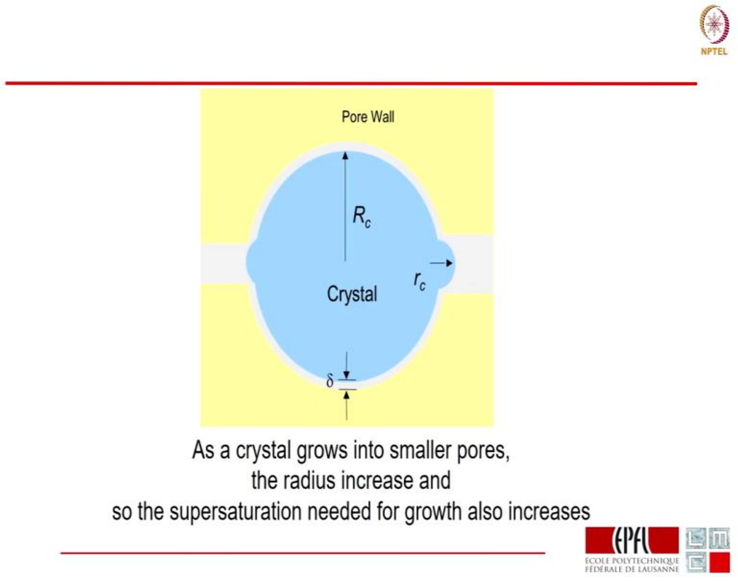

As a crystal grows into smaller pores,
the radius increase and
so the supersaturation needed for growth also increases

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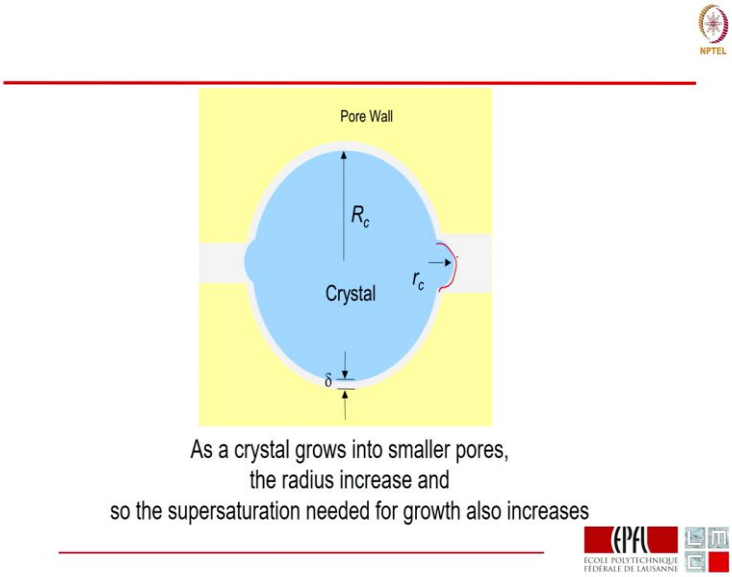

As a crystal grows into smaller pores,
the radius increase and
so the supersaturation needed for growth also increases

And this is why we think we are getting very slow reaction rates. We will come back to this in the next lecture.

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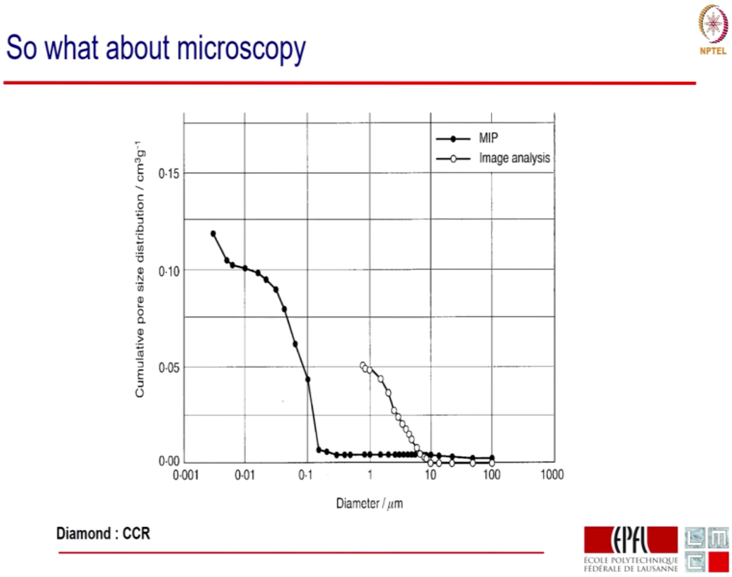

So what about microscopy

Diamond : CCR

So just to finish, let us look at what we get from microscopy and this is the classical paper which was published by Diamond some years ago when he said M I P is rubbish because it does not measure what is the same thing you measure by S E M. Well, what I would tell you is I think S E M is rubbish because it does not measure the same thing which you measure by

M I P. It is not really telling anything about the pores that are important in terms of properties determined, particularly in terms of durability.

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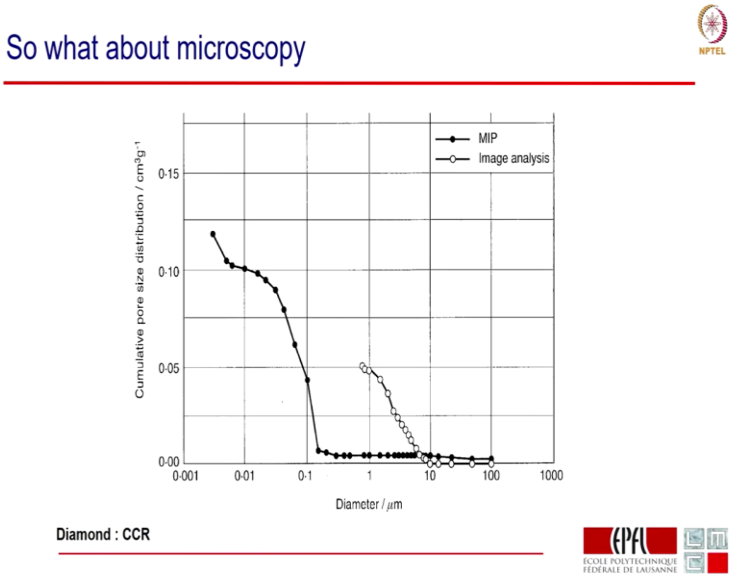

So what about microscopy

Diamond : CCR

So in this image analysis technique, he supposed we had all these pores coming in the range 1 to 10 microns. Well if you look at the well-cured paste, here is a well-cured paste and this is 30 microns.

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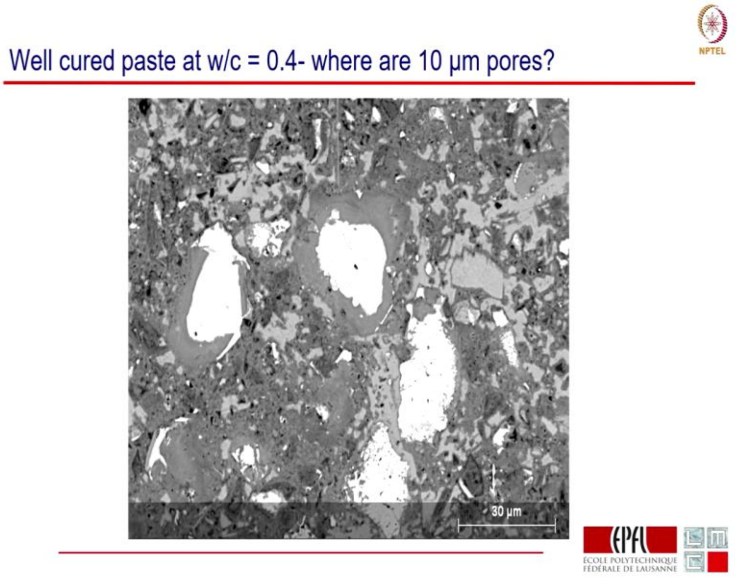

Well cured paste at w/c = 0.4- where are 10 μm pores?

There are not any 10 micron pores in that. I cannot see one single 10 micron pore in that. So I do not know why he had a paste with such high 10 micron pores.

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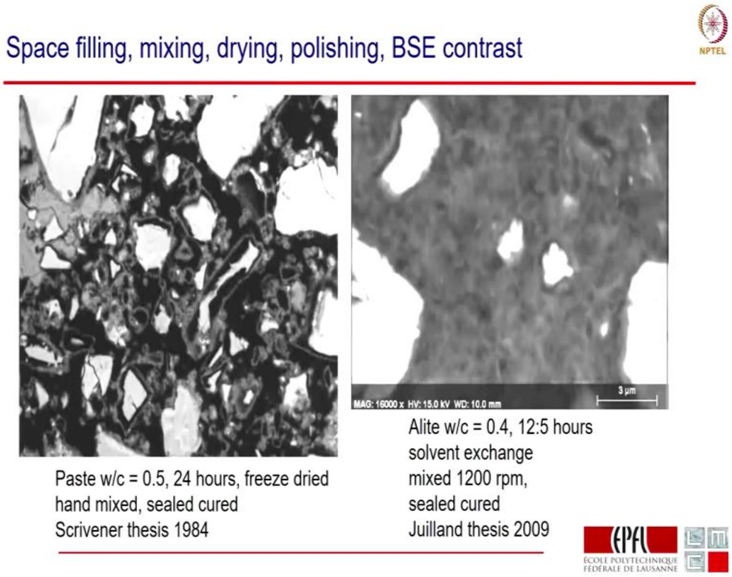

Space filling, mixing, drying, polishing, BSE contrast

Paste w/c = 0.5, 24 hours, freeze dried
hand mixed, sealed cured
Scrivener thesis 1984

Alite w/c = 0.4, 12:5 hours
solvent exchange
mixed 1200 rpm,
sealed cured
Juilland thesis 2009

I might speculate, because it depends a lot on how you look at your samples. And to illustrate that here is an image of a one day old paste I took in 1984 and we did not really know what we were doing. So this was a hand mixed example and it was very high contrast in S E M. so it was not properly mixed with very high contrast. And then over here we see one of this done at about younger time but it is done with proper mixing. By proper mixing we distribute well the hydrates and you can see the huge difference that you produce by proper mixing.

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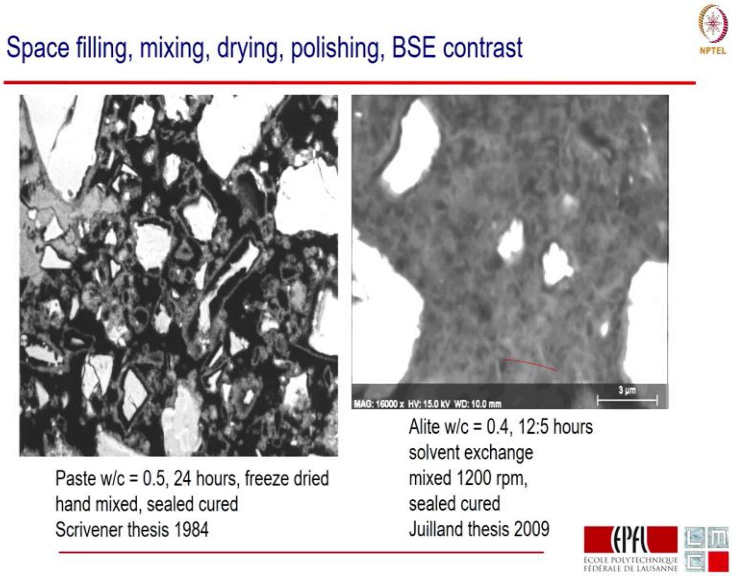

Space filling, mixing, drying, polishing, BSE contrast

Paste w/c = 0.5, 24 hours, freeze dried
hand mixed, sealed cured
Scrivener thesis 1984

Alite w/c = 0.4, 12:5 hours
solvent exchange
mixed 1200 rpm,
sealed cured
Juilland thesis 2009

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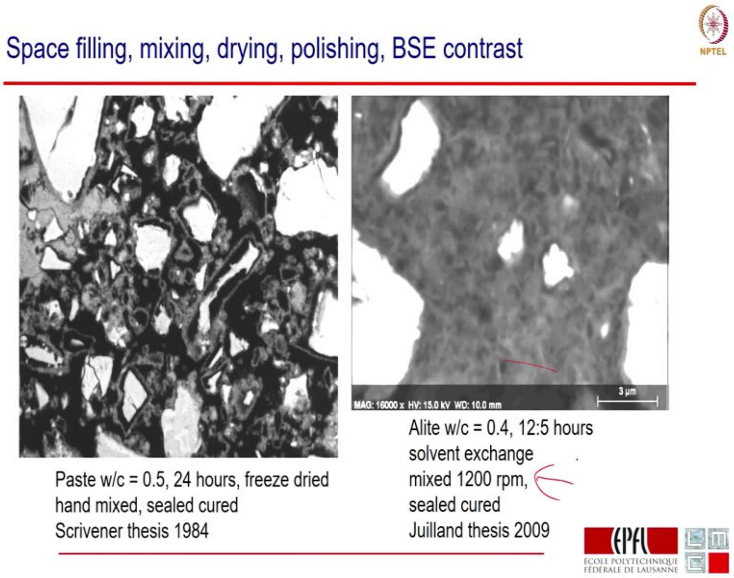

Space filling, mixing, drying, polishing, BSE contrast

Paste w/c = 0.5, 24 hours, freeze dried
hand mixed, sealed cured
Scrivener thesis 1984

Alite w/c = 0.4, 12:5 hours
solvent exchange
mixed 1200 rpm,
sealed cured
Juilland thesis 2009

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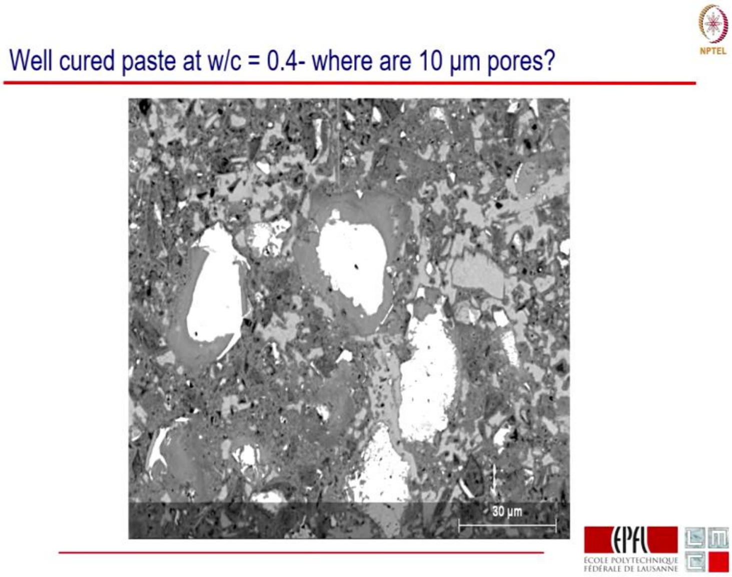

Well cured paste at w/c = 0.4- where are 10 μm pores?

So large pores space are really a problem of the fact that you have not mixed your sample like it would be mixed in a mortar. If you do that, then you do not get these very large pores. And to 0:29:12.0 (()) then you really have to go to M I P.

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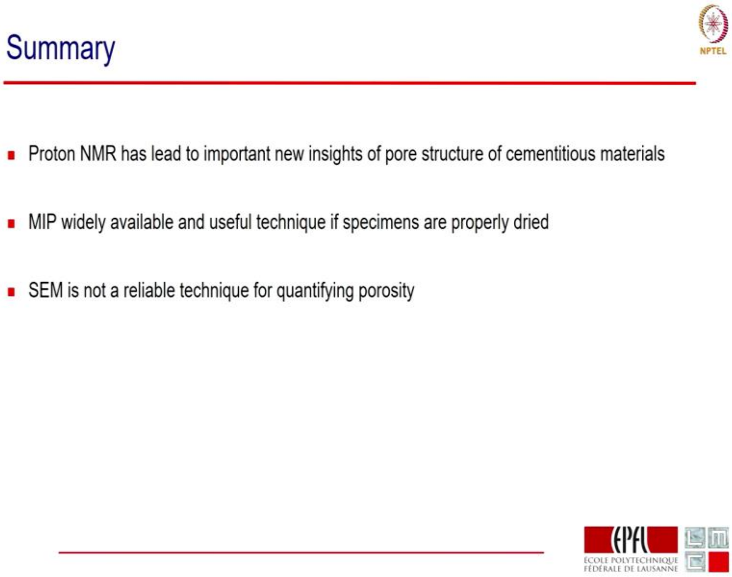

Summary

- Proton NMR has lead to important new insights of pore structure of cementitious materials
- MIP widely available and useful technique if specimens are properly dried
- SEM is not a reliable technique for quantifying porosity

So, just to summarize that last part, this is probably a different vision of porosity that you may have from standard text, because I think this new technique of proton N M R has really led us to very important new insights from the pore structure cementitious materials.

And very usefully what is shown is that, MIP which is a widely available technique is really very useful if you properly dry your samples by solvent exchange. And finally S E M is not really reliable for porosity.

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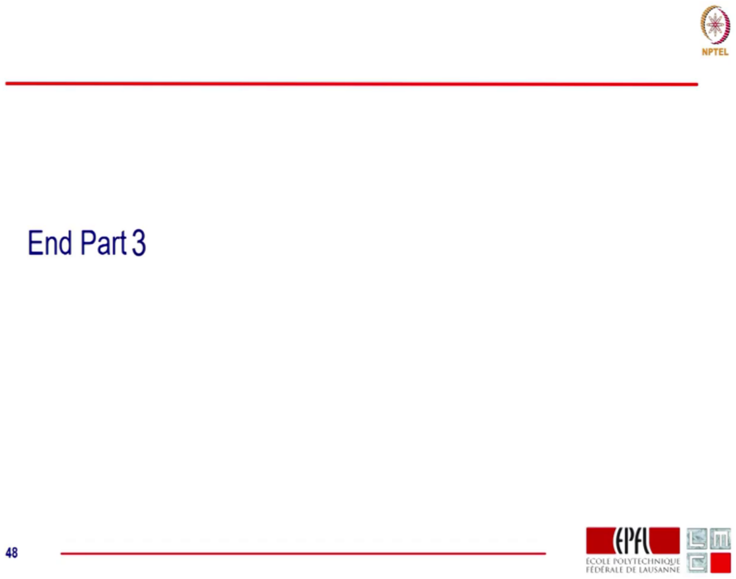

End Part 3