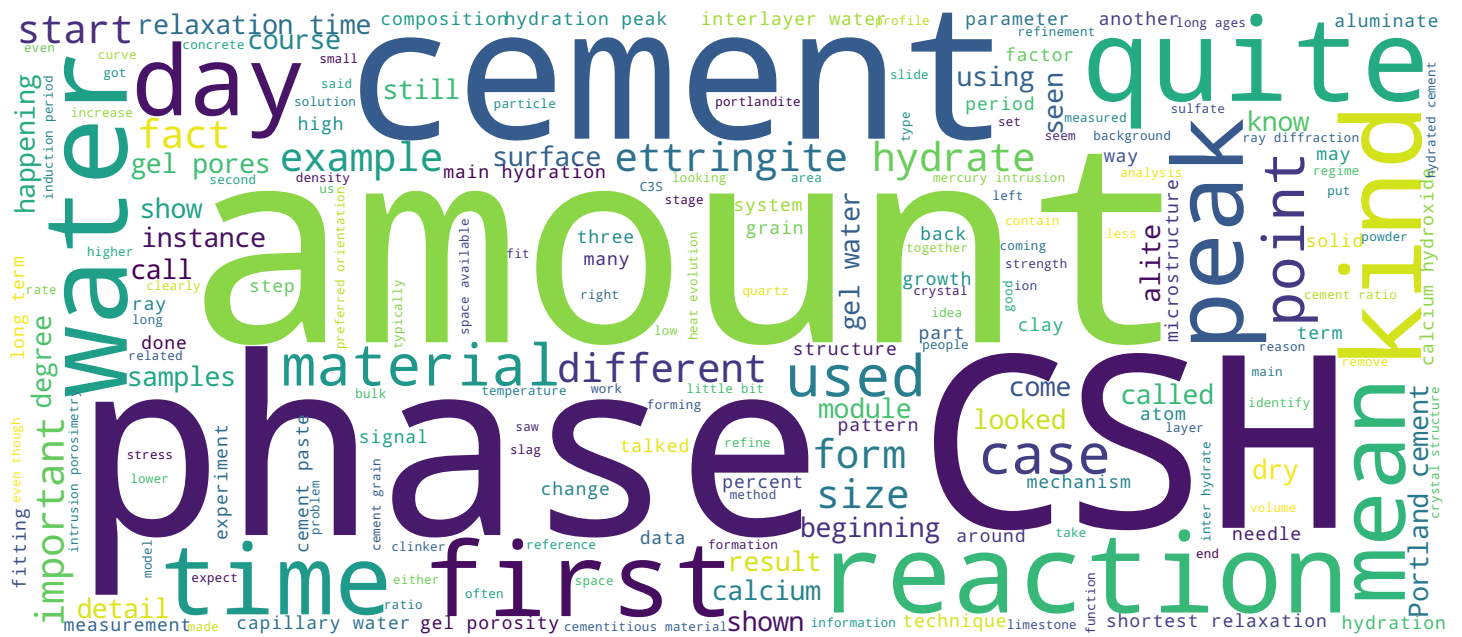


## Kinetics: after the main peak

### Cement Chemistry and Sustainable Cementitious Materials

Professor Karen Scrivener, FREng



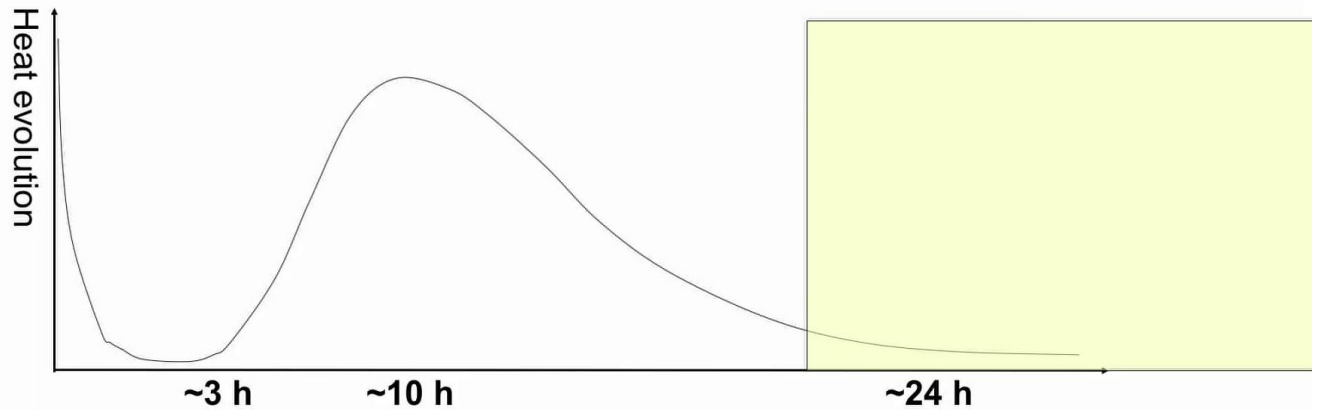
Search MOOC



Video



# Period III, slow ongoing hydration



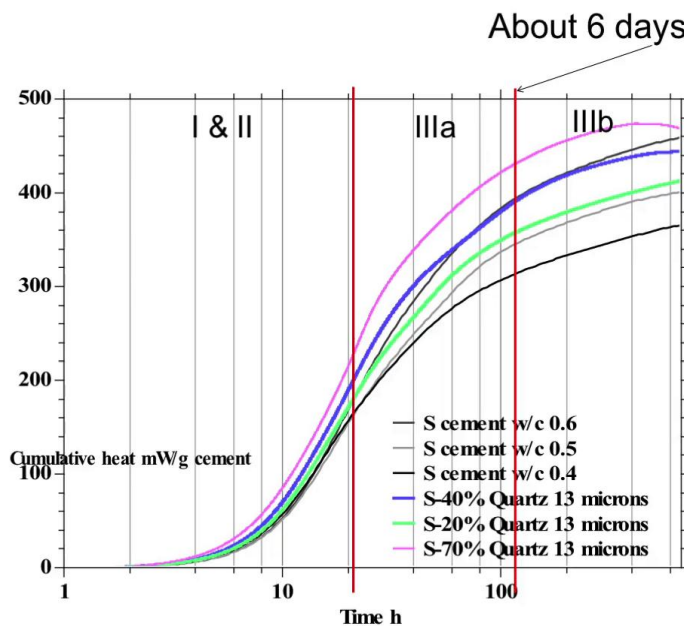
Hello and welcome back. In this module, we are going to look at the longer term hydration. Previously we have looked at the induction period, up to about three hours, then we have looked at the main hydration peak and we have seen that this is controlled by nucleation and growth of CSH. Now we are going to look in the longer term. And this period is really not been studied as anywhere near in as much detail as has this induction period and the main hydration peak. Perhaps because it is rather difficult to study because in terms of what you can measure, for example the heat evolution is shown here, there is not much going on. Or at least it seems so but that is very deceptive, because at this point here of about one day the degree of hydration would typically be about fifty percent and the amount of strength would be maybe 20-25% of the final strength. So there is an awful lot going on in this later period here beyond the first day. And in this module we are going to try and look at what some of these things might be. Although, I have to tell you now that we still don't really know that much.

Notes

Summary



# Cumulative heat curves: 2 regimes after main peak



Hydration of systems with different  $w/c$  or amounts of filler

IIIa. Space controlled

IIIb. "densification" similar for all systems

Thesis E.Berodier, EPFL 2014

If instead of looking at curves in the differential form, as we saw previously, if now we look at the integral curve, the cumulative heat curve, we can plot for example the variation of the water cement ratio and we can plot different mixtures with different substitutes of quartz. And we can kind of identify three different regimes. We can identify this regime here which we have already looked at. We have called this previous "periods one and two" and we can see that even though the details of this main hydration peak might vary a lot as we saw in the previous two modules, it is fairly similar. And then over here in the long term, we also see a very similar behaviour for all the systems. And we will come to that at the end of this module but at the minute we are calling this period "the densification period" for reasons I will explain. And then in the middle here, we see that this is where we get the biggest variation for all these different systems and what we have really done in these different systems is vary the amount of space available for the hydrates to deposit in. And this is why we call this "middle regime", which I have called 3A here, we call this a space controlled regime.

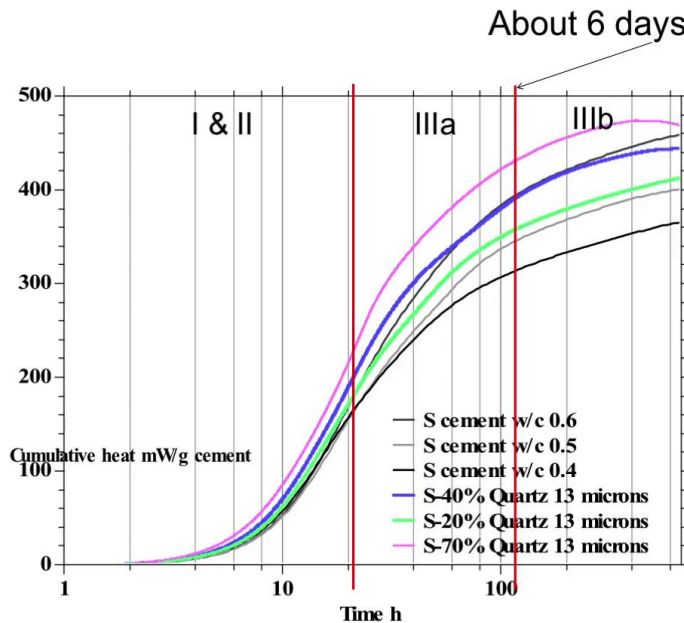
Notes

Summary



1m 20s

# Cumulative heat curves: 2 regimes after main peak



Hydration of systems  
with different  $w/c$  or  
amounts of filler

IIIa. Space controlled

IIIb. “densification”  
similar for all  
systems

Thesis E.Berodier, EPFL 2014

So basically what this means is that hydrates are continuing to form until they have used up all the easily available space. And this occurs around about six days for a water cement ratio of 0.4.

Notes

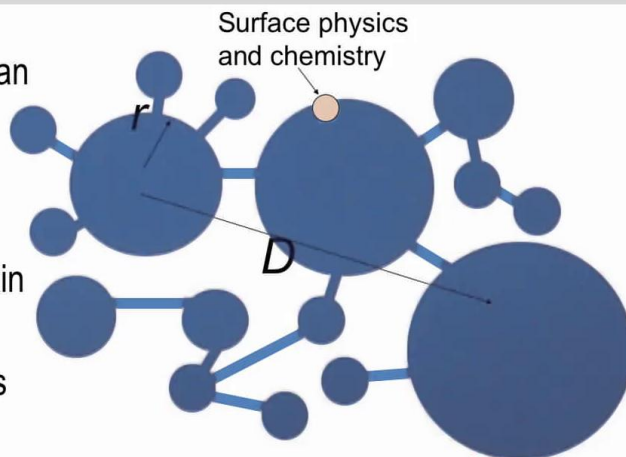
Summary



2m 53s

# Proton, $^1\text{H}$ 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



Now we can get other very interesting insights on this regime if we use this technique called “proton nuclear magnetic resonance”. So what we do with proton nuclear magnetic resonance is we depend on the behaviour of protons which are basically hydrogen atoms and by applying a magnetic field, we can align the little spins of these nuclei and then we can remove the magnetic field, the spins relax, they go back to the kind of random orientation they were in the first place and by looking at the timing of this relaxation, we can make various deductions about the pore sizes. And the real strength of this technique is that we don't have to dry the sample. So most techniques that been used classically to look at microstructure, you have to dry the sample before you look at it. In this case, it is exactly the opposite. In fact the pores need to have water in them to get the signal. And what we can do, we can do many different measurements in situ from the same sample. And here we see a sort of little schematic of a pore structure and you see these big pores and smaller pores and the essential aspect is that we have water molecules in these pores moving around and if they hit the surface then they relax very, very quickly.

Notes

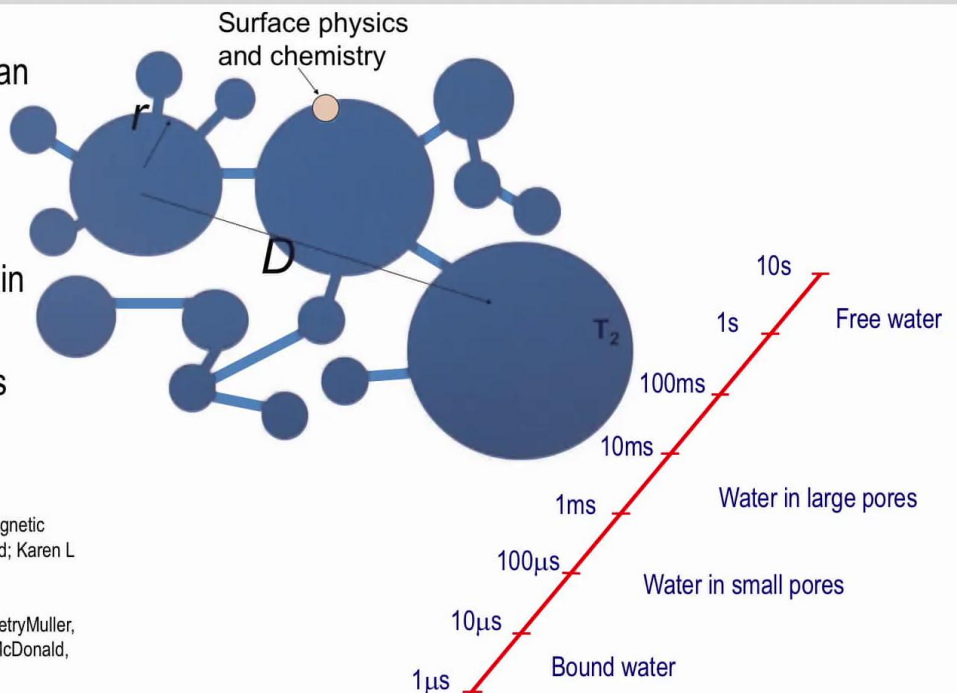
Summary



3m 08s

# Proton, $^1\text{H}$ 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  $^1\text{H}$  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  $^1\text{H}$ -NMR Relaxometry" Muller, Arnaud C. A.; Scrivener, Karen L.; Gajewicz, Agata M.; McDonald, P.M" J Phys. Chem. C 117 (1) 403-412 2013

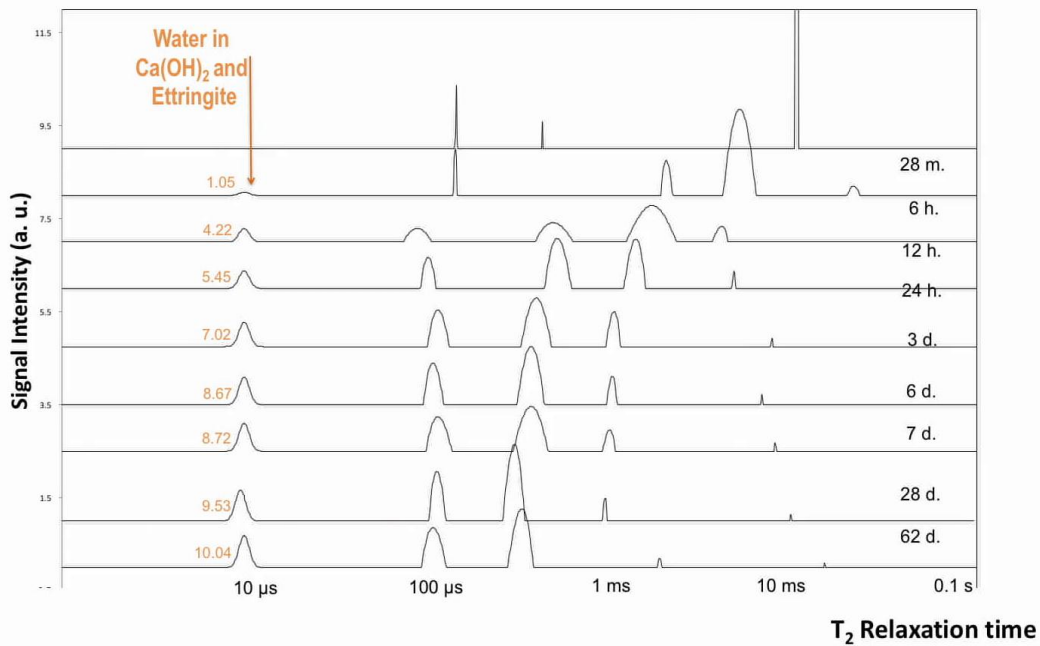
So this means if we have water like you may have in a bottle of water, this will have a relaxation time of about four seconds. And as we move to smaller pores, then because the water will have a very high probability of hitting the surface before too long, we will go to shorter relaxation times, small pores to shorter relaxation time still and the shortest relaxation times are for bound water which is found in the crystalline hydrates. And this is explained in a lot more detail in these references that are given here.

Notes

Summary



# Evolution of water populations over time



[Muller et al. 2013]

These are results from the work of Arnaud Müller. And we can see how these spectra evolve over time. And what we can identify in these spectra is different populations. So we start with the shortest one with the shortest relaxation time.

Notes

Summary

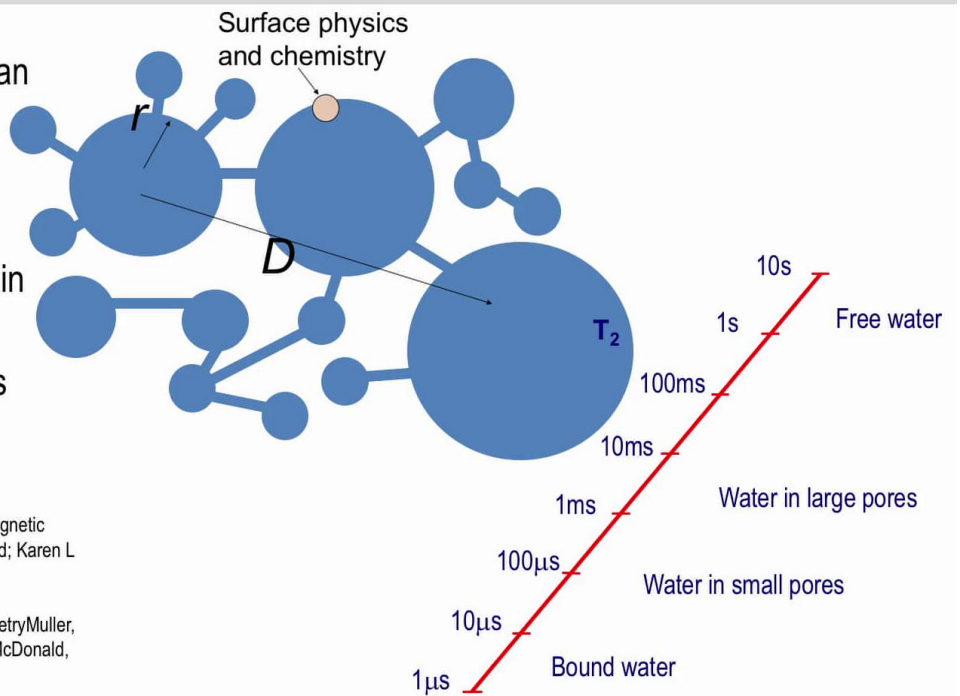


5m 13s



# Proton, $^1\text{H}$ 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  $^1\text{H}$  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  $^1\text{H}$ -1 NMR Relaxometry" Muller, Arnaud C. A.; Scrivener, Karen L.; Gajewicz, Agata M.; McDonald,

[Muller et al. 2013] 117 (1) 403-412 2013

And by analogy with this diagram here, the shortest relaxation time is expected to come with water that is firmly bound in crystals.

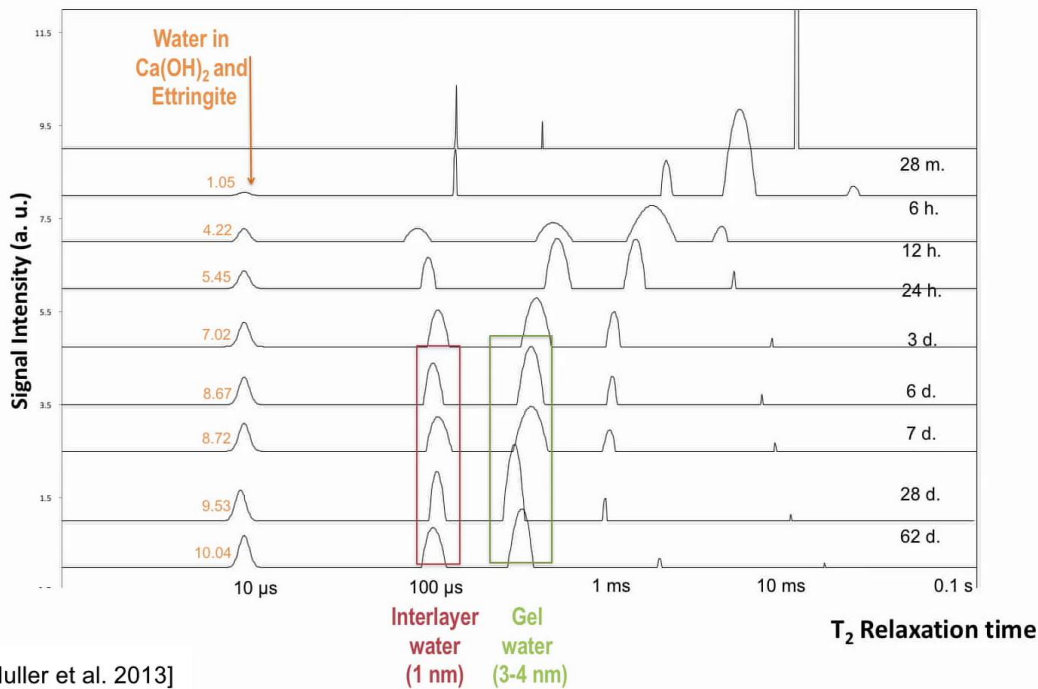
Notes

Summary





# Evolution of water populations over time



And this we can show to be the case by quantifying the signal here, we can see that it corresponds to the water which is in portlandite and in ettringite. And I should perhaps have said at the beginning here, that what is important in this series of experiments in these spectra is in fact we can quantitatively measure all the water in the cement paste. So this is the bound water. This has the shortest relaxation time and as you see here it matches really very, very well with water in the calcium hydroxide and the ettringite. So logically the next shortest relaxation time has to be coming from the interlayer water in the CSH. So this is the interlayer water in the CSH and from analyzing the signal, we can see that this is coming from dimensions of around one nanometer, which is roughly what we would expect to be the area for water in the interlayer the CSH. So this next clear population we can see here which starts a little bit bigger and then comes down to this defined size, is in fact what we call the gel water. So, when we looked at CSH we talked about the gel porosity and in those gel pores is the gel water, and we see this has a quite well defined characteristic size of about three to four nanometers.

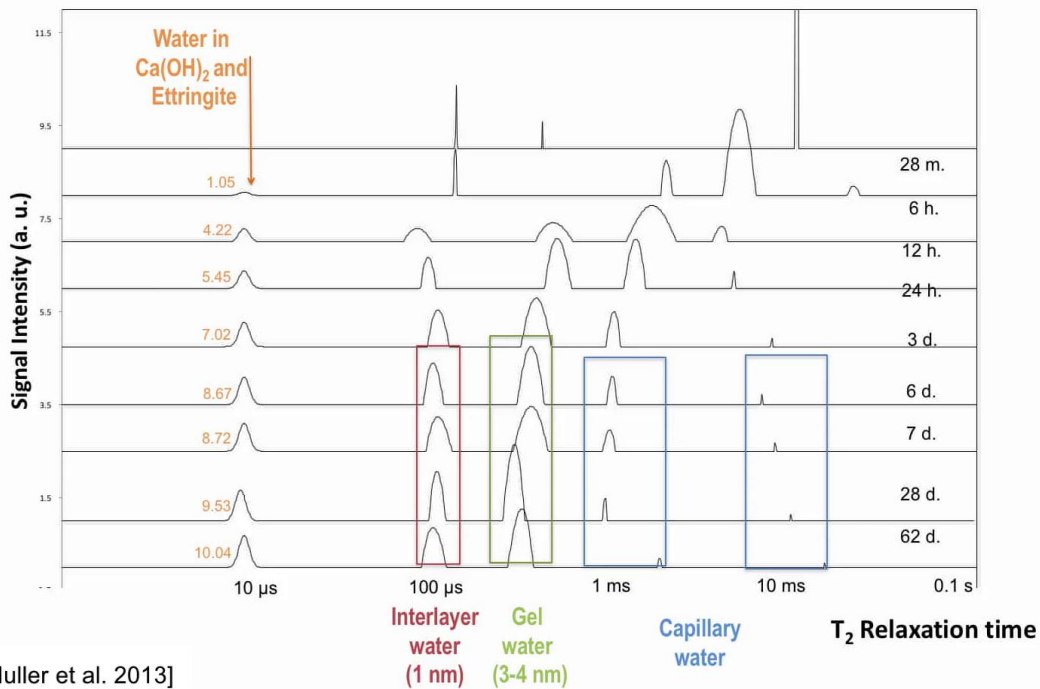
Notes

Summary



5m 46s

# Evolution of water populations over time



And finally, the rest of the water over here is now capillary waters. So going back to the beginning, we can see in the beginning we start with just capillary water, then we start to form CSH and then finally the gel pores. And at the end in these experiments which are done with sealed paste, we have very little capillary water.

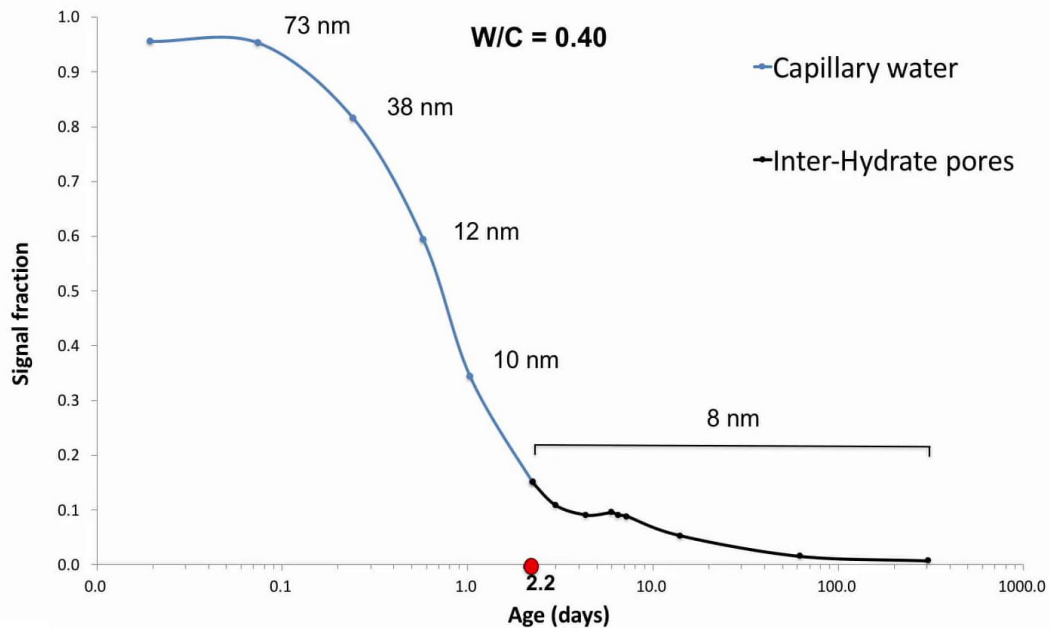
Notes

Summary



7m 24s

# Amount and size of capillary pores



[Muller et al. 2013]

So we can look in more detail at how those populations evolve over time in terms of their amount and also in terms of their size. So if we look at the capillary water, what we see is over the first day of course it is corresponding to this main heat evolution peak we have been talking about, the amount of capillary water decreases very sharply and also its size decreases. So it starts off with the characteristic size of around 73 nanometers and here already after one day, it is gone down to about ten nanometers. And then after this point here at about two days, we see that the amount decreases but the size no longer decreases. The size really stays constant as a size of about eight nanometers. And because of this consistency of size, we then decided to give a new name to this area, we call this “inter-hydrate pores”.

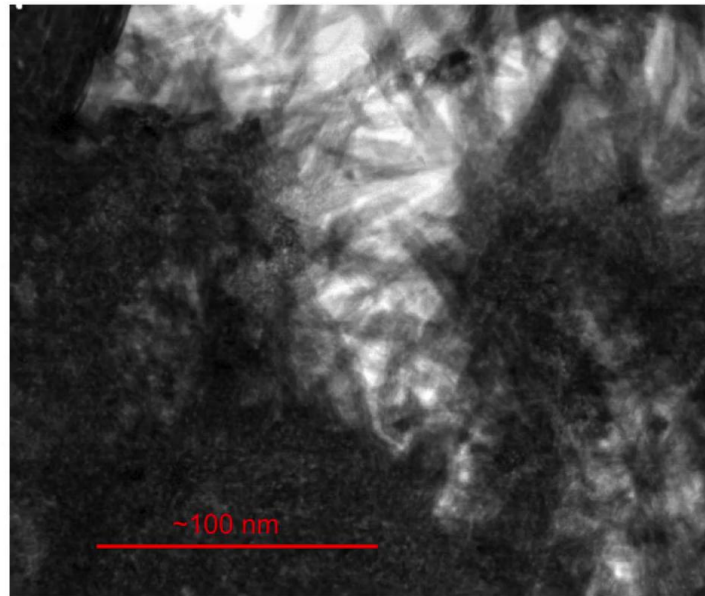
Notes

Summary



7m 50s

# Interhydrate pores



Thesis A.Bazzoni EPFL ,2014

Now why do we call it inter-hydrate pores, because if you look in the TEM and you see these needles of CSH like we talked about in the previous modules, you can see between these needles, we have spaces of about eight nanometers. And we really feel now that this is making up most of the capillary pore space of a well cured mature cement paste. It is this very complex spaces between these CSH needles.

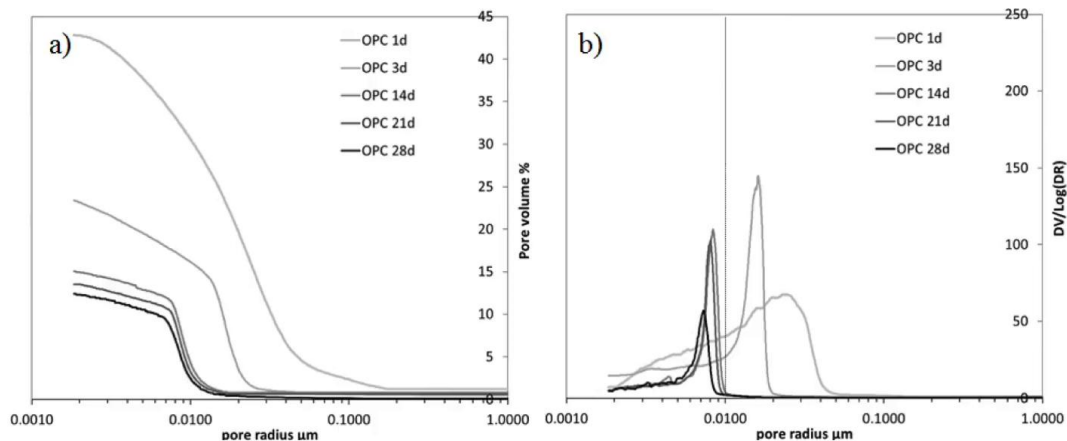
Notes

Summary



8m 55s

# MIP: Pore structure plain Portland cement



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

[Berodier and  
Scrivener 2015]

We can see a similar picture by using a very different technique which is mercury intrusion porosimetry. And many of you have probably heard a lot of negative things about mercury intrusion porosimetry but when we have compared mercury intrusion porosimetry to proton NMR, we actually have now a lot of evidence that mercury intrusion porosimetry is giving us a very good picture of what is happening in the pore space as long as you dry your samples correctly. And I really need to stress this point, because if you dry your samples by putting them in the oven, you form a lot of cracks, you get any kind of thing by MIP. If you do it by this technique we use which is called solvent exchange, where you dry your samples in isopropanol, then you can get really nice reproducible results. And what you see is that this breakthrough diameter here, when the mercury really starts to penetrate into the sample, this is going down quite rapidly during the first few days but by the time we are at about three days or fourteen days then after that point it doesn't go down anymore. So it goes down to a certain critical pore entry size and then it doesn't go down more even though the overall amount of the capillary porosity is continuing to decrease. So we think this fixed critical pore entry size here, is the same as the inter-hydrate space we saw here.

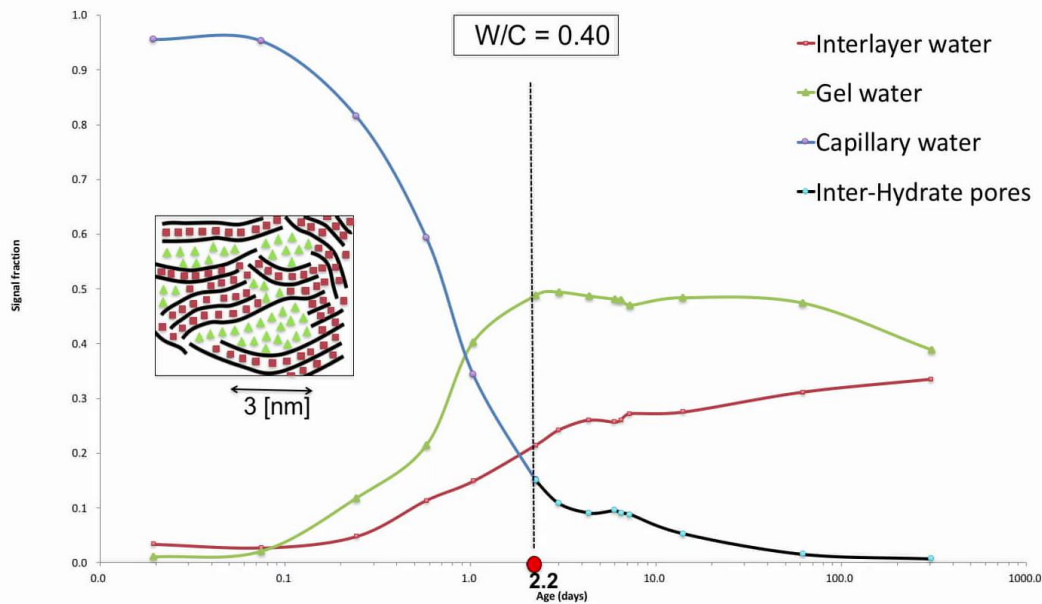
Notes

Summary



9m 31s

# Gel water



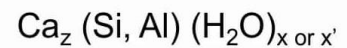
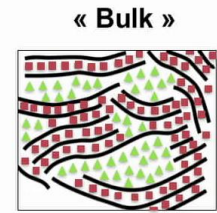
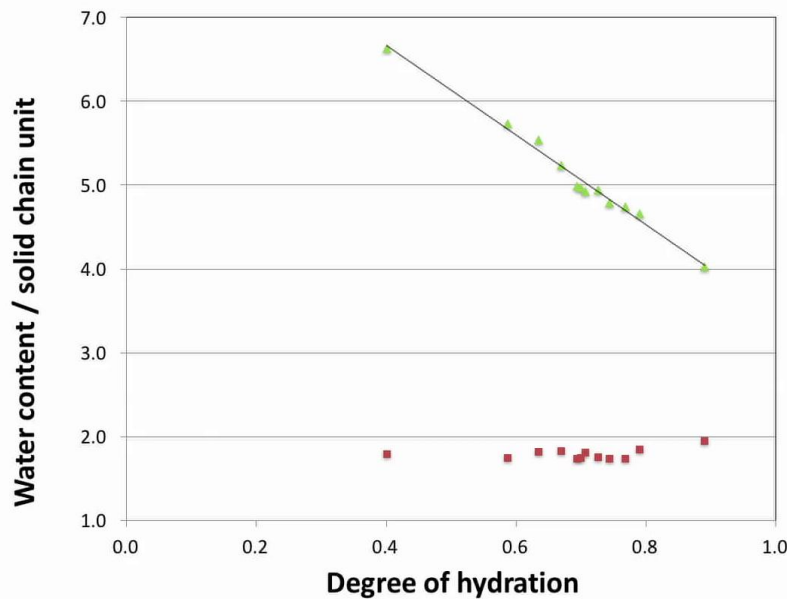
Now if we look at what is happening in the hydrates, we can now look at the interlayer water. So the interlayer water is between these sheets of CSH as shown in red here. And unsurprisingly during the main hydration peak this is going up quite fast and then subsequently, it is going up but more slowly. We add the gel water as we see here and at the beginning in the main hydration peak the gel water is going up in parallel in the same ratio as the amount of interlayer water but from this point at 2.2 days in this case of this white cement, we see that the gel water is really plateauing. And at very long ages it maybe even goes down a little bit. So the amount of gel pores is not a constant amount in all the CSH. The amount of gel porosity varies, we form a lot at the beginning and then really no more after a certain time. Very probably, this is related to formation of outer CSH, those needles we have been talking about quite a lot and then afterwards when we get the inner CSH, we really see that this doesn't contain any gel porosity.

Notes

Summary



# C-S-H water content



« Solid »

And from all these measurements, we can get now quite a lot of detail about what is happening in our CSH. We can look for example at the density and we can look either at the density of this kind of solid part, these are these nano crystalline regions we talked about quite a few lectures ago, and we can look at the amount that is forming in the bulk as we see with the gel porosity here. And the solid has quite a constant density over time of about just below 2.7, 2.8, whereas the bulk, the average density, is increasing because the proportion of gel pores is decreasing. So at the beginning we have quite a low density below 1.8. And by the time we are getting to a high degree of hydration, we are seeing that this is going to a density of about 2 to 2.1. which is very much in line with the kind of densities that have been estimated from other techniques. We can look also at the amount of water contained in the CSH. So again for the solid nano crystalline regions, the amount of water content is around 2 for each solid chain unit, whereas for the bulk the amount of water on average is decreasing because we have less water proportionally in the gel pores.

Notes

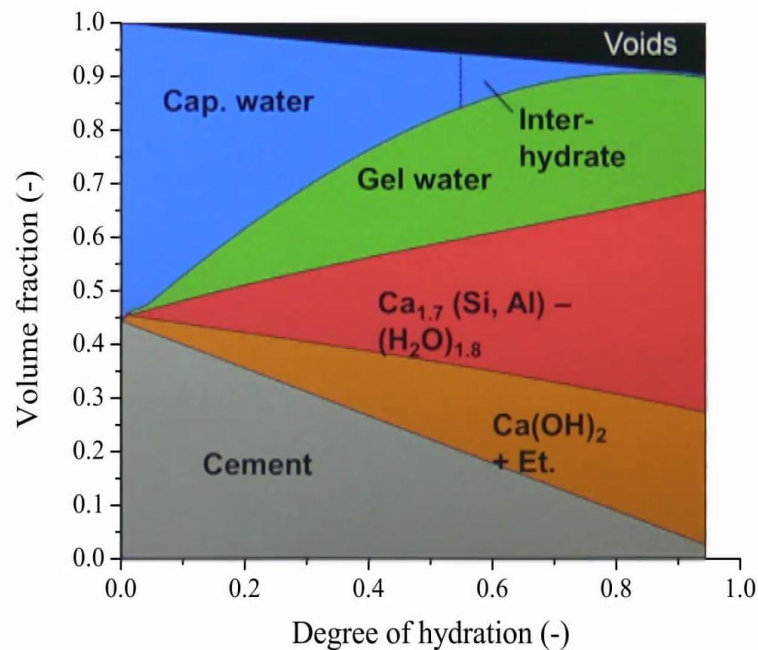
Summary



12m 45s



# Volume changes with hydration: update of Powers



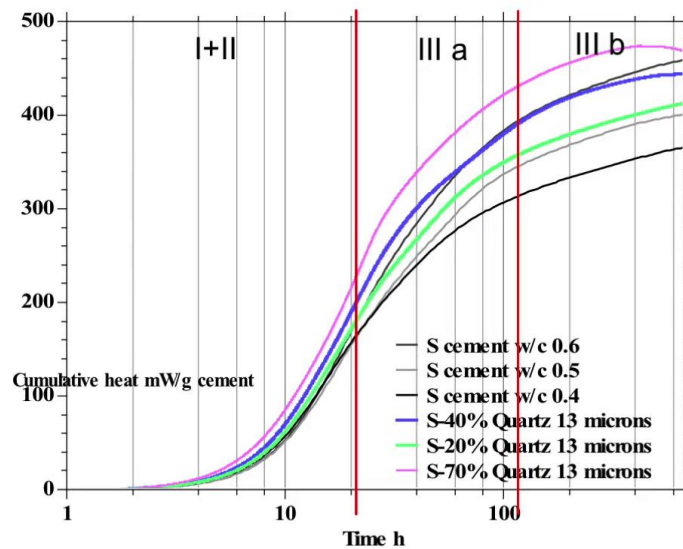
So from all this, we need to really make an update of the repetition of the solid volume over time, so this was done already about sixty years ago by Powers. And he measured the proportions at long times and then said "well OK I am just going to draw straight lines as a function of the degree of hydration". And we find a very good agreement between our repetition of the volumes at long ages here with what Powers found except that now we can differentiate the solid that he just measured as one single hydrate into CSH here and calcium hydroxide and ettringite here. The main difference we see is the amount of gel water is not a linear function of the degree of hydration. But it increases very rapidly at the beginning and then stays constant there after.

Notes

Summary



14m 17s



In stage III b  
Kinetics still do  
not fit with  
diffusion

E.Berodier

So let's go back to cumulative heat curves, to these different stages. We have looked in this middle zone, zone three A here, and we have seen that this is controlled by the amount of space available but what is happening in this very long term? Well again we can analyze the slope of these curves and we really don't see any indication that it fits with the kind of kinetics we would expect from diffusion.

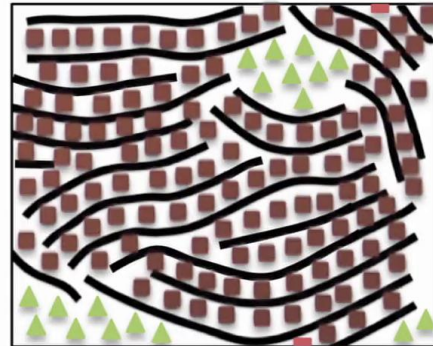
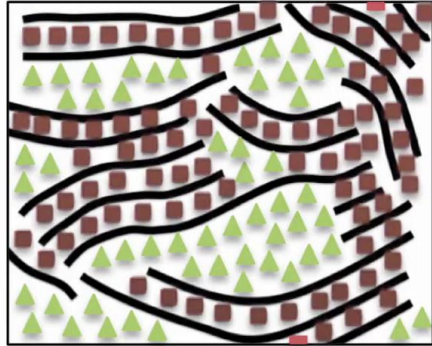
Notes

Summary



15m 16s

# Long term densification, possibility



What we could hypothesize at this stage, and I stress this is very, very tentative as an idea for a mechanism, is that what perhaps we have, we have initially CSH like this, where there are nanocrystalline regions in the gel pores and then at very long ages those gel pores are getting filled in by extra layers of CSH. So the amount of extra hydration between here and here is really very, very small but it is contributing to this densification and to some gain in mechanical properties. So I stress this is still quite a tentative idea here but it needs to be worked on more in the long term.

Notes

Summary



15m 45s

# Summary: long term



- In the longer term space filling almost certainly plays an important role up to a few days
- $^1\text{H}$  NMR confirms densification of C-S-H over time
  - need for refinement of Powers model: capillary and gel porosity are not linear functions of the degree of hydration.
- Very slow kinetics after few days, mechanism still unclear

So to summarize what we have seen in this lecture we have looked at some ideas of what is happening in the long term. And what really seems to be important, certainly in the first few days, is the amount of space available for the hydrate to form which are determining the rate of reaction. And after about a few days, say about six days, this is a typical water to cement ratio of 0.4, we only have pores below quite a small size which are left. And this small size does not allow the growth of hydrates in the classic way that we have talked about previously. And this kind of slowing down of the reaction then means we transit to a regime in which we have really more densification of the CSH. And that is really highlighted by the studies we have done on proton NMR, which also indicate that we need to refine the Powers model, because the development of the capillary and gel porosity are not linear functions of the degree of reaction. So after these few days we get this very slow reaction, which the mechanisms are still unclear and still a subject of ongoing work.

Notes

Summary



16m 29s

# Summary: long term



- In the longer term space filling almost certainly plays an important role up to a few days
- $^1\text{H}$  NMR confirms densification of C-S-H over time
  - need for refinement of Powers model: capillary and gel porosity are not linear functions of the degree of hydration.
- Very slow kinetics after few days, mechanism still unclear

So now we have really seen the mechanisms, we have been concentrating most of all on the silicate phases and what remains now is to look at the reactions of the aluminate phases, how this fit in, this will be in the next module, and then finally we will bring this all together to look at how the microstructure can be visualized in the scanning electron microscope for example. So thank you and see you next time.

Notes

Summary



17m 51s