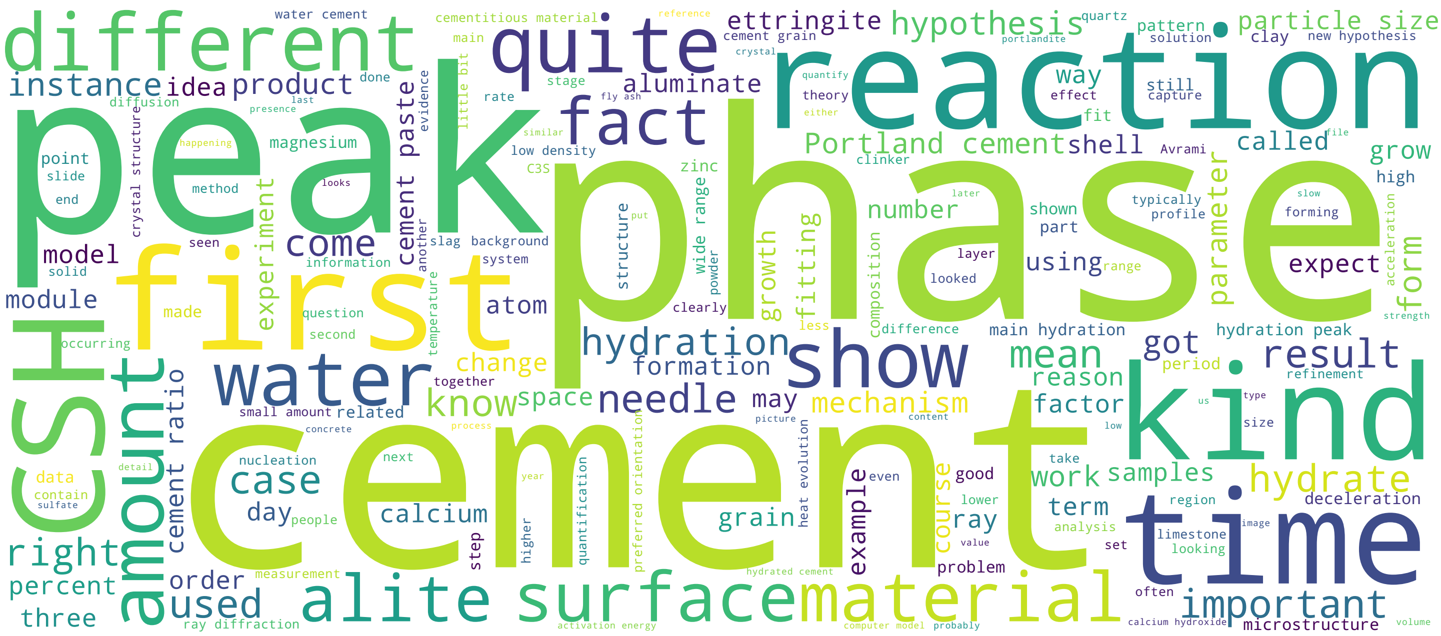
ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Kinetics: the Main Hydration Peak

Cement Chemistry and Sustainable Cementitious Materials

Professor Karen Scrivener, FREng

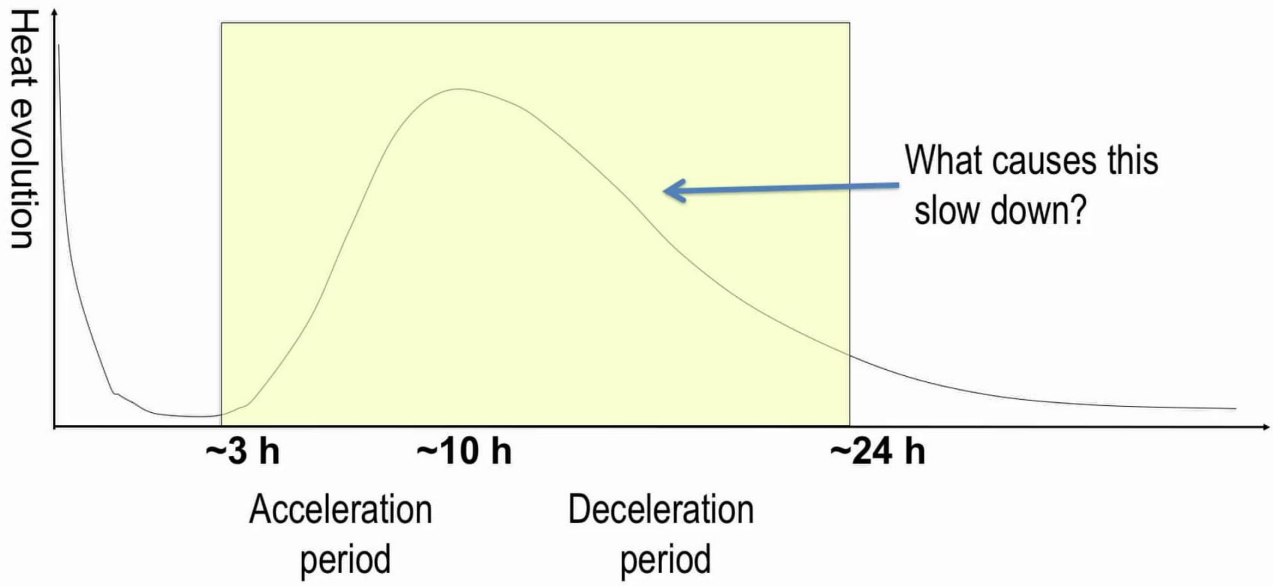


Search MOOC

Video

EPFL

Period II, main heat evolution peak



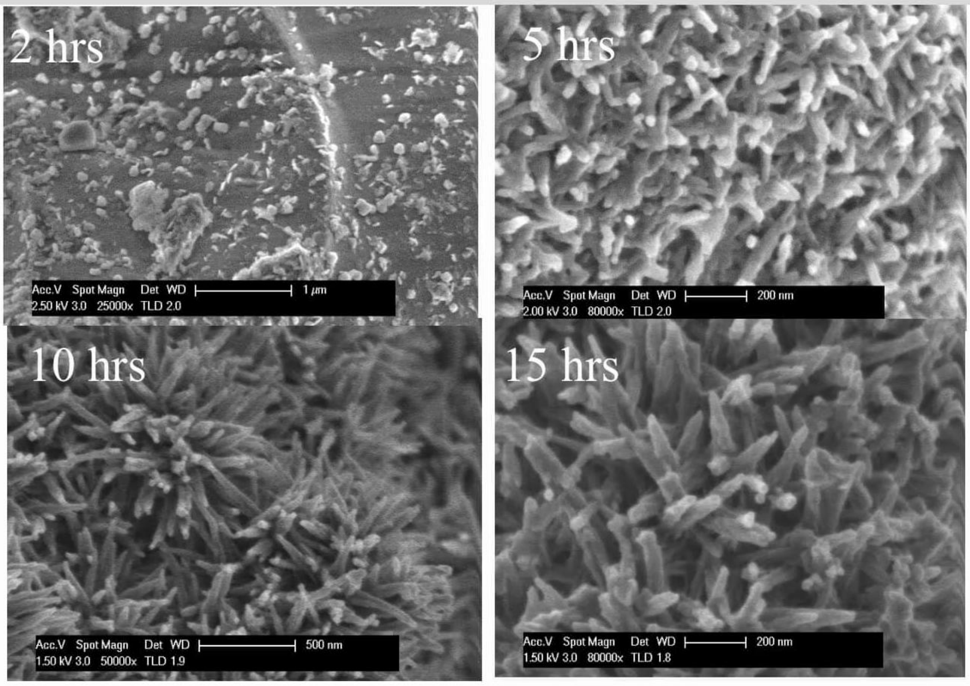
So OK, welcome back. Now we are going to look at the main hydration peak. So in the last module, we looked at the induction period, how that this is not related to protective membranes, it is just related to undersaturation and dissolution theory. And now in this module we are going to look at this main hydration peak, that is to say the period between about three hours and twenty four hours in which we have first this very strong acceleration in the rate of reaction and then this deceleration. And the main question that is really posed in this period is why do we go from this acceleration? Why doesn't it just continue accelerating to the deceleration because the amount of reaction at the peak here is still relatively modest.

Notes

Summary

0m 04s

End of induction period growth of C-S-H (& CH)



Berodier 2015

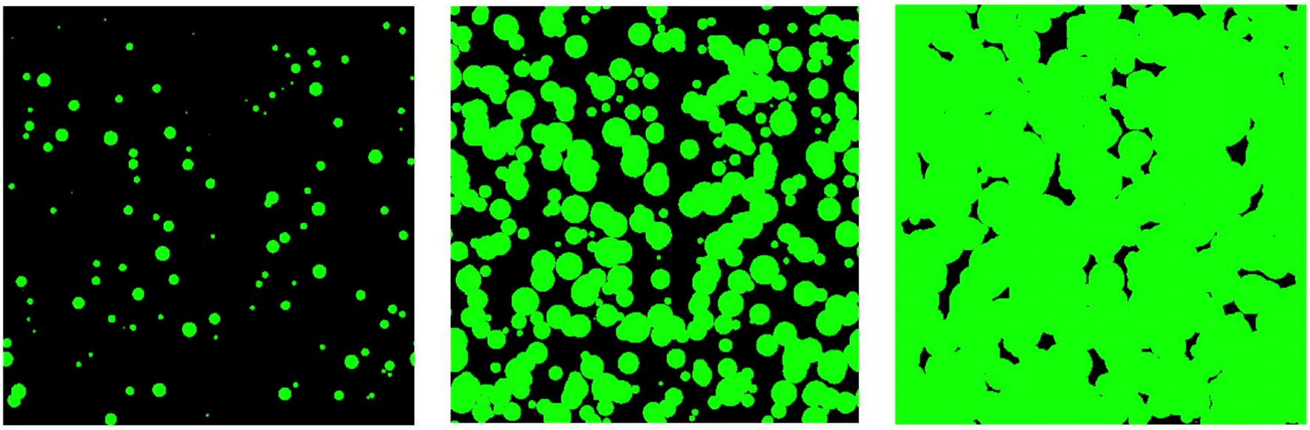
So in terms of what is happening in acceleration I think the situation is quite clear that here we are looking at the nucleation and then the growth of CSH. So on these slides, we can quite see at about two hours, we can see these little tiny nuclei, all the CSH which are forming and then those nuclei grow over time. And as they grow over time, they grow in this what we often call a kind of needle morphology, where this looks a little bit like a sea urchin. Now I am going to use the term needles but depending on the different conditions, sometimes they can look more like foils, even here we can imagine those needles are actually tapered foil, so you know don't worry too much about those those differences, we can find quite a lot of variation but it is all this kind of outward growth.

Notes

Summary

0m 57s

Avrami: Nucleation and growth



Developed for solidifying metals
Simple 3D nucleation and growth:
growth $\propto$ surface available

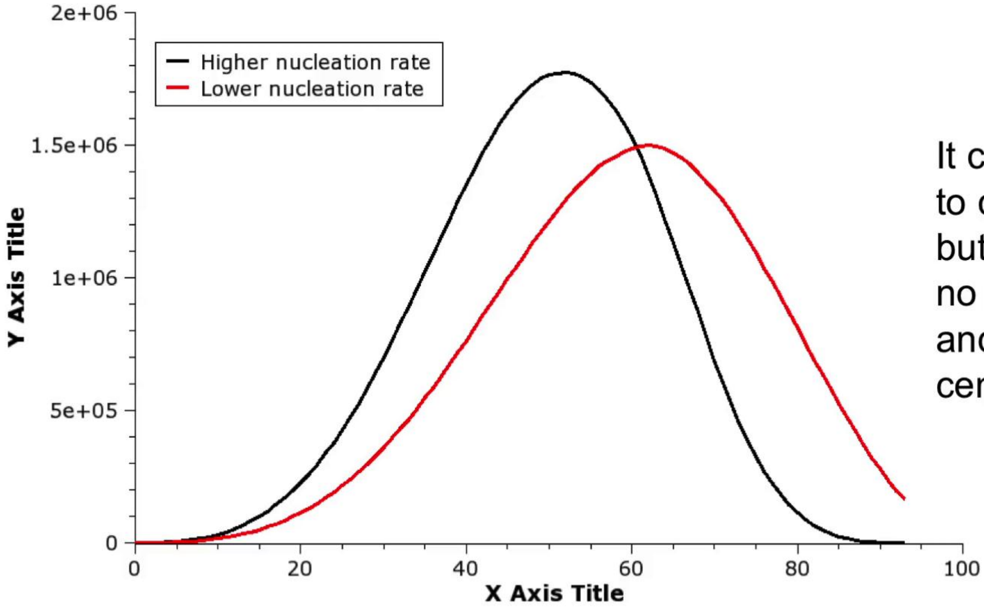
People have been studying nucleation and growth for a long time. These images here summarize the theory of Avrami and Avrami was one of the first people to really quantify these processes. And what Avrami was doing he was studying solidifying methods and in solidifying methods you have a liquid and then these nuclei represented in here form and then they grow and the rate of growth is proportional to their surface. So as first of all they get bigger the growth rate goes up and then as these nuclei grow into each other you can see the surface available for growth goes down, so you get this deceleration.

Notes

Summary

1m 58s

Avrami equation gives the right kind of peak



It can be FITTED to cement hydration, but parameters have no physical meaning and vary from one cement to another

So he analyzed this process in quite some detail, came up with some very powerful equations and this just shows a couple of his equations. And because this kind of form of reaction, where we have this peak, this looks rather similar to what we have got in cement paste, for about fifty old years, people have been trying to say “well can we apply this quantitative analysis to cement paste”? And indeed because it is such a simple shape, you can quite easily fit this to cement hydration. But the problem is that then you come up with parameters that have no physical meaning and vary enormously from one cement to another. So this really underlines the fact that to really understand the right mechanism, you have to do a very wide range of experiments and you have to analyze those quantitative.

Notes

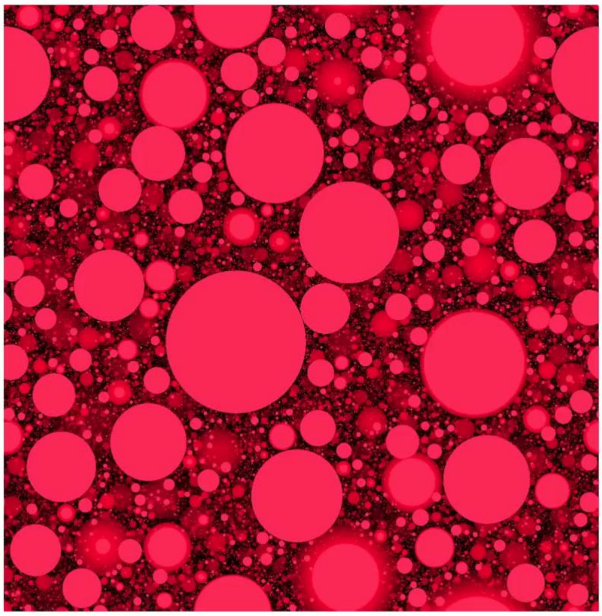
Summary

2m 40s

Need to test theories quantitatively

- Wide range of particle sizes is an important aspect
- Computer models can handle this complexity

μic model (pronounce "mike")
Is a model developed by Bishnoi at EPFL.
It used a vector representation of spheres to enable the hydration of millions of particle to be followed



Now in terms of doing the quantitative analysis, it is very useful to be able to rely on computer models. And one aspect which we need to capture in computer models is the fact that we have a very wide range of particle sizes. We have some cement particles that are about sixty microns in size, some are less than a micron in size and this means that in a typical box, so this would be a typical box of one hundred microns, we may have many millions of particles.

Notes

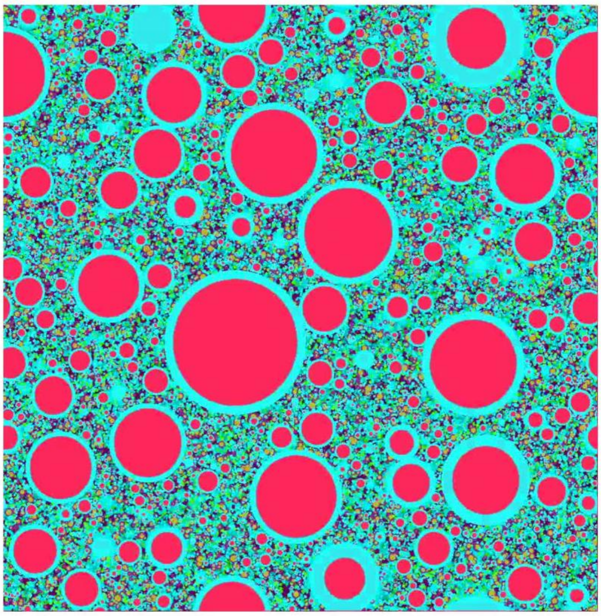
Summary

3m 39s

Need to test theories quantitatively

- Wide range of particle sizes is an important aspect
- Computer models can handle this complexity

µic model (pronounce “mike”)
Is a model developed by Bishnoi at EPFL.
It used a vector representation of spheres to enable the hydration of millions of particle to be followed



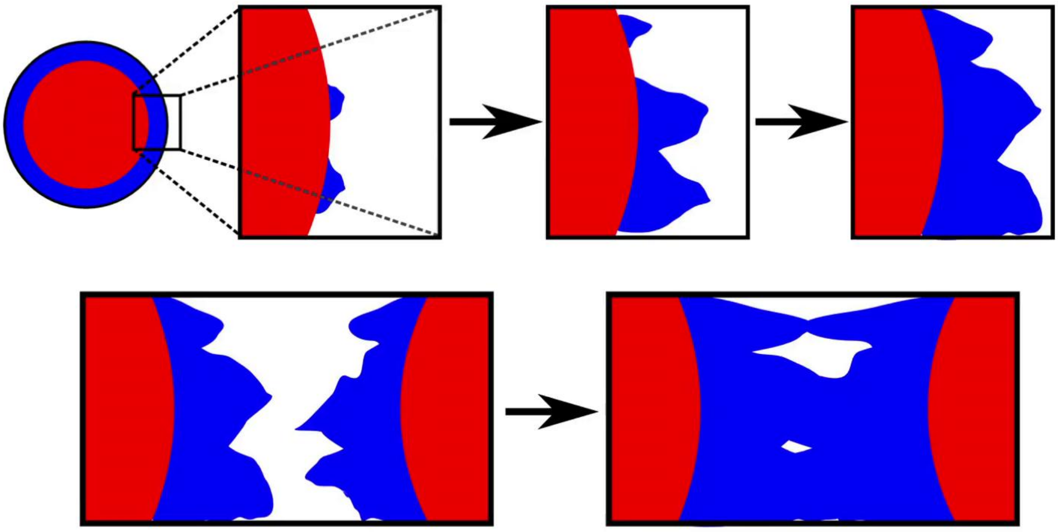
And this shot here shows the model we call µic (mike). µic is a model developed at EPFL by Shashank Bishnoi and it has this cute little logo, it is written like this but that is because it is µic (mike) for microstructure.

Notes

Summary

4m 10s

classic, compact product, boundary nucleation



Thesis Bishnoi EPFL 2008

OK so we can use this modeling platform to test different hypothesis. The first hypothesis we tested was this classical idea sometimes called boundary nucleation and growth, where we have our surface which is alite, we have the CSH growing on the surface and the growth rate is proportional to the surface of the CSH So that eventually growth will slow down when material from one grain impinges with the other.

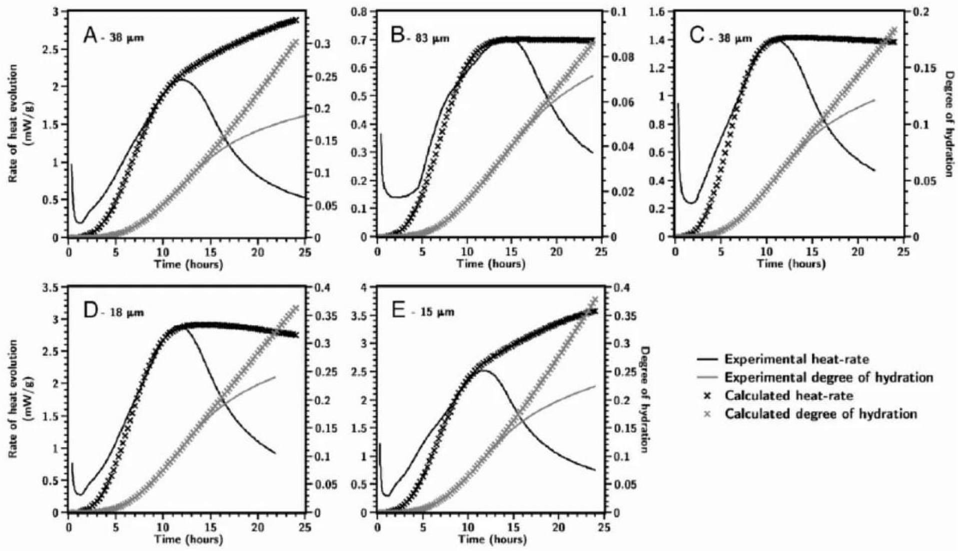
Notes

Summary

4m 28s

Modelling Nucleation and growth

classic, compact product, boundary nucleation



Deceleration not captured

No impingement of product

Thesis Bishnoi EPFL 2008

If we look at the results from this and what is quite important in these results I am going to show you, is that we tested this on a range of particle sizes from the same alite. So these numbers here tell you the average particle size of the different alite, but in fact we had the whole particle size distribution which we could simulate in the model. And what you can see here is that in this modeling we can capture very well this accelerating period but after the peak we get a very poor correspondence between the model shows and what the experimental result is. Basically we don't get the deceleration.

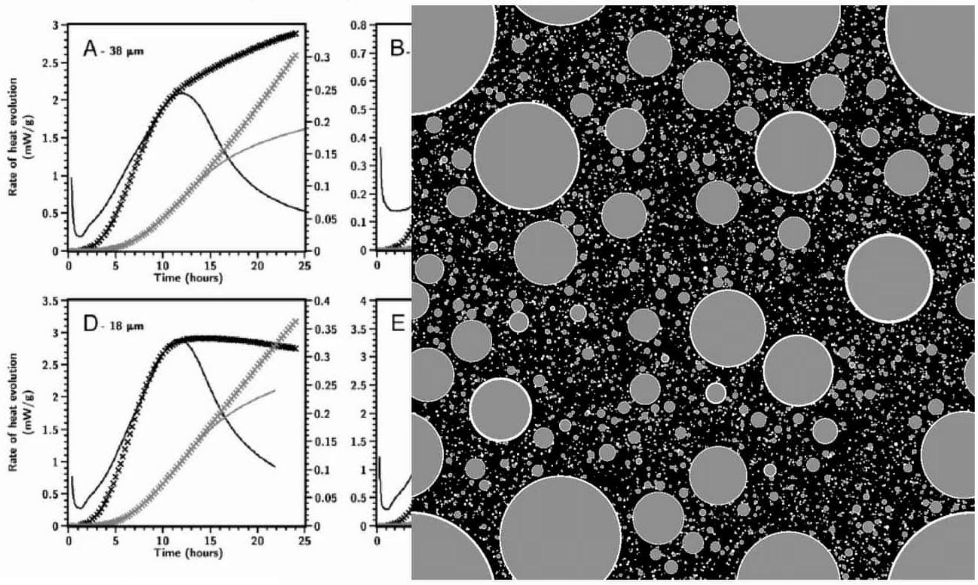
Notes

Summary

4m 59s

Modelling Nucleation and growth

classic, compact product, boundary nucleation



Deceleration not captured

No impingement of product

Thesis Bishnoi EPFL 2008

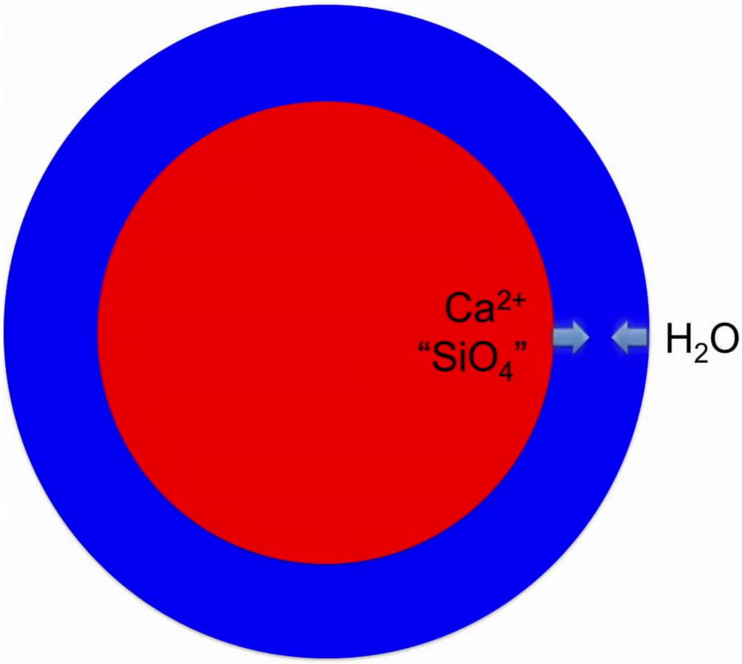
And if we look at the screenshot of the model at the peak, you can see here there is a very small amount of product, so it is not surprising we are not getting much impingement between the product. So what can be an alternative?

Notes

Summary

5m 46s

Diffusion



Many researchers have proposed that at the peak the layer of hydration products provides a barrier to the reaction and the rate limiting step is the diffusion of species through this layer

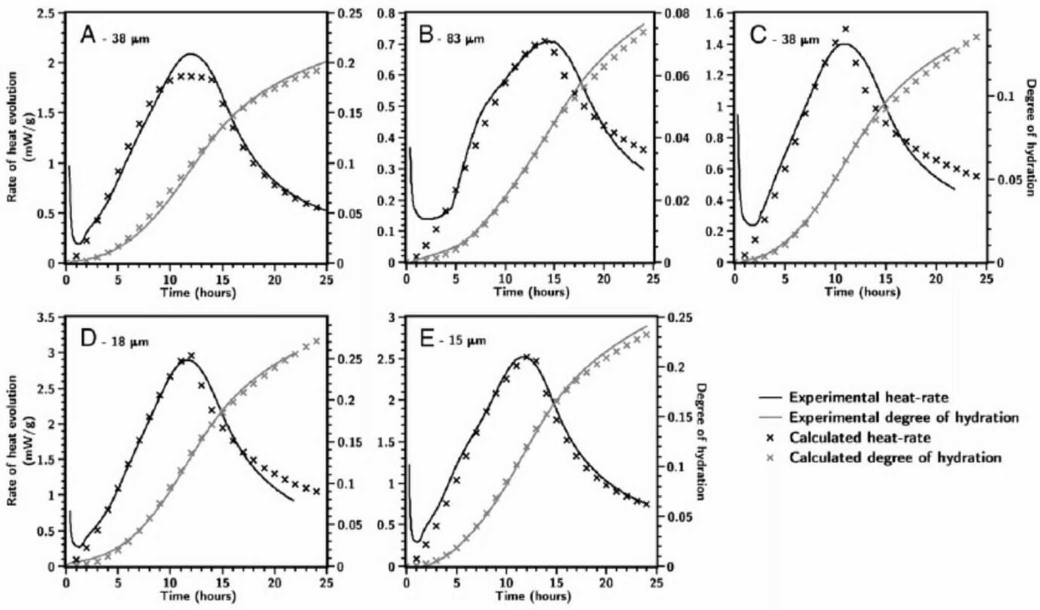
Well classically, many researchers have proposed that what happens at the peak is that we switch the mechanism, we go from a nucleation growth controlled mechanism, to the fusion controlled mechanism. And the idea is that we have our cement grain here, we have our solution out here, we have a product layer in-between and that either the water has to diffuse in, or the products have to diffuse out. Probably both but we don't know which one is rate limiting. So that again seems quite a nice hypothesis. It is a hypothesis that fits very well in a number of other reaction studies. And we can use our modeling platform to look at that and here we see the results.

Notes

Summary

6m 02s

Bishnoi 2008 : Post-peak "Diffusion"



Good fits were obtained but diffusion coefficient varied by 10x

And at first glance this looks OK because you see the model now fits fairly well with the experimental results. But, and this is a very important but, because we did the simulations on this wide range of different particle sizes and we see if you get them all to fit, we have got to vary all the fusion coefficient by ten times. Now this makes absolutely no sense whatsoever because this is exactly the same alite with forming exactly the same CSH and there is absolutely no reason that this diffusion coefficient of that CSH should change by an order of magnitude. Clearly what this shows is, you know, you can make a lot of mechanisms fit but you have to go further to really see what can be the right theory. So we really have to abandon this idea of diffusion and there are a number of other reasons why we should do this.

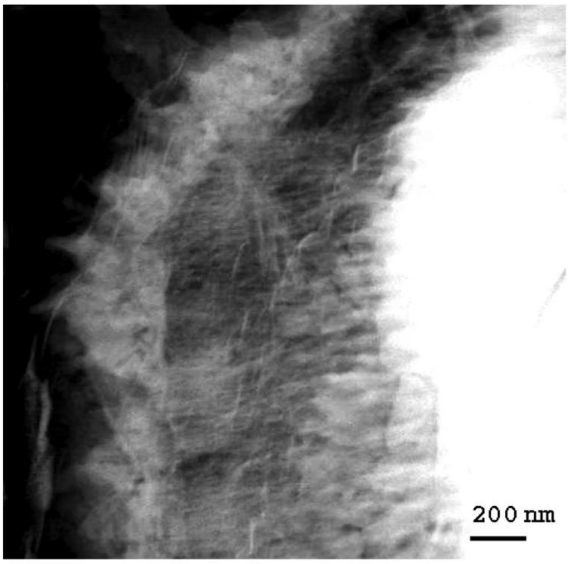
Notes

Summary

6m 55s

Evidence against diffusion

- Same C-S-H for different particle sizes, why should diffusion coefficient vary by 10X
- Success of maturity approaches: same activation energy throughout main hydration peak
  - Bond breaking / making processes typically have Ea > 40 kJ/mol
  - Transport controlled processes have Ea <~20 kJ/mol
- Low density region inside "shell" does not fill in until much later



[Gallucci et al. 2010]

So here we have the first reason I showed in the last slide that there is no reason why this diffusion coefficient should change by an order of magnitude but also those of you who have perhaps looked at different ways of calculation maturity will be familiar with the idea that we can use a single activation energy throughout that main hydration peak and we wouldn't expect that if we had a transition in mechanism. So if we went from a mechanism which is like nucleation and growth, which is to do with bond breaking and making, this would have a typical activation energy around forty kJ per mole, which is typically of the same order of what we find in cement paste, whereas transport control processes such as diffusion have much lower activation energies, less than around twenty kJ per mole. So there is no evidence from this activation energy. And thirdly, if we look at a micrograph, this is a taken at one day, so, you know, we are well past the heat peak here, and what we can see this is our alite grain on the right here, this is our CSH forming, we have got this kind of shell here but we really cannot in any way defend that this shell is acting as a diffusion barrier, because if the shell was acting as a diffusion barrier we would now expect to see this region of low density behind the shell, we would expect this to be right in contact with our alite grain.

Notes

Summary

7m 59s

Evidence against diffusion

- Same C-S-H for different particle sizes, why should diffusion coefficient vary by 10X
- Success of maturity approaches: same activation energy throughout main hydration peak
  - Bond breaking / making processes typically have Ea > 40 kJ/mol
  - Transport controlled processes have Ea <~20 kJ/mol
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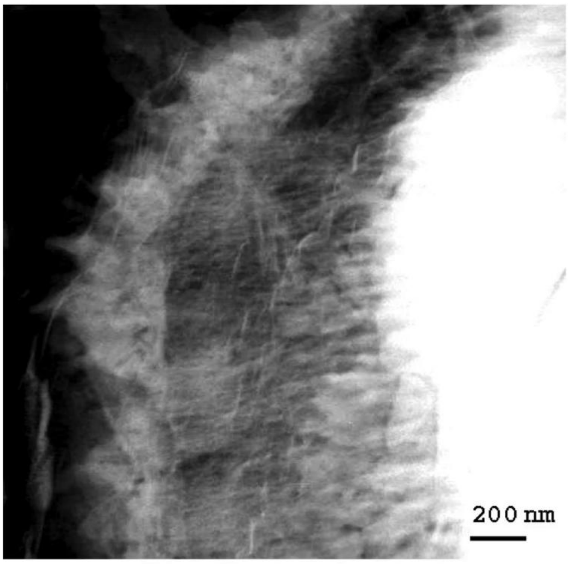


[Gallucci et al. 2010]

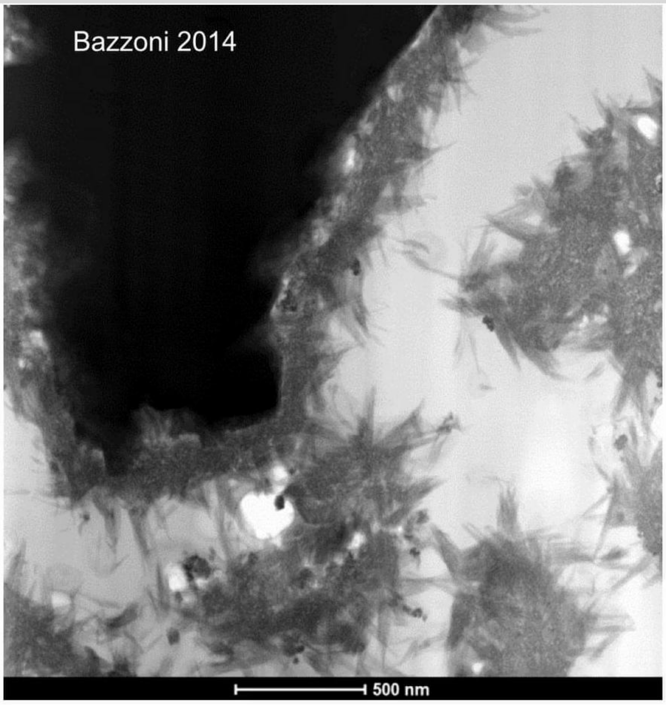
So these many reasons really are evidence that diffusion is not becoming the rate determining mechanism at this stage of the reaction.

Notes

Summary

9m 31s

But C-S-H does not grow in a compact manner with uniform density



Then with the work of Shashank Bishnoi, we really looked at this formation of product and this formation of product you can see, it is not really all that uniform, that is to say that the kind of an average density out here is quite a bit less than the density close to the particles.

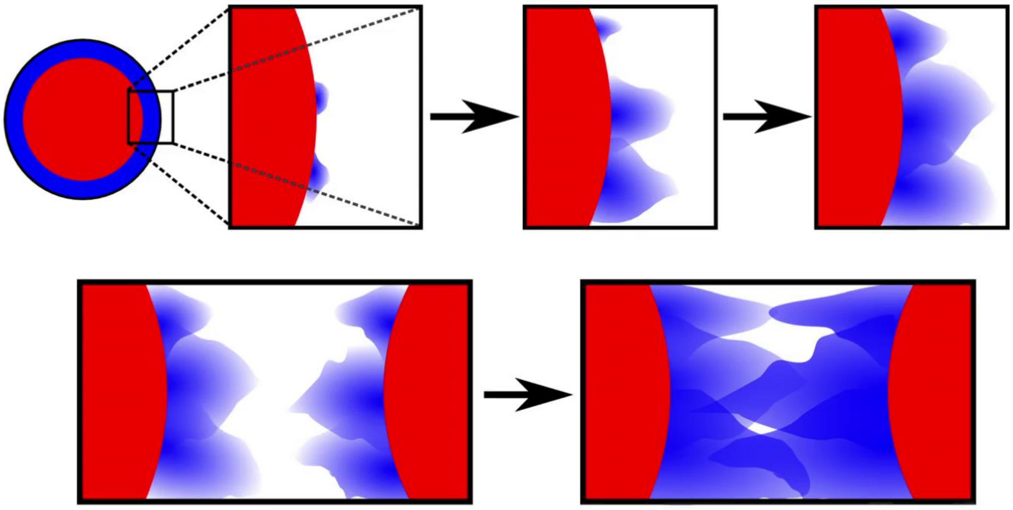
Notes

Summary

9m 43s

New hypothesis: densifying growth

rapid outward growth
in diffuse manner
(low packing density)
then densification



[Bishnoi 2014]

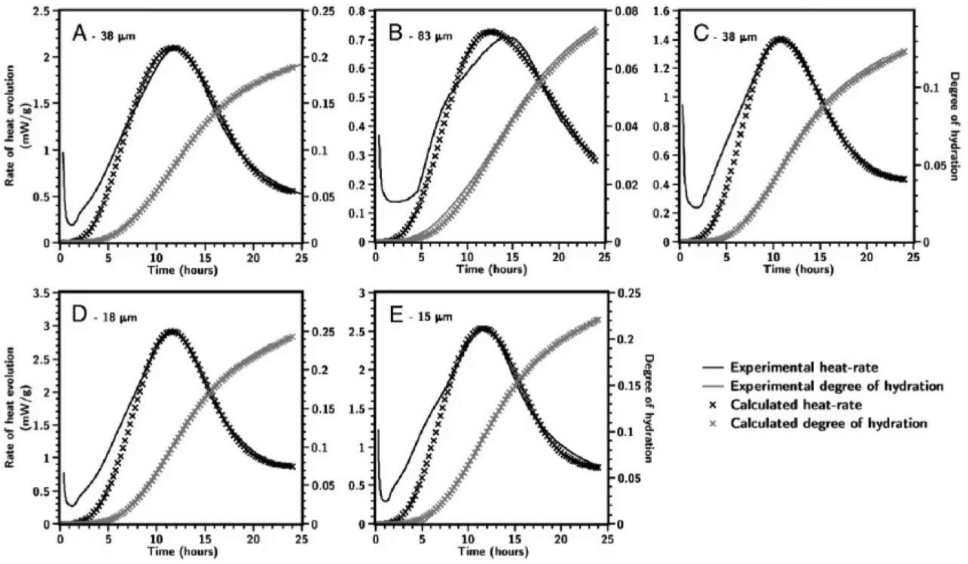
And so we put forward a new hypothesis that CSH was first forming in a low density way and then subsequently densifying. And because it is got this low density, then it can occupy more space and you can imagine to have impingement between the hydrates much earlier than you would otherwise expect.

Notes

Summary

10m 03s

Diffuse nucleation and growth



[Studying nucleation and gowth of C-S-H using μic - Shashank Bishnoi, Karen L. Scrivener *Cement* and *Concrete* Research, 39, (10), October 2009, 849-860]

Appears to work well

And this theory was developed quite rigorously and quantitatively and we see from these results here that it really appears to work very well and in 2009 we published this paper, where we put forward those hypothesis. Unfortunately, as is often the case in science, we then come to a counterexample which really shows that this new theory was not right either.

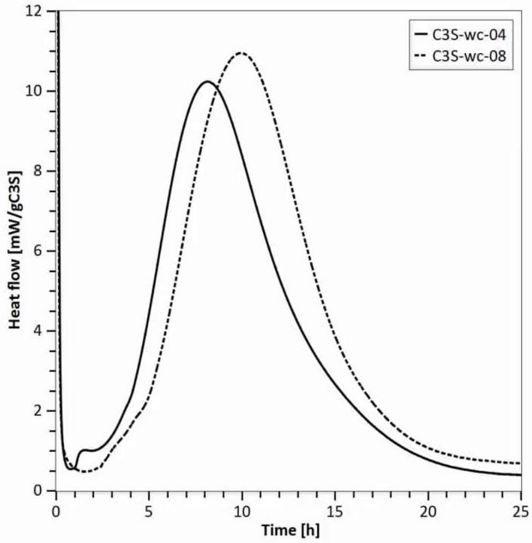
Notes

Summary

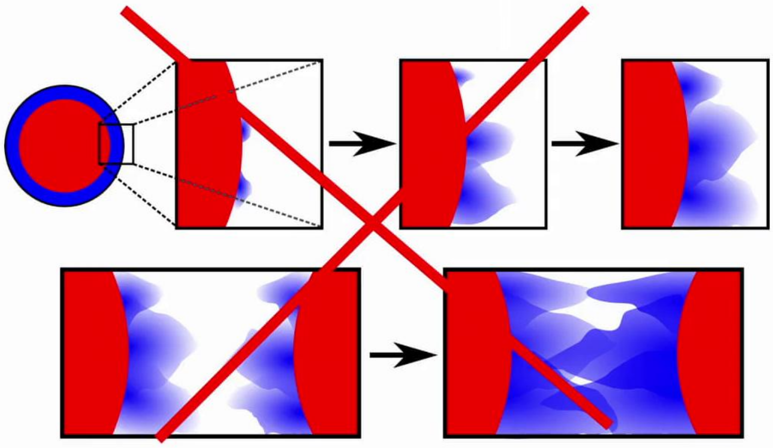
10m 27s

But: Impact of w/c

- Very low impact of W/C completely contradicts diffuse growth model



Bazzoni 2014



The critical experiment is this one which we did with Amélie Bazzoni but has also been done by a number of other people, where you can see we have a very different water to cement ratio, so here we have hydration with a water to cement ratio 0.4 and 0.8. According to this densifying growth theory, we would expect for the water cement to ratio 0.8 that there would be a lot more space and therefore to have a lot more hydration before this downturn. But in fact we don't see this, we face here just a little bit more hydration before we get this downturn. So unfortunately we have to abandon this new hypothesis.

Notes

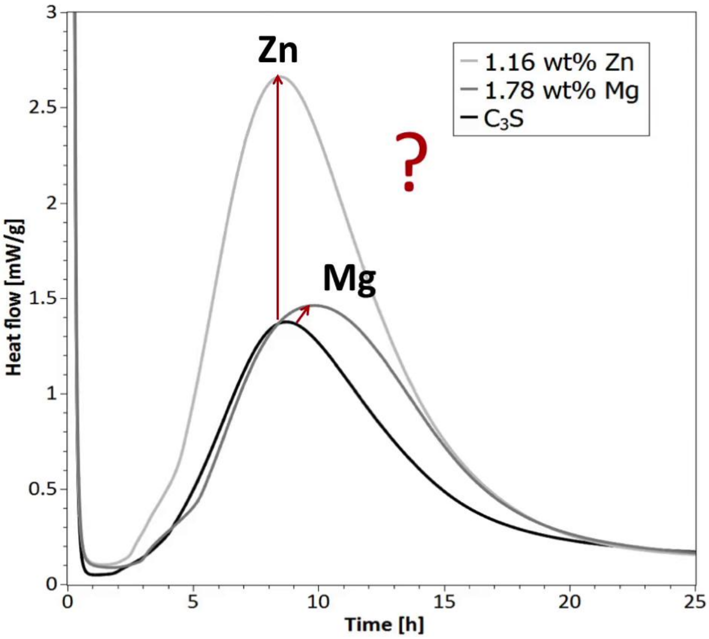
Summary

10m 56s

Impact of ions

- Alite with Zn and Mg
- Higher maximum heat with Zn
- Little change with Mg

[Bazzoni et al
J. Am Ceram Soc 2014
With Nanjing University of Technology]



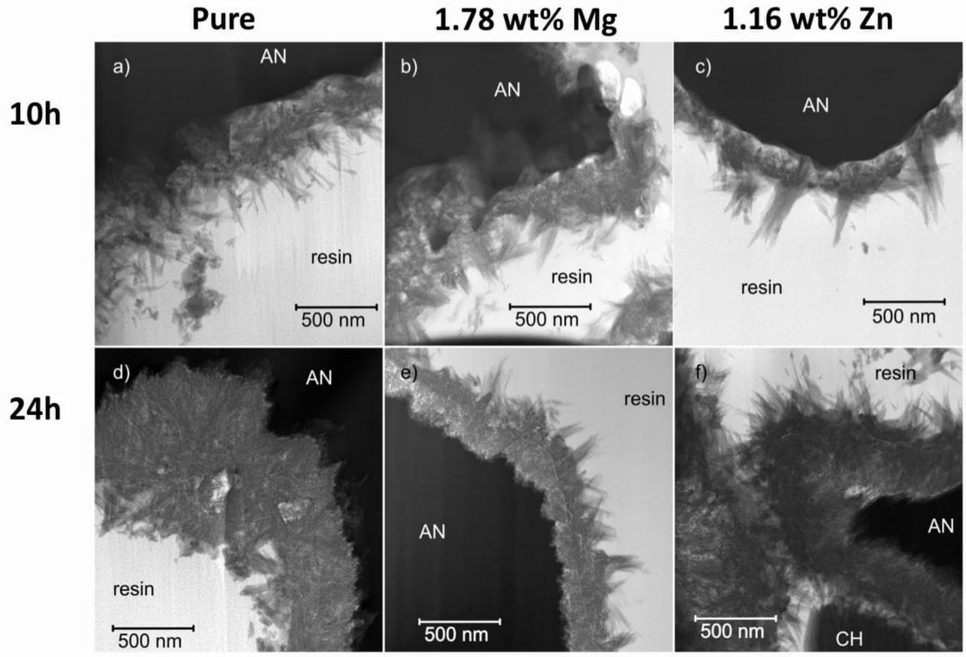
Also in the thesis of Amélie Bazzoni we had another source of alite which gave us a different perspective on this question. And this was really where we had alites which on the one hand contained small amounts of zinc, and on the other hand small amounts of magnesium. So we had the pure system magnesium and zinc. And what you can see in the calorimetry curves here is that the presence of low amounts of zinc gives you this vast increase in the amount of hydration that is occurring in this first heat evolution peak. So there must be something different that is occurring with the zinc-doped sample, which is telling us about what is controlling this main heat evolution peak.

Notes

Summary

11m 38s

Growth of needles



- Similar needles with Mg
- Longer needles with Zn

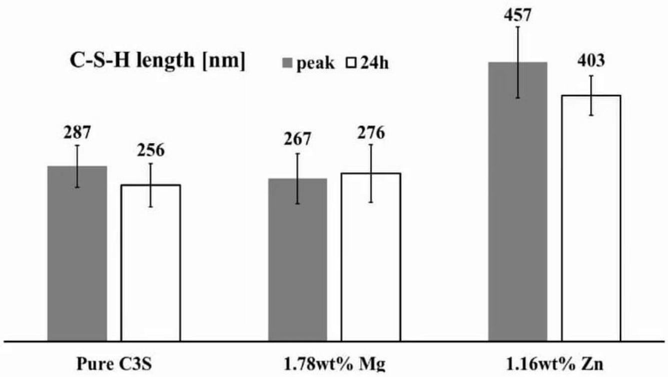
So when we made a more detailed investigation by transmission electron microscopy, what in fact we see here, we see these needles that are growing out from the C3S surface are much longer in the case of zinc than in the case of magnesium and the pure case.

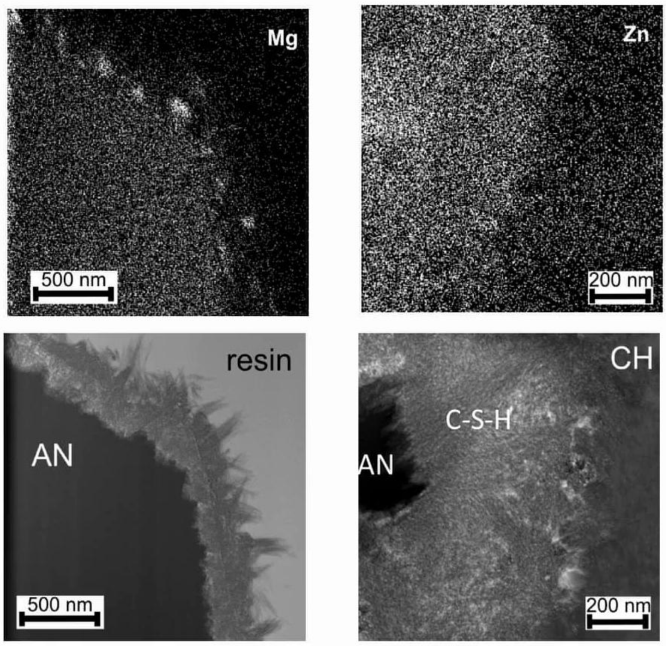
Notes

Summary

12m 30s

C-S-H needle length





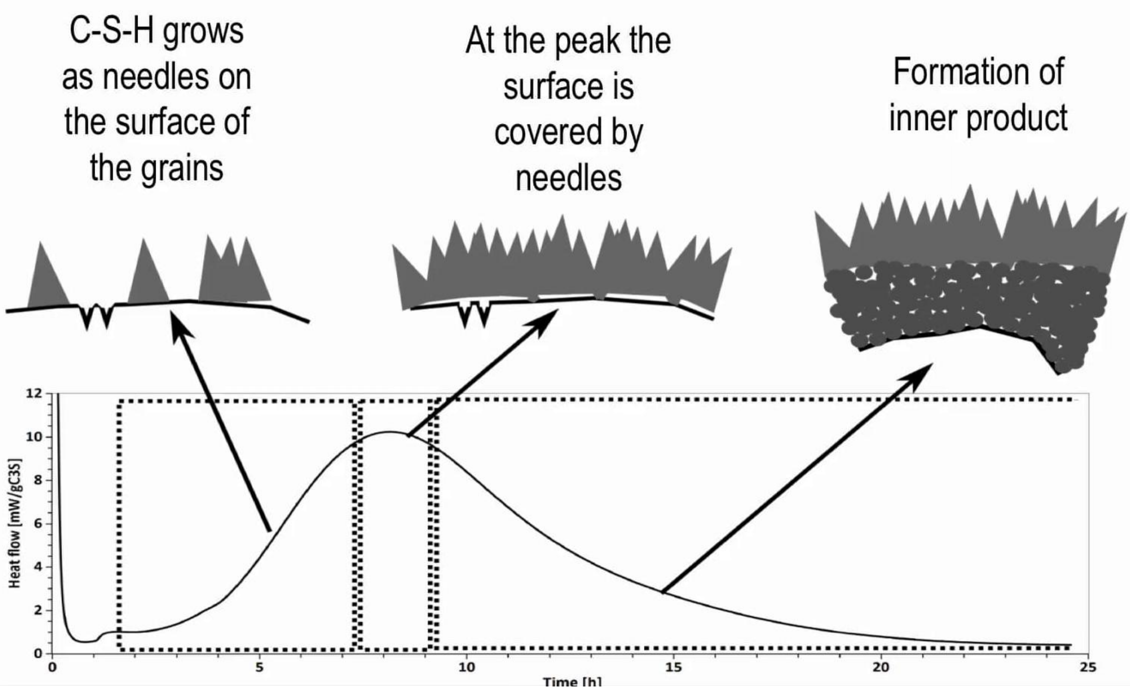
And we could quantify that. So here we see the quantification of the needles length. We don't know exactly the mechanism but we could see that the zinc is really incorporated into the CSH, whereas the magnesium is not really being incorporated at all, it is just occurring as these little isolated crystals.

Notes

Summary

12m 49s

Another new hypothesis



So this gave us a new hypothesis, yet another new hypothesis that the idea is we get this CSH growth in needles on the surface of the grain. By the time you get to the peak the surface is covered so no more needles can grow and as no more needles can grow, the rate of hydration starts slowing down and you get the formation of inner product. But as I have already said, the critical test of any hypothesis is whether it works quantitatively.

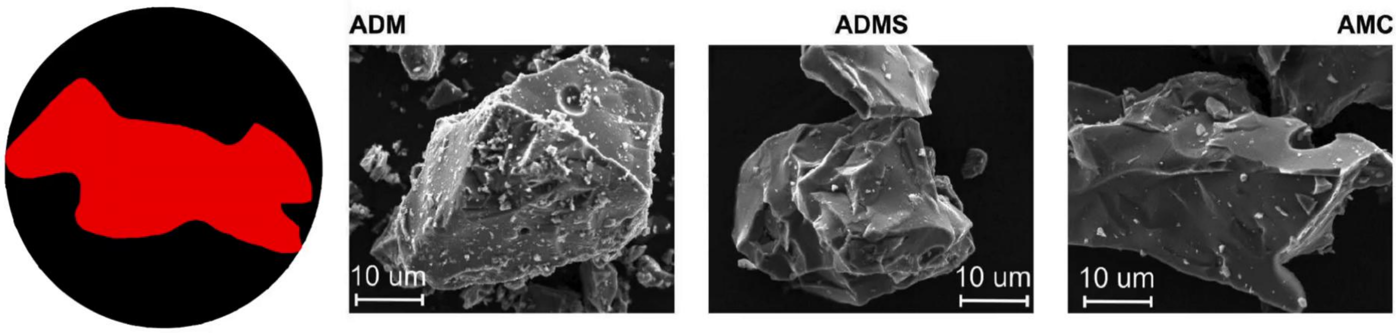
Notes

Summary

13m 11s

Needle model: [Ouzia et al. 2017]

- C-S-H growth as needles
- ALL parameters from experiment – **NO fitting**
- Algorithmic model allows form of particles to be accounted for.
- Consumption of small grains also included



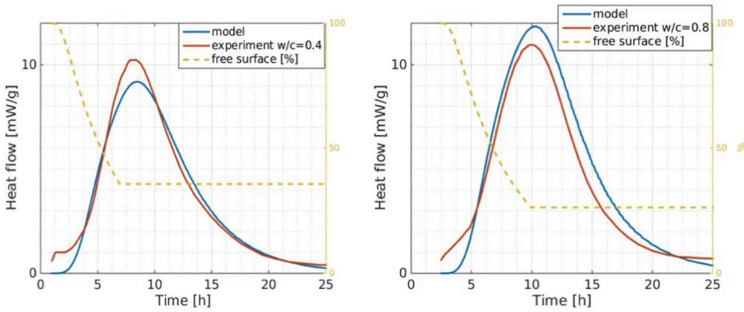
And for this we are now working on a new model, which is called the needle model which is being worked on by Alexandre Ouzia in our lab at the minute. And this hypothesis is we have CSH growth as needles. What is very, very important is that all the parameters can now come to experiment. There is no fitting in what I am going to show you here. And because it is an algorithmic model rather than a computer model, a model that works in terms of having a real microstructure, we can also calculate much more complex form for the grains and take account of the consumption of the small grains.

Notes

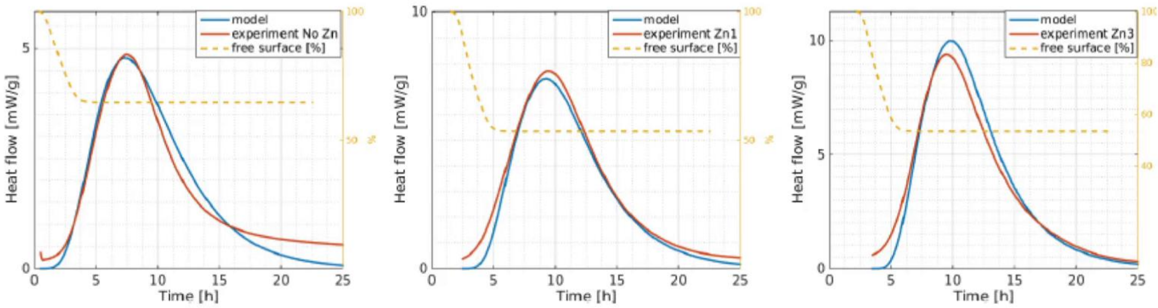
Summary

13m 43s

Needle model: [Ouzia et al 2017]



W/C variation



doping

And when we do that you can see now in these different simulations, this really works beautifully throughout the whole range of different variations we have already seen. It can really well capture this water cement ratio variation and it can really well capture the effect of the zinc doping. So hopefully, this is now the hypothesis which can be validated. Of course we are not at the end of the road because there are important open questions.

Notes

Summary

14m 26s

Open question?

- If mechanism is C-S-H growth: What controls this?

So if this mechanism is controlled by these needles that grow and then stop what is controlling this? Unfortunately today we can't answer that question but with work we have underway looking at the much more atomistic level, I am pretty confident we will be able to answer this in a year or so time.

Notes

Summary

14m 57s

Main peak, summary

- Many hypotheses can fit the form of the peak
- Need to look at a wide range of variables and have physically measureable parameters
- Growth of needles to a critical length seems best hypothesis

So let's come to the summary on this main peak. The first and foremost thing is that just because you can do occur fitting that doesn't mean the hypothesis is right. You can take many, many equations that have this simple form of peak and they look right. If you are going to differentiate between these different hypothesis you need to look at hydration with a wide range of variables. You need to work with the water cement ratio, particle size distribution, look at the dopants, all these different things are really really important to give you the range to test your hypothesis. And ideally you need to have physically measurable parameters because if you can do that and if you can avoid the fitting step then you can really be much more confident that your hypothesis is working. And having followed that process over the last few years we are now fairly confident that we can explain this by this growth in needles to a critical length as being the best hypothesis for this main hydration peak.

Notes

Summary

15m 16s