ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Kinetics: the "Filler" Effect

Cement Chemistry and Sustainable Cementitious Materials

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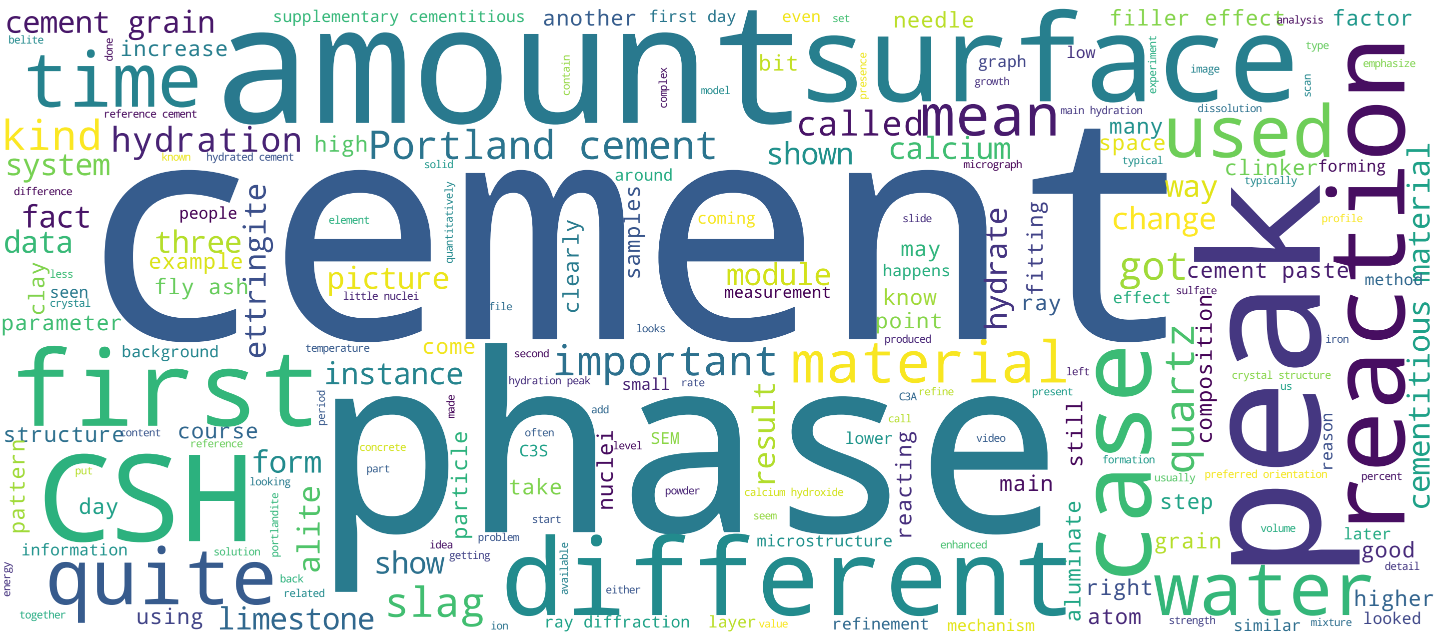

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Impact of SCMs on main heat evolution peak

- During the first day or so most SCMs do not react
- However their physical presence affects the hydration of the clinker component
- This is known as the “filler effect”

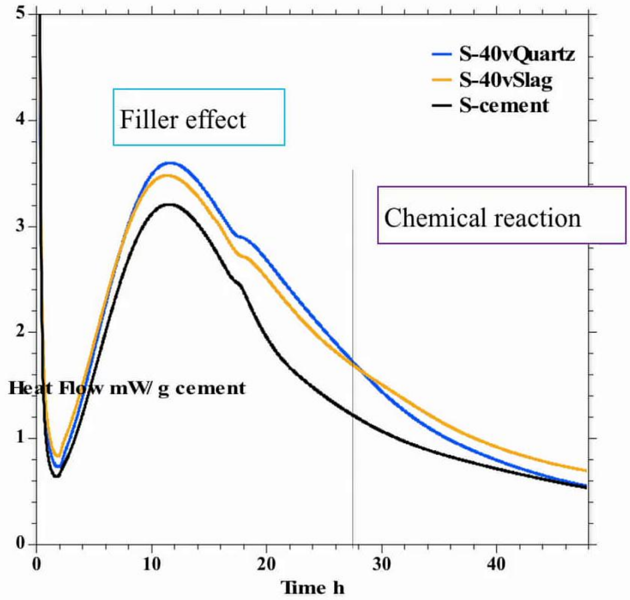
Hello, welcome back. So in the last module, we looked at the kinetics occurring in the main hydration peak and the mechanism for that. And before going to look on what happens in the longer term in this module we are going to look at what is called the filler effect, this is the impact that supplementary cementitious materials have on the hydration, not because they are themselves reacting, but because of their physical presence in the mixture. So during the first day or so most supplementary materials are not reacting, their physical presence affects the hydration of the clinker and this is what we mean by the filler effect.

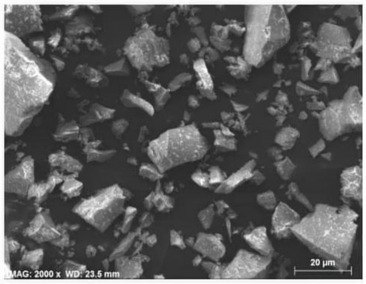
Notes

Summary

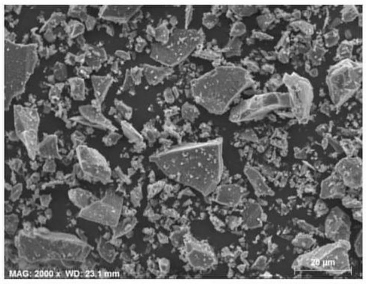
0m 04s

Physical effect on main hydration peak





Slag



Quartz

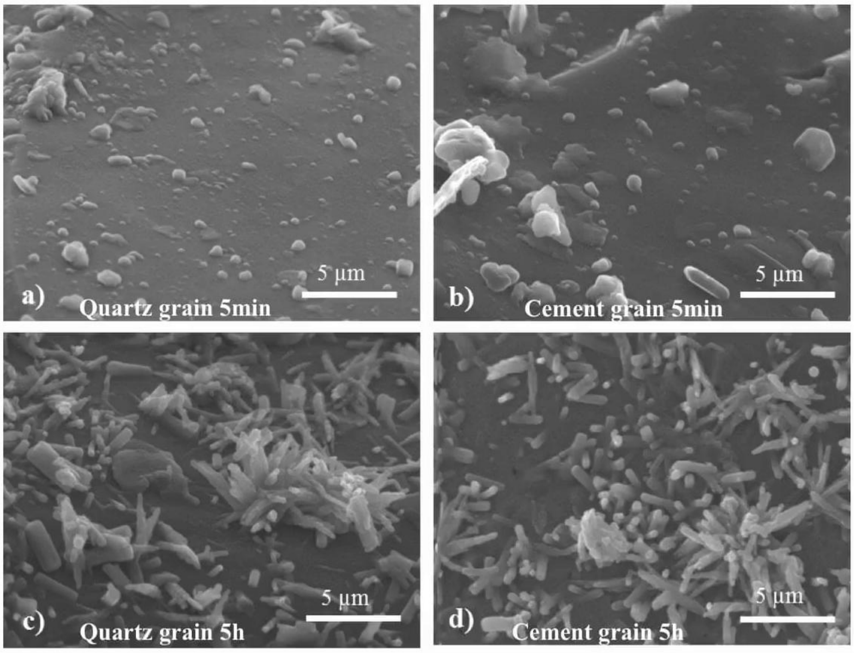
So we can see that by looking at this data here coming from different mixtures. So the first one in black is the reference cement and then we took this reference cement and we mixed it either with forty percent quartz as shown in blue here. Always forty percent slag as is shown in orange here. And the slag and the quartz were chosen but they had about the same particle size distribution as you can see by these images here. So we can see in the first day that when we take this calorimetry curves and we normalize them by the cement content, that is very important this is just as if there was a hundred grams of cement, reference cement in all cases. You can see that the reaction of that cement is enhanced in both cases. it is enhanced by the quartz, it is enhanced by the slag and pretty much in the same way in the two cases. Which really emphasizes that it is a purely physical effect because quartz is non reactive. We have checked that the amount of reaction even at twenty eight days is barely measurable. After the first day or so we can see now that the slag reactivity starts to be higher and this is indicating, this is actually the slag itself reacting. So over here we have the filler effect, here we have later on the chemical reaction.

Notes

Summary

0m 43s

Surface of quartz provides nucleation sites for C-S-H



System: Cement + 40% Quartz, hydrating together – pictures from same sample

When we look into the micrograph, why did we do this? The reason we did this was that most people have proposed that this filler effect is coming from the extra surface providing extra nucleation sites for CSH. And when we look in the SEM, this seems to be the case. So this was a system of cement and quartz, they are hydrating together, so the pictures are taken in exactly the same sample and here we see a cement grain, you can see these little nuclei forming on the surface and then you can see these needles of CSH forming. And here we see the quartz grains, it looks really the same. We have got the CSH nucleons surface from very early times and then from those little nuclei the CSH is forming. So the hypothesis seems to be correct.

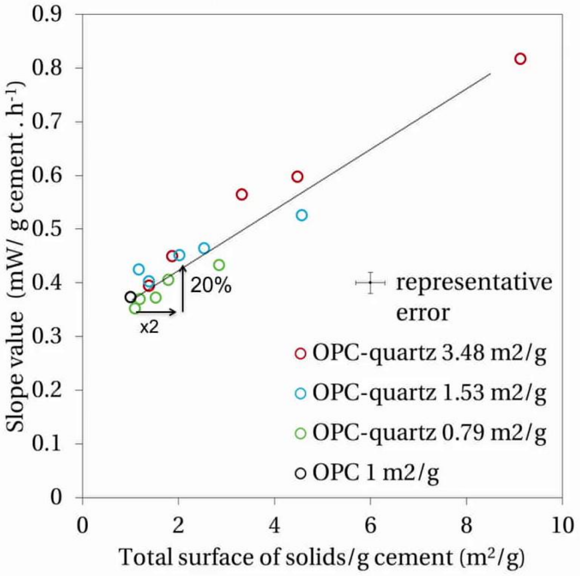
Notes

Summary

2m 22s

Hypothesis:

extra surface provided by SCM provides new site for nucleation



BUT:
Quantitatively, the effect of the surface is quite low compared to the surface provided

However, when we look at it now more quantitatively, it is not so good. So this graph here shows how the slope, that is to say the slope of that acceleration part, varies with the amount of surface. OK So this is the reference Portland cement down here. OK and if we increase the amount of surface by two times, so here we got twice the amount of surface, but we have only increased that acceleration slope by twenty percent. So the fact we had extra surface just doesn't add up because we would expect it to be twice as much there, which is clearly not the case. What can we suppose?

Notes

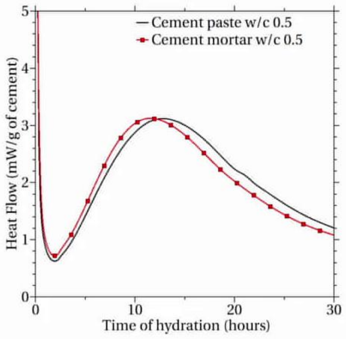
Summary

3m 18s

Mortar vs Paste

Cement paste =
water + cement grains (µm)

Mortar =
water + cement grains (µm)
+ sand (mm)



[Berodier & Scrivener 2014]

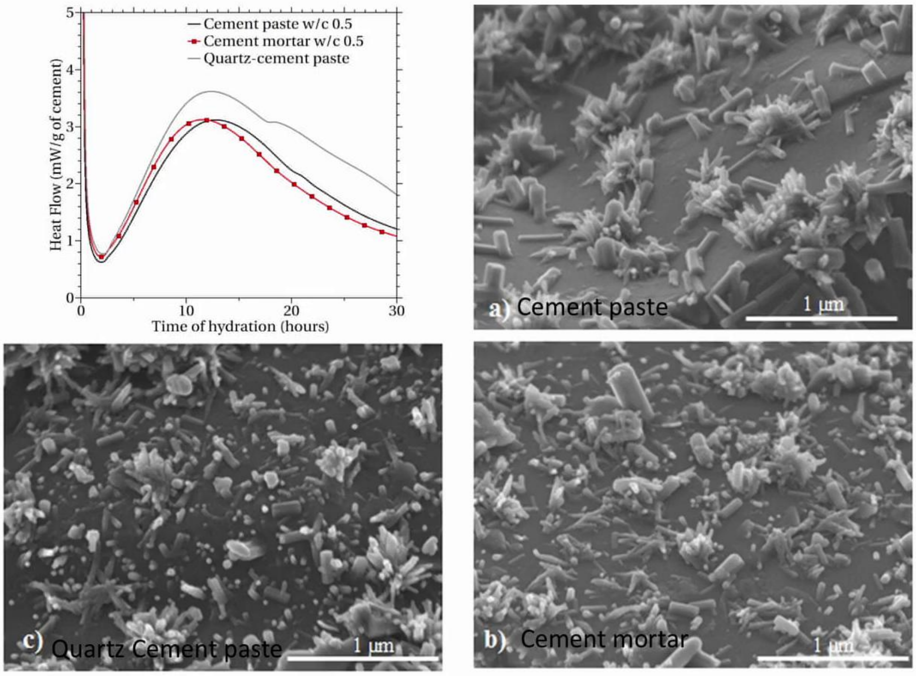
Well if we now go back to look at mortars versus cement pastes, so cement paste where we just have water and cement grains versus mortars where we have water cement grains and sand, we can see a similar acceleration or increase of that acceleration slope.

Notes

Summary

4m 09s

Mortar vs Paste



[Berodier & Scrivener 2014]

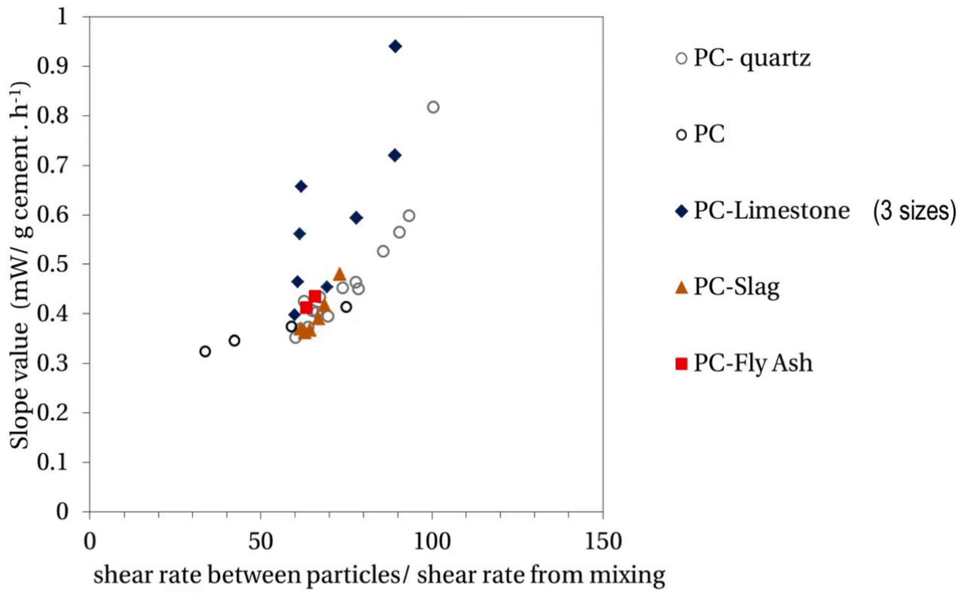
And if we look at the pictures in the SEM, We can see that here we have got just the plain cement, we have got some bits of CSH but also some bits of quite smooth surface. Here in the mortar we have got a much more confused picture with many more small nuclei on the surface of the cement grains, just by the presence of those large sand grains. And this picture here looks very, very similar to what we see in the quartz cement system. So what we can suppose is that in the mortar system, the presence of the sand grains during the mixing phase, is knocking those little nuclei off the surface, it is redistributing these nuclei through the space and by that shearing effect and redistributing the nuclei then we are getting more nuclei on the surface and we then get an acceleration effect.

Notes

Summary

4m 31s

Effect of Slag, Fly ash, Limestone



[Berodier & Scrivener 2014]

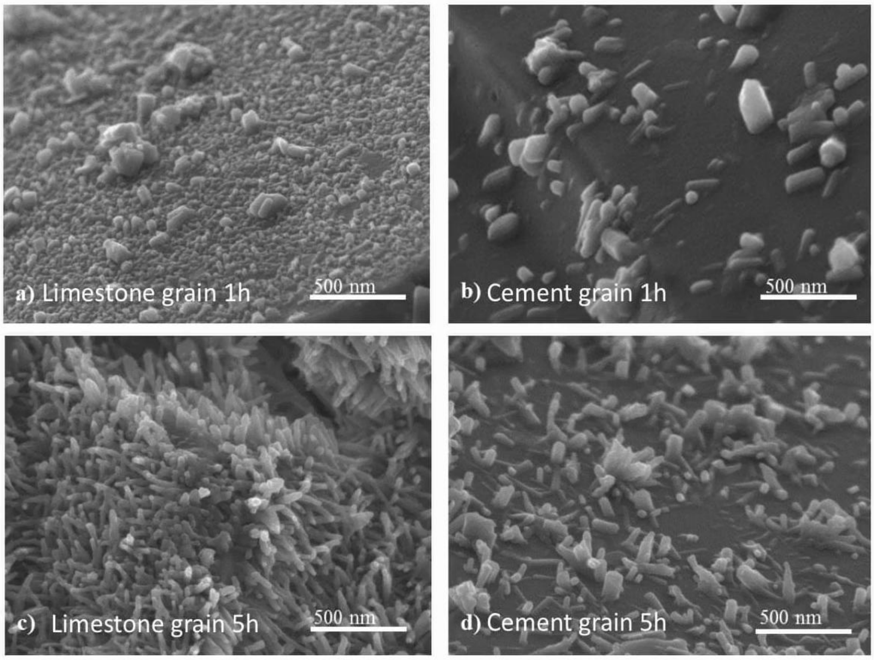
And again we can test this quantitatively. So now we can look at a variety of different systems, of different quartz with slag, with fly ash and we can plot all these results relative to the different shear rate between the particles. And we can see as the shearing rate is going up, the slope values is going up. So this is now our idea of why we get this physical filler effect. And as we see on this graph, the slag and the fly ash really act in very much the same way as we get with the quartz. However, if we now go through the effect with limestone we see that with limestone we get a very different reaction. We are getting much, much more accelerating effect from the limestone, even when we have the same shear rates.

Notes

Summary

5m 31s

Micrographs: Cement + 40% Limestone



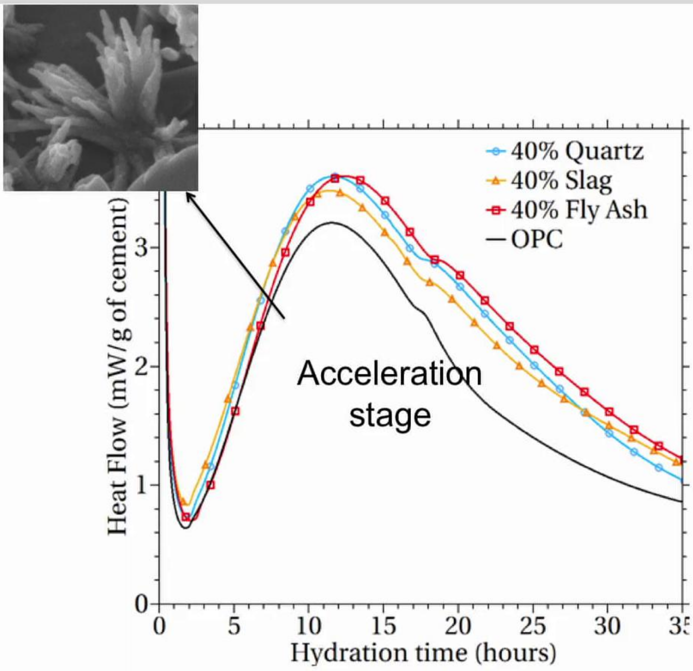
And now if we go in the SEM and look at this effect, we can see that on the limestone grains, we have got this very, very dense covering of nuclei, much, much denser than we have for the cement grains. And what it seems is that the low but measurable dissolution of the limestone grains is increasing the calcium concentration close to the surface and that helps to stimulate the nucleation of CSH. And once we form that much more dense number of nuclei here, then these grow as these dense clusters of needles. So this really emphasizes how limestone can have this very particular effect.

Notes

Summary

6m 24s

Summary: filler effect



- Although inert, SCM have a significant effect on the nucleation and growth of C-S-H
- Small increase in nucleation sites ***due to the higher shearing conditions***
- Some surfaces, e.g. calcite favor the nucleation of C-S-H and also change the growth

So if we just summarize that module here. Although they are inert, these supplementary cementitious materials do have a very significant effect on the nucleation growth of CSH. We have a small increase in nucleation sites due to high shearing conditions. But some surfaces for example calcite, also favour the nucleation of CSH and change the growth pattern. So now we have looked at the main hydration peak and what happens with supplementary cementitious materials, next time we will look at the longer term hydration. Thank you.

Notes

Summary

7m 11s