

C₃A

+

water



Rapid reaction
large platey hydrates



Stiffening
Flash set

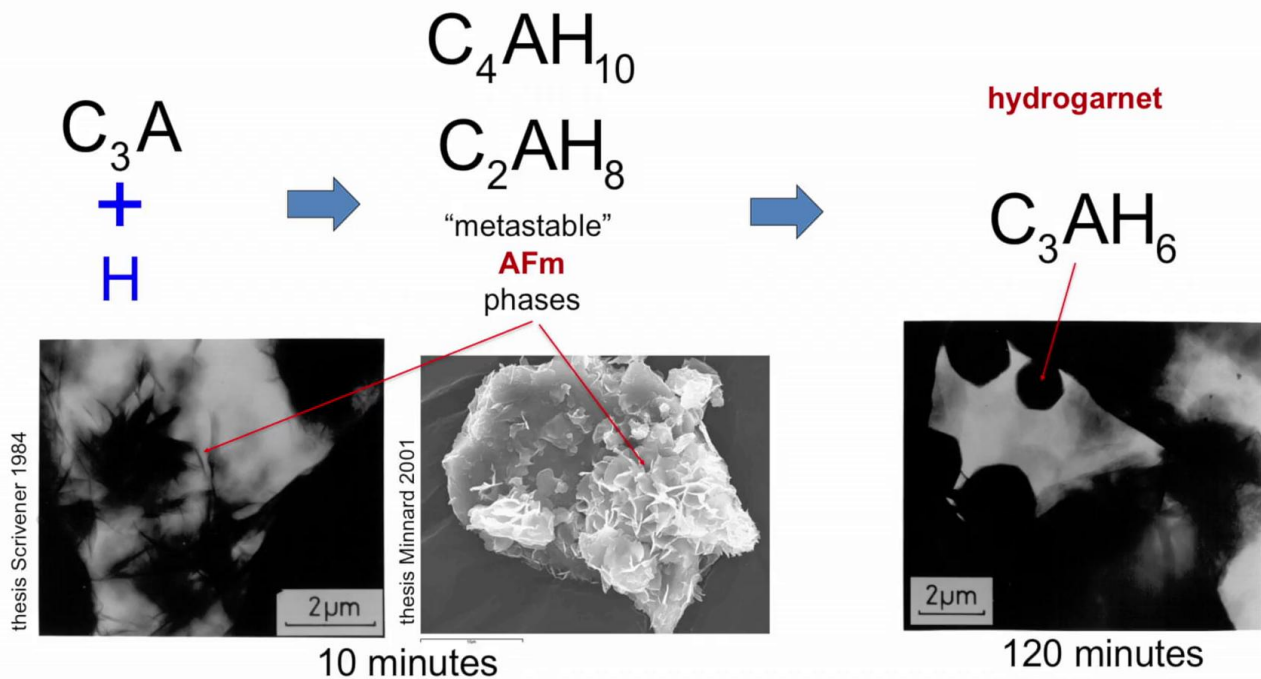
OK So hello and welcome back. So far we have talked mainly about the hydration of the calcium silicate systems. In this module we are going to talk about what happens with the aluminate systems. Many of you probably already know that if you just take tricalcium aluminate and you add water, then what you get is a very, very violent reaction. You get these large platy hydrates and the result of that is that we have what is called very rapid stiffening or flash set.

Notes

Summary



Hydration C_3A without sulfate



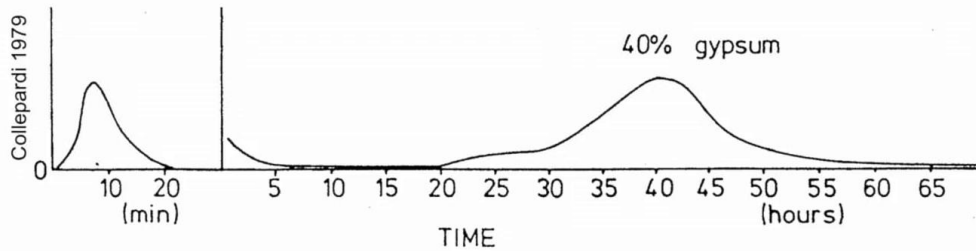
Now this shows some actual pictures of the reaction of C_3A . You can see either by the transmission micrograph here or in this scanning electron microscope, you can see these platy hydrates. And these platy hydrates are normally described as C_4AH_{10} or C_2AH_8 . These are a metastable AFM phases and over time they will transform to the hydrogarnet phase. So that is what happens without sulfate but that is not really what we are interested in for the purposes of cement.

Notes

Summary



0m 37s



The slowing down of the reaction is linked to absorption of sulfate ions on C_3A surface

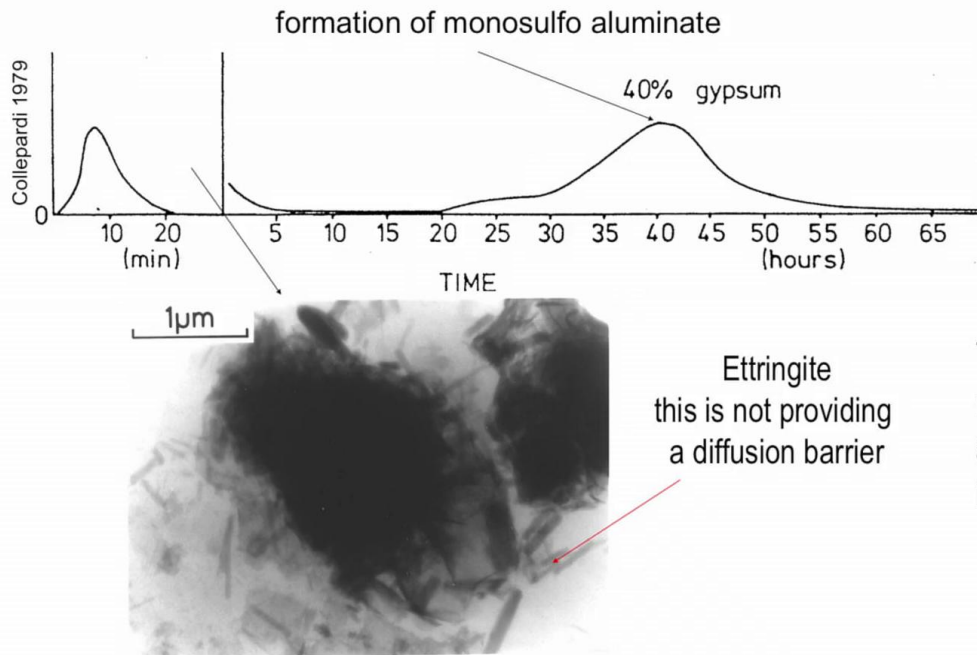
Because of course in cement we add gypsum and the reason for adding this gypsum is to control this reaction of the aluminate phase. So here we see the pattern of reaction with sulfate. This is an experiment where there was 40% of sulfate, for 100% C_3A and that is roughly or even a bit lower, the same as the sulfate C_3A ratio you would have in cement because typical Portland cements contain around six to eight percent C_3A and around five percent gypsum. And here we can see that we have a pattern of reaction where we have the last initial peak. And then we have this very long period, more than a day in which there is almost nothing happening and then we have this second peak here. OK so this period in which there is nothing happening is extremely important because we need to have this long period of induction to allow the silicates to react. Now most textbooks say that the reason for this very long induction period is because we have the formation of ettringite.

Notes

Summary



1m 14s



The slowing down of the reaction is linked to absorption of sulfate ions on C_3A surface

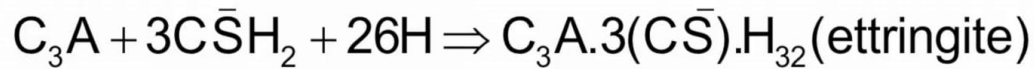
Now we do have the formation of ettringite, we can see in this picture here, these little rods, these ettringite, but these are not forming a barrier. You know it would be like trying to block water with a dam of spaghetti. The water can infiltrate through the spaces between the rod. So this is not the reason why the reaction slows down and in fact other experiments have shown that the real reason is because we have sulfate ions absorbing directly on the surface of the C_3A , which slow down the dissolution of the C_3A . Then in this case after about two days, we get the second reaction and during the second reaction, we get the formation of this phase calcium monosulfoaluminate.

Notes

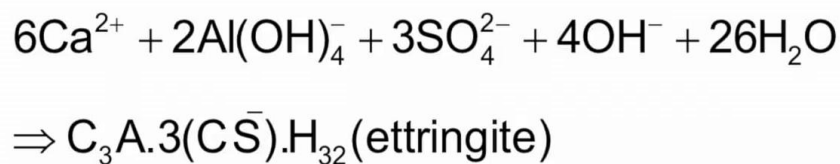
Summary



2m 37s



Reaction is through solution



Hypotheses of “topochemical” formation of ettringite are nonsense

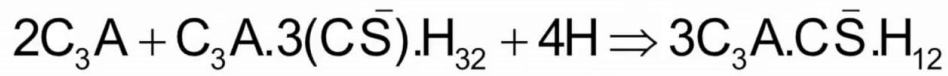
Now if we look at the chemical equations of these reactions, the formation of ettringite is usually written like this, we have C3A with the gypsum and water which forms this complicated formula here of ettringite, we discussed a few modules back, but in fact we should always remember that like all hydration reactions in cement, the reactions really going through a solution, we have calcium ions, aluminate ions, sulfate ions and and hydroxide ions which all come together to form this mineral ettringite. And in fact these calcium ions here don't necessarily come from the aluminate phase, they could come from the C3S for example. And I really want to stress that again a common myth in many textbooks is this idea you can get topochemical formation of ettringite and this is really absolute nonsense because the crystal structure of this phase is so completely different from what you have in the anhydrous materials. There is absolutely no way this is possible.

Notes

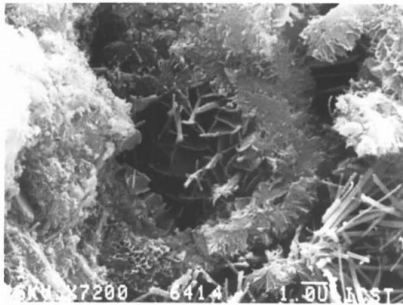
Summary



Exhaustion of sulfate



Calcium monosulfo aluminate
"AFm"



Paste at 7 days
Formation of monosulfo
inside C-S-H shell.
Ettringite remains outside grain

And then the second reaction here, can be described as a reaction of C3A with some of the ettringite already formed, to give us this calcium monosulfoaluminate. So we see that for the reaction of C3A to continue, some of the ettringite gets used up to form monosulfate. But not all the ettringite disappears. So this micrograph down here clearly shows that we still got a lot of ettringite in this space out here whereas inside this hydrate shell we have got these plates of monosulfoaluminates. So it is not all the ettringite that disappears.

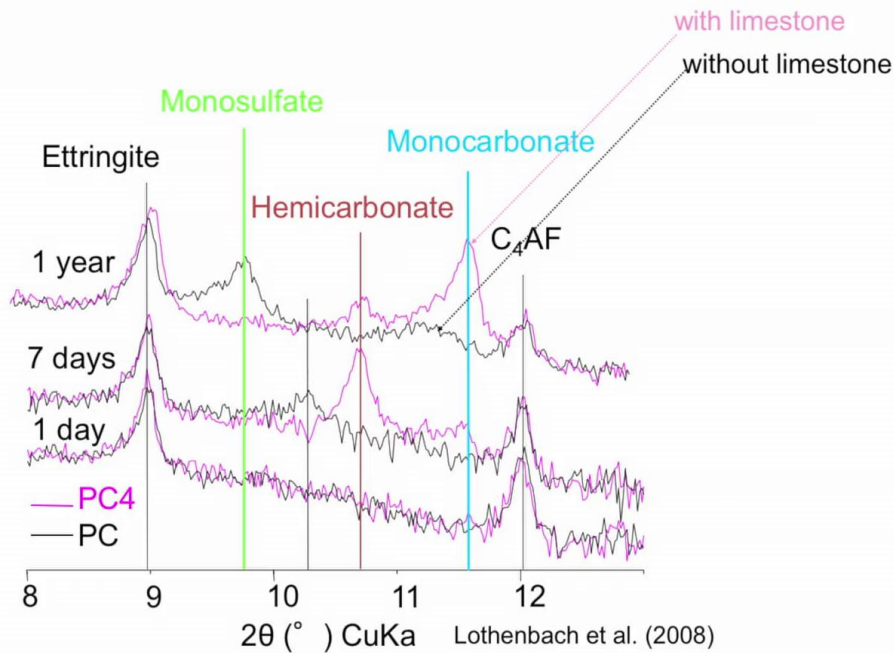
Notes

Summary



4m 43s

Afm phases: effect of limestone addition



As we talked about in the previous module, nowadays we have usually small additions of limestone in the cement and these small additions of limestone mean that instead of forming monosulfate, which we see here in the cement without limestone, what we actually form is now hemi or monocarboaluminate. So generally hemi and monocarboaluminates are replacing monosulfate in most cements you see today.

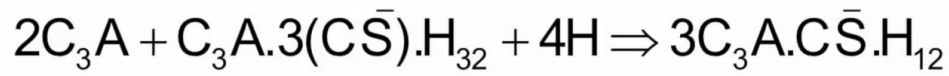
Notes

Summary

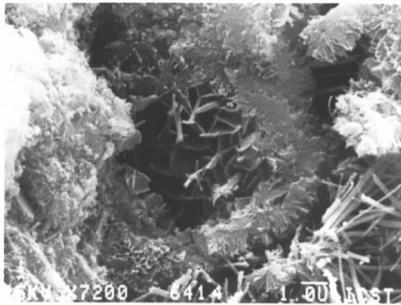


5m 27s

Exhaustion of sulfate



Calcium monosulfo aluminate
"AFm"



Paste at 7 days
Formation of monosulfo
inside C-S-H shell.
Ettringite remains outside grain

You won't really be able to see any difference in terms of the micrographs here, because the morphology of hemi and monocarboaluminate is very similar to what we have with monosulfate.

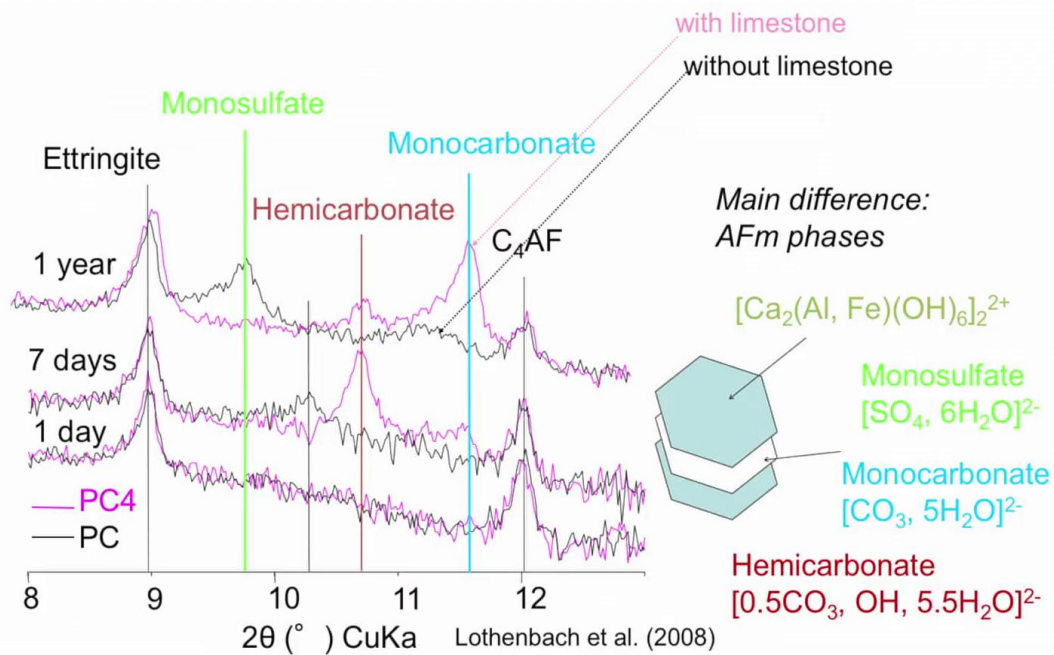
Notes

Summary



5m 58s

AFm phases: effect of limestone addition



We describe the differences between these AFm phases in the previous module on the aluminate hydrates.

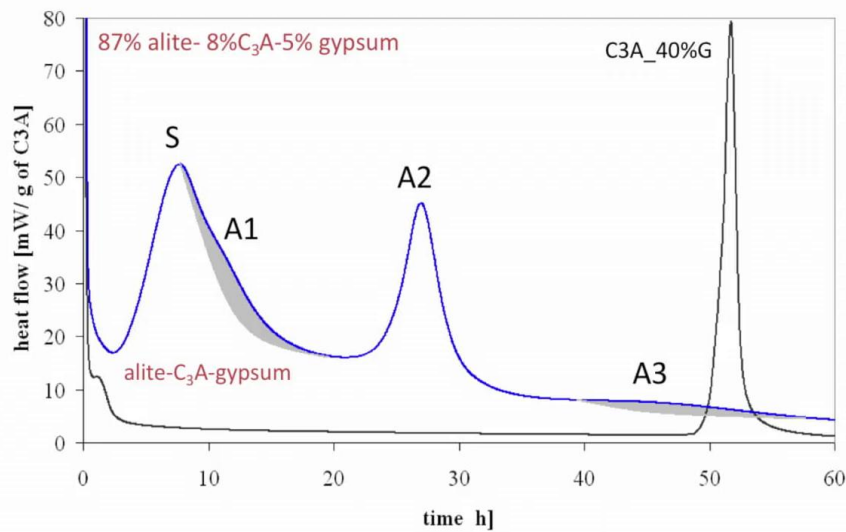
Notes

Summary



6m 11s

Mixture of Alite and C3A



- Multiple aluminate peaks when hydration occurs in the presence of alite

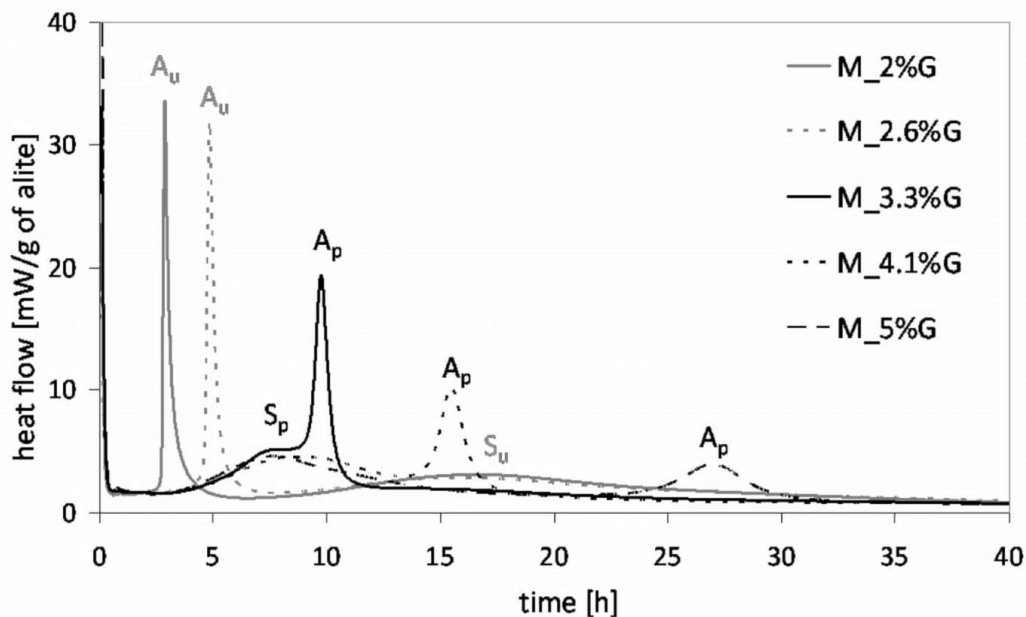
That is not the end of the story because when you put the alite and the C3A together, you get quite a lot of complex interactions. So this blue curve here shows the heat evolution we get from a synthesized clinker, which is composed of alite and C3A but no ferrite and the pure C3A and gypsum on its own. And what we see in the mixture, we can actually identify three peaks which are related to the reaction of the aluminate phases. We can see this kind of shoulder peak which we call A1, then we can see this quite pronounced peak A2, and finally this is rather small in defined peak, which we call A3. Now this A1 peak has often been said to be the formation of monosulfate but that is actually not correct as we are going to see.

Notes

Summary



Sufficient gypsum to ensure aluminate reaction after silicate



Quennoz and Scrivener 2013

Silicate reaction reduced if aluminate reaction occurs first,

Undersulfation, can be exacerbated with admistures

So before we go into that in more detail, the important point to emphasize is the need to have enough gypsum in your mixture, in order to make sure that the aluminate reactions or the main aluminate reactions are occurring after the silicate reactions. So here we see these same mixtures with progressively larger amounts of gypsum, and as we add more and more gypsum, you see this very strong peak here shifts later and later in time. Now if we have too low amounts of gypsum, then you see this big aluminate peak occurs before the silicate peak. And as a consequence, that silicate peak, which was here in the properly sulfated ones, gets shifted to much later ages and it is much lower. So this violent reaction of the aluminate really inhibits the reaction of the silicate phases and will be very damaging in terms of strength development. So this is very, very important that we need a proper amount of sulfate to make sure that this main aluminate peak is well after the silicate peak. In this case here, it would be preferable to go for this system here which is 4.1% gypsum, where you see the large peak is occurring really well after the silicate peak.

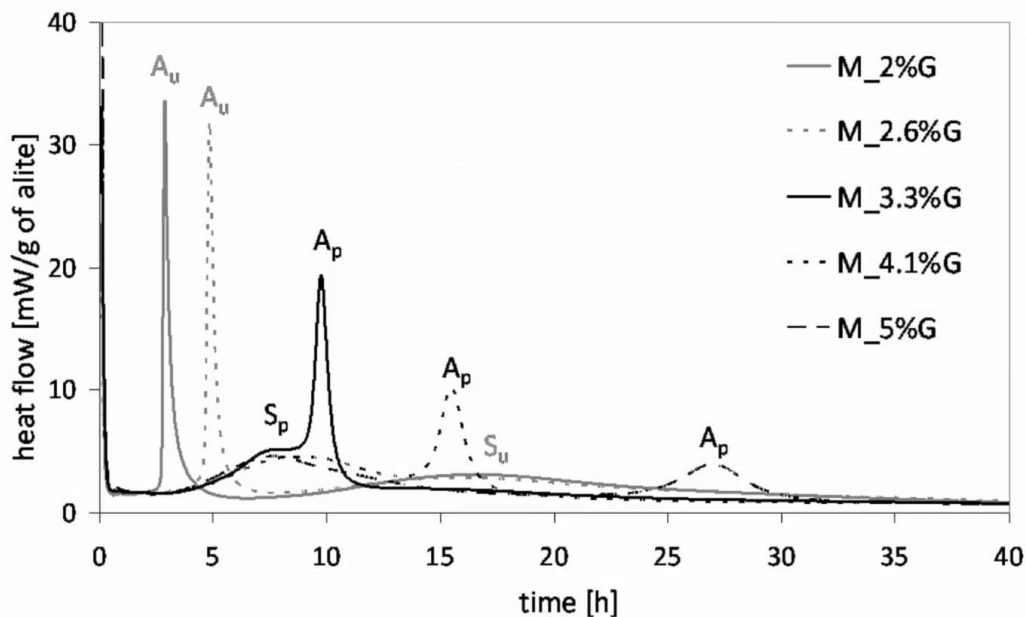
Notes

Summary



7m 26s

Sufficient gypsum to ensure aluminate reaction after silicate



Quennoz and Scrivener 2013

Silicate reaction reduced if aluminate reaction occurs first,

Undersulfation, can be exacerbated with admistures

If we went for this one here we would have a risk that we could destabilize this sulfation if we had any admixtures in the system. And this is a very common problem particularly in North America where people are adding not only admixtures but often supplementary cementitious materials like fly ash at the concrete stage. And when you have all these things coming together, you can quite easily destabilize the reactions and have this aluminate reaction occurring too early, with the consequence of really impeding the reaction of the silicates.

Notes

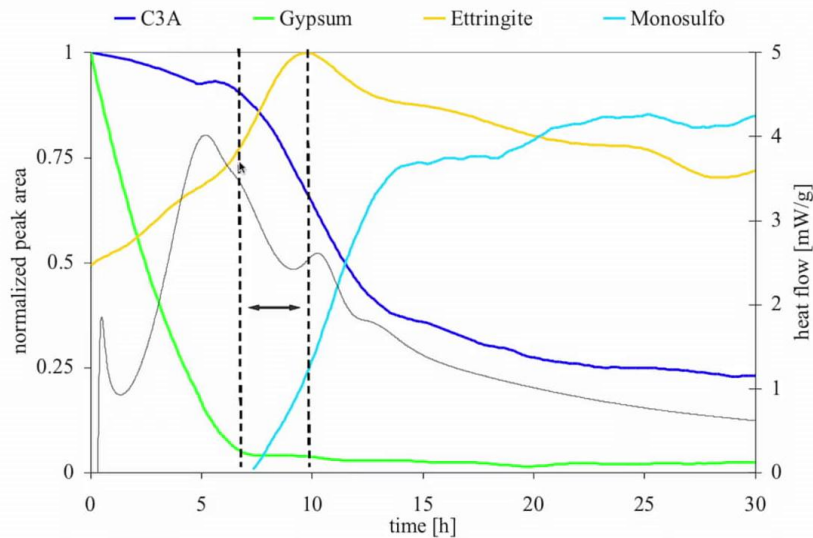
Summary



8m 59s

Multiple aluminate peaks

- Peak A1 → second formation of ettringite
[Scrivener, 1984]



So let's come back now to this peak A1. And here we see the calorimetry output, we can see this shoulder peak just here, this A1 peak and then this A2 peak here. Now it is really quite complex what is happening. If we look at the solid gypsum which is this green line here, we can see that the solid gypsum is more or less exhausted just at the point where we start to help the onset of this A1 shoulder peak. But, even though the solid gypsum seems to have been exhausted, we can see that during this A1 peak here, the main solid phase that is forming is in fact still ettringite. And see here on this yellow curve, the amount of ettringite is continuing to go up. And it is not really until somewhat later that we can see a significant formation of the monosulfate, more associated with this A2 peak. So how can this be? How can it be that even though the solid gypsum has been exhausted, we can still go on forming ettringite?

Notes

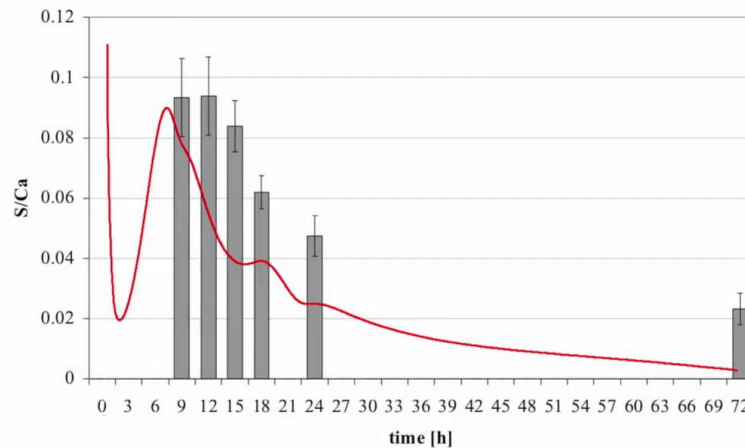
Summary



9m 44s

Multiple aluminate peaks

- Peak A1 → second formation of ettringite [Scrivener, 1984]
- Reaction of C_3A with sulfate ions desorbed from C-S-H



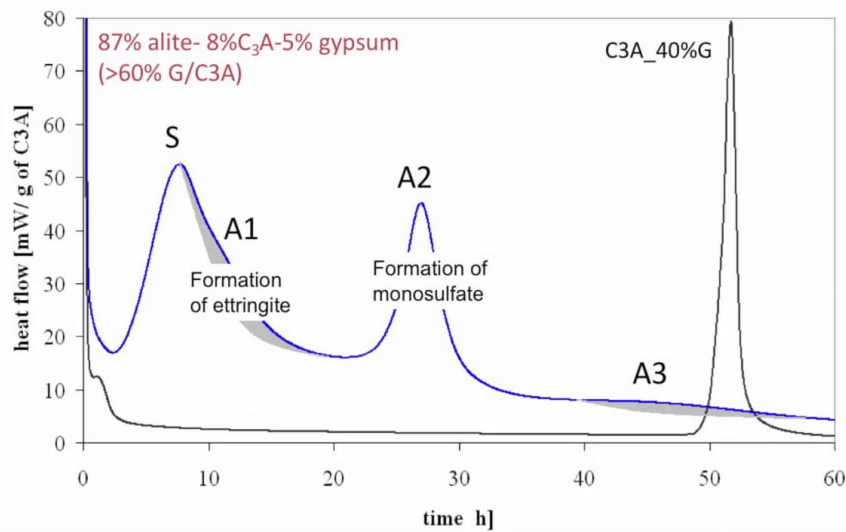
Well the reason is this, that sulfate can be absorbed on the calcium silicate hydrate. So during the acceleration part of the curve, the silicate is reacting. It is forming CSH and as it is forming CSH, because the sulfate in solution is quite high, quite a lot of it gets absorbed on the CSH. Here you can see measurements taken in the SEM of the ratios between sulfate and calcium in the CSH. So we can see here the sulfate on the CSH is quite high and then as we come through this A1 peak you can see it is really dropping. So this is the extra source of sulfate that we needed to keep forming ettringite as we are seeing in the previous slide here.

Notes

Summary



Mixture of Alite and C3A



- Multiple aluminate peaks when hydration occurs in the presence of alite

Let's come back to this peak here. We can now really confirm that this A1 peak is the formation of ettringite and this A2 peak is the formation of monosulfate. And it is also important to observe that this impact of sulfate being absorbed on the CSH also changes the time of this A2 peak, compared to a pure system. So here we see what was happening in a binary mixture of C3A and forty percent gypsum. We had this monosulfate peak at about 50 hours and now in this mixture, where we have got the equivalent of more than 60% of gypsum compared to the C3A, this A2 peak is only at about 25-30 hours. And the reason it has moved up here is that a lot of the sulfate is lost to the system because it gets absorbed on the CSH. So we have got quite a lot of complex interactions and you may have noticed I haven't yet said anything about the peak A3 because we still don't really know why we have this peak here. It is not really been possible to associate that with any obvious reaction.

Notes

Summary





- Presence of sulfate modifies reaction of aluminate (& ferrite) phase
- Small initial reaction, then induction period which should be long enough to allow silicate to react.
- When sulfate exhausted in solution, second burst of aluminate reaction with formation of ettringite from sulfate absorbed on C-S-H
- Monosulfate (or monocarbonate forms) typically after a few days

So what we are seeing in this module is that it is very important that the sulfate present from the addition of gypsum, drastically modifies the reaction of the aluminate and the ferrite phases. You get a small initial reaction during which sulfate ions are absorbed on the surface of the aluminate and then an induction period. And what is important is that this induction period must be long enough to allow the silicate to react. If it is not long enough, you will inhibit the silicate reaction and get very big problems of strength development. And then the solid gypsum is slowly reacting and when the sulfate in solution is exhausted, you get a second burst of the aluminate reaction but you are still forming ettringite with sulfate that was previously absorbed on the CSH. And then later, typically after a few days, we form calcium aluminate monosulfate or more typically hemi or monocarbo aluminate when we have small amounts of limestone in the cements. So that was the last module on the reaction kinetics and then in the final one in this group on hydration, we will talk about bringing all this together to look at the microstructure formation. Thank you.

Notes

Summary



13m 22s