



- For a properly regulated cement (enough rapidly soluble calcium sulfate added),
- hydration and structure development is dominated by the reaction of C_3S

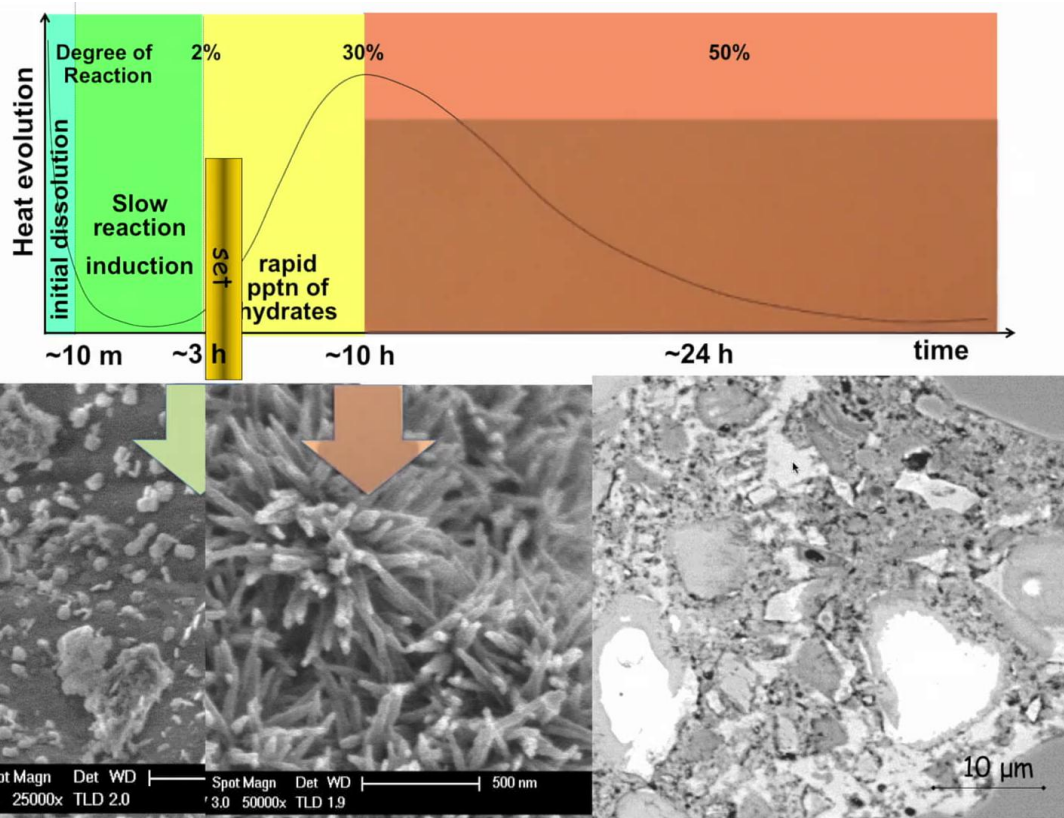
So welcome. This is the last module in the sequence about hydration reactions and in this one we bring together everything we have seen in the previous modules to look at how these results in the microstructure we have in hardened cement pastes. Now what I am going to talk about here is of course properly regulated cements, enough soluble calcium sulfate added, and as we saw in the last module, this means that the aluminate, main aluminate reactions, occurs after the silicate reaction. And it therefore means that the hydration and structure development is really dominated by the reaction of C_3S or alite.

Notes

Summary



0m 04s



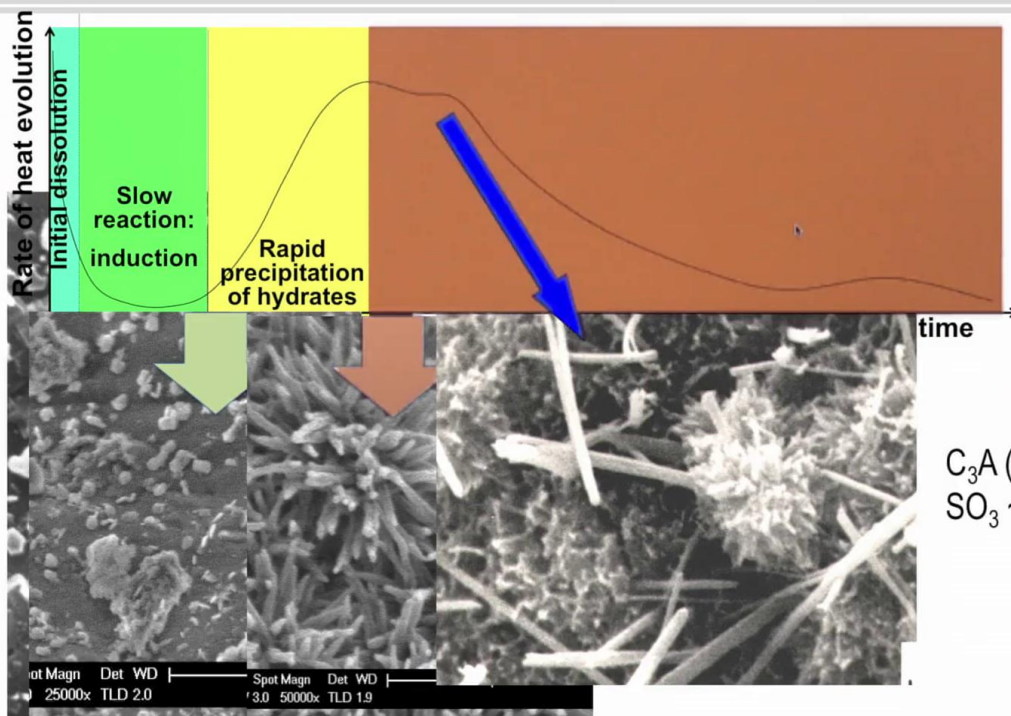
Now this is the calorimetry heat evolution curve we have seen several times before, we have talked about the mechanisms that control the reactions throughout this. First of all the induction period controlled by the buildup of ions in solution, then acceleration and deceleration controlled by the growth of the CSH needles on the surface and finally the slow ongoing reaction. And just to relate that to the physical properties, the setting of the cement is usually occurring at middle to beginning of the acceleration period. Now let's look at how this heat evolution curve is linked to what we see microstructurally. So if we first consider the case for the silicates, what we see at the end of the induction period is we get this first formation of CSH starting to grow on the surface of the grains. And then that CSH develops very rapidly as these needles, so by ten hours we see these long needles from the surface. And then the hydration goes on and finally we end up with the microstructure like this, where we have the cement grains which are embedded in this matrix mainly of CSH and ettringite, which is all this stuff here, and then some calcium hydroxide which is this stuff here.

Notes

Summary



Reaction of Portland cement:

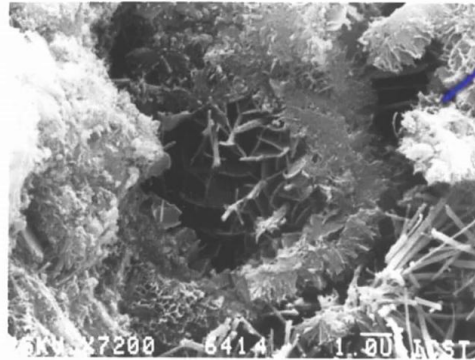
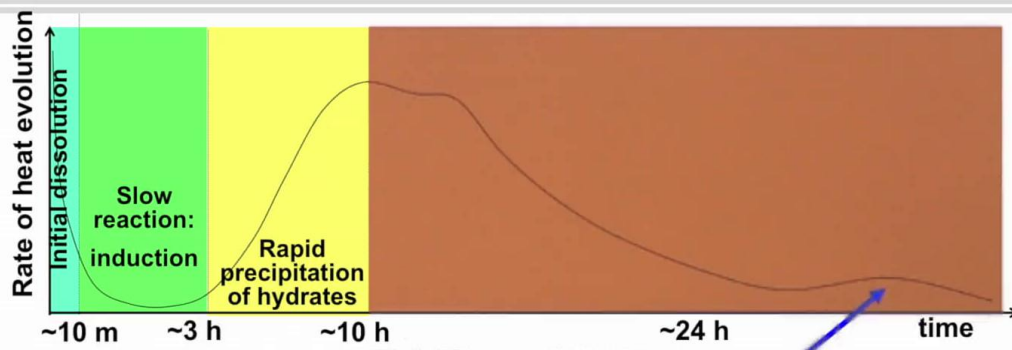


Now if we now add in the aluminate, so we have Portland cement rather than alite, during the very early reaction of the alite we can form some very small ettringite needles but again I would like to stress that it is not those very small needles that are inhibiting the reaction, it is the absorption of sulfate ions on the surface. And this absorption of sulfate ions on the aluminate suppresses the aluminate reaction so that it allows the silicates to react, so here we see the silicates reacting as before and then when we come to this shoulder peak here we see very clearly the second growth of ettringite, we see these long ettringite needles which are formed during that shoulder peak. And then as we go on we may not always see it but in this case we have got a small hydration hump here and this is associated with the formation of the monosulfate.

Notes

Summary





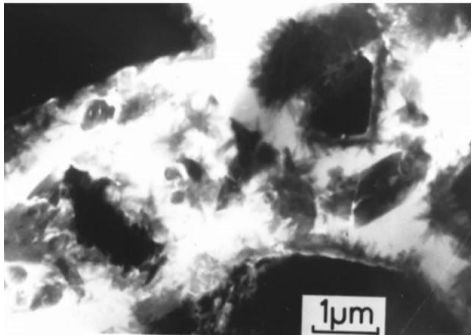
Monosulfate
In hadley grain
After 2-3
days hydration

Notes

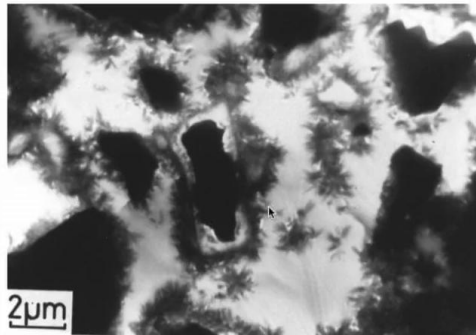
Summary



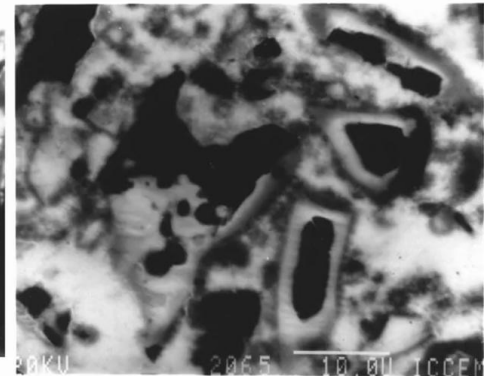
Formation of Hadley grains (thesis Scrivener 1984)



5hrs cement paste: ion thinned section



12hr cement paste: ion thinned section



18 hr cement paste:
SEM/BSE, inverse contrast

Now another aspect I want to mention is this formation of so-called Hadley grains. Now Hadley was a student working in the 70's who noticed that sometimes you could see that you had these kind of shells which appeared empty. And in fact we see that generally if we look at these transmission electron micrographs, we can see even from very early ages, even as early as five hours, we can see we get the small separation of the shell and the reacting grain. So what happens is we seem to form this layer of hydrates here and then the anhydrous grain goes on reacting but the products are deposited outside, probably because we have this preferential growth of the CSH needles that we discussed a few modules back.

Notes

Summary

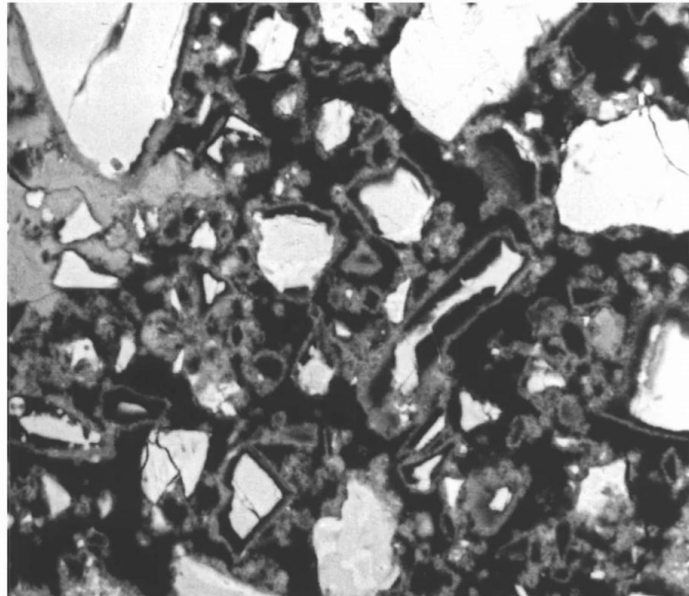


3m 30s

For some (as yet unknown) reason the outer C-S-H, which forms during the main heat evolution peak does not form in contact with the underlying grain.

This "shell" of hydrates seems to grow on the outside, so that the gap between the shell and the grain increases up to about 24 hours

The presence of aluminate seems to be important as these shells are not so clearly separated in the case of C3S



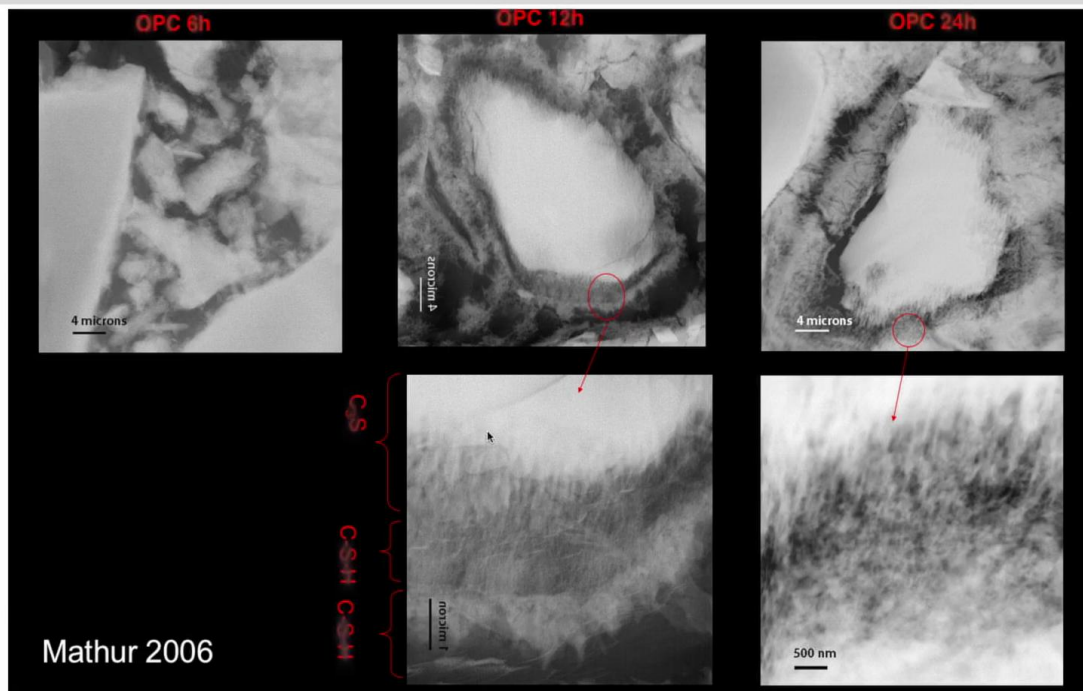
And this is just another micrograph, this time taken with backscattered electrons, where you can see just how generalized these gaps are around the anhydrous grains. Now we don't really know exactly why these form like this, but we can say that it is very much amplified by the presence of aluminates. We get a small separation in the case of pure C3S but it is very much more apparent when we have a Portland cement, when we have the silicates aluminates reacting together.

Notes

Summary



TEM studies



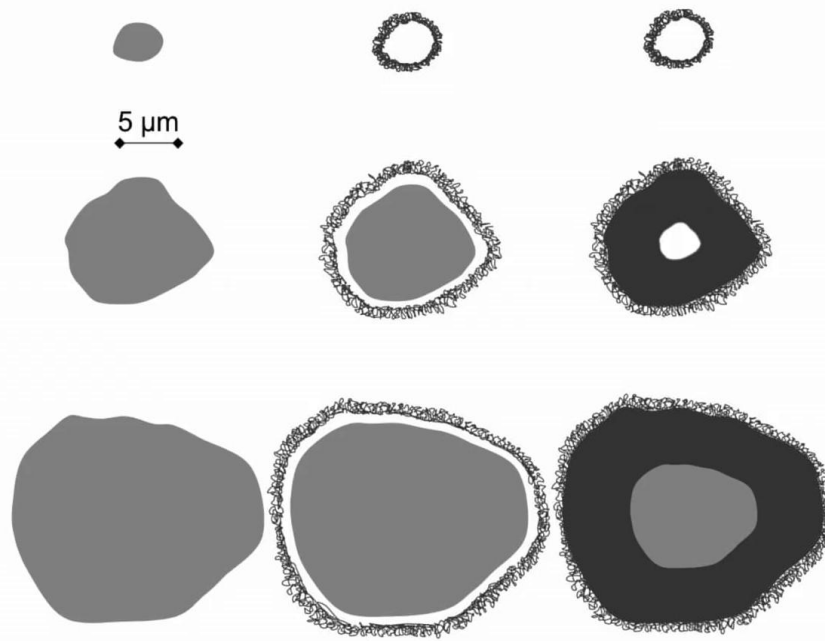
And here are other pictures again by transmission electron microscope. We can see that if we now have a very careful specimen preparation, we can see this very kind of fragile looking shell of hydrates but in fact the space in-between is not completely empty. It seems to be filled with a very dispersed diffuse product. And another interesting aspect is that this anhydrous grain here is not reacting evenly on the surface that is actually quite deep, itching along certain crystallographic directions.

Notes

Summary



5m 09s



The eventual evolution of these “Hadley” grains depends on the size of the grain. Large ones the gap fill in, small ones remain empty

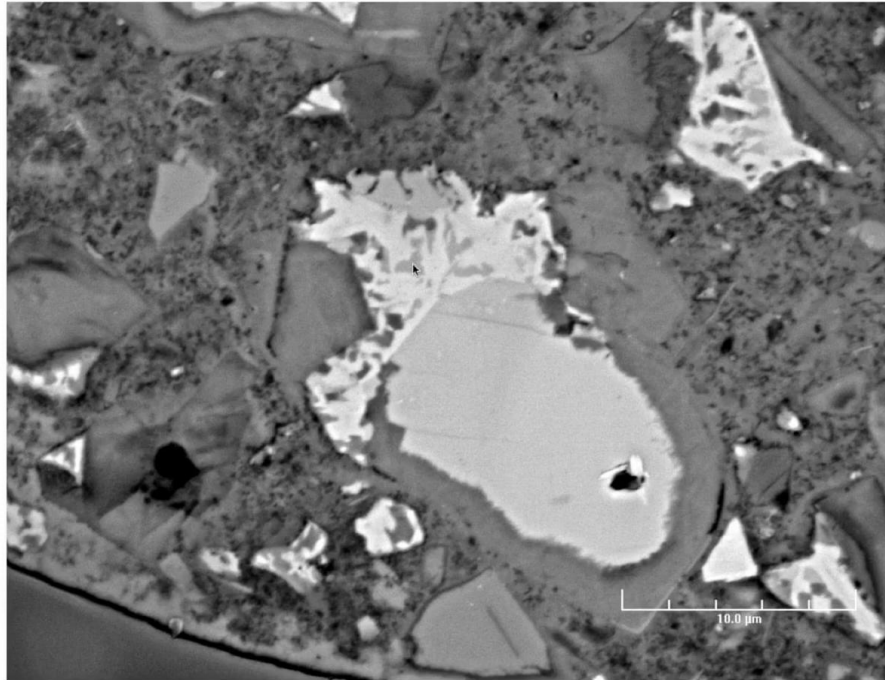
So what happens to these separated shells, all these Hadley grains over time really depends on the size of the grains. If we have very small grains, five microns or less, then these will very quickly react during the main hydration peak and they will leave this kind of shell of hydrates which persists indefinitely. If the grain is a bit bigger, so in the second case here we have a grain maybe about ten to fifteen microns, then after the main heat evolution peak, this anhydrous material will continue to react but it may leave a small hole in the middle. And finally if we have large grains, greater than say about fifteen to twenty microns, then during the later hydration this separation between the shell and the anhydrous grain completely fills in and disappears.

Notes

Summary



5m 51s



And we can see those in this micrograph here. If you look carefully at this micrograph you can see many little hollow shells which are small grains which completely reacted. So we have got this one here for example, we have got one down here which is slightly larger and therefore we have got a slightly thicker shell, we have got another one here and the more you look you can really see that these little hollow shells are everywhere. But for the larger grains, notably this one in the middle here, this separation has completely filled in and we get this thick rim of inner product. We can still see though that the surface of the reacting anhydrous grain is still quite rough. This roughness that emerged really quite early on is persisting because it seems we can have probably defects along certain crystallographic directions, which make them more soluble than others. Of course in this micrograph we can also see that of course we got the reaction of the alite, here we have got the interstitial phases, the ferrite and the aluminate. Now close to the surface the aluminate has all disappeared, but here where it is embedded in the ferrite, we can still see small regions of aluminate phases that have not reacted yet.

Notes

Summary



6m 55s

Overview, Scrivener 1984

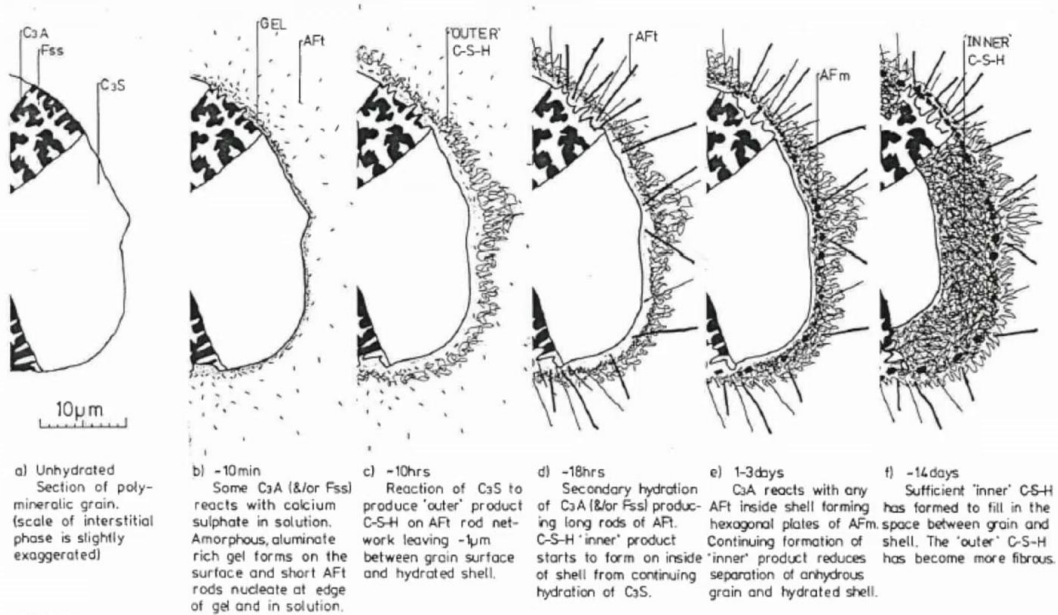


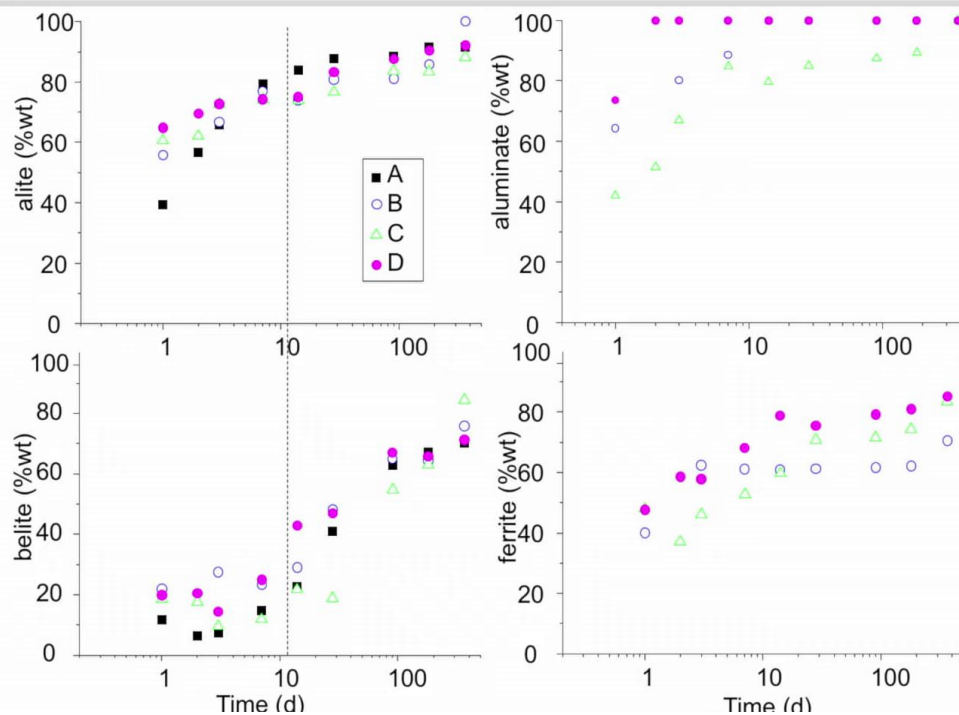
FIG. 6.1 Microstructural Development during the Hydration of Portland Cement

These aspects are brought together in this drawing I made quite some years ago now, which really summarized the micro structural development around one grain of cement.

Notes

Summary





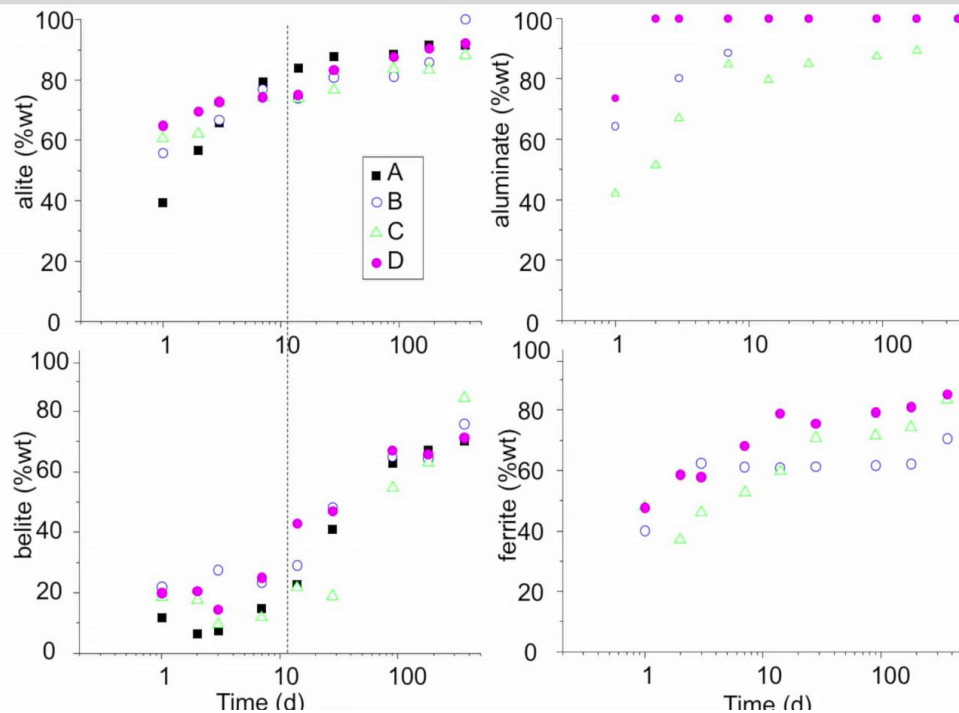
Another aspect which is important to talk about is to look at the different phases. So really we have very much emphasized the reactions of C3S and then of aluminate because these are the ones that react most. So in this graph here you see data from the literature for the 4 main phases, so we have alite here, we have aluminate here, belite here and ferrite here, and then we have very similar data for four different cements which were studied in the PhD of Vanessa Kocaba. Now what is very important is you can see that the alite is reacting most early on, that is to say one day we have degrees of reaction between 40% and 70%. Really very, very high. And then that is increasing at say about 28 days to about 80% and as we go on to 90-100 days, it is approaching 100%. The aluminate reaction, also very fast. You see we have high degrees of reaction at 1 day, again between 40 and 80% and in some cases it is very quickly going up to 100% in just a few days. In other cases where it is more embedded in ferrite for example then it may take somewhat longer. So now we come to the other two phases we have hardly discussed at all and we see in general the reaction of these two is much slower, notably the belite.

Notes

Summary



8m 42s



And this is very important. I said several times before that it doesn't make any sense to produce high belite cements because of the slow reactivity of the belite. But we almost see that there really is this interaction between alite and belite. That is to say while we have this fast reaction of alite as we see here, the reaction of belite is hardly happening at all. So alite reaction actually suppresses belite reaction. And it is really only after ten days and more when the alite has more or less all reacted that the belite reaction is starting to have any impact at all. Ferrite is a kind of intermediate case. In fact we see that at 1 day the degrees of reaction may be quite high, about 40%, that is similar to the aluminate, but then it really slows down. And the reason for this is this low solubility of iron in alkaline solution so that after a bit of the ferrite phases reacted you kind of clogged up the surface with first of all amorphous iron hydroxide, which really stops the rest of the phase reacting.

Notes

Summary



- Belite:-
little reaction before 10 days (thermodynamics)
- Aluminate:
fast, but slowed by ferrite in grey cements
- Ferrite:
slow but significant

That is just summarized here that we have little reaction before ten days and that is actually thermodynamically controlled, because of the reaction of the alite phase, it suppresses the dissolution of the belite phase. The aluminate is fast, but it can be slowed down by the presence of ferrite in grey cements. and that is actually thermodynamically controlled, because of the reaction of the alite phase, it suppresses the dissolution of the belite phase. The aluminate is fast, but it can be slowed down by the presence of ferrite in grey cements. And the ferrite is slow but it can quite be significant even at one day.

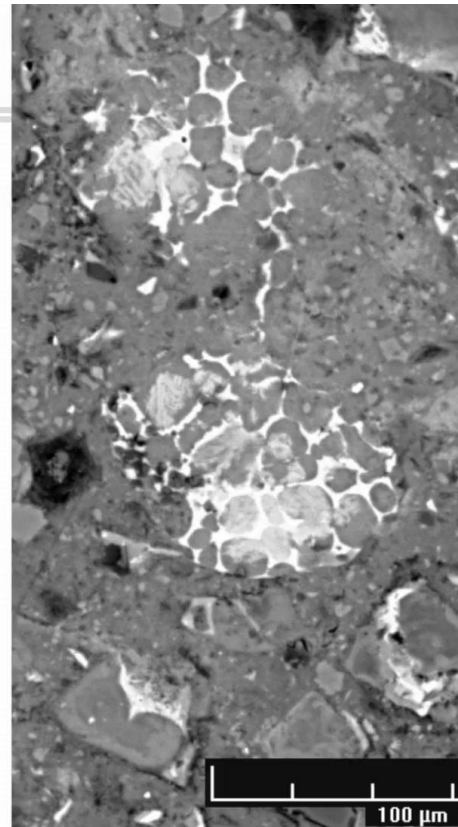
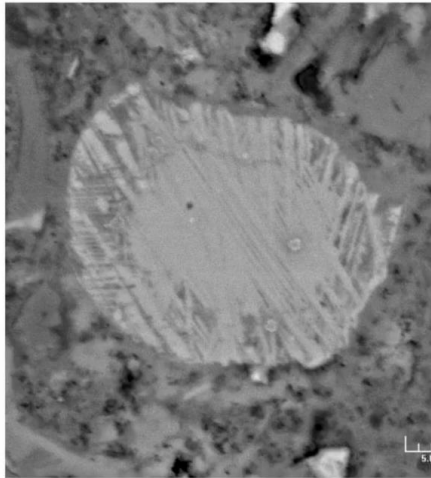
Notes

Summary



11m 52s

Reaction of Belite



Now if we look at the reaction of these phases in the microstructure, belite often gives us this very interesting pattern of reaction, we can see that certain striations have reacted, while others have not reacted. And the reason for this is that during the cooling of belite, you get these multiple phase transformations, which often occur by twinning and then solutes tend to accumulate in some twins and not in others. And it is generally the parts which have the high solute content which are more reactive and can react. So you see that the depth of reaction here is several microns but then we still have got a kernel in the middle which is unreacted. And this you can see even in very old cements, this micrograph here on the right comes from a piece of concrete that is about thirty years old and you can see these large clinker grain, this was a cluster of belite, this is quite typical in cements. You want to minimize these grains but they do occur and you see in this cluster of belite that quite a bit of the belite still hasn't reacted even after thirty years.

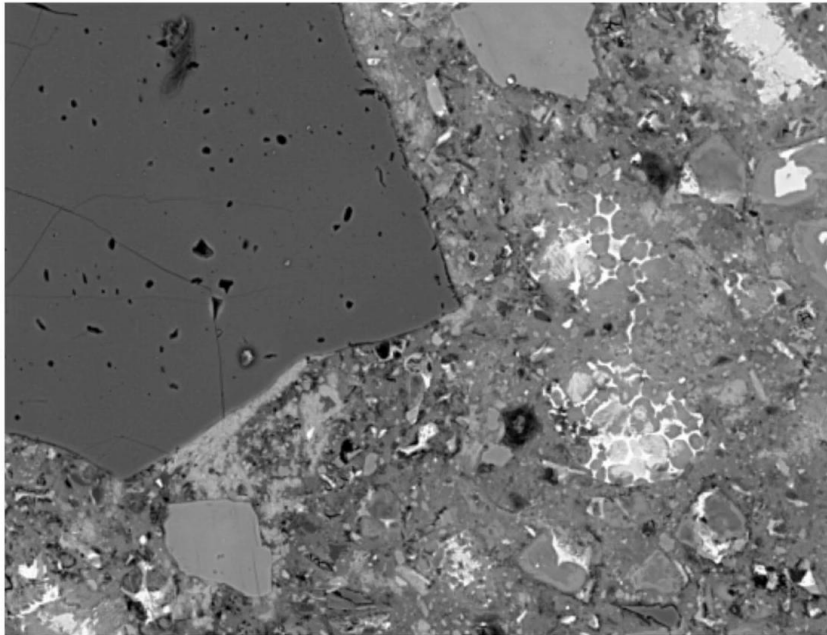
Notes

Summary



12m 20s

Old concrete, only belite and ferrite apparent



Now in that micrograph, this is like a zoom out of the one before, now the only unreacted phases we see in this thirty year old concrete, are really belite and of course the ferrite phase. This is the ferrite phase, these bright areas here.

Notes

Summary

13m 43s



Reaction of ferrite phase

- XRD shows reaction but in BSE appears unreacted
- Probable that A and C “leach” out leaving Fe “relic” of ferritic siliceous hydrogarnet

And if look at this backscattered electron image which is what we saw in the previous slide, it appears that the ferrite hasn't reacted even though when we go to the x-ray diffraction, it shows us that the ferrite phase has disappeared. And what happens is that the aluminate and calcium components kind of leach out, they disappear and form the normal hydrates leaving this relic of ferritic siliceous hydrogarnet. And this is what has been seen in quite old pastes, even after a few months or so, but the dominant phase from the ferrite is this siliceous hydrogarnet.

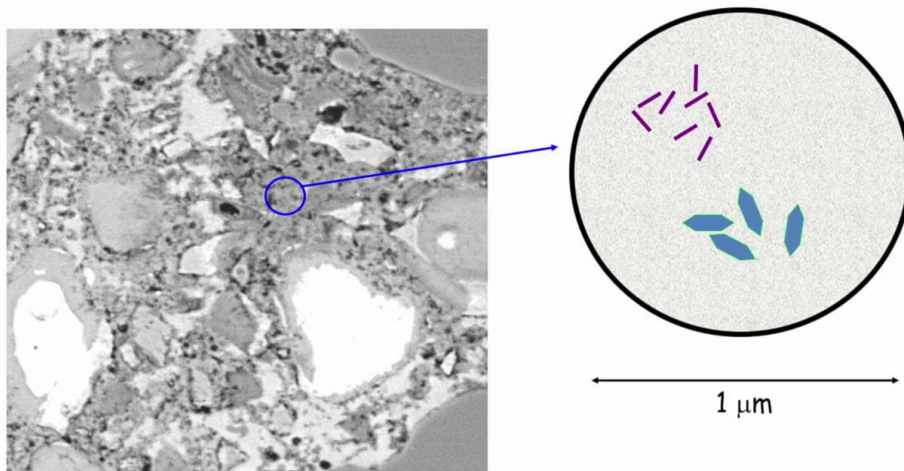
Notes

Summary



14m 04s

Aluminates in hardened cement paste



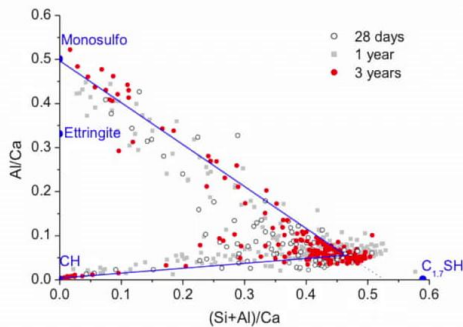
Intermixing of ettringite and/or Monosulfate at submicron scale

Now coming back to the overall microstructure, we have shown this micrograph several times and what I want to do here is to remind you that this hydrate phase that is between the grains, everything that isn't calcium hydroxide is really a very fine mixture of CSH with ettringite or with mono AFm phases, monocarbonate, monosulfate, really mixed at this very fine scale below one micron.

Notes

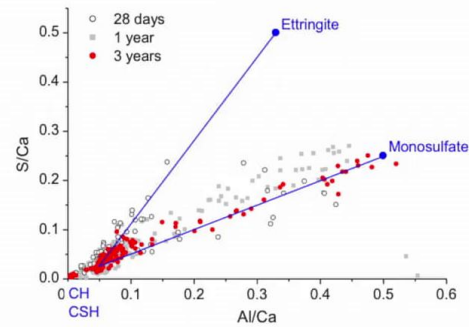
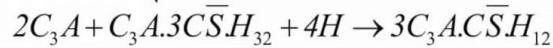
Summary





28 days. Formation of C-S-H, CH

ettringite and then monosulfate



1, 3 years. Further formation of C-S-H, CH

Reaction of ettringite into monosulfate

thesis Lamberet 2005

And we can see further evidence of this by looking at these microanalysis, if we make microanalysis and then we plot them on these graphs of alumina calcium versus silica to calcium or sulfur to calcium versus aluminate to calcium, we can see that what we have here, we have this cluster of points, we see here and we see here, which is CSH, but the fact we get points extending along these lines is really showing us that we have mixtures either of calcium hydroxide with portlandite, with calcium hydroxide along this line or with CSH with either ettringite or monosulfate. And we can see more clearly in this graph down here that we can differentiate much more easily between whether we have mixtures with ettringite or with monosulfate. So here this is at 28 days, we see we still got quite a lot of ettringite intermixed with the CSH, a little bit of monosulfate and as we go on, first to one year and then to three years, we still see this very gradual shift as further ferrite probably reacts to now getting much more points along the monosulfate line. But we always see this persistence of this spread, this cluster of CSH points due to the intermixing. And you know I want to emphasize that what we analyze here in the SEM, we are always analyzing a volume of 1 to 2 microns in dimension, which is why we see together these several different phases.

Notes

Summary



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 just to summarize this microstructure part, what we saw at the beginning was the same as what we saw in the reaction of the aluminate part that the presence of sulfate modifies the reaction, we get a smaller initial reaction and then this long induction period. When the sulfate in solution is exhausted, we get this second burst of aluminate formation. And then finally the monosulfate or monocarbonate formation.

Notes

Summary



17m 08s



- Hadley grain formation
- Belite reaction only significant after about 10 days (inhibited by alite reaction)
- Ferrite reacts to poorly crystalline ferritic siliceous hydrogarnet
- Aluminate phases mainly finely dispersed in C-S-H

And what we also saw in this module, we talked a little bit about Hadley grain formation where we get these separated shells. We talked about the rates of reaction of the different phases and really emphasize that the belite reaction is very slow, only significant after about ten days because it is inhibited by alite. We talked a bit about the ferrite, it seems to be unreactive, it certainly doesn't move much, it stays in the same place but in fact it seems to react to form this poorly crystalline ferritic siliceous hydrogarnet. And then at the end we emphasized the fact that the aluminate phases were the ettringite or AFm phases are mainly finely dispersed within the CSH. So that is the last one in this series about hydration. I hope you have found something interesting and enjoy the rest of the course on characterization methods. Thank you very much.

Notes

Summary



17m 37s