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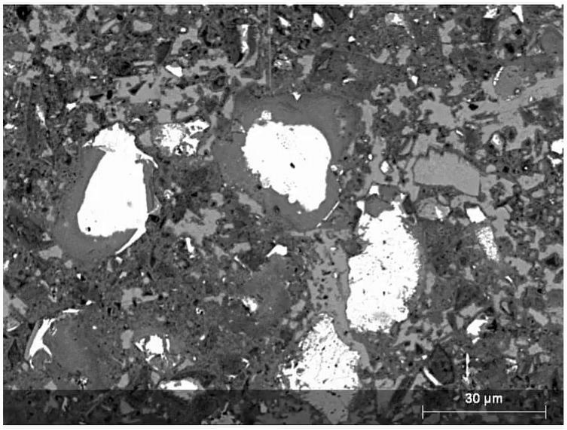
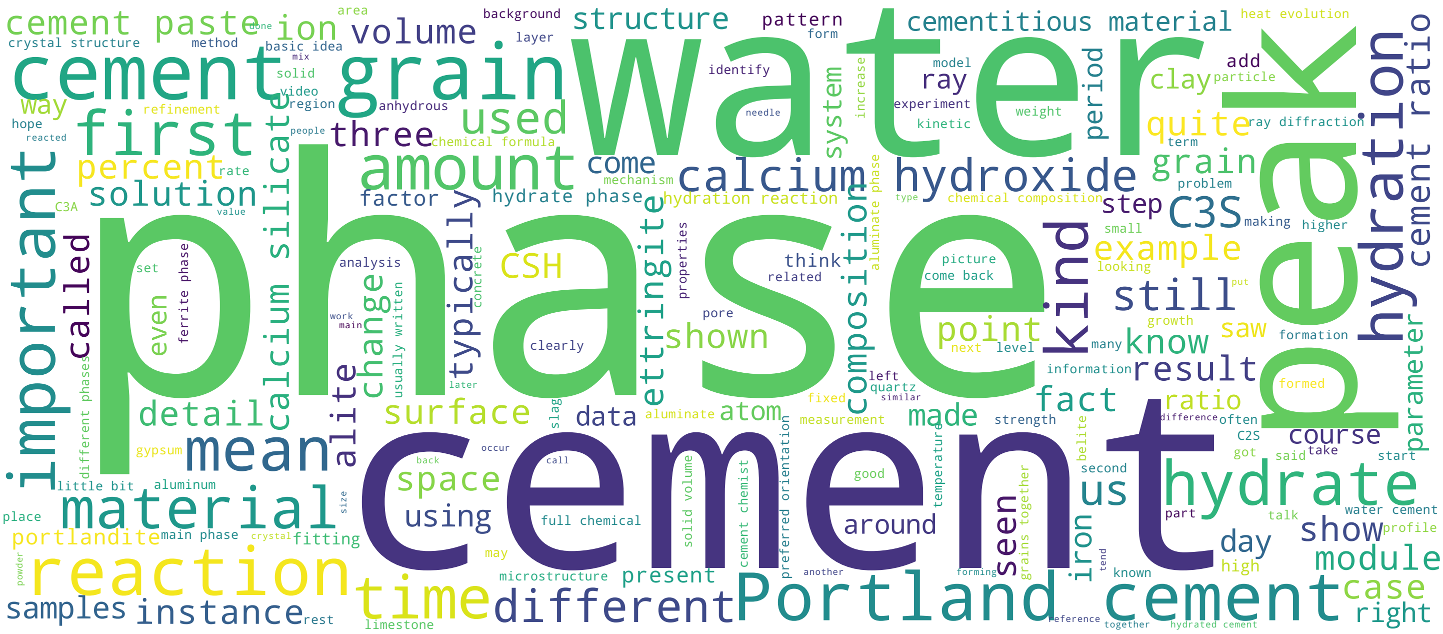


Hydration 1: Overview

Cement Chemistry and Sustainable Cementitious Materials

Professor Karen Scrivener, FREng



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Video

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Cement chemistry: Nomenclature

As cement is composed of oxides a particular notation is used to shorten chemical formulae

Calcium oxide or lime:	$CaO = C$
Silicon dioxide or silica:	$SiO_2 = S$
Aluminium oxide or alumina:	$Al_2O_3 = A$
Iron oxide:	$Fe_2O_3 = F$
"sulfate":	$SO_3 = \bar{S}$ or \$
Water:	$H_2O = H$

So welcome back. In this module, we will be talking about the hydration reactions. And this is clearly the fundamental aspect which is responsible for the behaviour of cementitious materials. In this first module I am going to give you an overview of what hydration is, the different phases we have present and how they contribute to this hydration process. In later videos, we are going to look in more detail at these individual hydrate phases and then the mechanisms of hydration. So before we go on we have a question of nomenclature. Now cement chemists are a little bit lazy and because we are generally dealing with oxides we have a shorthand to shorten the chemical formula. Now you need to know this but it is really quite simple. Basically, calcium oxide or lime, which is written Ca0 in full chemical notation, becomes simply C. Similarly, silicon dioxide or silica, which is SiO2 in the form location, becomes S, aluminum oxide or alumina, Al2O3, becomes A, iron oxide becomes F, sulfate becomes S bar or S dollar or dollar sign and water becomes H. So to give some examples you can see how the formulae are shortened.

Notes

Summary

0m 04s

Examples

Tricalcium silicate or alite: $Ca_3SiO_5 = C_3S$

Ye'elimite: $Ca_4Al_6SO_{16} = C_4A_3\$$

Calcium silicate hydrate: $Ca_XSiH_YO_{(X+2+Y)}$ = C-S-H

Hyphens indicate variable ratios of lime silica and water

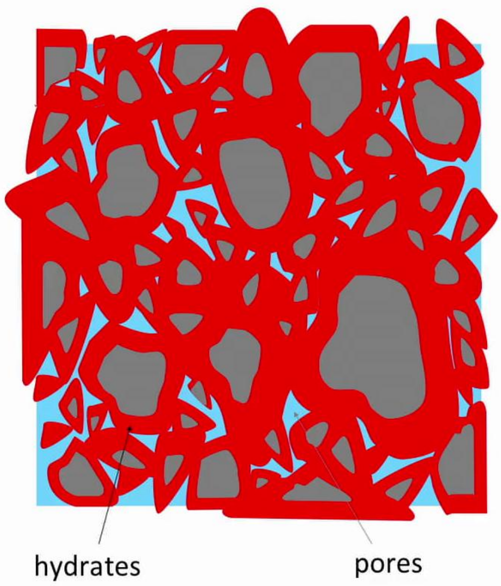
So if we talk about the main phase that is reacting in Portland cement, this is called tri calcium silicate or alite. And in the full chemical formula this has to be mentioned as Ca3SiO5. It is quite long but this can be simply shortened by the cement chemist notation to C3S and it is often also known by this name C3S. if we look at another reactive mineral that we may find in calcium sulfo aluminates cements, this is called ye'elimite, it is the mineral name, and the full chemical formula is even more complex Ca4Al6SO16 and this can simply be shortened to C4A3$ and that is often known by that phrase C4A3$. It is still a bit of a mouthful but not as bad as this one over here. If we now go on to the hydrates, notably calcium silicate hydrate, which is making up the majority of cementitious microstructures, we have a further complication that the stoichiometry of this phase is not fixed, it varies quite widely as we will talk about subsequently. In the full chemical formula, I have represented that variability by the X's and Y's but on the right here we see the way it is usually written by cement chemists that we use hyphens here to denote that the ratios between these different elements are not fixed and we normally call this phase C-S-H. So this is very important to remember this terminology.

Notes

Summary

1m 42s

How cement works:



The cement grains dissolve in the water

And then precipitate *Hydrates* – new solids which have higher volume and hold the grains together: creating a rigid solid

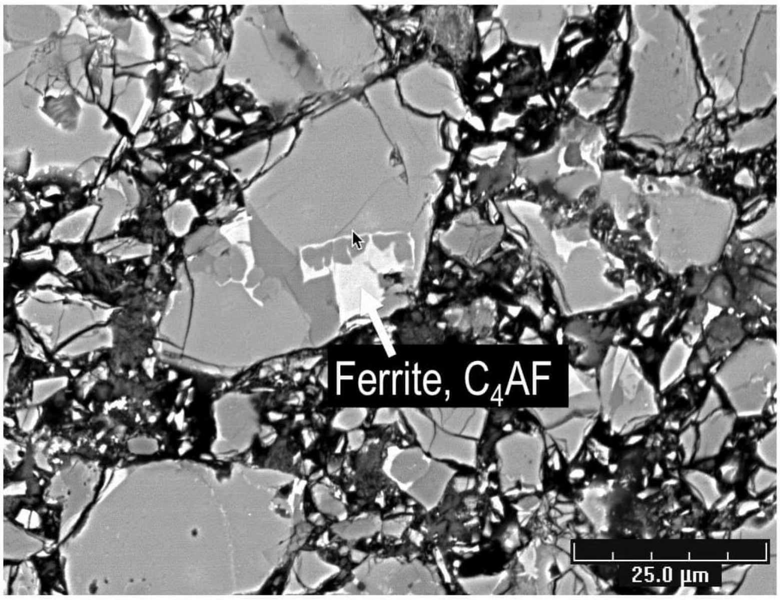
OK. So let's go back to the schematics. We saw these in the earlier lecture to give a very basic idea of how cement works and I really want to stress that it is all to do with volumes. So when we mix the grey powder with water what we have is these grey cement grains floating about in the water. And then the cement grains are dissolving in the water. This is exaggerated in the next picture here where you see the grains get smaller. So the ions that are in the cement grains are passing into the water and then they are making new combinations and those combinations are precipitating as the hydrates which we have seen here in red. So now we see the basic idea that these red hydrates are now joining the cement grains together and by joining the cement grains together you get a rigid solid which has strength but you will still have some areas where there is no material, may contain water, may contain air and these are known as pores. So it is very important to keep this basic idea of hydration as this change in solid volumes in your head. We can look at it another way.

Notes

Summary

3m 32s

Real cement



- Rough, angular grains
- Multi phase grains
- 4 main phases

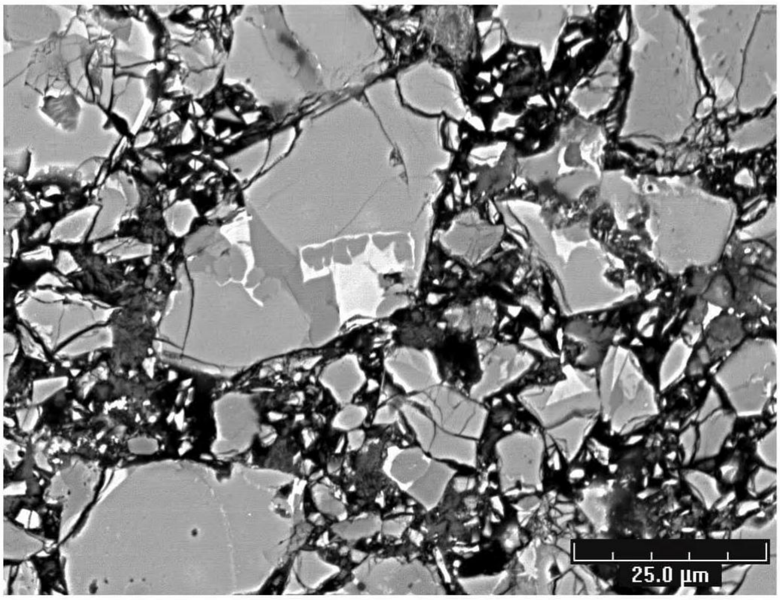
First of all in a real microstructure. So this is a picture of real cement grains. And what you can see in these cement grains is that they have got different levels of grey which means they have got different chemical compositions. And typically in cement we can identify four main phases. So we see this phase here which is called alite or C3S. This is the majority phase, generally will make up between 40 and 70 percent of the cement. Then we see some other grains like this one down here, a more rounded and this grain is made of what we call belite or C2S. So this is another calcium silicate phase but has somewhat less calcium than the C3S. This also means it is less reactive. And then in addition to these alite and belite we can see this darker phase which is the aluminate phase, or C3A, and this very bright phase, it is very bright because this is the phase which contains the iron which is called ferrite. And this is usually written as C4AF although you should be aware that the ratio of aluminum to iron is not fixed at 1 to 1. So these are the four phases that make up our Portland cement. So then what we see here is the different reactivity of these different phases.

Notes

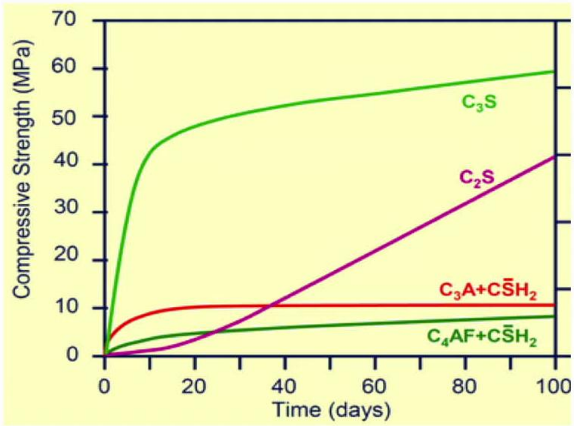
Summary

4m 55s

Real cement



- Rough, angular grains
- Multi phase grains
- 4 main phases

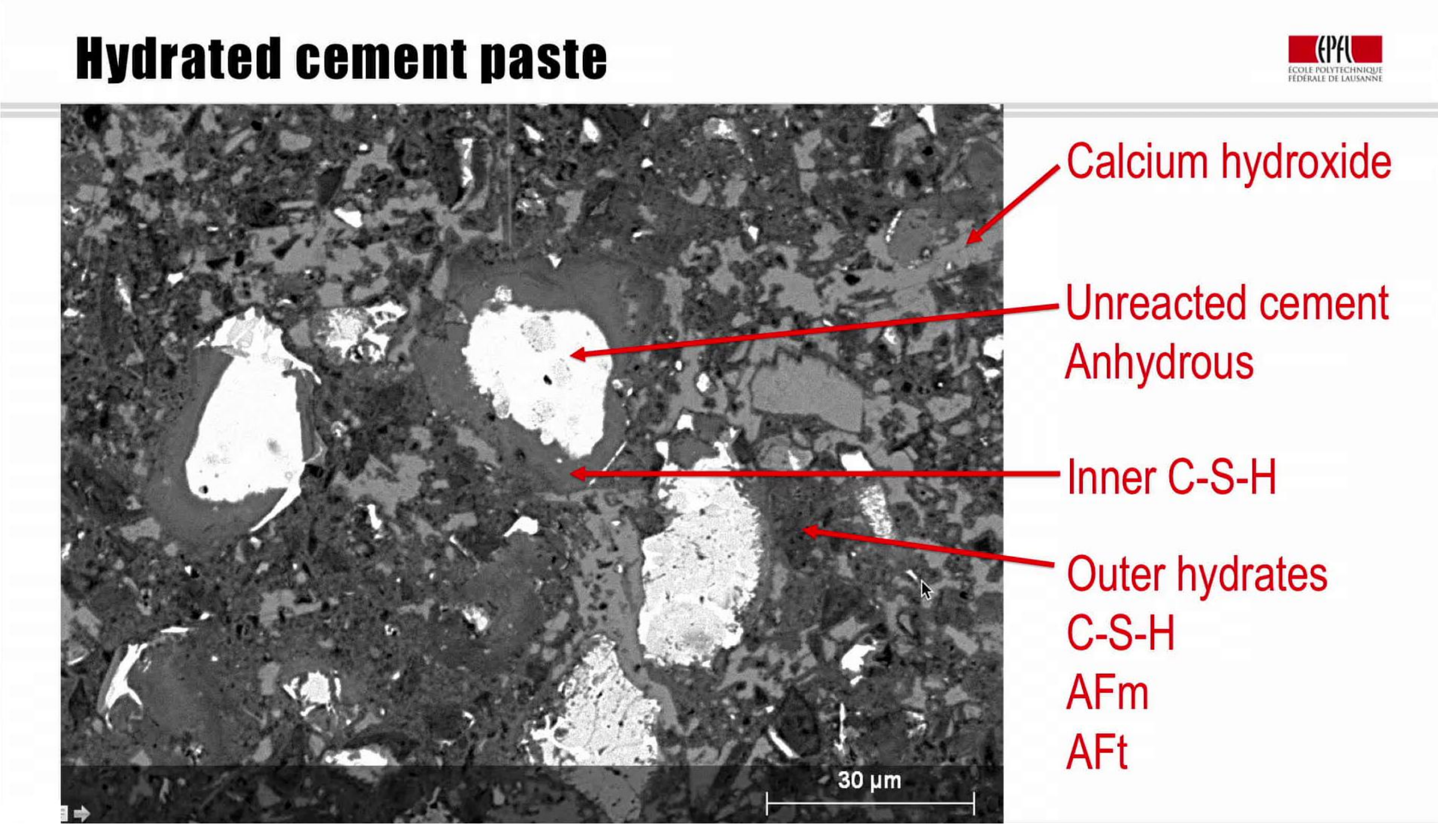


We can see that the compressive strength coming from C3S is by far the highest. And this is why generally we tend to try to maximize the amount of C3S in our Portland cement clinker C2S is very very much slower and as we saw in one of the earlier modules, this is why really it doesn't make any sense to make cement with high content and belite from an environmental perspective. It may make sense from a point of view of having low heat cements. The aluminate phases and the iron phases, we need some calcium sulfates. This is why we add the gypsum during grinding, as it has been mentioned before. These tend to react quite fast but they don't give such high strength as the C3S.

Notes

Summary

6m 31s



So now after hydration the clinker grains transform to give us the microstructure of the hardened cement paste. We can still see cement grains which haven't reacted. These are the bright areas here. But now in between these grains we can see the hydrates and we can identify in particular two different types of hydrates. We can identify these areas here which are lighter grey than the rest of the hydrates but still darker than the anhydrous. And these regions here are calcium hydroxide. Calcium hydroxide has a very simple formula of 1Ca(OH)2. And this is one of the main phases formed from the calcium silicates. And then apart from the calcium hydroxide, the rest of the hydrates have this kind of darker grey levels. We can still see that they are lighter than the pores which we can see in black such as here. And this other hydrates we can say it is in majority C-S-H. Around the cement grains we can see these nice rims. We call these rims have formed in the place of the cement grain which has reacted. And this is called inner C-S-H. Whereas now between the grains we have what we call outer hydrates and this is a very fine mixture of C-S-H of AFm and of AFt phases which we can't distinguish from each other at this level of resolution here.

Notes

Summary

7m 22s

Volume changes are critical

The ratio between cement and water are usually expressed by weight
For example a typical water to cement ratio (w/c) for concrete is 0.5:
for each gram of cement 0.5 gram of water is added.

But the development of properties is controlled by
the filling of space related to volumes.

How does a w/c of 0.5 in weight translate into volumes?

Given the density of cement is around 3 (g/cm^3),
calculate the relative volumes of cement and water just after mixing.

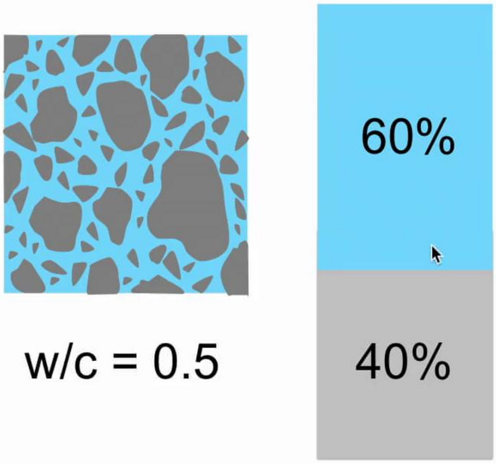
As I said before it is really these volume changes that are critical. The ratio between cement and water are usually expressed by weight. But we are interested in the volume ratio. So typically our water to cement ratio in weight terms would be said to be 0.5. And this means for each gram of cement present we add 0.5 grams of water. But the development of properties is controlled by the filling of space which is related to the volumes. So I think it is a nice little exercise if you can translate that water cement ratio by weight of 0.5 into volume. And I think you can switch off the video here. You can make this calculation for yourself. I will tell you that the relative density of the cement is around three. I hope you know that the relative density of water is one and then you should be able to make a nice simple calculation to calculate the relative volumes of cement and water just after mixing.

Notes

Summary

9m 14s

Volume changes



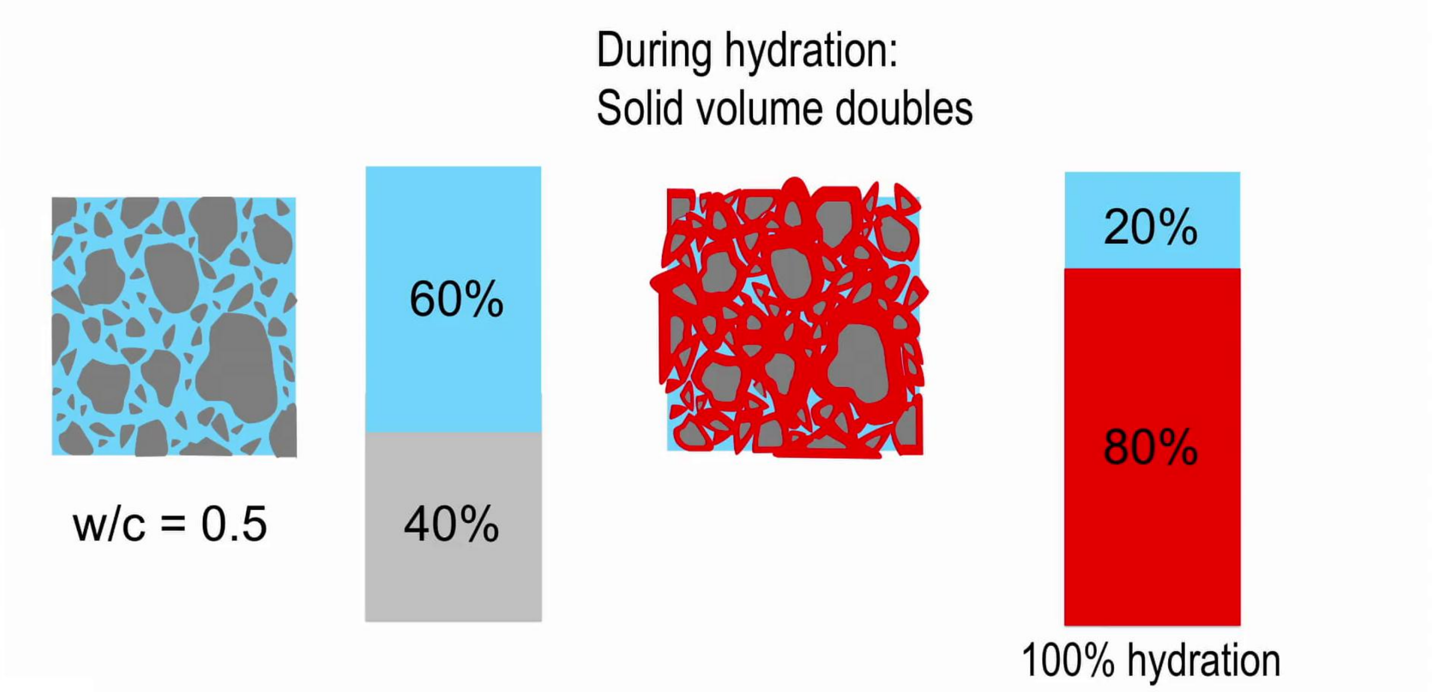
So I hope you manage to work that out. But when we have a water to cement ratio of 0.5 by weight this means that the relative volumes of cement and water at the beginning we have about 40 percent cement and about 60 percent water. So you see we actually have more water by volume than we have cement and we need that amount of water by volume to give us the fluidity. You know if any of you have made a cake that you have the grains of flour and you need to add a certain amount of liquid to make a flowable cake mixture and making a cement paste is really exactly like that. You have this grey powder which is the cement. You have to add a certain amount of water to fill the spaces between those cement grains and give you this flowable cement paste. Nowadays we can go to somewhat lower water cement ratios particularly if we use admixtures like super plasticizers - we will come back to that in another module. But if we don't have any super plasticizers then we would typically use this water cement ratio of 0.5. So that is the ratio between the solid and the liquid at the start.

Notes

Summary

10m 20s

Volume changes



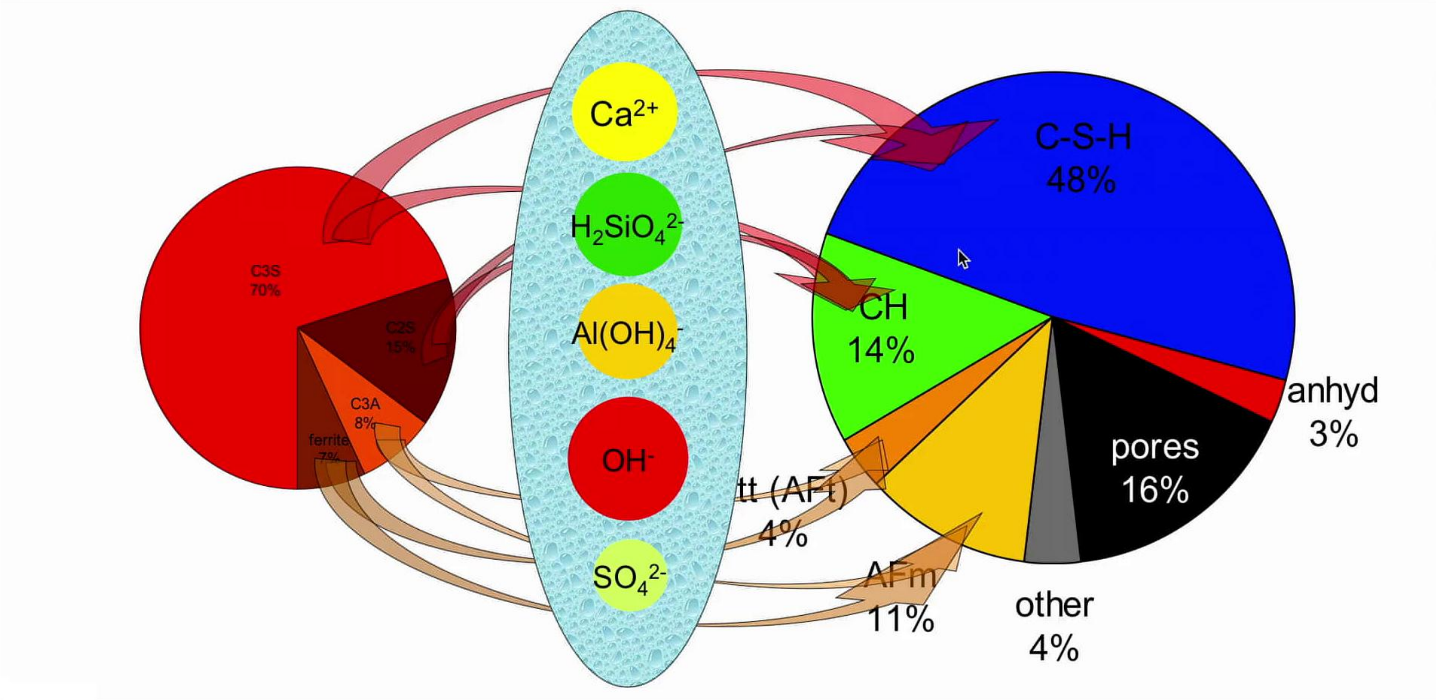
What then happens is we have this hydration reaction and during this hydration reaction, we have roughly a doubling of the solid volume so that this 40 percent here, this becomes now 80 percent and the rest that doesn't get filled by these hydrates will still remain as pores. And this is then why these hydrates occupy a higher volume. They can then bridge these cement grains together. They can give us this rigid pores solid that has strength. So please I really cannot emphasize enough just how important it is to think in terms of volumes.

Notes

Summary

11m 41s

Phases present – mature paste



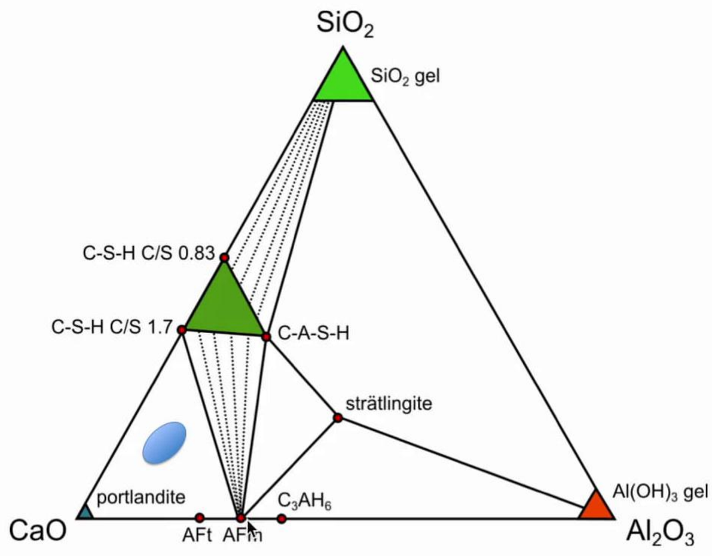
Now if we look in a little bit more detail at the different phases. What comes from what? What we have here on the left is we have the approximate compositions of a typical Portland cement. 70 percent C3S or alite, 16 percent C2S or belite, 8 percent C3A and 7 percent ferrite phase. And then, roughly speaking, the C3S reacts to give us this phase C-S-H and calcium hydroxide. We also get these two phases from the C2S while the aluminate phase and the ferrite phase react to give us these phases we call ettringite, or AFt, and AFm phases. And in subsequent videos we are going to see what is the chemical composition, the crystal structure of all these different hydrate phases. But what is really important to see is that C-S-H is really the most important. In a typical cement paste, mature cement paste, this makes up nearly half of the solid material. Now this kind of one to one correspondence is what is usually written down but in fact all of these hydrates, are formed what is called through solution. So first of all as we saw in the schematic, the cement phases dissolve. They form these different ions which go into the solution phase and you see in the solution we then get these ions of calcium, of silicate, of alumina, hydroxide, sulfate etc and then these ions combine in the different proportions to give us these hydrate phases which then precipitate from the solution.

Notes

Summary

12m 27s

Hydrates over view



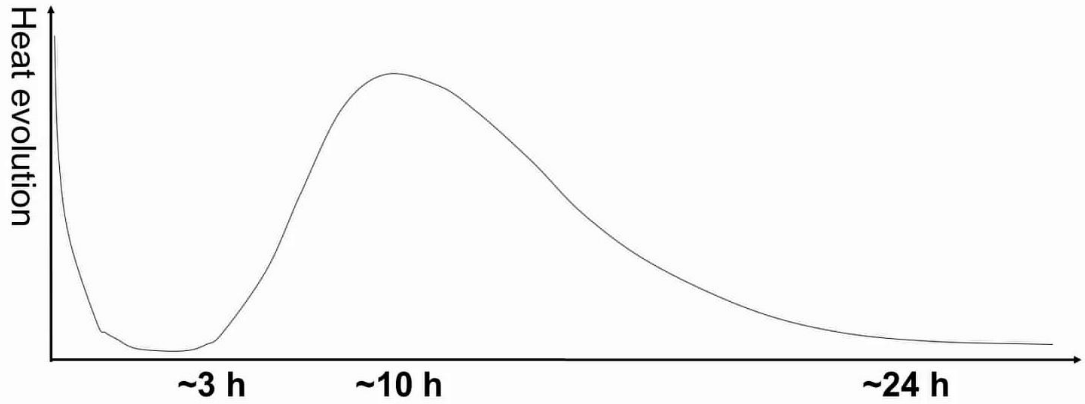
Another way we can look at these hydrates is in this ternary diagram where we plot the different hydrates in this triangle here of calcium oxide or in the hydrated form calcium hydroxide or portlandite, the Al(OH)3 hydrated aluminate gel and up here hydrated silica gel. And again here we can see that we have a very important phase of C-S-H. C-S-H, well we have quite a wide range of chemical compositions we will discuss in the next video. C-S-H, it can also contain quite significant amounts of aluminum. And then down here we have the various aluminate hydrates. Now if we look at the composition of Portland cement, which is shown by this blue area here, we can see that this composition of the Portland cement lies in this triangle bounded by C-S-H here, by portlandite or calcium hydroxide here and by the aluminate hydrate phases here.

Notes

Summary

14m 28s

Kinetics of reaction



Here we come back to the kinetics of the reaction. We have already mentioned this but in the context this is a very important aspect of Portland cement because this really determines their technological use. So we look at the kinetics of reaction we are generally measuring the amount of heat evolved and we see initially, we get this very short burst of heat but then the heat evolution is quite low during a period of several hours. And this period of low heat evolution means that we have the time to mix our cement or our concrete and to transport it to the building site, put it in place to build our walls etc. And then after three hours or so, the rate of reaction starts to increase rapidly and we get this main reaction which occurs during the first day. And in subsequent videos we are going to be looking at what are the mechanisms determine these different stages of the reaction.

Notes

Summary

15m 40s

Summary

- Hydration involves reaction of cement with water
- This increases the volume of solid,
  bridging space between the grains and forming a solid
- Essential aspect is volume change
- Silcates: C_3S and C_2S form calcium hydroxide and C-S-H
- Aluminate and Ferrite lead to formation of AFt and AFm phases

- In next few modules we will look at the structure of these hydrates in detail and the mechanisms controlling kinetics.

So to finish this video and just to summarize what we have seen here is hydration reaction involves the reaction of cement with water. And the critical aspect to this is the increase in solid volume which bridges the space between grains forming a rigid solid. So the calcium silicates, C3S and C2S, generally form calcium hydroxide in C-S-H while the aluminate and ferrite phases lead to the formation of these phases we call AFt and AFm. So in the next few modules we are going to look at the structure of these hydrates in detail and the mechanisms controlling kinetics. So we hope you will come back to listen to those.

Notes

Summary

16m 46s