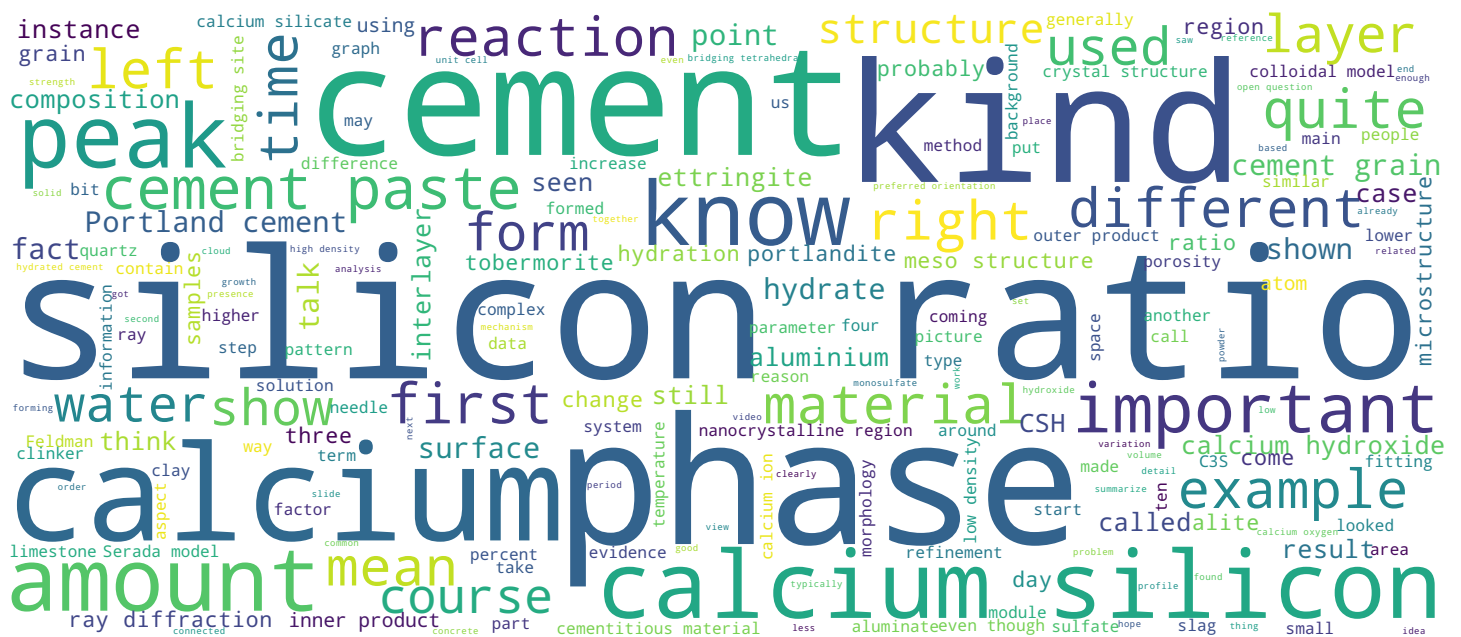
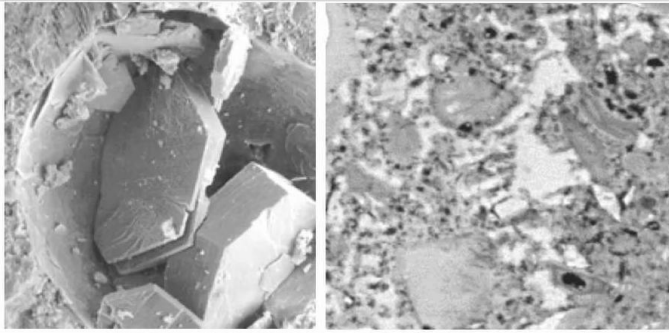


Professor Karen Scrivener, FREng



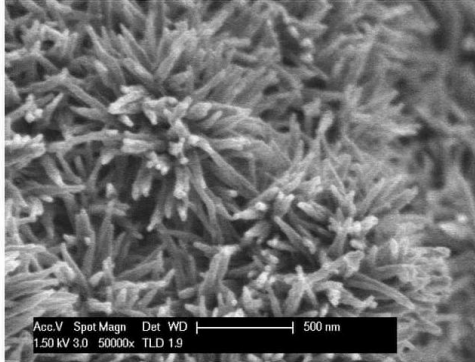
# Hydration of calcium silicates : $C_3S$ and $C_2S$



calcium hydroxide  
Hydrated lime  
portlandite  
 $Ca(OH)_2$   
CH

} crystalline  
Hexagonal  
morphology

~ 10-20% of hydrated paste



calcium silicate hydrate  
C-S-H

Nano crystalline  
multiple morphologies

~ 50-65% of hydrated paste

So welcome to this second video in the hydration module and in this module, this section we are going to talk about the C-S-H phase which as we have seen in the overview is the most important hydration product. So just as a reminder, what we saw in the overview was that when we have the calcium silicate phases hydrating, that is to say  $C_3S$  and  $C_2S$ , we form two hydrates. We have calcium hydroxide, it has lots of different names. Often referred to as portlandite or as CH. And this form is about ten to twenty percent of the hydrated paste. And then we have this phase calcium silicate hydrate, which is written in this nomenclature C-S-H which is a rather complex but even though it is complex we have to understand it and this is making up as we have seen more than half of the cement paste.

Notes

Summary





- “atomic” structure and composition
- “meso” structure
- “microstructure / morphology”

So what we are going to talk about in this video we are going to talk first of all about the atomic structure and the composition and then we are going to talk about the meso structure and then we are going to talk about the microstructure.

Notes

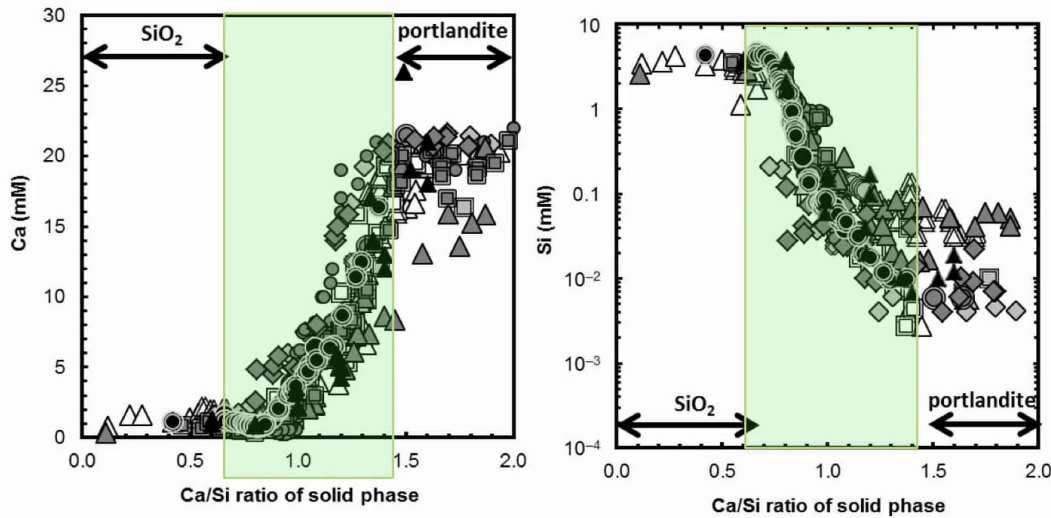
Summary



1m 06s

# Definite phase, reproducible behaviour

Variable calcium to silicate ratio, depending on composition of solution



Ca/Si =  
0.7 to 1.5  
for "synthetic" C-S-H

Lothenbach, Nonat (2015) CCR

Now the first point I really want to emphasize is the C-S-H really is a definite phase with a reproducible behaviour. When I came into the field more than thirty years ago, people often talked about C-S-H like it was this complete random unknown material. But what we didn't know before but what has been really clearly established is that it is a phase with a reproducible thermodynamic behaviour. And that is what I am trying to illustrate on these two graphs here. On these two graphs you see the results of many many different experiments carried out over the last eighty years or more on examining the C-S-H. And always, although there is a lot of scatter because of the experimental measurements, always we see that we get the same behaviour of C-S-H. And the other thing that is very important on this slide is we see that we have this variation in the calcium to silicon ratio of the C-S-H depending on the composition of the solution. So this variation in the calcium silicon ratio of the C-S-H is shown by the green boxes on these graphs. On the left of the green box we have the C-S-H co-existing with silica gel and on the right of the box we have the C-S-H co-existing with portlandite or calcium hydroxide.

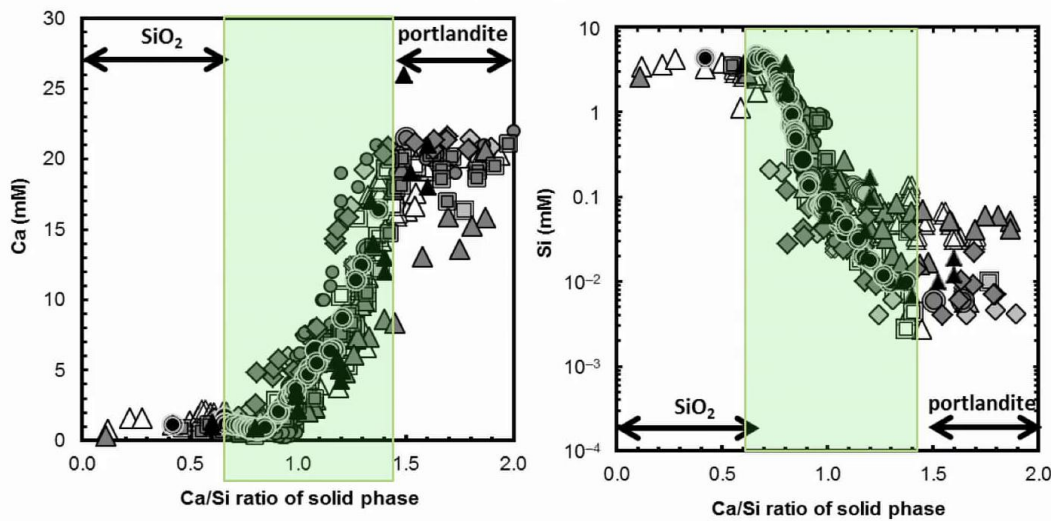
Notes

Summary



# Definite phase, reproducible behaviour

Variable calcium to silicate ratio, depending on composition of solution



**Ca/Si =**  
**0.7 to 1.5**  
for “synthetic” C-S-H

**1.7-2 PC pastes**

Lothenbach, Nonat (2015) CCR

And the co-existence with portlandite is of course the situation we are closer to when we are talking about cement paste. Now what is important here is that people who have tried to produce calcium silicate hydrate in the laboratory, that is to say we often call that synthetic C-S-H, mixing different solutions together, they really can make C-S-H with calcium to silicon ratios of 0.7 to about 1.5. However, when we go to cement paste, we can clearly see that in fact we have C-S-H of much higher calcium to silicon ratio in the range of 1.7 to 2. And this is still somewhat of an open question today why we can get these much higher calcium to silicon ratios. We now think it is really connected to the difficulty of precipitation of calcium hydroxide.

Notes

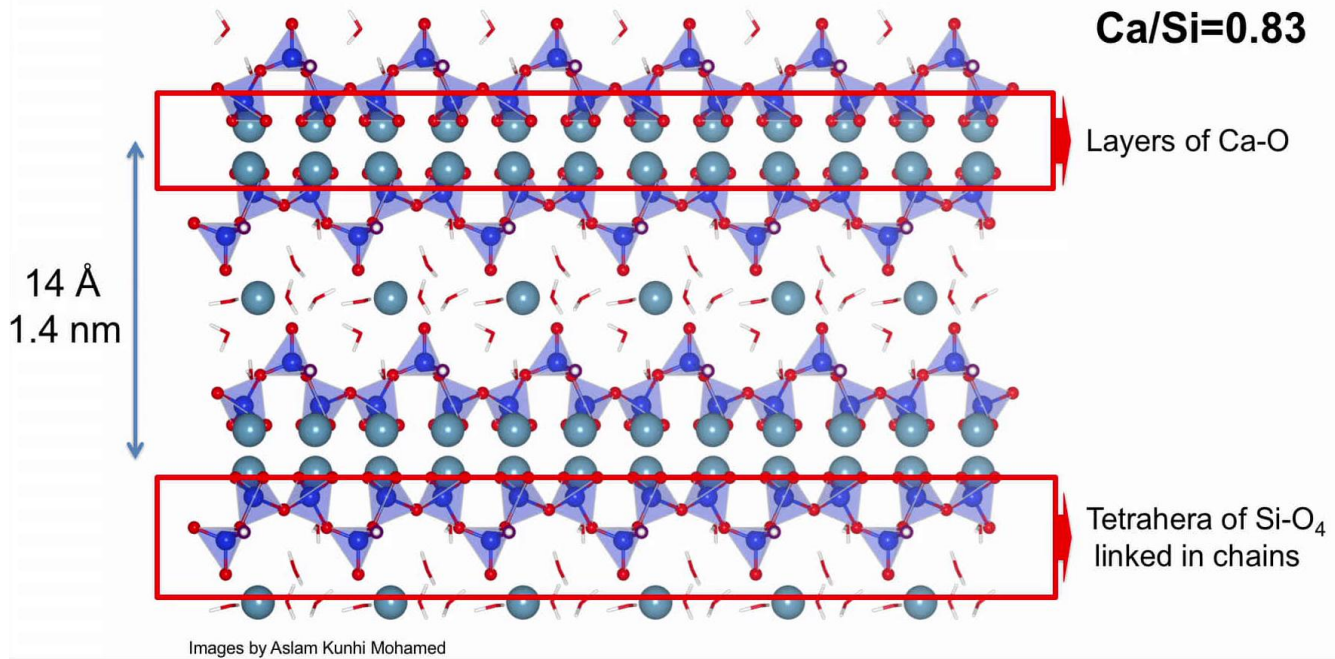
Summary



2m 57s



# Structure based on natural mineral tobermorite



For a long time it has been realized that C-S-H is related to the natural mineral tobermorite. And tobermorite is so called because it was found on the island of Tobermory which is located off the coast of Scotland. And this is the crystal structure of tobermorite. It has a calcium to silicon ratio of 0.83. And the main characteristics of this crystal structure are the following. First of all we have these layers of calcium and oxygen, so this is what you see here, you see the calcium atoms in this kind of turquoise colour and the oxygen atoms in red. So this is the layers of calcium oxygen and in fact these layers are very similar to the layers you have in calcium hydroxide. It is probably not a coincidence. And then on these layers what we see is these chains of silicate tetrahedra. So the silicate atoms are at the center of those blue tetrahedra and at the corners of these tetrahedra we have oxygen atoms. And this tetrahedral organization of silicon is very common in nature, it is what you have in quartz, it is what you have in glass, so you know it is really how silica prefers to be. But in this tobermorite what you see is we form these long chains and these chains have a repeating pattern of three.

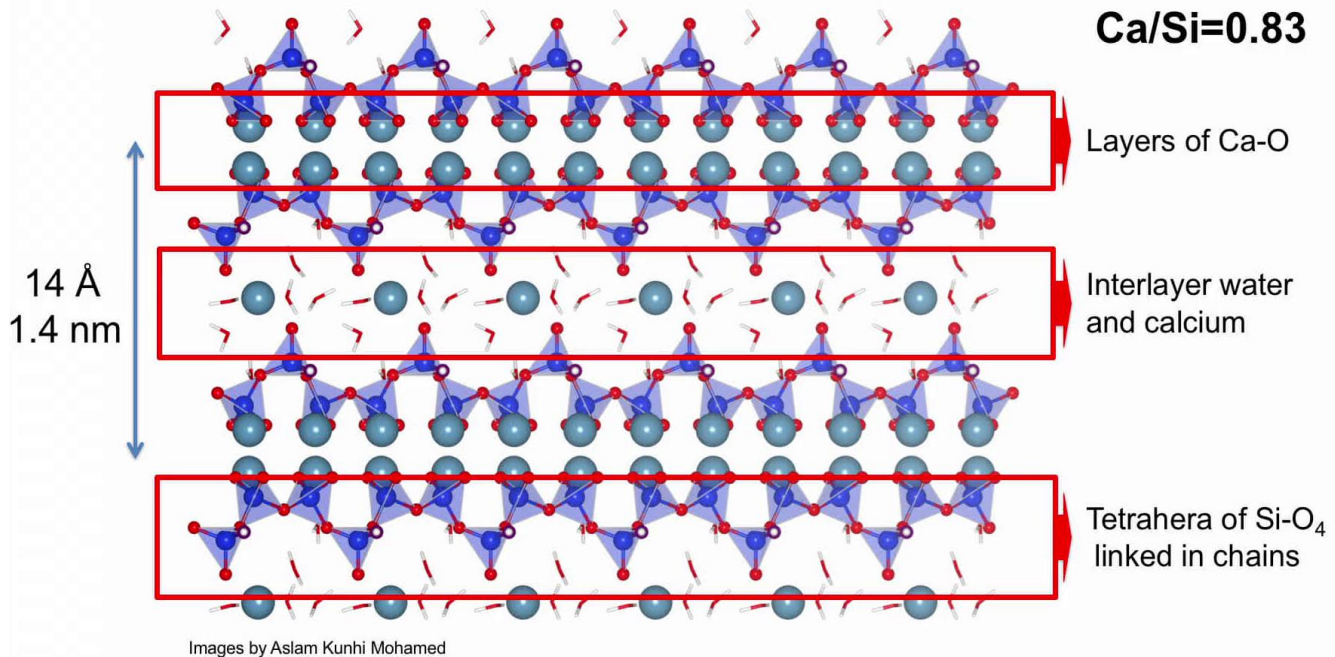
Notes

Summary



4m 00s

# Structure based on natural mineral tobermorite



So for the repeating pattern of three we use the word dreiketten, which in German means three chains. And you see we have two atoms which are attached to this calcium oxygen layer and then we have one tetrahedra which is sticking out from that layer. Then the third element of this tobermorite structure is what we call the interlayer, that is this region in here. And this region in here contains water molecules and also can contain calcium ions for example. And in more complex cases there are other ions such as alkali ions which can come into this space. So this is the structure of tobermorite. We know the structure with a very high degree of confidence because we can make single crystals of tobermorite and examine them by x-ray diffraction. So the question then is how do we go from this tobermorite structure to the structure of C-S-H? And the main problem here is of course we see here we have a calcium silicon ratio of 0.83, but we know that in the C-S-H we have in cement paste, the calcium silicon ratio is generally much higher than that. In paste it can be up to 2. So what people have really looked at is the ways in which we can change the calcium to silicon ratio. And I am going to try and illustrate that in the following slides.

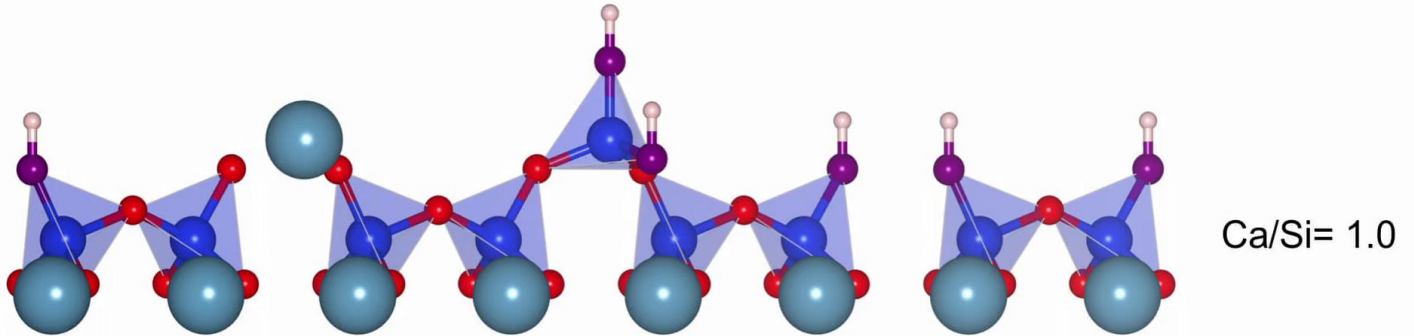
Notes

Summary



5m 34s

# Ways to vary C/S



## Calcium replacing two terminating hydroxides

Now the first and most simple way of varying the calcium silicon ratio is to omit these bridging tetrahedra. So we see these bridging tetrahedra here, if these are omitted, so for example here you see this one is missing, then we start to change the calcium silicon ratio, we have less silicon, the same amount of calcium and as we go through this sequence you can see on the right here it is telling you the calcium to silicon ratio and you see it is going up. So that is the first way we can introduce defects which increase the calcium to silicon ratio. But this is nowhere near enough to take us to the kind of calcium silicon ratios we know we have in cement paste. We need other mechanisms. And the second mechanism we can have is that instead of these hydroxide ions terminating here, we can replace these two hydrogens here with a calcium atom. So calcium is a doubly charged ion, hydroxide is singularly charged, so we can go from two hydroxide ions to one calcium ion. And this then because now we have more calcium, same amount of silicon, again the calcium to silicon ratio is increased. And here we see by replacing all the hydroxides with calcium, we can get quite a significant increase in the calcium silicon ratio.

Notes

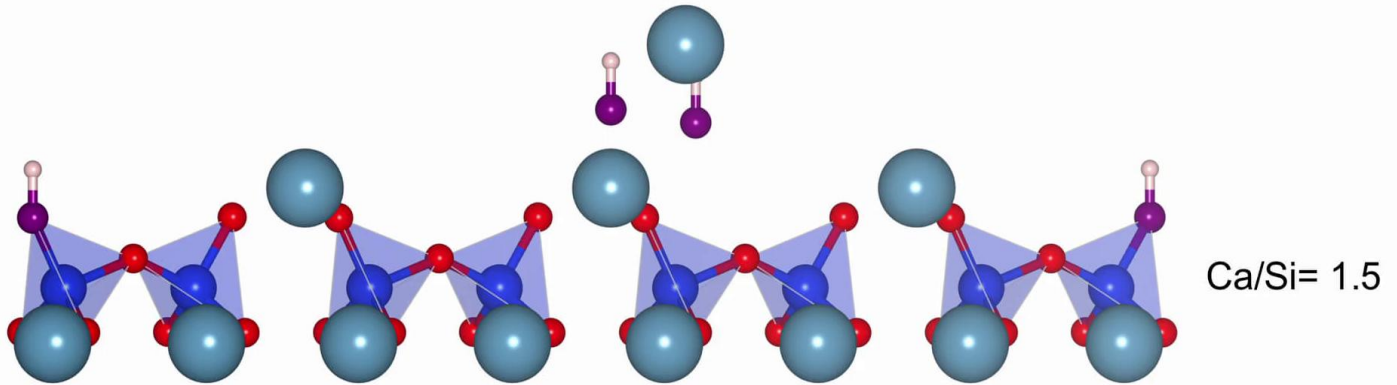
Summary



7m 18s



# Ways to vary C/S



## Calcium in interlayer

But what we see here with this version is that even though we have now omitted all the bridging sites, and we have got calcium replaced in the hydroxide, this is still not enough to get us through the calcium silicon ratios we see in C-S-H. So the next mechanism is to work on this interlayer and, you know, to have calcium ions in this interlayer. So here we see various different versions with calcium in the interlayer and now we are starting to really approach the calcium silicon ratios we find. So this example here is a calcium silicon ratio of 1.5, which is around about the upper limit we find for C-S-H precipitated from solution in the laboratory.

Notes

Summary



8m 53s

# 3 mechanisms

- Missing bridging tetrahedral
  - Calcium replacing terminating hydroxides
  - Calcium in interlayer
- 
- No unique way to get a given C/S
  - Structure probably has random organisation of these defects:
    - One reason for low crystallinity by X-rays

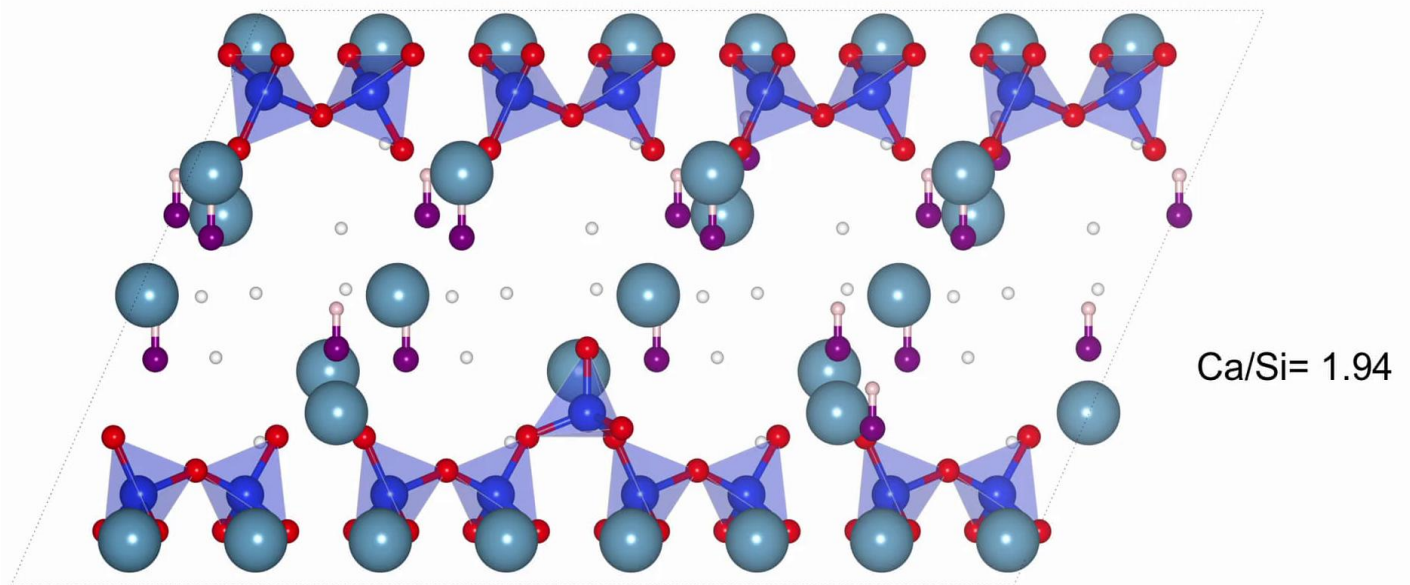
So just to summarize here, what we have seen is that there are three kinds of defects we can put in tobermorite. We can have missing bridging tetrahedra. We can have calcium replacing terminating hydroxides and we can have calcium in the interlayer. And really what is important is that there is no unique way to get a specific calcium silicon ratio, we can have different combinations of these three kind of defect mechanisms. And what we think is that the structure probably has a really random organization of these defects, This could be one reason for the low crystallinity, the fact that we generally don't see C-S-H by x-ray diffraction. Also the entropic effect of having this random organization of different defects could probably be an important element in stabilizing the C-S-H structure.

Notes

Summary



9m 46s



So here we show just some examples of the full unit cells of different calcium silicon ratios. Here we see this one here calcium silicon 1.4. Here we see calcium silicon 1.72. And here we see calcium silicon 1.94. So this is right now coming to the upper limits. You see that we have most of the bridging sites disappeared, we have mostly calcium ions terminating the tetrahedra and we have some calcium in the interlayer.

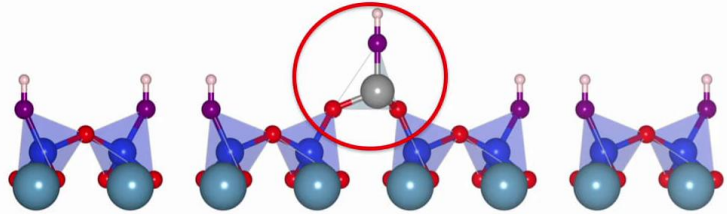
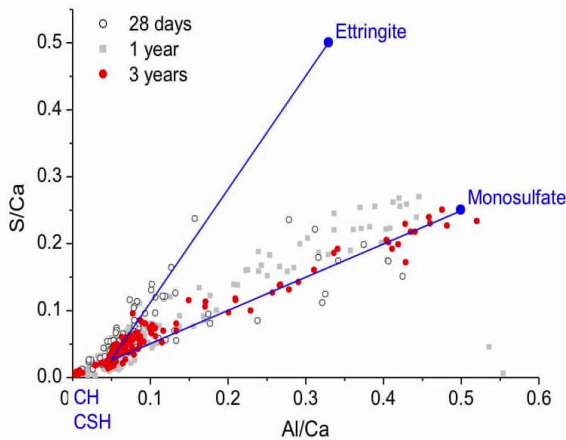
Notes

Summary



10m 47s

# C-S-H: Si substitution by Al



OPC pastes:  $\text{Al/Ca} \sim 0.05$ ;  $\text{Al/Si} \sim 0.1$   
Higher with Al rich SCMs

Location in bridging sites

The other aspect which is important to talk about is the presence of aluminium. So when we make micro analysis in the SEM - this is what is shown on the left here - then we can quite clearly see that this cloud of points here which corresponds to the C-S-H, this cloud of points has a displacement along the aluminium to calcium axis. So we can see that the intersection of these lines from ettringite to monosulfate is coming at an aluminium to calcium ratio of about 0.05. And this corresponds to an aluminium to silicon ratio of roughly 0.1, which is to say about one in ten of the silicon atoms are replaced by aluminium. Other studies have shown that the aluminium tends to be located in these bridging sites, that is to say the tetrahedral positions which are facing out and not in the tetrahedral positions which are attached to the calcium oxide sheets. And this ratio of about one to ten which we find in Portland cement paste can go quite substantially higher when we have supplementary cementitious materials which contain a lot of aluminium such as for example metakaolin.

Notes

Summary





- “atomic” structure and composition
- “meso” structure
- “microstructure / morphology”

Now I hope you have a fairly good idea of the atomic structure of composition and now we are going to look at the meso structure. And this area of meso structure is probably the area where we have still quite a few open questions and need to advance our understanding. So why do we think that C-S-H has a particular meso structure?

Notes

Summary



12m 44s



- No long range order
- “intrinsic” porosity of 26-28% (Powers)
  - “gel porosity”
  - Scattering experiments (neutron, X-ray) and proton NMR indicate “characteristic size” of about 4-5 nm

Well the experimental evidence for this goes back quite a long way. First and foremost is the observation that we have no long range order. That is to say in normal cement paste, we don't see specific peaks from the calcium hydroxide by x-ray diffraction. The second thing which was pointed out already by Powers back in the 1940's was that C-S-H has this intrinsic porosity. OK so what do I mean by intrinsic porosity? What I mean is that when you form the C-S-H, as you increase the amount of C-S-H that is formed, you increase the amount of this particular type of porosity. And this particular type of porosity is often referred to as gel pores. And now in the last twenty or so years, we have had a lot of evidence from different scattering experiments, from neutron scattering, from small angle x-ray scattering and most recently from proton NMR, which indicates that this gel porosity has a characteristic size of about four to five nanometers. And if we look at the kind of spectra we have from proton NMR then we can see a specific peak.

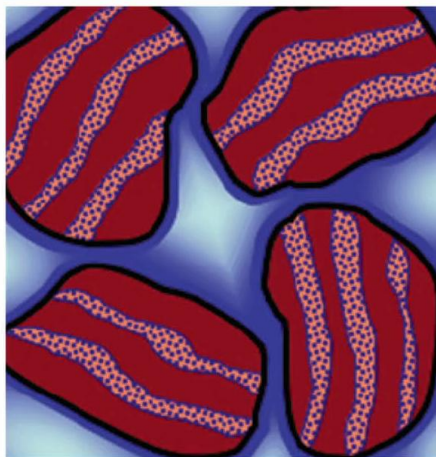
Notes

Summary

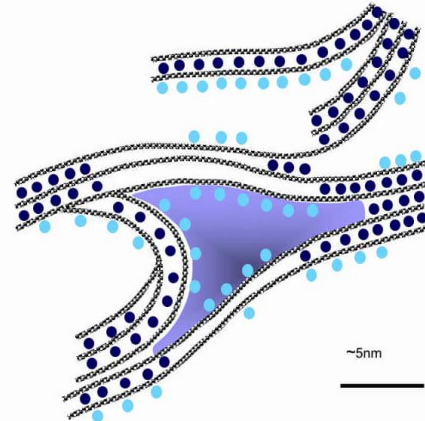
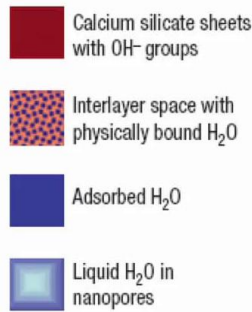


13m 07s

# Two schools of thought



“Jennings” model  
Discreet colloidal nanoparticles



“Feldman-Serada” model  
Linked nanocrystalline regions

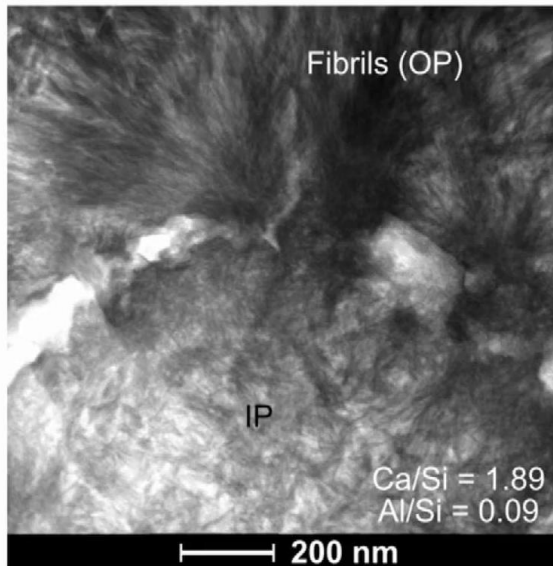
OK, so know that there are two schools of thought about the structure of C-S-H. So on the left here, we see the very widely cited model that originated with Jennings. And Jennings did a lot of work around this idea that you have this colloidal model of C-S-H. So what do we mean by this colloidal model? We mean in this colloidal model the little areas of C-S-H are discrete nano particles, which are not linked together. And these discrete nano particles are made up of about four or five layers of the C-S-H. On the right here what we see is the what is often called the Feldman-Serada model. Although not all aspects that we are going to talk about here were explained like that by Feldman and Serada. And in this Feldman and Serada model, we have nanocrystalline regions where the layers of C-S-H are quite well aligned and then those layers extend from one nanocrystalline region to another crystalline region. And this kind of arrangement of the layers leaves pockets where we have higher amounts of porosity, which we could relate to the gel porosity. OK so this model on the left is somewhat similar to what you have in semi crystalline polymers for those of you who have made studies in polymers. Now we have to say well what is the evidence for one or the other of these model?

Notes

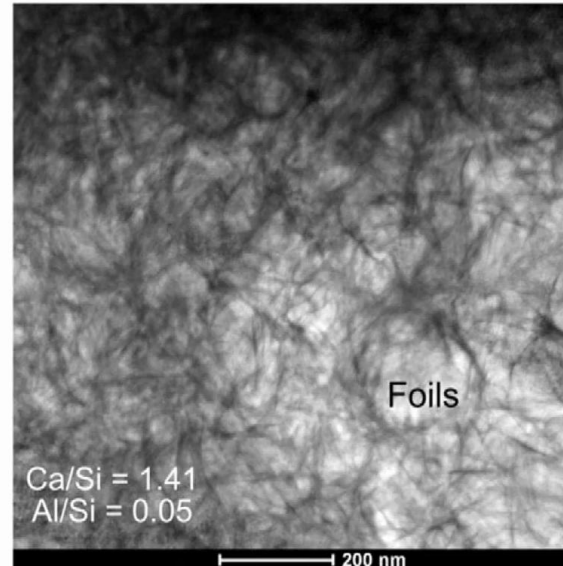
Summary



# C-S-H in cements



(a) Plain cement (PC), 90 days, 20°C



(b) PC 10SF, 90 days, 20°C

Rossen et al (2015) CCR 75

Well for me seeing is always believing and I think the best evidence is really coming from now from transmission electron microscopy. So these show you two transmission electron micrographs from cement paste. At this very fine level people are often distinguishing two types of morphology. The morphology we see on the left here with these kind of fibrils of C-S-H and the morphology we see on the right which is said to be kind of like foils. But in neither of these cases, even though we are quite high resolution here of two hundred microns, in neither of these cases do we really see any evidence for these colloidal particles. Of course we don't see the C-S-H layers either, so we don't yet have a full understanding of how this kind of microstructural model at this level might relate to this Feldman and Serada model either. But nevertheless, my personal feeling is that we have much more similarity, much more chance that the real structural C-S-H at that level is something like what we see in the Feldman and Serada model than it is in the colloidal model.

Notes

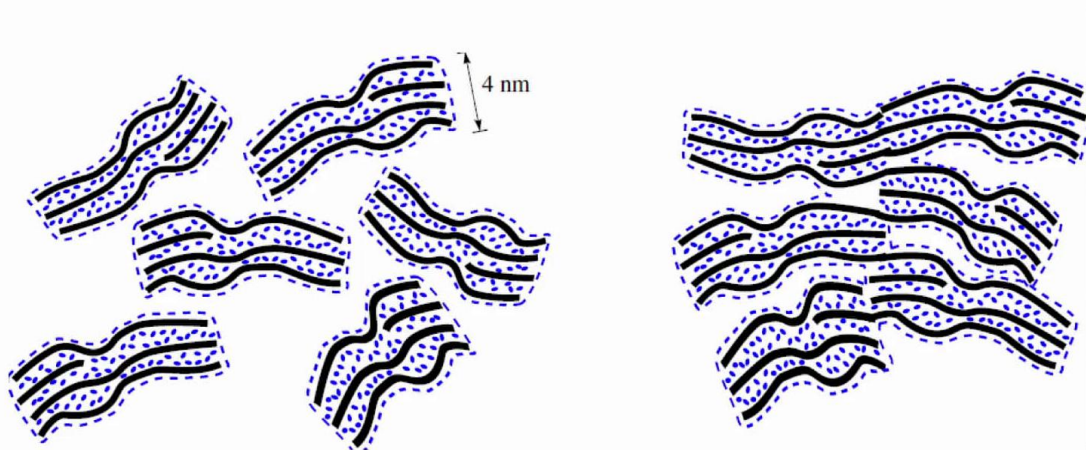
Summary



16m 20s

# Meso structure

- Two interpretations of nanocrystalline nature
- The main open question is whether they are discrete or linked by sheets



But at the end of the day, I think it is more important to focus on the similarities between these two schools of thought in contrast to the differences. So I have tried to show those similarities here that you know, this is the colloidal model on the left where we have these nanocrystalline regions which are not connected. This is the kind of alternative model on the right where we have nanocrystalline regions which are connected and you know for many points of view it is probably not so important which one is correct in terms of mechanical behaviour for example. We would expect to have quite high forces between these colloidal particles, which would be of the same order as breaking a few sheets as on the left. So that is probably what we can say at this point in time for the meso structure of C-S-H.

Notes

Summary



17m 48s



- “atomic” structure and composition
- “meso” structure
- “microstructure / morphology”

So finally in this short video, we are going to look at the microstructure.

Notes

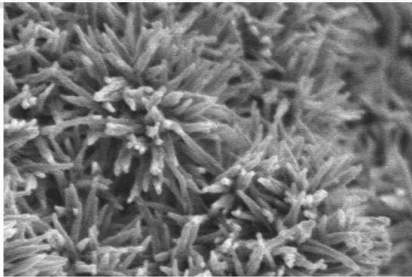
Summary



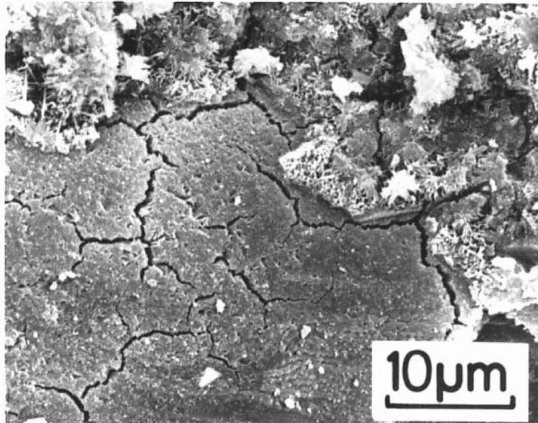
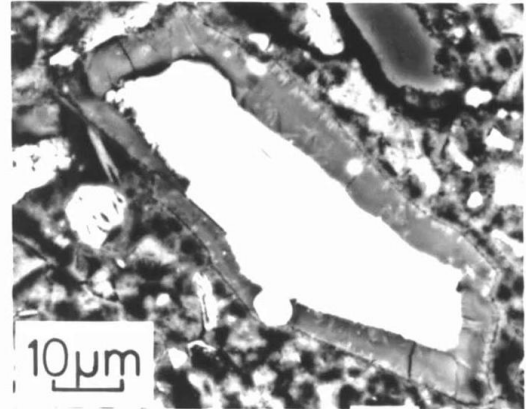
18m 48s



# Two microstructurally distinct forms



“Outer” or “early”  
“inner” or “late”



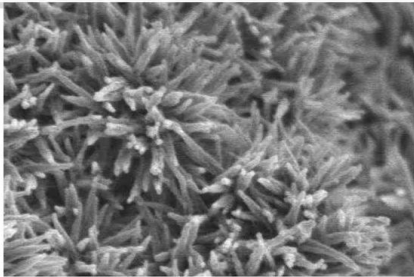
Here we now I think have a very clear picture and our very clear picture really shows us that we have two microstructurally distinct forms of C-S-H. So this picture on the top on the left here, this is what is often shown, this is this kind of needle-like sea urchin morphology and this is the kind of C-S-H that forms early on in the hydration process, it is the kind of C-S-H that nucleates on the surface of the cement grains and that is why we call the C-S-H outer product or early C-S-H. And then we are quite clear that at later times we get this C-S-H, this much more dense C-S-H, which we can see in this bottom micrograph on the left. We can see this is the outer C-S-H here and underneath it is this more dense C-S-H and it is more clear to see these two different forms in a cross section such as shown on the right, which is then imaged in backscattered electrons. So here we see an unhydrated cement grain. You can see this dent thick layer of inner product. It is called inner product because it is formed in place of the cement grain and just on the surface of that you can see this fine outer early product. Now those of you who have looked in the literature somewhat may also have noticed that there are all these terms high density and low density.

Notes

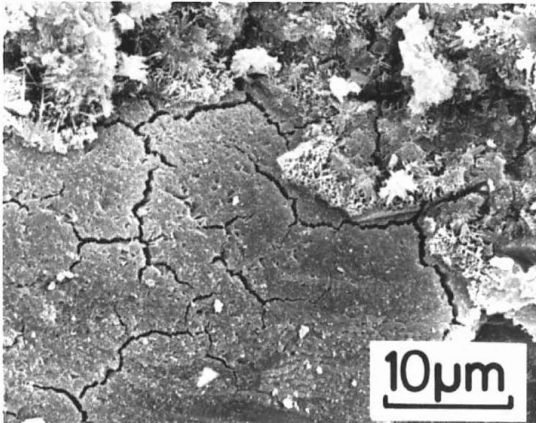
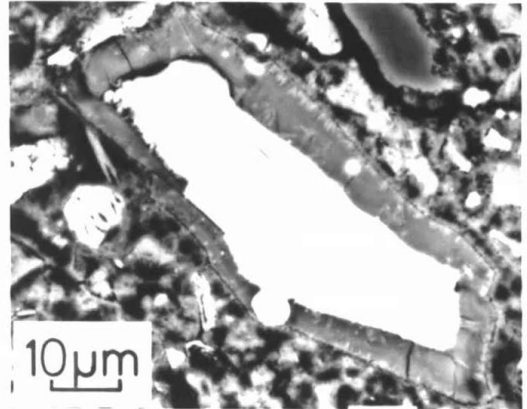
Summary



# Two microstructurally distinct forms



“Outer” or “early”  
“inner” or “late”



Also “high density” and “low density”

Some debate as to whether this is analogous  
to inner and outer

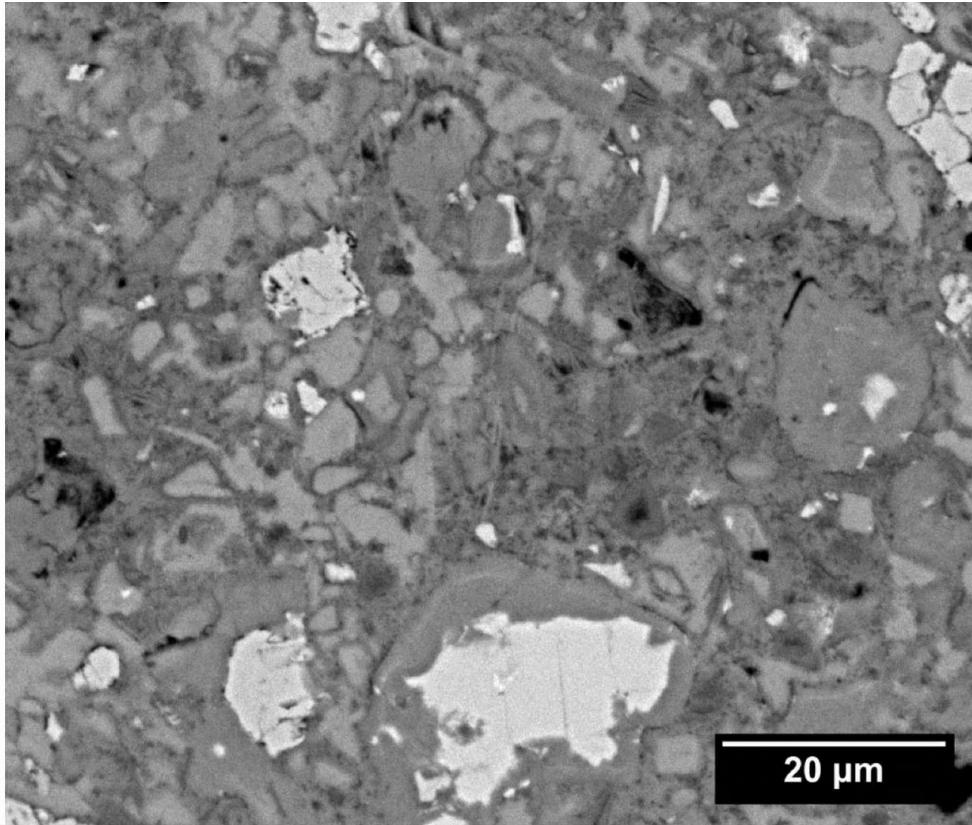
Of course from a simplistic point of view, we can say that the inner product is clearly high density and certainly in the initial stages the outer product is low density but there is still quite a bit of debate as to whether we can make a direct analogy between high density and low density and inner product and outer product. So that is still something under discussion. But these two different forms are quite clear.

Notes

Summary



20m 27s



So if we now come to look at an overall microstructure of a typical cement paste, we can clearly identify the original cement grains. So for example here we have a cement grain, here we have an original cement grain and in this paste dehydration it is quite advanced, so we have some regions of unhydrated cement paste such as here and here and these are surrounded by quite dense regions of the inner C-S-H. And then in the space between these large grains, we can identify this kind of outer C-S-H but still we can see indications of this needle structure that formed very early in the beginning.

Notes

Summary

21m 00s



# C-S-H summary



- Atomic level structure fairly well understood:
  - CaO sheets with chains (dimers) of  $\text{SiO}_4$  tetrahedra attached
  - Al substitutes for Si, in bridging sites
- Meso level structure less clear
- Nanocrystallites or nanocrystalline regions with characteristic scale of about 5nm

## Microstructure

- Outer, formed early through solution
- Inner formed later

So to summarize all that, what we have seen today, we have looked at the atomic level structure. This is now really very well understood through contributions that have been made from silicon NMR. We have seen that this is based on these sheets of calcium oxygen with mainly dimers of silica tetrahedra attached. And then we also may have aluminium substitution for silicon in the bridging site. The meso structure, we still have some open questions. We have either nanocrystallites or nanocrystalline regions with the characteristic size of somewhere in the region of five microns. And finally in the microstructure we can clearly identify first of all what we call outer product which forms early through a solution and then inner product which forms at later times. So I hope that I have given you some insight into the C-S-H hydrates. In the next video we will look at the aluminate hydrates. Thank you.

Notes

Summary



21m 49s