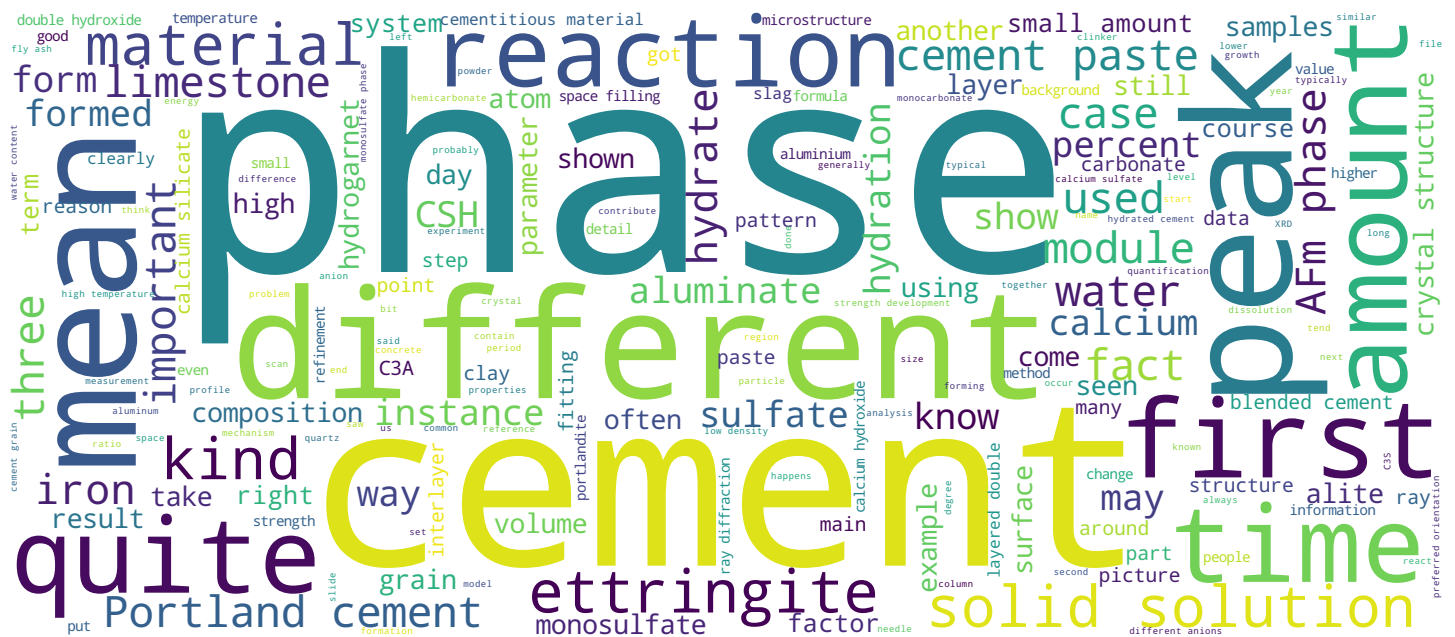
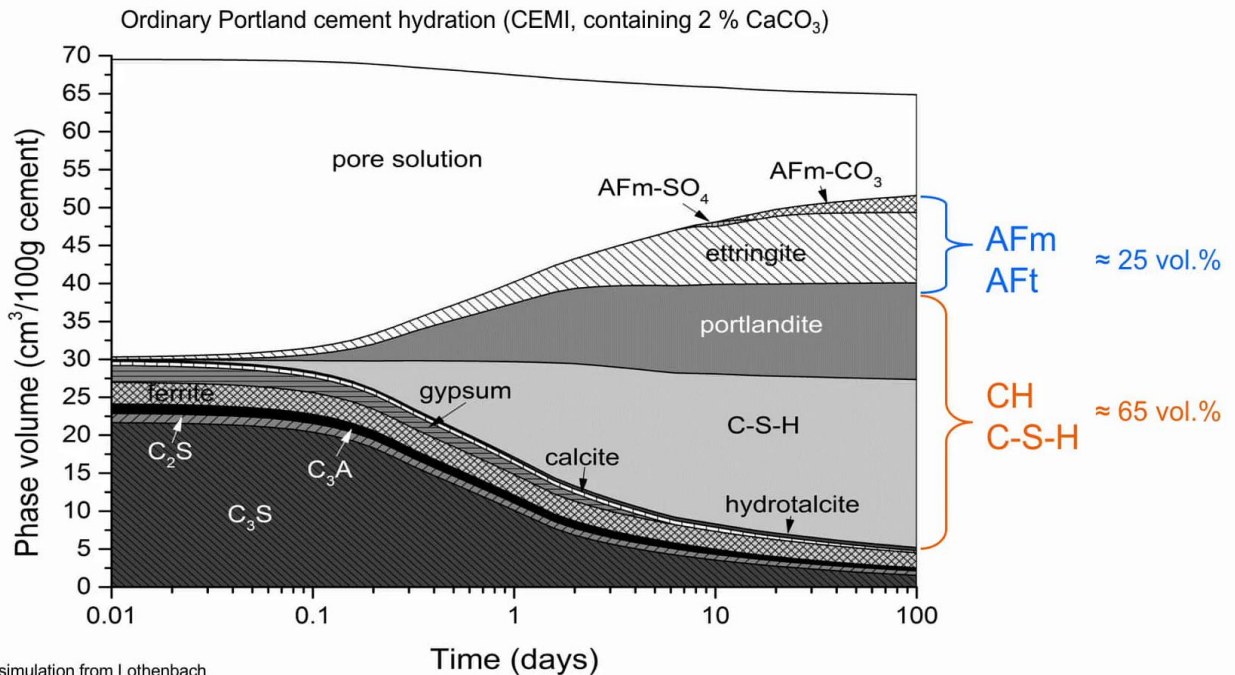


Cement Chemistry and Sustainable Cementitious Materials

Professor Karen Scrivener, FREng



Aluminate hydrates make up a about ¼ of volume



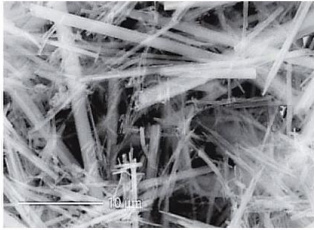
OK. so welcome back and welcome to this module on the aluminate for hydrates. In the last slides we saw about these hydrates that formed from the hydration of the calcium silicates spaces that is to say C3S mainly and C2S later on. And in this module we are going to look at the hydrates that formed from the aluminate, that is to say the C3A phase and the ferrite phase usually called C4AF. These phases are not as prevalent as the ones from the calcium silicate phases but nevertheless quite significant. So in this slide we see the phases that are formed from a typical ordinary Portland cement. And while the phase is from the calcium silicates, that is to say calcium hydroxide and C-S-H are making up about 65 percent of the volume of the final paste, the hydrates coming from the C3A and C4AF, that is to say this AFm and AFt, are still accounting for about 25 percent by volume. So this is a quite significant amount of the final volume of the paste.

- Notes

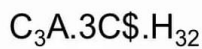
Summary



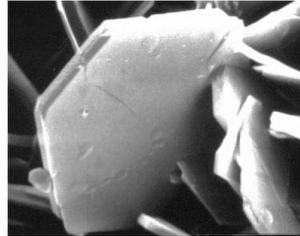
Calcium aluminate hydrates: overview



ettringite

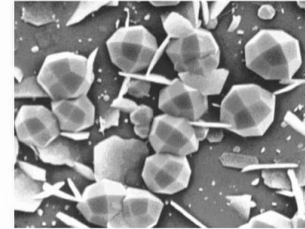


AfT – aluminate ferrite tri



AFm

aluminate ferrite mono



hydrogarnet

Now these aluminate hydrates broadly come in three families. First we have these rods which are called ettringite. Now the formula of ettringite is as written here as to say for each molecule of C3A, we have three molecules of calcium sulfate and then a lot of water. And what we are going to see in a lot of these hydrates, we can have a replacement of the aluminum ions by iron ions. These are very similar elements from a chemical point of view and because of that as well as the term ettringite, which means they are formed with aluminum, we also have this term AFt, so A and F means the possibility for having either alumina or iron oxide and T is the other anion, that is to say in this case the calcium sulfate, and here we have three calcium sulfates, so three gives us the word tri. Now the second family has many more variants depending on the different anions that we find. And for this reason we tend to use more often the generic word AFm standing for aluminate ferrite mono phase. And finally, we don't usually have very much of it in common cement paste, we have the hydrogarnet. And in the next slides we are going to look at each of these families in turn and see in more detail about their crystal structure and the possibilities of solid solution.

Notes

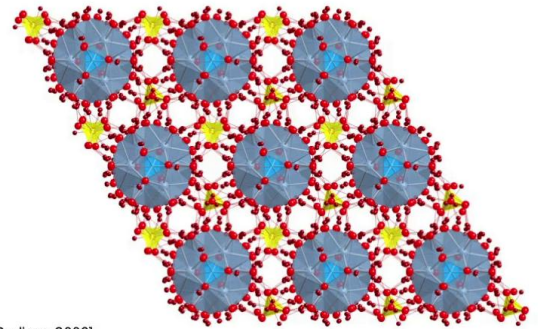
Summary



1m 14s

Ettringite or Aft phases

- $[\text{Ca}_3(\text{Al,Fe})(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2 \cdot \text{X}_3 \cdot x\text{H}_2\text{O}$
 - X is divalent anion
- Ettringite forms early on in cements pastes
- Some may later transform into AFm phases depending on sulfate and carbonate activity
- No systematic changes in composition reported for blended cements
 - Solid solution between (Al, Fe)[6], miscibility gap $0.3 < \text{Al}/(\text{Al}+\text{Fe}) < 0.6$ (Möschner et al., 2009)
 - Incomplete solid solution between CO_3 - SO_4 : ettringite stabilisation of AFt- CO_3 at low T (Matschei & Glasser, 2010)



Hartman & Berliner, 2006]

Ettringite was first found in the town of Ettringen, hence the name, and in nature it can form these very big crystals so if we look at this picture here we can see we can get these really huge crystals which have this hexagonal cross-section. There we can see the crystal structure is like this. So we have columns and in these columns we have the alumina and we have the calcium surrounded by lots of hydroxide ions and then in between the columns we have the sulfate molecules. More generally the formula is like this, so we have three calciums, either aluminum or iron, and then these hydroxide groups and the water molecules and then the X_3 . This can be a divalent anion. In this case we are talking about here it is sulfate. But another possibility is carbonate. So ettringite forms early on in cement pastes and some may later transform into the AFm phases that we are going to see later depending on the amount of sulfate and carbonate we have in the paste. So in most cement pastes and indeed most blended cements, there is not much variation in fact in the composition. The composition we find is pretty close to the stoichiometric ettringite.

Notes

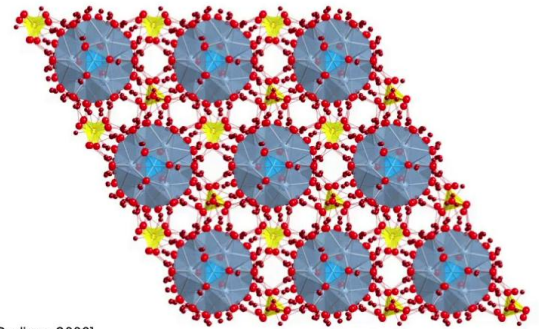
Summary



2m 53s

Ettringite or Aft phases

- $[\text{Ca}_3(\text{Al,Fe})(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2 \cdot \text{X}_3 \cdot x\text{H}_2\text{O}$
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 - Incomplete solid solution between CO_3 - SO_4 : ettringite stabilisation of AFt- CO_3 at low T (Matschei & Glasser, 2010)
- Ettringite
 - High water content
 - Low density: 1.8 g/cm^3
 - Good space filling



[Hartman & Berliner, 2006]

So even though we know we can have this solid solubility between aluminum and iron, in actual cement paste, because of the high alkalinity of the pore solution, not much of the iron actually goes into the ettringite phase. It is pretty much just the pure aluminum form. We have some solid solutions as I have mentioned between carbonate anion and sulfate and this can be stabilized at low temperature so at low temperatures we tend to get more carbonate going into the AFt phase. And the other important aspects about ettringite are that it has this high water content as we have seen. And because of this it actually has quite a low density. Okay, and because it has low density this means it fills up a lot of space. So in terms of filling space it makes a very positive contribution to strength development and other properties.

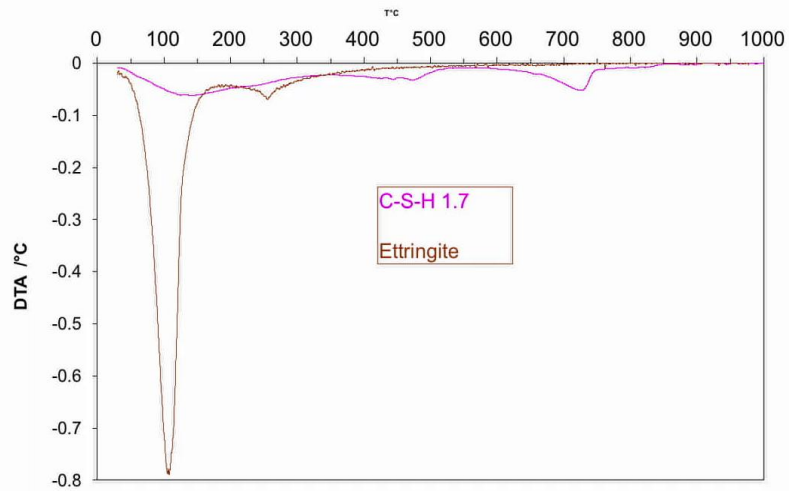
Notes

Summary



4m 17s

Decomposition of Ettringite and C-S-H in same range



Now in terms of stability the stability of ettringite thermal terms is very very similar to that of C-S-H. Here we see the thermal decomposition curves by DTA for ettringite and C-S-H. And we can see that the peak for the two is in a very very similar position at 120, 140 around that kind of temperature.

Notes

Summary



5m 15s

AFm phases: a subset of layered double hydroxides

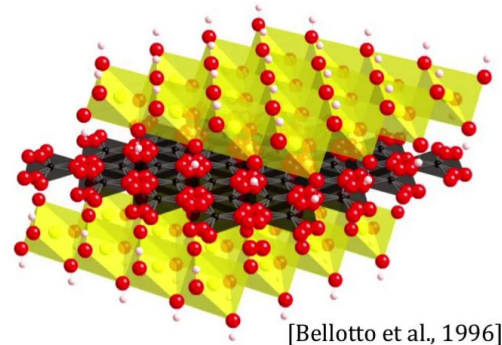
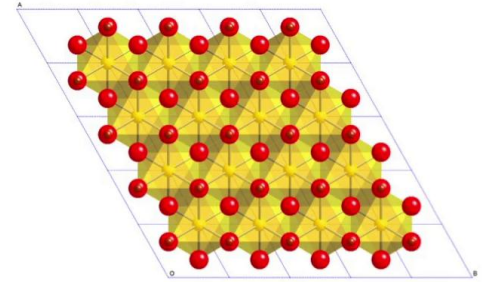
- LDH – hydrotalcite supergroup nomenclature

(Mills et al., IMA report 2012)

- $[(M_{1-x}^{2+}M_x^{3+})(OH)_2]^{x+}$ layers
- Anions** in interlayer, stacking leads to **polytypism**
- 8 groups within hydrotalcite supergroup
 - Hydrotalcite group ($M^{2+}:M^{3+} \approx 3:1$)
 - Quintinite group ($M^{2+}:M^{3+} = 2:1$)
 - ...
- Hydrocalumite group** ($M^{2+}=Ca^{2+}$, $M^{3+}=Al^{3+}$; $Ca:Al = 2:1$)



AFm phases



[Bellotto et al., 1996]

Now as we move to the second group, AFm phases, these are part of a much larger group of hydrates called layered double hydroxides. Some of you may have heard of layered double hydroxides because they are really researched quite a lot nowadays for their interesting electronic properties. And in this layered double hydroxide, we have layers of M2 and M3 ions and then between the layers we have these anions and the fact you can put in a lot of different anions leads to what is called polytypism. So in this larger family of layered double hydroxides, a large number of groups have been defined. There are in fact eight groups with this, what is called hydrotalcite in the supergroups. So there is hydrotalcite where you have three to one divalent to trivalent ions, the quintinite group where we have two to one divalent to trivalent so on. And finally we come to the hydracalumite group which is what interests us where these divalent ions are calcium and the trivalent ions are aluminum. And they exist in the ratio of two to one. So this is the AFm phases.

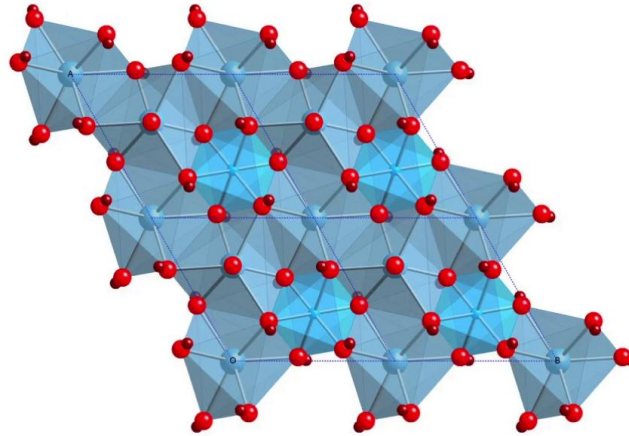
Notes

Summary



5m 38s

- LDH in cement: AFm phases
 - Main layer is a distorted brucite layer, Ca:Al 2:1
 - $\text{AFm-SO}_4^{2-} - \text{CO}_3^{2-} - \text{OH}^-$
 - What is extent of solid solution?



This is the kind of layer we have in those AFm phases. It is a distorted layer similar to what we have in brucites with two calciums to one aluminium. And then the anion that can go in between that gives us the AFm phases. Most commonly, well I mean the first one that gave its name to this group are the monosulfates where the anion is sulfate. But probably in fact more common today is where we have carbonate ions as in monocarbonate. And we can also have hydroxide ions as it is high in hydrocalumite, we can have chloride ions as Friedel's salt and even complex alumina silicate ions as strätlingite as we will see. Now one of the key questions in understanding these phases and particularly how much forms and what is their contribution to space filling, we need to know what is the extent of solid solution.

Notes

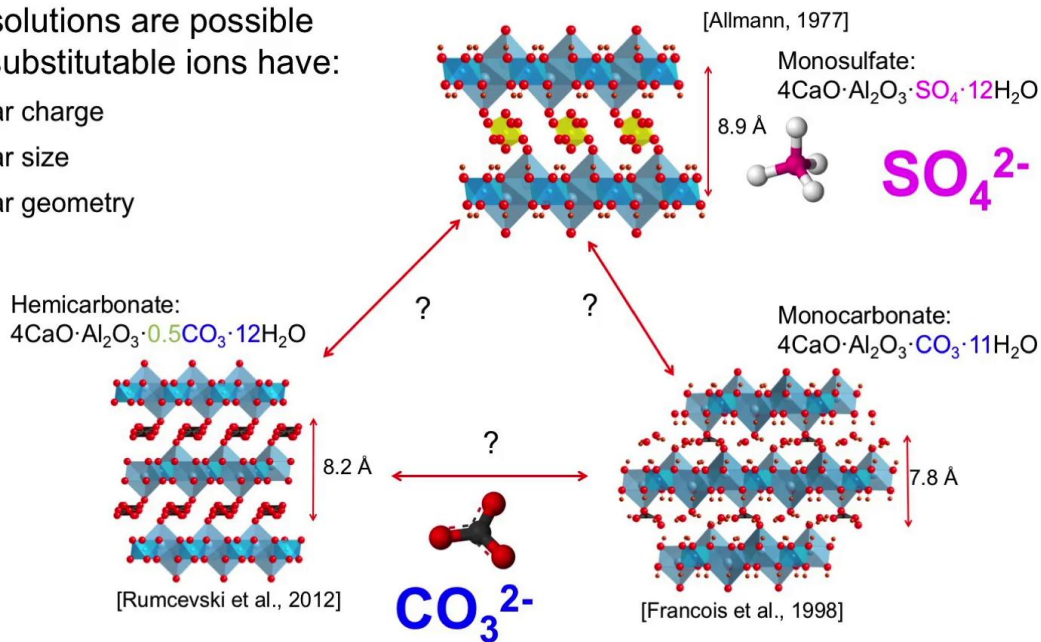
Summary



AFm solid solutions

- Solid solutions are possible if the substitutable ions have:

- Similar charge
- Similar size
- Similar geometry



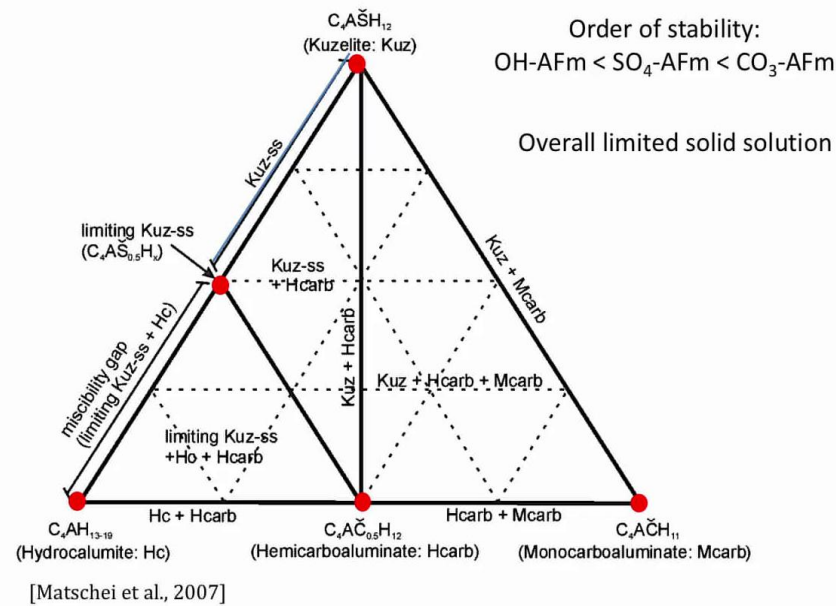
So if we take the three most common or if we take the most common substitution which is between sulfate and carbonate, we have these three phases, we have monosulfate we see at the top, we have the monocarbonate we see at the bottom on the right and the hemicarbonate which we see at the bottom on the left. Now because of the different anions in the interlayer you can see that the interlayer spacing for these crystal phases is quite different. 8.9 for the monosulfate. 7.8 for the monocarbonate and 8.2 for the hemicarbonate. So these may not seem that big but they are big enough such as in fact we find that these differences mean that we get really no solid solution between these different phases. And the transformation from one to another really occurs by dissolution and the reprecipitation of the new phases.

Notes

Summary



AFm phases: CO_3 – SO_4 – OH- phase diagram



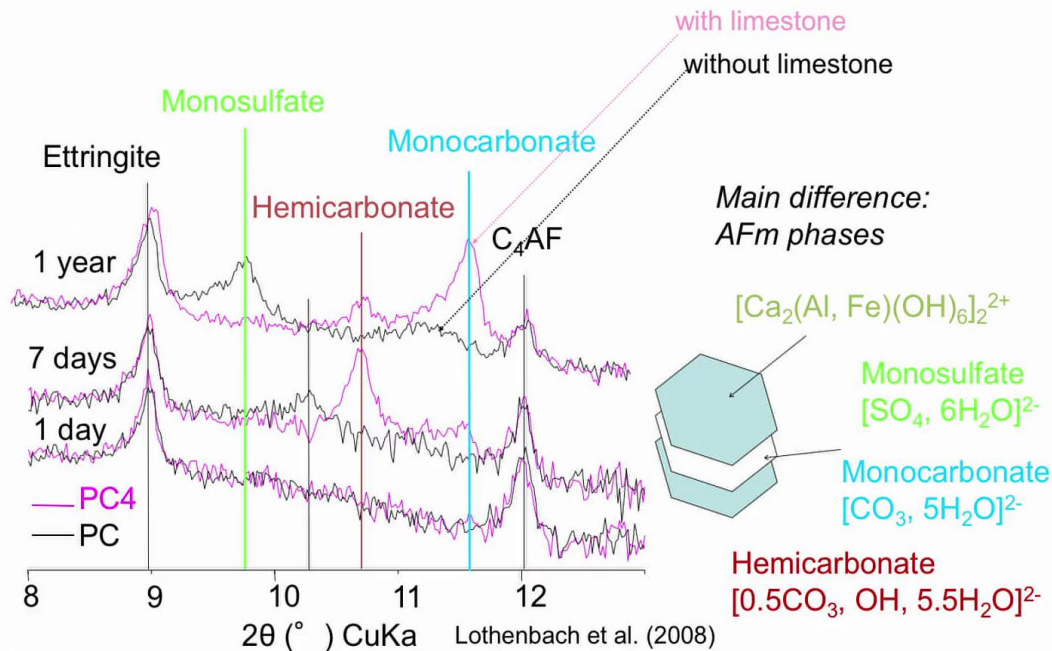
And if we look more broadly also including the hydroxide phases, the hydrocalumite phase down here, this shows us that really the only regions of solid solution we have are on this axis between the hydrocalumite and the sulfate form where we can have some solid solution. Otherwise there is really very little solid solution.

Notes

Summary



AFm phases: effect of limestone addition



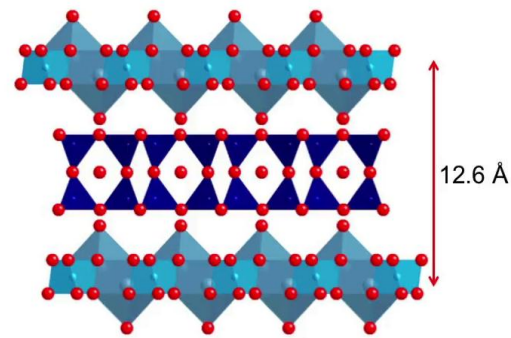
As I said classically when people are thinking about cement hydration they think about ettringite forming. And then most of the textbooks say yes there is monosulfate forming and this is what we can see happens in cement without limestone. Here you can see that on one day and seven days ettringite is dominating but by the time we get to one year we clearly have a lot of monosulfate phases. Now most cements made today do in fact contain a small amount of limestone, 3 or 4 percent is typical, because this amount of limestone has been shown to improve properties and at the same time give us a slight reduction in the net CO₂ emissions. And when we have those cements with limestone then we can see the picture changes quite dramatically. And instead of the monosulfate phase here we have instead forming first of all hemicarbonate at about 7 for about seven days. And later on monocarbonate, and this is what it is one reason why we get improved performance with this small amount of limestone because small amounts of limestone can react with the calcium aluminate from the cement forming these extra phases and this means we have more space filling and more strength.

Notes

Summary



- Compositional solid solution
 - Strätlingite (hydrated gehlenite)
 - $\text{AlSi}(\text{OH})_8^-$ groups in interlayer
 - Conditions of formation and solubility not well constrained
 - Occurrence
 - Low $\text{SO}_3/\text{Al}_2\text{O}_3$ ratio (MK, Class C FA)
 - Absence of CH



[Rinaldi et al., 1990]

Ok so finally in this AFm group, we are just going to have a quick look at this phase called strätlingite and this phase called strätlingite has this very complex alumina silicate groups in the interlayer. You can see now that this has increased quite dramatically the spacing of these interlayers from about seven or eight we had in the monosulfate monocarbonate cases to this value of 12.6. And this can be quite an important phase where we have very high contents of alumina and silica reacting in blended cements and thermodynamically it only forms once all the portlandite has been consumed. But in reality we can often find strätlingite where we still have small amounts of portlandite present.

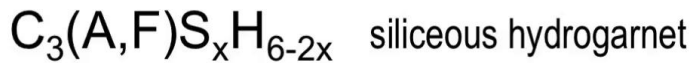
Notes

Summary

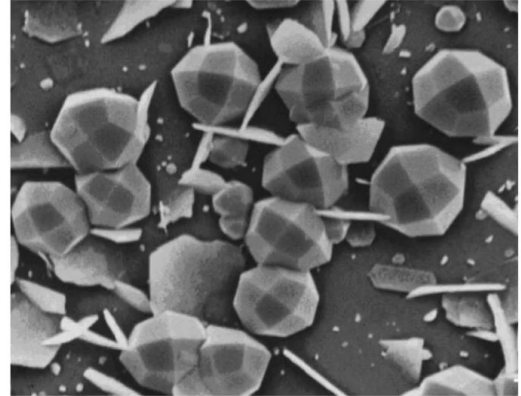


11m 07s

Hydrogarnets



- Solid solutions
 - $Al^{3+} \leftrightarrow Fe^{3+}$
 - $SiO_2^0 \leftrightarrow 2 H_2O$
- Low water content
 - **High density:** 2.5 g/cm³
 - Less space filling



[Pöllmann 2012]

So finally in this module we are going to look at the hydrogarnets and the classic formula for hydrogarnet is this formula C_3AH_6 which is also known as the mineral katoite. And more generically what we see again we can have solid solution between alumina and iron but now we can have a solid solution between one silicate group and two water groups. So this is why they call hydrogarnets, because if all the water was replaced by silicate this would be the garnet structure, and in reality we always have quite a bit of water. And in this case this is actually the phase where most of the iron goes to in Portland cement paste. So I said that the iron because of its low mobility in high alkaline solutions didn't go much into the ettringite, doesn't go much into the AFm phase but it does form the siliceous hydrogarnet which there ends up being quite a lot of. But it is rather poorly crystalline. So not often well detected by XRD. Now other important aspects about this phase is it has got a low water content and because it has got low water content it has a high density and this means that it is less space filling. So if we had a lot of hydrogarnets as we would get if we cured at a high temperature, this also contributes to the relatively poorer strength at high temperatures because this phase occupies less space.

Notes

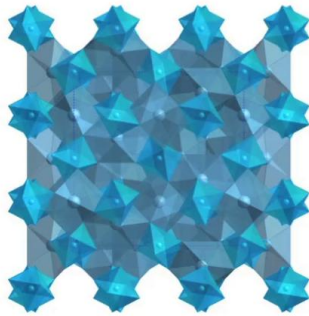
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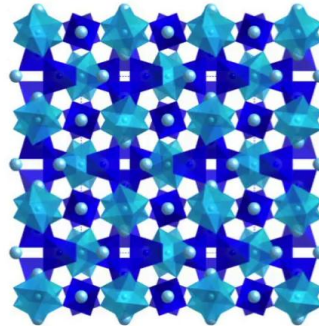
11m 59s

Hydrogarnets

- Si[4] connects Al[6] in siliceous hydrogarnet
- Thermodynamically predicted phase in many blended cements
- Location of most of iron in mature pastes



Hydrogarnet
[Cohen-Addad et al., 1964]



Siliceous hydrogarnet
[Sacerdoti & Passaglia, 1985]

So here are some other pictures of the crystal structures of the hydrogarnet. It is a sort of three dimensional structure in which four coordinated silicon connect the six coordinates of the aluminium. It is predicted to form quite a lot in blended cement. But as I said really not much except for the iron.

Notes

Summary



13m 37s

Summary



- Aluminate containing hydrates constitute an important part of the hydrate assemblage (~ 25 vol.% in mature pastes)
- They contribute to space filling (strength development) in the same way as C-S-H and portlandite
- Ettringite can be substituted, but fairly pure in Portland pastes
- AFm phases solid solution is important; limestone favours carboaluminates
- Hydrogarnet forms only at long ages (high temperatures)

So if we summarize this module, what we have seen in this module is that if the aluminate containing hydrates are a very important part of this hydrate phase assemblage they make up about typically 25 percent of the volume in mature paste. They do contribute to space filling and therefore they contribute to strength development very much in the same way as C-S-H. In paste as long as we have a continuous C-S-H phase with ettringite and monosulfate finally buried in it, then they are contributing in same way to strength development. Ettringite can be formed with different substitutes. But in most Portland cement paste, most blended cement paste, it is really very close to the stoichiometric formula. In AFm phases on the other hand, solid solution is much more important and limestone as we find almost ubiquitously present in modern cements that favours the formation of carboaluminates rather than monosulfate phases as you have properly learnt in the past. Final type, hydro garnets forms only at long ages or at high temperatures. OK. So thank you very much.

Notes

Summary

