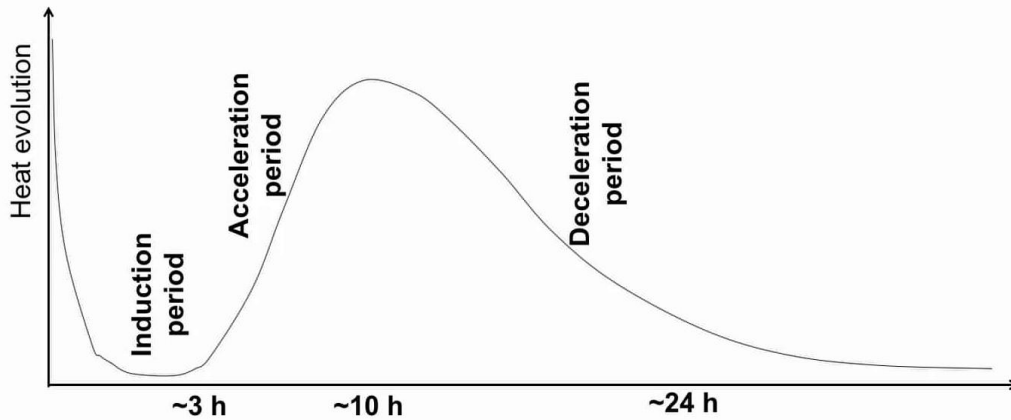


Kinetics are key

underlying mechanisms not well understood



So hello again. Having looked at the different hydrates that forms, calcium hydroxide, calcium silicate hydrates, these phases that come from the aluminates, now we are going to look at how these different hydrates form in time, the kinetics of the hydration reaction. Here we are going to look first of all at the hydration of the calcium silicate phases. And this shows the typical hydration curve for tricalcium silicate. What you see is that initially we get a very high rate of heat evolution and then very quickly the rate of heat evolution, that is to say the rate of reaction, falls away and we get this period of very slow reaction during a few hours. And this is usually called the induction period. Now from a practical point of view this is very important because this induction period gives us the time to mix our cement or concrete, to move it on to site, to place it in the forms and produce the kind of concrete element we want to have in our buildings. And then after typically something like three hours the reaction takes off again.

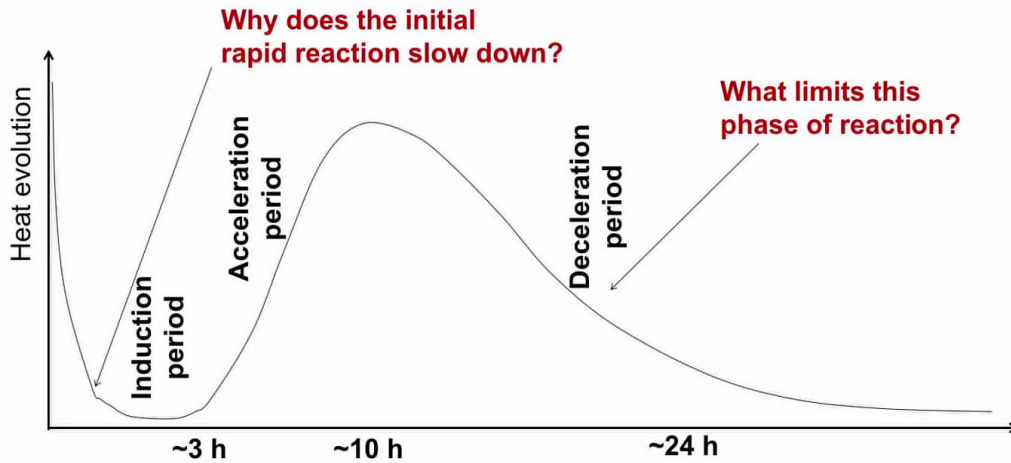
Notes

Summary



Kinetics are key

underlying mechanisms not well understood



We have what is called the acceleration period, after about ten hours then it starts to slow down again and what we call the deceleration period and after the first day or so, the rate of heat reaction is really quite low, even though at 24 hours we may only have formed about twenty five percent or less of the final strength of our concrete. So there is quite a lot happening after the first day but it is happening much more slowly, so it is more difficult to follow from the point of view of this heat evolution. And in particular, in terms of these kinetics, there are two questions that have occupied researchers. First of all this initial slowdown, why do we get this initial slowing down? Then why do we get this second slowing down for the deceleration period?

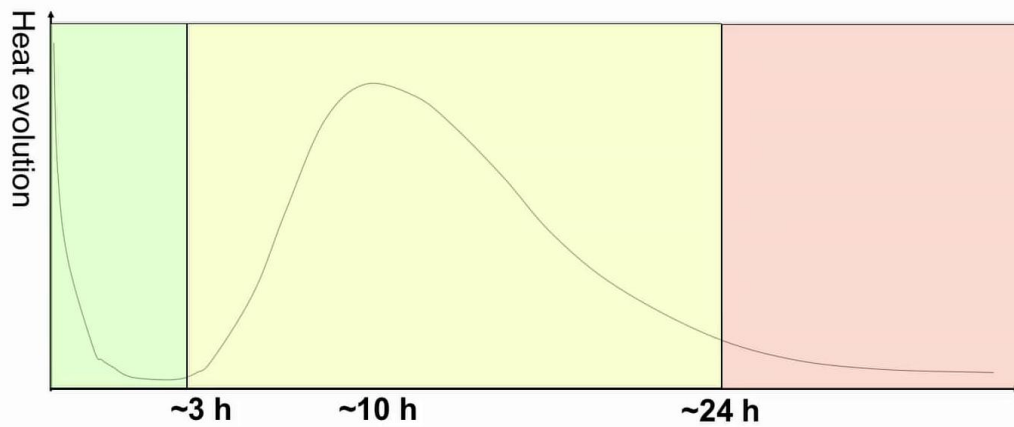
Notes

Summary



1m 15s

Three periods



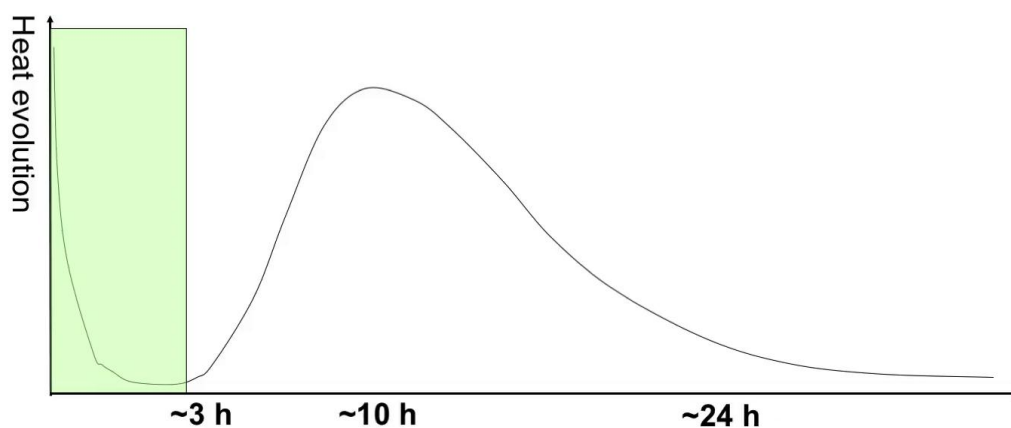
And in these modules we are going to look individually at three separate periods. We are going to look at this first period of the initial heat evolution and the induction period, then we are going to look at this main heat evolution peak here. And then we are going to look at the slow ongoing reaction. There is quite a lot happening in this final period. In fact a lot of the strength is developing during this time but it is quite difficult to see because it is quite difficult to measure what is happening due to the very low rate of heat evolution.

Notes

Summary



Induction period



Right, so in this first one on the kinetics, we are going to look at this induction period.

Notes

Summary

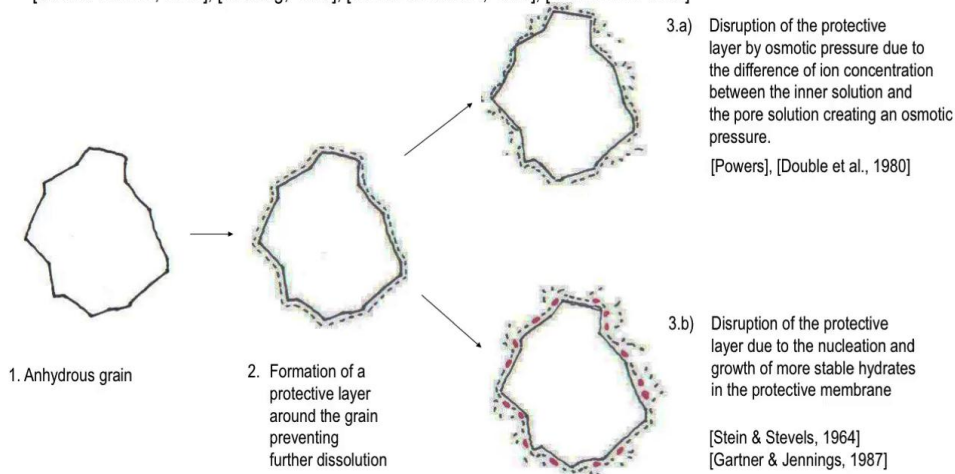


2m 45s

Different theories about the induction period

A) PROTECTIVE MEMBRANE LAYER

[Stein & Stevels, 1964], [de Jong, 1967], [Kondo & Daimon, 1968], [Brown et al. 1985]



No direct evidence

It seems kind of odd that the reaction should start fast and then slow down and to explain this what is classically being advanced has been this idea that we have this protective membrane forming around the grains. And many people over the years have advanced this kind of hypothesis, then there has been all kinds of different theories as to why this layer should suddenly disappear and this is why in fact one of the main weaknesses of this theory, that nobody really has come up with a coherent idea of why the membrane forms and then suddenly disappears after some time. But perhaps nowadays it is more important to realize that there is really no evidence for this protective layer. Back in the 60's when people first came up with this idea, the fact we couldn't see it wasn't really too much of a problem but nowadays where we have very advanced characterization tools, this is really a big issue. I mean it is like the emperor's new clothes.

Notes

Summary



2m 51s

Portland cement observed in the cryo SEM

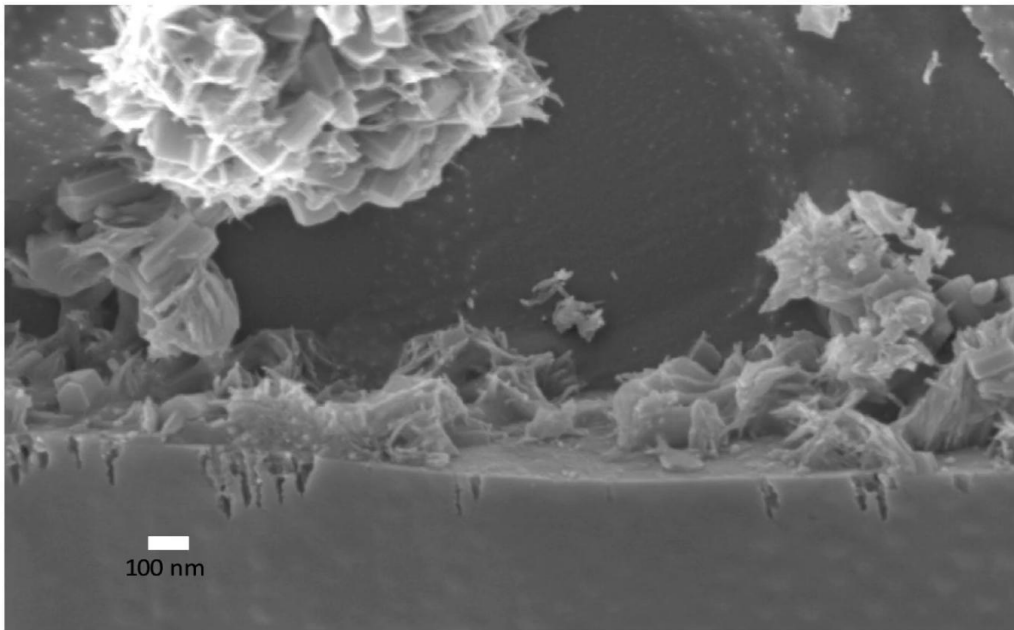


Image from Luc Nicoleau

Here we see a picture which I think is particularly important, it was lent to me by Luc Nicoleau and what we see, this was made in a cryo S.E.M. So in a cryo S.E.M. what happens? You take a cement paste, you freeze it, you break it, you put the broken frozen sample into the microscope and then sublime the water. So it is a kind of gentle way of drying but you do have to eventually remove the water because electrons can't penetrate through water, so you have to remove the water first. And what we can see here, we can see this is an alite grain here which is being fractured. Along the surface of this alite grain we see the hydrates. So here is CSH here. We don't really see much calcium hydroxide here, we see a little bit of ettringite for example down here, a little bit up here. But very clearly these hydrates don't give a continuous membrane on top of this cement grain. And in fact we can see these pits, we are going to come back to these pits, they are very very important. And particularly on these pits we can see there is no indication of any kind of covering. And this micro office has quite a high resolution, the bar here tells you about one hundred nanometers scale, so you know even if there was a layer only a few nanometers thick we would expect to see some indication of it.

Notes

Summary



4m 00s

Portland cement observed in the cryo SEM

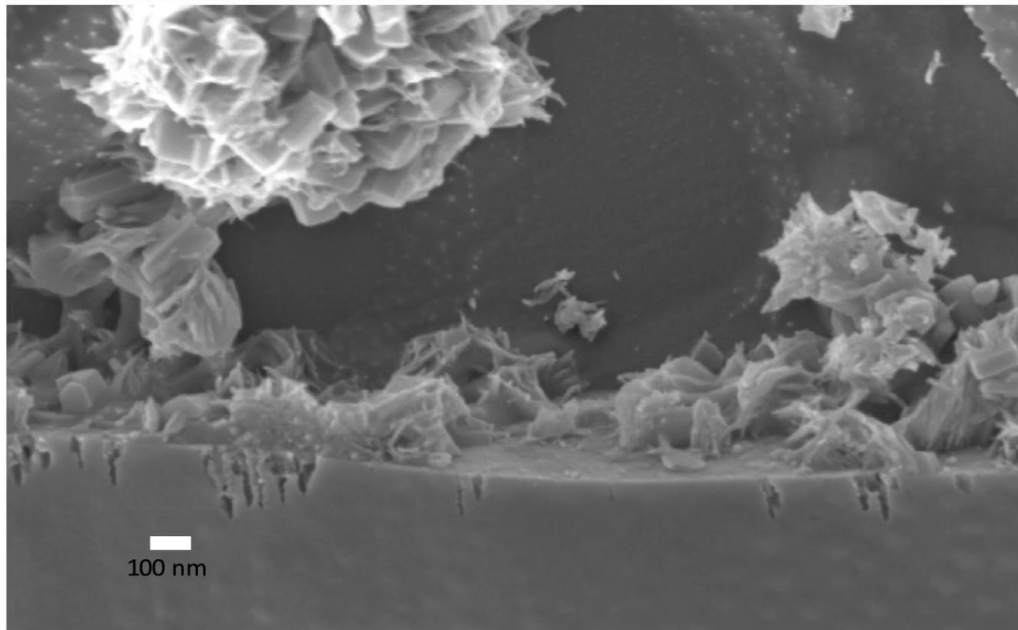


Image from Luc Nicoleau

So really this theory of the protective membrane that most people have been promulgating for a number of years now really just doesn't hold up to examination.

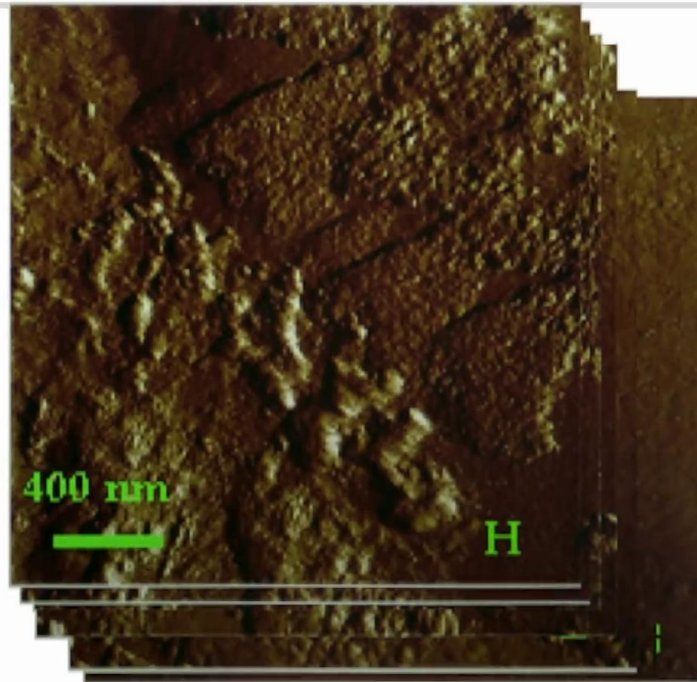
Notes

Summary



5m 39s

AFM wet cell



Thesis Helène di Murro U. Bourgogne

And here is another sequence where we can see in this case what is happening under water. So this sequence was taken in the wet cell of atomic force microscope. And as we run the sequence as we do here, here we run the sequence, we can see that we get this rough area forming here and then after a while we start to see these steps. OK these steps here. And the steps are moving as we have dissolution at those steps. Those are particularly important things to observe here, first of all a rough area forming and then moving to these steps which retreat.

Notes

Summary

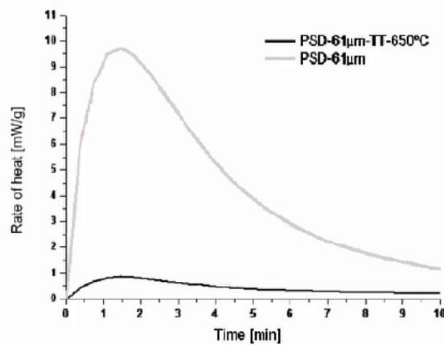


5m 52s

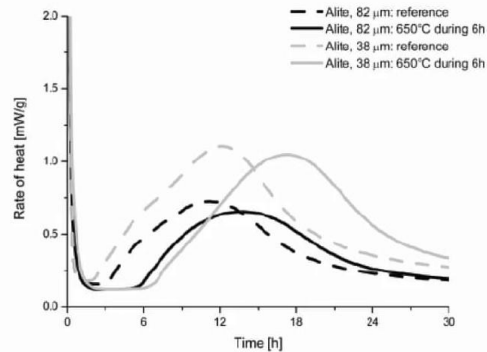
Effect of annealing

alite of narrow particle size distribution

First dissolution peak



Main hydration peak



This cannot be explained by protective layer theory

Now another observation which completely to my mind refutes the protective layer theory is this experiment we did about annealing. So we took alite and one part of the alite was then heated up to anneal it, to remove defects and you can see here this dramatic effect the annealing has on the hydration kinetics. It really extends this induction period, but after this induction period, then the hydration seems pretty much the same as it was for the unannealed sample. And over here we see the first peak and we see for the annealed sample, the initial heat evolution is much lower than from the non annealed sample. Now how could this be explained by a protective layer theory. If we were going to say “well maybe the layer is thicker in the case of the annealed sample”, that doesn't correlate with what we see from the first evolution peak. And you know if we had a different kind of layer forming, why should we expect the hydration to be the same afterwards. This is just one example of experimental results that cannot be explained by this theory and more results are discussed in the paper by Juilland et al. which can be found in the references.

Notes

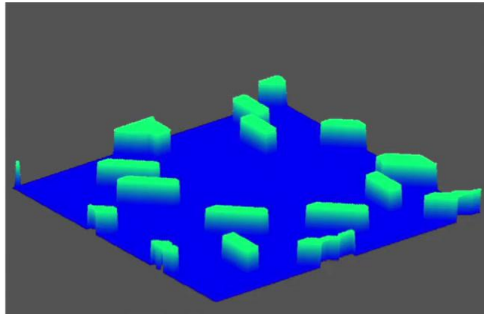
Summary



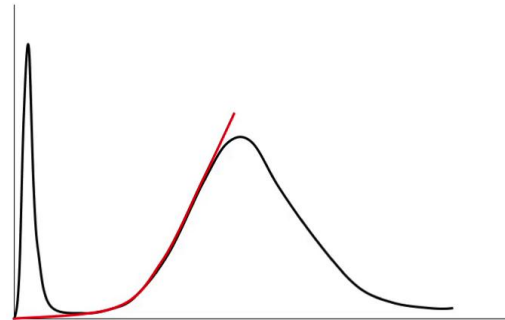
Different theories about the induction period

B) NUCLEATION THEORY

[Fierens and Verhaegen, 1976],[Odler and Dorr, 1979],[Gauffinet et al., 1998]



[Garrault et al., 2007]



Formation of nuclei on surface controls early reaction.
Growth of the nuclei is the rate limiting factor.

What explains initial slow down?

So the alternative theory is really just to say well we have nucleation and growth and nucleation and growth is a very well known phenomenon in many reactions, in metals, from aqueous solutions, many many chemical processes, we can make a simple model of nucleation and growth as is shown on the left here where we have these little islands which are represented in the nuclei of CSH and as they grow, they give this acceleration peak. So in terms of the acceleration peak as we will see in the next module, this can be very well explained by nucleation and growth. But what we are missing here is any explanation of why we have this slow down from the first dissolution. So to understand this slowdown better, I think we need to go to the work that has been done in geochemistry.

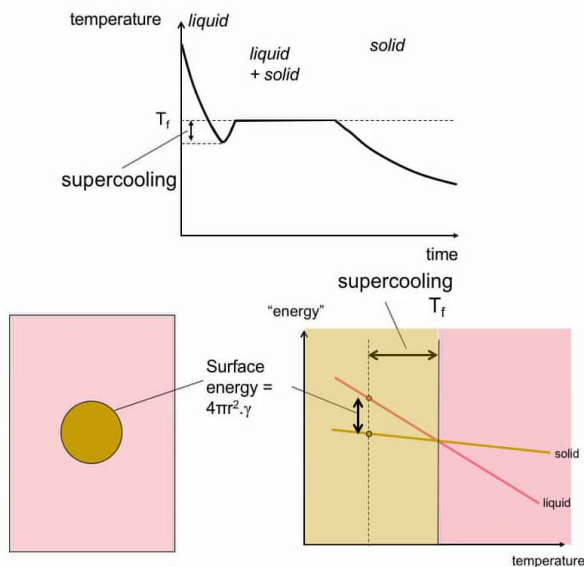
Notes

Summary



8m 05s

Dissolution = negative growth



Growth: example solidification of metals

Supercooling due to need to form surface of nuclei

Now here I want to introduce this idea of dissolution being a negative form of growth. And the little diagrams over on the left here will probably be familiar to those of you who studied classical metallurgy and material science and have looked at the solidification of metals. So it is well known in the solidification of metals, solidification of just about anything in fact, that we don't get the solid forming exactly at the melting temperature, the temperature of fusion as indicated here. And this is because we have super cooling and we need this super cooling because we need to go to this point here where there is an energy difference between the liquid and solid, and that energy difference is sufficient to give the surface energy to form the first nuclei. So those of you who are familiar with that, just look at any classical material science textbook you will find a more detailed explanation. Now, when we come to think about dissolution, if we have dissolution from a smooth surface, this is always also going to require energy for forming the extra surface, so here we have an imaginary surface and here we have a little bit of dissolution going on and you see dissolution means that we have to get this extra surface that is shown there.

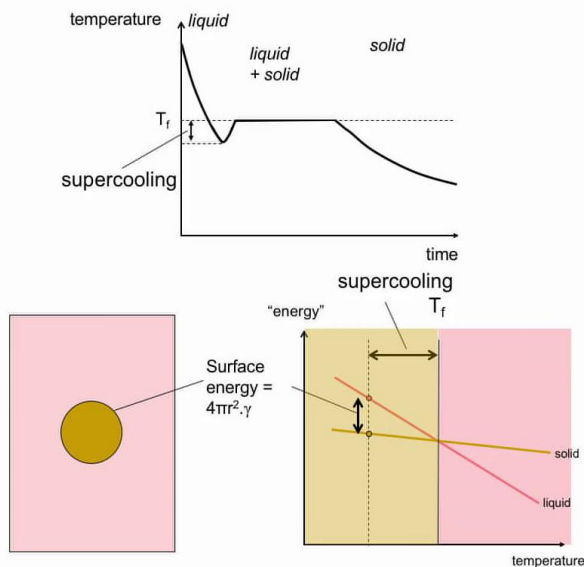
Notes

Summary



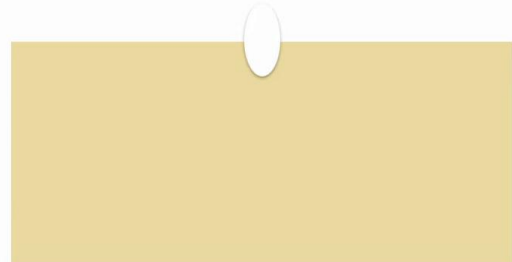
9m 02s

Dissolution = negative growth



Growth: example solidification of metals
Supercooling due to need to form surface of nuclei

Dissolution from smooth surface also
requires energy for extra surface



This energy comes from
the undersaturation of the solution

And then in this case, this extra surface energy needs to come from the under saturation of the solution. That is to say if the solution contains less ions than it can do at saturation, it has a higher energy, it can be used to produce this extra surface. So this analysis has been developed quite rigorously in the theology of chemistry and in the next slide we see two examples from works published in this area.

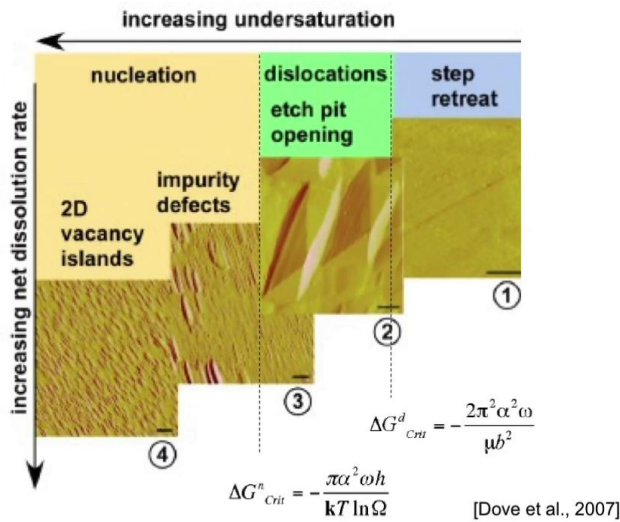
Notes

Summary

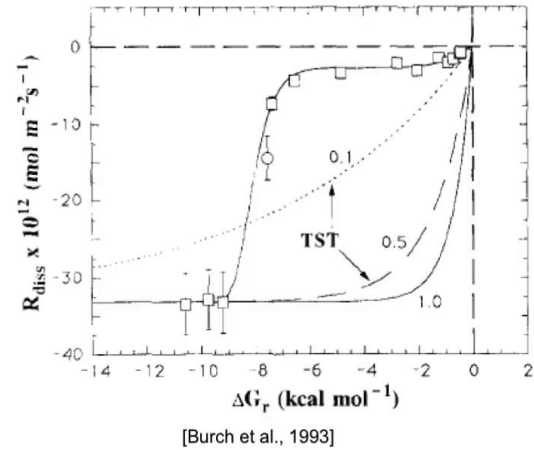


Study of theories of dissolution from Geochemistry

dissolution as negative growth



Albite dissolution at 80° C and pH 8.8



So the first example shows pictures of the different modes of dissolution of quartz. Standard quite high temperature, and I really want to underline that because of this idea of dissolution as being the negative of growth, we see that the undersaturation is increasing as we go to the left and the dissolution rate is increasing as we go down. So this is kind of the opposite to what we would expect on a normal axis system. And then we see here for the quartz that a very high degrees around the saturation, we have got a lot of excess energy due to that undersaturation so we can form a lot of these very small etch pits, these 2D vacancy islands. As we move a little bit closer to saturation, we see that these etch pits tend to focus on dislocations or other kind of defects we have in the crystal structure and as we come close to saturation, we change radically the mode of dissolution and instead of forming pits, we form this step retreat. And remember that picture we saw in the AFM of dissolving alite, how we saw that first of all we formed a rough surface which is similar to these first three pictures here and then we went to step retreat.

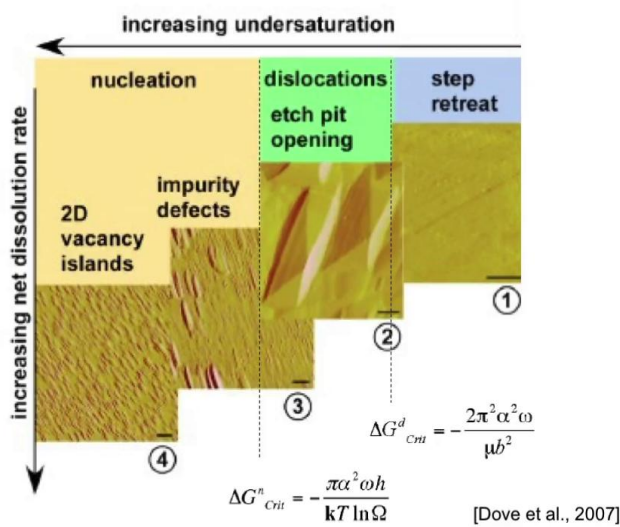
Notes

Summary

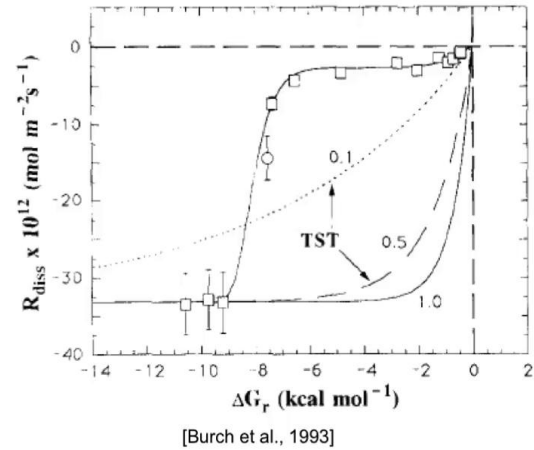


Study of theories of dissolution from Geochemistry

dissolution as negative growth



Albite dissolution at 80° C and pH 8.8



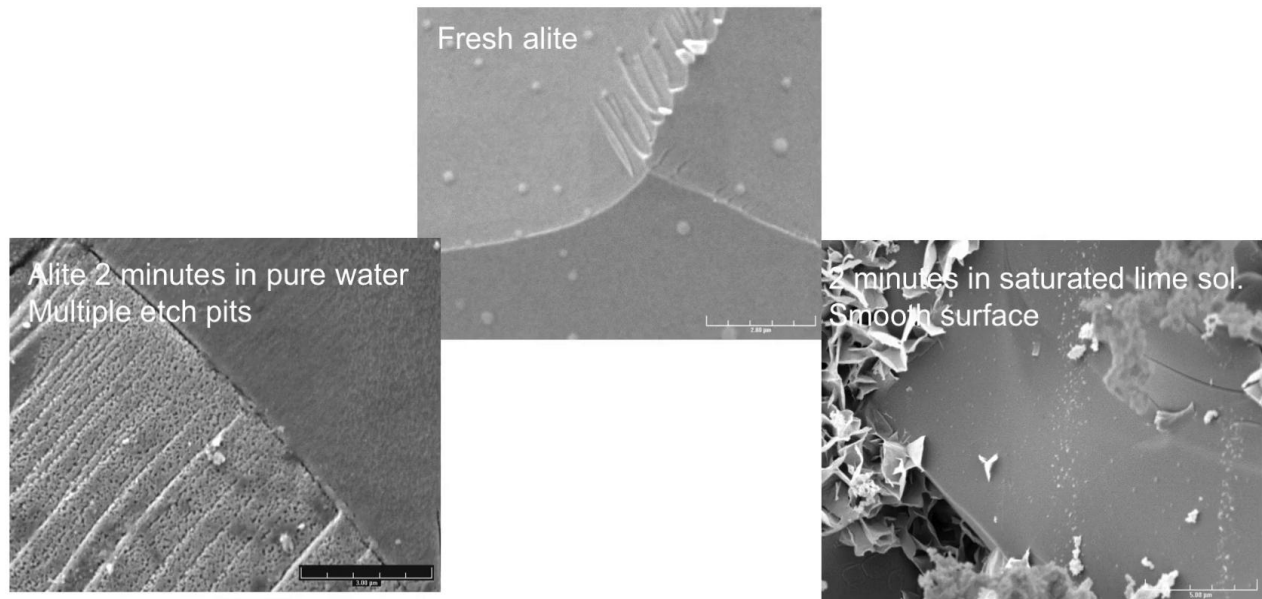
Now on the right here, we see how this translates quantitatively in terms of the rate of dissolution as a function of the Delta G. Now the delta G can just be derived from the difference between the equilibrium saturation and the actual under saturation. So what you see from the experimental points here is we get this sudden transition from a fast dissolution at high delta Gs to a slow dissolution and this transition occurs when we are still in fact quite far away from the equilibrium saturation which is here. And this step function cannot at all be captured by these other lines on here which shows what you would predict from a classical transition state theory, as is used in chemistry. So this transition between fast solution and slow dissolution is quite abrupt. Now the question is this is being well proven for many minerals, but does it apply for cement minerals? Well you know my first question is “well why not”? You know if it applies for all other minerals, why should the minerals we have in cement clinker be any different?

Notes

Summary



Does this apply to alite?



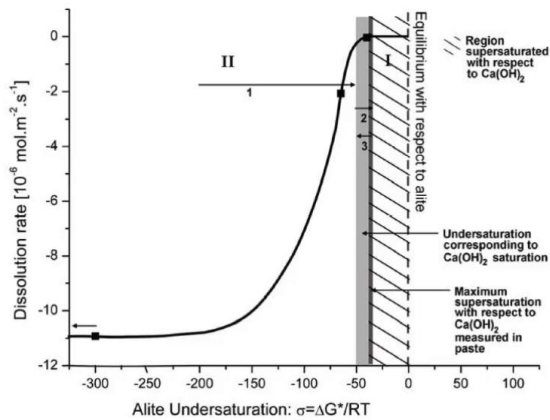
And in fact we see that they are not any different, this is a classical experiment done by Patrick Juilland a few years ago in my laboratory. What we see in the middle here, we see the alite which was freshly produced in the laboratory. And then he took this fractured alite and either dipped it in pure water and when we dipped it in pure water as you see on the left hand side, what we see is that very quickly we get this very rough surface forming with these etch pits. Because we have got a high undersaturation with the pure water, we rapidly form these etch pits and we can see it has got very strong crystallographic relationship, because we have actually got two alite grains here and we can see that one grain is being heavily attacked whereas the other grain is remaining relatively unattacked because it is probably in the wrong orientation. Whereas on the right hand side here, if we take exactly the same alite and now put it in saturated lime solution, so saturated lime solution is getting much closer but less undersaturated with respect to alite, we see that now we no longer got the energy required to give us these etch pits and we have got really just smooth surface.

Notes

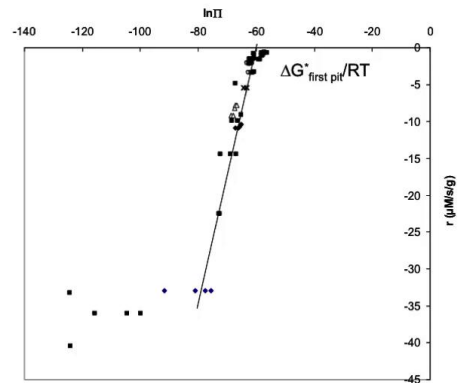
Summary



Evolution of the rate of dissolution



[Juilland et al. 2009]
From theory



[Nicoleau et al. 2011]
From experiment

So there was really the defining experiment and then when we made a theoretical analysis, we could see on the left here from this classical paper of Juilland et al. in 2009, we see that this is the undersaturation and the dissolution rate has this step function which occurs around the level of saturation of Portlandite. And then Luc Nicoleau and André Nonat really show that we could have exactly the same behavior experimentally. So here, we have a theoretical treatment here, experimental treatment here, and quantitatively, they really match extremely well.

Notes

Summary



Rate of Dissolution: modelling

$$\text{Rate} = k_{\text{diss}} \cdot a_{\text{SSA}} (SI_{\text{max}} - SI_{\text{alite}}) + a_{\text{SSA}} \cdot c_{\text{step_retreat}}$$

$SI_{\text{alite}} = \text{IAP}/K_{\text{sp}}$ of alite

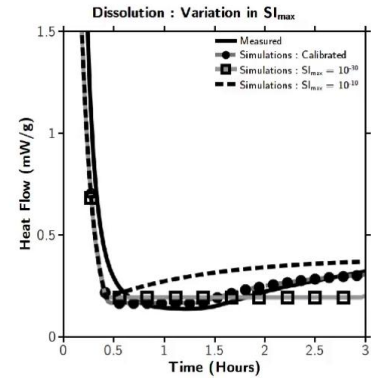
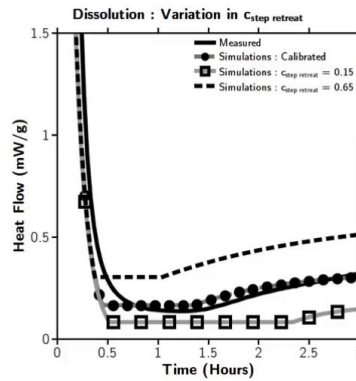
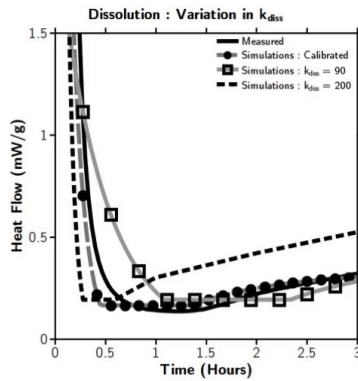
SI_{max} = Critical undersaturation of alite

a_{SSA} = Specific surface area

k_{diss} , SI_{max} and $c_{\text{step_retreat}}$ are calibrated from model systems

Fast dissolution regime

Step-retreat regime



[Kumar et al. 2012]

We could then take the same theoretical framework but apply it in a completely different way, so if we now take a model where we are trying to fit the calorimeter curves, we can find that we get the best fitting here when we get values for this step function, exactly the same as I showed you in the previous slide.

Notes

Summary



15m 57s

Induction period, summary



- No evidence for protective layer, **cannot** explain many experimental results
- Dissolution as a function of undersaturation:
 - Based on solid theoretical foundation from geochemistry;
 - Excellent agreement between, theory, experimental measurement of dissolution and modelling fit to calorimetry curves;
 - Can explain all experimental observations.

Coming to the summary here, I think what is very important in this module is that the most common theory you will find in your textbooks really is just not true. I mean I am sorry I know this is very destabilizing for people trying to learn about cement chemistry, but it is really very important, you know. It is not uncommon in science for one theory to be proven for a long period of time and then for somebody to come along and say that no it is not like that. And those of you who studied the history of science maybe know about the phlogiston which was kind of a negative oxygen, which was believed to explain a lot of things in metals. You can go read about that in your spare time. But really I want you to come away from this to really understand that there is no protective layer forming, there is no experimental evidence for it and most of the experimental results cannot be explained by that. But on the other hand we can explain this initial slowdown by dissolution as a function of the undersaturation. And this has a very sound theoretical framework from geochemistry. There is excellent agreement between theory, experimental measurements and what we can do with modeling and really we can explain all the experimental observations. So thank you and I hope that has been useful for you.

Notes

Summary



16m 22s