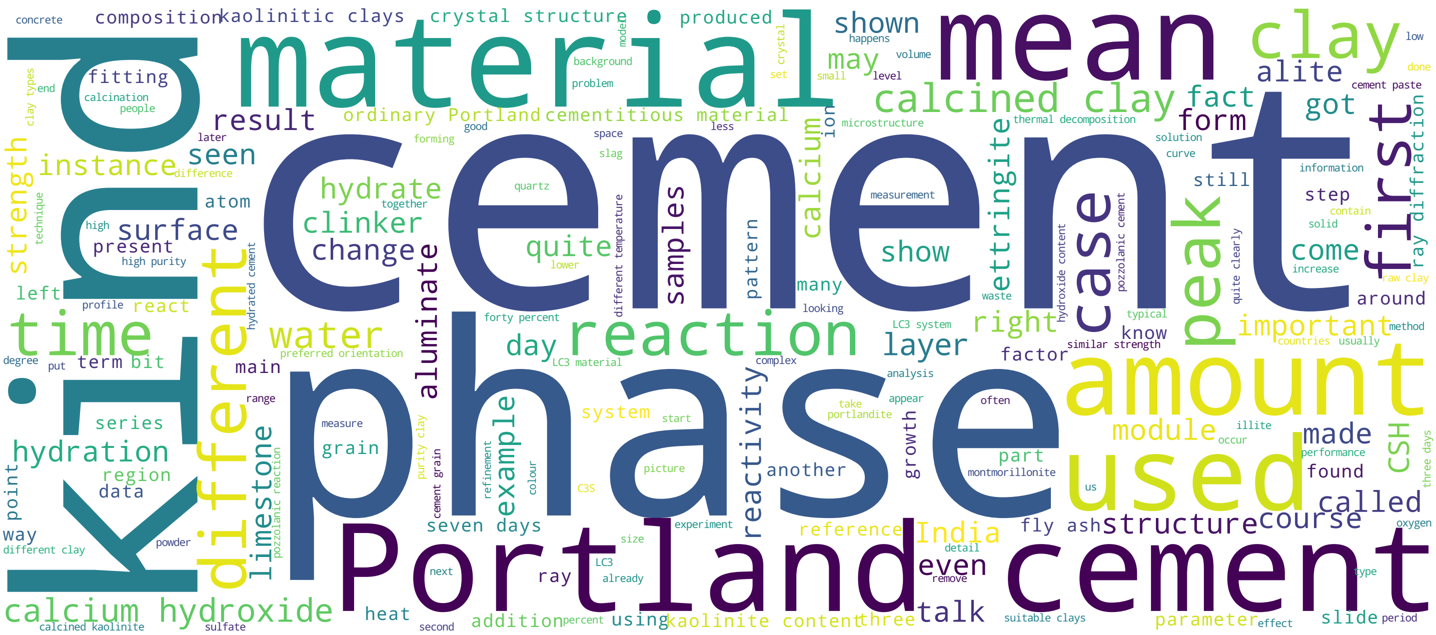
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Introduction 4:
LC³: limestone calcined clay cement

Cement Chemistry and Sustainable Cementitious Materials

Professor Karen Scrivener, FREng



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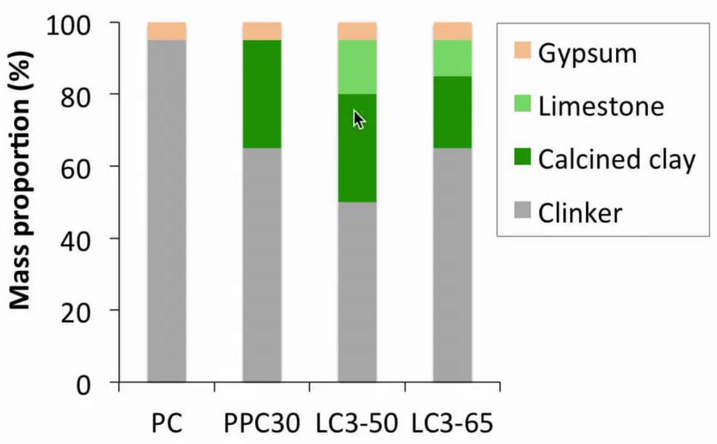
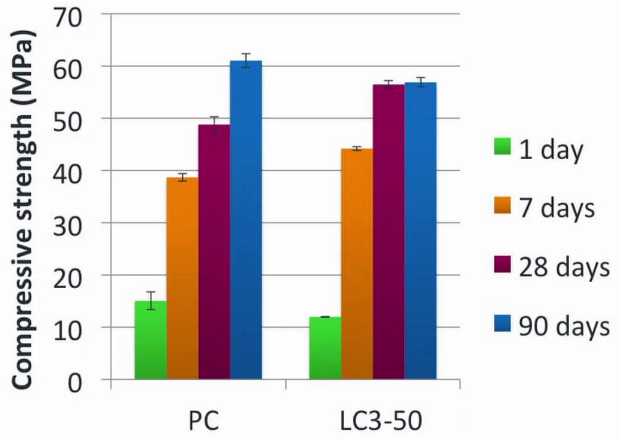
Video

EPFL

What is LC^3



LC^3 is a family of cements, the figure refers to the **clinker** content



- 50% less clinker
- 30% less CO_2
- Similar strength
- Better chloride resistance
- ASR resistant

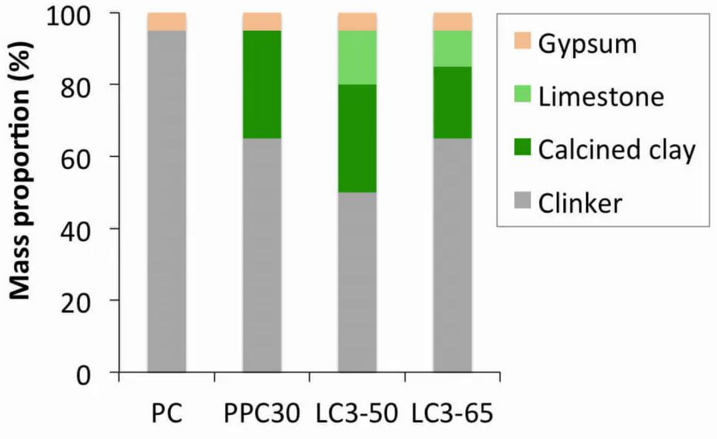
So welcome to video number four in this introductory module. And in this video we are going to talk about LC3 or limestone calcined clay cement. So what is limestone calcined clay cement? This is actually a family of cements and often we talk about LC-350 or LC-365. The figure in this case refers to the clinker content. So here we see on the left, we see the composition of ordinary Portland cement where we have about 95% clinker, and 5% addition of calcium sulfate or gypsum. When we have typical Portland pozzolanic cements as shown here, we will have about 70% clinker and about 30% pozzolan, which can be typically something like fly ash but can also be calcined clay. And usually because of the reactivity of these pozzolanic additions, 30% is the maximum level of addition we find in practice. However, what is very special about the LC3 family, is now instead of adding just calcined clay on it is own, we add calcined clay together with limestone. And what we find is that we can add an extra 15% of limestone, we can remove 15% more of the clinker, and we can get the same performance as in the pozzolanic case here. So on the right here we see some strength results for LC3-50.

Notes

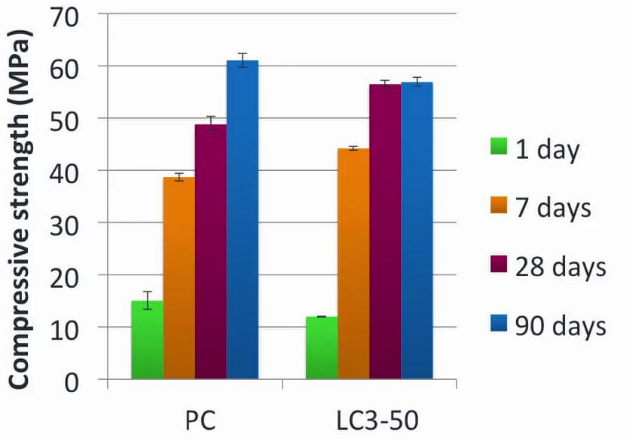
Summary

0m 04s

What is LC³



LC³ is a family of cements, the figure refers to the **clinker** content



- 50% less clinker
- 30% less CO_2
- Similar strength
- Better chloride resistance
- ASR resistant

You see that one day the strength is somewhat lower than it was for the ordinary portland cement, But already by only 7 days, the strength of the LC3-50 system has surpassed that of the ordinary portland cement and it is still higher at 28 days. So this is quite remarkable because it means that for only 50% of the clinker, we have the same performance. This also means we have about 30% less CO2. We get as I said similar strength. And in some respect, we have quite a big improvement in the properties, particularly in respect to chloride penetration and to alkali silica reaction.

Notes

Summary

1m 49s

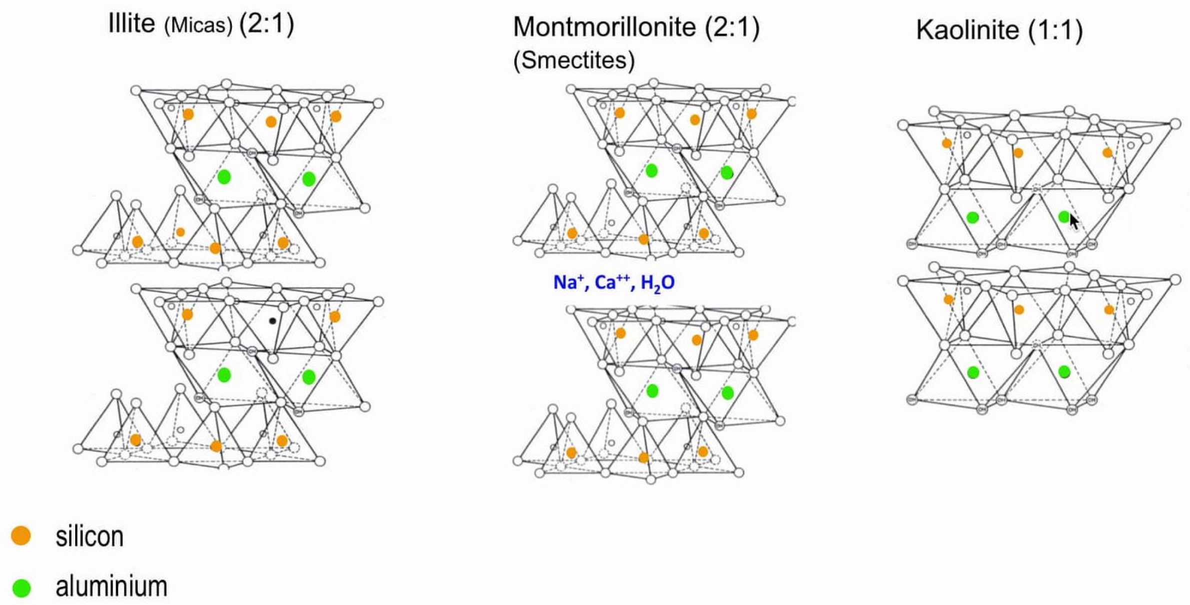
So in this module, what we are going to talk about is what types of clays can be used, how they can be calcined and where we can find the kind of suitable clays in the world today.

Notes

Summary

2m 38s

Three basic clay structures

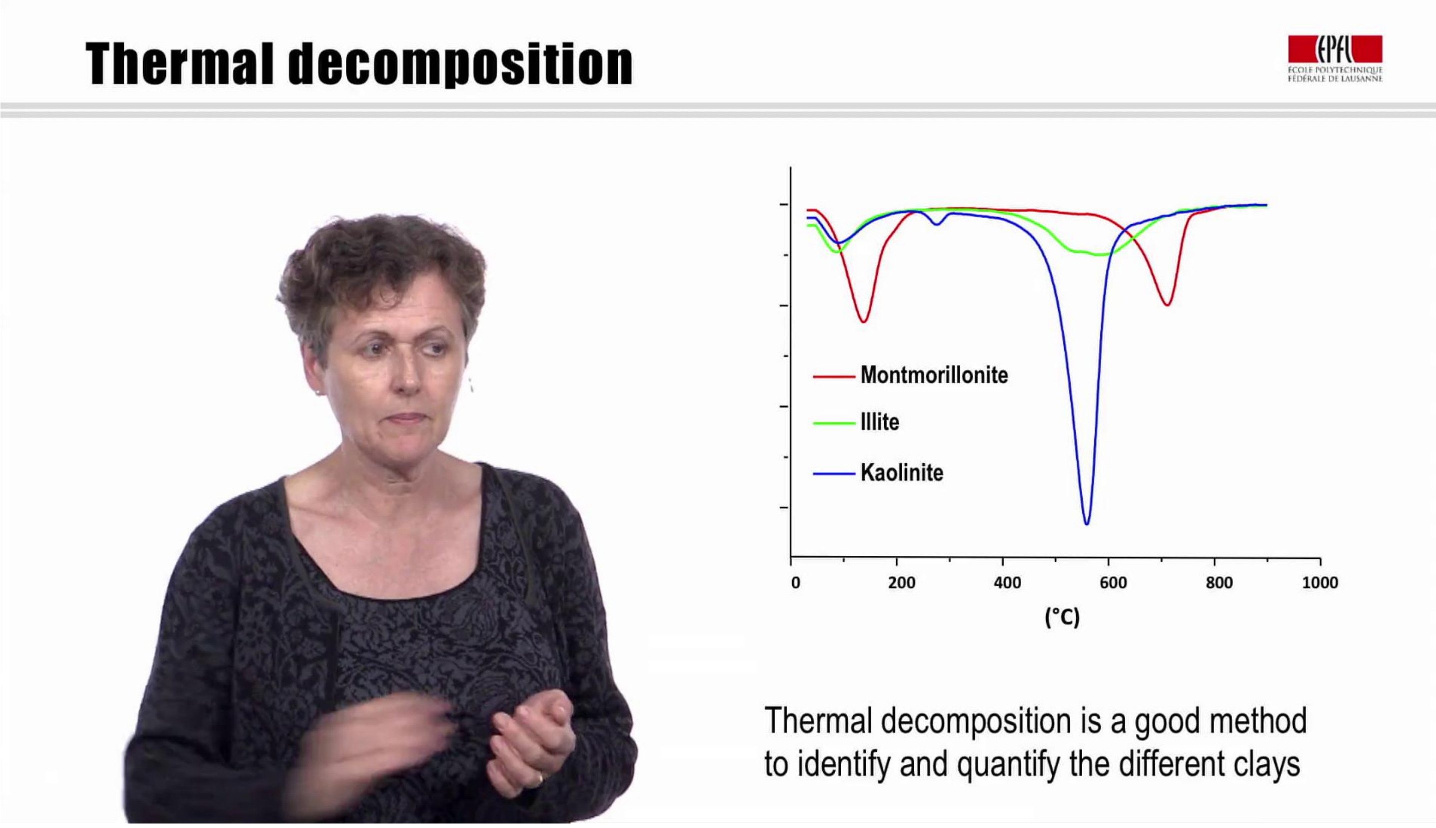


So what we see in this slide here are the crystal structures of the basic clay types. All the clays are layer structures, so here we see the layers, and these layers are alumino-silicate layers. So we see the orange dots represent the silicon atoms which are found in little tetrahedra. So in a little cage of oxygens. And the green atoms represent the aluminium, which are found in octahedral cages of oxygen. Now the two materials on the left here, the illites and the montmorillonites are called 2:1 clays. What these means is that we have two silicate layers here, and here we have sandwiched the aluminium layer in the middle. And the difference between illites and montmorillonites is mainly in terms of the ions that are found between the layers and the montmorillonite usually has alkali ions and more water between the layers. And finally on the right here, we have the kaolinite structure, and the kaolinitic clays are what is called 1:1 clays and this means in the layers we have one layer of silicate and one layer of aluminate.

Notes

Summary

2m 51s



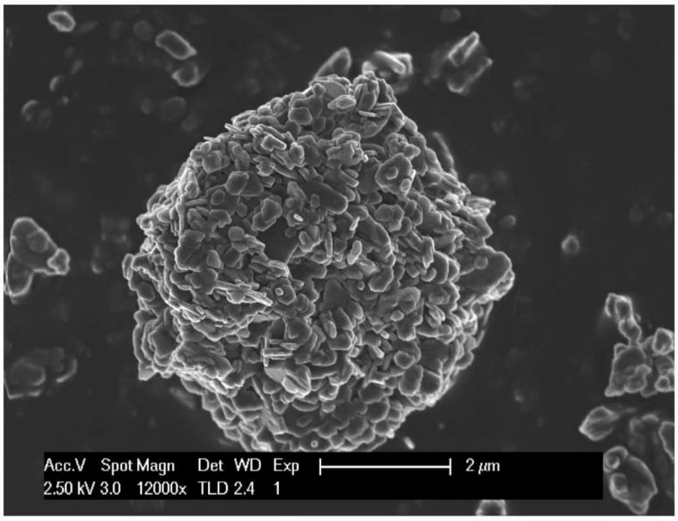
In this slide here, what we see is the thermal decomposition of the different clay types. And we can see that these have a thermal decomposition in different ranges. What do these peaks represent? They represent the amount of heat that is absorbed by the material as it is heated up And this heat is absorbed due to the loss of hydroxide from the structure which is called dehydroxilation. And we can see that these different clay types have dehydroxilation in different temperature ranges. The clearest dehydroxilation is this one here for the kaolinite which occurs between about 450 and 650 degrees. And this signature provides a very good way of determining how much kaolinite you have in any clay you may want to investigate. All you do is to make this kind of thermal decomposition. You can even quite simply do it by heating your material in two different ovens one at say 400 and one at 700 and looking at the weight loss between these two temperatures. Of course as you can see there will be a small interference if you also have some illite in your sample. But these kind of effects can be determined by looking at something like an x-ray diffraction diagram.

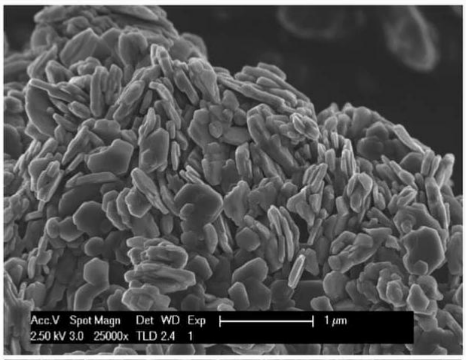
Notes

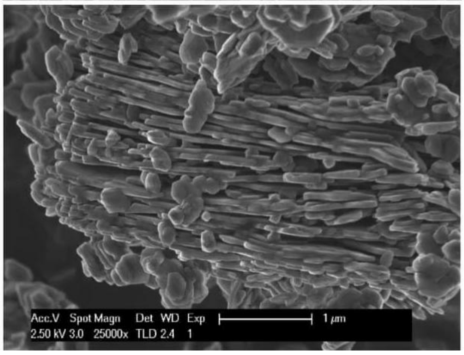
Summary

4m 16s

Kaolinitic clay structure







If we look in the electron micrograph, we can see this layered clay structure, we can see that the clay is made up of little platelets. Here we see the raw clay before dehydroxilation, here we see the clay after dehydroxilation. Basically at this level in the SEM you dont see any change in the morphology, it appears to be very similar.

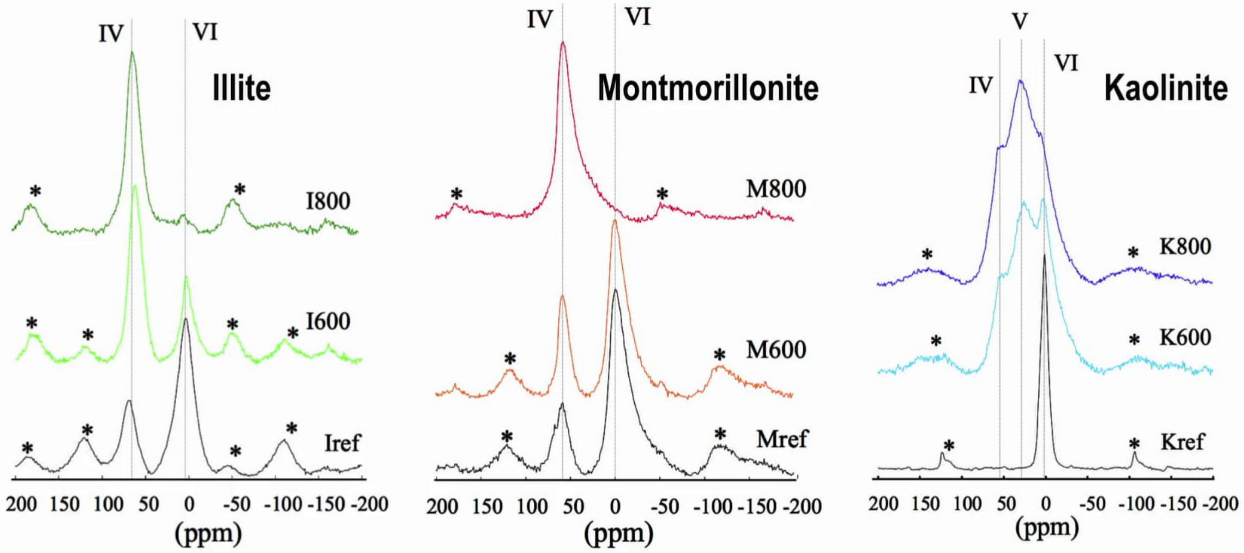
Notes

Summary

5m 47s

Effect of calcination by ^{27}Al NMR

Illite, montmorillonite: Al groups trapped in the crystal structure
Kaolinite: higher amount of hydroxyl groups + formation of $Al^{(V)}$ groups



We have to use other techniques to really see what is happening within the crystal structure. And particularly useful in this regard is solid state NMR, when we study 27 aluminium ion. So nuclear magnetic resonance, or NMR, is a technique that can be used to look at the local environment of a particular species. So we see for the two 2:1 clays, illites and montmorillonites, that as we heat these materials, we get a transition of the aluminium from the octahedral coordination in the raw clay. Octahedron has six apexes so this is also called a six coordination to a tetrahedral coordination or a four fold coordination. What is quite clearly different in the kaolinitic clays is that as well as the shift from octahedral coordination to tetrahedral coordination, we see quite clearly the emergence of this five fold coordinated site and this five fold coordinated site is the indicative of a disordered or semi-amorphous sight, which is what means that it is easier for it for react. So this is a very important difference between what happens in thermal decomposition between the 2:1 clays and the 1:1 kaolinitic clays. The 1:1 kaolinitic alays had this disordered aluminium which is then the atoms that can go on and react without cementitious materials.

Notes

Summary

6m 12s

Calcined clay

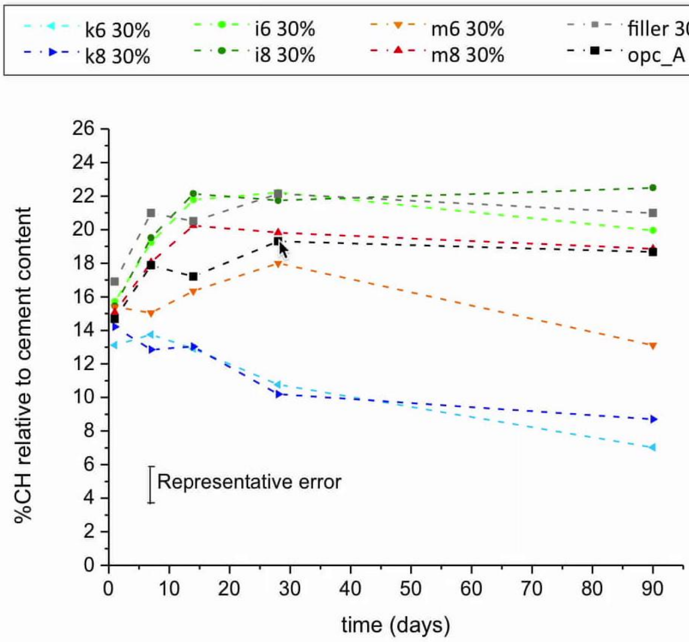
Here we see the appearance of these calcined clays depending on the other materials that are present in the clay, the colour of the clay can change over the whole spectrum from white to reddish colour if there is a lot of iron oxides present. You can actually control the colour that comes out in the end by the conditions of oxidation and reduction in the kiln.

Notes

Summary

7m 57s

Reactivity of the different clays



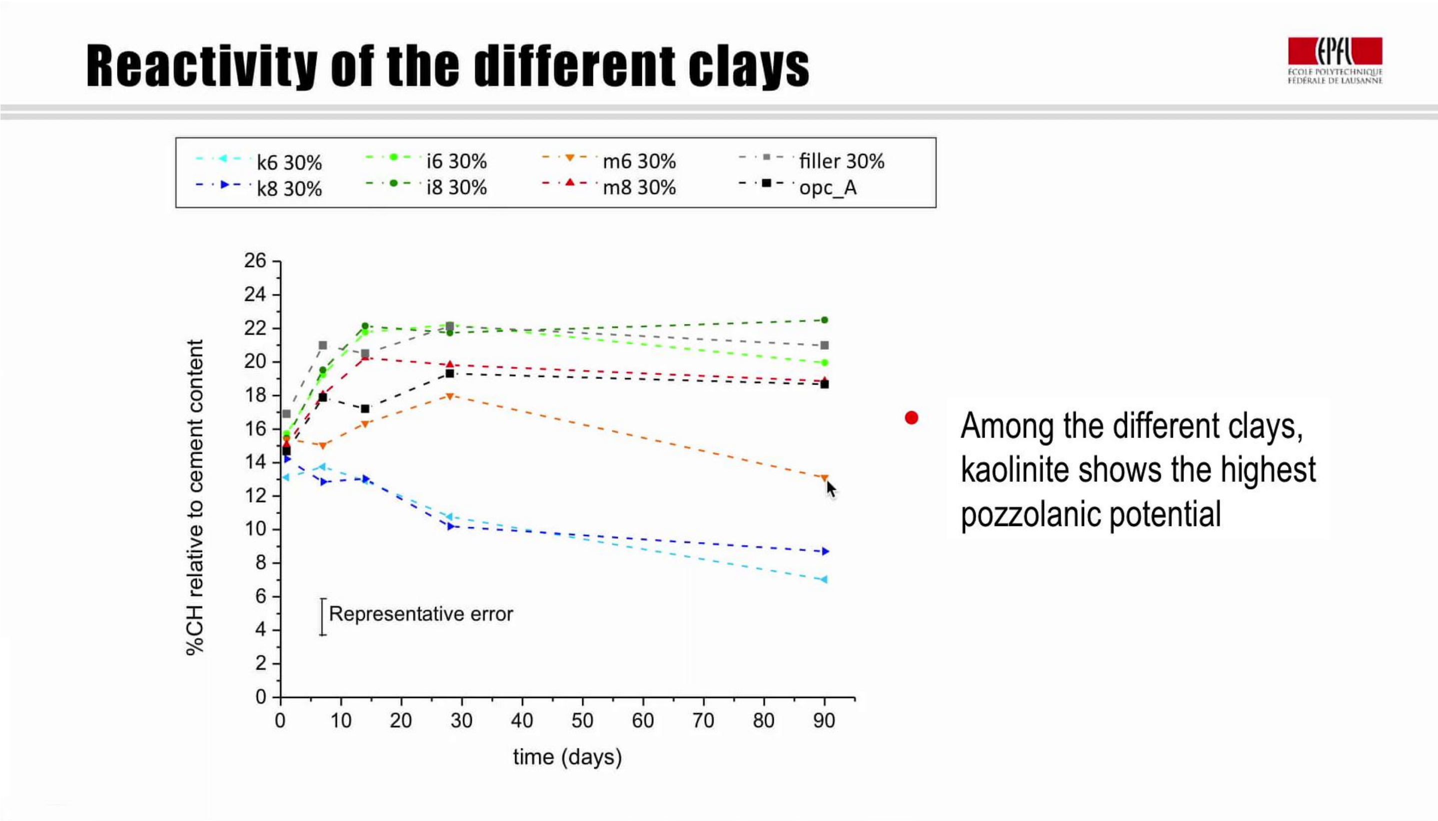
- Among the different clays, kaolinite shows the highest pozzolanic potential

OK in this slide here, what we see is the pozzolanic reaction, all of these different clay types in cement. So the pozzolanic reaction basically involves the reaction of the pozzolan, the calcined clay in this case, with calcium hydroxide that comes from the cement. And this code here, K stands for kaolinitic, I stands for illitic, M for montmorillonite clays. And as references we have got the plain OPC and the plain OPC with just an inert filler which in this case was quartz. So we can see how the different clays react by looking at their consumption of calcium hydroxide relative to the amount of the cement, the clinker based cement, OPC. And in most cases, we see that the amount of calcium hydroxide produced is actually somewhat higher than the reference which is this curve in black, which is the plain Portland cement. And the amount of calcium hydroxide is somewhat higher purely due to a filler effect as in this grey curve here, where the fact that you have a dilution of the cement by the clay gives a bit more room for the cement to react so it produces a bit more calcium hydroxide.

Notes

Summary

8m 23s



In sharp contrast, we see the kaolinitic clays here we have much lower calcium hydroxide contents, this calcium hydroxide content gets lower and lower with time and this is a typical signature of the pozzolanic reaction of the calcined clay. Even in very early ages we can see the calcium hydroxide content is very much reduced compared to the Portland cement reference. Finally we perhaps want to look at this montmorillonitic clay here which does seem to show some reaction at later ages.

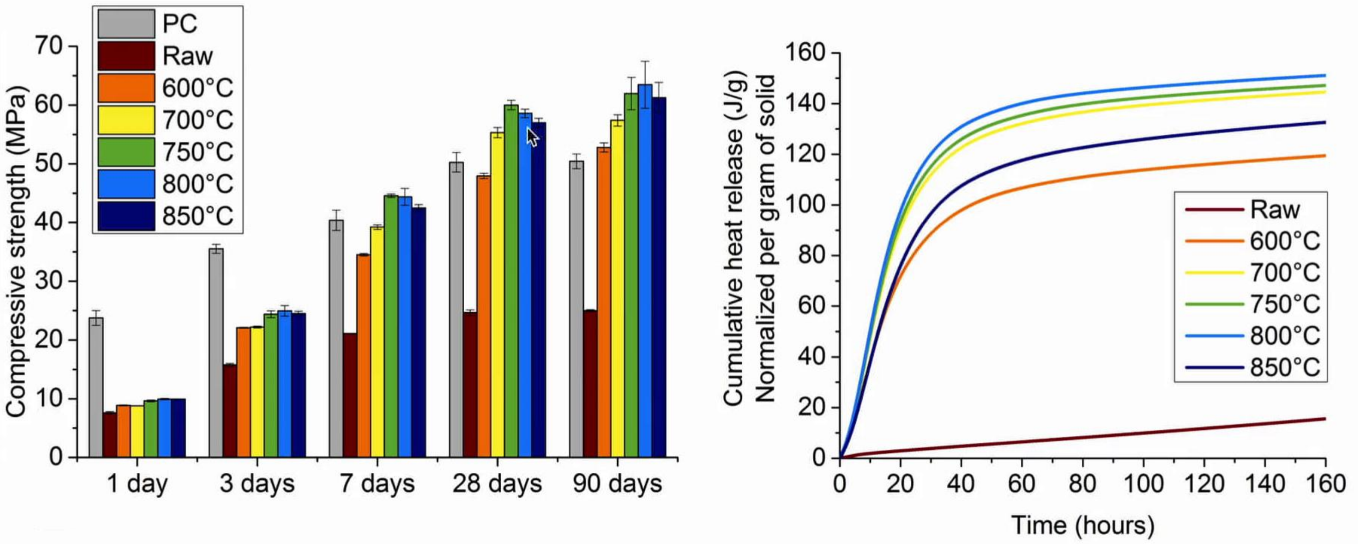
Notes

Summary

9m 51s

Effect of calcination temperature on reactivity

- Highest reactivity for a calcination temperature of 800°C
- 600°C: incomplete dehydroxylation of kaolinite
- 850°C: effect of coarsening / sintering / rearrangement and decrease of specific surface



What should be the optimum temperature for the calcination? In this graph, here we see for a particular clay that has been calcined at different temperatures, how the strength varies over time. So the different temperatures we have used are the plain raw clay with no calcination at all, 600,700,750,800 850. And the raw clay, it is just reacting as a filler, so you see the strength development is really quite poor. The calcined clays even from three days are giving a very significant increase which is indicative of their reaction. And we see by seven days that for this particular clay which contained about forty percent kaolinite, for the optimum calcination temperatures, this strength is surpassing that of the Portland cement. We see that the strength is increasing from 600 to 700 to 750. 800 is about the same and by the time we get to 850 then we see in this particular case the strength is going down. And this is what we have observed in most cases that the optimum calcination temperature is in this range, 750 to 800. It may be somewhat lower if you have small contents of calcite in the clay.

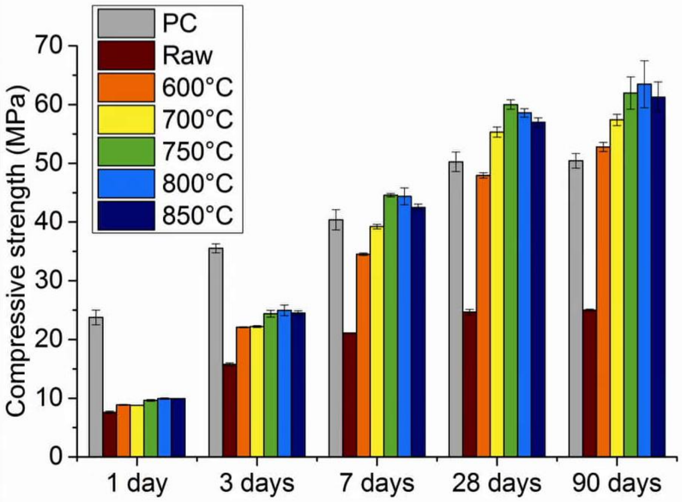
Notes

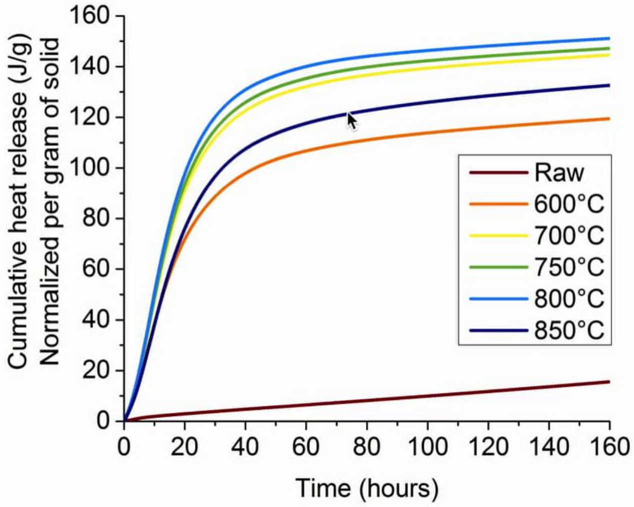
Summary

10m 31s

Effect of calcination temperature on reactivity

- Highest reactivity for a calcination temperature of 800°C
- 600°C: incomplete dehydroxylation of kaolinite
- 850°C: effect of coarsening / sintering / rearrangement and decrease of specific surface



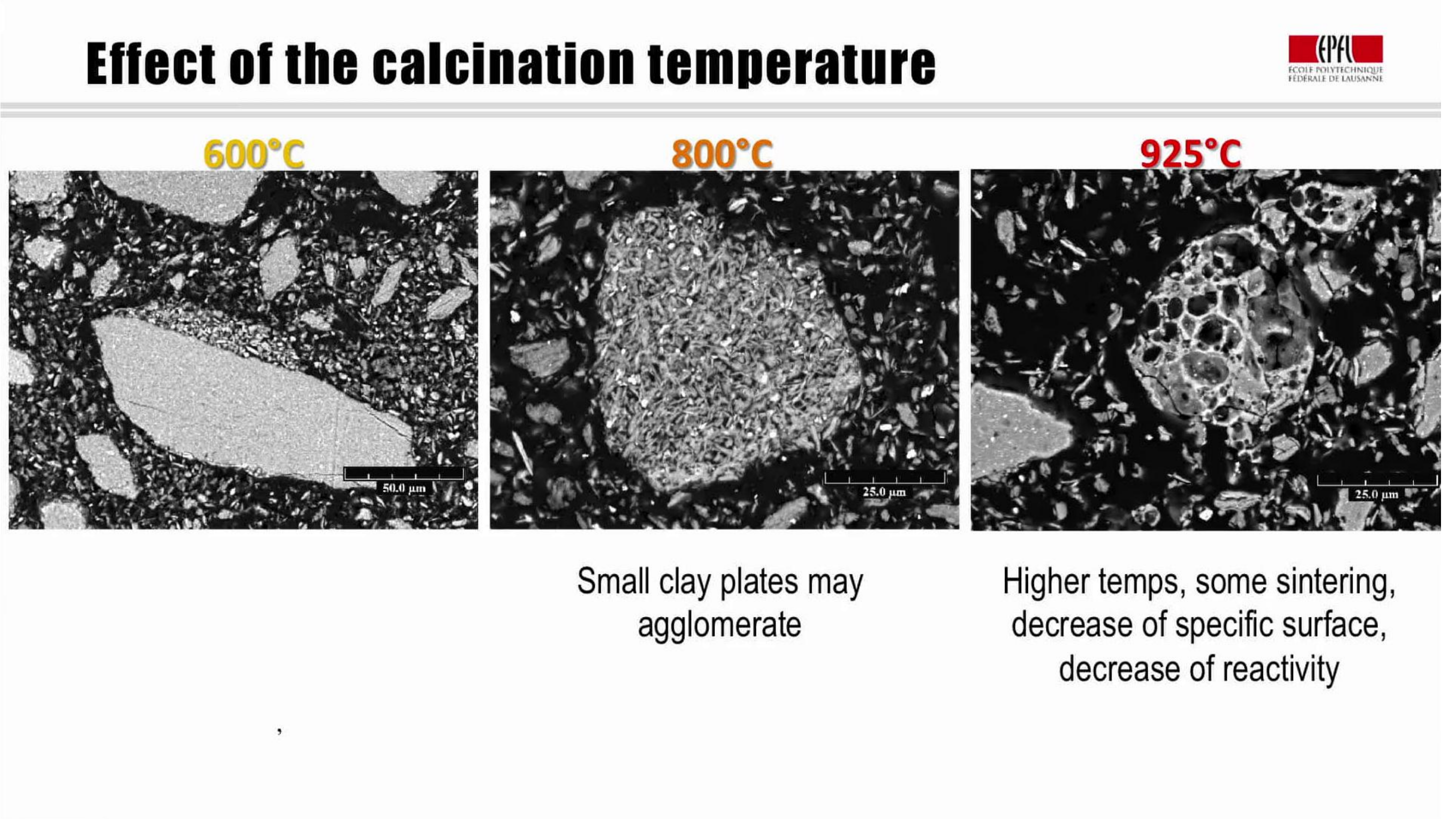


Instead of having to do this series of strength tests, what we see on the right is the results of a reactivity test which we will talk about later in the series and here we can use much smaller amounts of clay and study the heat evolution in what is called a calorimeter but we can see the same trend, we can see the raw material has no reactivity, at 600 we get modest reaction this increases through 700, 750, 800 and then by 850 there is a clear decrease in reactivity.

Notes

Summary

12m 09s



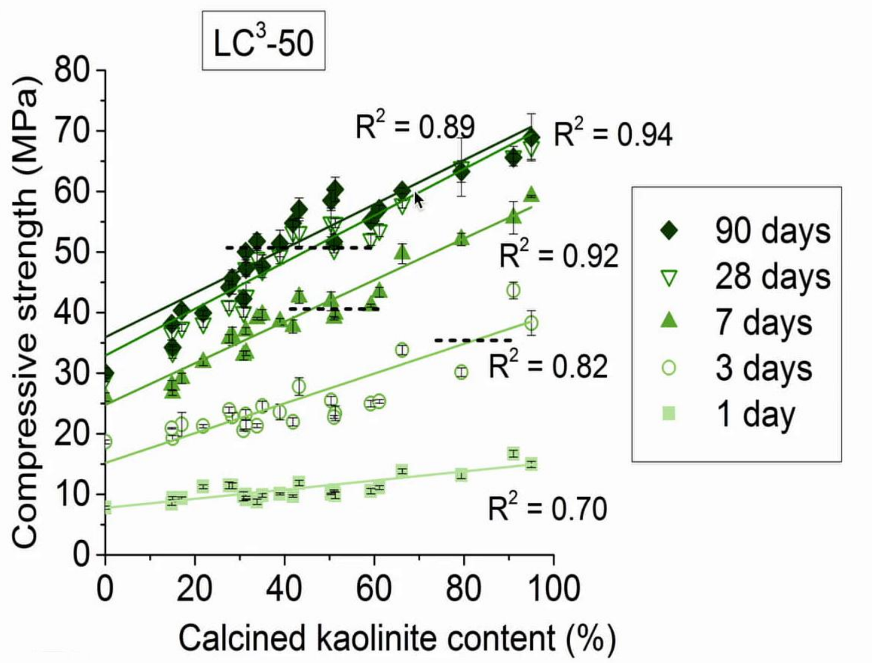
Now why do we have this decrease in reactivity? We can see that in this series here, this is the clay calcined at 600. We can see these agglomerates of these tiny clay platelets. Again we can see these agglomerates at 800 and now when we go at higher temperatures, in this case we have gone right up to 925, we now can see that we no longer see the individual platelets but we see these kind of glassy looking grains and what happens is we have had a small amount of liquid phase forming which actually sinters these clay particles together. And if we have this happening, then we will get a very strong decrease in reactivity.

Notes

Summary

12m 51s

Impact of clay grade on strength development



- Calcined kaolinite content is the overwhelming parameter
- Linear increase of strength with the grade of calcined clays
- Similar strength to PC for blends containing 40% of calcined kaolinite from 7d onwards
- Minor impact of fineness, specific surface and secondary phases

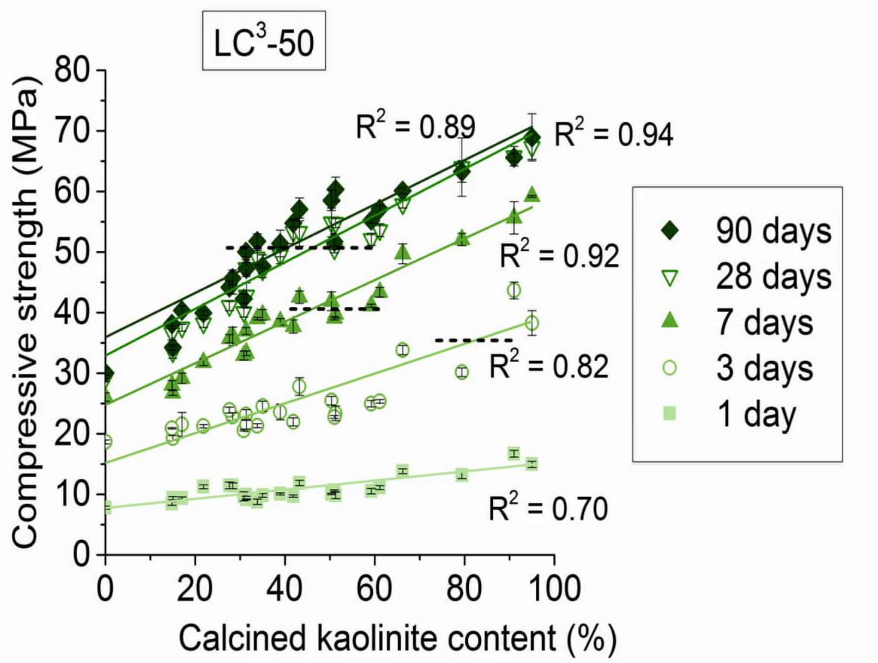
So the critical question now is what grade of clay do we need to be able to make these LC3 materials? So at EPFL here, we have studied a wide range of clays from around the world. These clays had different origins, some came from Latin America some from India, other parts of Asia etc, even from Europe and the fineness of this clay, the production method of the clay, the minor phases that were present in addition to clay, all of these vary quite widely between the different materials. If they weren't calcined, we have calcined these clays and then we use them in the LC3-50 system and measure their strength in the European mortar bar test. And what we see quite clearly here is that we get a very clear correlation between the calcined kaolinite content, that is the amount of kaoline which was in the original clay that had been broken down during the calcination, between the calcined kaolinite content and the compressive strength development. So we have different curves here for the different ages for one day, for seven days, three days, for seven days twenty eight days, ninety days. And in addition to this strong correlation with the calcined kaolinite content, we have indicated here by this dotted line, we have indicated the reference strength of the plain Portland cement.

Notes

Summary

13m 43s

Impact of clay grade on strength development



- Calcined kaolinite content is the overwhelming parameter
- Linear increase of strength with the grade of calcined clays
- Similar strength to PC for blends containing 40% of calcined kaolinite from 7d onwards
- Minor impact of fineness, specific surface and secondary phases

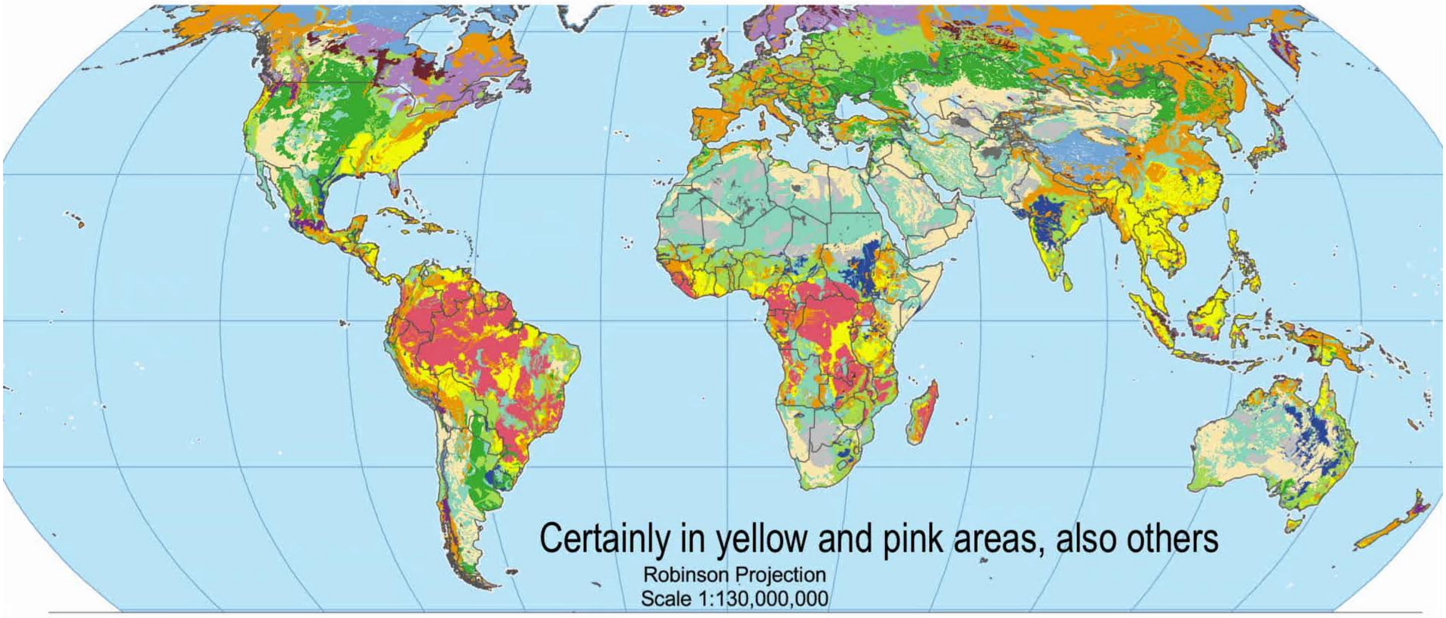
So you can see the three days if you have a kaolinite content of over eighty percent, you can meet the same strength as your ordinary Portland cement. Whereas if you are prepared to wait a bit longer, to about seven days, then if you have a kaolinite content of between forty and fifty percent, you will get a similar strength to your ordinary Portland cement. So this is very important because it means for this LC3 system, we don't need to use very high purity clays. High purity clays notably used to produce metakaolin have to have very strong requirements for colour, for purity etc., which makes them very expensive. Whereas these kind of clays which contain much lower amounts of kaolinite, only say forty/fifty percent, are generally waste materials which are consequently much cheaper.

Notes

Summary

15m 29s

Availability of suitable clays: kaolinitic



Natural Resources Conservation Service - USDA

So the kind of clays we want to use are very widely distributed around the Earth. And this is a soil map which gives an indication of what kind of clays you are likely to find below the surface and it is a rather simplistic representation but we can be quite sure that in all the regions where we have this yellow colour or this pink colour, there we will certainly have abundant clays and we see that this is really very very widely available in the central equatorial subtropical region, going through China, Southeast Asia, India, Africa and Latin America. And in fact we have seen in India where we have made much more detailed studies that suitable clays are not confined only to these yellow and pink regions but we actually have very large amounts of suitable clays, for example in this region of India, in Gujarat and Rajasthan, which on this soil map would appear not to be so suitable. So the main message here is that the kind of clays we need are incredibly abundant throughout the world, the reserves are virtually unlimited. These are just the countries in the equatorial subtropical regions where the growth in demand for cement is strongest.

Notes

Summary

16m 26s

In many regions suitable clays stockpiled as wastes

And in many of these countries, what we can find is that the suitable clays are currently stockpiled as waste. So this picture comes from a quarry in India. This is a quarry where they are extracting high purity clay for producing metakaolin which is then used for ceramics or in the paper industry and this huge mountain here is just waste. This is material which has too low quality for exploitation at the present time, but this waste here is a very suitable quality for blending with cement.

Notes

Summary

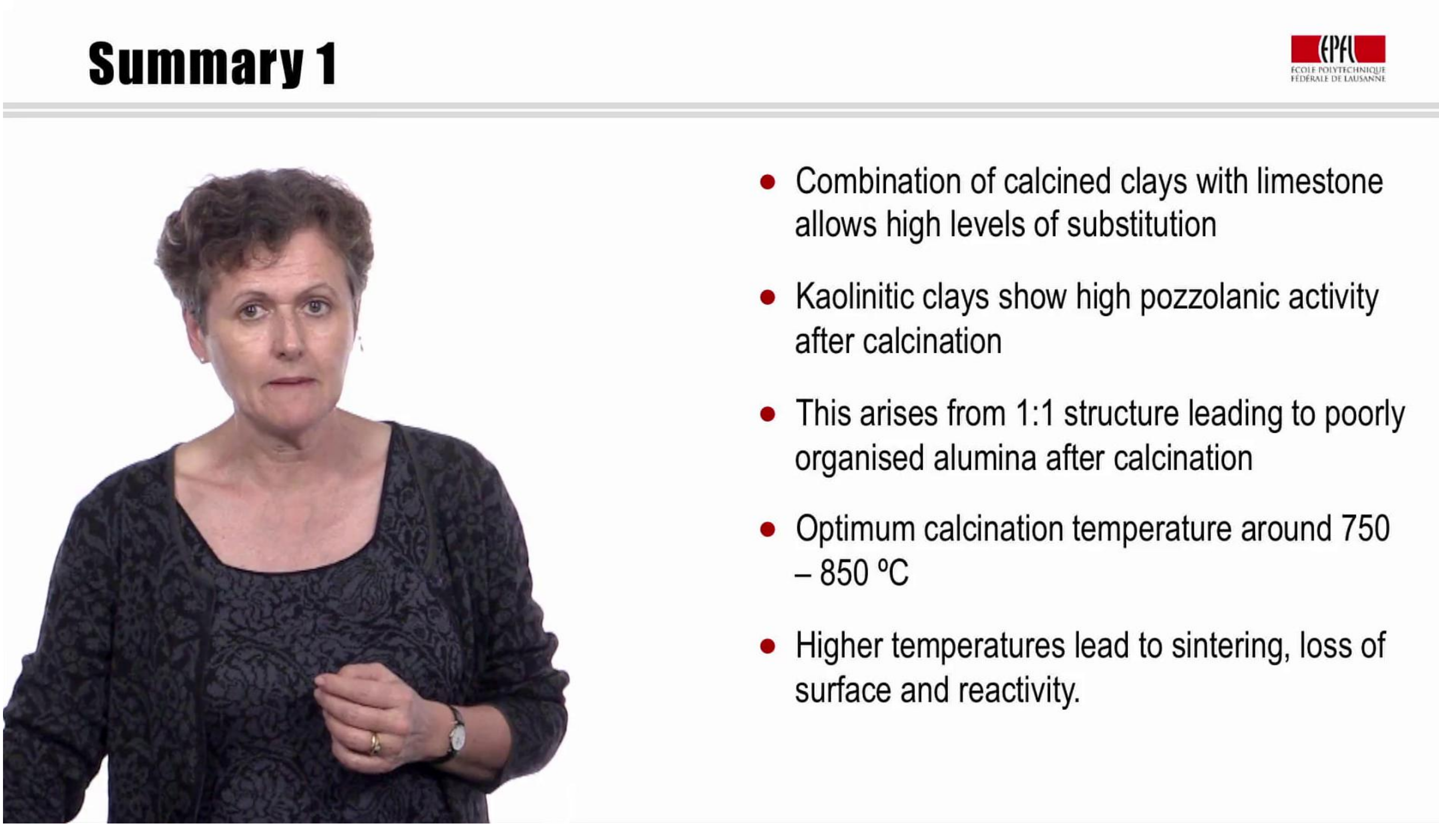
17m 56s

And we have taken those kind of waste materials, we have made full scale trial productions. This just shows a couple of houses produced from these productions. This one in Cuba here. This one in India. All the materials, the concrete blocks, the render, here the roof tiles etc, these are all produced with LC3 material. And they were actually produced, they could be produced by totally unskilled workers in the same factories without special training, just purely with a one to one replacement, taking one bag of the cement that was used before either OPC or pozzolanic cement with fly ash and replacing that with LC3. And in this case in India we made a more detailed calculation of the CO2 savings and we could calculate that about seven tons of CO2 were saved just in this one single house by using LC3 materials compared to the existing materials.

Notes

Summary

18m 35s

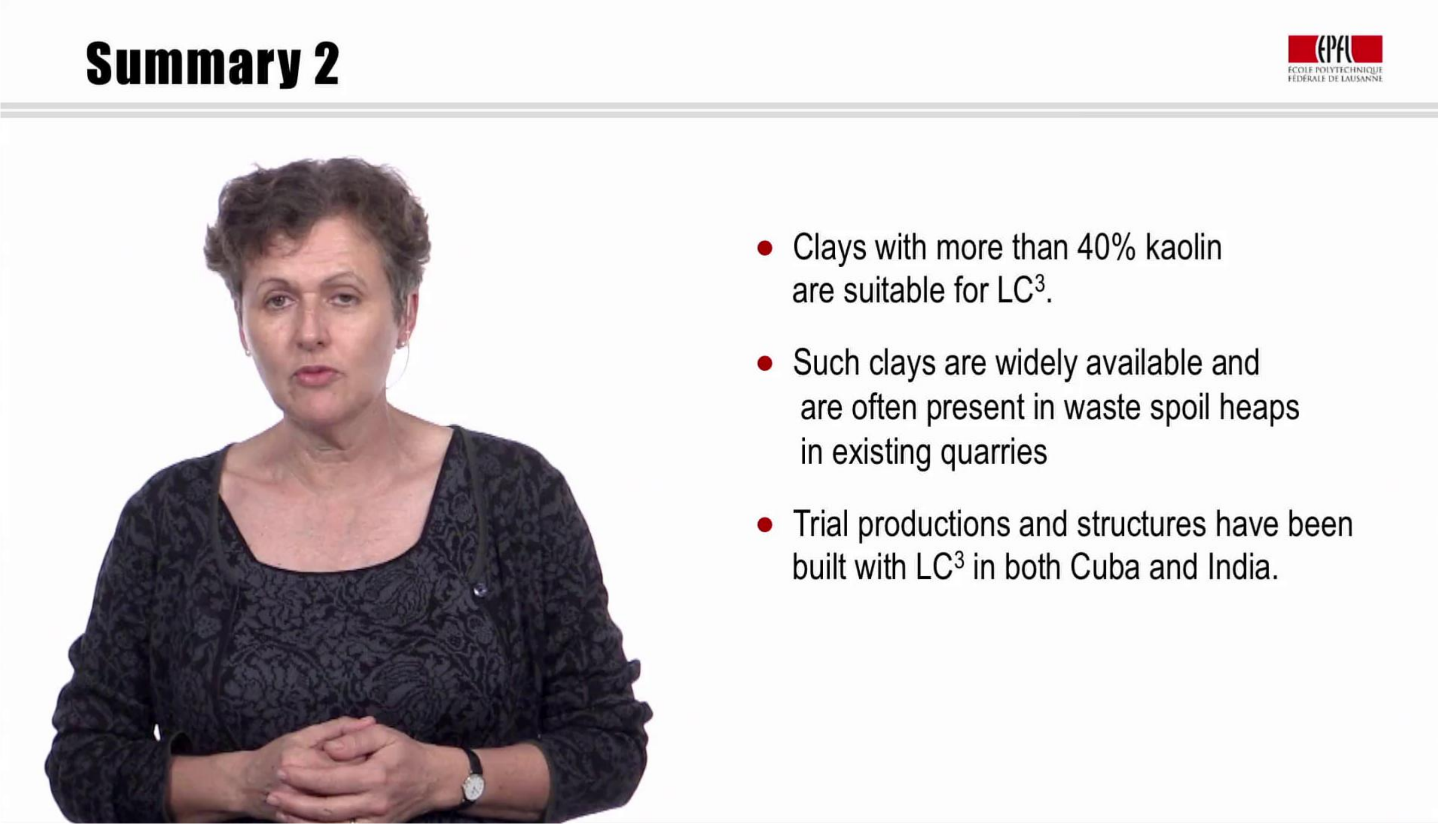


So let's look at what we have seen in this module. What we have seen is how we can use a combination of calcined clay with limestones to go to much higher levels of substitution than is typical in pozzolanic cements. We have seen that it is really the kaolinitic clays which have the potential to give these high pozzolanic activity after calcination. And this high pozzolanic activity results from their one to one structure which means we get poorly organized alumina after calcination. The optimum temperature for the calcination is in this range 750 to 850. If we go to higher temperatures then we may get sintering, a loss of surface and reactivity.

Notes

Summary

19m 38s



If we look at the performance in mortars and concretes we see that if we have got more than about forty percent kaoline, this can be very suitable for use in LC3 blends, even in a mixed system you can get a similar strength after about seven days and we are sure you could get even better earlier strength by optimizing the grinding parameters. These kind of clays, with forty percent or more kaolinite, are very widely available around the world, particularly in the regions where the growth in demand for cement is highest. And we have made trial productions of LC3 in both Cuba and India. So this short video completes the introductory module. I hope that you will be interested to come back and listen to the module on hydration which follows this.

Notes

Summary

20m 29s