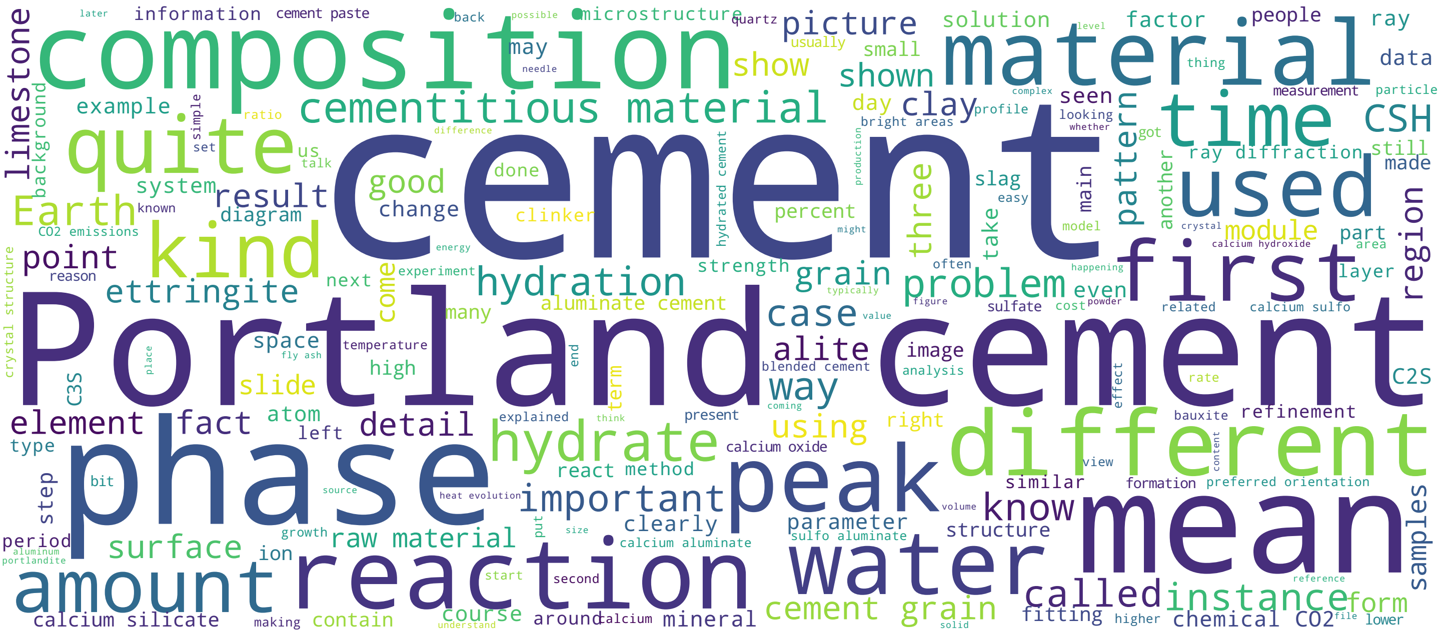
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Introduction 2: Why "Portland" cement

Cement Chemistry and Sustainable Development

Professor Karen Scrivener, FREng



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Why Portland cement

- > 99.99% of cement made today is based on “Portland” cement or more precisely Portland cement ***clinker***
- *Clinker* is the marble sized nodules which come out of a cement kiln, which is then ground to make the grey powder we know as cement.

- The name “Portland”, was chosen by Joseph Aspdin who patented the term in 1824 to highlight the similarity in appearance (when set) to Portland Stone – then a highly regarded building material.

OK! So welcome back. In this second unit of this introductory module I have called it “why Portland cement”. And what we are going to look at in this module is why the composition of cement is as it is. Why Portland cement? 99.99% of cement made today is based on what we call Portland cement or more precisely Portland cement clinker. So clinker is these nodules you see in the picture here and that is the material that comes out of the cement kiln. And the name Portland this is purely a marketing name, this was chosen by Joseph Aspdin who was the person who patented the term “Portland cement” in 1824 and what he wanted to do, he wanted to highlight the appearance of his new material to Portland stone which was then regarded as the best building material in England. So don't worry about this word Portland, it is purely a marketing term.

Notes

Summary

0m 04s

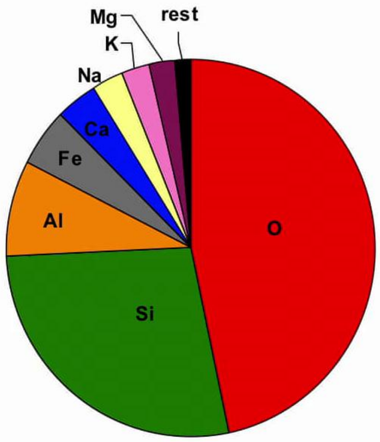
So the dominance of this type of cement is really not by chance. It is a direct consequence of the raw materials which we have available on Earth.

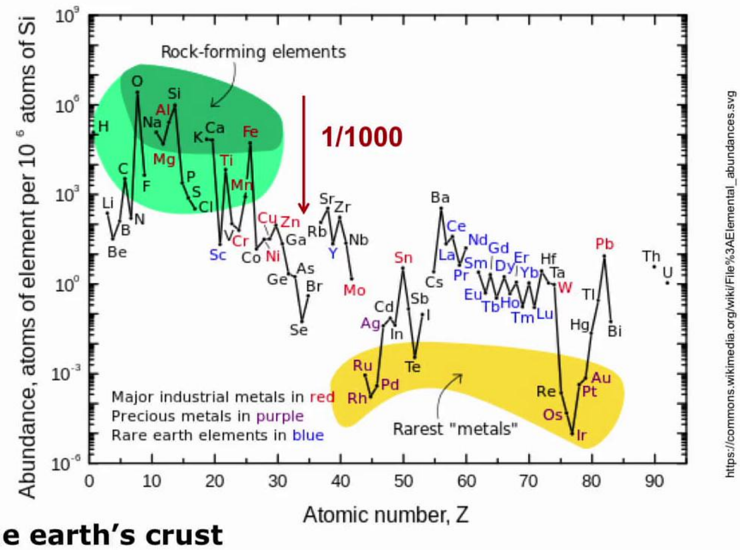
Notes

Summary

1m 08s

We do not have a lot of options!





Only 8 elements constitute >98% of the earth's crust

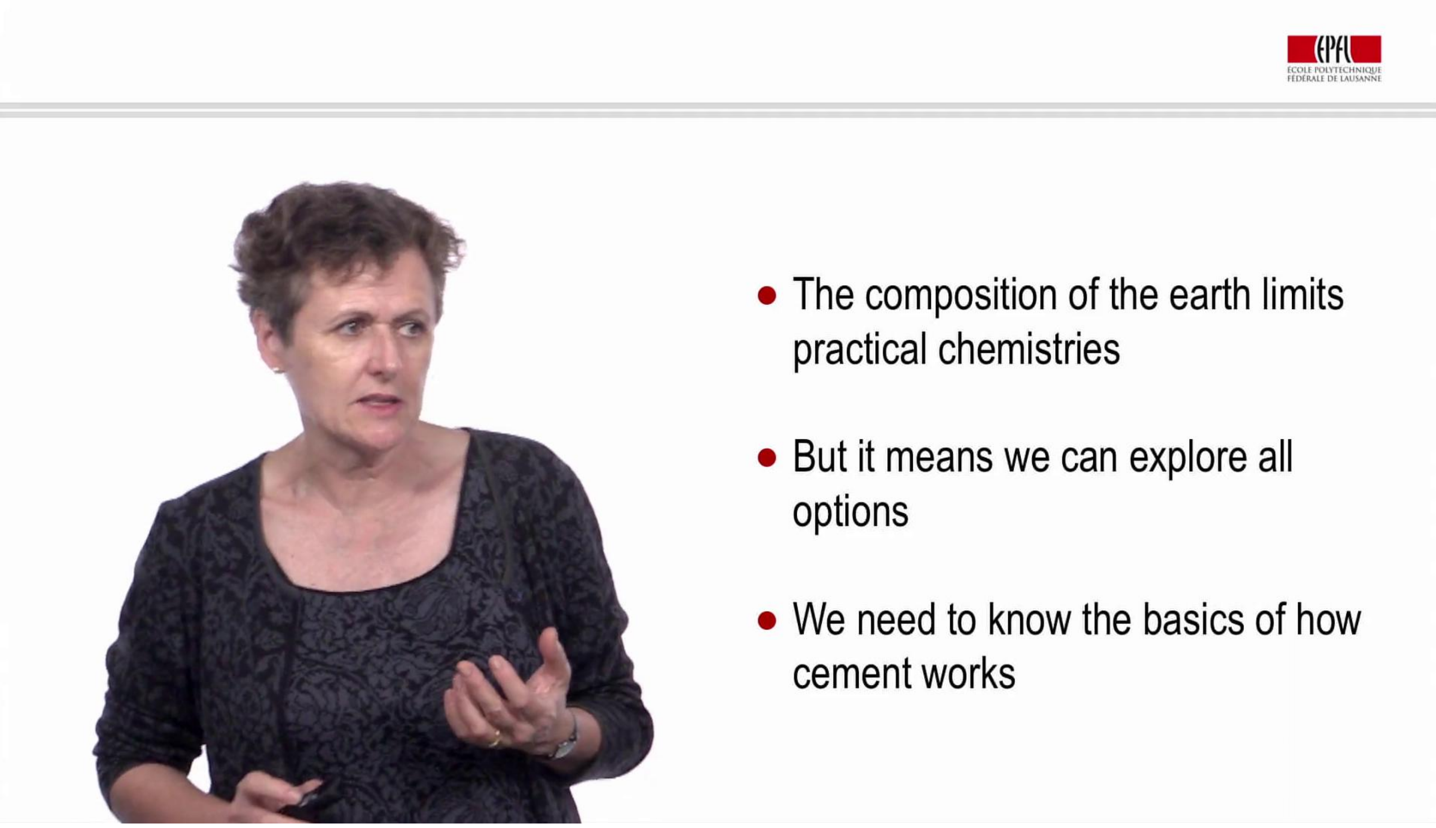
Even elements we regard as common are more than 1000 times LESS abundant that the elements found in cement – cost and geographical distribution

So here on the left we see the composition of the Earth's crust and it is really remarkable to see that we have just eight elements, that is to say oxygen, silicon, aluminium iron, calcium, sodium, potassium, magnesium. These together make up more than 98% of the Earth's crust. This is quite remarkable but those of you who may have done some astronomy will realize that it is a direct consequence of the formation of elements in stars. And it also means that this is not just the composition of the Earth but will be the similar composition for all the rocky planets we can imagine in the universe. What this means is that even elements we regard as quite common, like for example copper, are very very much less abundant than these eight rock forming elements, like for example silica. And this relative abundance of one to a thousand will translate in terms of the availability and the cost of these materials. So having seen in the last module the very large amount of the cement that is produced, clearly we can't think about making cement out of all the other elements that is in that remaining 2%.

Notes

Summary

1m 19s



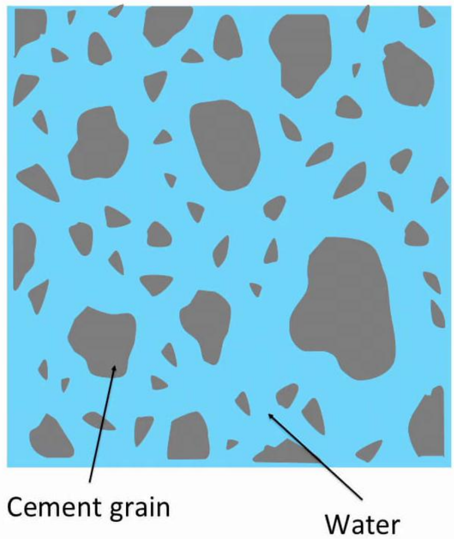
So now we can understand that it is the composition of the Earth which limits the practical chemistries we can have to cementitious materials. But looking on the bright side, it also means that we can explore all possible options, it means that there is no kind of breakthrough out there that we haven't discovered there yet. And what we need to really know in a bit more detail is how cement works to understand how these different elements can be used. So this is what I have illustrated in the next few slides.

Notes

Summary

2m 42s

How cement works:



The cement grains dissolve in the water

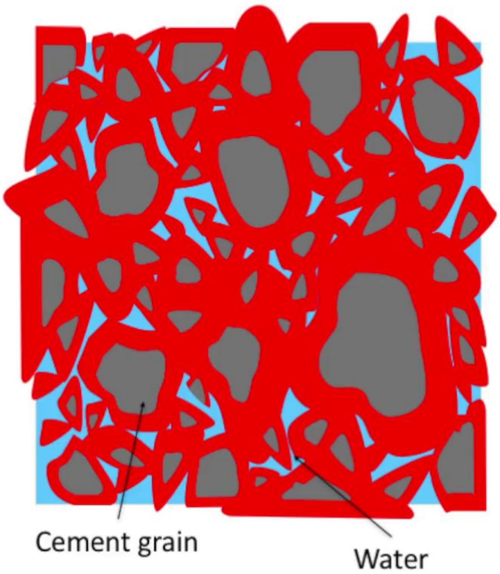
So this schematic here really tries to explain this. When you mix grey cement powder with water, what you have is grains just floating about and that is very convenient because it means you have a florable material, you can cast into molds you can make into different shapes. And then we have a chemical process whereby these gray cement grains are dissolving and then the ions are reacting with the water to give us this new solid which I have called the hydrates.

Notes

Summary

3m 18s

How cement works:



The cement grains dissolve in the water

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

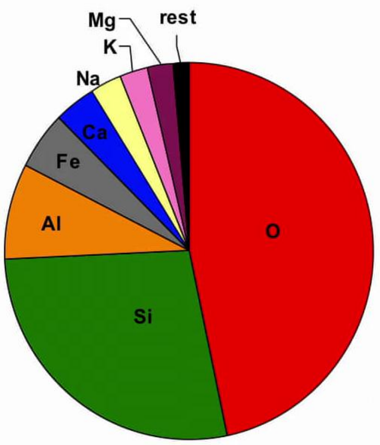
So in this image here, the red areas are the cement hydrates. And these have a higher volume of solid and therefore it holds the cement grains together, creating a rigid solid.

Notes

Summary

3m 52s

What about the different oxides



Na_2O, K_2O — **Too soluble**

Fe_2O_3, MgO — **Too low mobility in alkaline solutions**

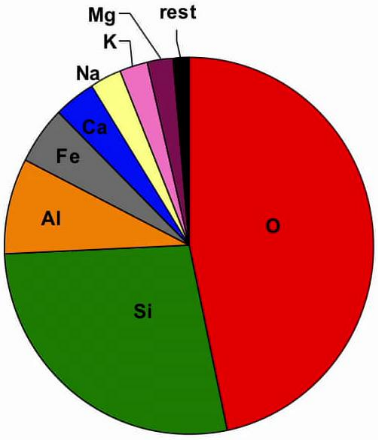
So let's go back and look at this composition of the Earth. Most of those elements are associated with oxygen as oxides and look at whether these different oxides can react to give us a cementitious material. Now if we take the two alkali oxides, sodium and potassium, the problem here is these produce very soluble salts. So maybe in your chemistry lessons you've used sodium hydroxide and you will know that you can have very strong sodium hydroxide because a very high amount can go into a solution without precipitating. So clearly this is no good for producing solid hydrates which hold the structure together. On the other hand, if we look at iron oxide and magnesium oxide, the problem here is that these oxides have fairly low mobility in alkaline solutions which is the solutions we have in cementitious materials.

Notes

Summary

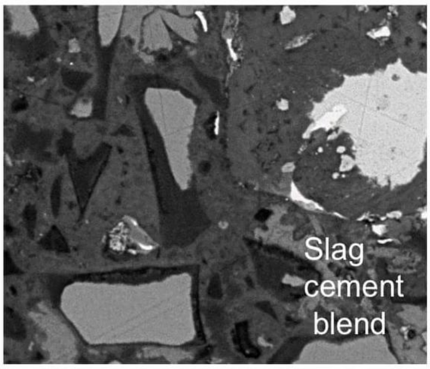
4m 05s

What about the different oxides



Na_2O, K_2O — **Too soluble**

Fe_2O_3, MgO — **Too low mobility in alkaline solutions**



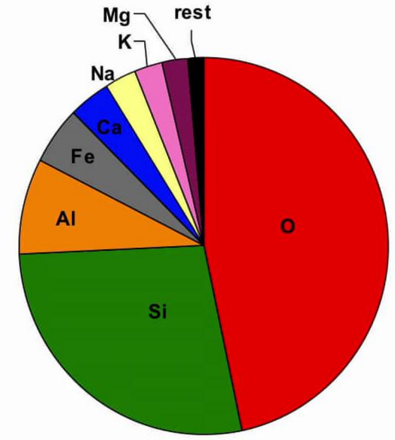
So what we can see in this image here, this is just a piece of concrete taken from a normal concrete wall, and in this image we have some very bright areas and these very bright areas are where all the iron oxide is located. And in fact those bright areas are exactly the same as in the original cement grains. During that whole thirty years that iron in the cement grains has just stayed in the same place. So it is not doing any harm but basically it means it is not going out into solution, it is not precipitating new solids and therefore making very little contribution to the bonding and the development of strength. It is a similar story for magnesium. Here in this picture now we see a blended cement, we are going to talk about that in a few modules time and in this blended cement, the darker grains, such as in the center of the picture here, you see are now surrounded by a region of dark products and these darker project products are because all the magnesium that was in that slag grain is concentrated there in that area. And same situation, this magnesium has not moved into the space between the grains, it has not really contributed to bridging the space between them.

Notes

Summary

5m 03s

What about the different oxides



Na_2O, K_2O — **Too soluble**

Fe_2O_3, MgO — **Too low mobility in alkaline solutions**

CaO, SiO_2, Al_2O_3 — **The most useful**

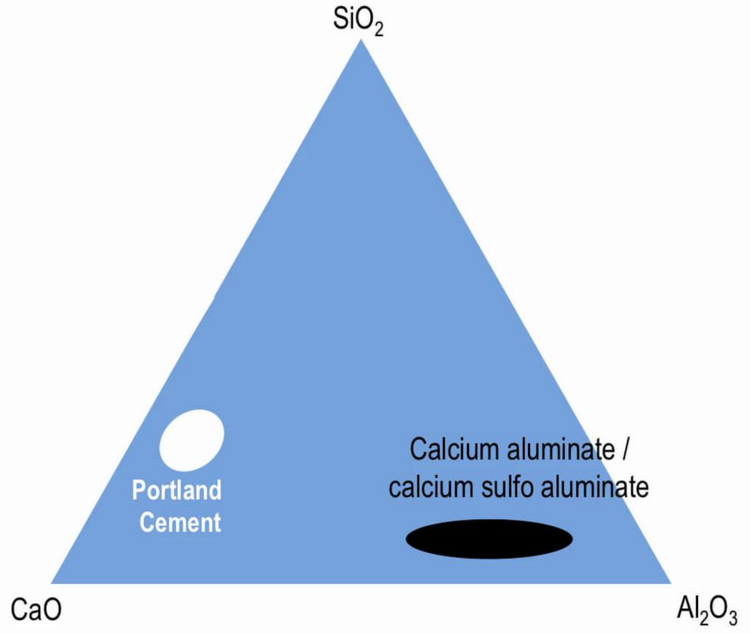
So this means we end up with just three oxides which are really the most useful and of the essential component for the Portland cement we have today.

Notes

Summary

6m 32s

Hydraulic minerals in the system $CaO-SiO_2-Al_2O_3$



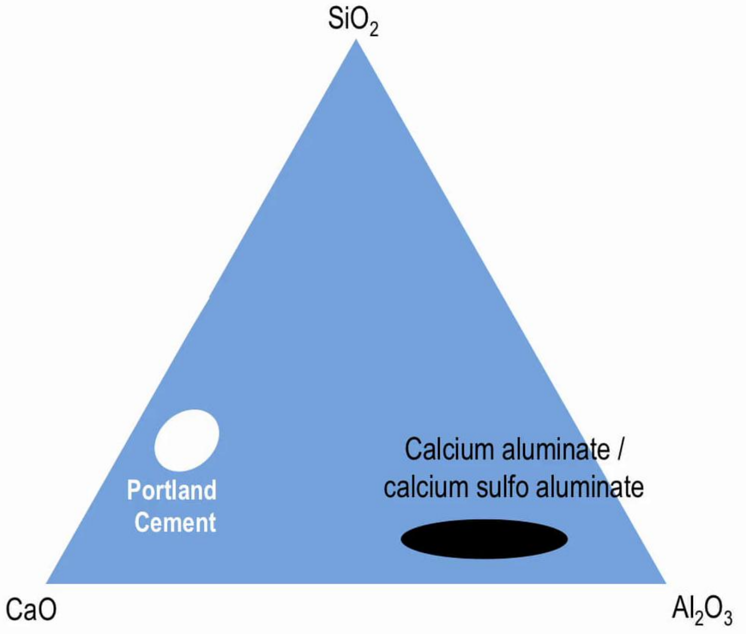
So this is really in no way a coincidence that we have ended up with this composition because if we now look at that ternary system between calcium oxide, silicon dioxide and alumina, we see the composition of Portland cement. And in fact Portland cement as we see it here, this is composed of calcium silicates. There is really only one other region in this diagram where we have minerals that will react with water in the way we previously saw and give us cementitious materials and that is this region here which is the region where we find calcium aluminate cements and calcium sulfo aluminate cements. Small amounts of sulfur is the sort of extra dimension which is not shown in this diagram here. So these other compositions, calcium aluminate, calcium sulfo aluminate, have a lot of advantages because they have less calcium and you see they are further away from that calcium oxide corner, it means they have less calcium oxide and therefore there is less CO2 produced chemically during the production of these phases. So that sounds very good but the problem is that it is not so easy to make these because the raw materials we need are not so widely available.

Notes

Summary

6m 42s

Hydraulic minerals in the system $CaO-SiO_2-Al_2O_3$



Much less CaO, therefore less CO_2

BUT, what sources of minerals are there which contain $Al_2O_3 >> SiO_2$?

Bauxite – localised, under increasing demand for Aluminium production, EXPENSIVE

And we have to ask the question, what sources of minerals are there which contain much higher amounts of aluminium to silica. Most minerals have about the same ratio of silicon to aluminum, as in Portland cement, about two to one, and to get a composition down here in this alumina rich part of the diagram we have to go to materials like bauxite. Now bauxite is much more localized than the materials used for making Portland cement. It is estimated that only ten countries contain about ninety percent of the reserves of bauxite And of course bauxite is the first raw material for aluminium production. So the consequence of all this means that it is rather expensive and it means that you cannot produce calcium aluminate cement or calcium sulfo aluminate cement for the same cost as producing Portland cement.

Notes

Summary

8m 13s

“Chemical” CO_2 emissions of hydraulic minerals

Clinker compound:	Chemical CO_2 emissions, kg/tonne
Alite (C_3S)	579
Belite (C_2S)	512
Tricalcium Aluminate (C_3A)	489
Tetracalcium Alumino-Ferrite (C_4AF, “Ferrite”)	362
Quicklime (CaO)	786
Wollastonite (CS) [a major component in Solidia clinkers]	379
Ye’elimite ($C_4A_3$$) [made with $CaSO_4$ as sulphur source]	216
Periclase (MgO) [made from magnesium carbonate]	1100
Periclase (MgO) [made from basic magnesium silicate rocks]	0

Belite rich clinkers <10% reduction more than offset by slower kinetics

Good reduction potential

We can look at this effect of chemical CO2 and how it is related to composition in more detail on this slide here. So at the top we see the two calcium silicates which are present in Portland cement. These are known as tricalcium silicate or C3S, Dicalcium silicate or C2S. And many people have proposed that what we should be doing is making Portland cement with more C2S as opposed to C3S. But the problem here is that the reduction in chemical CO2 is really very marginal. It is only around ten percent and that is more than offset by the much slower kinetics of C2S. So the strength development is much slower and because the strength developed is much slower this would mean that in practical situations where people need a given strength at a given time then they will use more cement and using the more cement will completely cancel out this ten percent save. So belite rich clinkers really don't contribute at all to lowering CO2 emissions. Down here we can see the figures for ye’elimite, that is this complex phase called C4A3$, and as I said on the previous slide this has a good reduction potential in terms of lowest chemical CO2. But we have the problem of the cost of the raw materials.

Notes

Summary

9m 13s

"Chemical" CO_2 emissions of hydraulic minerals

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Quicklime (CaO)	786
Wollastonite (CS) [a major component in Solidia clinkers]	379
Ye'elimite ($C_4A_3\$$) [made with $CaSO_4$ as sulphur source]	216
Periclase (MgO) [made from magnesium carbonate]	1100
Periclase (MgO) [made from basic magnesium silicate rocks]	0

Alite and Belite (579, 512): Belite rich clinkers <10% reduction more than offset by slower kinetics

Ye'elimite (216): Good reduction potential

Periclase from magnesium carbonate (1100): Much worse than calcium silicates

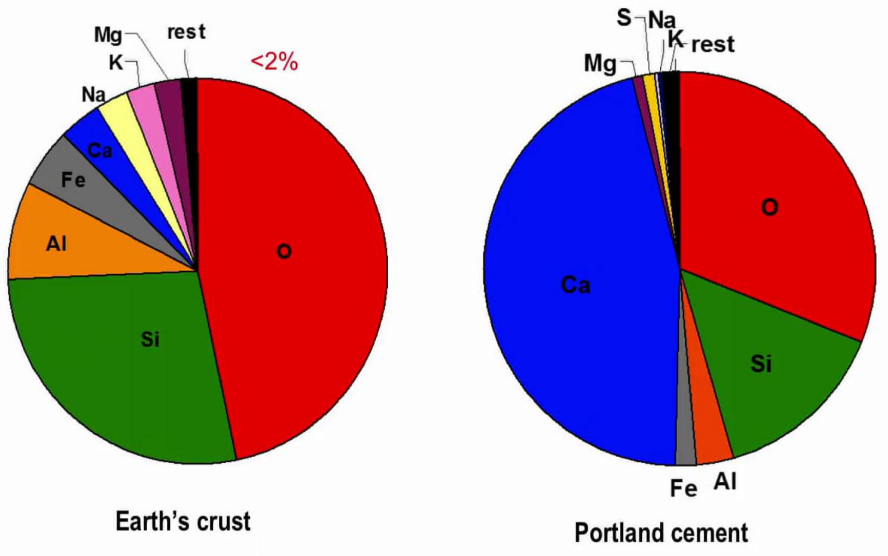
And finally on this slide I want to point out this line here because many people nowadays are proposing that we should use magnesium based cements, there can be context in which this might be possible, not now, but if somebody can invent a way of producing magnesium based cements from magnesium silicate rocks it might be interesting, but what's happening at the minute most people are using magnesium carbonate and what you can see here very clearly is that this chemical CO2 emissions from breakdown of magnesium carbonate are way higher than they are from the calcium silicate phases we had in Portland cement.

Notes

Summary

10m 51s

Composition of cement compared to earth's crust



Limestone:
very widely distributed
provides the high amounts
of calcium

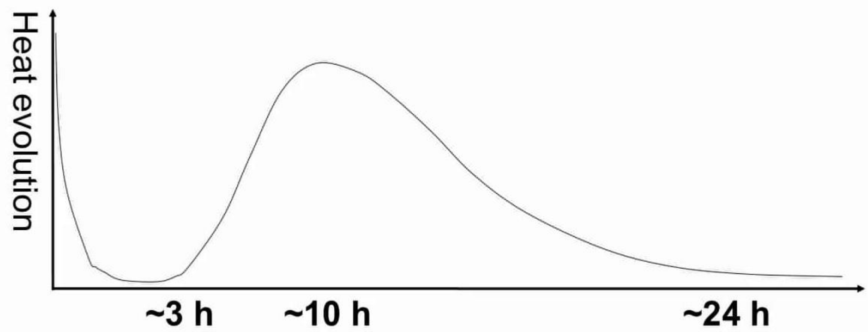
So here we come back to that composition of the Earth we have discussed in detail and we compare it with the composition of a typical Portland cement. And you can see the elements present are similar. The big difference between the Portland cement and the composition of the Earth is the dominance of this sector for calcium. And this is as we explained in the last lecture where the chemical CO2 is coming from but from a practical point of view it is very easy to make things with this composition because limestone, which is usually very pure calcium carbonate, is very widely distributed across the globe and it could mean that you can make these Portland cement out of limestone. The other elements are generally coming from something like clay, but you can make this almost everywhere in the world and therefore transportation of the final product is minimised.

Notes

Summary

11m 36s

Portland cement is amazingly robust



- Open time of several hours
  – easy to manipulate with admixtures
- Hardens in matter of days

So the other important aspect is the pattern of reaction of the Portland cement. And this is shown in this diagram here which plots the heat evolution, which is a signature of the rate of reaction. And what we can see is at the beginning of the reaction, we have a burst of reaction, and then we have this period here where the reaction remains slow for several hours. For a practical point of view this is extremely important as it gives us time to mix the cement and transport it to the building site. And then after about three hours the reaction takes off again. Now this pattern of reaction means that it is very very simple to use cementitious materials.

Notes

Summary

12m 38s

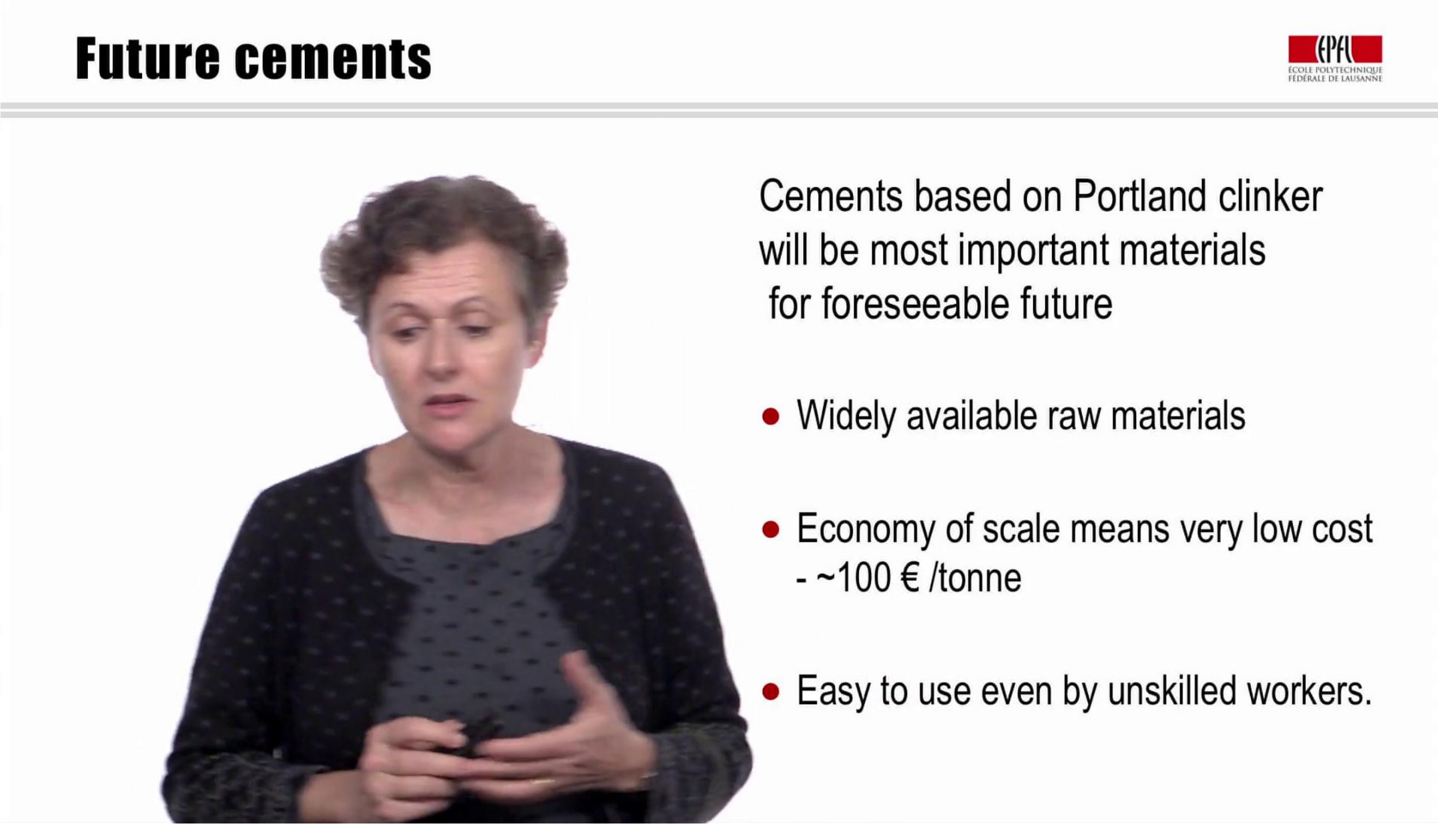
Can be mixed almost anywhere

Here we see a picture from India where people are making concrete under really quite rustic conditions. But nevertheless because it is such a robust chemical reaction it still works, it still gives very good quality building materials.

Notes

Summary

13m 25s

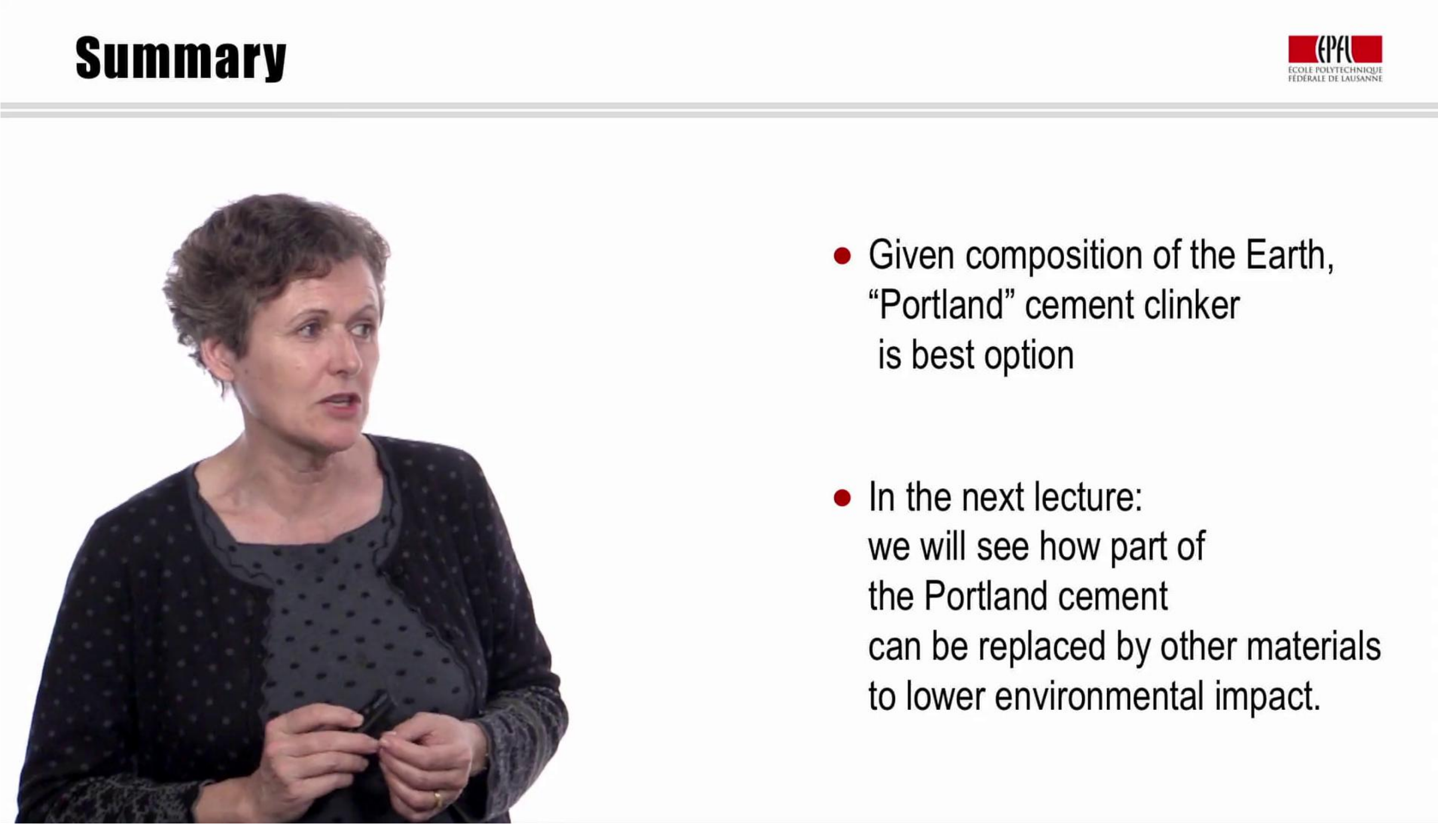


Really well we are going to see that for all these reasons I have explained to you here, cement based on Portland clinker will be the most important materials for the foreseeable future. They can be made from widely available raw materials, there is an incredible economy of scale leading to very low cost and they are very easy to use even by unskilled workers.

Notes

Summary

13m 41s



Given the composition of the Earth, this composition Portland cement clinker, really is the best option but in the next lecture, what are we going to see is how by replacing part of this Portland cement we can lower environmental impact. So thank you very much.

Notes

Summary

14m 08s