ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Lecture 3:
Lowering Environmental Impact

Cement Chemistry and Sustainable Cementitious Materials

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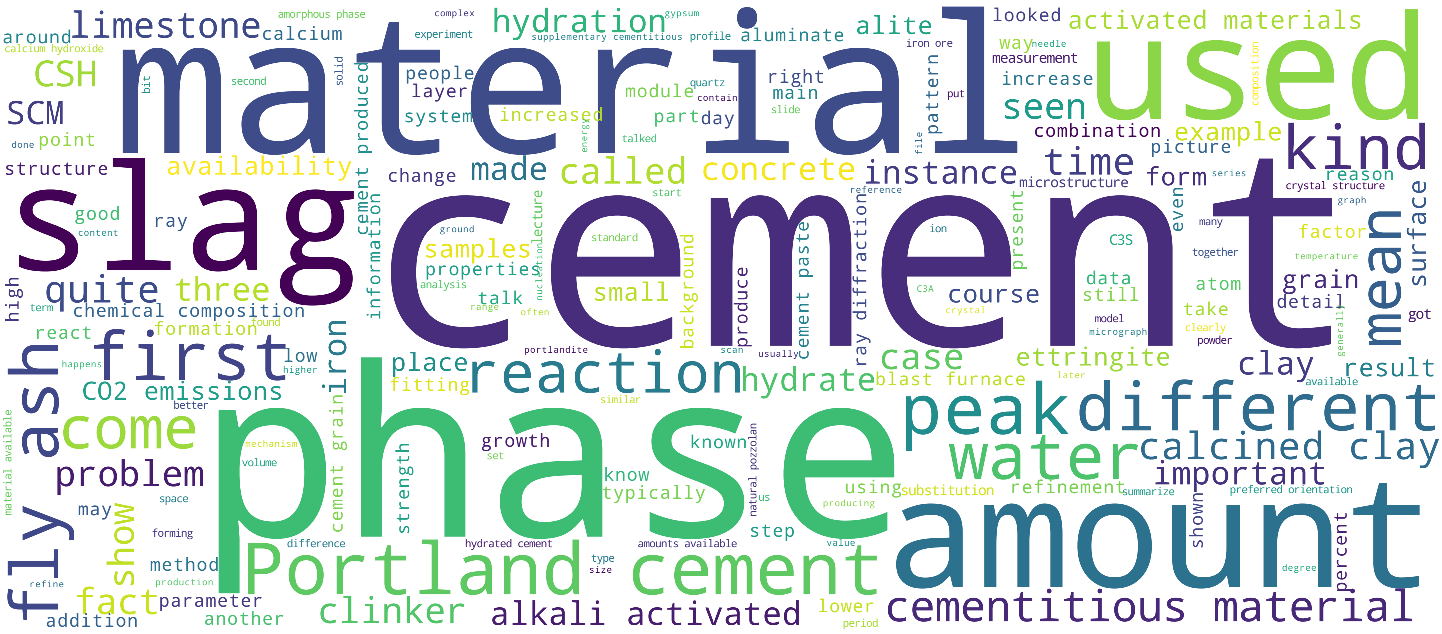

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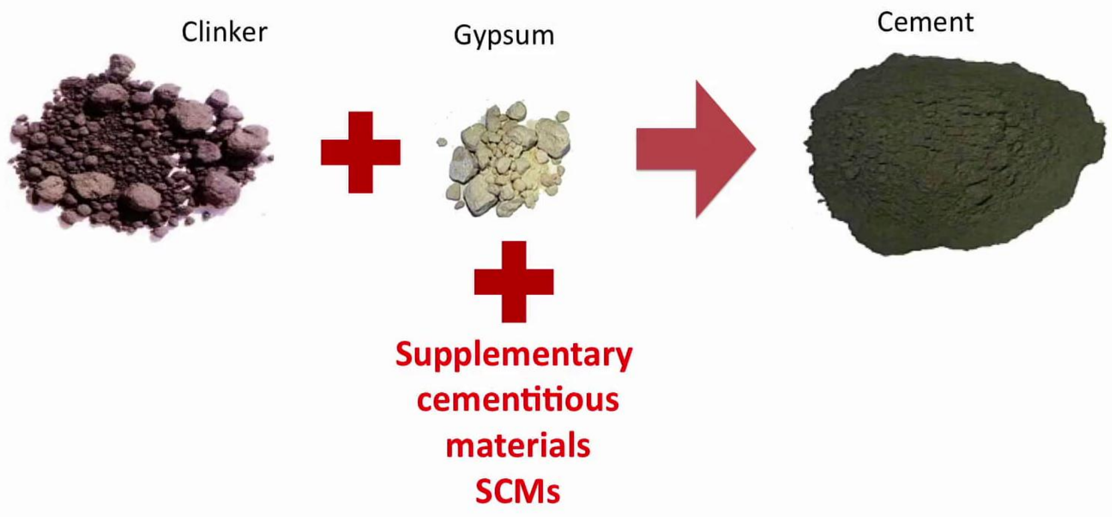
Video

EPFL

Do we need to rely only on clinker?

Traditionally Portland Cement consists of clinker ground with about 5% of calcium sulfate (e.g gypsum)



Now the majority of cement contain other materials as a partial substitution for clinker.

So welcome to the third video in this introductory module series. In this module, we are going to talk about how we can lower the environmental impact of cementitious materials by replacing part of the Portland cement clinker with other cementitious materials. So classically, cement has been clinker which is ground with a small addition of calcium sulfate, normally referred to as gypsum, to produce cement. And this is what we call Ordinary Portland Cement, O.P.C. or Plain Portland Cement. 50 years ago this made up practically all the cement produced but nowadays the vast majority of cement produced also contain what are known as supplementary cementitious materials or SCMs Now what are these SCMs?

Notes

Summary

0m 04s

Supplementary cementitious materials

Often by-products or wastes from other industries

Local availability very important!

Some examples are limestone which comes from the quarry. Fly ash which comes from burning coal to produce electricity. Slag which comes from blast furnaces where iron ore is is reduced to iron. And natural pozzolans which are found in nature and finally calcined clays. Now these are often bright products a waste from other industry and their availability will vary considerably from place to place.

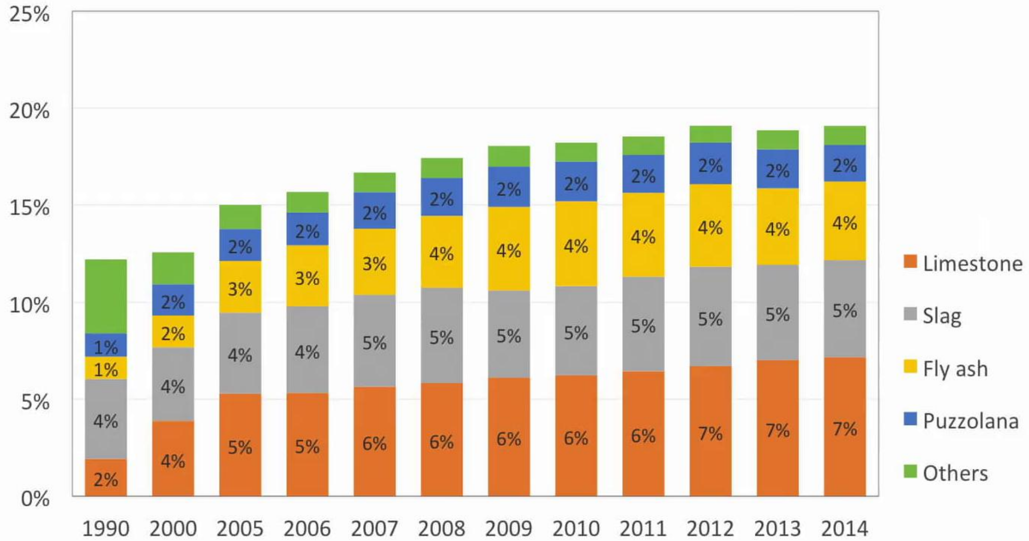
Notes

Summary

0m 57s

Evolution of Clinker substitution

Clinker substitution most successful strategy to reduce CO_2



- Only 3 substitutes used in quantity
- Almost no progress in last 5 years

If we look at the overall level of substitution of SCMs in cements around the world, we can see in this graph here that just three materials make up the overwhelming majority of the substitutes, namely limestone slag and fly ash. Secondly we can see that while a few years ago the level of substitution was increasing, for the last five or six years it has remained almost static.

Notes

Summary

1m 31s

Limestone

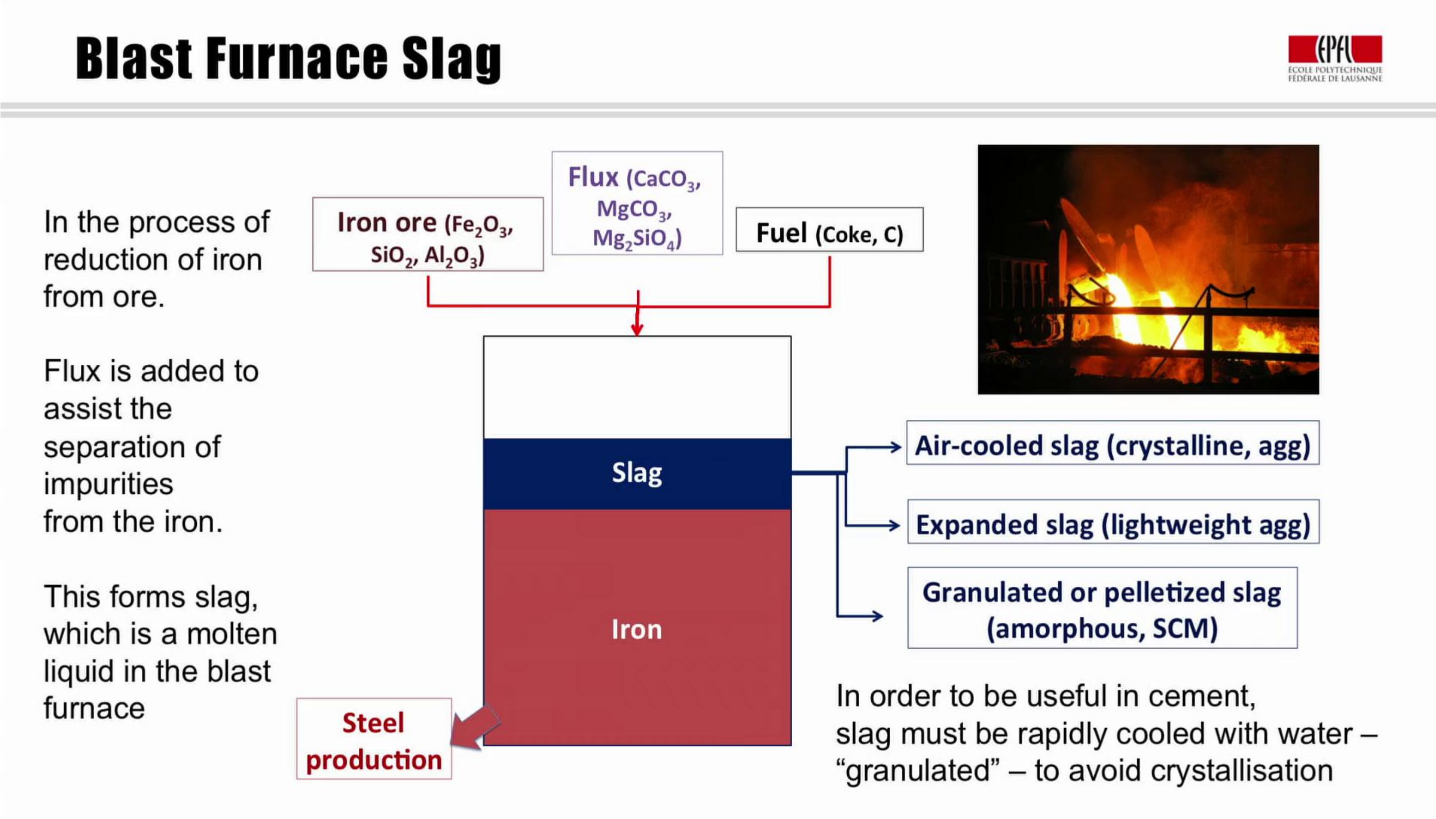
- From quarry, but does not pass through kiln so does not loose its CO_2
- Interground during milling
- Up to about 5% properties enhanced:
  - Small amount reacts with aluminates
  - Fine particles enhance nucleation of C-S-H and packing
- High purity limestone not needed (but required in many standards)

Now before we look at the reasons for this let's look at these different SCMs in a bit more detail. So first we have limestone. This comes through from the same quarry where limestone is excavated for producing the clinker, but the important thing here is because it doesn't pass through the kiln it doesn't lose it CO2. It is typically interground with the cement during milling and we find that if we have small levels of addition up to about five percent it actually enhances the properties and this is due to the fact that a small amount of the limestone does react with the aluminate phases and also because the fine limestone particles enhance the nucleation of the CSH and give a denser microstructure. Now we don't actually need to use high quality limestone, although this is often required in standards.

Notes

Summary

2m 03s



The second material is blast furnace slag. This schematic here shows that we have iron which comes from the iron ore and slag is the material which is used to help the separation of the iron from the impurities in the iron ore. This material is liquid in the blast furnace and then it is poured off. And depending on the cooling, we can either have crystalline material which really can only be used as aggregate, which is air-cooled slag. We can also make expanded slag which can be used as lightweight aggregate but what we are really interested in is when we quench this slag which is what is known as granulation, and by this very fast cooling with water, then we produce amorphous phases and these amorphous phases can then dissolve in water and react like the cement grains.

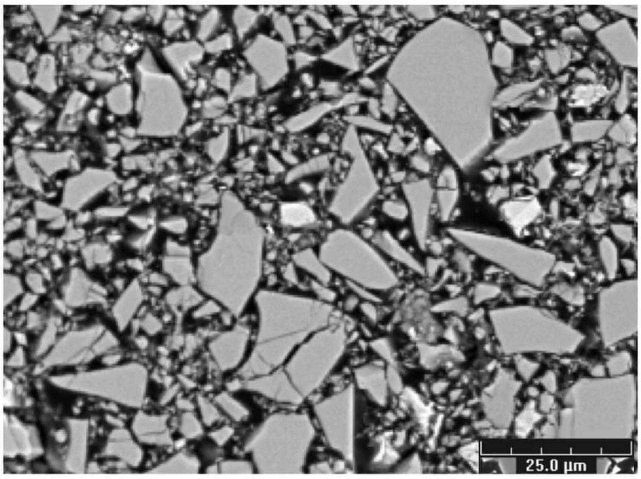
Notes

Summary

3m 00s

Ground Granulated Blast-furnace slag

- 90-100 % amorphous
- Sharp edged and irregular glassy material
- High CaO content (30-50%): **latent hydraulic** material
- **30-70%** replacement of cement typical (even 90% possible)



[Kocaba, 2008]

And here we see a picture of the slag, we can see these angular grains. They are made up about 90% percent or more are amorphous material. And then this is ground and the break up of this glass gives these sharp irregular glassy materials. This has a very high calcium oxide content and produces what is called a latent hydraulic material. Because of the high calcium content then we can replace very high amounts of clinker in cement. Typical replacement levels are in the range from 30-70% percent.

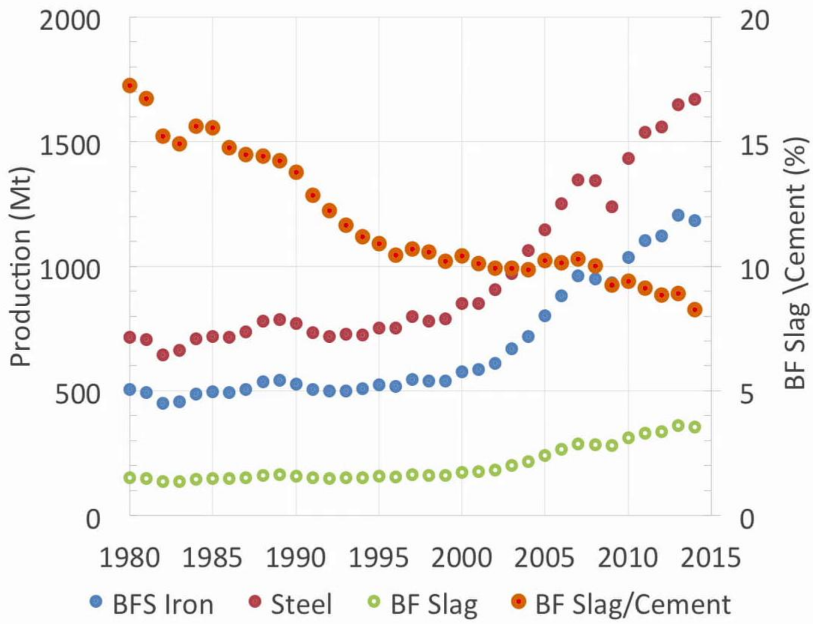
Notes

Summary

4m 03s

Evolution of slag relative to cement

- The faster growth of cement use relative to steel and increased recycling of steel mean that the proportion of slag relative to cement has decreased dramatically in the past decades.
- At present, globally, the annual production of slag is about **8%** or the production of cement
- 90-95% of this is already used blended to make cement or incorporated at the concrete level.
- This trend will continue



Now the problem with slag is that the growth in availability of slag has been not as fast as the growth in availability of cement. So at present, the annual production of slag is only around eight percent of the production of clinker and this proportion is unlikely to increase because we are producing more or more iron and steel from recycled materials and this means there is less slag available from blast furnaces.

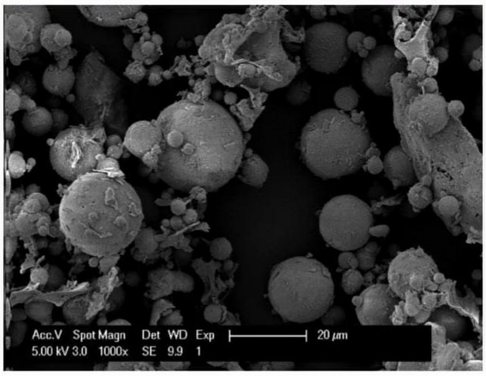
Notes

Summary

4m 43s

Coal fly ash

- Incombustible inorganic material in coal
- Recovered from **exhaust gases** by electrostatic or mechanical precipitators (baghouses)
- Mainly composed of **spherical glassy particles** (1-300 µm), formed as rapidly cooled droplets reactive phase)
- A significant portion of refractory **crystalline phases** persists (unreactive)
- Less reactive than slag, typically used at around **30%** in blends,



Next we move to fly ash and as I have said, this is the incombustible material which is in the coal. What happens is that during the burning of the coal, little droplets of water form, these droplets then are carried in the flue gas and subsequently recovered by electrostatic precipitation to avoid their dispersion into the atmosphere. Now because they are very small, they cool quite quickly and this quick cooling again leads to the formation of amorphous or glassy material. So we have much lower proportion of amorphous material. We typically find the that the core of these grains is crystalline, because of this reason and the chemical composition where it contains less calcium, this is less reactive than the slag and the typical levels of addition we can make are up to around thirty percent.

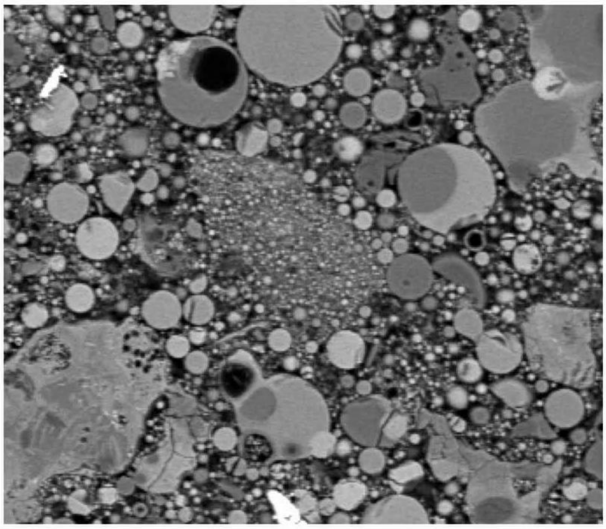
Notes

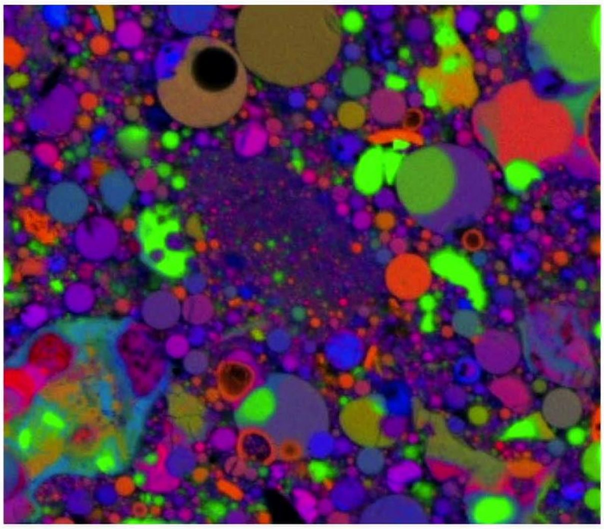
Summary

5m 14s

Coal fly ash

- Very heterogeneous material – and variable material





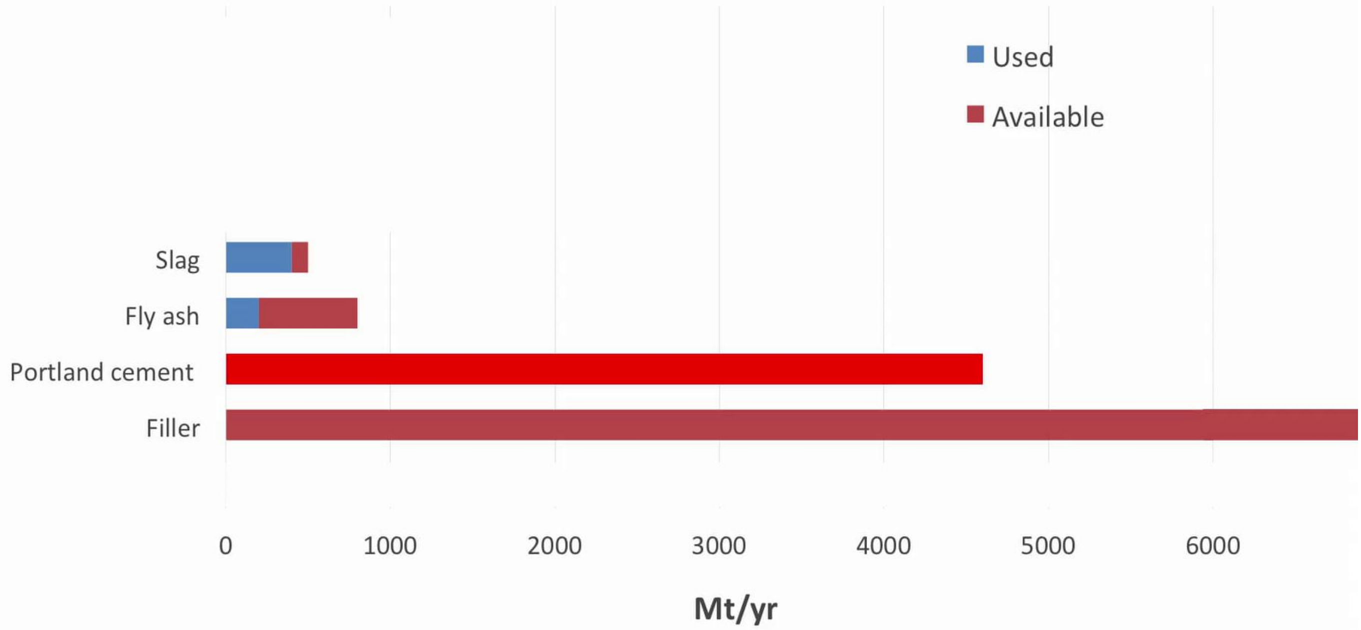
Now the other problem with fly ash is that it is a very heterogeneous material. In this micrograph here we can see the different grey levels indicate the different chemical composition and on the right here we have made a chemical mapping of that fly ash and the different colours indicate different chemical compositions. So what you can really see is that the chemical composition varies considerably from place to place and this makes it quite tricky to determine how fly ashes react and means that one fly ash can behave quite differently from another fly ash.

Notes

Summary

6m 15s

Availability of SCMs



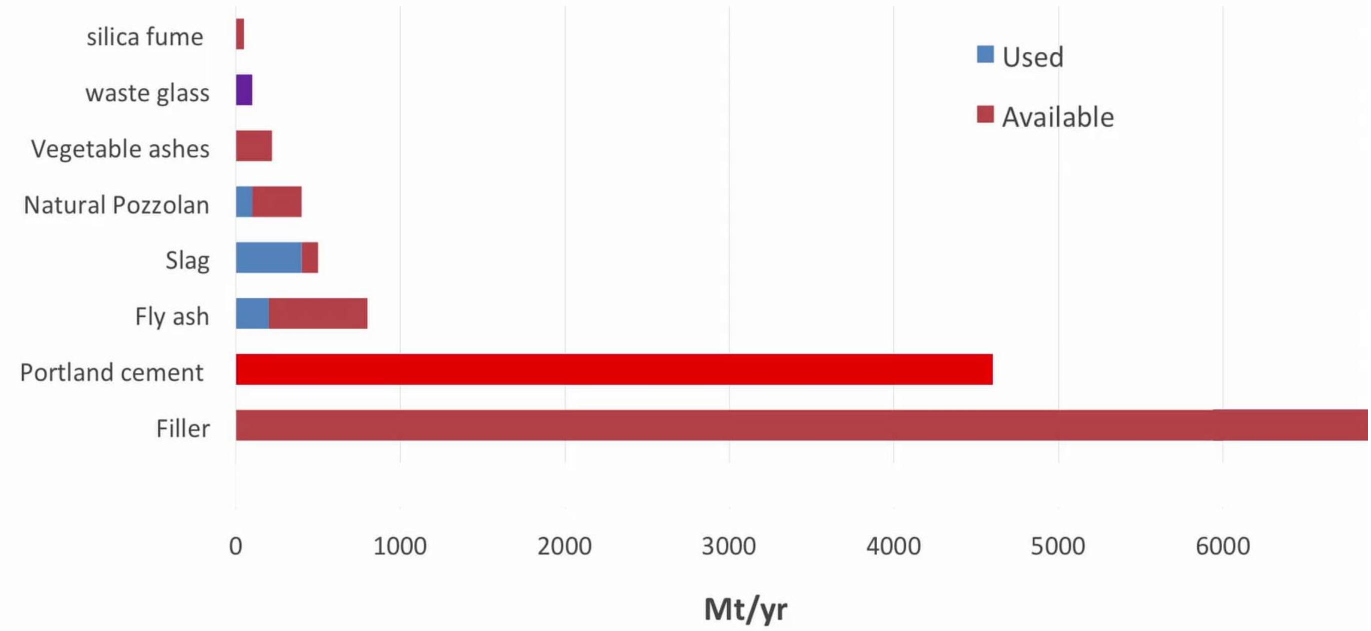
So in this series of slides, we can look at the availability of these SCMs compared to Portland cement. So this red bar shows the amount of Portland cement produced in the world today, just over four billion tonnes. And if we look at these common replacement materials, slag and fly ash, we see that the amounts available are much lower than the amount of Portland cement. So slag, we have about eight percent compared to portland cement and the vast majority of this is already used either blended with cement or added at the concrete stage. When we come to fly ash, overall we have a somewhat higher amount but because of that variability, the amount that can be used with cement is quite a bit lower. And these two materials together make up only around fifteen percent of the amount of Portland cement produced today. Now people have looked for other materials that can be blended in. The other material we have is limestone, we have talked about earlier and there is effectively unlimited amount of this material available. But the problem is that we can't have very high amounts without diluting the properties of the cement. And generally if we have additions above about ten percent or so then the strength and other properties of the cement tends to decrease.

Notes

Summary

6m 56s

Availability of SCMs



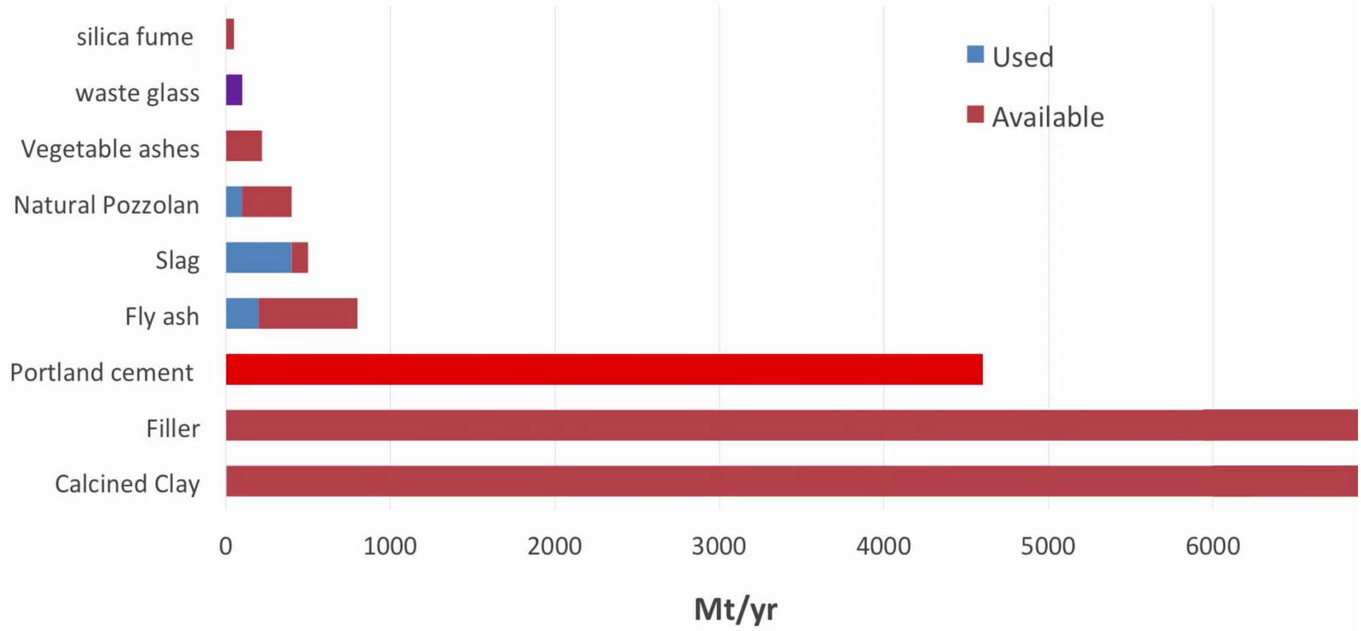
Now people have looked at other materials to use as SCMs which we see now here on the top. We see natural pozzolan. The amounts used today are really quite small. This could perhaps be increased, but nevertheless, geographically, the distribution of natural pozzolan is very uneven. People have considered vegetable ashes, so notably the ash produced by burning rice husks can be an active addition in cementitious materials. But the amounts available are really quite small and there are a lot of other problems with these vegetable ashes such that they are only produced seasonally, they tend to be produced in rural areas where the big demand for cement is in urban areas and currently many of these agricultural waste are used as fertilizers so if they are taken off the land, they may lead to a problem of soil fertility. People have talked about waste glass, but really we see that the amounts of this are very, very small and of course it is much, much better to recycle waste glass into new bottles. And finally of course silica fume which is a very high performance additive widely used to produce high performance concrete but the amounts available are really very very small. So what else can we have?

Notes

Summary

8m 28s

Availability of SCMs



Now what we really see is that there is only one material that is available in the kind of quantities we really need and this is calcined clay. And the amounts of calcined clay really are virtually unlimited.

Notes

Summary

10m 02s

So to summarize that, what we see is that there is no magic solution. Blended cements with SCMs will be the best solution for sustainable cement for the forseeable future. The traditional SCMs we have are only about fifteen percent compared to the amount of cement we produce and the only material available in viable quantities apart from these is calcined clay. And even more interesting is the use a combination of calcined clay with limestone which we will talk about in another video of this module.

Notes

Summary

10m 19s

There is no magic solution

Limestone
Calcined
Clay
Cement
LC3

- Blended with SCMs will be best solution for sustainable cements for foreseeable future.
- Traditional SCMs (slag + fly ash) only about 15% available compared to cement.
- **Only other material available in viable quantities is calcined clay**.
- Even more interesting is the use of a combination of calcined clay with limestone
- We will talk about this in more detail in another lecture

So this material, this material with that combination of calcined clay and limestone is what we call limestone calcined clay cement or LC3.

Notes

Summary

10m 57s

Alkali activated materials - Geopolymers

- The low availability of slag is the main reason alkali activated materials (AAMs) will not contribute significantly to lowering global CO_2 emissions.
- All formulations which harden at ambient temperature contain mainly slag
- If slag is diverted from use in cement blends and concrete to use in AAMs:
  - It may be true that the AAM has lower CO_2 emissions, but globally the emissions of other concrete will increase
  - Then the CO_2 emissions of the alkali activator must be considered
  - These two effects mean that CO_2 emissions may even be increased on a global level
- There are very few countries where the supply of slag would favour the use on AAMs

So before summarizing this, I just want to say a short word about alkali activated materials or geopolymers. The low availability of slag is the main reason why alkali activated materials will not contribute significantly to lowering global CO2 emissions. All the formulations of alkali activated which harden at ambient temperature contained today contain mainly slag. And as we have seen the availability of slag is really very low. So if slag is diverted from use in cement blends and concrete to be used in alkali activated materials, then we may be able to say that these alkali activated materials have a lower CO2 emissions, but globally the emissions of other concrete will increase and in fact what we need to consider is also the CO2 emissions of the alkali activator. And for these two reasons, the CO2 emissions may be increased at a global level. And in fact there are very few countries which have really abundant supplies of slag which would favour the use of alkali activated materials, so one exception in this case is Japan.

Notes

Summary

11m 07s

Summary (1/2)

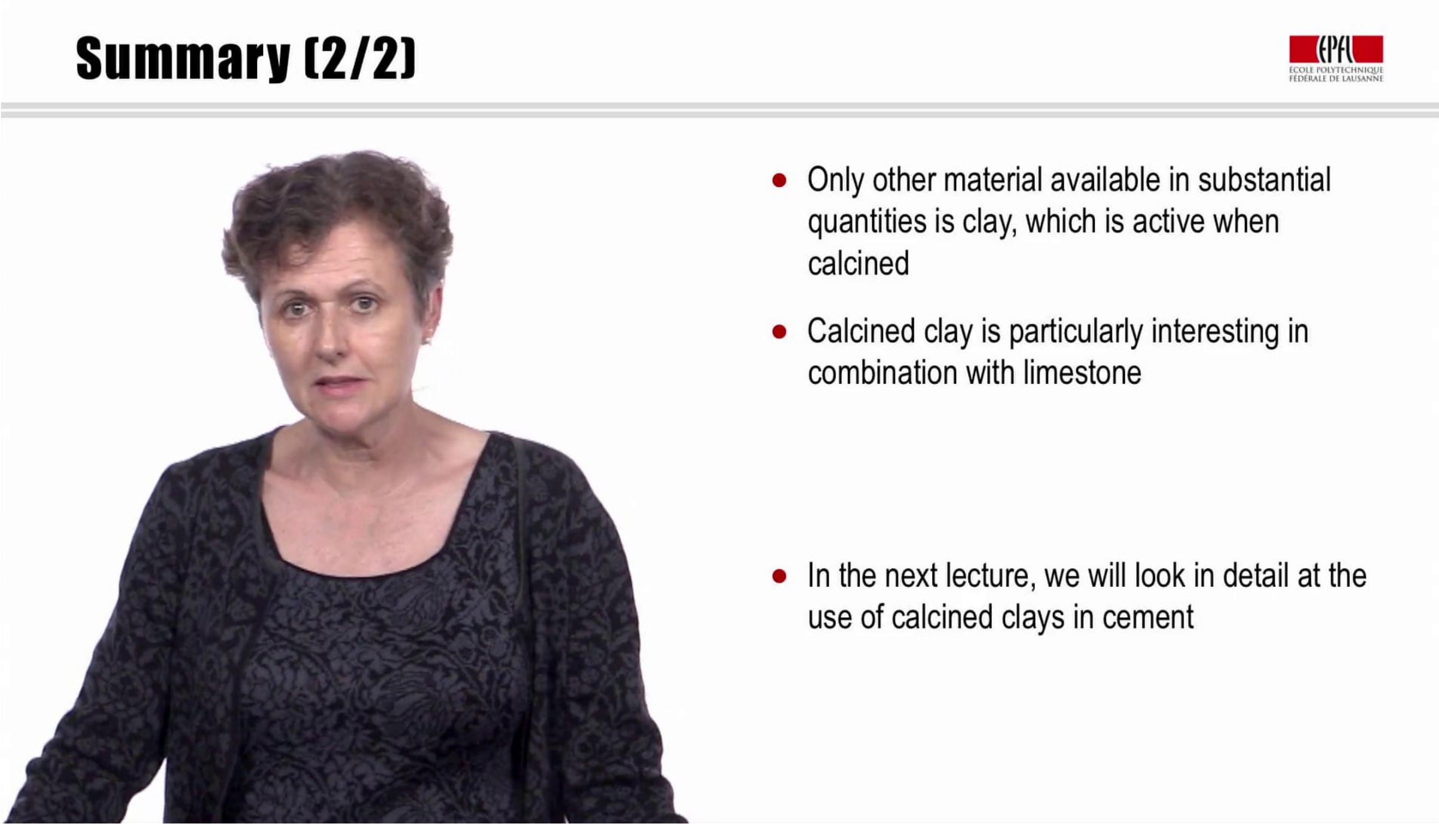
- Supplementary cementitious materials are an effective way to reduce the amount of clinker in cement (or concrete) and hence reduce CO_2 emissions
- Over the past few decades the average level of substitution has increased to around 20%, made up mainly of slag, fly ash and limestone.
- Further progress is limited by the availability of these SCMs
- This is also the main reason that AAMs cannot have significant environmental impact.

OK so let's summarize what we have seen in this lecture. In this lecture we have seen that supplementary cementitious materials are an effective way to reduce the amount of clinker in cement or in concrete and hence to reduce CO2 emissions. Over the past few decades, the average level of substitution has increased to around twenty percent and this is made up mainly of slag, fly ash and limestone. Further progress in this respect is mainly limited by the availability of these SCMs and this limited availability is also the main reason that alkali activated materials cannot have a really significant impact on lowering overall emissions from cementitious materials.

Notes

Summary

12m 23s



What we have seen is that the only other material available in the kind of quantities we need is clay which is active when calcined and this is particularly interesting when used in combination of limestone. So in the next lecture we are going to look in detail at the use of calcined clays for cement and concrete. So thank you for listening and I hope to see you next time.

Notes

Summary

13m 13s