Context

Cement Chemistry and Sustainable Cementitious Materials

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Outline

- Context
- CO_2 footprint
- Why Portland
- Lowering Environmental Impact: SCMs

MOOC-Title

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Let's start with a little quiz!

» Which of these sectors / technologies has the highest annual CO_2 emissions?

» Cement and concrete	» 6-8
» Iron and steel	» 7
» Clothing	» 10
» Passenger transport, road	» 9.5
» Food loss/ waste	» 6

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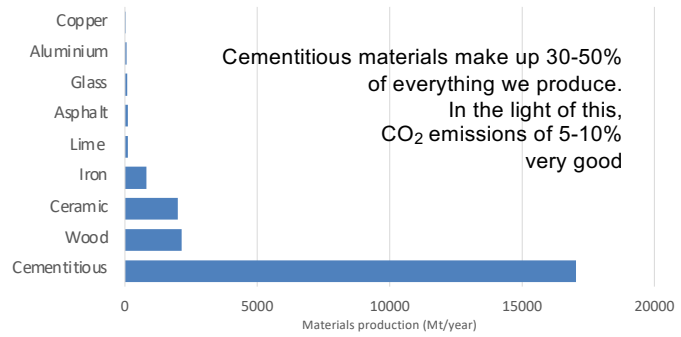
Cement based materials cannot be replaced



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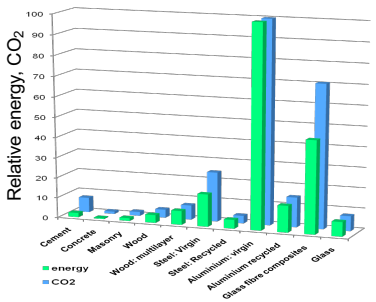
Concrete is an environmentally friendly material

Material	MJ/kg	kgCO₂/kg
Cement	4.6	0.83
Concrete	**0.95**	**0.13**
Masonry	3.0	0.22
Wood	8.5	0.46
Wood: multilayer	15	0.81
Steel: Virgin	35	2.8
Steel: Recycled	9.5	0.43
Aluminium: virgin	218	11.46
Aluminium recycled	28.8	1.69
Glass fibre composites	100	8.1
Glass	15.7	0.85

ICE version 1.6a
Hammond G.P. and Jones C.I
2008 Proc Instn Civil Engineers
www.bath.ac.uk/mech-eng/sert/embodied/



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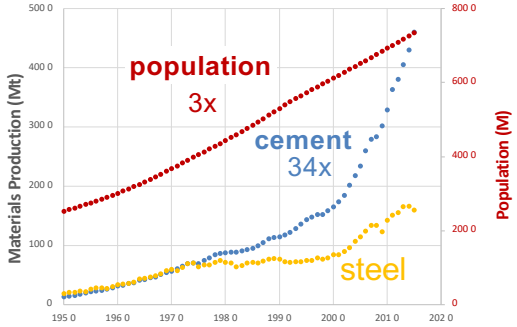
Growth in cement use in last 70 years



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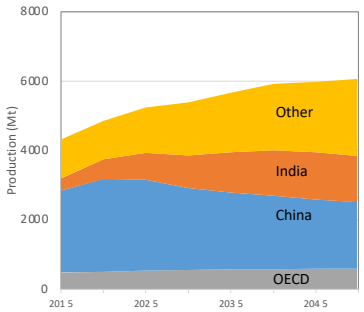
Forecast growth



We need solutions for people in developing countries

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How to meet this challenge sustainably

Solutions need to be:

- Practical,
  usable by unskilled workers
- Economically viable

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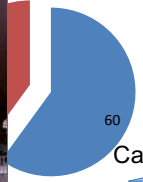
Origins of CO_2 emissions in cement production

1 tonne of cement leads to the emission of 650 – 900 kg CO_2



$CaCO_3$ ➔ $CaO + CO_2$

Limestone 80% of raw material

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Summary

- Importance of cement as a material
- Good environmental impact
- Origins of CO_2 emission

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Why "Portland" cement

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Why Portland cement

- > 99.999% 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.

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- The dominance of Portland cement is not by chance.
- It arose as a consequence of the raw materials available on earth.

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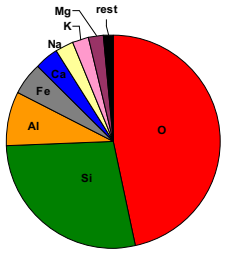
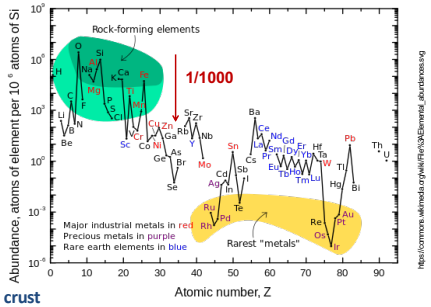
We do not have a lot of options!





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

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- The composition of the earth limits practical chemistries
- But it means we can explore all options
- We need to know the basics of how cement works

MOOC-Title

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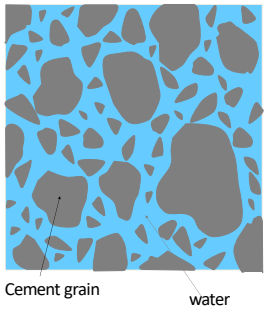
How cement works:



We mix the grey cement powder with water.

To start with the grains are just floating about in the water and we can cast the concrete into moulds

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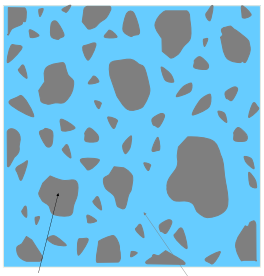
How cement works:



The cement grains dissolve in the water

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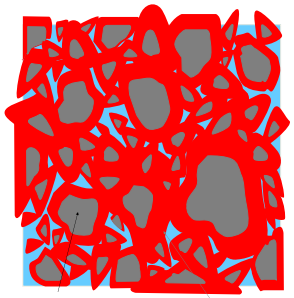
How cement works:



The cement grains dissolve in the water

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

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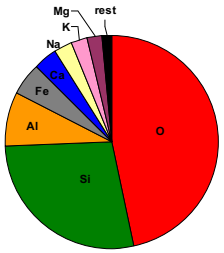
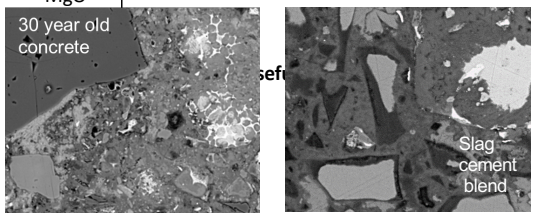
What about the different oxides



Na_2O
K_2O
Too soluble

Fe_2O_3
MgO
Too low mobility in alkaline solutions



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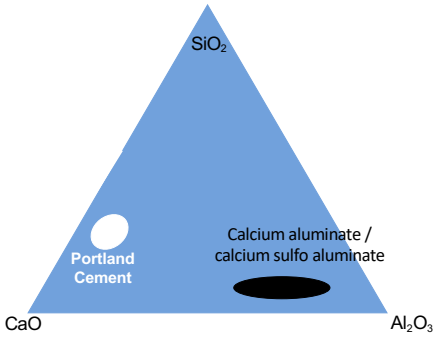
Hydraulic minerals in the system $CaO-SiO_2-Al_2O_3$



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

Important limitations of supply. Even if all current production of bauxite switched to CSA production could only fill 15% of demand

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"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

Much worse than calcium silicates

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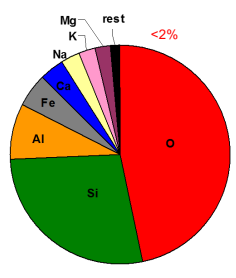
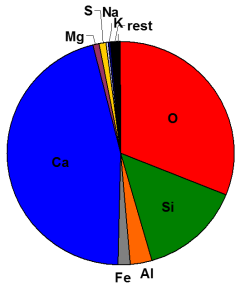
Composition of cement compared to earth's crust



earth's crust



Portland cement

Limestone: very widely distributed provides the high amounts of calcium

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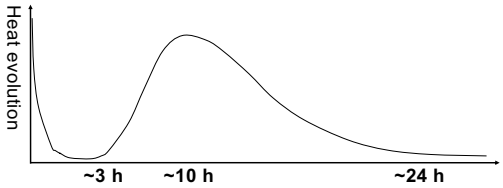
Portland cement is amazingly robust



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

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Can be mixed almost anywhere

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Future cements

- Cements based on Portland clinker will be most important materials for foreseeable future
  - Widely available raw materials
  - Economy of scale means very low cost - ~100 € /tonne
  - Easy to use even by unskilled workers.

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Lowering Environmental Impact

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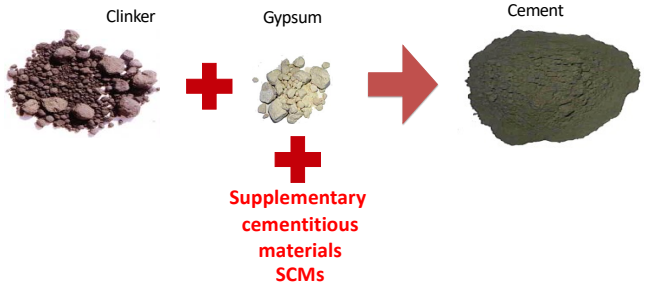
Do we need to rely only on clinker?

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.

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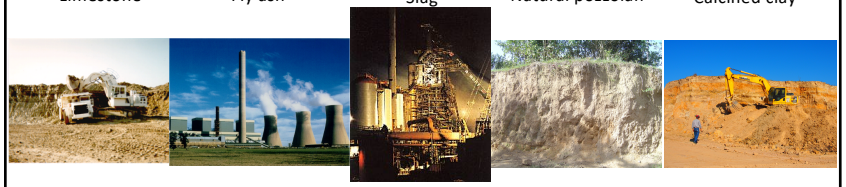
Supplementary cementitious materials



Often by-products or wastes from other industries

Local availability very important!

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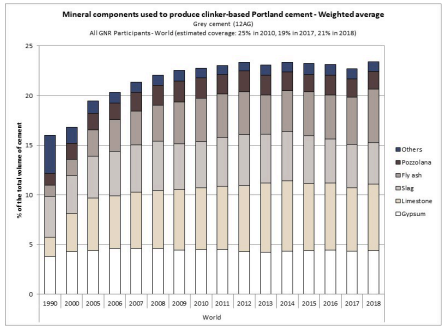
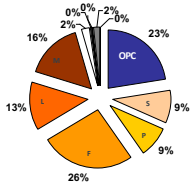
Clinker substitution

LOW CARBON LOW COST LOW CAPITAL



Breakdown of cement types



Holcim 2010

S Slag Cement
P Pozzolan Cement
F Fly Ash Cement
L Limestone Cement
M Multiple Blend Cement
Masonry Cement

Source GCCA GNR (getting the numbers right)

EPFL

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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)

MOOC-Title

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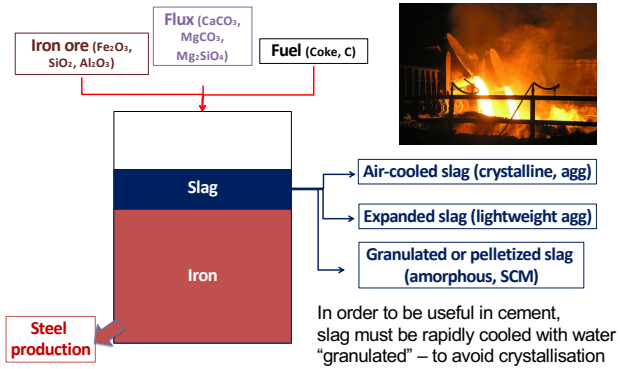
Blast Furnace Slag

In the process of reduction of iron from ore.

Flux is added to assist the separation of impurities from the iron.

This forms slag, which is a molten liquid in the blast furnace



In order to be useful in cement, slag must be rapidly cooled with water – "granulated" – to avoid crystallisation

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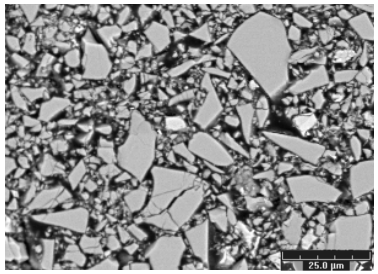
Ground Granulated Blast-furnace slag

- 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]

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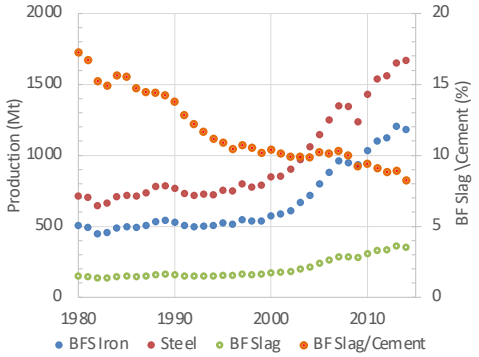
Evolution of slag relative to cement

- 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



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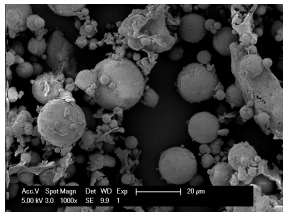
Coal fly ash

- 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,



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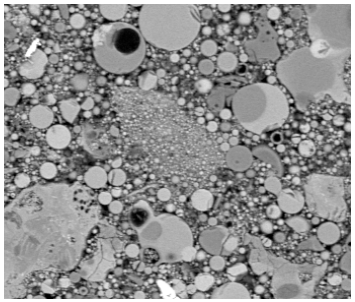
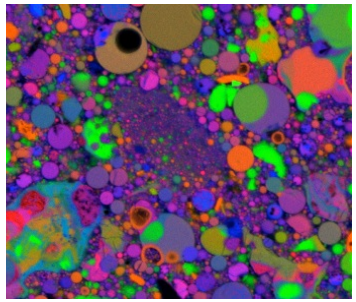
Coal fly ash

- Very heterogeneous material – and variable material





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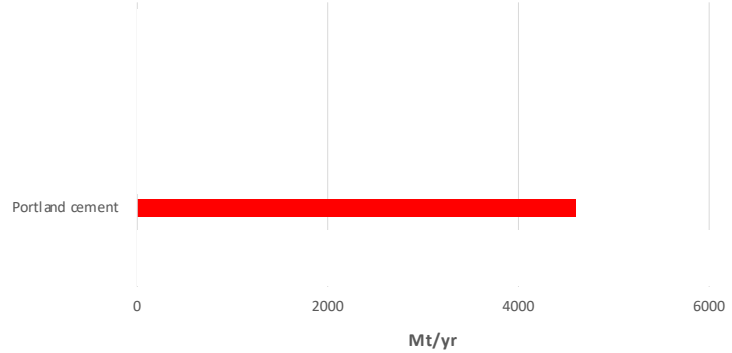
Availability of SCMs



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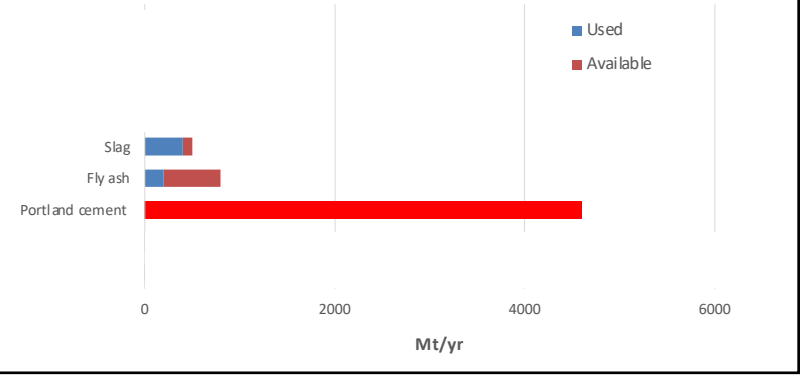
Availability of SCMs



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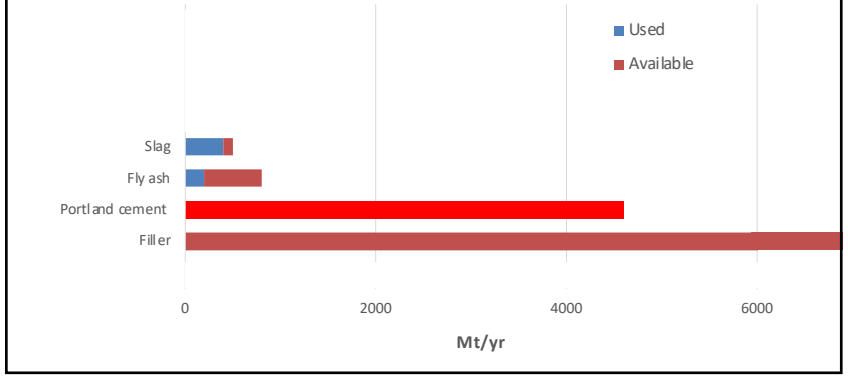
Availability of SCMs



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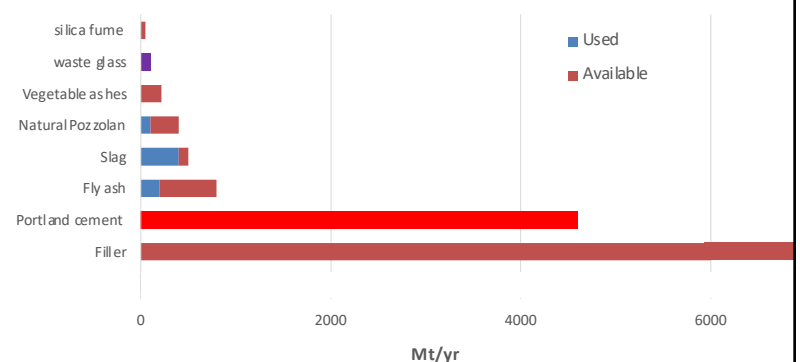
Availability of SCMs



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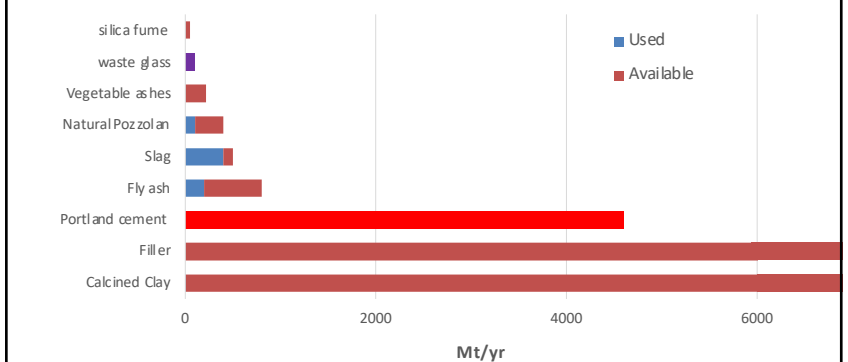
Availability of SCMs



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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

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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

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Summary

- 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.
- Only other material available in substantial quantities is clay, which is active when calcined
- Calcined clay is particularly interesting in combination with limestone

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Limestone Calcined Clay Cement

UN environment

LOW CARBON LOW COST LOW CAPITAL

Eco-efficient cements: Potential economically viable solutions for a low-CO_2 cement-based materials industry

Karen Scrivener, EPFL, Switzerland

Vanderley John, USP, Brazil

Ellis Gartner, Imperial College, UK

2016

Can be downloaded free at multiple sites.

Just google

RILEM YouTube Scrivener

https://www.youtube.com/watch?v=a7fpWA19aYc

EPFL

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