LAFARGE

bringing materials to *life*

ALTERNATIVE BINDERS FOR CONCRETES WITH REDUCED CO_2 EMISSIONS

Ellis GARTNER, LCR

The Challenge: Can we develop low-CO_2 alternatives to Portland Cement, with global market potential?

- Current best available manufacturing technology for OPC is already very energy-efficient.

- OPC manufacturers are already attempting to use more and more local industrial by-products, but supplies are limited.

- CO_2 sequestration approaches are already being addressed by the energy industries, but they look very expensive to us!

- Therefore, the objective of this talk is to draw attention to the fact that some alternative approaches exist. Such approaches necessitate a good understanding of “cement science”.

Approximate worldwide consumption of materials

(Global construction needs can never be met without concrete!)

CEMENT: 2740 Mt

CONCRETE: ≈ 25000 Mt (≈ 10 km^3)

GYPSUM PRODUCTS: ≈ 130 Mt

TIMBER: ≈ 3200 Mt (≈ 4 km^3);

[the Earth’s sustainable limit is ≈ 2500 Mt]

(of this, < 1000 Mt is used in construction and ≈ 300Mt for paper and cardboard)

STEEL: 1350 Mt

(of this, ≈ 600 Mt is used in construction, about 500 Mt of it for concrete reinforcement)

ALUMINUM: 32 Mt

FIRED CLAY PRODUCTS: ≈ 400 Mt (bricks, tiles, ceramic articles, etc.)

PLASTICS: 120 Mt

GLASS: ≈ 100 Mt

Approximate Embodied Energies *(data from Australia – ref. 2)*

Material	Embodied Energy: GJ/t	GJ/m^3
Aggregate (sand, stone, gravel)	**0.02-0.10**	**-**
Cut stone (local)	**0.8**	**1.9**
Asphalt paving	**3.4**	**7.1**
Fiber-cement board	**9.5**	**13.6**
Concrete tiles, blocks, bricks, pavers	**0.8-1.2**	**1.5-3.0**
GRC boards	**7.6**	**14.8**
Average pre-cast concrete elements	**2**	**5**
Ready mix concrete, 17.5 MPa	**1.0**	**2.4**
Ready mix concrete, 40 MPa	**1.6**	**3.9**
Adobe blocks, (straw stabilized)	**0.47**	**0.75**
Rammed soil cement *(e.g. blocks)*	**0.8**	**(≈2)**
Ordinary fired clay bricks and tiles	**2.5**	**5.2**
Glazed clay bricks and tiles	**7.2**	**14.8**
Float glass and laminated glass	**15.9-16.3**	**40-41**
Plasterboard	**6.1**	**5.9**
High-density polyethylene	**103**	**97**
Expanded polystyrene board	**117**	**2.3**
Paper products	**12-36**	**-**
Softwood timber, rough-sawn, air-dried	**0.3**	**0.17**
" " " " kiln-dried	**1.6**	**0.88**
MDF *(medium-density fiberboard)*	**11.9**	**8.3**
Steel (general)	**32-35**	**250-275**
Steel (recycled)	**9-13**	**70-100**
Aluminum (virgin) products	**191-227**	**516-613**
Aluminum (recycled) products	**8-43**	**22-116**

Selected Estimates of “Embodied CO_2”:

Average CO_2 emission per unit of fossil fuel heating value = 100 kg/GJ

(Natural gas gives only 64 kg/GJ, fuel oils give over 80 kg/GJ, whereas coals and cokes typically give 100 - 120 kg/GJ)

Based on the average fuel value, but adding the raw-materials CO_2 emissions for cement manufacture, we calculate the following:

Un-reinforced concrete (in place): ≈ 140-260 kg/t, or ≈ 350-650 kg/m^3

Clay bricks and tiles: ≈ 250-720 kg/t, or ≈ 520-1480 kg/m^3

Typical processed wood products: ≈ 800-1200 kg/t, or ≈ 800-1500 kg/m^3

Mild steel: > 3000 kg/t, or ≈ 25000 kg/m^3

Lightweight expanded polystyrene: ≈ 230 kg/m^3

Factors Influencing the "CO_2-Efficiency" of Concrete.

The CO_2 emissions associated with the manufacture of hardened concrete objects or structures can be broken down into the following major contributions:

(A) CO_2 emissions associated with the raw materials (cement, aggregates, water, etc.)

(B) CO_2 emissions associated with the energy used in concrete mixing.

(C) CO_2 emissions associated with the delivery (of both the raw materials and the fresh concrete) and the placing and finishing of the concrete.

Here, I will only deal with (A). This is composed of:

1 Aggregates, e.g.: gravel; crushed rock; sand; lightweight aggregates

2 Water (sometimes partly substituted by air voids or bubbles on a volume basis)

3 Binder (cementitious powders plus any fine fillers that are not counted as aggregate)

4 Chemical admixtures (usually water-soluble chemicals added to the mix water)

Here, I will only treat (3) and to some extent (4)

The importance of raw materials choice

(examples using extremely simplified chemical equations!)

Conventional portland cement manufacture:

$3CaCO_3 + SiO_2 \Rightarrow Ca_3SiO_5 + 3CO_2$

300 *60* *(> 1300°C)* *228* *132* *(mass units)*

limestone + silica ⇒ C_3S (cement) + carbon dioxide

The 'cement-sulfuric acid' process:

$3CaSO_4 + SiO_2 + 3H_2O \Rightarrow Ca_3SiO_5 + 3H_2SO_4$

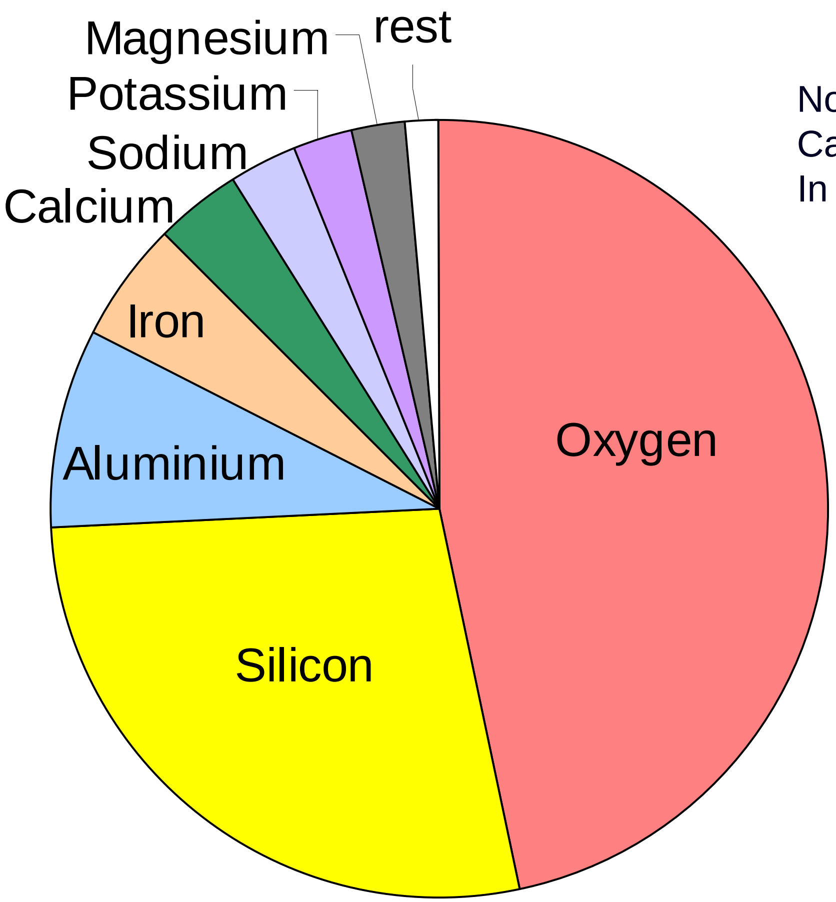
408 *60* *54* *(> 1300°C)* *228* *294*

anhydrite + silica + steam ⇒ C_3S(cement) + sulfuric acid

The Raw Materials must be Abundant!

- Current world cement production is now over 2.7Gt/year and still increasing. The main component is still always portland clinker.
  - *This involves decarbonating about 3 Gt/yr. of limestone, containing about 1.3 Gt of “fossil” CO_2, (independent of combustion-derived CO_2)*
  - *Supplies of conventional clinker substitutes (granulated BF slag, fly ashes and natural pozzolans) are limited, especially from good quality sources.*
- Alternative cements must be based on minerals available in quantities comparable to the demand and well-distributed world-wide, or at least readily available in many key locations.
  - *Cements based on less abundant minerals are unlikely to be produced in quantities large enough to have much impact on global CO_2 emissions.*
  - *Due to the low cost of cement per tonne, transportation costs are a major factor in any economic analysis.*

Proportions of the principal elements in the Earth’s crust



Note: Portland Clinker contains
Ca, O, Si, Al and Fe
In that order of concentration

Other elements abundant
enough to be considered
include H, C, S, N, Cl & P

Pertinent Mineral Resources

Mineral	**Resources and Distribution**	**Supply / Possible Demand for Cement Use**
Limestone (calcite):	Very abundant and very widespread	Very high
Silica (& *silica-rich clay)*	Very abundant and very widespread	Very high
Gypsum, Anhydrite *(& other sulfur sources)*	Abundant and fairly widespread *(includes FGD gypsum from fuels)*	Acceptable (*due to increasing use of FGD)*
Bauxites *(alumina sources)*	Abundant but poorly distributed; *impure grades much more common*	Acceptable only if very impure grades can be used
Alumina-rich clays *(kaolinites)*	Abundant but poorly distributed; *impure grades much more common*	Acceptable only if very impure grades can be used
"Natural Pozzolans" *(reactive volcanic ashes)*	Fairly abundant, but *very variable and very poorly distributed*	Interesting only in certain locations
Magnesite (Magnesium carbonate)	Much less abundant than calcite, and *very poorly distributed.*	Adequate for magnesia *but not for cements.*
Phosphate Rock: (Calcium phosphate)	Relatively uncommon and *very poorly distributed*	Priority need for fertilizers, *not for cements!*
Iron Ore	Very abundant and fairly widespread	High
Coal *Combustion residues*	Very abundant and fairly widespread *Fly ash (and also FGD gypsum)*	Acceptable *Adequate for cements*
Alkaline sodium compounds *(e.g. trona)*	Relatively uncommon and *very poorly distributed*	Can be manufactured from salt if necessary

Clinker Manufacturing Issues

- The current best technology for clinker manufacture uses only ≈ 3 GJ/t in kiln fuel energy, and there is little room for improvement on this, for good thermodynamic reasons.
- The gases that leave the stack are similar to those of most fossil-fuel-burning power plants. Systems being developed for CO_2 capture, concentration and subterranean sequestration in the electric power industry could also be applied to cement plants. Some joint research is in progress but projected costs are high.
- Oxygen enrichment of combustion air could save some kiln fuel and facilitate CO_2 capture, but the energy used to generate the oxygen is high, so projected overall energy costs for capture are still high.

Theoretical Enthalpy Balance for OPC Manufacture

***Note:** Assumes dry limestone and clay as kiln feed, and ignores any heat losses, either in combustion gases or by conduction, radiation, etc.; (based on Lea, 3rd Edn., p126)*

Kiln section	Temperature range	Process	Enthalpy required, kJ/g (GJ/t) of clinker
Preheater	20 – 900°C	heating raw feed to 900°C	+1.53
“	about 450°C	dehydration of clays	+0.17
“	20 – 900°C	cooling CO_2 and H_2O	- 0.59
Calciner	about 900°C	dissociation of calcite	+1.99
“	about 900°C	reactions of dehydrated clays	- 0.04
Rotary Kiln	900 –1400°C	heating feed from 900 to 1400°C	+0.52
“	900 –1400°C	formation of clinker phases	- 0.31
Clinker cooler	1400 – 20°C	cooling of clinker to 20°C	- 1.51
		Net heat required:	+1.76

Raw Materials CO_2 per unit mass and volume for the major cement compounds of interest

Cement Compound	Raw Materials	RM CO_2 in g/g	RM CO_2 in g/ml
M (magnesia, periclase)	magnesite	1.092	3.91
C (calcia, quicklime)	limestone	0.785	2.63
C_3S (alite)	limestone + quartz	0.578	1.80
β-C_2S (belite)	limestone + quartz	0.511	1.70
C_3A (tricalcium aluminate)	limestone + alumina	0.489	1.50
C_4AF (calcium aluminoferrite)	as above + iron oxide	0.362	1.29
NS (sodium metasilicate)	soda + quartz	0.361	-
CA (monocalcium aluminate)	limestone + bauxite	0.279	0.83
$C_4A_3\$$ (calcium sulfoaluminate)	as above + anhydrite	0.216	0.56

Generic technical and scientific problems to be addressed for concretes made with new binders:

1. The prediction of concrete durability
2. The control of fresh concrete properties and early-age curing procedures
3. Variability of raw materials
4. Concrete life cycle and recycling issues

The prediction of concrete durability

- Durability is probably the most problematic issue involved in the development of alternative binders, since there are few reliable and rapid durability tests that are not based on “chemical assumptions”!
- What can we do to minimize “autogenous cracking”?
- We must be very careful to distinguish between the durability of the concrete matrix and the durability of the final article. The majority of concrete durability issues seem to be related to the durability of reinforcing steel, not of the matrix itself. Can we decouple the two?
    - Should concrete essentially be considered to be an anti-corrosion paint for steel? If so, perhaps the matrix is currently too cheap!
    - Couldn’t we work with the steel producers on alternative steels that would resist corrosion in matrices with pH <9, or with high chloride? This would remove many of the barriers to alternative binders.
    - Are there realistic alternatives to steel reinforcement?

The control of fresh concrete properties and early-age curing procedures

- The relationships between mix design and the rheological properties of fresh concrete are reasonably well understood for Portland cement-based binders, but less so for alternative systems with low or zero Portland clinker contents.

- Rheological properties of concern include both the “yield stress” and the “viscosity” as functions of time, temperature, shear rate, etc. A simple slump test is not sufficient to characterize fresh concrete properties for many applications.

- Setting times and rates of strength development at early ages can be critical for many applications, and alternative binders can be very different from Portland cements in this respect.
    - For example, high-volume fly ash concretes (HVFAC) usually set and gain strength very slowly compared to OPCs.

Variability of raw materials

- The responsibility for dealing with raw materials variability may rest more or less with the concrete maker, depending on “local tradition”.
  - Should we allow concrete makers to take full responsibility for this? It could be the best way to optimise raw materials use, but are they technologically and scientifically equipped to do it?
  - The input of the academic community could be critical in this respect.
- With by-product SCMs (especially fly ashes), existing product standards for use in concrete are based on low substitution levels. But some alternative binders (e.g. HVFAC and “geopolymers”) involve high substitution levels at which variations in by-product quality can have an enormous impact.
  - New standards will be needed.

Concrete life cycle and recycling issues

- Recycling of as much as possible of old concrete as close as possible to its source is evidently desirable.

- Could alternative binder systems make recycling easier?

- The issue of CO_2 uptake by existing concrete structures is pertinent.
    - Steel corrosion protection requires low carbonation rates
    - Concrete recycling can help reduce life-time CO_2 emissions

- It would be advantageous for the concrete industry to choose binders on the basis of the final application, i.e. whether or not the concrete will be reinforced with steel, and, if it will be, then what type of exposure conditions it will be subject to.

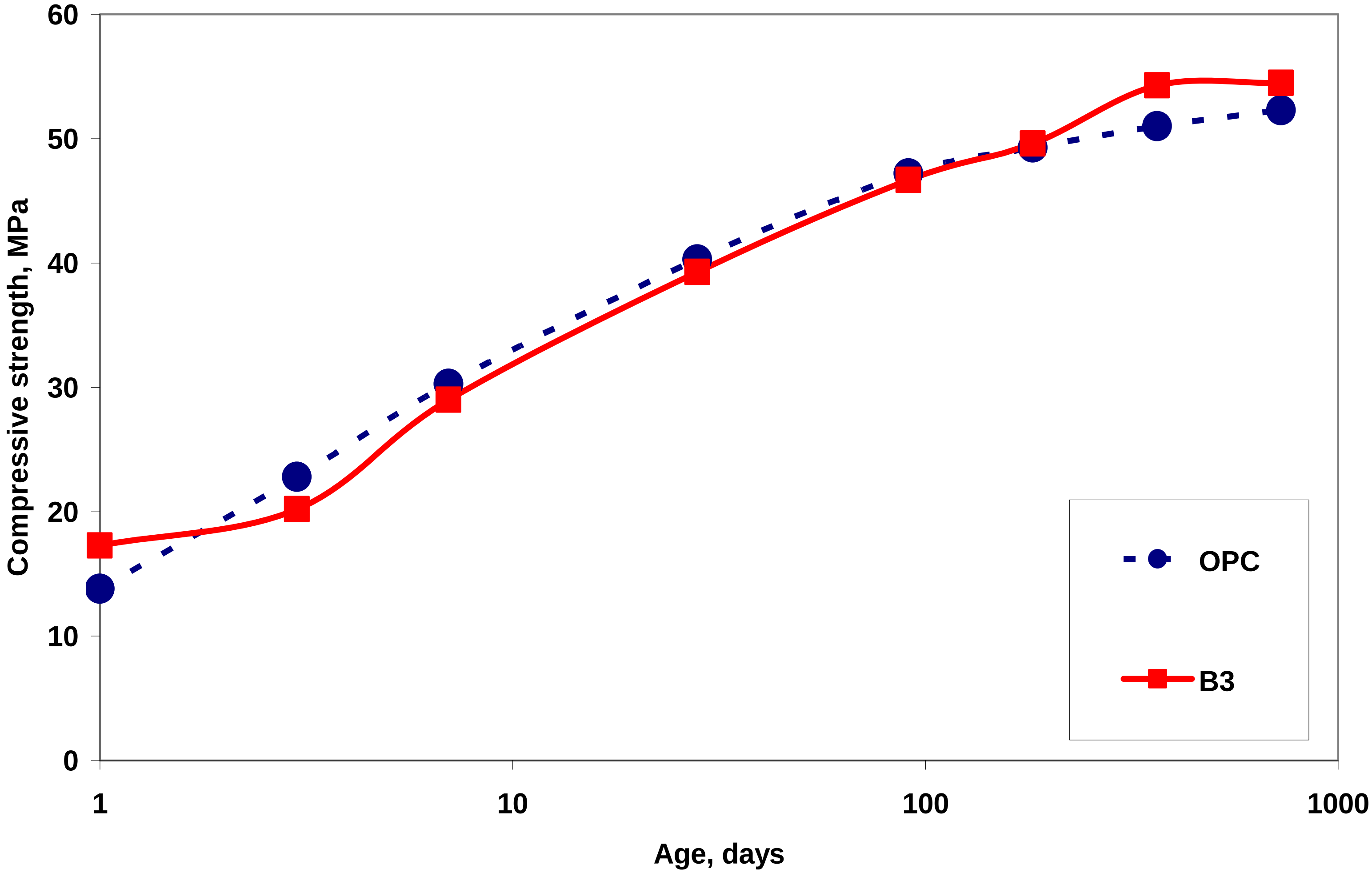
What are the alternatives to OPC-based cements?

- Manufacture of clinkers based on calcium sulfoaluminate (CSA) plus belite and other phases, looks promising.
  - Such clinkers could be made in existing OPC plants.
  - China has already developed norms for this type of ‘TCS’ cement.
  - Raw materials costs are higher than for OPC in almost all locations, but perhaps not so high as to be uneconomic once projected CO_2 emissions costs (taxes) have been factored in.
- An oft-proposed alternative system is “pozzolans” activated by alkali hydroxides or silicates (usually called “geopolymers”).
  - Unfortunately, the potential CO_2 savings vs. OPC have often been exaggerated by ignoring the large amounts of energy used to make the activators and sometimes also the pozzolans.
  - Raw materials supply will be a problem unless new manufacturing plants are added, both for the activators and the pozzolans.

Lafarge’s novel Belite-CSA-Ferrite (BCSAF) cements:

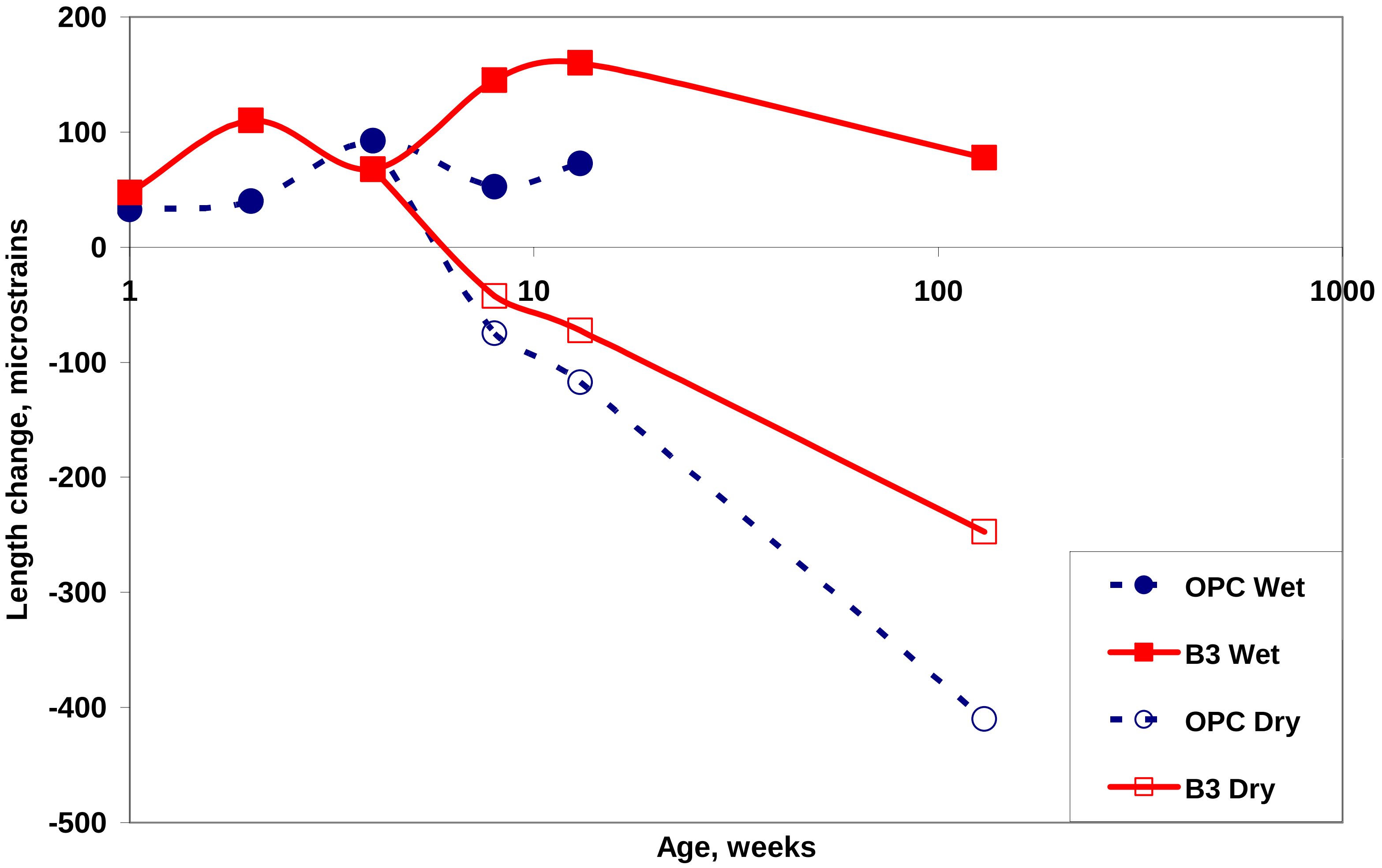
- Lafarge has recently patented a class of cement clinkers based on belite, CSA and calcium aluminoferrites, these three phases usually being present in the clinker in that order of abundance.
- These BCSAF clinkers can be used to make cements in the usual way, by intergrinding with gypsum, anhydrite, and other SCMs.
- BCSAF cements are somewhat outside the range of the Chinese CSA (TCS) cements, and may be considered in some respects to be intermediate between them and PC-based cements.
- In their overall elemental composition, BCSAF cements can be close to high slag content PC-based cements; but they do not require a source of slag. This makes them potentially capable of production in much larger volumes than slag-based cements.
- Unlike PC-slag cements, BCSAF cements can have high early-age strengths due to the reactivity of the CSA (ye’elimite) phase.
- A pilot-scale test batch of a BCSAF cement was made by LCR and subsequently tested under by the BRE as part of a public project.

BRE concrete data at w/c = 0.55, 300kg/m^3 for pilot batch of BCSAF (B3) compared to OPC (CEM I 42.5) (at 20°C).



Dimensional stability of B3 concrete

(vs. OPC concrete, at 20°C, either in water or at 65% RH)



CONCLUSIONS

- To have the potential to significantly reduce global CO_2 emissions from cement manufacture 'Low CO_2' cements must:
    - Be able to produce concrete with appropriate physical and durability properties
    - Be based on locally-available raw materials (even if some materials are globally available, transportation energy costs can be high).
- Cements based on CSA plus belite, ferrites, and calcium sulfates are a promising option. They hydrate to form mainly ettringite, C-S-H & AFm phases.
- Preliminary concrete tests of this approach to this have shown promising strength and durability results, but much more work is needed to establish data for Codes and Standards etc.