The Future of Cementitious Materials: Durability Implications

Professor Karen Scrivener
Concrete and sustainable development

- There are a lot of misconceptions about cement and concrete with respect to sustainable development.

- If we want to improve things we have to start from a correct assessment of the situation.

- We hear a lot about the fact that cement and concrete account for some 5-8% of man-made CO$_2$.

- What we don’t realise is that this is amazingly good for a material which makes up around half of everything produced.

- Here I am going to discuss how we can continue to improve environmental impact and the implications for durability.
The importance of concrete: Global figures (2005)

- (a) 34 GT of products  
- (b) 30 GT of CO$_2$e

<table>
<thead>
<tr>
<th>Material</th>
<th>Per year</th>
<th>A = % of $a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concrete</td>
<td>17.1 GT</td>
<td>50.2%</td>
</tr>
<tr>
<td>Steel*</td>
<td>0.74 GT</td>
<td>2.4%</td>
</tr>
<tr>
<td>Timber</td>
<td>2.2 GT</td>
<td>6.5%</td>
</tr>
</tbody>
</table>

(a) Resource consumption minus: major wastes (agricultural waste, mine tailings); grazed crops; fossil fuels – Krausmann et al *Ecol Econ* 68 (2009) 2696. (b) Estimate derived from various sources. *Virgin steel not including rebar. **IPCC estimate of emissions owing to forestry operations & thus upper bound. Full details of calculations & data sources available on request.

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*Slide Phil Purnell, University Leeds*
Concrete is an environmentally friendly material
Best able to satisfy the demands of the world population

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

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

Given these low figures, local supply is key
to avoid transport costs
Comparison on basis of functional unit

Energy of producing 1m of column to support 1000 tonnes

Energy of producing 1m of pipe

<table>
<thead>
<tr>
<th>Material</th>
<th>Fuel (litres)</th>
<th>Energy (kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concrete</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>Brick</td>
<td>230</td>
<td>190</td>
</tr>
<tr>
<td>Steel</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Concrete</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Concrete is the only viable solution

- From these slides we can also see that there is no possible substitute for concrete to satisfy the needs of the world's population for buildings and infrastructure.
- For example, the amount of wood used per year is about 1/10th the amount of concrete, and this level is already judged to be unsustainable – we are cutting down forests faster than we are replanting them.
- Compressed earth is still used in rural situations, but due to the low strength, you need to use much greater quantities than concrete for the same application.
- Real danger of depleting soil in heavily populated rural areas.
- Now more than half the people in the world live in urban areas.

- But we need to see if we can continue to reduce the environmental footprint **AND** satisfy the growing demand.
Demand is forecast to rise: to meet the demands of a growing world population
Origins of CO$_2$ emissions in cement production

1 tonne of cement leads to the emission of 650 – 900 kg CO$_2$

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$$
“Chemical CO$_2$”

- Most of the CO$_2$ emission associated with cement production comes form the decomposition of limestone
- This situation is particular to cement
- Alternative energy sources will not help, as with most other industrial processes.
- If we lower this chemical CO$_2$, we will *inevitably* change the *chemistry* of the cement
- And so the way it reacts and performs
- To introduce low carbon solutions, engineers will have to understand and deal with different cement chemistries.
Let's look a bit more at possibilities for low carbon chemistries
The resources of the earth mean we do not have a lot of options!

The composition of the Earth’s Crust limits the possible chemistries. But the limited range mean we can explore all options.
What about the different oxides

- $\text{Na}_2\text{O}$
- $\text{K}_2\text{O}$
- $\text{Fe}_2\text{O}_3$
- $\text{MgO}$

Too soluble

Too low mobility in alkaline solutions

30 year old concrete
Most important system CaO-SiO$_2$-Al$_2$O$_3$
There is no magic bullet solution

- Despite the frequent press articles, there is no magic bullet solution.
- A radically different material will be a niche product with less than 0.1% of the market (e.g., calcium aluminate cements, calcium sulfo aluminates).
- The ability to save 5-10% CO$_2$ on every m$^3$ of concrete is orders of magnitude more important.
- But under the current approach, each small increment of change takes years to reach the field due to large empirical data base which need to be built up.
Possible routes

- New clinker chemistries

- Increasing clinker substitution

- “Clinker free”, alkali activated materials
Other hydraulic minerals

- **SiO₂**
- **CaO**
- **Al₂O₃**

C₃S 74% CaO (proportional to CO₂)
C₂S 65% CaO
CA 35% CaO
C₄A₃S $\equiv$ 37% CaO?

(3CA + C$)

- Here we see real potential to reduce CO₂

BUT, what sources of minerals are there which contain Al₂O₃ >> SiO₂?
Bauxite – localised, under increasing demand for Aluminium production, EXPENSIVE
Most promising approach – reducing the clinker factor

↓ CO₂

Process optimisation

↓ clinker factor

SCMs – Supplementary Cementitious Materials

Clinker + Gypsum → Cement

Limestone + Fly ash + Slag + Natural pozzolan

Often by-products or wastes from other industries
Typical reductions in clinker factor

Source: HOLCIM
Figures from ~2000

- Metakaolin
- Rice husk ash
- Silica fume
- Burnt shale
- Natural pozzolana
- Blast furnace slag
- Fly ash
- Cement
- Limestone

Fly ash: significant volumes with low performance

Used in cement
Reserve
Alkali activated materials (Geopolymers)

- Tried and tested
- Known durability
- Presence of cement adds robustness
- Uses existing technology

**Use in blends**

**Use in alkali activated binder**

- Questionable CO$_2$ reduction
- Non robust behaviour for setting and flow
- Handling strong alkalis on site
- Production of alkali not enough to make significant substitution
- Durability questionable

Components:
- Fly ash
- Slag
- Calcined clays
Portland cement clinker, blended with SCMs is likely to be best solution for sustainable cements for foreseeable future.

Limited supplies of currently widely used SCMs (notably slag and fly ash).

Very alternatives available in quantities comparable to Portland clinker.

For example, collected and not reused waste glass, (subject of much research) estimated only to be 10-20 million tonnes worldwide!

At present each new SCM needs extensive testing to be accepted in standards.

Only material really potentially available in viable quantities is calcined clay.

High Kaolin content clays in great demand, metakaolin about 3 times price of clinker.

Low Kaolin content clays (down to about 40%) also perform well.
Limestone- Alumina synergy

- It is now realised that limestone can react with alumina to form monocarboaluminate (and hemicarbo aluminate)
- In normal Portland cements the extent of reaction is limited (2-3%), but the extra volume of hydrates can explain the optimal strength at 5% addition of limestone (see several publications of Matschei et al).
- With a more rapidly available source of alumina – from metakaolin or calcined clays – this effect becomes much more interesting to allow higher levels of substitution
- Metakaolin “MK” plus limestone
  - \((\text{Al}_2\text{O}_3) : 2\cdot(\text{SiO}_2) + \text{CaCO}_3\)
- Formation of monocarbo aluminate “Mc” (AFm)
  - \(\text{Al}_2\text{O}_3 + \text{CaCO}_3 + \text{Ca}^{2+} + \text{OH}^{-} \Rightarrow \text{C}_4\text{A}_\text{CH}_{11}\)
Coupled addition of calcined clay and limestone

Very promising route to low carbon cements

Cement substitution by a combination of metakaolin and limestone

M. Antoni a,*, J. Rossen a, F. Martirena b, K. Scrivener a

a EPFL STI-IMX—Laboratoires des Matériaux de Construction, Station12, CH-1015 Lausanne, Switzerland
b CIDEM—UCLV, Universidad Las Villas, Santa Clara, Cuba
Compressive strengths

- Combined addition gives better strength than OPC at 7 & 28d for replacement of 45%
- ~90% for 60% addition

Fast synergetic effect between metakaolin and limestone
Promising mechanical results at early age

- Synergetic effect already observed at 3 days
- Higher strength for blended systems from 3 days onwards
Use of low grade clays from lab to field
Pilot production in Cuba, calcination 40% kaolinite clay
Pilot production in Cuba, grinding, 48% clinker, 30% calcined clay 15% limestone, 7% gypsum
Pilot production in Cuba, Hollow concrete blocks

10-11-12 September
Production of 10938 of hollow blocks 500x200x150mm
Pilot production in Cuba, Pre-cast concrete elements

2nd - November
Production of big pre-cast concrete elements of 25 Mpa
CO$_2$ emissions per ton of cement vs relative strength
Potential CO$_2$ emission reduction

- **P-35 BY SIG B-45**: 33.4% reduction
- **PP-25 BY SIG B-45**: 22.2% reduction
- **P-35 BY PP-25**: 14.4% reduction

Emission reduction (Kg CO2/t substituted cement)
Cost vs relative strength

Production cost (dollars/ton of cement) vs Compressive strength variation (%)

- PP-25
- Ref. OPC
- SIG B-45ind_gd
- SIG B45ind
- SIG B45lab
1st International Conference

Calcined Clays for Sustainable Concrete

June 23rd - 25th 2015

The Swiss Tech Convention Center
Durability implications
The basis for user confidence

New developments can only be successful if we can provide the basis in understanding and performance tests for users to have confidence in the many potential solutions.

This can only come (on a reasonable timescale) through:

- A systematic, science-based understanding of cementitious processes and materials at the nanoscale:
- Extended across all the scales involved in cement and concrete production to:
- Provide the multidisciplinary assessment and prediction tools needed to assess the functional and environmental performance of current and new materials.
Generic approach for SCMs
ASR
Durability positive aspects - ASR

- Alumino silicate SCMs are highly effective in controlling ASR
- Alkalinity of pore solution lowered due to absorption of K, Na by C-S-H

- But alumina in the SCMs can also directly inhibit reaction of silicates
There is a clear influence of aluminium ions on aggregates gel formation!
Contribution of SCMs to reducing ASR will be very important in the future to enable use of marginal aggregates.

Understanding relative contribution of silicate and aluminate components important to design optimal concrete.
Chloride ingress
Durability positive aspects - chlorides

- Most SCMs refine pore structure

- This leads to dramatic reductions of diffusion
- Aluminate hydrates can also bind chlorides
Ponding results, 2 years

![Graph showing total chloride content vs depth for PC, MK30, and MK-B45. The graph illustrates the decrease in chloride content with increasing depth for each material.](image)
Durability: Cl Migration test

- SIMCO Procedure, 14d long, 10 V applied:
  Modified version of Rapid Chloride Penetration Test (RCPT) (ASTM C1202 -97 )
  Current and Voltage at surface sample daily monitored
  [Cl\textsuperscript{-}] monitored in downstream solution
  GOAL: Estimate the diffusion coefficient of ionic species in cementitious materials

- Materials: 28 days old mortars, w/b=0.5
  - Heidelberg OPC, MK30, B45
  - B45i-Pontezuela own interground

- Total [Cl\textsuperscript{-}] profile by grinding/acid dissolution in the samples is being investigated too to improve/validate the model
Migration test

PC and B45 mortars (w/c = 0.5, 28 days)

PC Mortar
\[ D_{OH} = 19 \times 10^{-11} \text{ m}^2/\text{s} \]

B45 Mortar
\[ D_{OH} = 1.6 \times 10^{-11} \text{ m}^2/\text{s} \]

12 fold decrease in diffusion rates
However

Carbonation
Reducing calcium content; reduces buffer to carbonation

All CaO content can react with CO$_2$, not just portlandite

CH + CO$_2$ $\rightarrow$ CaCO$_3$ + H$_2$O

C-S-H + CO$_2$ $\rightarrow$ various intermediates $\rightarrow$ CaCO$_3$ + SiO$_2$nH$_2$O + H$_2$O

Aluminate hydrates + CO$_2$ $\rightarrow$ CaCO$_3$ + hydrated alumina

Ferrite hydrates + CO$_2$ $\rightarrow$ CaCO$_3$ + hydrated alumina + iron oxides
Effects more pronounced with poor curing

From BRE via MDA Thomas, UNB
Longer term carbonation,

In long term diffusion of gas through carbonated layer dominates rate

M.D.A. Thomas
Supplementary cementitious materials in Concrete
Is carbonation important?

- Carbonation takes place in environments which are too dry for active corrosion.
- Conversely, conditions with enough humidity for active corrosion will only carbonate very slowly.
- Can be dealt with by correct design and cover depths.
Is this concrete vulnerable to carbonation corrosion
Need to beware of inappropriate “performance” tests
In both cases, all hydrates tend to carbonate, not only portlandite as often assumed.

Only Calcite forms for PC, small amounts of Aragonite and Vaterite additionally form in B45.
All hydrates show again carbonation, to a much larger extent. Anhydrous phases also show partial carbonation.

In PC, mostly calcite forms with carbonation, with small amount of vaterite.

In B45, mostly aragonite forms, then calcite and vaterite,
- Change in carbonated phases, changes in microstructure

- Major factor in long term carbonation is the diffusion of gas through the CARBONATED layer
Sulfate
Sulfate attack

Pure Portland and slag blends have completely different failure mechanism. Conventional expansion tests NOT appropriate for blends.
To master new solutions, we need approaches based on mechanisms.
Coordinated research approach needed for More sustainable cementitious materials

nanocem
Nanoscience for Sustainable Cement and Concrete
THE INDUSTRIAL-ACADEMIC RESEARCH NETWORK ON CEMENT AND CONCRETE

Nanoscience for Sustainable Cement and Concrete

11 Industrial partners
22 Academic partners
# Nanocem Road map

## MAT
### fundamental and analytics

<table>
<thead>
<tr>
<th>AREA</th>
<th>Focus</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mat 1:</strong> PHASE ASSEMBLAGES&lt;br&gt;f (chem, t, T, rH)</td>
<td>Thermodynamics&lt;br&gt;Effect of surfaces&lt;br&gt;Kinetics&lt;br&gt;Arrangements</td>
</tr>
<tr>
<td><strong>Mat 2:</strong> STRUCTURE FORMATION&lt;br&gt;Rheology, admixtures&lt;br&gt;f (chem, t, T, rH) curing and mixing</td>
<td>Surface forces&lt;br&gt;Surface reactions</td>
</tr>
<tr>
<td><strong>Mat 3:</strong> MICROSTRUCTURE /POROSITY&lt;br&gt;Transport processes&lt;br&gt;f (chem, t, T, rH)</td>
<td>Porosity description&lt;br&gt;Water transport&lt;br&gt;Nano/micro &quot;indicators&quot;</td>
</tr>
</tbody>
</table>

## PEA
### Performance assessment

<table>
<thead>
<tr>
<th>AREA</th>
<th>Focus</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PEA 0:</strong> Rheology</td>
<td>Paste to concrete&lt;br&gt;Segregation&lt;br&gt;Robustness</td>
</tr>
<tr>
<td><strong>PEA 1:</strong> Mechanical /structural</td>
<td>Setting, Strength, creep, Shrinkage, cracking</td>
</tr>
<tr>
<td><strong>PEA 2:</strong> Protection of reinforcement</td>
<td>Chloride (CP8): take binding into account&lt;br&gt;Passivation and corrosion rate&lt;br&gt;Carbonation</td>
</tr>
<tr>
<td><strong>PEA 3:</strong> Other attacks</td>
<td>Freeze / thaw and scaling&lt;br&gt;“sulfate” + other ions&lt;br&gt;Crystallisation pressure&lt;br&gt;Long term dimensional stability&lt;br&gt;Expansion</td>
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<tr>
<td><strong>PEA 4:</strong> Service life modelling</td>
<td>Realistic service conditions</td>
</tr>
<tr>
<td><strong>PEA 5:</strong> Impact on environment</td>
<td>Leaching impact on Environment</td>
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</table>
10th Anniversary OPEN MEETING
Tuesday, April 8, 2014
9:30 – 16:00
Lausanne, Switzerland

First announcement
http://www.nanocem.org
Key messages

- Portland cement already has low environmental impact, challenging to improve further
- Blending with SCM is the most viable option
- Problem is limited supplies of well established SCMs
- Calcined clays (with limestone) can be next step forward
- Range of materials will become more diverse - Local
- More sustainable use of concrete requires better understanding of mechanisms
- Danger in “performance” test designed for Portland cement
- To progress we need a co-ordinated effort between industry and the academia.
Thank you
Questions
Acknowledgements

LMC, EPFL and friends