HOW TO MAKE CEMENTS AND CONCRETES WITH LOWER CO$_2$ EMISSIONS

Ellis GARTNER, Lafarge Central Research, France
<table>
<thead>
<tr>
<th>Material</th>
<th>Consumption (Mt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEMENT</td>
<td>2740</td>
</tr>
<tr>
<td>CONCRETE:</td>
<td>≈ 25000</td>
</tr>
<tr>
<td>GYPSUM PRODUCTS:</td>
<td>≈ 130</td>
</tr>
<tr>
<td>TIMBER:</td>
<td>≈ 3200</td>
</tr>
<tr>
<td>STEEL:</td>
<td>1350</td>
</tr>
<tr>
<td>ALUMINUM:</td>
<td>32</td>
</tr>
<tr>
<td>FIRED CLAY PRODUCTS:</td>
<td>&gt; 400</td>
</tr>
<tr>
<td>PLASTICS:</td>
<td>120</td>
</tr>
<tr>
<td>GLASS:</td>
<td>≈ 100</td>
</tr>
</tbody>
</table>

*Approximate worldwide annual materials consumption (these numbers are only very rough estimates in some cases)*

- The Earth’s sustainable limit is ≈ 2500 Mt
- Of this, < 1000 Mt is used in construction and ≈ 300 Mt for paper and cardboard
- Of this, ≈ 600 Mt is used in construction, about 500 Mt of it for concrete reinforcement
## Approximate Embodied Energies


<table>
<thead>
<tr>
<th>Material</th>
<th>Embodied Energy: GJ/t</th>
<th>GJ/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aggregates (sand, stone, gravel)</td>
<td>0.02-0.10</td>
<td>-</td>
</tr>
<tr>
<td>Cut stone (local)</td>
<td>0.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Asphalt paving</td>
<td>3.4</td>
<td>7.1</td>
</tr>
<tr>
<td>Fiber-cement board</td>
<td>9.5</td>
<td>13.6</td>
</tr>
<tr>
<td>Concrete tiles, blocks, bricks, pavers</td>
<td>0.8-1.2</td>
<td>1.5-3.0</td>
</tr>
<tr>
<td>GRC boards</td>
<td>7.6</td>
<td>14.8</td>
</tr>
<tr>
<td>Average pre-cast concrete elements</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Ready mix concrete, 17.5 MPa</td>
<td>1.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Ready mix concrete, 40 MPa</td>
<td>1.6</td>
<td>3.9</td>
</tr>
<tr>
<td>Adobe blocks, (straw stabilized)</td>
<td>0.47</td>
<td>0.75</td>
</tr>
<tr>
<td>Rammed soil cement (<em>e.g.</em> blocks)</td>
<td>0.8</td>
<td>(≈2)</td>
</tr>
<tr>
<td>Ordinary fired clay bricks and tiles</td>
<td>2.5</td>
<td>5.2</td>
</tr>
<tr>
<td>Glazed clay bricks and tiles</td>
<td>7.2</td>
<td>14.8</td>
</tr>
<tr>
<td>Float glass and laminated glass</td>
<td>15.9-16.3</td>
<td>40-41</td>
</tr>
<tr>
<td>Plasterboard</td>
<td>6.1</td>
<td>5.9</td>
</tr>
<tr>
<td>High-density polyethylene</td>
<td>103</td>
<td>97</td>
</tr>
<tr>
<td>Expanded polystyrene board</td>
<td>117</td>
<td>2.3</td>
</tr>
<tr>
<td>Paper products</td>
<td>12-36</td>
<td>-</td>
</tr>
<tr>
<td>Softwood timber, rough-sawn, air-dried</td>
<td>0.3</td>
<td>0.17</td>
</tr>
<tr>
<td>&quot; &quot; &quot; &quot; &quot; &quot; kiln-dried</td>
<td>1.6</td>
<td>0.88</td>
</tr>
<tr>
<td>MDF (<em>medium-density fiberboard</em>)</td>
<td>11.9</td>
<td>8.3</td>
</tr>
<tr>
<td>Steel (general)</td>
<td>32-35</td>
<td>250-275</td>
</tr>
<tr>
<td>Steel (recycled)</td>
<td>9-13</td>
<td>70-100</td>
</tr>
<tr>
<td>Aluminum (virgin) products</td>
<td>191-227</td>
<td>516-613</td>
</tr>
<tr>
<td>Aluminum (recycled) products</td>
<td>8-43</td>
<td>22-116</td>
</tr>
</tbody>
</table>
Selected Estimates of “Embodied CO$_2$”:

CO$_2$ emission per unit of gross heating value vary with the type of fuel: Natural gas gives only 55 kg/GJ, fuel oils give over 70 kg/GJ, whereas coals and cokes mostly fall in the range 90 - 110 kg/GJ

Using the conservative assumption that the main fuel is coal/coke, we have an average value of 100 kg/GJ. Adding the raw-materials CO$_2$ emissions for cement manufacture, I estimate the following values:

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

Mild steel: $\approx 3000$ kg/t, or $\approx 25000$ kg/m$^3$

(∴ “global average concrete with associated steel” $\approx 500-800$ kg/m$^3$)

Clay bricks and tiles: $\approx 250-720$ kg/t or $\approx 520-1480$ kg/m$^3$

Typical processed wood products: $\approx 800-1200$ kg/t or $\approx 800-1500$ kg/m$^3$

Lightweight expanded polystyrene: $\approx 230$ kg/m$^3$
Portland Cement – the basics:

- Finely ground homogenised mixture of raw materials (limestone, clay, etc.,) heated to >1400°C in rotary kiln to form nodules of “clinker”: typically, ≈80% basic calcium silicates, plus ≈20% calcium aluminates and ferrites as “fluxing” phases.

- Cooled clinker is ground to fine powder with ≈5% gypsum to make “pure” Portland Cement. But most modern cements also contain other ingredients known as “supplementary cementitious materials” (SCMs) to reduce cost, energy requirements and CO₂ emissions.

- Portland cements harden when mixed with water because of hydration reactions that form mainly calcium silicate hydrates (C-S-H).

- SCMs vary in hydraulic reactivity and thus in their ability to substitute for PC clinker. The most effective are blast-furnace slags but their global supply is very limited. Coal fly ashes can be used but are less reactive. Other materials such as some limestones and volcanic rocks can be used but are even less reactive so substitution levels are lower.
Simplified Portland Cement Chemistry

Tricalcium silicate is the major component (>60%) of a modern PC clinker. It is produced by reaction of limestone and silica at >1300°C:

$$3\text{CaCO}_3 + \text{SiO}_2 \Rightarrow \text{Ca}_3\text{SiO}_5 ("\text{C}_3\text{S}\") + 3\text{CO}_2$$

Other major phases: $\text{Ca}_2\text{SiO}_4 (\text{C}_2\text{S})$; $\text{Ca}_3\text{Al}_2\text{O}_6 (\text{C}_3\text{A})$; $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10} (\text{C}_4\text{AF})$

The CO$_2$ emissions associated with decarbonation of limestone are referred to as “raw materials” (RM) CO$_2$ emissions, to distinguish them from the CO$_2$ emissions derived from fuel combustion (FD). For an energy-efficient modern kiln, RM CO$_2 \approx 60\%$, FD CO$_2 \approx 40\%$.

Hydration of tri- and di-calcium silicates is mainly responsible for the binding power of cement and also gives “portlandite” which maintains the high pH necessary to prevent corrosion of steel in concrete:

$$(\text{C}_3\text{S}, \text{C}_2\text{S}) + \text{H}_2\text{O} \Rightarrow "\text{C-S-H}" + \text{Ca(OH)}_2 \text{ (portlandite)}$$

The main binding phase in concrete, “C-S-H”, is an amorphous “gel”.

Ellis Gartner, ECI CO2 Summit, Vail, June 2010
Schematic illustration of a modern precalciner kiln

- Raw feed
- Calciner vessel
- Back-end fuel
- Tertiary Air duct
- Clinker cooler
- Clinker

Feed drying, + filters

Ellis Gartner, ECI CO2 Summit, Vail, June 2010
Theoretical Enthalpy Balance for OPC Manufacture

(*note: the best modern kilns require ≈ 2.8 GJ/t*)

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)

<table>
<thead>
<tr>
<th>Kiln section</th>
<th>Temperature range</th>
<th>Process</th>
<th>Enthalpy required, kJ/g (GJ/t) of clinker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preheater</td>
<td>20 – 900°C</td>
<td>heating raw feed to 900°C</td>
<td>+1.53</td>
</tr>
<tr>
<td></td>
<td>“ about 450°C</td>
<td>dehydration of clays</td>
<td>+0.17, +1.11</td>
</tr>
<tr>
<td></td>
<td>“ 20 – 900°C</td>
<td>cooling of CO₂ and H₂O (gases)</td>
<td>- 0.59</td>
</tr>
<tr>
<td>Calciner</td>
<td>about 900°C</td>
<td>CaCO₃ ⇒ CaO + CO₂</td>
<td>+1.99, +1.95</td>
</tr>
<tr>
<td></td>
<td>“ about 900°C</td>
<td>reactions of dehydrated clays</td>
<td>- 0.04</td>
</tr>
<tr>
<td>Rotary Kiln</td>
<td>900 – 1400°C</td>
<td>heating feed from 900 to 1400°C</td>
<td>+0.52, +0.21</td>
</tr>
<tr>
<td></td>
<td>“ 900 – 1400°C</td>
<td>formation of clinker phases</td>
<td>- 0.31</td>
</tr>
<tr>
<td>Clinker cooler</td>
<td>1400 – 20°C</td>
<td>cooling of clinker to 20°C</td>
<td>- 1.51, -1.51</td>
</tr>
</tbody>
</table>

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**Net heat required:** +1.76
Typical ball mill used to grind clinker to make cement (usually run in closed circuit with an air separator)

Power consumption 35-40 kWh/t to produce cement of 340 m²/kg. A mill with a power of 10 MW produces 250-286 t/hr of cement.
Electrical energy use in cement manufacture cannot be neglected:

- Portland Cement manufacture usually requires about 100kWh of electrical energy per tonne of product. Almost half of this is used in the fine grinding of clinker (and other components) to make the cement. Some supplementary cementitious materials (e.g. granulated slags) require even more energy for fine grinding than PC clinker.

- $100\text{kWh/t} = 0.36\text{GJ(e)/t} \approx 1\text{GJ/t}$ primary fuel equivalent. For coal-derived electricity, $1\text{kWh} \approx 1\text{kg CO}_2$; thus, typically about 100kg of $\text{CO}_2$ are emitted from the production of the electricity required to make one tonne of cement. This is over 10% of the total emitted $\text{CO}_2$.

- Evidently, purely electrical processes for clinker manufacture cannot be considered seriously unless it can be guaranteed that the electricity would be obtained mainly from non-fossil energy sources.
The importance of raw materials choice in determining RM-derived CO$_2$ emissions:

**Conventional portland cement manufacture:**

\[
3\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{Ca}_3\text{SiO}_5 + 3\text{CO}_2
\]

\[
300 \quad 60 \quad (>1300 \degree \text{C}) \quad 228 \quad 132 \quad \text{(mass units)}
\]

limestone + silica \(\Rightarrow\) C$_3$S (cement) + carbon dioxide

**The ‘cement-sulfuric acid’ process:**

\[
3\text{CaSO}_4 + \text{SiO}_2 + 3\text{H}_2\text{O} \rightarrow \text{Ca}_3\text{SiO}_5 + 3\text{H}_2\text{SO}_4
\]

\[
408 \quad 60 \quad 54 \quad (>1300 \degree \text{C}) \quad 228 \quad 294
\]

anhydrite + silica + steam \(\Rightarrow\) C$_3$S(cement) + sulfuric acid
If we want to replace Portland Cement with a new binder, we will have to base it on very abundant raw materials!

Proportions of the principal elements in the Earth’s crust:

- Oxygen
- Silicon
- Aluminium
- Iron
- Calcium
- Sodium
- Potassium
- Magnesium
- rest

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

- **Based on their terrestrial abundance, we can consider the following:**
  - Limestones and dolomites (abundant and widespread)
  - Quartz (abundant and widespread)
  - Hydrous aluminosilicates (e.g. clays) - (abundant and widespread)
  - Basic aluminosilicate rocks (e.g. feldspars) - (abundant and widespread)
  - Ultra-mafic rocks (e.g. peridotites) (abundant but localized)
  - Amorphous volcanic rocks (e.g. tuffs, pumices) (abundant but localized)
  - Iron ores (abundant but localized)
  - Coal (containing sulfur and aluminosilicates) (abundant but localized)

- **Pure calcium sulfates, sodium carbonates, bauxites, magnesites and phosphate ores are not sufficiently abundant or widespread to serve as the major ingredients in cement manufacture**
Raw Materials CO$_2$ per unit mass and volume for the major cement compounds of interest

<table>
<thead>
<tr>
<th>Cement Compound</th>
<th>Raw Materials</th>
<th>RM CO$_2$ in g/g</th>
<th>RM CO$_2$ in g/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>M (magnesia, periclase)</td>
<td>magnesite</td>
<td>1.092</td>
<td>3.91</td>
</tr>
<tr>
<td>C (calcia, quicklime)</td>
<td>limestone</td>
<td>0.785</td>
<td>2.63</td>
</tr>
<tr>
<td>C$_3$S (alite)</td>
<td>limestone + quartz</td>
<td>0.578</td>
<td>1.80</td>
</tr>
<tr>
<td>$\beta$-C$_2$S (belite)</td>
<td>limestone + quartz</td>
<td>0.511</td>
<td>1.70</td>
</tr>
<tr>
<td>C$_3$A (tricalcium aluminate)</td>
<td>limestone + alumina</td>
<td>0.489</td>
<td>1.50</td>
</tr>
<tr>
<td>C$_4$AF (calcium aluminoferite)</td>
<td>as above + iron oxide</td>
<td>0.362</td>
<td>1.29</td>
</tr>
<tr>
<td>NS (sodium metasilicate)</td>
<td>soda + quartz</td>
<td>0.361</td>
<td>-</td>
</tr>
<tr>
<td>CA (monocalcium aluminate)</td>
<td>limestone + bauxite</td>
<td>0.279</td>
<td>0.83</td>
</tr>
<tr>
<td>C$_4$A$_3$S (calcium sulfoaluminate)</td>
<td>as above + anhydrite</td>
<td>0.216</td>
<td>0.56</td>
</tr>
</tbody>
</table>
Generic technical and scientific problems to be addressed for concretes made with new binders:

1. Prediction of concrete service lifetimes (esp. reinforced concrete)
   - Should concrete still be considered to be a cheap “anti-corrosion paint” for steel?
   - Are there any realistic alternatives to mild steel reinforcement?

2. Control of fresh concrete properties and early-age curing procedures
   - Setting times and rates of strength development are critical for many applications. New binders might be very different to Portland cements in this respect.

3. Variability of raw materials (especially critical for high-SCM systems)
   - 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 equipped to do it?
   - Industrial by-products are inherently variable and sources are highly localised
   - New standards will be needed and may vary widely with location.

4. Recycling issues
   - Could alternative binder systems make recycling easier?
   - Concrete recycling could help reduce life-time CO₂ emissions
Currently proposed alternatives to PC-based binders

The following systems are currently being investigated by various groups:

1. Reactive aluminosilicates activated by lime and/or alkalis
   - e.g. HVFAC (high-volume fly ash cements), and “Geopolymers”

2. Systems based on MgO hydration and carbonation

3. Systems based on re-precipitation of calcium and magnesium carbonates

4. Systems based on calcium aluminates + silicates with higher A/S than PC

In all of the above systems the raw materials are sufficiently abundant to be of global interest, but the practical performance and manufacturing costs are not yet known in detail.
Activated aluminosilicate binders

- This category extends all the way from fairly standard portland-pozzolan blended cements to pure alkali-activated aluminosilicates.
- The attraction is the ability to use readily-available resources of either man-made by-products (especially fly ashes) or natural pozzolans.
- Insofar as these materials are available locally in a dry state, they can be considered to have low associated energy and CO\(_2\) costs.
- Alkaline activators (R\(_2\)O) might help reduce overall CO\(_2\) emissions if:
  1. One mole of R\(_2\)O replaces several moles of CaO in the products
  2. The R\(_2\)O can be obtained at a reasonably low energy and CO\(_2\) cost
- The calcium source does not have to be PC clinker or lime.
  - It can be slag – but unused slag resources are very limited.
  - It can be gypsum, but then the alkali source must provide all the alkalinity.
Generalized “Geopolymerization”

“Geopolymer” is a trademark copyrighted by J. Davidovits. The term has no generally-accepted scientific meaning but is nonetheless widely used!

We can define “geopolymerization” by the following generalized reaction between a pozzolan and an alkali (silicate) solution:

\[
A_xS_y + RS_z + nH \rightarrow RA_xS_{(y+z)}H_n
\]

The value of \(z\) can vary from zero (pure alkali hydroxide) to over 2 (water glass). It is not clear what the optimum value of \(z\) may be for any given property, or why. However, there is good evidence that \(x = 1\) and \(n\) is small, probably < 1.
Are alkali-activated cements a practical alternative?

- Alkali activators are usually either NaOH (manufactured via the electrolysis of NaCl solutions in the “chlor-alkali” process), or sodium silicates (usually made by melting soda + silica in a glass furnaces.

- Both of these process are capital- and energy-intensive, and the CO$_2$ emissions per mole of R$_2$O are greater than for CaO (in PC or lime).

- Major global manufacturing capacity increases would be needed if significant volumes of alkali-activated binders were to be used worldwide.

- The bulk of the binder (>80%) is typically a mixture of pozzolans and calcium sources (slags, clinker, gypsum, etc.). The reactions are complex and raw materials quality control will be a major issue. The durabilities of AAC products are also not yet well established.

- It is not certain that sufficient volumes of pozzolan will be available at an acceptable cost. Manufacture of artificial pozzolans specifically for cement uses could be energy-intensive (e.g. calcination of clays.)
MgO-based binders

- MgO-based binders have been used for many years in the form of “Sorel Cements,” based on the formation of hydrated basic magnesium chlorides or sulfates. But these binders have limited applications due to high raw materials costs and poor water-resistance in use.
  - They behave like stronger (but more expensive) gypsum plasters

- More recently it has emerged that very reactive MgO (usually produced by low-temperature calcination of MgCO$_3$) can act as an hydraulic binder on its own, and can be strengthened further by carbonation:
  - MgO + H$_2$O $\Rightarrow$ Mg(OH)$_2$ ; Mg(OH)$_2$ + CO$_2$ $\Rightarrow$ MgCO$_3$.$n$H$_2$O, etc.
  - Atmospheric carbonation of Mg(OH)$_2$ is normally slow, but some MgCO$_3$ can also be included in the initial cement mixture.
Are MgO-based binders a practical alternative?

- Conventional methods for producing MgO (decarbonation of magnesite rock or treatment of seawater or Mg-rich brines with lime followed by calcination) are too expensive and emit too much CO₂.

- It has been suggested that it may be possible to extract MgO at a low cost (both in energy and CO₂) from common basic magnesium silicate rocks such as olivine or serpentine. If true, this would be a significant breakthrough in accelerating the natural weathering processes by which basic rocks slowly absorb atmospheric CO₂, e.g.:

\[
\text{Mg}_2\text{SiO}_4 + 4\text{CO}_2 \Rightarrow 2\text{Mg}^{++} + 4\text{HCO}_3^- + \text{SiO}_2 \downarrow \Rightarrow 2\text{MgCO}_3\downarrow + 2\text{CO}_2 \uparrow
\]

- Even if the overall CO₂ balance of the above process is negative in the long term (as claimed by some), there is as yet no proof that the resulting MgO-based binders will give suitable performance for all construction applications in which Portland-based cements are used. There is also the issue of what to do with the by-products (e.g. SiO₂).
Alkaline Earth Carbonate-based binders

- It is known that amorphous calcium carbonates can be precipitated from highly supersaturated solutions and stabilized by certain cations (e.g. Mg$^{2+}$). More recently, it has been shown that these amorphous phases can be used as hydraulic cements (see Combes et al, Biomaterials, 2006):

\[
\text{CaCO}_3 \text{ (amorph)} \Rightarrow (\text{aq. soln + nuclei}) \Rightarrow \text{CaCO}_3 \text{ (calcite or aragonite)}
\]

*Note: these appear to be hydraulic cements without hydration!*

- While such cements may have useful biological applications (e.g. bone cements), the manufacturing processes seem too expensive and the product performance too poor for construction applications. Of course, this situation could change if better manufacturing processes could be developed and if the strengths of the hardened products could be increased. However, such cements are essentially pH-neutral and would not be expected to protect reinforcing steel, so they would probably not be of much use for conventional reinforced concretes.
Calcium sulfoaluminate-based cements

- Manufacture of clinkers based on calcium sulfoaluminate ($C_4A_3$) plus belite and other phases (e.g. ferrites) looks promising.
  - Unlike CAC, CSA clinkers can be made in existing OPC plants.
  - China has already developed norms for this type of cement (TCS).
  - Raw materials costs are usually much higher than for OPC in most locations, but certain compositions may become cost-competitive once projected CO$_2$ emissions costs have been factored in.
  - 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.
Lafarge’s novel Belite-CSA-Ferrite (BCSAF) cements:

- BCSAF clinkers can be used to make cements in the usual way, by intergrinding with gypsum, anhydrite, and various 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 $\text{C}_4\text{Al}_3$ (ye´elimite) phase.

- $\text{CO}_2$ reductions of the order of 25% for concretes of equivalent performance seem feasible – (see report by K. Quillin, BRE, 2007)
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 be able to significantly reduce global CO$_2$ emissions from concrete manufacture, ‘Low CO$_2$’ binders must be developed that:
  - Can produce concretes with appropriate physical and durability properties
  - Will be based on locally-available raw materials (since transportation energy costs can be high).

- Development of new materials standards and construction codes will be needed, and the materials users will have to be re-educated!

- Cements based on CSA plus belite, ferrites and calcium sulfates appear to be a promising medium-term option. Preliminary concrete tests have shown promising strength and durability results.

- Another promising binder class currently under development is alkali-activated aluminosilicate binders; but these systems are very complex and variable. It is not yet clear what might be the sources of raw material and CO$_2$ savings for such binders on a global basis.

- More speculative long-term possibilities include binders based on MgO extracted from basic rocks, and binders based on calcium or magnesium carbonates; but few reliable data are yet available.