LOW CARBON CEMENTS AND CONCRETES IN MODERN CONSTRUCTION

A John W Harrison
Managing Director TecEco Pty. Ltd. and private researcher.

ABSTRACT: A multidisciplinary analysis and review of low carbon cements and concrete is provided. Options are set out in a table and explained in the context of a wide range of disciplines and concepts.

The paper takes a lateral thinking approach and calls for a change in mindset, teaching methods and the way standards are written so that the business model of cost cutting prevalent in the industry can change. It finds that significant de-carbonation will result not so much by changing the chemistry of existing cements or by developing new ones but by focussing on properties affecting lifetime energies and making CO₂ and other wastes resources to manufacture synthetic carbonate aggregates and introducing carbon capture during manufacture or Portland and other hydraulic cements.

Keywords: Aggregate, Business models, Carbon capture, Cement, Concrete, De-carbonation, Gaia Engineering, Industrial ecology, Limestone, N-Mg Process, Nesquehonite, Reactive magnesia, Sustainability, Synthetic carbonate, Waste utilisation.

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INTRODUCTION

There are some significant problems facing humanity including climate change, ocean acidity and food shortages, land degradation and water pollution by wastes. At the 2007 “Driving CO2 Reduction” National Conference held in Melbourne on 13 & 14 September 2007 M K Singh stood up and said “I want the cement industry to be the saviour of the world”. Concrete can be and those in the industry who take on this challenge will succeed. We must however think outside the square and develop new technical paradigms1.

Cement production was 3.4 billion tonnes in 2011 and the concrete produced with it roughly 28 billion tonnes. The annual carbon emissions from the cement in this huge material flow amount to roughly 2.9 billion tonnes of carbon dioxide, or 8.8%2 of total anthropogenic carbon emissions making cement a significant source of emissions. If other associated supply chain releases are included, significantly more.

China and India between them are now consuming 40 times more cement and concrete than the USA. India currently produces around 210 million tonnes of cement, second to China at around 2 billion tonnes (25).

There is a solution to global warming, salinity and many other global problems and it is potentially very profitable. TecEco Gaia Engineering utilises the huge flow of concrete to create an enormous CO2 sink and I will explain this as I go through the options and issues for cement and concrete in modern construction.

According to the British Research Establishment (BRE) we cannot address de-carbonation without changing the composition of cement and fuel derived emissions will diminish slowly for purely economic reasons (19). Papers describing numerous different binder formulations abound and I have written some of them.

![Figure 1 - Predicted Global Cement Demand and Emissions (19)](image)

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1 The technology paradigm defines what is or is not a resource.

2 The Chinese government (16) estimate that 861 kg (net) of CO2 are emitted for every tonne of Portland cement clinker produced. The production of 3.4 billion tonnes cement would results in emissions of 2.9 billion tonnes CO2. Global emissions are around 33 billion tonnes (17) so the current contribution of cement production globally as 2.9/33 x 100%, or 8.8%.
The BRE are applying the wrong emphasis. The composition of cement does not have change so much as the composition of concrete. Cement is only around 10% of concrete. The use of a high proportion of SCM’s coupled with synthetic carbonate aggregates made from flue CO2 and waste magnesium ions and other materials effecting properties\(^3\) would make concrete made with any hydraulic cement currently associated with emissions a very green material with net sequestration.

Mehta summarised some of the techniques used by architects for dematerialisation (15) but did not consider the effect of dematerialisation on lifetime or operational energies and TecEco have realised the potential of carbon capture during manufacture.

\[\text{Figure 2 - Mehta's Triangle (15)}\]

These and other alternatives are summarised with reference to Table 1 that follows. I then address the options, dealing with those that have been dealt with in the literature adequately more briefly than others that have not.

\(^3\) The inclusion of additions that introduce properties such as thermal capacity and lower heat transfer rates have significant scope to reduce lifetime or operational energies. Many of these additions can be sourced from waste streams.
<table>
<thead>
<tr>
<th>Option</th>
<th>Description</th>
<th>Players</th>
<th>Drivers</th>
<th>Barriers</th>
<th>Standards &amp; Guides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alternative Binders</td>
<td>Numerous and described in Table 2 - Future Binder Contenders with Differentiated Supply Chain Options</td>
<td>Scientists</td>
<td>Sustainability and profit.</td>
<td>Conservatism, out dated software. Prescription standards and approvals systems (see <a href="http://www.tececo.com/sustainability.permissions_rewards.php">http://www.tececo.com/sustainability.permissions_rewards.php</a>)</td>
<td>A few guides and draft standards (e.g. with Geopolymers)</td>
</tr>
<tr>
<td>CO₂ Capture during Manufacture</td>
<td>Reduce process emissions. Cements that involve calcination can be made without releases.</td>
<td>Scientists, TecEco and Calix.</td>
<td>Sustainability, carbon taxes.</td>
<td>Inability to think laterally. Fear of change</td>
<td>Common sense!</td>
</tr>
<tr>
<td>Replacement of Portland cement by Limestone</td>
<td>Blending with Limestone with cement to reduce net emissions has met with some success and is now incorporated into many standards. There are however issues.</td>
<td>Cement technologists</td>
<td>Economic cost/benefit, sustainability, Leed, GBC, r &amp; d &amp; procurement Policies.</td>
<td>Buyer hesitancy.</td>
<td>New standards emerging because industry driven.</td>
</tr>
<tr>
<td>Event</td>
<td>Description</td>
<td>Stakeholders</td>
<td>Challenges</td>
<td>Solutions</td>
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<td>------------------------------------------------------------------------------------------------------</td>
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<tr>
<td>Replacement of cement by SCM’s</td>
<td>Blended cements that contain a high volume of replacement materials (SCM’s) such as fly ash, slag cement (gbfs), pozzolans, silica fume, rice husk ash etc. High replacement cement concretes often have improved properties such as rheology, less shrinkage, greater durability etc. The use of reactive MgO makes the use of higher proportions of SCM’s possible.</td>
<td>Cement technologists</td>
<td>Economic cost/benefit, sustainability, Leed, GBC, r &amp; d &amp; procurement Policies.</td>
<td>Conservatism, out dated software. Prescription standards and approvals systems (see <a href="http://www.tececo.com/sustainability.permissions_rewards.php">http://www.tececo.com/sustainability.permissions_rewards.php</a>)</td>
<td>Mix design methods. LCA &amp; LCCA. New better software.</td>
</tr>
<tr>
<td>Product Differentiation and Specialisation</td>
<td>Mineral composites other than concrete with just stone aggregate can improve sustainability. E.g. composites with a high “R” value</td>
<td>Materials scientists</td>
<td>Economic cost/benefit</td>
<td>Inability to think outside the box. Fear of change</td>
<td>Standards, LCA &amp; LCCA</td>
</tr>
<tr>
<td><strong>Changing the emphasis</strong></td>
<td><strong>An emphasis other than on the binder to improve sustainability. E.g. Use of synthetic carbonate aggregate. A greater focus on properties having a high impact on lifetime energies.</strong></td>
<td><strong>Scientists</strong></td>
<td><strong>Sustainability, economic cost/benefit. Technical merit</strong></td>
<td><strong>Inability to think outside the box. Fear of change. Technical issues (?).</strong></td>
<td><strong>Common sense!</strong></td>
</tr>
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<td>--------------------------</td>
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<td>--------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------</td>
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</tr>
<tr>
<td><strong>The Right Business Model</strong></td>
<td><strong>Although not a technical matter the right business model is essential for progress to be made.</strong></td>
<td><strong>Consultants</strong></td>
<td><strong>Profitability in a changing business environment</strong></td>
<td><strong>Conservatism, standards and legislative environment.</strong></td>
<td></td>
</tr>
<tr>
<td><strong>The Right Framework to Operate in</strong></td>
<td><strong>Legislative restrictions and standards throughout the world are prescriptive in nature and this and a lack of training is holding back innovation. There is a strong need to throw away dogma for what it is and get back to science.</strong></td>
<td><strong>Scientists and Consultants</strong></td>
<td><strong>The need to change</strong></td>
<td><strong>Conservatism, inability or unwillingness to change.</strong></td>
<td></td>
</tr>
</tbody>
</table>
ALTERNATIVE BINDERS

There are a large number of alternative binders and many options to improve the energy and emissions associated with their manufacture. Given necessary brevity and the fact that they have been dealt with extensively by others most of them are presented as Table 2 - Future Binder Contenders with Differentiated Supply Chain Options on the next page. Data on production emissions with and without capture in most cases is included.

Noticeably the hydraulic cement group dominated by Portland cement is the largest and there are many variants providing high early strength, sulphate resistance etc. Many of the new cements are variants of a Portland cement theme.

Hydraulic Cements

There is significant potential for carbon capture with cements made with a calcination step such as most if not all hydraulic compositions. This potential is covered in more detail under the heading ALTERNATIVE MANUFACTURING PROCESSES on page 15.

Slag-lime or slag – Portland Cement (PC) cements. Slag is made from ground granulated blast furnace slag (GBFS) which is a waste and latently hydraulic. It can be used with activators such as Portland cement (PC), lime and/or reactive magnesia (according to our patents) to make a cement.

Calcium sulfoaluminate cements \& belite calcium sulfoaluminate cements are low energy cements that can be made from industrial by products such as low calcium (class F) flyash and sulphur rich wastes. The main hydration product producing strength is ettringite. Their use has been pioneered in China and more recently in the UK.

Calcium aluminate cements are hydraulic cements made from limestone and bauxite. The main components are monocalcium aluminate CaAl_2O_4 (CA) and mayenite Ca_{12}Al_{14}O_{33} (C12A7) which hydrate to give strength. Calcium aluminate cements are chemically resistant and stable to quite high temperatures.

Belite cements can be made at a lower temperature and contains less lime than Portland cement and therefore has much lower embodied energy and emissions. Cements containing predominantly belite are slower to set but otherwise have satisfactory properties. Many early Portland type cements such as Rosendale cement were rich in belite phases. (See http://www.tececo.com/links.cement_rosendale.php.)

Reactive magnesia blended with other hydraulic cements and Supplementary Cementitious Materials (SCM’s) Reactive magnesia (rMgO) is a powerful new tool in

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4 We include for convenience GBFS in our definition of hydraulic cements in our patents in most countries and claim the right to reMgO GBFS mixes. Beware of infringements. We do not think reactive magnesia (rMgO) a good activator but it is an excellent additive and facilitates more rapid dissolution

5 The NRMCA’s CIP 30 – Supplementary Cementitious Materials includes pozzolans which by themselves do not have any cementitious properties and other materials such as ground blast furnace slag that do.
hydraulic cement blends. 15-30% improvement in compressive strength and greater improvements in tensile strength, much faster setting, better rheology and less shrinkage and cracking, less bleeding and long term durability have been demonstrated with 50 % replacement and more of PC by flyash and GBFS. We believe autogenous shrinkage has been solved.7

rMgO is an ideal additive as it aids the dissolution of SCM’s and contributes positively to many other properties (See REPLACEMENT OF CEMENT BY SCM’S on page 20.) 7

Chemical Cements

Magnesium Phosphate Cements are chemical cements that rely on the precipitation of insoluble magnesium phosphate from a mix of magnesium oxide and a soluble phosphate. They include some of the oldest binders known8 and are potentially very green if the magnesium oxide used is made with no releases or via the nesquehonite (N-Mg route) which is part of the TecEco Gaia Engineering solution (See ALTERNATIVE MANUFACTURING PROCESSES on page 15). It would also be good if a way is found to utilise waste phosphate from feedlots9.

Carbonating Cements

Reactive Magnesia Based Carbonating Binders can, like lime, be used for full thermodynamic cycle binders such as carbonating mortars. Reactive Magnesia (rMgO) has the advantage of also taking on water of crystallisation so the solid produced for input mass ratio is higher than for lime based carbonating binders. rMgO can also be made without releases10.

Lime Based Carbonating Binders can, like magnesia, be used for full thermodynamic cycle binders such as carbonating mortars. As water of crystallisation is not also taken up, the solid produced to input mass ratio is lower than for magnesium based carbonating binders which is a disadvantage.

Other Cements

Geopolymers are potentially very green but suffer from a number of fundamental flaws that will restrict their use and increase risk outside factory environments where they are currently being mainly used. They suffer from the nanoporosity durability flaw and the fact that water is not consumed in their setting with the result that making them fluid enough for easy placement is difficult.

6 The magnesia must be reactive and be wary of imitations that are not

7 Much more detailed information is available in the TecEco web site in the downloads area.

8 Dung + MgO in ancient Indian stupas.

9 Thereby solving an environmental pollution problem.

10 See under the heading ALTERNATIVE MANUFACTURING PROCESSES on page 14.
Because geopolymers are nanoporous soluble aggressive agents can get into them and attack aggregates. What makes them risky to use is the variability of results obtained. The problem is that the amount of water added is critical - too much and they are insufficiently alkaline or too little and they cannot be placed. Getting over these problems has been the main area for research and some success has been achieved as geopolymer premix concretes are commercially available as at the time of writing in Australia for non-structural applications.

Sialites are a neologism for rocks made in a manner mimicking natural rock forming processes.\(^{11}\) The technology is not new as it has been known by some for years how to solidify some fly ashes\(^{12}\) for example.

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\(^{11}\) The name Sialite is attributable to Dr Henghu Sun and others of the Pacific Resources Research Center in California, in collaboration with Tsinghua University in Beijing; see (24) for a description.

\(^{12}\) depending on the composition
<table>
<thead>
<tr>
<th>Cements Based on</th>
<th>Process</th>
<th>Process CO₂ (tonnes CO₂ / tonne output)</th>
<th>Decarbonation CO₂ (tonnes CO₂ / tonne output)</th>
<th>Total Emissions tonnes CO₂ / tonne output</th>
<th>Re-absorption tonnes CO₂ / tonne output in 1 year</th>
<th>Net Emissions (Sequestration) (tonnes CO₂ / tonne output in 1 year)</th>
<th>Example of Cement Type</th>
<th>Type applies to/propone nt</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>Conventional</td>
<td>.266</td>
<td>0.498</td>
<td>.764</td>
<td>.004</td>
<td>.760</td>
<td>Ordinary portland cement</td>
<td>Most dense concretes</td>
<td>Normal premix. No supplementary cementious or pozzolanic materials</td>
</tr>
<tr>
<td>PC</td>
<td>Permeable block formulation</td>
<td>.266</td>
<td>0.498</td>
<td>.764</td>
<td>.144</td>
<td>.620</td>
<td>Carbonated ordinary Portland cement blocks</td>
<td>Gas permeable substrate</td>
<td>No supplementary cementious or pozzolanic materials</td>
</tr>
<tr>
<td>42% PC 8% MgO 25% Flyash 25% GBFS</td>
<td>.199</td>
<td>.209</td>
<td>.408</td>
<td>.001</td>
<td>.407</td>
<td>Ternary mix with MgO additive.</td>
<td>Most dense concretes</td>
<td>Faster setting and higher early strength</td>
<td>1</td>
</tr>
<tr>
<td>Material</td>
<td>Process</td>
<td>Temperature</td>
<td>Recapture</td>
<td>Most dense concretes</td>
<td>Notes</td>
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<tr>
<td>PC</td>
<td>With capture</td>
<td>.266?</td>
<td>.266?</td>
<td>.004</td>
<td>.266?</td>
<td>Recapture during calcination.</td>
<td>No supplementary cementious or pozzolanic materials</td>
<td></td>
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</tr>
<tr>
<td>MgO 750-1000°C</td>
<td>Conventional</td>
<td>.240</td>
<td>1.092</td>
<td>1.322</td>
<td>-1.092</td>
<td>.240</td>
<td>Eco-Cements sorel &amp; magnesium phosphate cements.</td>
<td>Historic and conventional Sorel and Mg phosphate cements. TecEco Eco-Cement Force carbonated pure MgO (Cambridge University)</td>
<td></td>
</tr>
<tr>
<td>MgO &lt;750°C</td>
<td>Tec-Kiln (with capture)</td>
<td>.240</td>
<td>.240</td>
<td>-1.092</td>
<td>-.851</td>
<td>Eco-cement Brucite (MgO) boards</td>
<td>TecEco, Cambridge University Sorel and Mg phosphate cements. TecEco Eco-Cement Force carbonated pure MgO (Cambridge University)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>MgCO₃ ·3H₂O</td>
<td>.378</td>
<td>.007</td>
<td>.385</td>
<td>-1.092</td>
<td>-.706</td>
<td>Eco-cement concrete, pure MgO concretes</td>
<td>TecEco, University of Rome La Sapienza.</td>
<td>TecEco, University of Rome La Sapienza.</td>
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<tr>
<td>&lt;450 °C</td>
<td>Conventional calcination</td>
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<tr>
<td>MgO</td>
<td>MgCO₃ ·3H₂O Tec-Kiln (with capture)</td>
<td>.378</td>
<td>-1.085</td>
<td>-.706</td>
<td>-1.092</td>
<td>-1.798</td>
<td>Eco-cement concrete, pure MgO concretes</td>
<td>TecEco</td>
<td>N-Mg route TecEco</td>
</tr>
<tr>
<td>&lt;450 °C</td>
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<tr>
<td>MgO</td>
<td>MgCO₃ ·3H₂O Tec-Kiln (with capture)</td>
<td>.369</td>
<td>-.743</td>
<td>.374</td>
<td>-.874</td>
<td>-1.248</td>
<td>Eco-cement concrete, pure MgO concretes</td>
<td>TecEco</td>
<td>N-Mg route TecEco</td>
</tr>
<tr>
<td>&lt;450 °C</td>
<td>20% PC 80% MgO</td>
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<tr>
<td>MgO</td>
<td>MgCO₃ ·3H₂O Tec-Kiln (with capture)</td>
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<td>&lt;450 °C</td>
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<tr>
<td>MgO</td>
<td>MgCO₃ ·3H₂O Tec-Kiln (with capture)</td>
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<td></td>
<td>Silicate route</td>
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<tr>
<td>CaO</td>
<td>Conventional</td>
<td>.266</td>
<td>.785</td>
<td>1.051</td>
<td>.785</td>
<td>.266</td>
<td>Carbonating lime mortar</td>
<td>Calera, British Lime Assn &amp; many others</td>
<td></td>
</tr>
</tbody>
</table>

1
<p>| | | | | | | | | |</p>
<table>
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</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>CaCO₃</td>
<td>Tec-Kiln (with capture)</td>
<td>.266</td>
<td>.266</td>
<td>.785</td>
<td>-.518</td>
<td>Carbonating lime mortar</td>
<td>Calera, British Lime Assn &amp; many others</td>
</tr>
<tr>
<td>C3S</td>
<td>Conventional</td>
<td>?</td>
<td>0.578</td>
<td>&gt;0.578</td>
<td>?</td>
<td>&gt;0.578</td>
<td>Belite cement</td>
<td>Chinese &amp; others</td>
</tr>
<tr>
<td>C2S</td>
<td>Conventional</td>
<td>?</td>
<td>0.511</td>
<td>&gt;0.511</td>
<td>?</td>
<td>&gt;0.511</td>
<td>Tri calcium aluminate cement</td>
<td>Increased proportion</td>
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<tr>
<td>C3A</td>
<td>Conventional</td>
<td>?</td>
<td>0.594</td>
<td>&gt;0.594</td>
<td>?</td>
<td>&gt;0.594</td>
<td>Calcium sulfoaluminate cement</td>
<td>Chinese &amp; others</td>
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<tr>
<td>C4A3S</td>
<td>Conventional</td>
<td>?</td>
<td>0.216</td>
<td>&gt;0.216</td>
<td>?</td>
<td>?</td>
<td>Calcium sulfoaluminate cement</td>
<td>Chinese &amp; others</td>
</tr>
<tr>
<td>Geo polymers</td>
<td>Flyash + NaOH</td>
<td>0.16</td>
<td>0.16</td>
<td>0.16</td>
<td>Geopolymer Alliance, Geopolymer Institute, University Melbourne</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Notes to Table 2 - Future Binder Contenders with Differentiated Supply Chain Options


Much of the thermodynamic data used in this table has been calculated using TecEco’s LCA Tool downloadable from the TecEco web site at [http://www.tececo.com/files/spreadsheets/TecEco-CementLCA15Jan2013.xls](http://www.tececo.com/files/spreadsheets/TecEco-CementLCA15Jan2013.xls). The tool is in the form of an editable Excel spread sheet with no password that calculates energy and emissions to the factory gate only. Please send any corrections or suggestions to a.john.w.harrison@tececo.com
ALTERATIVE MANUFACTURING PROCESSES

So far the industry response has mostly been to:

- Modernise and upgrade plant
  - Convert wet to dry plant processes
  - Convert shaft to rotary kilns
  - Install preheating, more efficient burners etc.
  - Improve grinding and other efficiencies.
- Burn cheaper waste fuels. Burning waste materials with high calorific value including timber, tyres, solvents, waste oil, animal fats, carbon waste from the aluminium industry (14) etc. has met with opposition in some countries because of the associated pollution.
- Reduce kiln temperatures and adjust the composition of cement accordingly with more aluminates and less alite\textsuperscript{13}.

Capture during Manufacture

Significant sequestration can be achieved with capture of CO\textsubscript{2} from kilns but the problem, which has not been solved yet for any form of sequestration, is what to do with it. One approach taken by Ramesh Suri of ACC in 2006/7 was to use Algae to consume the CO\textsubscript{2} and produce bio fuel\textsuperscript{14}. The problem lies in the sheer volume of CO\textsubscript{2} produced and in making the sequestration process profitable. To meet this challenge TecEco is developing the N-Mg sub-process of Gaia Engineering that will sequester huge amounts of CO\textsubscript{2} as synthetic carbonate that can be used as aggregate or as feedstock to make rMgO for its cements\textsuperscript{15}.

Manufacturing taking Advantage of full Thermodynamic Cycles

The manufacture and use of Portland cement does not involve a full thermodynamic cycle and there is therefore little point in splitting the process into the endothermic\textsuperscript{16} and exothermic\textsuperscript{17} sub processes\textsuperscript{18} with one or two exceptions such as the manufacture of Syngas\textsuperscript{19}.

\textsuperscript{13} Pers comm. WA (Tony) Thomas – Chief Engineer Concrete, Boral Construction Materials

\textsuperscript{14} http://www.tececo.com/files/newsletters/Newsletter64.htm

\textsuperscript{15} See www.gaiaengineering.com home page and some of the latest movie downloads at http://www.gaiaengineering.com/movies.php

\textsuperscript{16} Calcination of limestone.

\textsuperscript{17} Reaction of quicklime (CaO) with clays, shales etc to produce clinker.

\textsuperscript{18} More processes result in more process energy.

\textsuperscript{19} Dr Sheila Devasahayam at the SMaRT Centre, School of Materials Science and Engineering, The University Of New South Wales, is researching pyroprocessing CaCO\textsubscript{3} with an additive to produce Syngas
Figure 3 - Options for Portland Cement Manufacture.

It is a different situation with carbonating cements containing rMgO such as TecEco Eco-Cement. Recapture occurs with net sequestration possible if CO₂ is also captured during calcination.

Figure 4 – Manufacture of MgO from Magnesite with and without Capture

The real game changer and pinnacle of industrial ecology is our N-Mg sub process of Gaia Engineering that will produce large quantities of nesquehonite (MgCO₃·3H₂O) from waste magnesium cations such as found in oil process water and bitterns and if this source runs out then from any brine containing Mg⁺ (step 1).
Nesquehonite can then be calcined in our Tec-Kiln without releases (step 2) to make rMgO and the CO₂ fed back into the process (step 1) to precipitate more nesquehonite.

The rMgO is then used as a binder to agglomerate massive amounts of nesquehonite to make synthetic carbonate aggregate or in TecEco Eco-Cements where it re carbonates (step 3). The sequestration into synthetic carbonate aggregate without saturating the market for aggregate is sufficient to solve the global carbon problem as can be seen from the graph in Figure 6 below.
Figure 7 - The Sequestration Potential for Synthetic Carbonates in Concretes

Eco-Cement binders according to TecEco Pty. Ltd.’s patents are ideal for agglomerating synthetic carbonate aggregate and from the graph the total sequestration possible given 2011 – 12 concrete production is over 22 billion tonnes which is around 2/3 of that needed to consume all anthropogenic emissions. As a matter of proportion, the particular cement used in the future becomes less important in relation to the total sequestration possible in concrete if the focus is also on aggregate.

TecEco call this breakthrough technology Gaia Engineering and it is a whole new way of thinking about industrial ecology and associated molecular flows. Gaia Engineering can profitably solve the problem of global warming and related problems such as ocean salinity and in doing so mitigate other problems such as pending food shortages\textsuperscript{15}. 

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Assumptions & \multicolumn{1}{c|}{Values} \\
\hline
Tec-Cement concrete with synthetic magnesium carbonate aggregate & \multicolumn{1}{c|}{Total Sequestration} \\
Percentage by weight of cement in concrete & 12.00\% \\
Percentage by weight of MgO in Tec-Cement & 9\% \\
Percentage by weight Ca(OH)\textsubscript{2} in cement & 25\% \\
\% of Ca(OH)\textsubscript{2} in concrete that carbonates & 10.00\% \\
Proportion cement that is flyash and/or CFA & 20\% \\
1 tonne Portland Cement & 0.857 Tonnes CO\textsubscript{2} \\
Proportion concrete that is aggregate & 80\% \\
CO\textsubscript{2} captured in 1 tonne aggregate & 1.081 Tonnes CO\textsubscript{2} \\
Net CO\textsubscript{2} sequestration 1 tonne MgO (N-Mg route, 1 complete recycle) & 1.795 Tonnes CO\textsubscript{2} \\
CO\textsubscript{2} captured hydration and carbonation of 1 tonne CaO (in PC) & 0.765 Tonnes CO\textsubscript{2} \\
\hline
\end{tabular}
\caption{Source USGS: Cement Pages}
\end{table}
REPLACEMENT OF PORTLAND CEMENT BY LIMESTONE

Limestone is now routinely being added to Portland cement in varying proportions around the world and some success is being claimed mainly as a result of the improved particle packing.

Compton and Chandler make it clear that Portland cement is not the best possible additive however when they say “limestone is generally considered to be the poorest potential performer of the available suite of mineral additions and as such considerable effort is focused on developing Portland-limestone cements that achieve the current general purpose Portland cement performance” (2)

By adding limestone to Portland cement the industry may be reducing the effectiveness of better and more suitable mineral additions such as rMgO and supplementary cementing materials (SCM’s) classified and ground as necessary to optimise particle packing. The SCM’s most commonly used include fly ash, ground granulated blast furnace slag and silica fume. Greater consumption of such wastes should be encouraged not compromised by a lowering of pH caused by the addition of limestone.

Hooton, Nokken and Thomas make it clear “One area where there is very little data is on the influence of limestone cements when used in conjunction with SCM’s. A question that needs to be answered is whether the use of limestone cements will reduce the replacement levels of SCM’s that
can effectively be used.” (8) A theoretical analysis of the issue is on our TecEco and Gaia Engineering web sites.  

At the present time “considerable effort is focussed on developing Portland-limestone cements that achieve the current general purpose Portland cement performance” (2). The goal is to find out just how much ground limestone can be added without compromising the properties of normal cements too much. The argument is that “limestone is the obvious choice for most cement manufacturers. It is a fundamental raw material at cement plants, and high grade limestone is readily available through its use as a supplement to amend raw meal chemistry. Limestone is abundant, pure and soft and makes an ideal mineral addition to be inter-ground with clinker and gypsum during cement milling” (1)

Given the theoretical evidence I present on the TecEco web site it is essential that cement that consists of clinker and gypsum in the right ratio with 5 % or less of limestone and nothing else continues to be made available for downstream blending as the economics of other mineral additions will change and many work much better such as rMgO which would otherwise compete with limestone for interstitial sites between cements grains.

Reactive magnesia blended with Portland cement and SCM’s results in significant improvements in properties as detailed in the next section. The problem is that best results are achieved if it is fine enough to also fill interstitial sites between grains of Portland cement.

**REPLACEMENT OF CEMENT BY SCM’S**

Portlandite should not be left in a concrete because it is far too reactive. On the other hand consuming it all in the pozzolanic reaction also has technical issues. Mistakes are routinely made. Portland cement can be blended with pozzolans such as flyash which will consume Portlandite (Ca(OH)₂) in the pozzolanic reaction. It is important however that not all of the Portlandite is consumed as calcium will start leaching from CSH if it is. As an alternative pH buffer we recommend the addition of rMgO which hydrates to brucite. The equilibrium pH of Brucite is approximately 10.5 and the pH of CSH around 11.2 (22). The pH of a CSH and Brucite assemblage in equilibrium will not fall much below 10.5.

According to the 12th plan in India around 10 million tonnes of GBFS are produced annually (10). In a recent article by Dr Yashpal Singh a figure of around 175 million tonnes of flyash was estimated for 2012 (20).

As most SCM’s are wastes their use is obviously more sustainable than digging up limestone, grinding it and adding it to cement and the paradox is that the use of limestone may compromise the use of SCM’s as explained in the previous section.

20 In the technical areas of www.tececo.com and www.gaiaengineering.com under the heading “Ground Limestone in Portland Cement - A Good Idea or Lost Opportunity”.

21 Preferably none at all

22 Properties will change and CSH is thought to become more brittle (5).
In many parts of the world builders are negative about the use of SCM’s because when added, concretes take longer to gain strength. Grinding cement finer to compensate for the negative chemical effects of limestone should have been considered as one way of making it more reactive with SCM’s such as flyash however this costs money. Another is to air classify pozzolans increasing their reactivity.

A way of accelerating the setting of mixes containing a high proportion of SCM’s is to include about 8-10 % rMgO as a proportion to PC in a mix. The reason is because when dissolved in water Mg\(^{2+}\) has a profound effect on the polarity of all species in solution that can be polarised. Of particular interest in relation to cement are water and its disassociation species.

![Figure 9](image)

**Figure 9** – **The Mg\(^{++}\) ion drags electrons to it exposing more electro positive protons**\(^{23}\)

\(\text{Mg}^{++}\) is a strong kosmotrope and strongly attracts electrons and brucite (including microcrystallites) has a strongly charged surface. Water dipole strength is increased and propagated in mix water. Water and its disassociation species such as hydroxides have reduced negative electron clouds around protons. Dissolution of SCM’s by proton wrenching occurs more readily, speeding up reactions and making their use more acceptable to builders\(^{24}\).

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\(^{23}\) Water is in equilibrium with hydroxide and hydronium ion ions. When acidic or basic compounds are dissolved the equilibrium is pushed towards more hydronium or hydroxide ions respectively. 

\[ \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \]

The hydronium ion is highly solvated and \(\text{H}_3\text{O}^+\), \(\text{H}_2\text{O}_2^+\) and \(\text{H}_4\text{O}_3^+\) are increasingly accurate descriptions of the environment of a proton in water. Chemists represent a hydronium ion as just a hydrogen ion (H\(^+\), as in the figure) in place of H\(_3\)O\(^+\)

\(^{24}\) See the web page Reactive Magnesia - A Theoretical Explanation of Properties in the technical area at [www.tececo.com](http://www.tececo.com)
With about 8-10% of reactive magnesia (rMgO) added, 50% or more of (SCM’s) can be used and the resulting concretes still outperform ordinary Portland cement concretes. This may not be achievable with higher additions of inter-ground limestone. Surely the goal should be to use SCM’s most of which are wastes.

The focus of my efforts in the past few years has been to find ways of making reactive magnesia much more cheaply so it will be blended with Portland cement and SCM’s as a matter of routine as it should be. Readers should however be aware that some manufacturers are actively selling magnesia for use in concrete without stating the reactivity in possible breach or circumvention of our patents and possibly dangerously as well because magnesia that is not highly reactive can cause dimensional distress in the proportions we recommend and does not act in the same way.

DEMATERIALISATION

Dematerialisation is a technique for reducing the materials used by design and has been practiced for many years by some architects. As the subject was covered by Mehta extremely well (15) I will not elaborate. I refer readers to Figure 2 - Mehta's Triangle on page 3 and comment that the impact of dematerialisation on lifetime energies must be considered.

MIX OPTIMISATION

Mix optimisation is mostly an art and should be a science. It is not practiced widely enough and there are a lot of shortcuts in the software used. More often than not the “rule book” of prescriptive standards is religiously followed without questioning why. For example the use of gypsum to prevent flash set even when blended with SCM’s.

![Figure 10 The Change in the Surface Charge of Metal Oxides with pH. (21)](image)

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An important aspect is particle size and charge. It is not just what is in the mix but the particle size range of each component and how they fit together in 3D space. The smaller the average size of each addition the more particle charge becomes important\(^\text{26}\).

What is or is not included should be carefully considered with end use in mind and many changes are suggested in this paper. RMgO for example accelerates first set because it goes negative at the surface as the pH rises as demonstrated in Figure 10 above.

It is important to realise that packing considerations apply to all components in a mix, not just the cement and that small component substitutions can make a big difference to properties and the amount of cement required to achieve a given strength. Less cement for a given strength is more sustainable.

A pioneer in this field is de Larrard from France\(^\text{13}\)(12) and the TecSoft\(^\text{27}\) project at TecEco has been initiated to implement some of his math.

Mix optimisation is also too focussed and should be better connected with need as discussed in the section with the title PRODUCT DIFFERENTIATION AND SPECIALISATION. on page 23.

**PRODUCT DIFFERENTIATION AND SPECIALISATION.**

It has been said in the industry that “all that is grey is great, all we make goes out the gate”. Significant amounts of energy would be saved with specialisation for differentiated market niches. Market penetration would also increase with the development of new concrete product.

With rising energy costs and an urgent need to improve sustainability additions to cementitious composites that improve lifetime or operating performance are an import part of a profitable future. Many waste streams can offer a wider range of properties for purposes such as thermal insulation or weight reduction. With the use of rMgO any toxics are encapsulated as well as immobilised and bonding to alternative included materials such as agriculture or domestic wastes is dramatically improved as are fire resistant properties. Concretes with high thermal mass for heat retention and concretes with greater elasticity and plasticity for road pavement are other examples.

New mineral composites incorporating waste streams with low thermal flow characteristics will be in high demand (e.g sawdust blocks) in the future and will drive this differentiation. Cementitious composites such as concrete can take a lead role in reducing lifetime energies and become part of the solution instead of the problem.

**CHANGING THE EMPHASIS**

It is essential to think of concrete not just cement as each component has a role in the performance at every stage. It we think whole of concrete as recommended by Ken Hover\(^\text{9}\) and many others then it becomes much easier to understand the material and issues concerning it such as sustainability.

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26 It is not well known that electrostatics plays a significant role in the setting of concrete\(^\text{11}\)

27 See www.tecsoft.com.au
There is too much emphasis on strength and not enough on durability and properties. As discussed under the heading PRODUCT DIFFERENTIATION AND SPECIALISATION. On page 23 concretes with a wider range of properties such as low conductance or light weight could play a major role in reducing the lifetime or operational energies of structures.

About seven years ago now I realised that aggregate is 80% or more of most concretes and therefore represented an opportunity to sequester huge amounts of carbon dioxide as synthetic carbonate in our Gaia Engineering process explained in this document under the heading Capture during Manufacture on page 15 and in a lot more detail at www.gaiaengineering.com.

THE RIGHT BUSINESS MODELS

For a long time a cost cutting model has dominated the efforts of players in our industry however if we are to move forward and fulfil the potential of solving many of the world’s problems this will have to change. New innovation based business models will have to be adopted.

![Figure 11 - Increases in Business Performance by Innovation status 2008 – 9 (4)](chart.png)


Most governments have realised that innovation is important and in relation to this some interesting statistics are coming out of the Department of Industry, Innovation, Science, Research and Tertiary Education in Australia that conclusively demonstrate that innovative companies perform better (See Figure 11).

Companies in the construction sector including the concrete industry do not spend much on research as shown in Figure 12. The main reason why is because our industry is bound by a framework of standards, legislation and conservatism that has resulted in low margins. It is no wonder cost based business models prevail.
Figure 12 – Australian R & D Expenditure by Industry Size (Bubble diameter) Employment and Gross Value Added. (3)
THE RIGHT FRAMEWORK TO OPERATE IN

The concrete industry in most countries operates with a restrictive framework of standards and guides and supporting legislation that breeds conservative managers who do not innovate and a cost cutting business model. Our engineers are taught to rely on out of date dogma not rely on science or their common sense. Change must occur if we are to move forward on sustainability and take advantage of emerging opportunities for carbon trading. Given the lack of training and education at the base level this will be a difficult challenge.

An Inappropriate Permissions and Rewards Systems

At Concrete Solutions 09 (6) I spoke about the tremendous potential for players in the concrete industry to make money as a result of inevitable change yet many barriers still exist as I have discussed. One of the greatest remains our ill-conceived permissions and rewards systems designed with the false notion that they protect the status quo. There is a rising current of change that I helped initiate and prescriptive standards and inappropriate legislation is getting in the way.

Standards for cement and concrete are still prescription based in most countries and even the Green Building councils in the US, Australia and elsewhere have fallen into the same trap of locking in the status quo and stifling innovation. Prescriptions should be confined to guidelines on how to do things. Standards should set out minimum performance requirements in a chosen range of categories. In order to take advantage of carbon trading the industry should also consider using standards, modified as suggested, as a way of providing benchmarks for minimum embodied energy and emissions. Existing standards could be relegated to a role as guides.

Legislative Frameworks fall into the same trap as standards with too much restriction although some governments such as my own here in Australia pay lip service to the need for change as evidenced by renaming departments with the word “innovation” included. The way forward surely lies in better education and training and the conversion of standards to guides. The concrete industry produce and place the most used and important materials in construction yet in many countries no qualifications of even basic training are required by those practically involved. This deplorable situation must improve and hopefully the training is not rote but such that it awakens minds to the possibilities.

The Right Policies to support Research and Development to Improve Sustainability

Few governments have ever managed to get the mix of stick, incentive and procurement right or even remotely efficient. The level of control continues to increase without the leadership to drive it. As Lord Stern made clear in his review of the economics of climate change (23) there are huge opportunities for emissions reduction in building and construction, not just in reducing the embodied energy and emissions of the materials we make but by changing the way we design structures and the way we utilise the materials we use to build them.

The biggest problem is that governments do not follow their policies through the supply chain. It is no good supporting the Research and development of for example carbon capture methods without

28 See also http://www.tececo.com/sustainability.permissions_rewards.php
making sure there are financial sticks and/or incentives to encourage the changes required to the process of making cement.

**Back to Science**

There are too many non-scientific dogmas in the cement and concrete industry.

At TecEco we have relied on science to explain what we observe. By using science rather than applying dogma it is easier to understand what is really happening and see a way forward for improvement.
CONCLUSIONS

It is time cement companies adopted a business model that connects innovation with profitability. In many other industries profitability is understood to be a function of research and development and that the regular release of new technically improved product generates revenue growth. Progress towards de-carbonation will be slow unless this occurs.

Engineers should be taught science not dogma and standards need to be rewritten as benchmarks not prescriptions. The legislative framework in many countries needs a broom through it and governments need to realise that the concrete industry could in fact be the saviour of the world as M K Singh bravely arose and said29.

All this can only be achieved if there is a change in mindset, a strong desire to move the agenda towards greater sustainability forward, a willingness to throw away the rule book, a whole new modern scientific lateral thinking.

Last century there were many different mineral cement contenders and Portland cement was only one of them. By 1900 it emerged as the dominant formulation. In the future a new differentiation of product based on properties will probably occur and this will be a good thing as it will result in greater margins and product more suited to particular use such as, for example, the development of binders suitable for utilising wood waste to make insulating composite products for the outside of buildings including rMgO for fire retardation. The major barrier to implementation will be the mindset of our managers and out dated prescription based standards.

John Phair said at the conclusion to his paper that “Further developments and new techniques must continue to be introduced into the cement and concrete industry. Green chemistry will play a significant role in facilitating a holistic industrial ecological approach to cement from a fundamental level. This will provide distinct alternatives to an OPC dominated cement market.” (18). There will be greater diversification and alternatives but in my view the market will still be PC and PC derivative based but only if new formulations and production processes that include capture are implemented such as our N-Mg process which produces synthetic carbonate aggregate.

Chemistries that fix known “sleeper” issues such as Portlandite content will need to be embraced including our own Tec and Eco-Cement technologies. With the use of a high proportion of SCM’s, particularly if pre - blended the addition of gypsum and limestone are questionable. As Paul Hawken makes clear in “The Ecology of Commerce,” concrete that is more durable is more sustainable(7).

By adopting a whole of concrete approach there is much more scope for sustainability. The obvious target in construction is to lower lifetime or operational energies so we should be thinking properties as well as strength and durability and this will require product diversification.

Paradigm changes such as our Gaia Engineering project will modify the supply chain to focus on carbon capture and then use the CO2 produced to manufacture synthetic carbonate aggregate.

A new approach to cement and concrete formulation cannot evolve without the realisation that concrete can be part of the solution not the problem.

29 See Introduction
Portland cement concretes are the most ubiquitous and will probably remain so because immense economies of scale make them relatively cheap and sustainability problems can be overcome by carbon capture with CO₂ used as synthetic carbonate aggregate and a reformulation excluding limestone and gypsum and including reactive MgO and a mix of classified fine and normal SCM’s in high proportion.

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