

An overview of alternative mineral binder systems including novel concrete technologies addressing practical supply chain issues including energy

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Abstract

Regardless of whether global warming is occurring or not there is little doubt that the imposition of carbon taxes is seen by government as a resource tax with sound economic, environmental and moral justification.

The cost of energy is likely to rise more rapidly than prices generally in the future and carbon taxes are inevitable. At the same time the output of wastes in the world keeps growing. It is also well known amongst experts that we could make much better and greener concrete and composites with more attention to the chemistry and physics of mineral composites such as particle packing and particle charge and granular physics. I also suggest that future changes will occur in the way we manufacture cements as the opportunity is there to do so in a much more environmentally sound way.

The building and construction industry can and must adapt to global pressures and increasing pressure on the bottom line. Rather than shirk at perceived costs it is essential to boldly consider these times of change as an immense opportunity to make money to survive. Yet where are the R & D budgets of the big players? Our conclusion is that the industry must adopt the model embraced by most other industries and innovate to grow and make money.

Future concrete will be made with much lower embodied energies and emissions and incorporate more waste materials for their physical and chemical properties. Gypsum for example is a waste that is in the supply chain of some cements containing sulphur. Components particles will be engineered for their chemistry, strength, charge and fit from the nano sizes up and there are many to choose from. This paper discusses the drivers, technical options, targets, economics and supply chains as well as barriers to change.

Background

Drivers for Change

CO₂ Emissions and Common Sense

The use of binders like Portland cement will continue to grow and continue to release to the atmosphere significant amounts of CO₂ unless we do something about it (See Figure 1 - Predicted Global Cement Demand and Emissions) The evidence is that CO₂ is a global warming gas and this is not disputed by the counter consensus to the IPCC (1). Whether we believe climate change is occurring or not or not¹, the atmospheric status quo has worked well for humans as the Holocene had been a remarkably stable period in earth's history. Why risk change - common sense and cost suggest reducing rather than increasing embodied energy and emissions hence releases.

The Rising Cost of Energy

We have now passed peak oil according to the IEA. (2). As a consequence and in spite of the recent financial crisis all forms of energy will become more expensive (See Figure 2 - Energy Outlook to 2035).

¹ The debate seems to have become a matter of belief not science unfortunately

Businesses exist in pursuit of the bottom line and it is therefore not just necessary to seek cheaper alternative sources of energy but reduce the embodied energies of products like cement and concrete

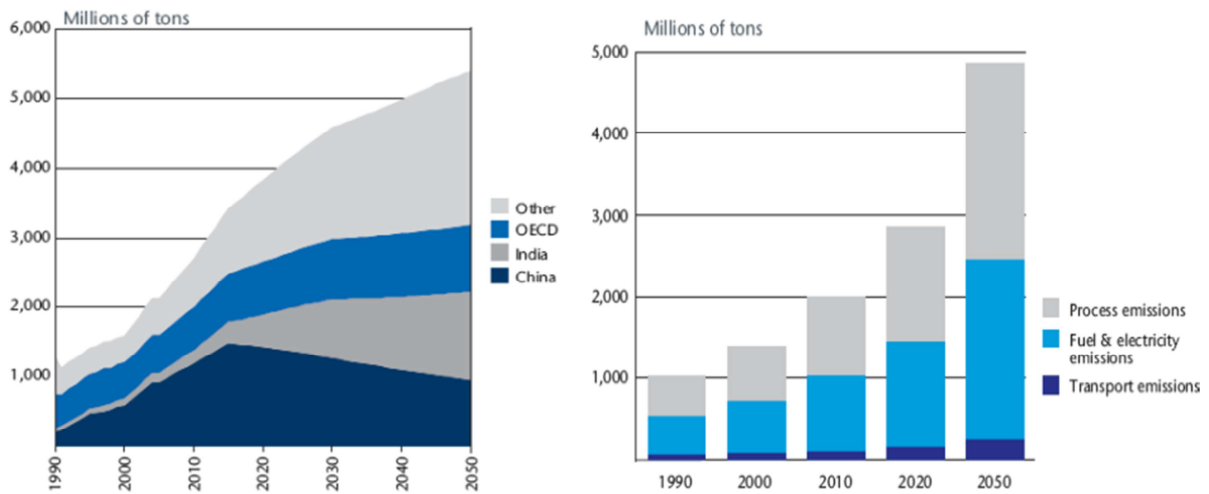


Figure 1 - Predicted Global Cement Demand and Emissions (3)

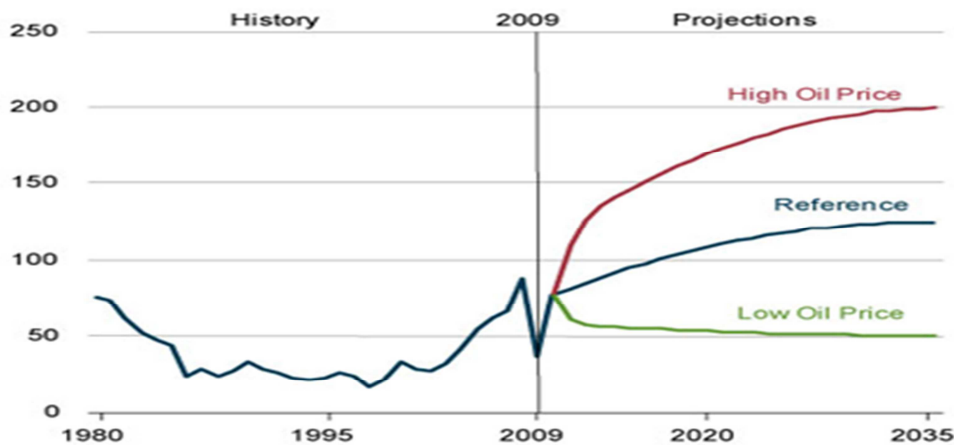


Figure 2 - Energy Outlook to 2035 (4)

Population Growth, Our Footprint and the Need to Recycle

The seven billionth person on this planet will be born this year; each person produces about 0.5 tonne of waste per year totalling 3.5 billion tonnes (Veolia). Malthus (6) may have been right after all and as a precautionary measure the three R's adage² applies more today than it ever did. In some countries like Taiwan, disposal of wastes is a real issue. Fortunately new technologies have improved the input potential of wastes and they will increasingly become components in future composites on the basis of their physical as well as chemical properties.

Technical Options

There are a large number of possible binders however Portland cement is the most ubiquitous and will remain so for the simple reason that water is a component making concrete made with it easy to place. Because of immense economies of scale Portland cement is also very cheap in spite of the energy manufacture consumes. It has dominated in the ultimate test – that of the market and with some

² Reduce, reuse and recycle

modifications suggested PC based or at least hydraulic cements³ will be able to satisfy most of the requirements of the future. The other main advantage of Portland cement or related cements is that they are extremely forgiving or operator error. Not all agree with the proposition that they will continue to dominate so to properly analyse the argument criteria must be set as a guide⁴ and tools such as decision matrices employed. See

³ Including derivatives and variants of PC. i.e other hydraulic compositions

⁴ Comparing different technologies is always subjective to a greater or lesser extent and thus a source of argument.

Table 1 - Example of a Decision Matrix to Decide Binder Systems of the Future. Note that the example decision matrix reflects the authors options and is not a consensus view.

There are a large number of potential candidate binders and many options to improve the energy and emissions options for their manufacture. Given the necessary brevity of this paper they are presented as Table 2 - Future Binder Contenders with Differentiated Supply Chain Options.

According to the BRE we cannot address decarbonation without changing the composition of cement and fuel derived emissions will diminish slowly for purely economic reasons (3). Added to their conclusions should be the need to change processes. The potential for sequestration of process changes to full or part thermodynamic cycle binders (these binders are usually also hydraulic) with recycling of CO₂ into aggregates is not understood by many writers on the subject (See Supply Chain Options).

Supply Chain Options

Table 2 includes a number of supply chain options for different types of cement and as they make a huge difference to the embodied energy and emissions as well as cost of binders a profitable avenue for improvement is in the way binders are manufactured. For example thermodynamic cycle binders that have a calcination step can be made without releases. This opportunity is there for Portland cement to be made in a split process, the calcination step being in a closed system.

The same but much easier, potentially less costly options also exist for magnesium binders with even more potential capture because of the lower molecular weight of magnesium.

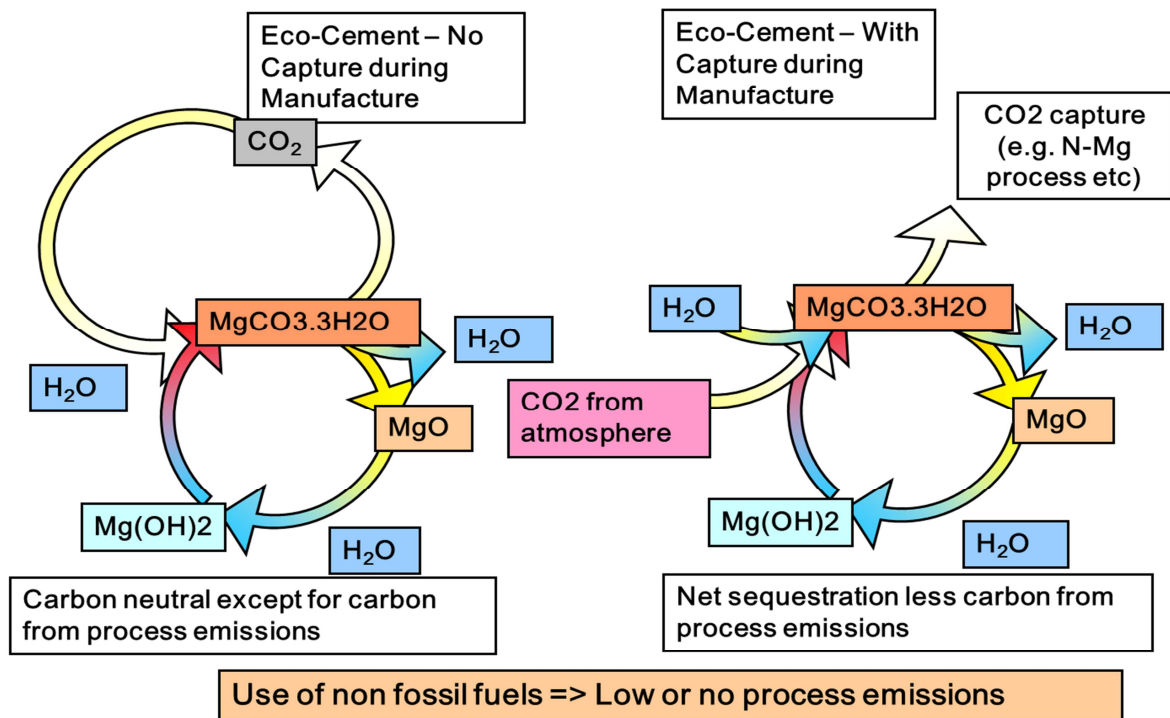


Figure 3 - The Potential of Full or Partial thermodynamic Cycle MgO Binders for Carbon Capture

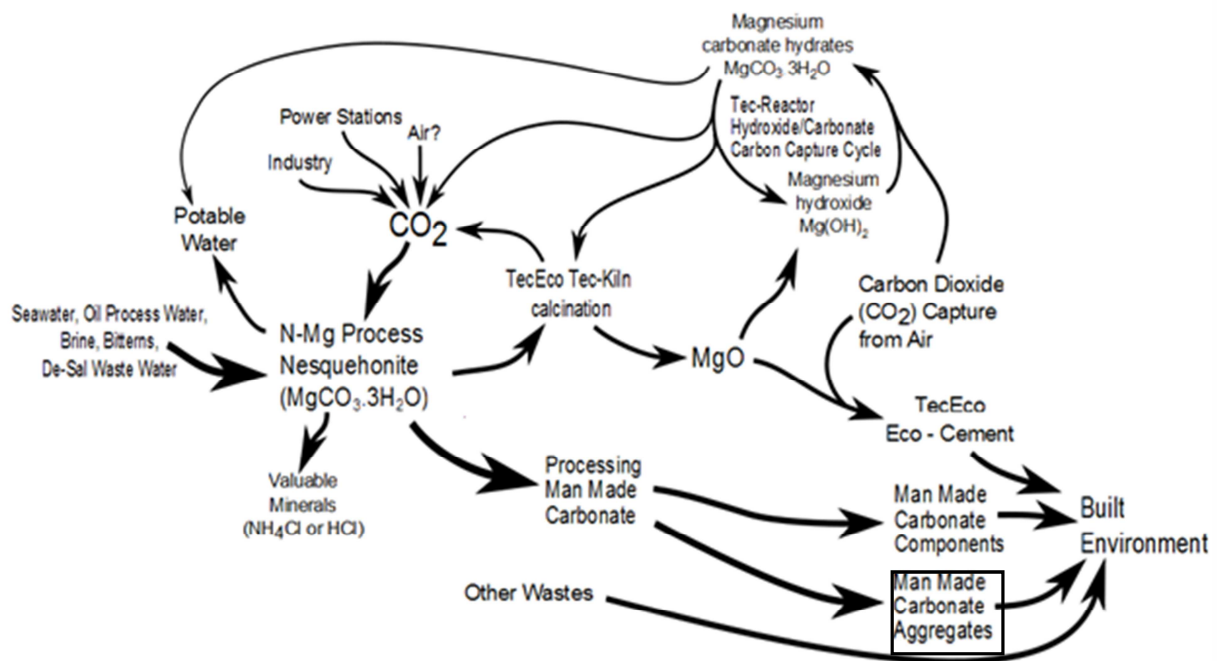


Figure 4 - The N-Mg Process for Low Temperature Manufacture of MgO from Nesquehonite

Recently the author spoke about a low temperature route via nesquehonite in London and Rome and this is now being intensively investigated by others. (See Presentations 50 and 51 at http://www.tececo.com/document.conference_presentations.php and Figure 6 - The N-Mg Process for the Low Temperature (<450 oC) Production of MgO from Brines). A vital component of this exciting new process is a kiln we have designed that will calcine without releases. Unfortunately for intellectual property reasons this is highly secret.

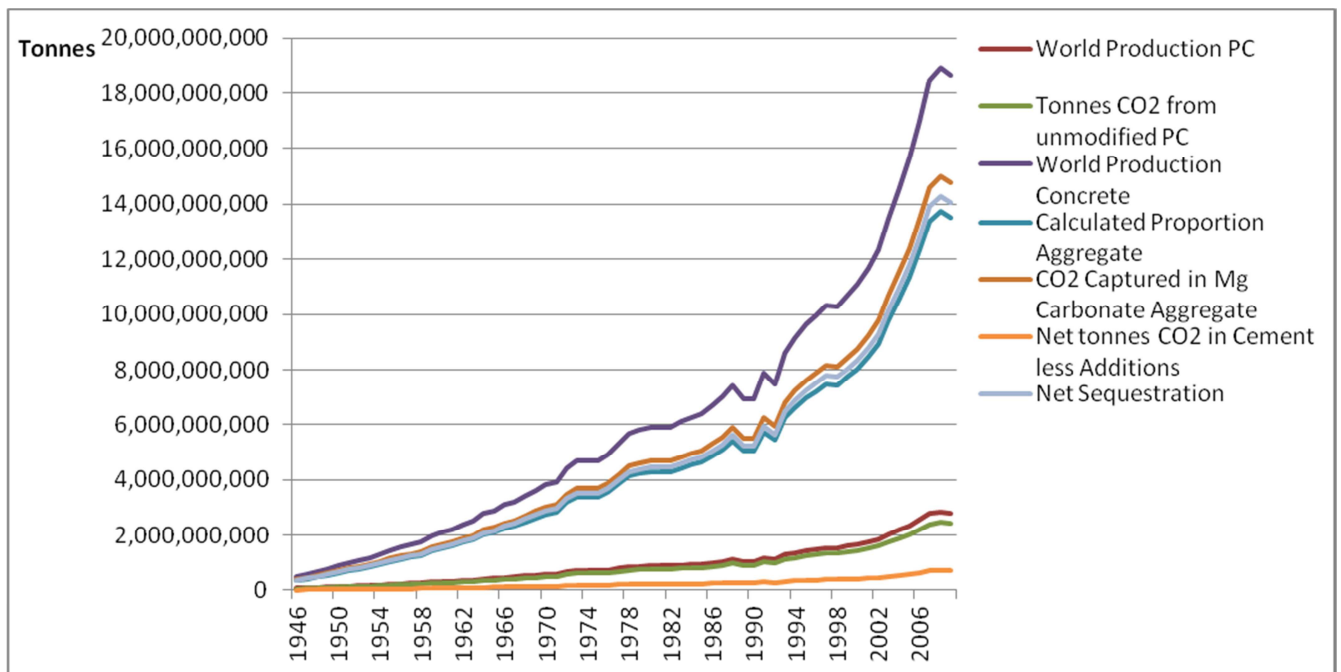


Figure 5 - The Potential of Man-Made Carbonate Aggregate for Sequestration

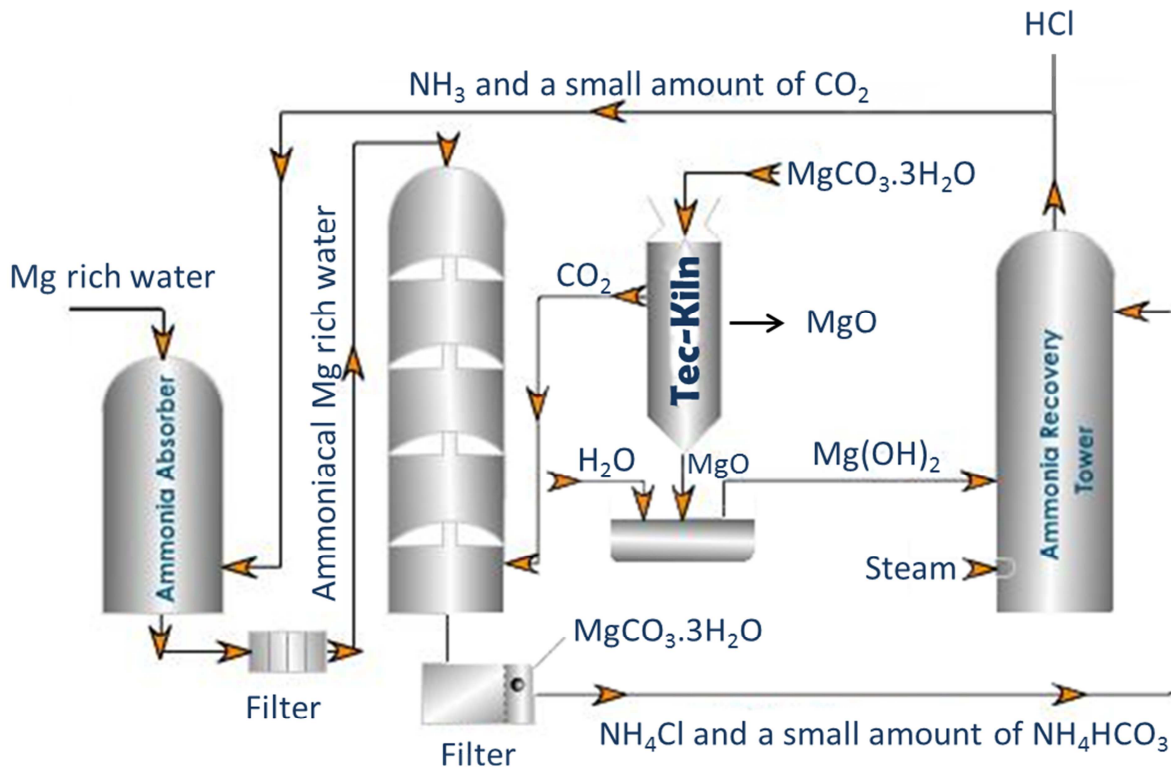


Figure 6 - The N-Mg Process for the Low Temperature (<450 °C) Production of MgO from Brines

Other Technical Options

Mainstream binders are likely to remain thermodynamic cycle hydraulic in nature with increasing use of waste streams such as fly ash and GBFS made possible by blending with reactive magnesia. Our claim is that 50% replacement binders can be made to outperform ordinary Portland cement binders. This is a big claim but it has been achieved. See Presentations 50 at http://www.tececo.com/document.conference_presentations.php

We agree with the BRE (3), the price of energy is likely to lead to innovation in kiln technology and fuels and with this in mind we have invested considerable effort in developing our kiln that will calcine without releases.

Cement Contenders

A few of the many possible binders are listed below with comments. A more complete list is included as Table 2 - Future Binder Contenders with Differentiated Supply Chain Options which contains tabulated data on CO2 emissions

The Hydraulic Cement group are the largest and there are many alternatives even without considering variants providing high early strength, sulphate resistance etc.

Hydraulic Cements

Note that few people when writing about either calcium or magnesium cements have understood the potential of the thermodynamic cycle for carbon capture with hydraulic compositions. (See Supply Chain Options, above and Figure 3 - The Potential of Full or Partial thermodynamic Cycle MgO Binders for Carbon Capture).

Portland cement could be made in a split process with CO2 capture and reincorporation in man-made carbonate cements or with greater impact aggregates. (See Supply Chain Options above). Eventually this will be done and when it is, Portland cement and related hydraulic cements are a clear leader in every criteria for the future. See

Table 1 - Example of a Decision Matrix to Decide Binder Systems of the Future.

Slag-lime or slag – PC cements are made from ground granulated blast furnace slag (GBFS) which is not hydraulic but can be "activated" by addition of alkalis such as, most economically, lime. (We consider slag cements a variant of Portland cement)

Supersulfated cements have potential as they are made mostly from GBFS and gypsum which are wastes and only a small amount of PC or lime. The main hydration product is ettringite and they show good resistance to aggressive agents including sulphate but are slow to set. (A derivative)

Calcium aluminate cements are hydraulic cements made from limestone and bauxite. The main components are monocalcium aluminate CaAl_2O_4 (CA) and mayenite $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (C12A7) which hydrate to give strength. Calcium aluminate cements are chemically resistant and stable to quite high temperatures.

Calcium sulfoaluminate cements & belite calcium sulfoaluminate cements are low energy cements that have the potential to be made from industrial by products such as low calcium fly ash and sulphur rich wastes. The main hydration product producing strength is ettringite. Their use has been pioneered in China (A derivative)

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 like phases. (a variant, See http://www.tececo.com/links.cement_rosendale.php.)

PC - MgO – GBFS – fly ash blends. MgO is the most powerful new tool in hydraulic cement blends since the revelation that reactive magnesia can be blended with other hydraulic cements such as Portland cement. 25-30% improvements in compressive strength and greater improvements in tensile strength, faster first set, better rheology and less shrinkage and cracking less bleeding and long term durability have been demonstrated. It is also possible autogenous shrinkage has been solved.

MgO blended with other hydraulic cements, pozzolans and supplementary cementitious materials (SCM's). Amazingly very little real research has been done on optimised blends particularly with cements other than Portland cement.

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 known (dung +MgO) and are potentially very green if the magnesium oxide used is made with no releases or via the nesquehonite (N-Mg route) suggested by the author and a way can be found to utilise waste phosphate from intensive agriculture and fisheries e.g. feedlots. (Thereby solving another environmental problem.)

Carbonating Cements

Magnesium Based Carbonating Binders can, like lime, be used for thermodynamic cycle binders such as carbonating mortars. As water of crystallisation is also taken on the solid produced for input mass ratio is higher than for lime based carbonating binders.

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

Other Cements

Geopolymers are potentially very green but suffer from a number of fundamental flaws that will restrict their use. 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.

Barriers to Change

An Inappropriate Permissions and Rewards Systems

At Concrete Solutions 09 (7) I spoke about the tremendous potential for players in this industry to make money as a result of inevitable change yet the greatest barrier remains our ill-conceived permissions and rewards systems.

Standards for cement and concrete are still prescription based and even the Green Building council has 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 relay minimum performance in a chosen range of categories and in order to take advantage of carbon trading the industry must consider using them to account for embodied energy and emissions.

Conservatism

The truth is that for years we have made concrete badly. New ideas and understandings are very hard to move forward and the pace of change has been slow. Yet our understanding of mineral binder systems of all kinds has never been greater.

Low Margins

Largely as an outcome of its own ineptitude the industry is cost restricted rather than profit driven. Low or no budgets for R & D have resulted in stagnating innovation which in itself is not seen as fundamental to profit and which instead is driven by cost cutting in what is considered a somewhat uniform market. It need not be so.

Lack of Information about New Binders

There is a preponderance of information on Portland cements but little on alternative variant and derivative hydraulic binders. Sheffield University, The BRE, Sheffield University, Lafarge and the Chinese lead the field with their work on aluminates and sulphated cements.

With my own work and that of Cambridge university and Imperial College London more information is being collated on magnesium binders but they have still got off to a bad start with far greater effort going into "me too" compositions such as Novacem are attempting to patent or into process dead ends such as being pursued by Cambridge University where carbonation rooms are required. We need less process, not more, simpler not more complicated manufacturing processes.

A Sample Decision Matrix

Pugh decision matrices are one of several tools to compare options but unfortunately do not eliminate subjectivity and must be properly designed to give the right answer⁵.

In

⁵The old adage about asking the right questions to get the right answer applies.

Table 1 - Example of a Decision Matrix to Decide Binder Systems of the Future we have attempted to develop some criteria for just six future binder options and immediately ran into subjectivity and assumptive issues. We were confronted with decisions such as should we consider current technology paradigms or what is possible. Our offering is based on what is possible.

Table 1 - Example of a Decision Matrix to Decide Binder Systems of the Future

		ALTERNATIVES											
Decision Model		Mg-Hydraulic		PC		Geopolymer		Mg-Carbonate		MgO		C ₄ A ₃ S	
Criterion	Weight	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score	Rating	Score
Ease of Placement	10	9	90	8.5	85	3	30	7	70	0	0	7	70
Cost	8	8	64	8.5	68	9	72	7	56	0	0	7	56
Safety	7	8	56	8	56	4	28	8	56	0	0	8	56
Compressive Strength	6	8	48	7.5	45	7.5	45	6	36	6	36	6	36
Tensile Strength	5	9	45	7.5	37.5	7.5	37.5	6	30	6	30	6	30
Durability	5	9	45	7	35	7	35	8	40	8	40	8	40
Use of Pozzolanic Wastes	5	9	45	7	35	7	35	4	20	4	20	4	20
Use of Other Wastes	5	9	45	4	20	5	25	9	45	9	45	4	20
Embodied Energy	8	7	56	7	56	8	64	7	56	7	56	7	56
Embodied Emissions	8	7	56	7	56	9	72	5	40	5	40	5	40
Thermal Mass	4	8	32	8	32	8	32	7	28	7	28	7	28
Thermal Flow	4	8	32	8	32	4	16	9	36	9	36	9	36
Supply Chain	7	8	56	9	63	4	28	5	35	4	28	5	35
Total	82	107	670	97	621	83	520	88	548	65	359	83	523

Score = Rating * Weight

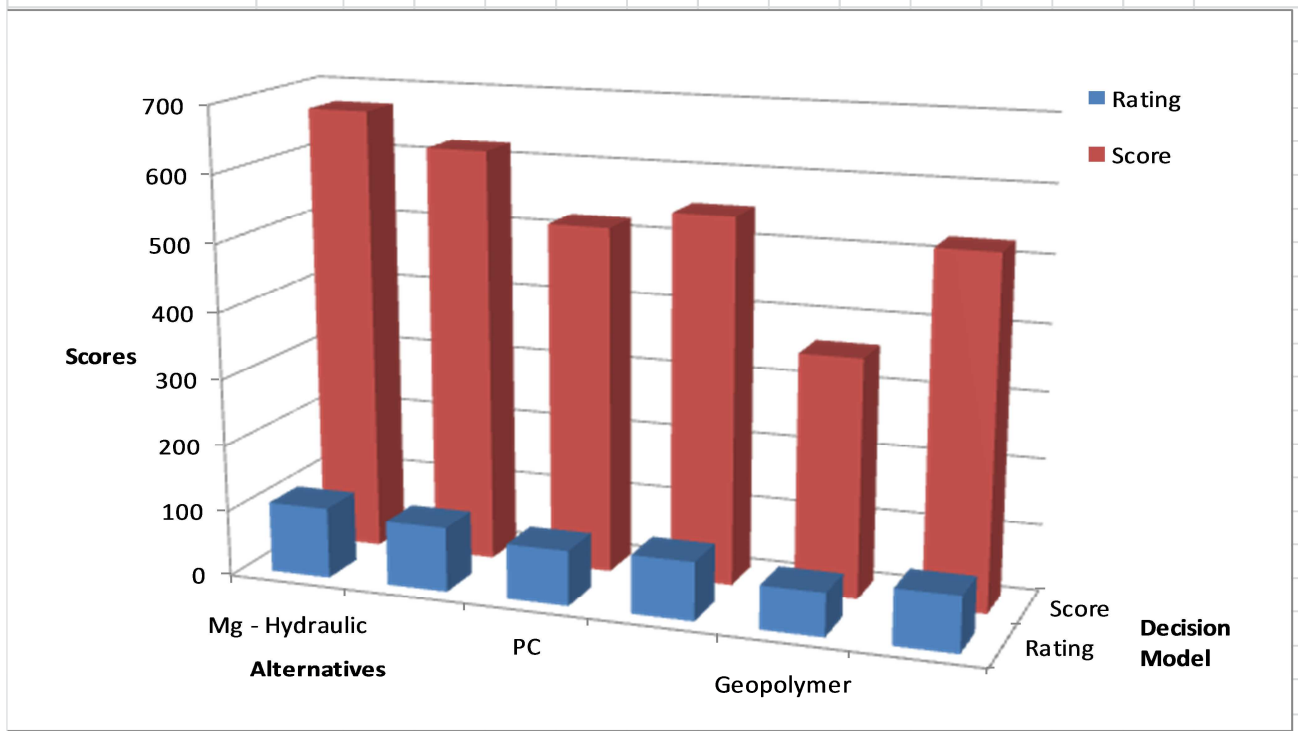


Figure 7 - The Decision Model from Data in Table 1

Table 2 - Future Binder Contenders with Differentiated Supply Chain Options

Cements Based on	Process	Process CO ₂ (tonnes CO ₂ /tonne Compound)	Decarbonation CO ₂ (tonnes CO ₂ /tonne Compound)	Emissions (if no kiln capture – tonnes CO ₂ /tonne Compound)	Absorption (tonnes CO ₂ /tonne Compound, Assuming 100% carbonation 1 year)	Net Emissions (Sequestration) (tonnes CO ₂ /tonne Compound, Assuming 100% carbonation 1 year)	Example of Cement Type	Apply to	Comment	Notes
PC	Conventional	.370	0.498	.868	.004	.864	Ordinary Portland Cement	Most dense concretes	No supplementary cementitious or pozzolanic materials	1
PC	Permeable Block formulation	.370	0.498	.868	.144	.724	Ordinary Portland Cement	Most dense concretes	No supplementary cementitious or pozzolanic materials	1
PC	Split Process – Lime then clinker	.40 ?		.40?	.004	.40?.	Split process lime with recapture then clinker	Most dense concretes	No supplementary cementitious or pozzolanic materials	1

Modified Ternary Blends (50% PC)	Split Process – Lime (with capture) then clinker	.185		.185	.002	.183	Ternary mix with MgO additive.	Most dense concretes	Faster setting and higher early strength	2
MgO 750-1000°C	Conventional	.403	1.092	1.495	-1.092	.403	Sorel & Magnesium Phosphate cements.	Historic and Conventional Oak Ridge spin offs.	Mg Phosphates potentially v. green.	3
<750 °C	MgCO ₃ + Tec-Kiln	.056		.056	-1.092	-1.036	Eco-cement concrete, pure MgO concretes Novacem concretes	TecEco, Cambridge & Novacem	TecEco Eco-Cement Force carbonated pure MgO	3
<450 °C	MgCO ₃ .3H ₂ O Conventional	.693	1.092	1.784	-2.184	-.399	Eco-cement concrete, pure MgO concretes Novacem concretes?	TecEco, Cambridge & Novacem	Mg Solvay process University of Rome, initial absorption is 1.092	3
<450 °C	MgCO ₃ .3H ₂ O + Tec-Kiln	.038		.038	-2.184	-2.146	Eco-cement concrete, pure MgO concretes Novacem concretes?	TecEco, Cambridge & Novacem	N-Mg route University of Rome	3

	Silicate route							Novacem	After Klaus Lackner?	
CaO	Conventional	.453	0.785	1.237	.785	.453	Carbonating lime mortar	Calera, British Lime Assn. & many others	Small net sequestration with TecEco kiln	4
C3S	Conventional	?	0.578	>0.578	?	>0.578				5
C2S	Conventional	?	0.511	>0.511	?	>0.511	Belite cement	Chinese & others		5
C3A	Conventional	?	0.594	>0.594	?	>0.594	Tri calcium aluminate cement	Increased proportion		5
C4A3S	Conventional	?	0.216	>0.216	?	?	Calcium sulfoaluminate cement	Chinese & others		5
Geo polymers	Fly ash + NaOH	0.16				0.16		Geopolymer Alliance, Geopolymer Institute, University Melbourne		6

Notes to Table 2 - Future Binder Contenders with Differentiated Supply Chain Options

1. <http://www.tececo.com/files/spreadsheets/TecEcoCementLCA20Jan2011.xls>
2. <http://www.tececo.com/files/newsletters/Newsletter93.php>
3. <http://www.tececo.com/files/spreadsheets/TecEcoCementLCA20Jan2011.xls>
4. <http://www.tececo.com/files/spreadsheets/TecEcoCementLCA20Jan2011.xls>
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6. <http://www.geopolymers.com.au/science/sustainability>

Change

Change is inevitable and will be accelerated by carbon taxes and associated trading as they are a source of revenue and policy implementation that governments cannot resist. To ride the wave of change profitably it will be necessary for the industry to learn rapidly and take on the model from that almost guarantees survival and that is that innovation is essential for future profits. Product differentiation will also lead to higher margins.

Future Challenges

Fireproofing Houses

One salutary lesson from bushfires is that we cannot continue to make houses like pizza ovens as we have done for years. The challenge is to develop fireproof insulating materials for the outside and magnesium binders are a strong contender for this because of their ability to bond to just about anything. Thermal capacity could then be used on the inside where it should be for better thermal performance

Thermal Performance

Given rising energy costs it is imperative we design houses with better thermal performance. New composites incorporating waste streams with low thermal flow characteristics will be part of this future (e.g. sawdust blocks)

Housing for the poor in the Third World

New cheaper better binders allowing a much greater range so fillers and aggregates are essential to meet the challenge of housing for the third world.

Earthquake Resistance

Introducing more tensile strength using reactive magnesia is essential for the improving earthquake resistance.

Use of Wastes

It is logical to utilise wastes for their chemical and physical properties and magnesium based binders are uniquely excellent for this purpose because their strong polar bonding capacity.

Reduced Energy Consumption

Reduced process energy requirements will help drive the development of new processes

Conclusions

There is a huge archive of performance based information on Portland cements and relatively little is known about other new cements except perhaps geopolymers. This lack of data is a major barrier to uptake. It is time cement companies took their heads out of the sand and adopted the model from most other industries whereby profitability is understood to be a function of research and development and the release of new product. For example at this point in time very little is known about the effect of adding reactive magnesia to derivative and variant hydraulic cements such as belite – sulphoaluminates or calcium aluminates. Would doing so fix known issues such as rate of set, stability and dimensional issues? These and other important questions need to be answered

Differentiation of product based on properties 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 products for the outside of buildings. As mentioned the major barrier will of course be out dated prescription based standards.

John Phair was right when he 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. (8)

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