TecEco Pty. Ltd.
Sustainable Technologies

Low Carbon Cements and Concrete in Modern Construction

Gaia Engineering
www.gaiaengineering.com

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

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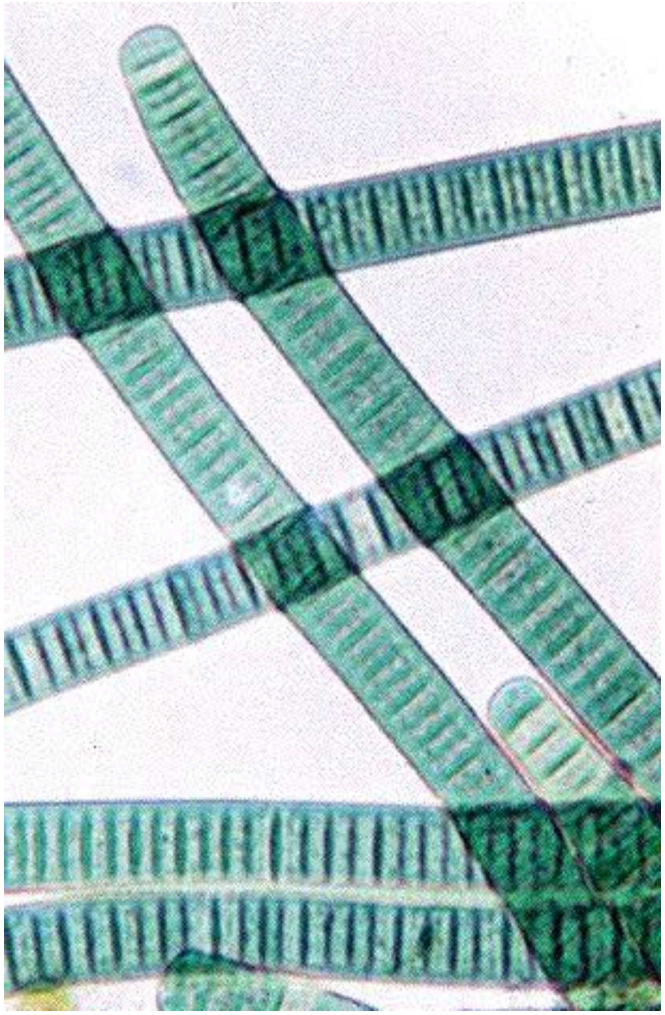
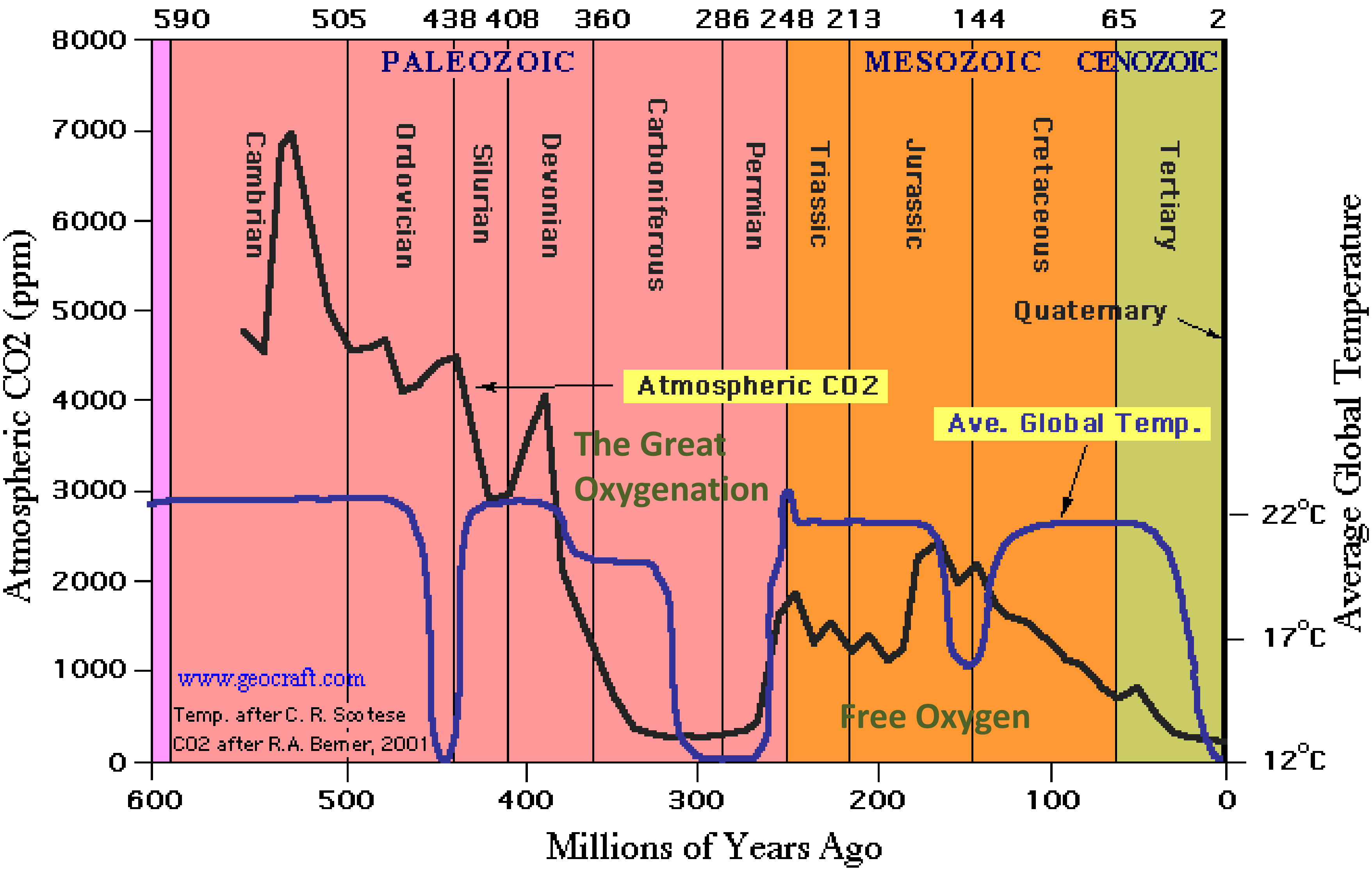
A Brief History of How Life on Earth Controls the Climate



- The first life on earth began about 3.5 billion years ago.
- The first oxygen was released by cyanobacteria.
  - Initially consumed by free iron in the oceans and precipitated to form iron ore.
  - Then started forming our atmosphere about 2.4 billion years ago.
  - Chloroplasts in plants evolved from them.
  - Life has controlled climate ever since

Paleoclimate



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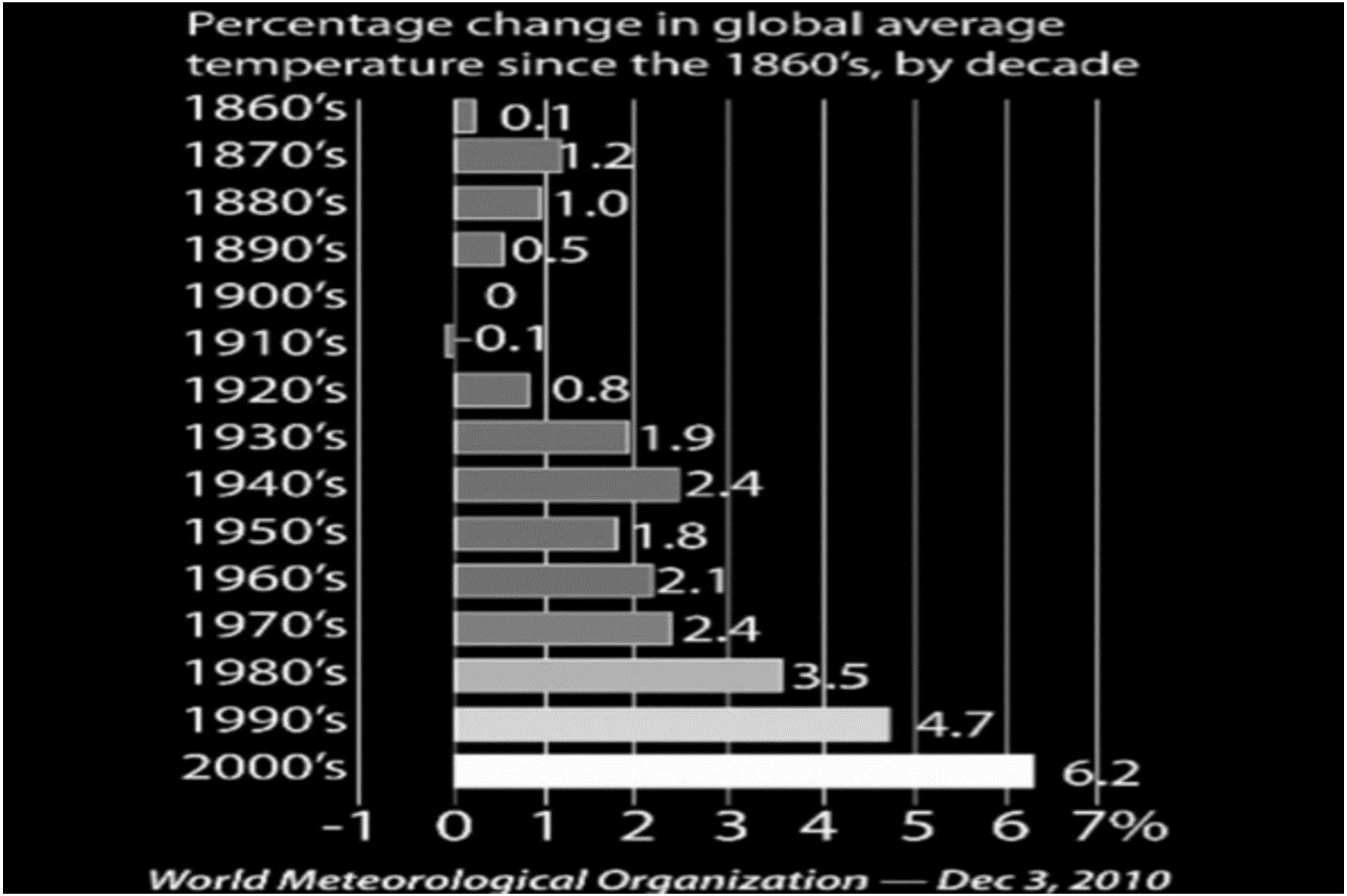
The Industrial Revolution – Machines

The Result - A Rising Rate of Warming



Net Atmospheric Emissions

For Global Anthropogenic Emissions:

According to recent research published in *Nature*, carbon emissions from burning fossil fuels and producing cement reached 9.1±0.5 Pg Carbon (9.1 billion tonnes carbon, or 33 billion tonnes carbon dioxide) in 2011.

Source: Peters, G.P., Marland, G., Le Quere, C., Boden, T., Canadell, J.G. and Raupach, M.R. 2012. Rapid growth in CO2 emissions after the 2008-2009 global financial crisis, Nature Climate Change, 2: 2-4

For Portland Cement:

Using the latest figures available which are from the Chinese Ministry of Environment Protection (MEP 2011) and they agree with the numbers I have from our LCA model.

877 kg of CO_2 are emitted for every tonne of Portland cement clinker produced, 820 kg from direct processes and 57 kg from indirect sources (the burning of coal for the electric power needed). MEP also estimates that waste heat recycling in the industry saves 16 kg CO_2 emissions – making 861 kg for each tonne of cement produced This is close to the figure TecEco have in their LCA downloadable under Downloads\Tools on the TecEco web site. Using these figures, the production of 3.4 billion tonnes cement would thus lead to emissions of 2.9 billion tonnes CO_2.

The current contribution of cement production globally is therefore 2.9/33 x 100%, or 8.8%.

The Techno Process

Extract, Process, Build, & Manufacture, Use, Dispose

Underlying Molecular Flows

Extract	**Process, Build & Manufacture**	**Use**	**Dispose or Waste**
Methane NOX & SOX Heavy Metals CO_2 etc.	NOX & SOX Heavy Metals CO_2 etc.	NOX & SOX Heavy Metals CO_2 etc.	Methane NOX & SOX Heavy Metals CO_2 etc.
Embodied & Process Energy	Embodied & Process Energy	Lifetime Energy	Process Energy

These are the releases and impacts we look at with LCA and LCCA

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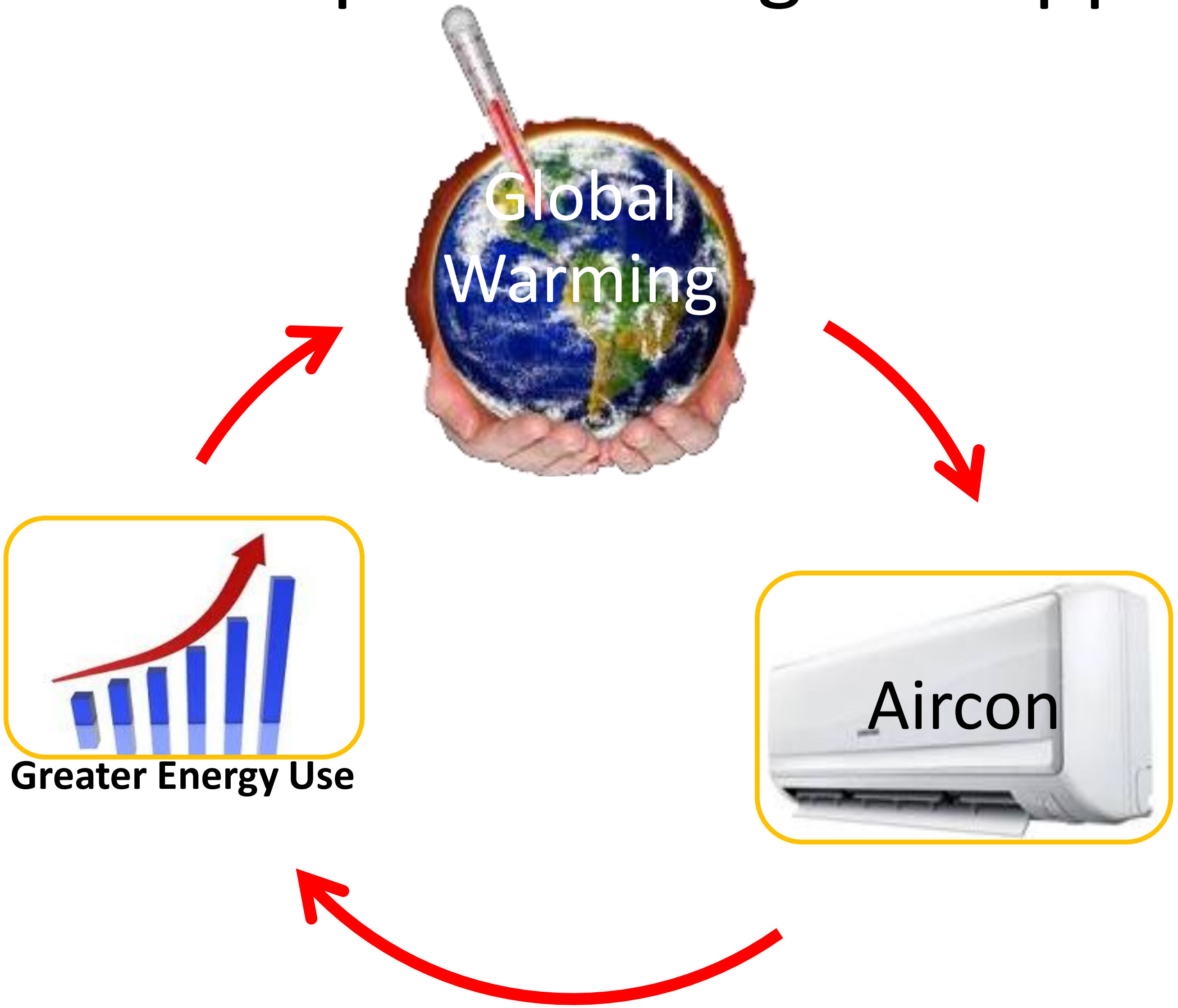
A Doom Cycle or Environmental Catastrophe Waiting to Happen?



"We have to find a way through this debacle"

Wouldn't it be Great if we Could Add Technical Value to Wastes.

The technical paradigm defines what is or is not a resource!

Wastes have physical and chemical properties that add value in composites!

Reactive magnesia as an additive to Portland cement that improves polar bonding and sticks to just about any waste.

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We Can Add Technical Value to Wastes – Including CO_2 – and Improve Concrete as a Material doing so!

The Indian Culture is the right base to start from but we need to dig into our minds

By Adding Value to Wastes –Jobs are Created. The Lifetime as well and Embodied Energy Performance of Concretes can be Improved.

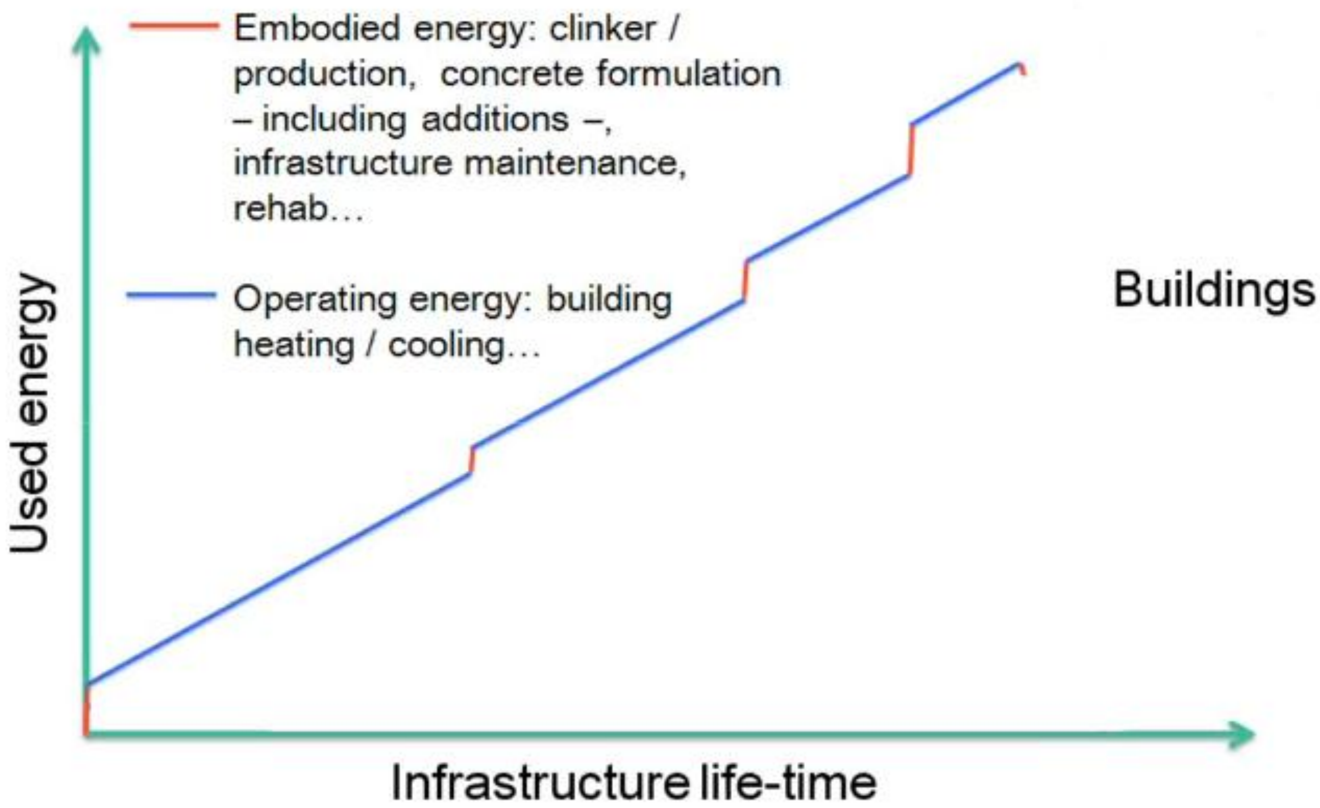
Many people can live much better if we can find ways of technically using wastes for their physical and chemical properties thereby turning them into resources and in so doing adding to their value.

We can do this and reactive magnesia (rMgO) is the technical key but it needs to be much cheaper.

Huge Potential for Doing it Better

- All that is grey is not great.
  - We not only need to think not only whole of concrete but expand our thinking to all composites utilising any mineral binder.
- The rising cost of energy will determine that
  - The future is for mineral composites
    - In which wastes including CO2 add useful properties such as fire resistance, tensile strength, thermal capacity or resistance.
    - Cementitious composites will be important if we are to reduce lifetime energies as required by the IEA Cement 2050 Roadmap.

Embodied Energy and Emissions over Time



The properties of materials chosen have a big influence on the lifetime or operational energies of buildings.

$$E_{emb} = \alpha\, E_{oper} \text{ with } \alpha = 10\ \% \text{ at } 70\ y$$

[13] Source: Slide in presentation by Prof Roland Pellenq, MIT Concrete Sustainability Hub

Conclusions from Introductory Slides.

- 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".
  - Cementitious composites 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 paradigms.
- A fundamental truism of industrial ecology is that the technology paradigm defines what is or is not a resource.
- A broader range of cementitious composites will be required if we are to dramatically reduce lifetime energies of buildings
- There is a way to profitably capture and store CO_2

  – more to follow

Concrete Today

- The mineral composite we build with.
- Next to water the most used.
  - Global 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%[1] of total anthropogenic carbon emissions.
  - 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.[2]

[1] MEP. Technical Requirements for Environmental Labeling Products: Low-carbon Cement (Discussion Paper) [Internet]. Ministry of Environment Protection, China; 2012. Available from: http://www.mep.gov.cn/gkml/hbb/bgth/201112/W020111208396803781008.pdf (in Chinese).

[2] USGS. Mineral Commodity Summary - Cement [Internet]. 2012, (2012):Available from: http://minerals.usgs.gov/minerals/pubs/commodity/cement/mcs-2012-cemen.pdf.

Construction and Concrete

- Buildings account for ~40% of the materials and ~33% of the energy consumed by the world economy. [3]
  - 7 billion M3 per annum [2]
  - 5% - 10% of CO_2 emissions depending on the authority.
- Concrete infrastructure expenditure a huge investment for governments at all levels but has high multipliers in an economy.
- A cost cutting volume business model for many players in the supply chain. Arguably models should be innovation based.
- Concrete production and use a good indicator or the state of a country's economy.
- Already one of the most environmentally friendly building materials – significant improvements are possible however.

[3] Rees, W. E. (1999). The Built Environment and Ecosphere: A Global Perspective. Building Research and Information. British Columbia, William E Rees. 27: 206-220
[4] Wallenvik, Olafur, Carbon Footprint of High Performance Versus Conventional Vibrated Concrete

We Can Recycle Safely and Profitably in Concrete !

- Cementitious composites are a safe repository for wastes <u>provided we regulate the pH</u> for the minimum solubility of heavy metals.
  - The use of rMgO in hydraulic cement compositions achieves this.
  - Somebody please tell the EPA in the US!

- Waste CO_2 and waste magnesium ions can be combined to form magnesium carbonates which can be the foundation of manufactured aggregates that can be combined with vast volumes of other wastes because of their polar nature.
- I use the word "can" because all my company needs is money.

The Good News!

- 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 sink for CO_2 and other wastes in aggregates and I will explain this as I go through the options and issues for cement and concrete in modern construction.
- The IEA Cement 2050 Roadmap mentions carbon capture and storage and significant reductions in operational or lifetime energies.
  – Our Gaia Engineering is a technically feasible profitable way forward.

Drivers for Innovative Change

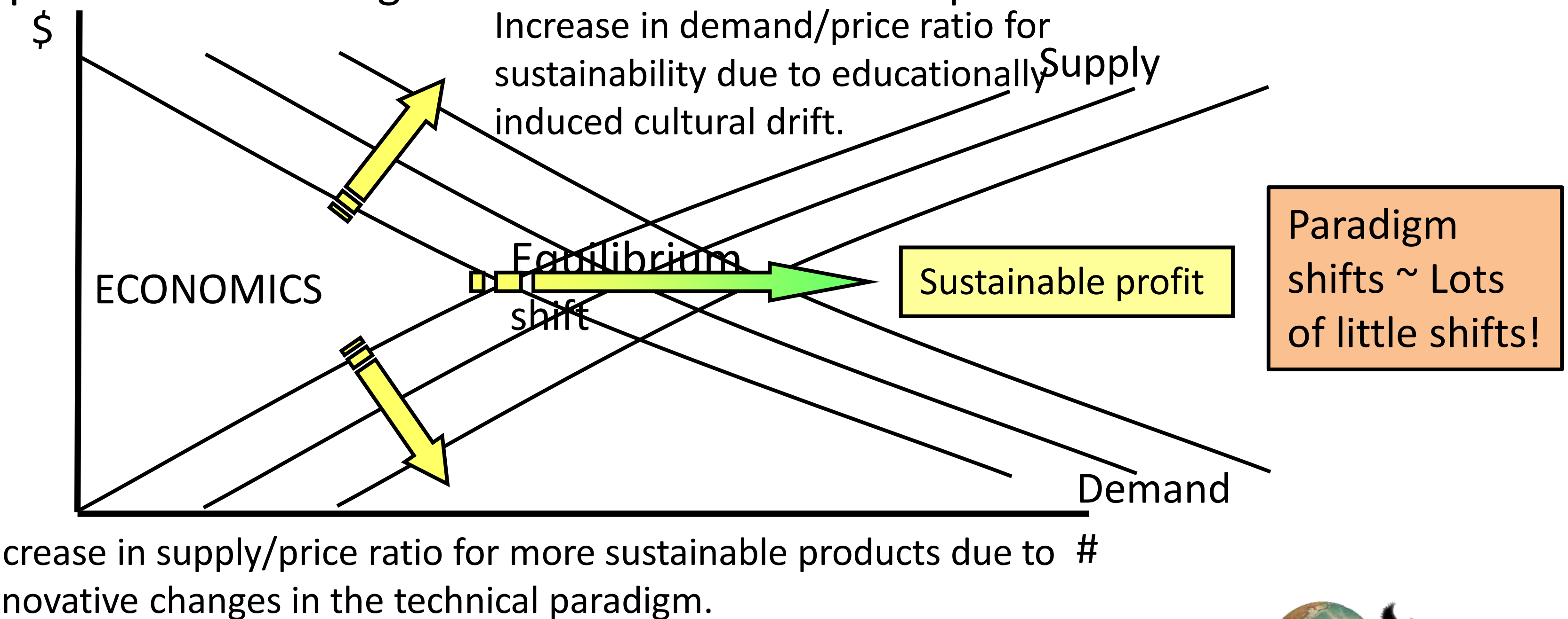
- Stakeholder demands for greater sustainability
  - Brundtland definition and triple bottom line.
  - The precautionary principle & intergenerational equity
  - Every improvement counts but paradigm improvements really matter – If implemented!, but
  - Quick fixes = paradigm changes
- Economic Cost Benefit given
  - Rapidly rising energy costs
  - Carbon taxes
    - Construction activities contribute over 35% of total global CO_2 emissions[3] so carbon taxes will have a big impact.
- > Sustainability can deliver > profit.
- Competition – Leed, the Green Building Council etc.
- Improved technical understanding and practice
- Government research and development as well as procurement policies
- The need to change!

Legislation and control will not get us there. Changing technical paradigms will.

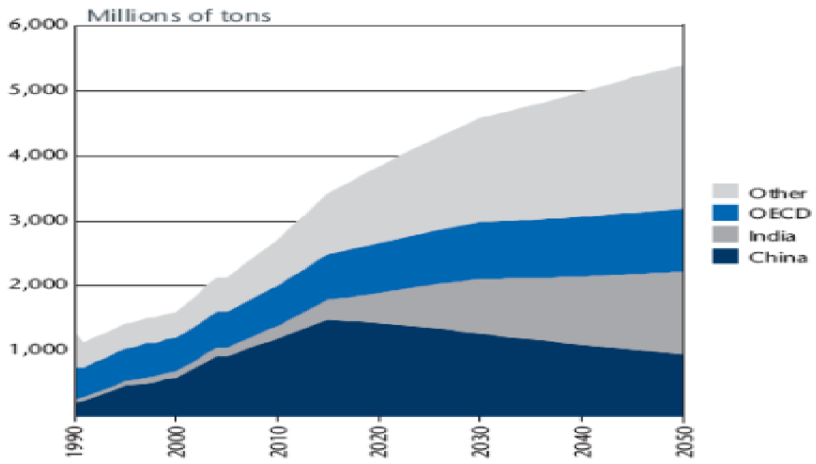
[3]UNEP (2001). Energy and Cities: Sustainable Building and Construction Summary of Main Issues, IETC Side Event at UNEP Governing Council, Nairobi, Kenya, UNEP.

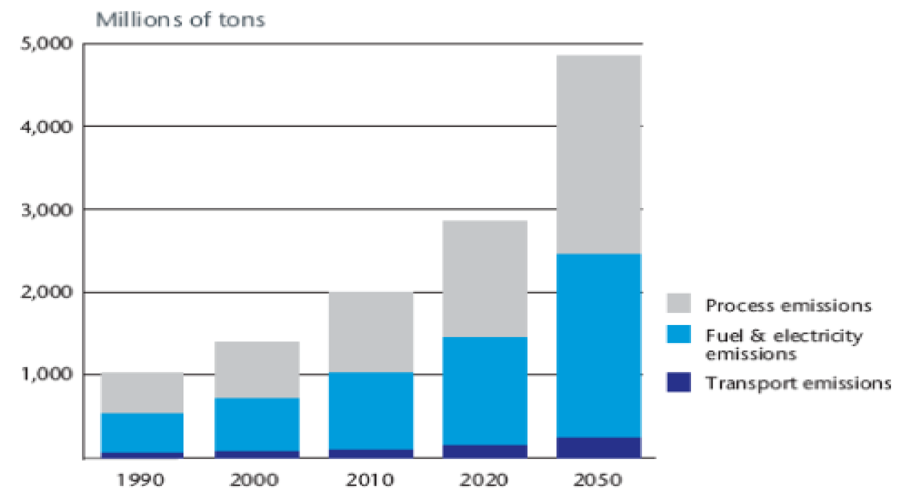
Better more cost effective concrete is more sustainable

- Concrete is not a perfect material yet. E.g. It shrinks, it cracks, it is not as durable as we would like and has a limited range of properties.
  - See how we fix many these issues in Part 2 - the section on reactive MgO
- Better concrete is not hard to make and there are huge opportunities for change
- Improvements through innovation = Sustainable profit!



Predicted Global Cement Demand, Emissions and Compositional Change

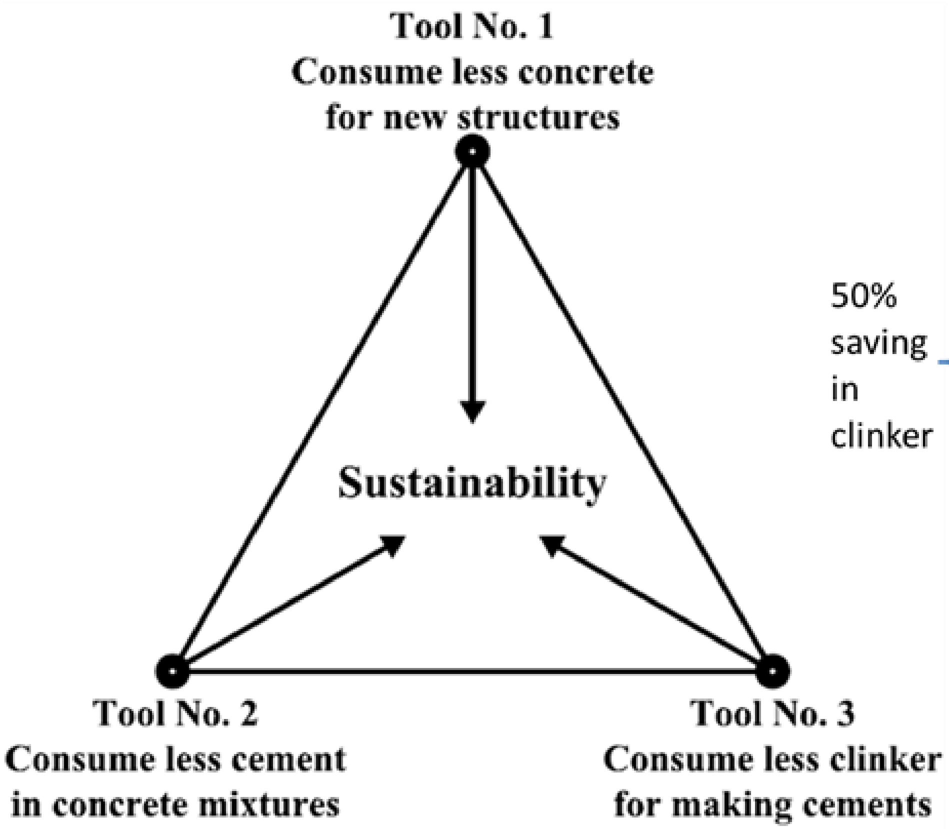




- According to the British Research Establishment (BRE) we cannot address de-carbonation without changing the composition of cement and fuel derived emissions will diminish slowly for purely economic reasons [1]
- The BRE may be wrong however. The composition of cement does not have change so much as the composition of concrete. Cement is only around 10% of concrete. **At TecEco we believe Portland cement is here to stay if rectified the way we say!**

[1] Quillin K. Low-CO2 Cements based on Calcium Sulfoaluminate [Internet]. Available from: http://www.soci.org/News/~/media/Files/Conference%20Downloads/Low%20Carbon%20Cements%20Nov%2010/Sulphoaluminate_Cements_Keith_Quillin_R.ashx

Mehta's Triangle



50% saving in clinker

30% saving in cement

1. **Consume less concrete**

Dematerialisation

2. **Consume less cement**

Longer period for strength, better particle packing. Etc.

2. **Consume less clinker**

Replacement by pozzolans and SCM's

Mehta summarised some of the techniques for dematerialisation[1] but did not consider the effect on lifetime energies

[1] MEHTA PK. Global Concrete Industry Sustainability. Concrete International. 2009, **Vol 31**(2):4.

Ways to make Cement and Concrete More Sustainable.

Option	Description	Players	Drivers	Barriers	Standards & Guides
Alternative Binders	Numerous and described in Table 2 - Future Binder Contenders with Differentiated Supply Chain Options	Scientists (Cement Chemists)	Sustainability and profit.	Conservatism, out dated software. Prescription standards and approvals systems (see http://www.tececo.com/sustainability.permissions_rewards.php.)	A few guides and draft standards (e.g. with Geopolymers)
CO_2 Capture during Manufacture	Reduce process emissions. Cements that involve calcination can be made without releases.	Scientists. TecEco and Calix.	Sustainability, carbon taxes.	Inability to think laterally. Fear of change	Common sense!
Replacement of Portland cement by Limestone	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.	Cement technol-ogists	Economic cost/benefit, sustainability, Leed, GBC, r & d & procurement Policies.	Buyer hesitancy.	New standards emerging because industry driven.

Ways to make Cement and Concrete More Sustainable.

Option	Description	Players	Drivers	Barriers	Standards & Guides
Replacement of cement by SCM's	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.	Cement technologists	Economic cost/benefit, sustainability, Leed, GBC, R & D & procurement Policies.	Conservatism, out dated software. Prescription standards and approvals systems (see http://www.tececo.com/sustainability.permissions_rewards.php.)	Mix design methods. LCA & LCCA. New better software.
Dematerial-isation	Innovative architecture and engineering. More durable concretes. $KgCO_2^e/MPa$	Architects & Engineers	Economic cost/benefit, sustainability, Leed, GBC, r & d & procurement Policies.	Prescription standards and approvals systems (see http://www.tececo.com/sustainability.permissions_rewards.php.)	Design codes, LCA & LCCA

Ways to make Cement and Concrete More Sustainable.

Option	Description	Players	Drivers	Barriers	Standards & Guides
Mix Optimisation	Appropriate particle packing, better admixtures and use of Brucite hydrates to release water for more complete hydration	Cement technologists	Economic cost/benefit, sustainability.	Conservatism, inappropriate software. Prescription standards and approvals systems (see http://www.tececo.com/sustainability.permissions_rewards.php.)	Mix design methods. LCA & LCCA. New better software.
Product Differentiation and Specialisation	Mineral composites other than concrete with just stone aggregate can improve sustainability. E.g. composites with a high "R" value	Materials scientists	Economic cost/benefit	Inability to think outside the box. Fear of change	Standards, LCA & LCCA
Changing the emphasis	An emphasis other than on the binder to improve sustainability. E.g. Use of synthetic carbonate aggregate.	Scientists	Sustainability, economic cost/benefit. Technical merit	Inability to think outside the box. Fear of change. Technical issues (?).	Common sense!

Ways to make Cement and Concrete More Sustainable.

Option	Description	Players	Drivers	Barriers	Standards & Guides
The Right Business Model	Although not a technical matter the right business model is essential for progress to be made.	Consultants	Profitability in a changing business environment	Conservatism, standards and legislative environment.	
The Right Framework to Operate in	Legislative restrictions and standards throughout the world are prescriptive in nature and this and a lack of training is holding back innovation	Consultants	The need to change	Conservatism, inability or unwillingness to change.	

	Critical
	Important
	Relevant
	A Furphy

Alternative Binders (A Summary)

- Hydraulic Cements
  - Slag-lime or slag – Portland Cement (PC) cements
  - Calcium sulfoaluminate cements & belite calcium sulfoaluminate cements
  - Calcium aluminate cements
  - Belite cements
  - Reactive magnesia blended with other hydraulic cements and Supplementary Cementitious Materials (SCM's)
- Chemical Cements
  - Magnesium Phosphate Cements

Alternative Binders

- Carbonating Cements
  - Reactive Magnesia Based Carbonating Binders
  - Lime Based Carbonating Binders
- Other Cements
  - Geopolymers
  - Sialites

Please see pages 7 - 9 and Table 2 in the paper "**LOW CARBON CEMENTS AND CONCRETE IN MODERN CONSTRUCTION" UKIERI Conference, Jalandhar, India 5 – 8 March 2013.** for advantages, limitations, associated energies, supply chain options and more detail !

The LCA spreadsheet we used to calculate energies and emissions is on our web sites covering hydraulic binders and soon there will be a LCCA!

Alternative 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[1] 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[2].

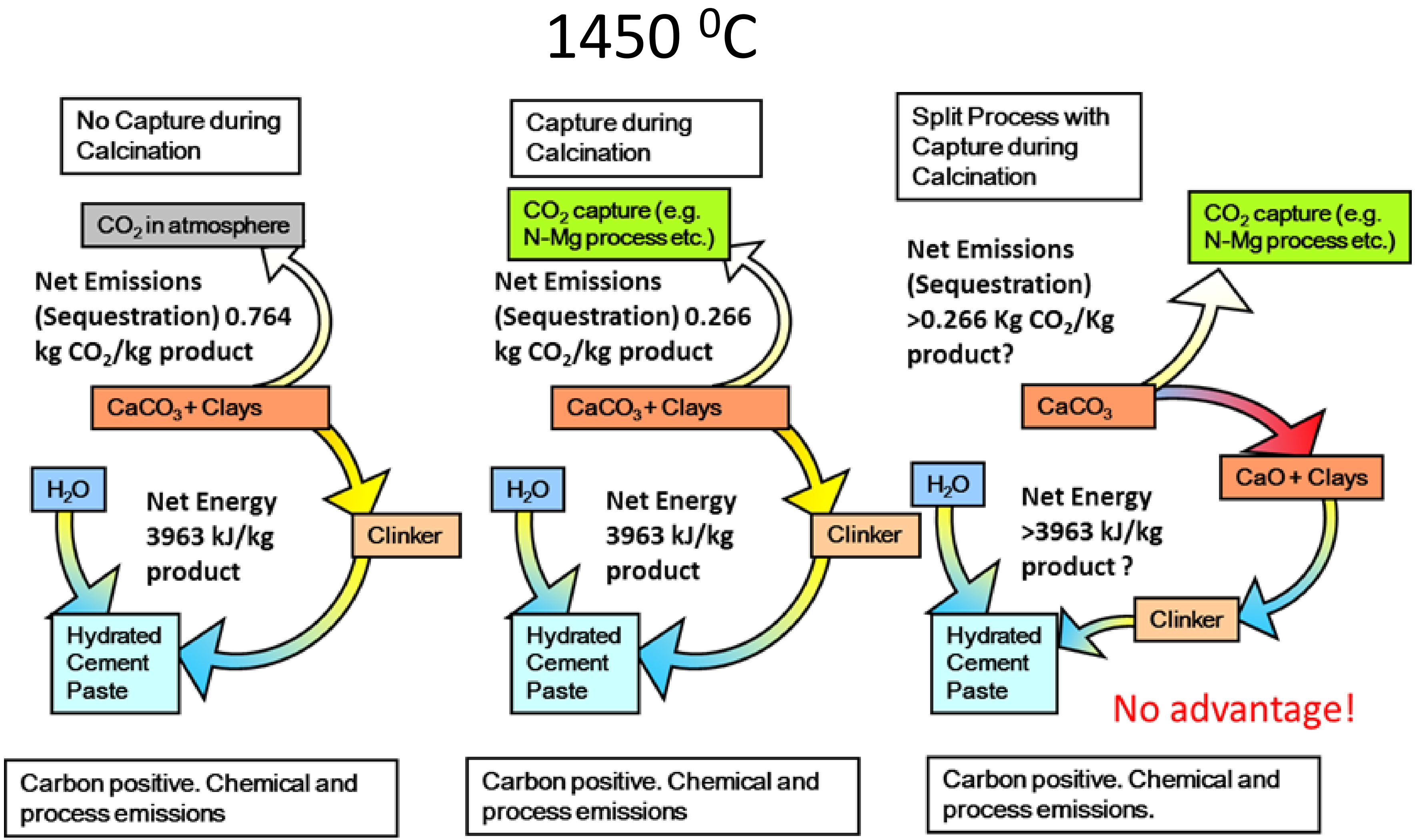
[1]Mcgrath T M Sustainable cement and concrete. Concrete in Australia. 2012, **38**(1):15-15.
[2]Pers comm. WA (Tony) Thomas – Chief Engineer Concrete, Boral Construction Materials

Manufacturing taking Advantage of full Thermodynamic Cycles

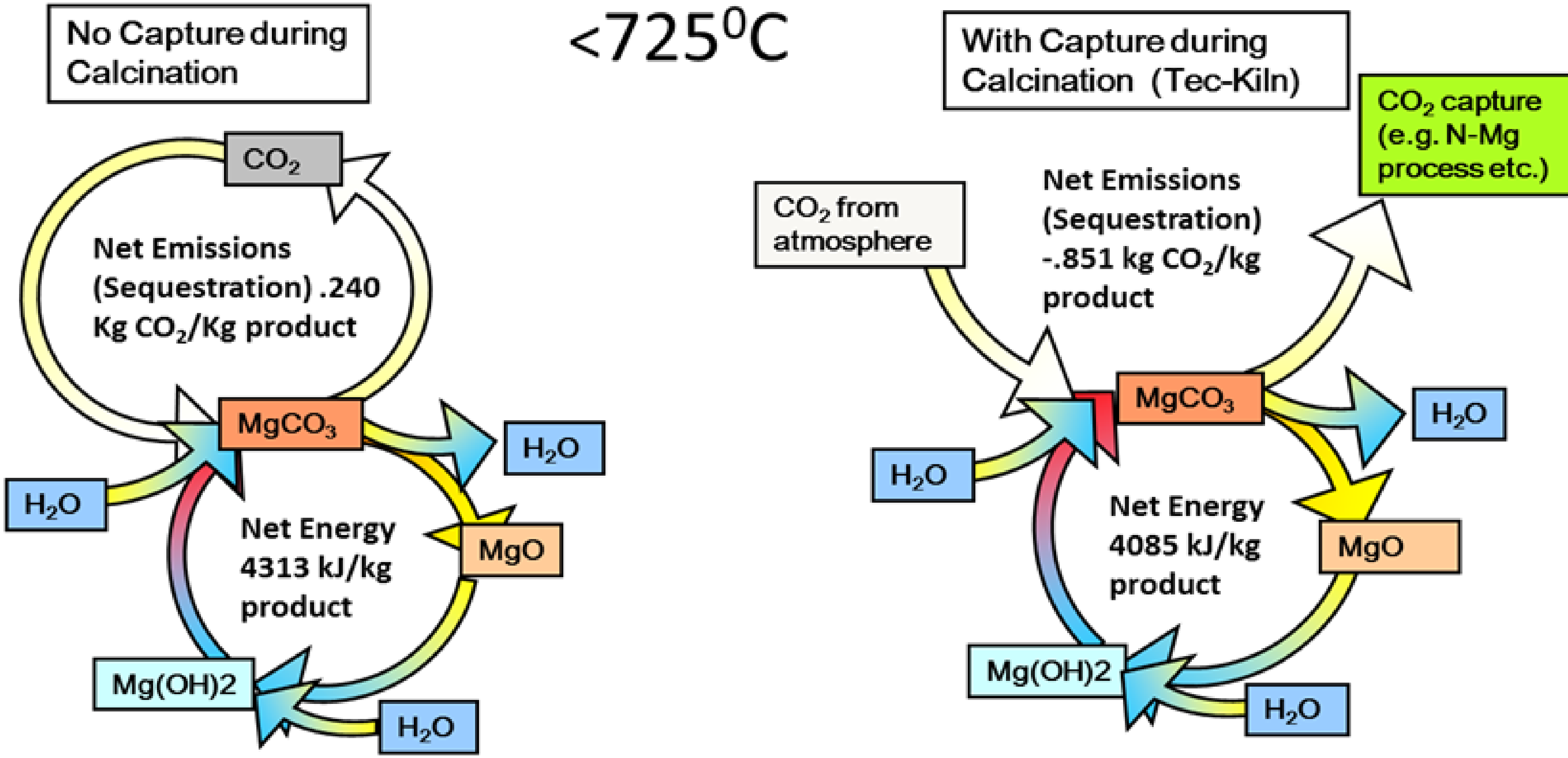
- The manufacture and use of Portland cement does not involve a full thermodynamic cycle.
  - there is therefore little point in splitting the process into the endothermic and exothermic sub processes with one or two exceptions such as the manufacture of Syngas[1].
- There is however a great deal of merit in capturing CO_2 during manufacture and our Gaia Engineering focusses on how to do this profitably in a sustainable way.

[1] Dr Sheila Devasahayam at the SMaRT Centre, School of Materials Science and Engineering, The University Of New South Wales, is researching pyroprocessing CaCO3 with an additive to produce Syngas

Options for Portland Cement Manufacture



Options for Carbonation Binders like TecEco Eco-Cement are Greater



Carbon neutral except for carbon from process emissions

Net sequestration

Capture During Manufacture

- Significant sequestration can be achieved with capture of CO_2 from cement and lime kilns which are a concentrated point source.
  - Recognised as important by the IEA Cement 2050 Roadmap.
  - The problem, which has not been solved yet for any form of sequestration, is what to do with the enormous volume of CO_2 produced
  - TecEco have developed the **N-Mg** sub-process of **Gaia Engineering** that will profitably sequester huge amounts of CO_2 as synthetic carbonate that can be used as aggregate with or without other wastes and / or as feedstock to make rMgO for our patented cements.

Gaia Engineering

www.gaiaengineering.com

A Solution to Global Warming

Gaia Engineering and the new TecEco "N-Mg" process to profitably sequester massive tonnages of CO_2 in the built environment as synthetic carbonate concretes.

This presentation is available for download on our web sites shown below

Gaia Engineering

- We realised that the answer to the worlds problems lay in an industrial ecology that utilised wastes including CO_2 and bitterns, de-sal waste water or oil process water to create valuable products for the worlds biggest market which is building and construction.
- By including the manufacture of not only TecEco patented cements but aggregates in the concept of synthetic carbonate built environment a solution to global warming can be achieved.

TecEco have changed the technical paradigm in favour of making CO_2 and other wastes resources

Gaia Engineering Summary

Gaia Engineering
www.gaiaengineering.com

- 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 ($MgCO_3.3H_2O$) from waste magnesium cations such as found in oil process water, bitterns and waste from de-sal plants 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 CO_2 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 with or without other wastes such as fly ash to make synthetic carbonate aggregate or in TecEco Eco-Cements where it re carbonates (step 3).

The Concept of a Carbonate Built Environment

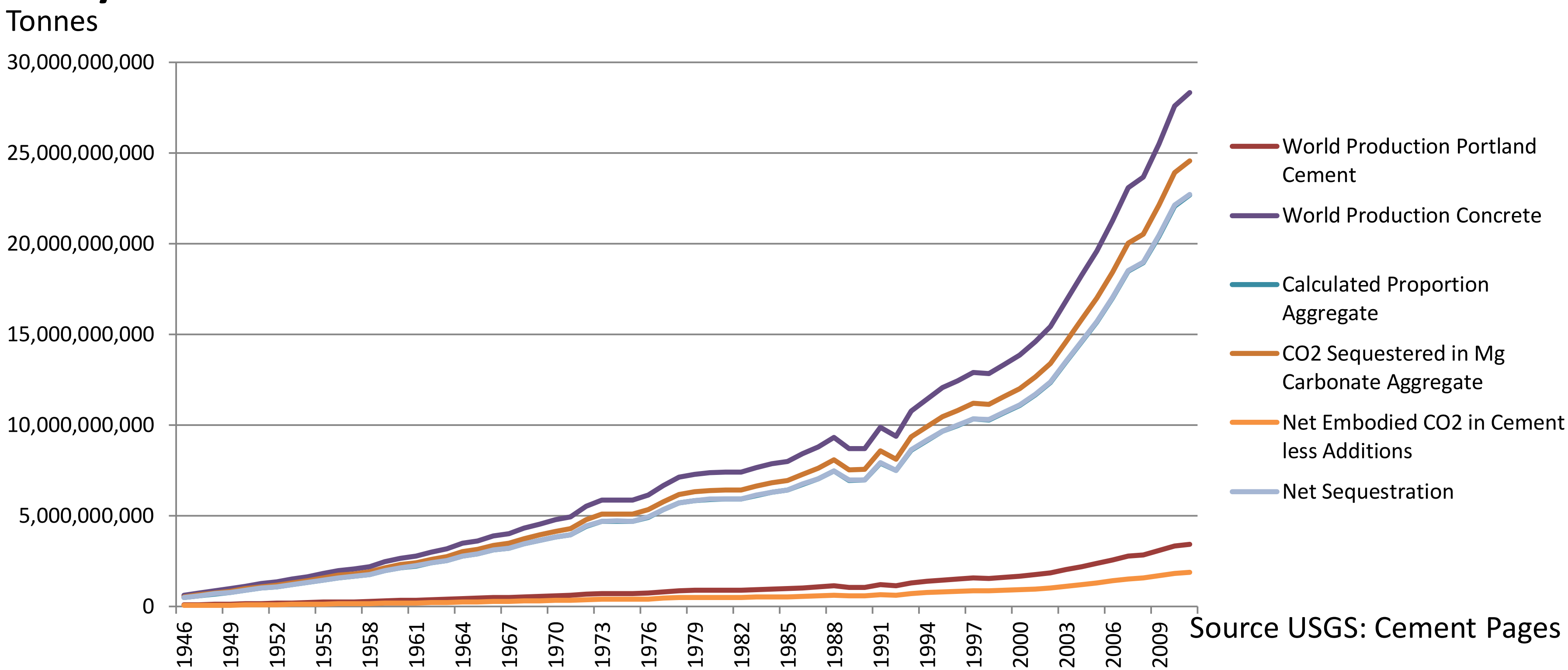
John Harrison from TecEco has for many years been advocating the carbonate built environment solution to global warming

13th July 2002 – Fred Pearce in New Scientist about TecEco magnesium cement technology:

"THERE is a way to make our city streets as green as the Amazon rainforest. Almost every aspect of the built environment, from bridges to factories to tower blocks, and from roads to sea walls, could be turned into structures that soak up carbon dioxide- the main greenhouse gas behind global warming. All we need to do is change the way we make ~~cement~~." (By including aggregates and considering concrete as a whole the potential for sequestration is much greater.)

All we have to do is change the way we do things and do what a big old tree does – make our homes out of CO2.

The Sequestration Potential for Synthetic Carbonates in Concretes



Source USGS: Cement Pages

Assumptions		
Tec-Cement concrete with synthetic magnesium carbonate aggregate		
Percentage by weight of cement in concrete	12.00%	
Percentage by weight of rMgO in Tec-Cement	9%	
Percentage by weight Ca(OH)2 in cement	29%	
% of Ca(OH)2 in concrete that carbonates	10.00%	
Proportion cement that is fly ash and/or GBFS	20%	
1 tonne Portland Cement	0.867	Tonnes CO2
Proportion concrete that is aggregate	80.0%	
CO2 captured in 1 tonne aggregate	1.084	Tonnes CO2
Net CO2 sequestration 1 tonne rMgO (N-Mg route, 1 complete recycle)	1.794	Tonnes CO2
CO2 captured hydration and carbonation of 1 tonne CaO (in PC)	0.785	Tonnes CO2

The Viability of Sequestration Technologies

- A viable Sequestration Technology must be:
  - Simple
  - Scalable
  - Have low up front capital costs (post combustion)
  - Low environmental impacts
  - Produce saleable products with insatiable markets
  - Easily implemented and
  - Deployable over a wide geographical area
- It should also ideally
  - Be industrially symbiotic and
  - address one or more other major problems facing the planet.

ECRA Concepts – Not Viable

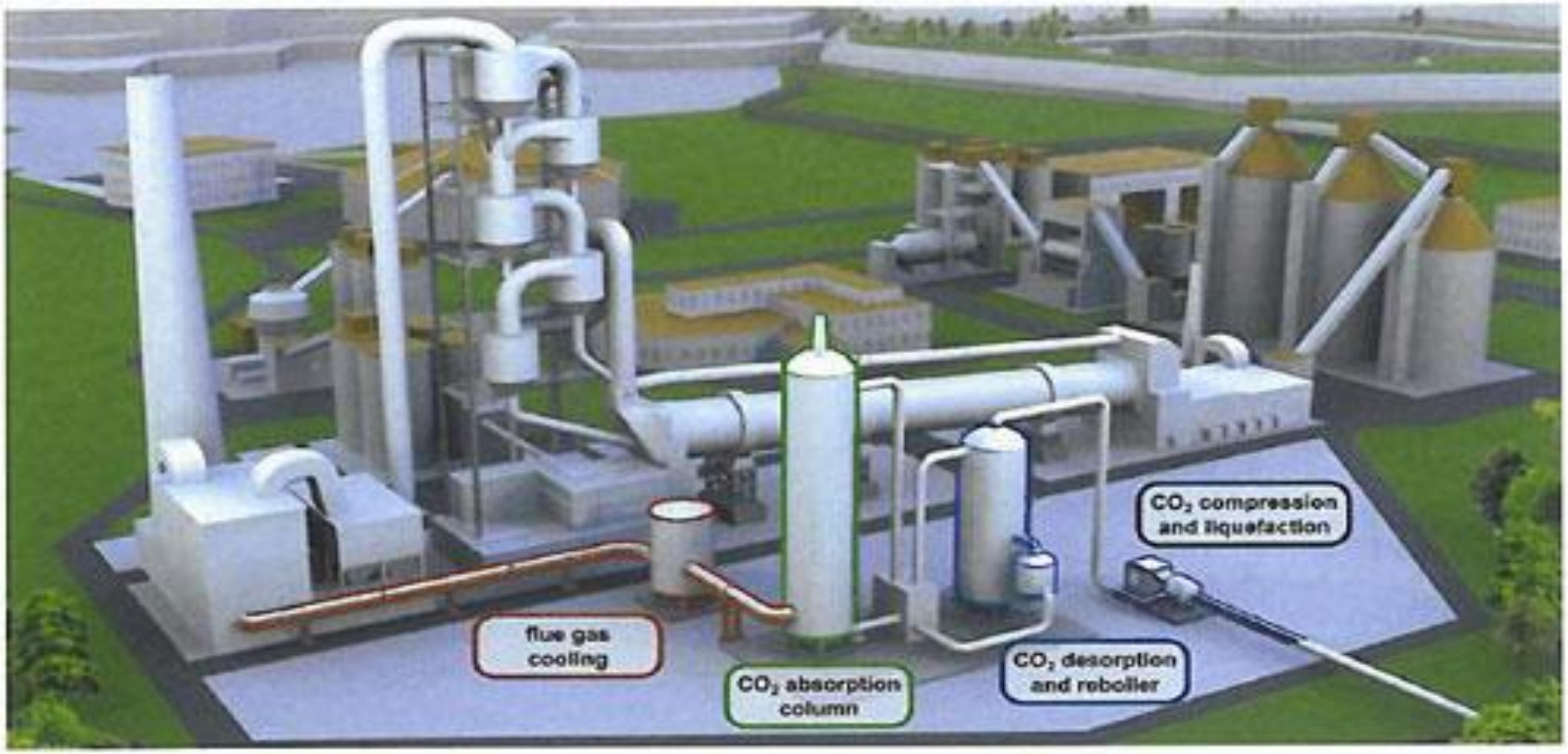


Figure 1. General arrangement of post-combustion CO_2 capture in a cement plant. The full animation can be seen at www.ecra-online.org.

No efficient means of capture, no viable means of storage.

Oxyfuel combustion ridiculously expensive

http://cement.mineralproducts.org/special_features/a_carbon_capture_and_storage.php

Viability of Gaia Engineering

- Gaia Engineering satisfies all the criteria set on the previous slide and is a magnificent example of industrial ecology in action.
- It can utilise many waste streams and nothing is produced that cannot be utilised.
- It is the only potentially profitable solution.
- There are environmental advantages not impacts.

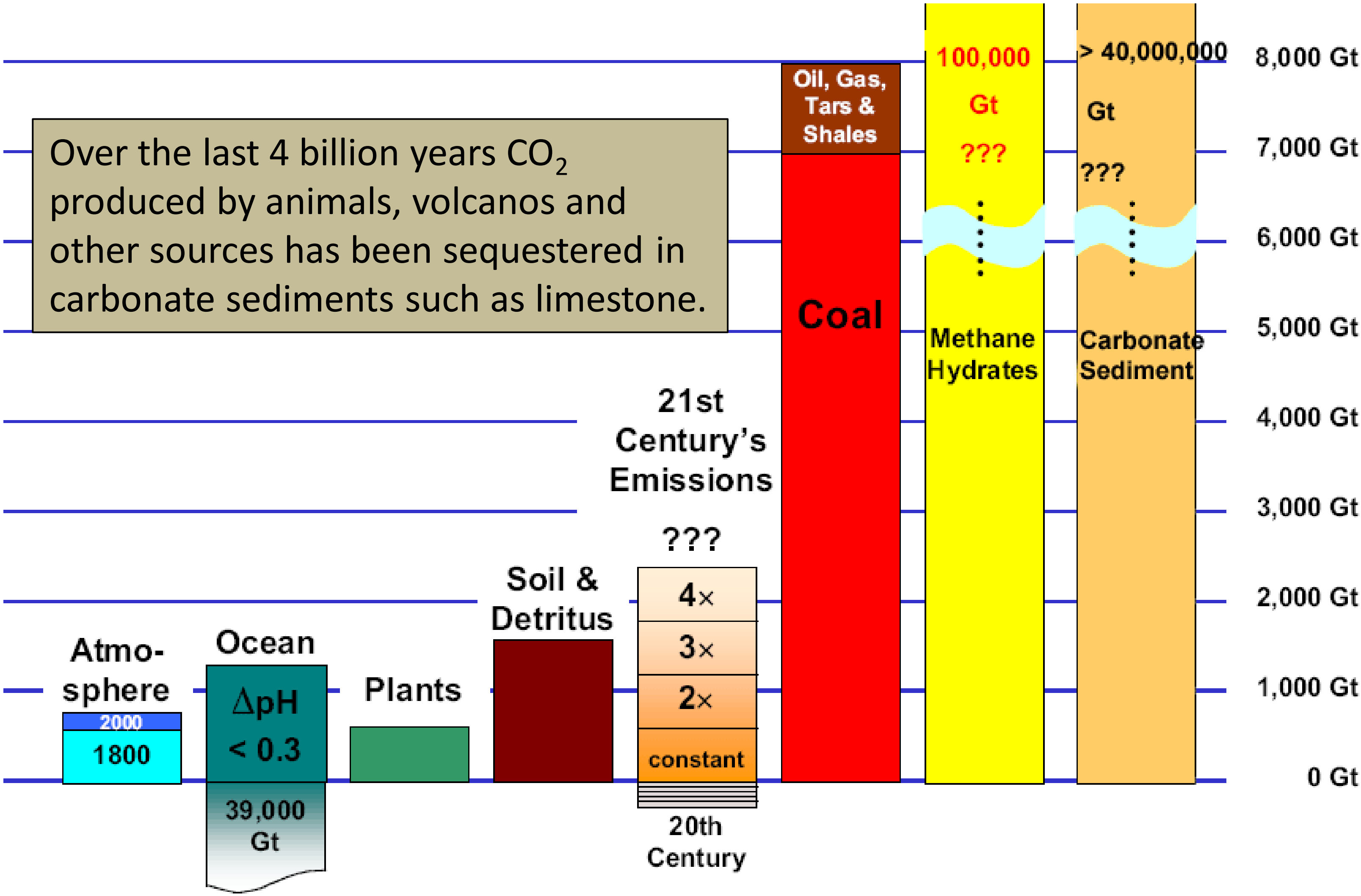
Gaia Engineering

- The process is scalable and can use intermittent energy from non fossil fuel sources. It can add value using the energy available without having to store it. Gaia Engineering can produce synthetic carbonate concrete and building products with it.
- The built environment represents what we do on this planet and is a large insatiable market for synthetic carbonate building products at the right price.
- Gaia Engineering addresses other problems such as waste utilization and the production of cleaner water.

Why is Gaia Engineering Low Cost?

- Gaia Engineering has much lower costs than older processes such as developed by NETL some years ago because:
- There are less process steps.
  - Gaia Engineering involves no mining, no transport, no grinding and no need to process silicate.
- No wastes are produced that cannot be used or recycled.
- The output from the process is saleable.
- A draft LCCA will soon be on our web sites

Natural Carbon Sinks

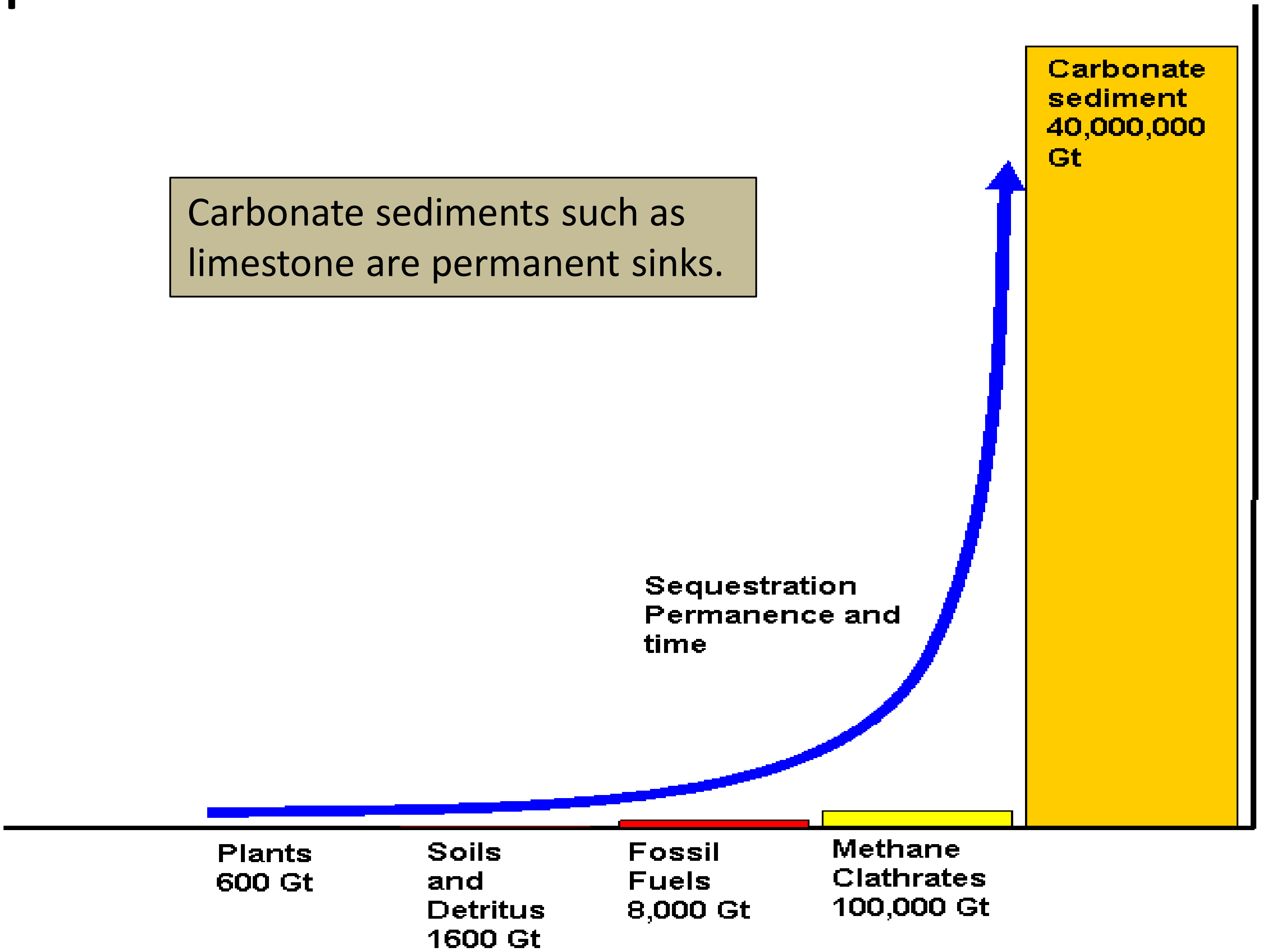


Carbon Sinks and Anthropogenic Actual and Predicted Consumption of Carbon

Modified from Figure 2 in Ziock, H. J. and D. P. Harrison. "Zero Emission Coal Power, a New Concept." from http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/2b2.pdf. by the inclusion of a bar to represent sedimentary sinks.

Sequestration Permanence

Carbonate sediments such as limestone are permanent sinks.



Data from Figure 2 in Ziock, H. J. and D. P. Harrison. "Zero Emission Coal Power, a New Concept." from http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/2b2.pdf. by the inclusion of a bar to represent sedimentary sinks.

What Carbonate?

The following table lists principal metal oxides of Earth's Crust. Theoretically up to 22% of this mineral mass is able to form carbonates.

Oxide	Percent of Crust	Carbonate	Enthalpy change (kJ/mol)	Comment
SiO_2	59.71			Too difficult
Al_2O_3	15.41			Too difficult
CaO	4.90	$CaCO_3$	-179	Feasible
rMgO	4.36	$MgCO_3$	-117	Feasible
Na_2O	3.55	Na_2CO_3		Too soluble
FeO	3.52	$FeCO_3$		Too difficult
K_2O	2.80	K_2CO_3		Too soluble
Fe_2O_3	2.63	$FeCO_3$		Too difficult
	21.76	All Carbonates		

Table Source: http://en.wikipedia.org/wiki/Carbon_sequestration

Magnesium Carbonates

- Because of the low molecular weight of magnesium, it is ideal for scrubbing CO_2 out of the air and sequestering the gas into the built environment:
- More CO_2 is captured than in calcium systems as the calculations below show.

$$\frac{CO_2}{CaCO_3} = \frac{44}{101} = 43\%$$

$$\frac{CO_2}{MgCO_3} = \frac{44}{84} = 52\%$$

- At 2.09% of the crust magnesium is the 8th most abundant element
- Sea-water contains 1.29 g/l compared to calcium at .412 g/l. Many brines contain much more.

Seawater Reference Data	g/l H_20	Cation radius (pm)
Chloride (Cl^{--})	19	167
Sodium (Na^+)	10.5	116
Sulfate ($S04^{--}$)	2.7	?
Magnesium (Mg^{++})	1.29	86
Calcium (Ca^{++})	0.412	114
Potassium (K^+)	0.399	152

Magnesium Minerals

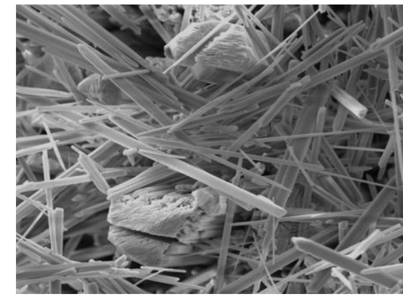
Mineral	Formula	Class	Molar volume	Hard ness	Habit	Reference for Habit
Brucite	$Mg(OH)_2$	Brucite	24.40		Blocky pseudo hexagonal crystals. Platy or foliated masses and rosettes - fibrous to massive	http://webmineral.com/Alphabetical_Listing.shtml http://en.wikipedia.org/wiki/Brucite Notes 1, 2, 3
Brucite Hydrates	$Mg(OH)_2.nH_2O$	Brucite hydrates	?	2.5	Not much known about them!	http://webmineral.com/Alphabetical_Listing.shtml
Pokrovskite	$Mg_2(CO_3)(OH)_2{\cdot}0.5(H_2O)$	Basic	66.79	3	Brown radiating tufts.	http://mineralbliss.blogspot.com/2010/03/different-pokrovskite-habits-possible.html
Artinite	$Mg_2(CO3)(OH)_2{\bullet}3(H_2O)$	Basic	105.81	2.5	Bright, white acicular sprays Forms crusts of acicular crystals, elongated [010]. Also botryoidal masses of silky fibers; spherical aggregates of radiating fibers; cross-fiber veinlets.	http://webmineral.com/Alphabetical_Listing.shtml http://www.mindat.org/min-377.html
Hydromagnesite	$Mg5(CO3)4(OH)_2.4H_2O$	Basic	221.86	3.5	Include acicular, lathlike, platy and rosette forms Crystals small, occurring as tufts, rosettes, or crusts of acicular or bladed crystals elongated [001] and flattened {100}. Massive, chalky.	http://webmineral.com/Alphabetical_Listing.shtml http://www.mindat.org/show.php?id=1979&ld=1
Dypingite	$Mg5(CO3)4(OH)_2.5H_2O$	Basic	181.45	181.45	Numerous individual crystals or clusters. Globular - Spherical, or nearly so, rounded forms (e.g. wavellite).	http://webmineral.com/data/Dypingite.shtml

Magnesium Minerals

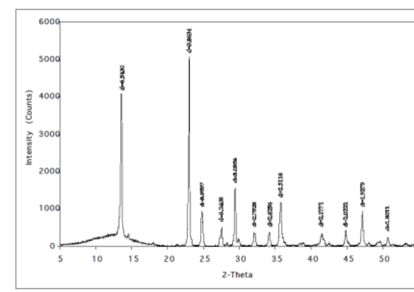
Mineral	Formula	Class	Molar volume	Hard ness	Habit	Reference for Habit
Giorgiosite	$Mg_5(CO_3)_4(OH)_2$ .5-6H_2O	Basic	183.93	3.5	Fibrous and spherulitic, admixed with other species in powdery masses.	http://www.mindat.org/min-1979.html
Magnesite	MgCO3	Normal or "self setting"	28.11	3.9	Usually massive Crystals usually rhombohedral {1011}, also {0112}; prismatic rare [0001] with {1120} and {0001}, or tabular {0001}. Scalenohedral rare. Massive, coarse- to fine-granular, very compact and porcelainous; earthy to rather chalky; lamellar; coarsely fibrous	http://webmineral.com/Alphabetical_Listing.shtml http://www.mindat.org/min-2482.html
Barringtonite	MgCO3·2H_2O	Normal or "self setting"	42.53	2.5	Glassy blocky crystals	http://webmineral.com/Alphabetical_Listing.shtml
Nesquehonite	MgCO3·3H_2O	Normal or "self setting"	74.79	2.5	Acicular prismatic needles Crystals prismatic, elongated along [010], {001}, {010}, {011}, {101}. {110} deeply striated parallel to [010]. Forms radial sprays and coatings, also botryoidal.	http://webmineral.com/Alphabetical_Listing.shtml http://www.mindat.org/min-2885.html
Lansfordite	MgCO3·5H_2O	Normal or "self setting"	102.59	2.5	Glassy blocky crystals Minute short-prismatic crystals [001]; also stalactitic.	http://webmineral.com/Alphabetical_Listing.shtml http://www.mindat.org/min-2324.html

Why Nesquehonite for Synthetic Carbonate Binder and Aggregate?

- Nesquehonite has an ideal shape that contributes strength to the microstructure of a composite like concrete
- Nesquehonite can be
  - manufactured easily using the N-Mg sub-process at room temperature with little energy
  - used directly in many products such as acoustic panels, non structural panels, insulation etc.
- Nesquehonite is
  - Stable over a wide PT range. It changes with heat to $MgCO_3$ which is even more stable.
  - A source input for the manufacture of reactive magnesia used in our cements
  - Used to make our synthetic carbonate and waste aggregate



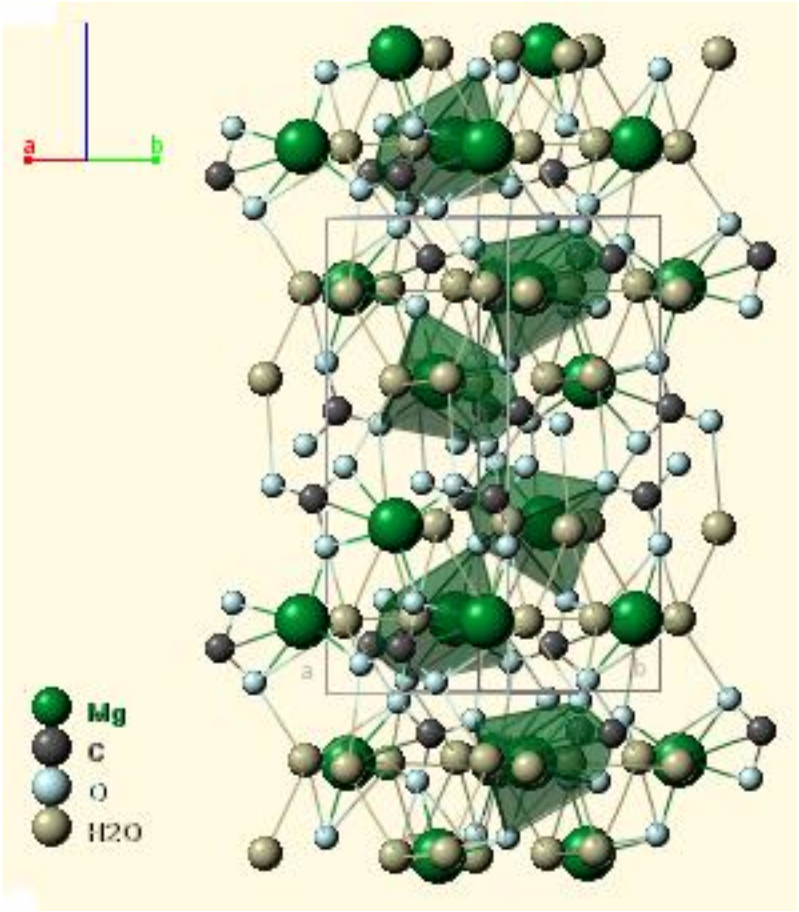
Nesquehonite courtesy of Vincenzo Ferrini, university of Rome.



XRD Pattern Nesquehonite

$$Mg^{++} + 3H_2O + CO_3^{--} \Rightarrow MgCO_3 \cdot 3H_2O$$

Structure of Nesquehonite



Infinite chains of MgO_6 octahedra and CO_3 groups <u>hydrogen bonded</u> together. Note that the atomic arrangement in nesquehonite shows no close relationship to those of the other known hydrated magnesium carbonates

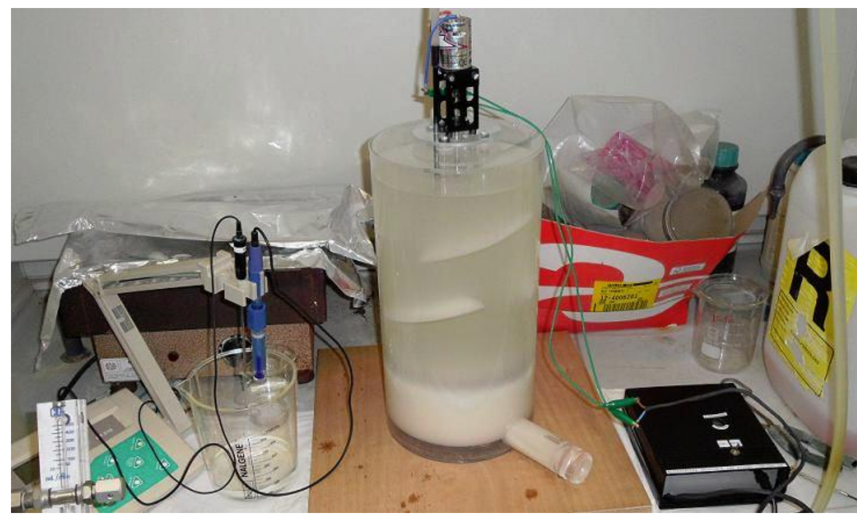
Giester, G., Lengauer C. L. , and Rieck B. , The crystal structure of nesquehonite, MgCO3.3H 2 O, from Lavrion, Greece, Mineralogy and Petrology (2000) 70: 153–163

Stephan G W , MacGillavry C H , Acta Crystallographica, Section B , 28 (1972) p.1031-1033, The crystal structure of nesquehonite, MgCO3*3H2O

The Production of Nesquehonite

A batch process is working and has been built by colleagues at the University of Rome, La Sapienza

TecEco's role
Conversion of a batch to continuous automated process. Tec-Kiln development



Source pictures : De Vito, Caterina, Ferrini,Vincenzo & Mignardi, Silvano, Ex situ CO2 mineralization via nesquehonite: a first attempt for an industrial application. Department of Science, Univeristy of Rome.

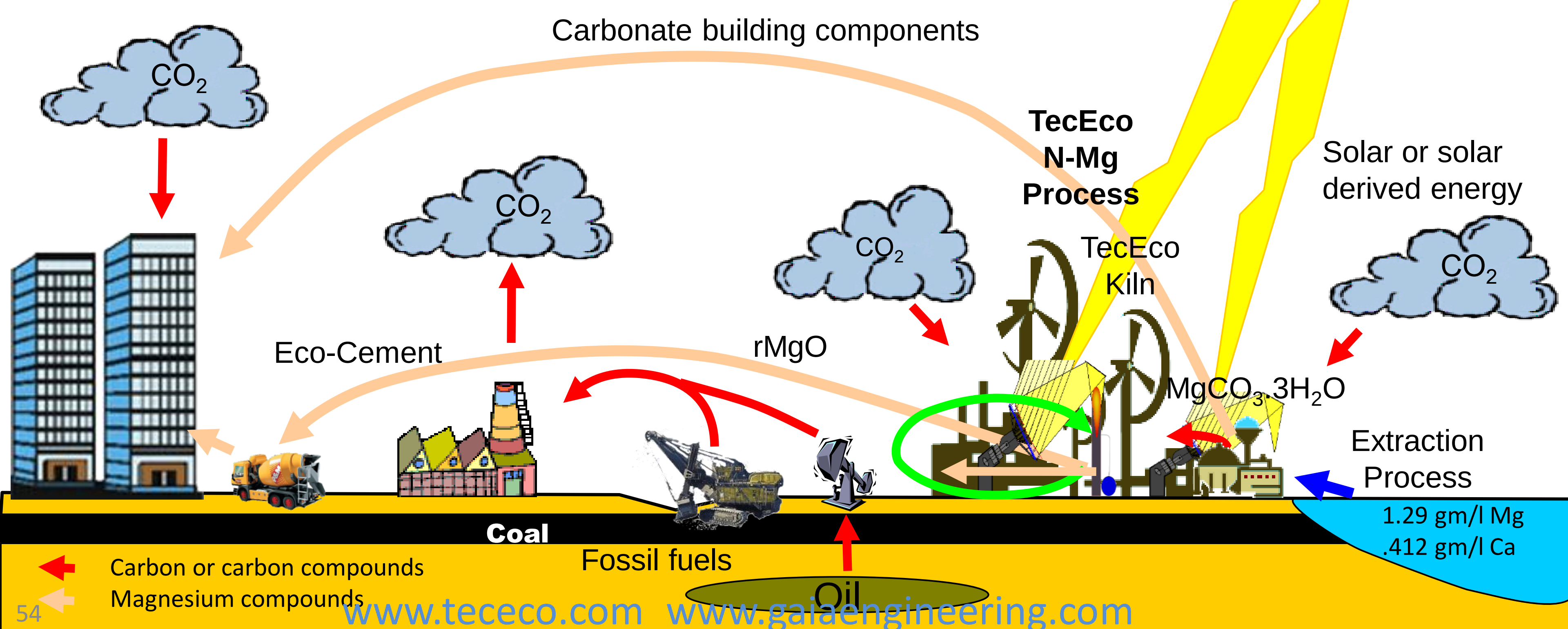
Manufactured Aggregates – Using Synthetic Carbonates, Fly ash and other Wastes

- Sand and stone aggregate are in short supply in some areas.
  - Note that rMgO will neutralise salts and humus.
- Nesquehonite is an ideal mineral for the manufacture of rMgO (our binder) as well as synthetic carbonate.
  - rMgO => Mg(OH)2 => MgCO3.3H20 has high molar volume growth
  - Ideal microstructure
  - Stability
  - Ideal low pH
  - Polar bonds in composites making it suitable for binding wastes
- Nesquehonite sequesters significant amounts of CO_2

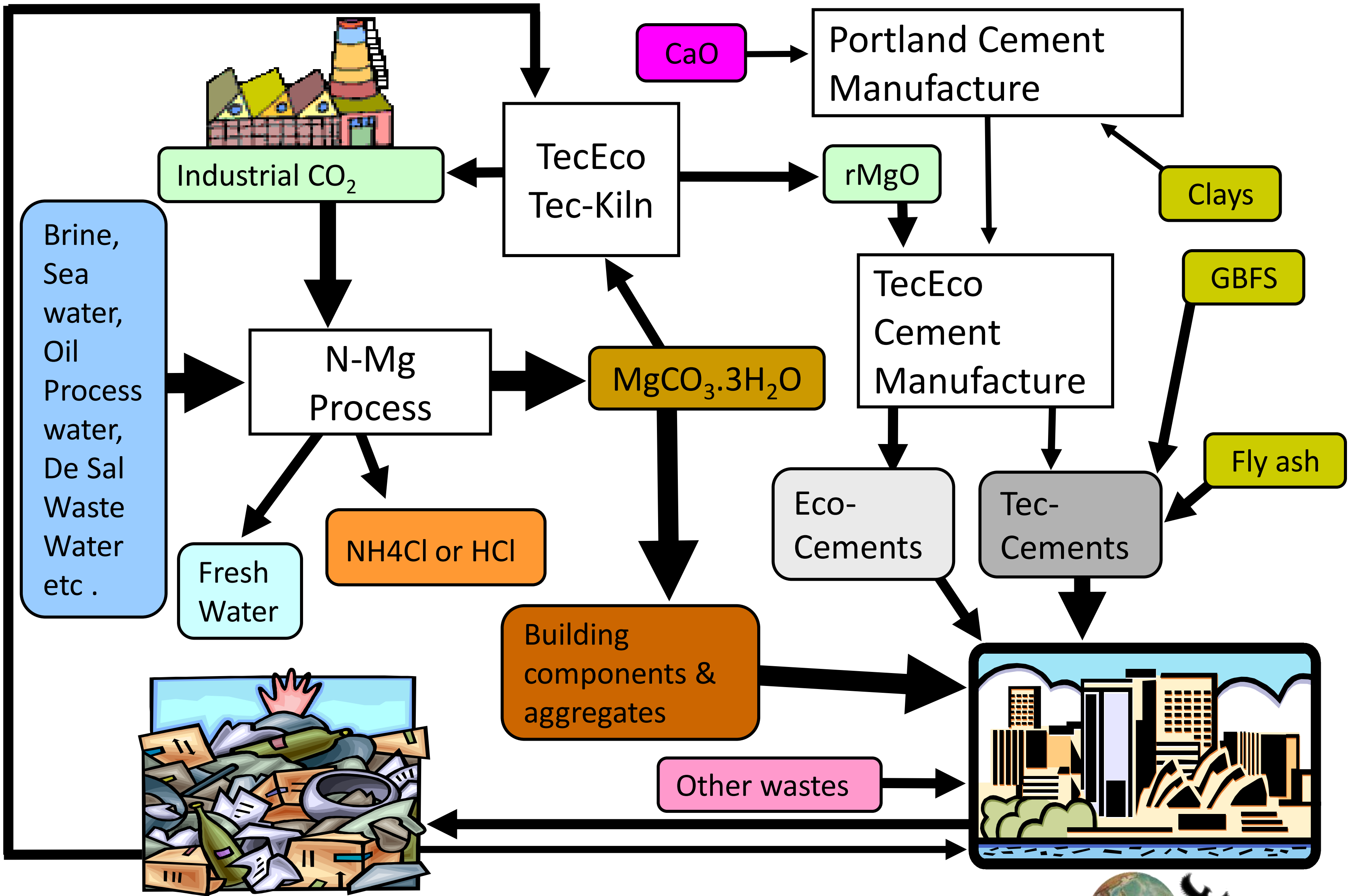
Gaia Engineering Overview

Inputs:
Atmospheric or industrial CO_2, brines (e.g. de-sal and process waste water, other wastes
Outputs:
Carbonate building materials, HCl, fresher water.

Gaia Engineering is an industrial ecology that delivers profitable outcomes whilst reversing underlying undesirable moleconomic flows from other less sustainable carbon emitting processes.



Gaia Engineering



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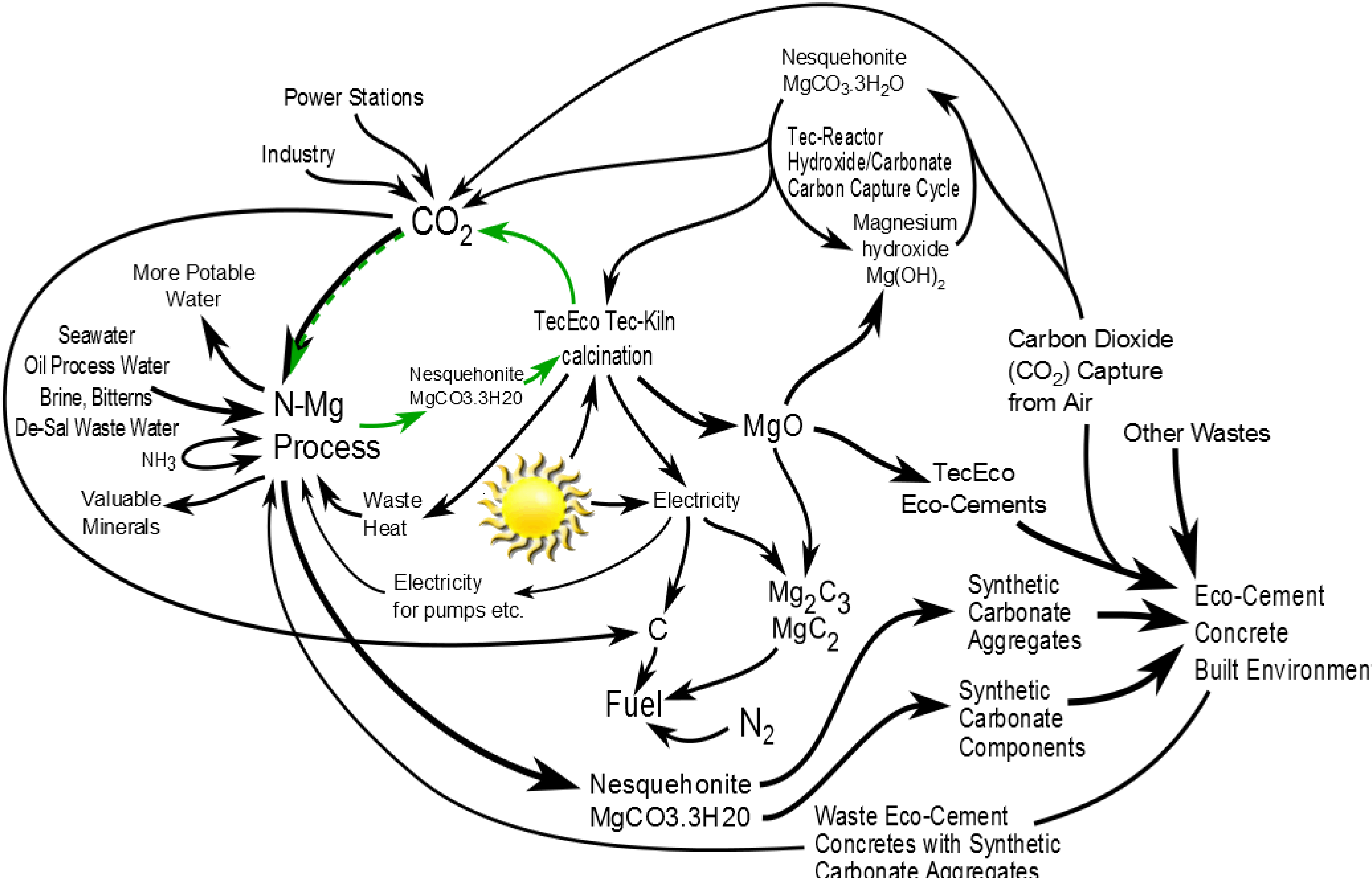
Gaia Engineering



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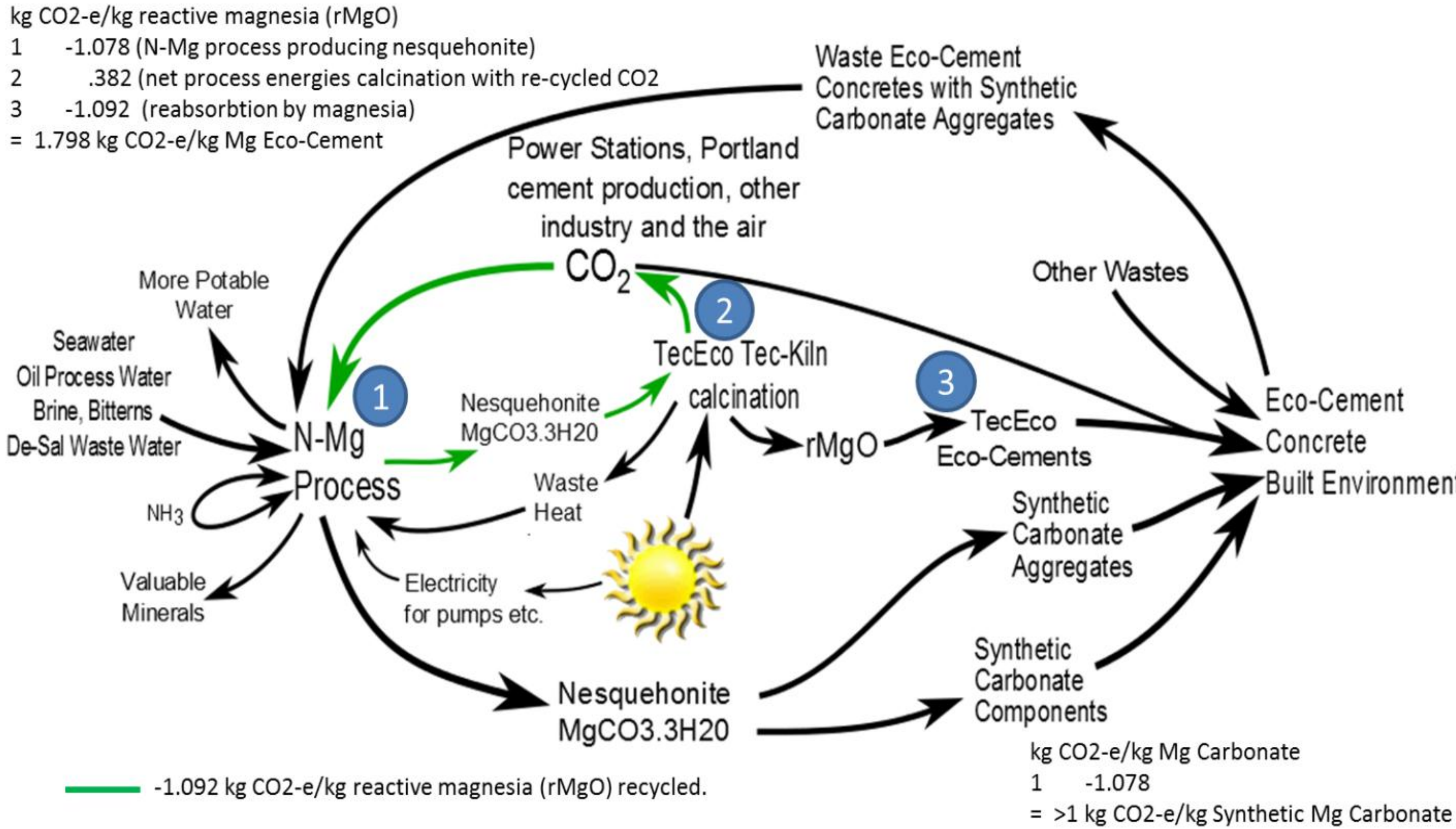
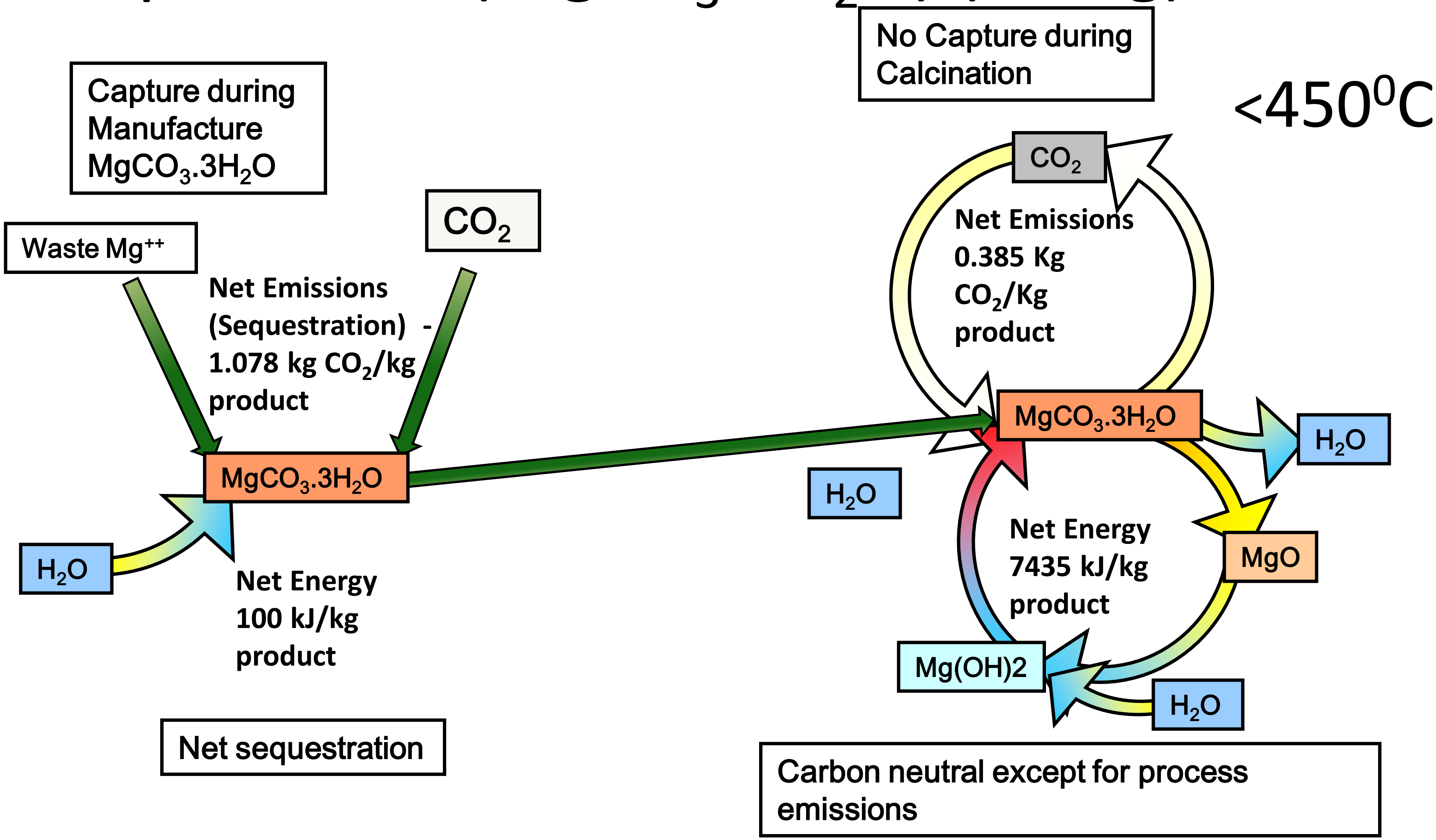
Gaia Engineering Simplified



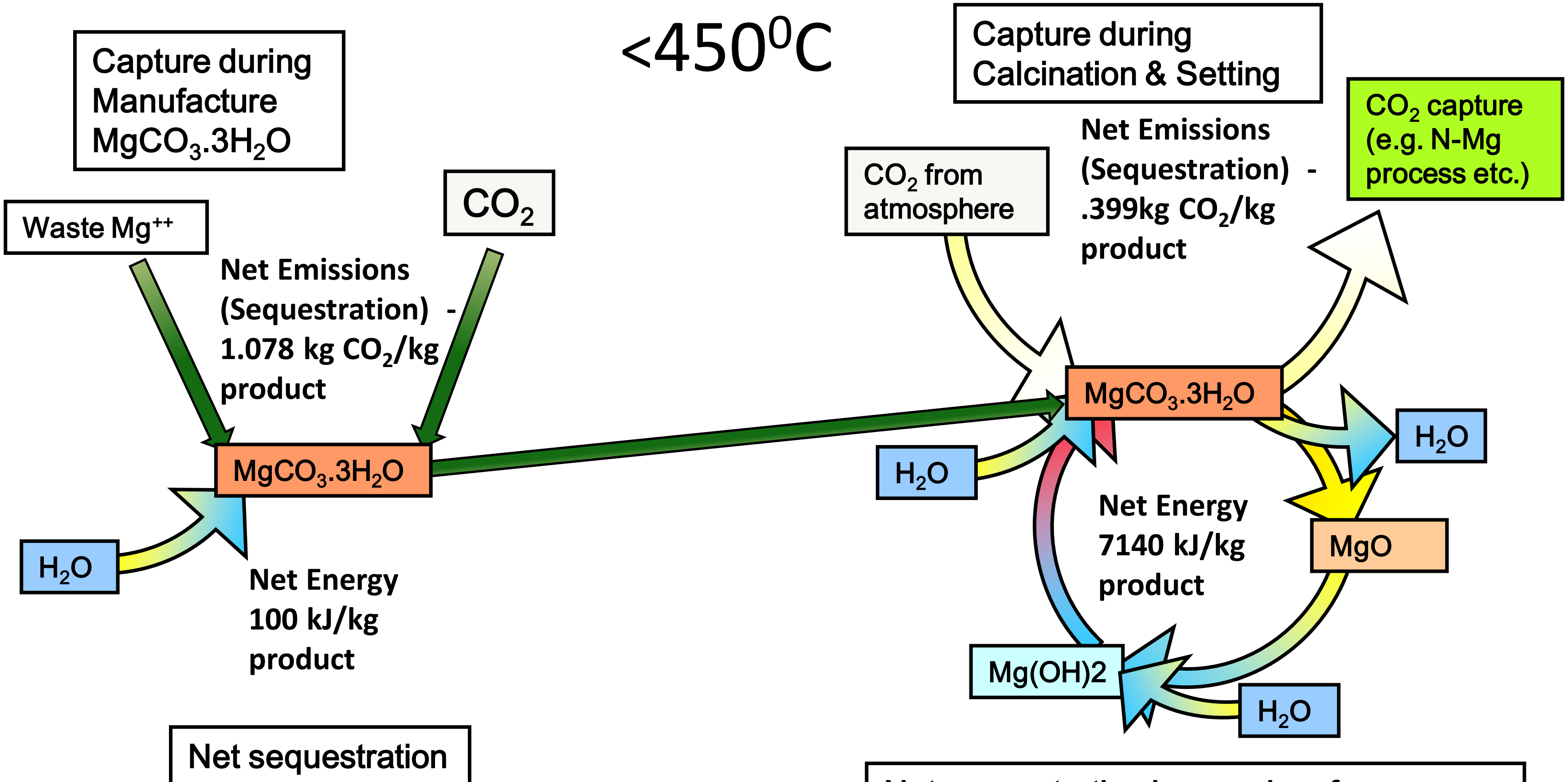
The Potential of CO_2 Release and Capture - Nesquehonite ($MgCO_3.3H_2O$) (N-Mg) Route



Use of non fossil fuels => Low or no process emissions

[17] Source Data: http://www.tececo.com/files/spreadsheets/TecEcoCementLCA14Feb2011.xls

The Potential of CO_2 Release and Capture - Nesquehonite ($MgCO_3.3H_2O$) (N-Mg) Route



Use of non fossil fuels => Low or no process emissions

[17] Source Data: http://www.tececo.com/files/spreadsheets/TecEcoCementLCA14Feb2011.xls

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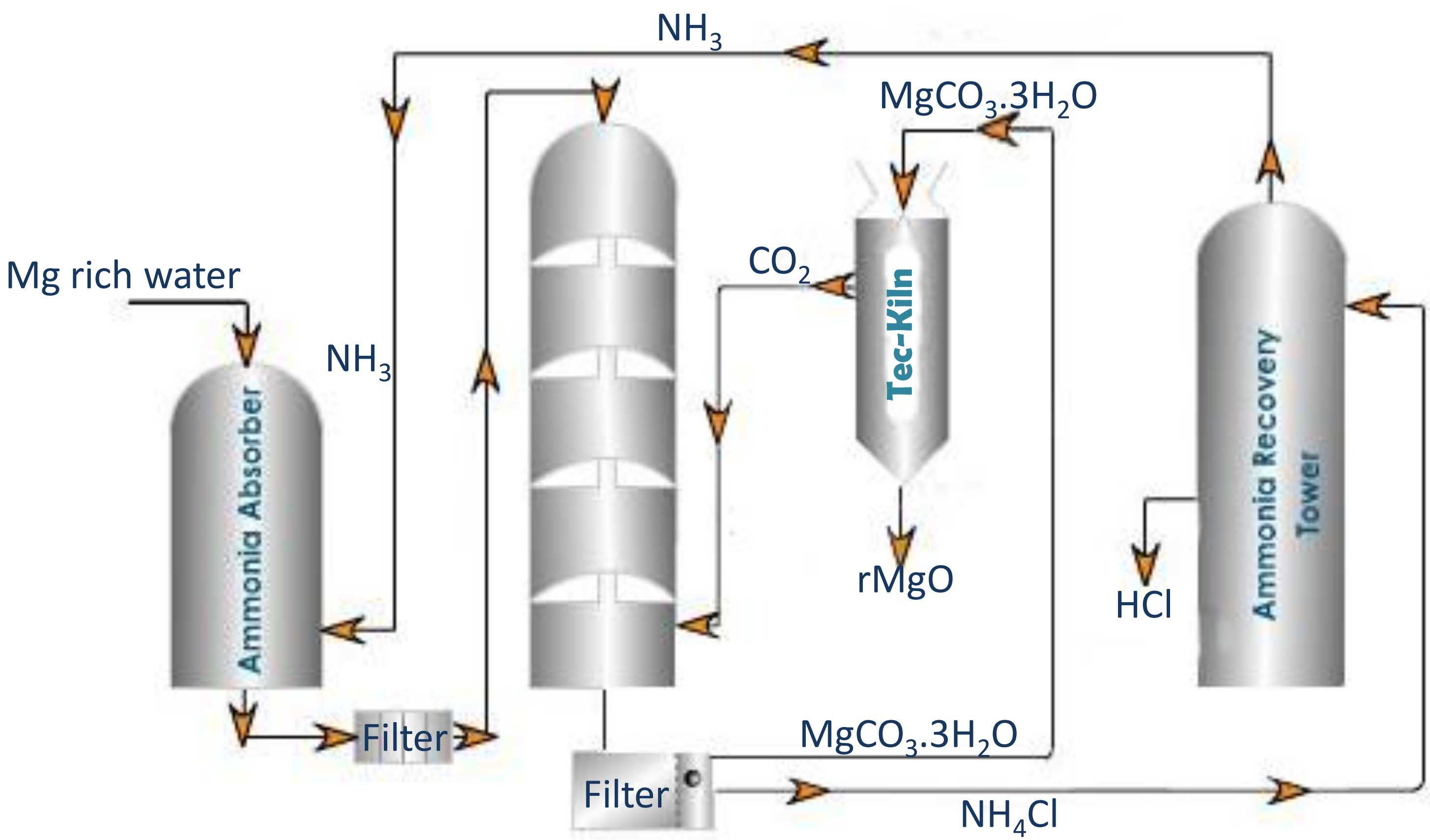
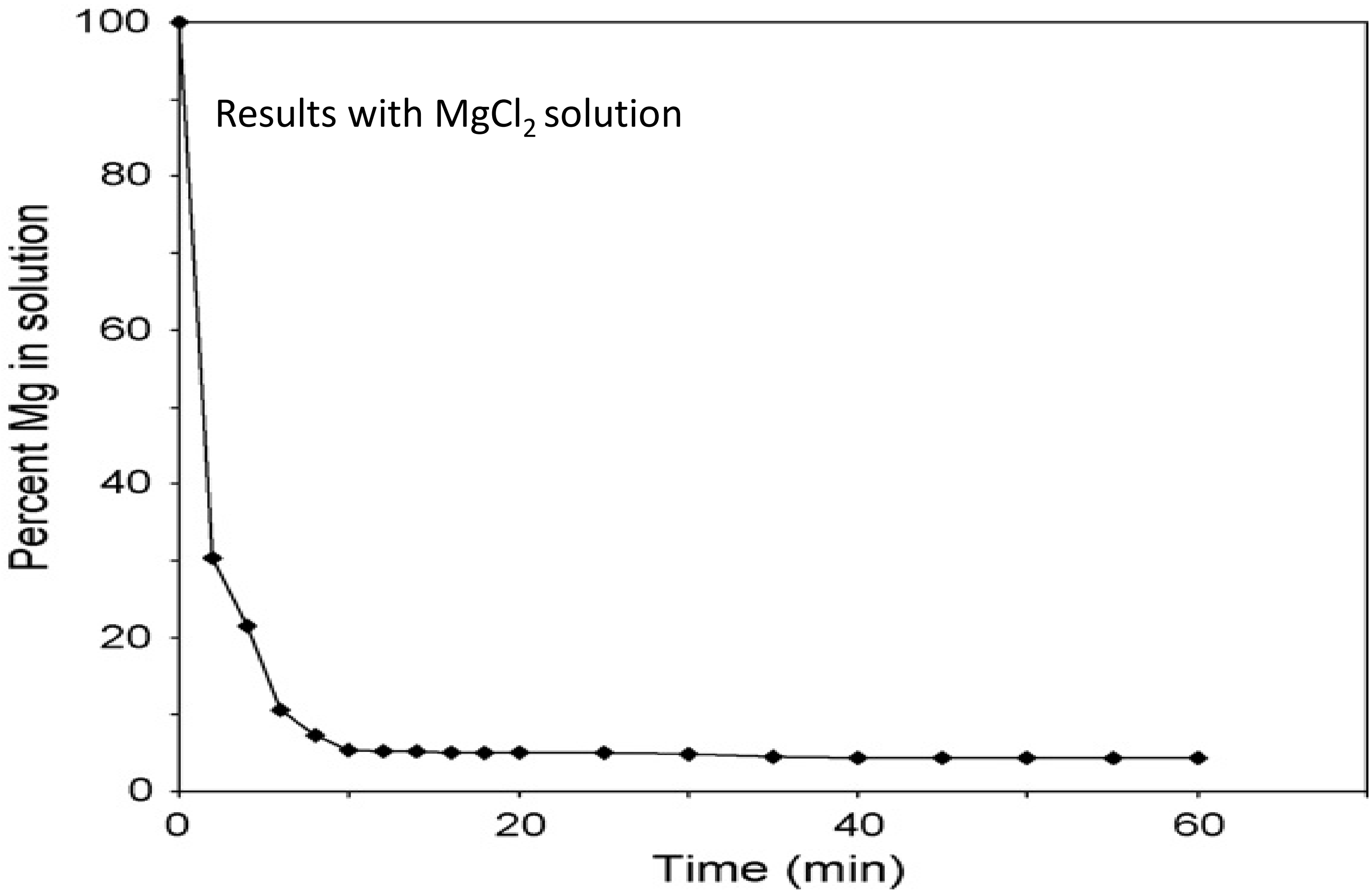
The N-Mg Process



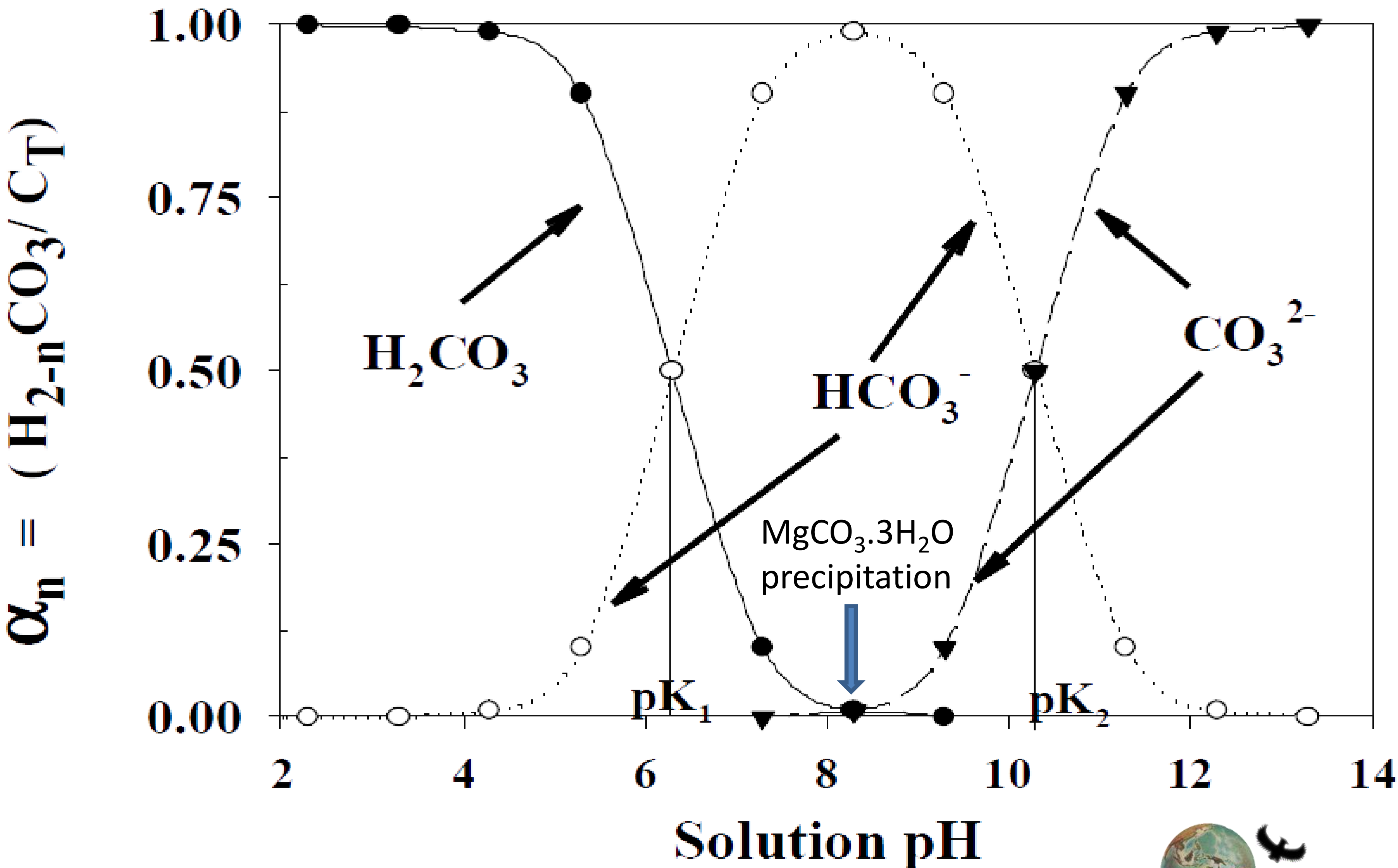
The process is not dissimilar to the well know Solvay process

Rapid Low Cost Production of Carbonate



Source pictures : Ferrini, V., De Vito, C. & Mignardi, S., 2009. Synthesis of nesquehonite by reaction of gaseous CO 2 with Mg chloride solution: Its potential role in the sequestration of carbon dioxide. Journal of Hazardous Materials, 168.

Speciation of Carbonate pH dependent



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Precipitation of Nesquehonite

The overall reactions are pH dependent and as follows:

1. $CO_2 + H_2O <=> H_2CO_3$ (aq)
2. H_2CO_3 (aq) < = > **H^+** (aq) + HCO_3^{--} (aq)

3. Mg^{++}(aq) + HCO_3^{--} (aq) + $3H_2O$ => ↓$MgCO_3.3H_2O$ (nesquehonite) + **H^+** (aq) (results in acidification)

4. NH_4OH + **H^+** (aq) => NH_4^+ (aq)+ H_2O (results in neutralisation . Excess ammonia results in pH adjustment to produce a preponderance of HCO_3^- (aq) consumed in reaction 3. (See also the previous speciation graph. It is also possible that ammonia complexes assist the precipitation of nesquehonite ($MgCO_3.3H_2O$)).

5. NH_4^+ (aq) + Cl^{-} (aq) => NH_4Cl (used industrially or used to make HCl by evaporating off ammonia)

   Our preferred option is to use our Tec-Kiln to produce rMgO for our cements and a small amount to dissolve in water to produce $Mg(OH)_2$

6. $Mg(OH)_2 + NH_4Cl$ => $MgCl_2 + NH_4OH$ (much less because most of the cycle Mg has been precipitated out as nesquehonite by the consumption of CO2. Both are recycled back in the process)

Agglomeration of Synthetic Carbonates, Fly ash and other Wastes

- Sand and stone aggregate are in short supply in some areas.
- Nesquehonite is an ideal micro aggregate so why not agglomerate it and/or other magnesium carbonates to make synthetic (manufactured) aggregate?
- MgO binders will be suitable for this purpose and TecEco are seeking funding to demonstrate the technology.
- TecEco can already agglomerate fly ash and nesquehonite without additional energy. We just can’t tell you how as we have not had the money to pursue a patent.

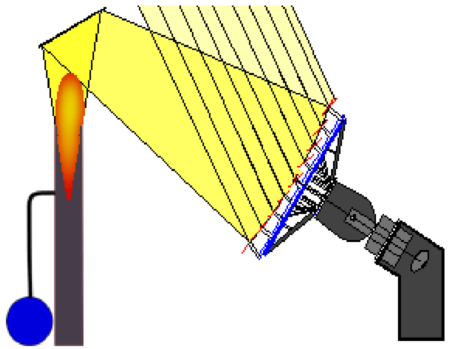
The TecEco Tec-Kiln

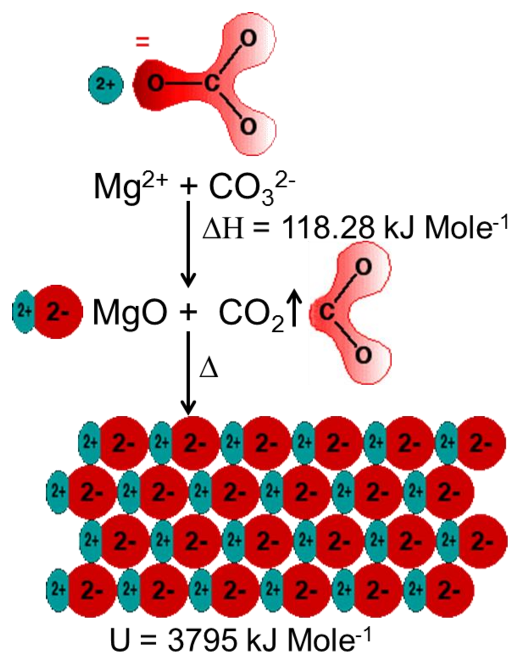
An obvious future requirement will be to make cements without releases so TecEco are developing a top secret kiln for low temperature calcination of alkali metal carbonates and the pyro processing and simultaneous grinding of other minerals such as clays.

The TecEco Tec-Kiln has no releases and is an essential part of TecEco's plan to sequester massive amounts of CO2 as man made carbonate in the built environment .

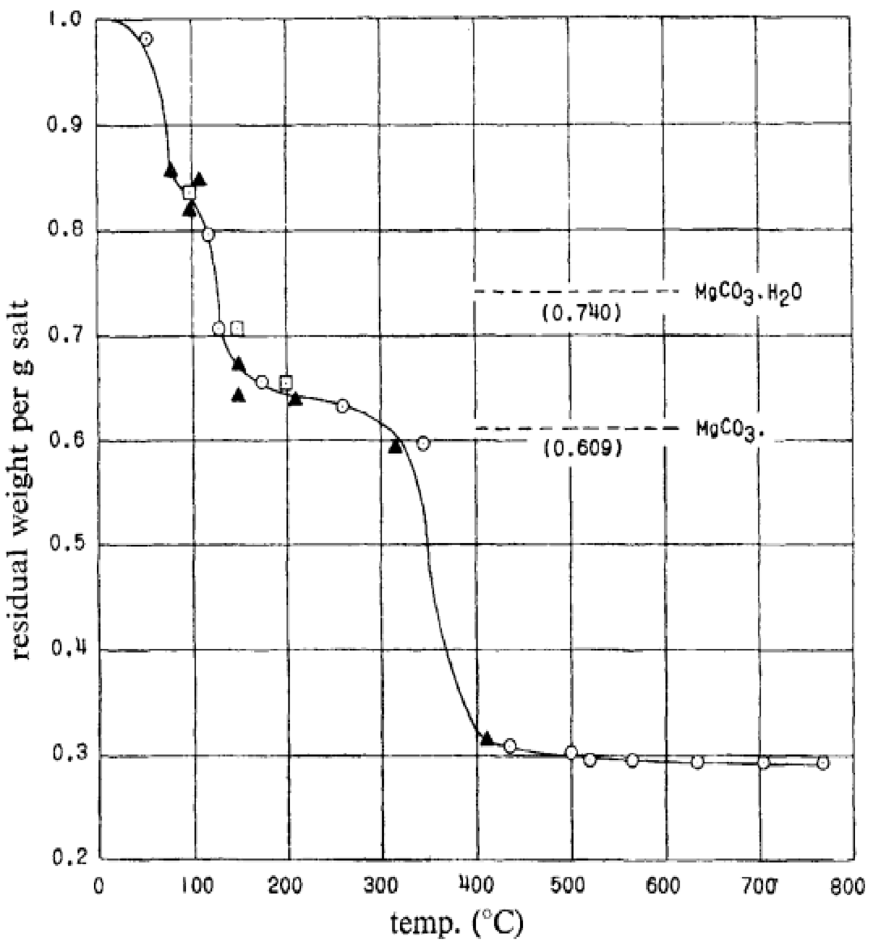
The TecEco Tec-Kiln has the following features:

- Operates in a closed system and therefore does not release CO2 or other volatiles substances to the atmosphere.
    - The CO2 produced will be recycled in the N-Mg process.
- Can be powered by various potentially cheaper non fossil sources of energy such as intermittent solar or wind energy and is energy smart.
- Grinds and calcines at the same time thereby running 25% to 30% more efficiently.
- Produces more precisely definable product. (Secret as disclosure would give away the design)





The Calcination of Nesquehonite (Tec-Kiln, N-Mg route)



Source: Dell, R. M. and S. W. Weller (1959). "The Thermal Decomposition of Nesquehonite MgCO3 3H20 And Magnesium Ammonium Carbonate MgCO3 (NH4)2CO3 4H2O." Trans Faraday Soc **55**(10): 2203 - 2220.

Scope for Reducing Energy Using Waste Heat?

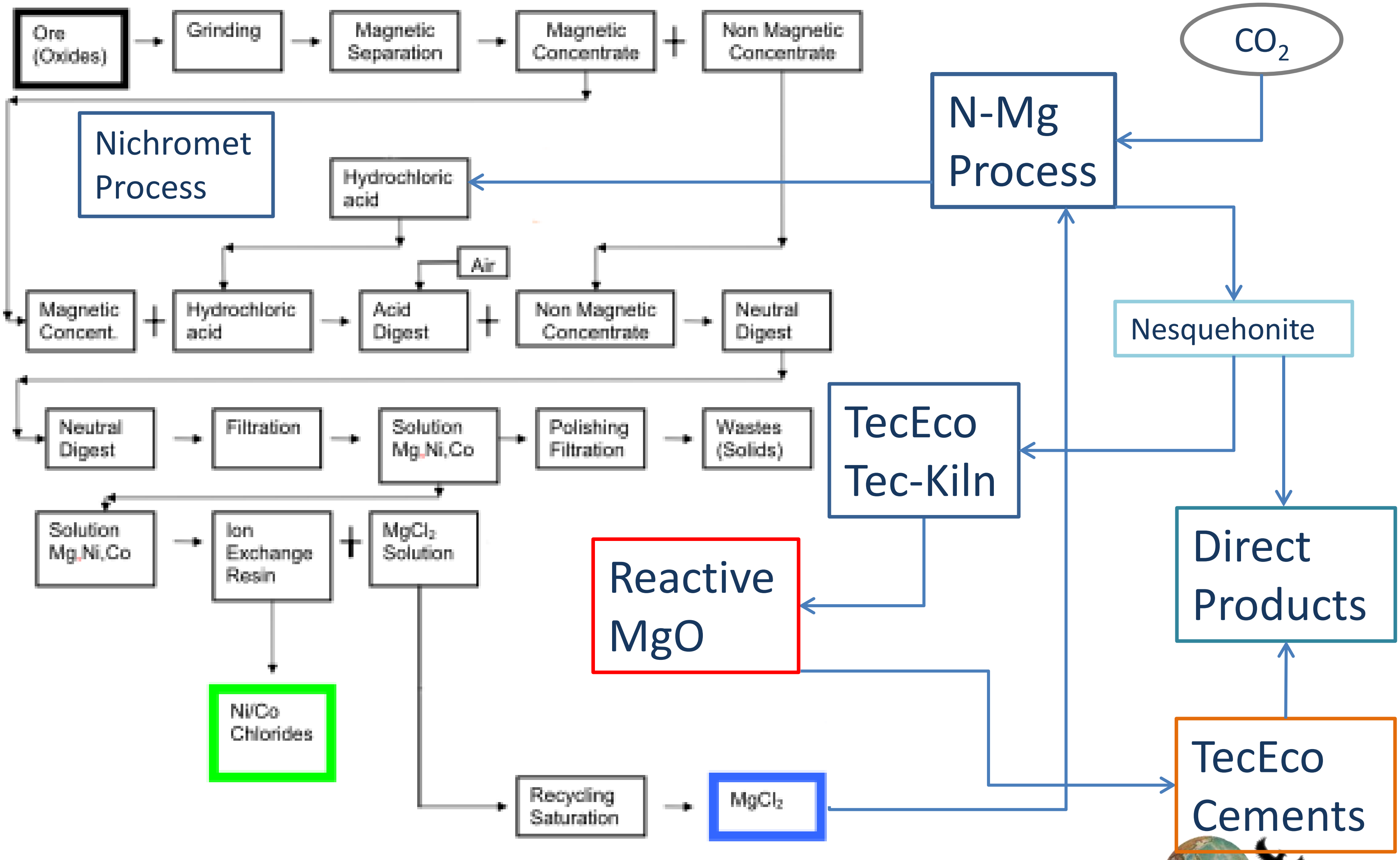
Initial weight loss below 100°C consists almost entirely of water (1.3 molecules per molecule of nesquehonite). Between 100 and 150°C volatilization of further water is associated with a small loss of carbon dioxide (~3-5 %).

From 150°C to 250°C, the residual water content varies between 0-6 and 0-2 molecules per molecule of MgC03. Above 300°C, loss of carbon dioxide becomes appreciable and is virtually complete by 420°C, leaving rMgO with a small residual water content.

Energy could be saved using a two stage calcination process using waste energy for the first stage.

1 mole of nesquehonite (solid) gives 3 moles of water (gas) and one off CO_2 (gas). This is a significant molar volume expansion and could be used to drive a turbine or pistons to generate electricity.

Gaia Engineering - An Example of Geomimetric Industrial Symbiosis!



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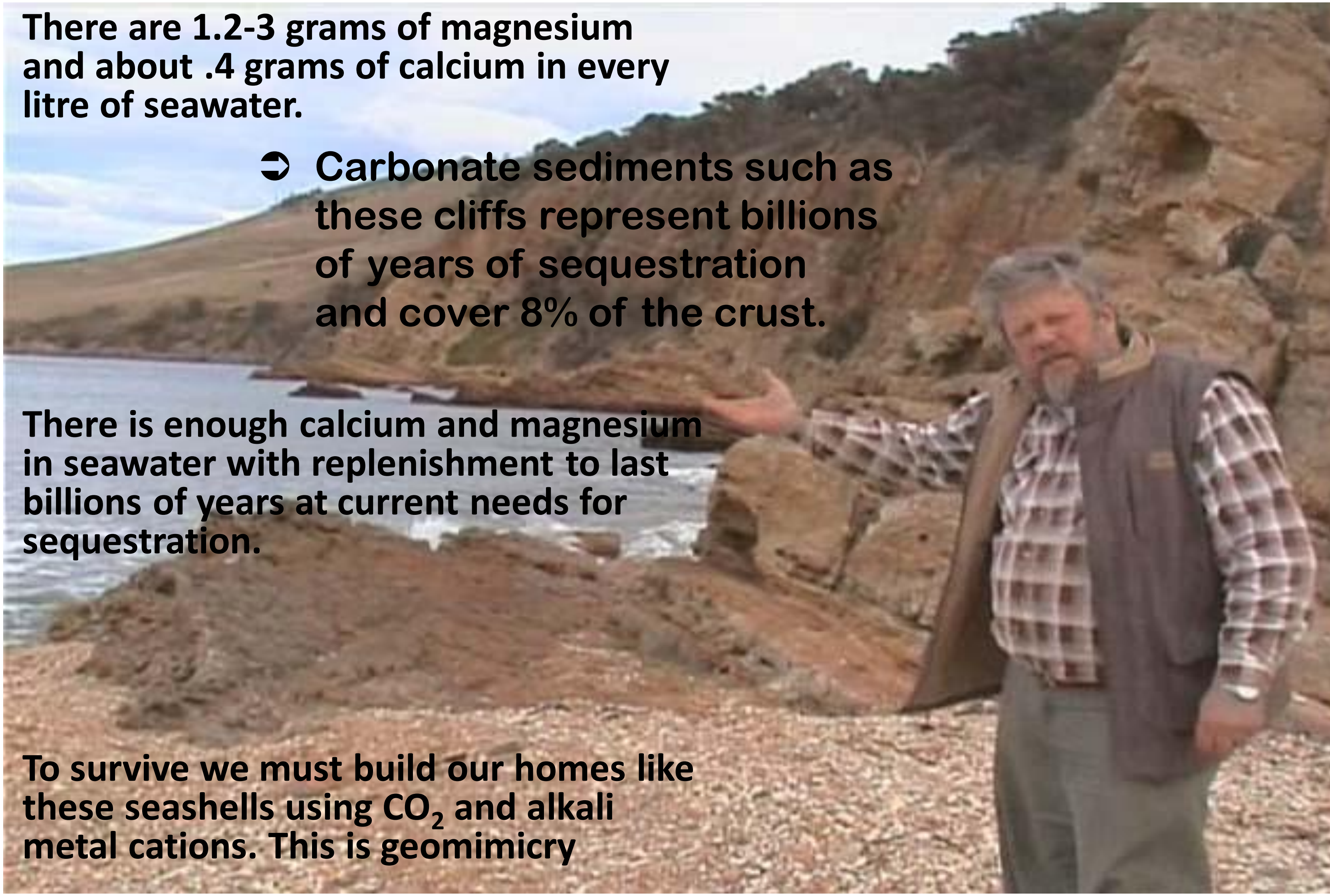
Geomimicry



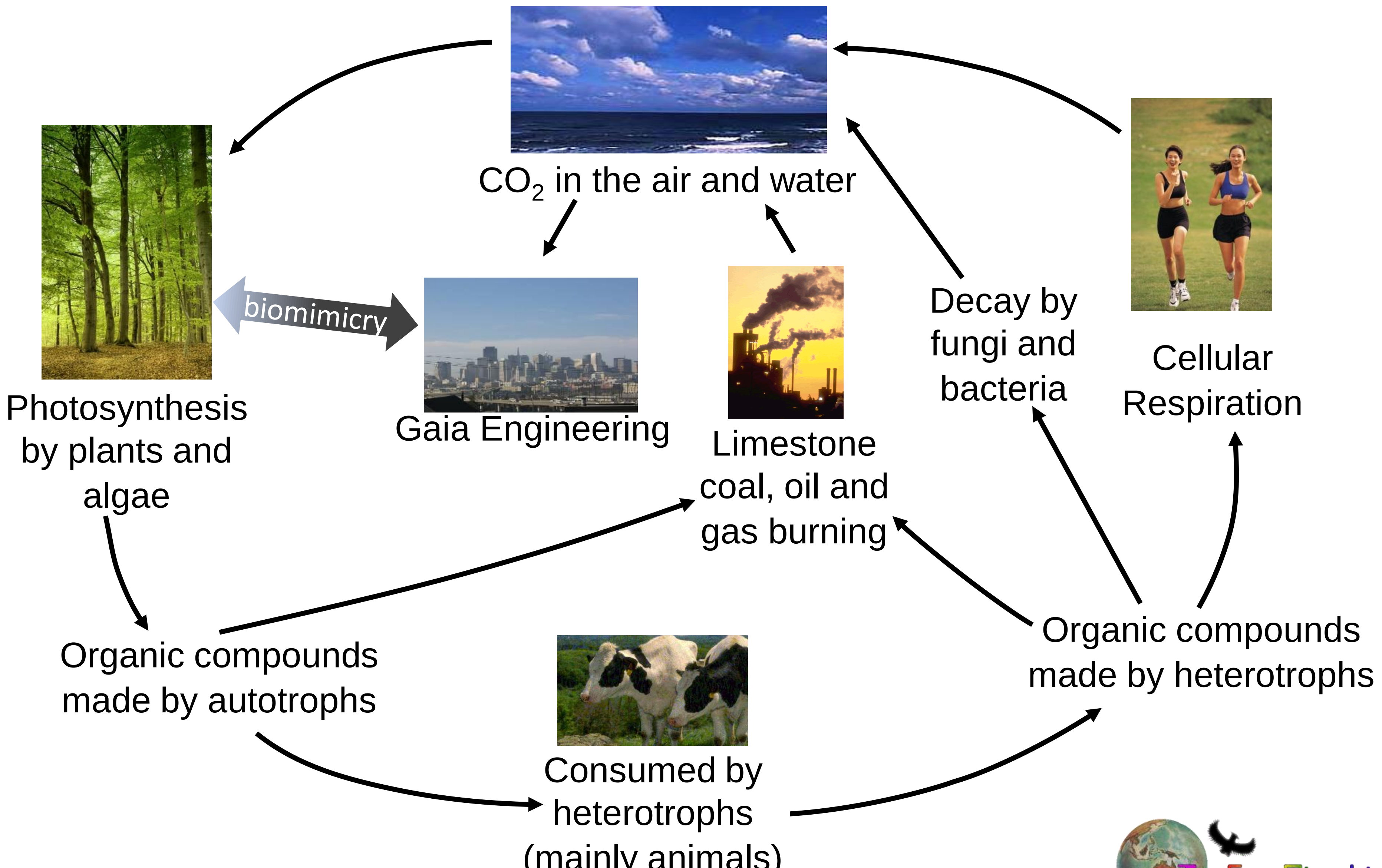
- **There are 1.2-3 grams of magnesium and about .4 grams of calcium in every litre of seawater.**

  ➲ **Carbonate sediments such as these cliffs represent billions of years of sequestration and cover 8% of the crust.**

- **There is enough calcium and magnesium in seawater with replenishment to last billions of years at current needs for sequestration.**

- **To survive we must build our homes like these seashells using CO_2 and alkali metal cations. This is geomimicry**

Gaia Engineering can Balance the Carbon Cycle



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Replacement of Portland Cement by Limestone

- On the surface seems to be a good idea
- Makes sense in relation to particle packing
- Not however the best possible additive in terms of the chemistry
  - pH is buffered down and pozzolanic and other important reactions including carbonation in our Eco-Cements is compromised.
- "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"[1]
- We agree. Reactive magnesia (rMgO) or even ground SCM's work much better as the resulting chemical reactions are beneficial. **It may be that gypsum is not required with rMgO resolving a number of other issues.**
- I suggest the industry stop trying to be alchemists and go do a course in chemistry 101.
- In the meantime please continue to make "Limestone Free Cement" for the benefit of down process blenders.

[1]Compton M, Chandler J., Elevated limestone mineral addition impacts on laboratory and field concrete performance. Concrete in Australia. 2012, **38**(1):27 - 33.

Replacement of Cement by SCM's

- Portlandite should not be left in concretes because it is far too reactive.

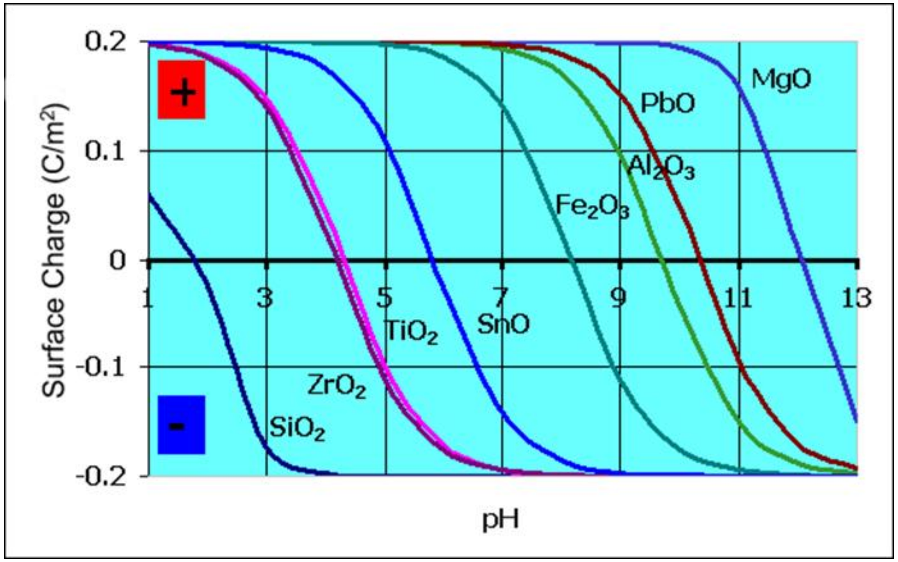
Portlandite should be replaced by an alternative pH buffer

- Portland cement can be blended with pozzolans such as fly ash 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 and is ideal for immobilising heavy metal cations*.

* Important if we are to use wastes like fly ash.

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.
- A pioneer in this field is Francois de Larrard from France.
- The next area to consider in in mix design software is volume stoichiometry and particle charge affects.



Particle charge is very important in relation to the rapid setting and strength gain in high SCM Tec-Cement mixes.

Product Differentiation and Specialisation

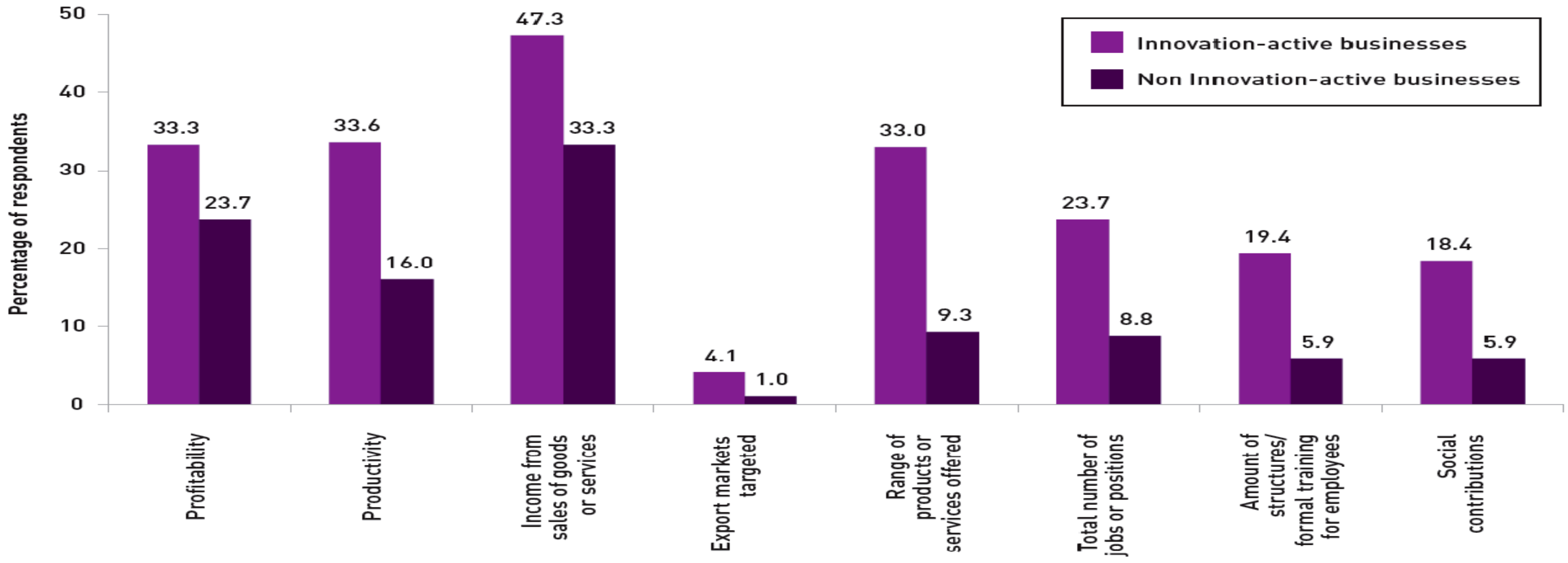
- New mineral composites incorporating waste streams that add properties sought such as thermal flow resistance, fire resistances etc. are required.
  – Important in relation to reducing the lifetime energies of structures
  – Important in relation to adding value to waste streams facilitating their conversion to resources and reducing pollution
- To allow this to be achieved prescription based standards need to be scrapped and relegated to the role of practice guides.
- Broadly based performance criteria are essential.

Changing the Emphasis

- In relation the sustainability more emphasis should be placed on aggregates as they comprise 80% of concrete.
- A greater emphasis on properties not prescriptions.
- A wider emphasis on the range of cementitious composites.
  - Addressing lifetime energy, sound insulation and a wide range of other requirements other than just strength and thermal mass.

The Right Business Models

- Cost cutting business models will not get the industry to where it needs to go
- **Innovation based business models** and appropriate changes to standards are required.



Source: ABS (2010) *Selected Characteristics of Australian Business*, 2008–09, cat. no. 8167.0.

Increases in Business Performance by Innovation status 2008 – 9

Cost rather than Profit Based Business Models

- Most corporations in the concrete industry have business model that relies on significant turnover and cost cutting to deliver profit.
  - Research and development budgets that deliver innovations and potentially more profitable product are generally small.
  - A focus on cost instead of cost effective.

If the industry believe in "cutting edge" research then they are going to have to practice what they preach and support innovation.

In Australia there is now benchmark support for R & D and commercialisation

Examples of Other Huge Change Opportunities

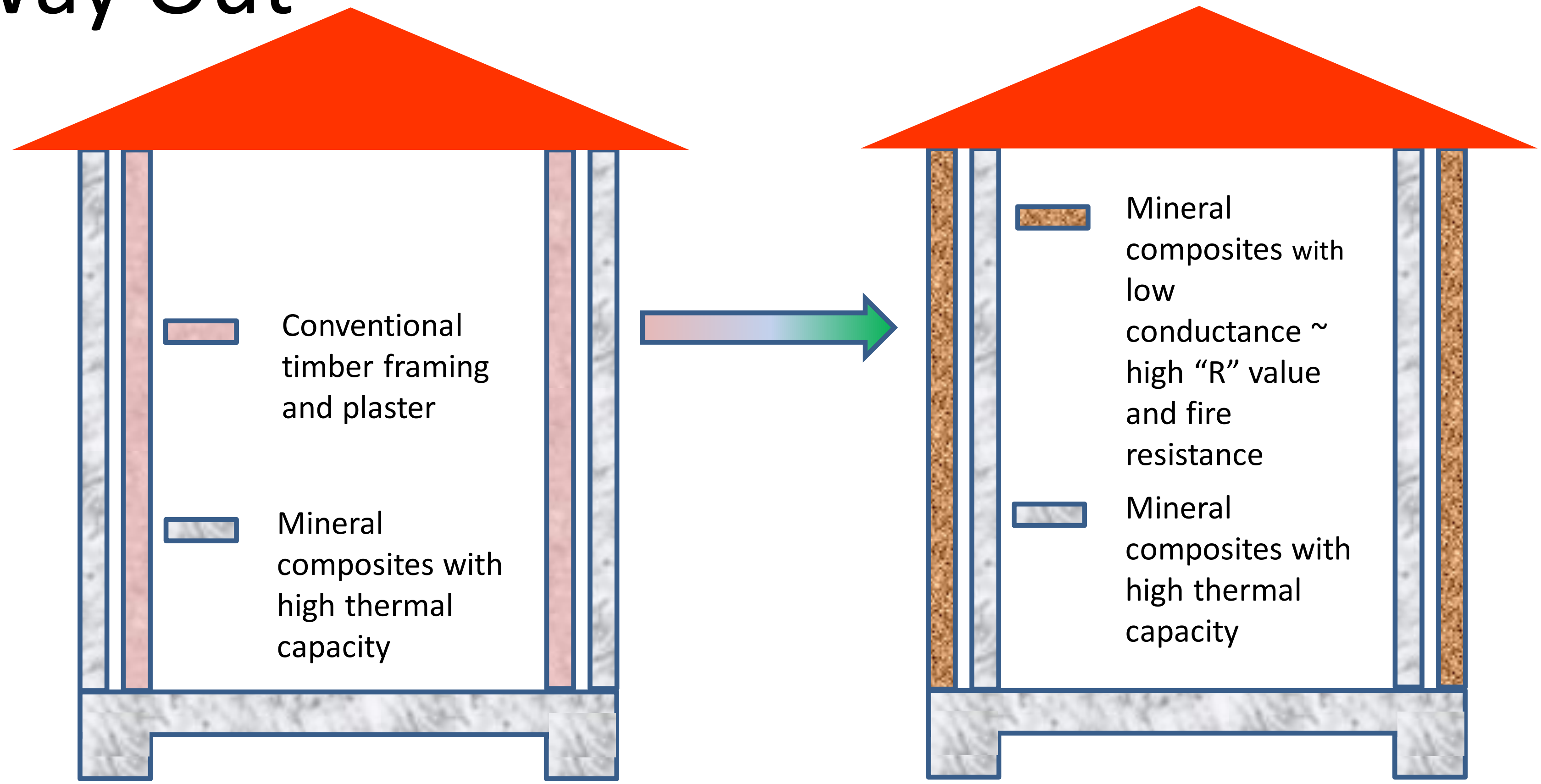
- A wide variety of possible end uses with higher potential margins for which current solutions are sub-optimal.
  - E.g. Addressing properties affecting lifetime energy.
    - E.g. Mineral composites with higher "R" value viz.
    - Boards made with mineral binders & wastes - **"MgO boards"**
    - Exterior structural panels with insulating properties
- Huge opportunities for reducing the cost base and improving the properties of concretes by focusing on the process by which they are made and what they are made with.
  - A few tweaks to the formulations
  - Major changes to the process and some
  - Lateral thinking in relation to aggregates => Synthetic carbonate aggregate.

See Part 2 for the ramifications of using reactive MgO

- De-materialization through design (Reductions in Kg CO_2^{-e}/Mpa)[7]
- Improvements in durability. Missing from the current analyses for sustainability

[7] Wallenvik, Olafur, Carbon Footprint of High Performance Versus Conventional Vibrated Concrete

Innovation – Turning Buildings the Right Way Out



Mineral composites with high "R" value can easily be made using reactive magnesia because of the polar bonding capacity (See Part 2). Hydration and carbonation products of reactive magnesia are all fire retardants. Imagine the reduction in lifetime energies if we started constructing buildings the right way out!

Barriers to Innovation and Change

- Out of date and inappropriate legislative restriction.
  - See other presentations
- A prescription rather than performance based standards and approvals system. and other presentations as well as what I have to say.
- A corrupt patent System.
  - Governments tend to issue patents to anyone for the money
  - A lack of know how in patent offices as a result of low pay
- Lack of transparency in relation to new products.
  - Secret formulations more often than not in breach of other people's ip.
- Knowledge should be free
  - Wikipedia v Science Direct etc.

Conflicting

- Greenwash.
- A focus on cost instead of cost effective
  - Little or no support for "cutting edge research" (See Lionel Lemay's presentation[4])
- Conservatism (Goes without saying?)
- A low level of skills in the industry

[9] Lobo, Colin, The role of Performance Based Specification in Sustainable Development
[10] Mansour, Wassim, Towards Performance-based Specification – Case Studies on Construction Projects in Abu Dhabi
[11] Lemay, Lionel, Life cycle Assessment of Concrete Structures

The Right Framework to Operate In - Standards

- 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
  - cost cutting business model.
- 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.
- Performance based standards are essential. Existing standards should be converted to guides.

The Standards and Approvals Systems

- Far too often our standards and approvals ratings are prescription based stifling innovation and change.
- Even Leeds in the US and the Green Building Council in Australia make the same mistake
- Standards should be based on a list of metrics for properties including embodied energy and emissions, thermal capacity and conductance, strength (compressive, shear and flexural) etc.
- This means that many existing standards should be relegated to being "codes of practice"
- Proper audit process instead??

See Colin Lobo's presentation (NRMCA)

The Right Framework to Operate In – Legislative Framework

- Too much restriction stifles innovation.
- A better approach would be better training in the industry.
- Few governments have ever managed to get the mix of stick, incentive and procurement right or even remotely efficient.
- Governments do not follow their policies through the supply chain.
  - Procurement policies must follow R & D support.
- UKIERI and other bodies need to take a greater leadership role.

Conservatism

- With the exception of perhaps the architectural fraternity players in the construction industry are generally conservative
- There is little incentive and a lot of risk in using new materials that have reduced embodied energies and emissions and substantial impact on reducing lifetime energies.
- One of the reasons for this conservatism is the legal liability of designers and engineers.
- Perhaps prescription standards should become codes of practice and greater support given for testing of new materials.
- Audited procedures and less reliance on standards?

The Low Level of Skills in the Industry

- There is an appallingly low level of skills in the concrete industry.
  - Electricians and plumbers must have licenses in most countries yet concrete placers and finishers seldom have any training at all.
  - Most civil engineers are taught very little and understand less about the material they use every day.
- It is no wonder we have the attitude that all that is grey is great, all we make goes out the gate. (With affront meant to Grey Matters)
  - any diversion is risky!
- This terrible situation needs to change.
  - Congratulations to the NRMCA re their producer training programs but what about placers and finishers?
- Quality control should go beyond testing, it must include risk management through training.

A Corrupt Global Patent System

- Patents are taken far to literally; the intent and purpose are almost irrelevant.
- Most patent examiners are basically incompetent – How could they be otherwise?
- The revenue raised is of greater importance to the grantee government than the value of the so called monopoly rights given.
- <u>Patents are an invitation and challenge to others to steal ip.</u>
  - Many secret formulations end up being identified as stolen ip.
- Governments do not protect the ip they "grant" they let the players fight it out in court.
- It follows that patents are little more than meat for dogs to fight over.
  - Consider geopolymers for example and my own experience.

The Role of Reactive MgO – An Update on TecEco Technology

An update on recent advances in Tec and Eco-Cements including the use of high proportions of fly ash and SCMS with added reactive magnesia

Reactive Magnesia is the most powerful new tool in cement chemistry

TecEco Cements

- **Eco-Cements** have relatively high proportions of magnesia which in permeable materials carbonates adding strength and durability. Eco-Cement formulations are generally used for bricks, blocks, pavers, pervious pavements and other permeable cement based products. See http://www.tececo.com/products.eco-cement.php

- **Enviro-Cements** are made using large quantities of reactive magnesia which reacts to form Brucite. Brucite is unique to TecEco Cements and is an ideal mineral for trapping toxic and hazardous wastes due to its layered structure, equilibrium pH level, durability and low solubility. See http://www.tececo.com/products.enviro-cement.php

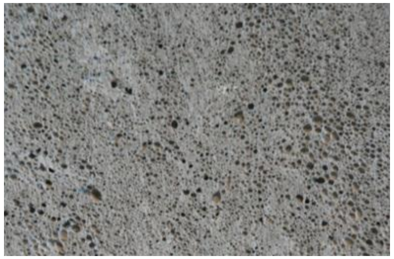
- **Tec-Cements** are cement blends that comprise of a hydraulic cement such as Portland cement mixed with a relatively small proportion of reactive magnesia and optionally pozzolans and/or supplementary cementitious materials which react with Portlandite removing it and making more cement or are activated by Portland cement. They offer a solution to many of the technical problems that plague traditional cement formulations caused by the reactivity of lime (Portlandite) and have significant advantages including faster setting even with a high proportion of non PC additions. See http://www.tececo.com/products.tec-cement.php

TecEco Eco-Cements

Eco-Cements are blends of one or more hydraulic cements and relatively high proportions of reactive magnesia with or without pozzolans and supplementary cementitious additions. They will only carbonate in gas permeable substrates forming strong fibrous minerals such as lansfordite and nesquehonite. Water vapour and CO2 must be available for carbonation to ensue.

Light colour = low albedo

Eco-Cements can be used in a wide range of products from foamed concretes to bricks, blocks and pavers, mortars renders, grouts and pervious concretes such as our own permeacocrete. Somewhere in the vicinity of the Pareto proportion (80%) of conventional concretes could be replaced by Eco-Cement.



Left: Recent Eco-Cement blocks made, transported and erected in a week. Laying and Eco-Cement floor. Eco-Cement mortar & Eco-cement mud bricks. Right: Eco-Cement permeacocretes and foamed concretes

Forced Carbonation ~ Optimisation

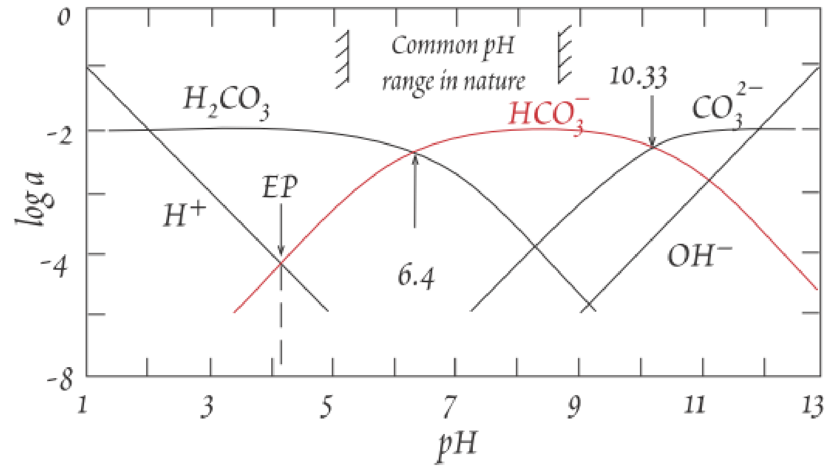
	Forced Carbonation (Cambridge)	Kinetic Optimisation (TecEco)
Steps	Multistep process	Less steps = lower costs
Rate	Variable	Varying on weather conditions (wet dry best and gas permeability)
% Carbonation in 6 months	70% (reported, could be more if permeable)	100%
Ease of general implementation	Require point sources CO_2	Can be implemented very quickly
Can use large quantities of fine wastes	Can use large quantities of fine wastes like fly ash that are not necessarily pozzolanic	Fine wastes tend to reduce gas permeability
Safety	Are carbonation rooms safe?	No issues
Key requirements	Special carbonation rooms	Optimal kinetics including gas permeability
Physical rate considerations	Doubling the concentration of CO2 doubles the rate of carbonation.	Doubling the pore size quadruples the rate of carbonation.
Other issues	Able to be sealed with paint etc. as pre carbonated	Some sealing paints will slow down carbonation

[20] According to ECN "The CO_2 concentration in power station flue gas ranges from about 4% (by volume)for natural gas fired combined cycle plants to about 14% for pulverised coal fired boilers." At 10% the rate increase over atmospheric could be expected to be 10/.038 = 263 times provided other kinetic barriers such as the delivery of water do not set in. Ref: http://www.ecn.nl/en/h2sf/products-services/co2-capture/r-d-activities/post-combustion-co2-capture/ accessed 24 Mar 08.

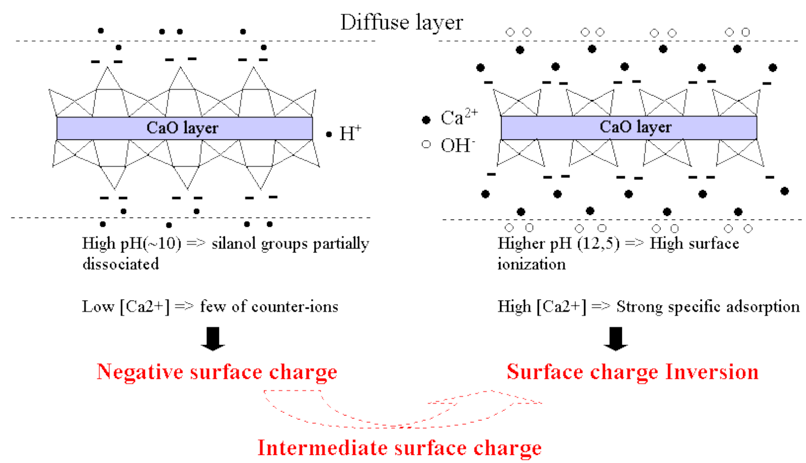
Forced carbonation of silicate phases as promoted by some is nonsense

Carbonation Optimisation

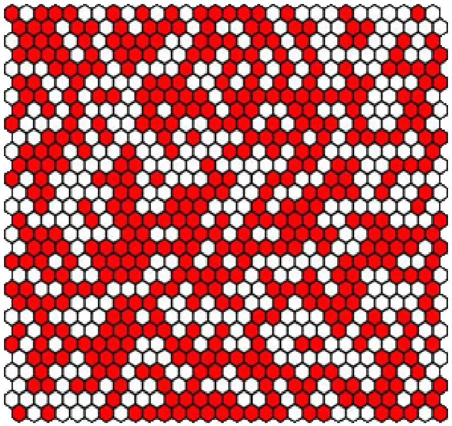
- Dissolution of MgO
  - Gouging salts e.g. $MgSO_4$, $MgCl_2$ and NaCl (Not used by TecEco)
  - Various catalysing cations e.g. Ca^{++} and Pb^{+} and ligands EDTA, acetate, oxalate citrate et (Not used by TecEco)
  - Low temperature calcination = Low lattice energy = high proportion of unsaturated co-ordination sites = rapid dissolution. See http://www.tececo.com/technical.reactive_magnesia.php



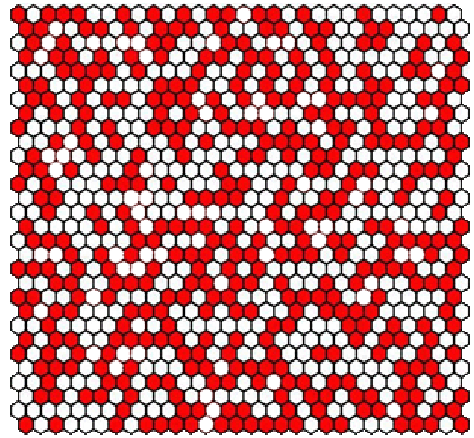
- Carbonation – High concentration of CO_3^{--} at high pH as a result of OH^- from Portlandite
- Possible catalysis and nucleation by polar surface of calcium silicate hydrate at high pH
- Wet dry conditions. Wet for through solution carbonation, dry for gas transport.
- Gas permeability
- Carbonate shape is important (next slides)



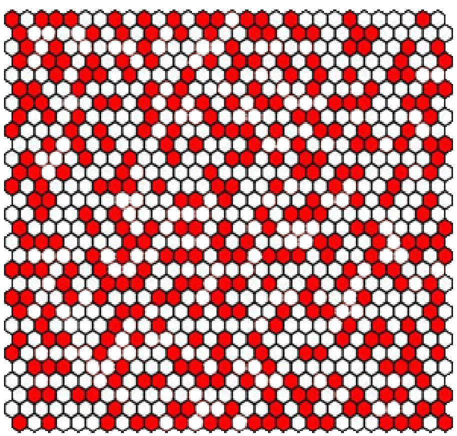
Particle Packing – Percolation and Porosity ~ Permeability



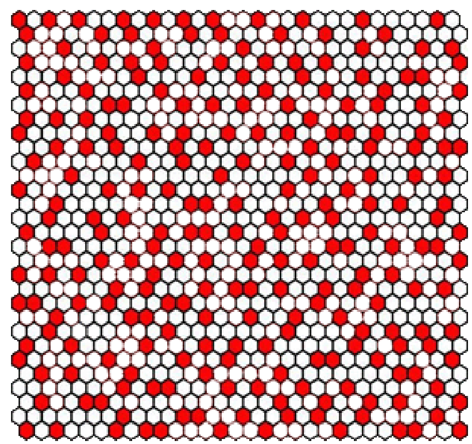
1. Red connected, white disconnected



2. Red partially connected, white partially disconnected



3. Red partially disconnected, white partially connected



4. Red disconnected, white connected

Shape effects particle packing (Olafur Wallevik presentation[21]) and the angle of repose (Bagnold[22]). The latter is therefore a proxy guide to shape.

Eco-Cements are deliberately not perfectly packed. Whereas in Tec-Cements the opposite occurs

[21]Wallenvik, Olafur, Carbon Footprint of High Performance Versus Conventional Vibrated Concrete

[22]Bagnold, Ralph A, The Physics of Blown Sand and Desert Dunes

Economics of Magnesium Carbonate Binder Based Masonry Products

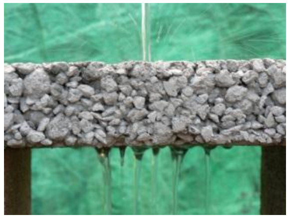
Material	Normal (kg)	Eco-Cement (kg)	
PC	200	80	
Reactive MgO		120	
Total Cementitous	200	200	13.89%
7mm Basalt	310	310	
3mm Dust	190	190	
Bottom Ash	660	660	
Total Aggregate	1160	1160	80.56%
Total Batch	1360	1360	
Water (litres)	80	80	
Total	**1440**	**1440**	
Binder Costs			
Cost PC	$90.00	$36.00	
Cost MgO	$0.00	$90.00	
Sub Total	$90.00	$126.00	
Less Carbon credit	$1.45	$3.58	
Net Cost Binder	**$88.55**	**$122.42**	
Assuming			**Actual**
GP Cement	$ 0.45	Kg	$ 0.45
Reactive MgO	$ 0.75	Kg	$ 0.75
Value Carbon Capture	$ 0.025	Kg	$ 0.025
% PC Capture	29.00%	%	
% MgO Capture	100.00%	%	

What this embedded spreadsheet demonstrates is that Magnesium Carbonate Block formulations are uneconomic unless the price of reactive MgO approaches that of PC or there is a high price for carbon or alternatively less MgO can be used!

Because of molar volume growth less can be used but we must still address supply chain issues.

This embedded spreadsheet looks only at the binder price and assumes all other factors remain the same

Permeacocretes

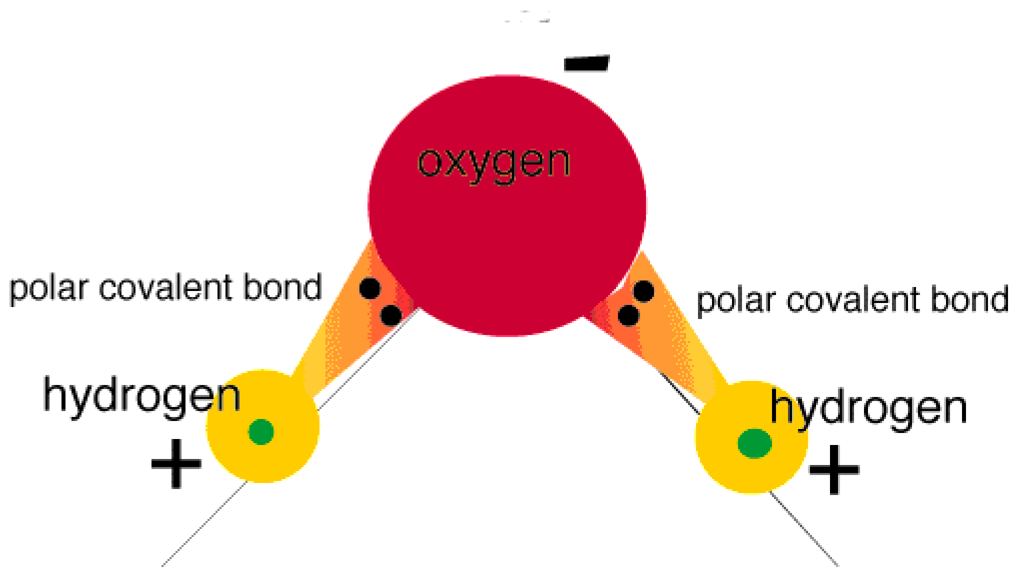


- Permeacocretes are an example of a product where the other advantages of using reactive MgO overcome its high cost.
- The use of MgO gives an ideal rheology which makes it possible to make permeacocrete pervious pavements using conventional road laying equipment therefore substantially reducing labour costs.
- There are many other advantages of pervious pavements see http://www.tececo.com/files/conference%20presentations/TecEcoPresentationSGA25Mar2010.ppt
- We are developing a low cost method of mechanised placement.

Tec-Cements

- Tec-Cements (5-20% MgO, 80-95% OPC)
  - contain more Portland cement than reactive magnesia. Reactive magnesia hydrates in the same rate order as Portland cement forming Brucite which uses up excess water reducing the voids:paste ratio, increasing density and possibly raising the short term pH.
  - Reactions with pozzolans are more affective. After much of the Portlandite has been consumed Brucite tends to control the long term pH which is lower and due to it's low solubility, mobility and reactivity results in greater durability.
  - Other benefits include improvements in density, strength and rheology, reduced permeability and shrinkage and the use of a wider range of aggregates many of which are potentially wastes without reaction problems.

Water – Fundamental to Concretes



Polar Bonding

Diagrammatic representation of a water molecule having polar covalent bonds between the Oxygen atom and the Hydrogen atoms. (Note the angle is supposed to be 104.5 ^{o}C)

In a polar covalent bond, the electrons shared by the atoms spend a greater amount of time, on average, closer to the oxygen nucleus than the hydrogen nucleus. This is because of the geometry of the molecule and the great electronegativity difference between the hydrogen atom and the oxygen atom.

The result of this pattern of unequal electron association is a charge separation in the molecule, where one part of the molecule, the oxygen end, has a partial negative charge and the hydrogens have a partial positive charge.

The Electrostatic Nature of Cements made with Water

The surface tension of water is 73 dynes per cm at 18^{o}C compared to ethyl alcohol at 24 dynes per cm.

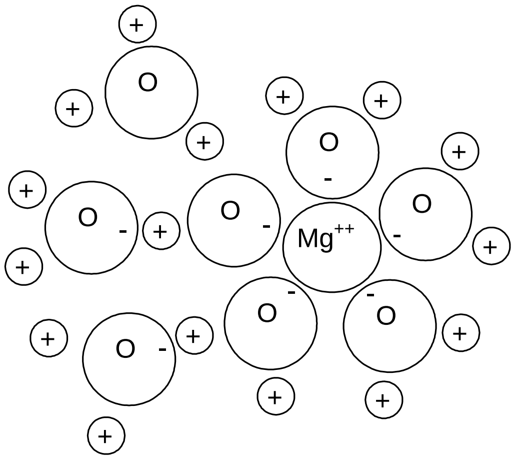
Hydrogen bonding is attributed to the ability of water to adhere to or "wet" most surfaces; such substances are said to be hydrophilic (water-loving). A hydrogen bond is only about 10 percent of the strength of a covalent bond, but it is responsible for most of the unusual properties of water (high freezing and boiling points, high heat capacity, high heats of fusion and evaporation, solvency, and high surface tension).

Water has an exceptionally large dipole moment (1.87 x 10-18 e.s.u.) relative to most other inorganic compounds. Dipole moment is the product of the distance between the charges multiplied by the magnitude of the charge in electrostatic units (e.s.u.).

[23]Refer: Labbe, Christophe, Nonat, Andre, 2007, The Cement Cohesion: An Affair of Electrostatics, Lutam Symposium on Swelling and Shrinkage of Porous Materials, Petropolis, Brazil

Wet Stage Properties of Tec-Cement Concretes

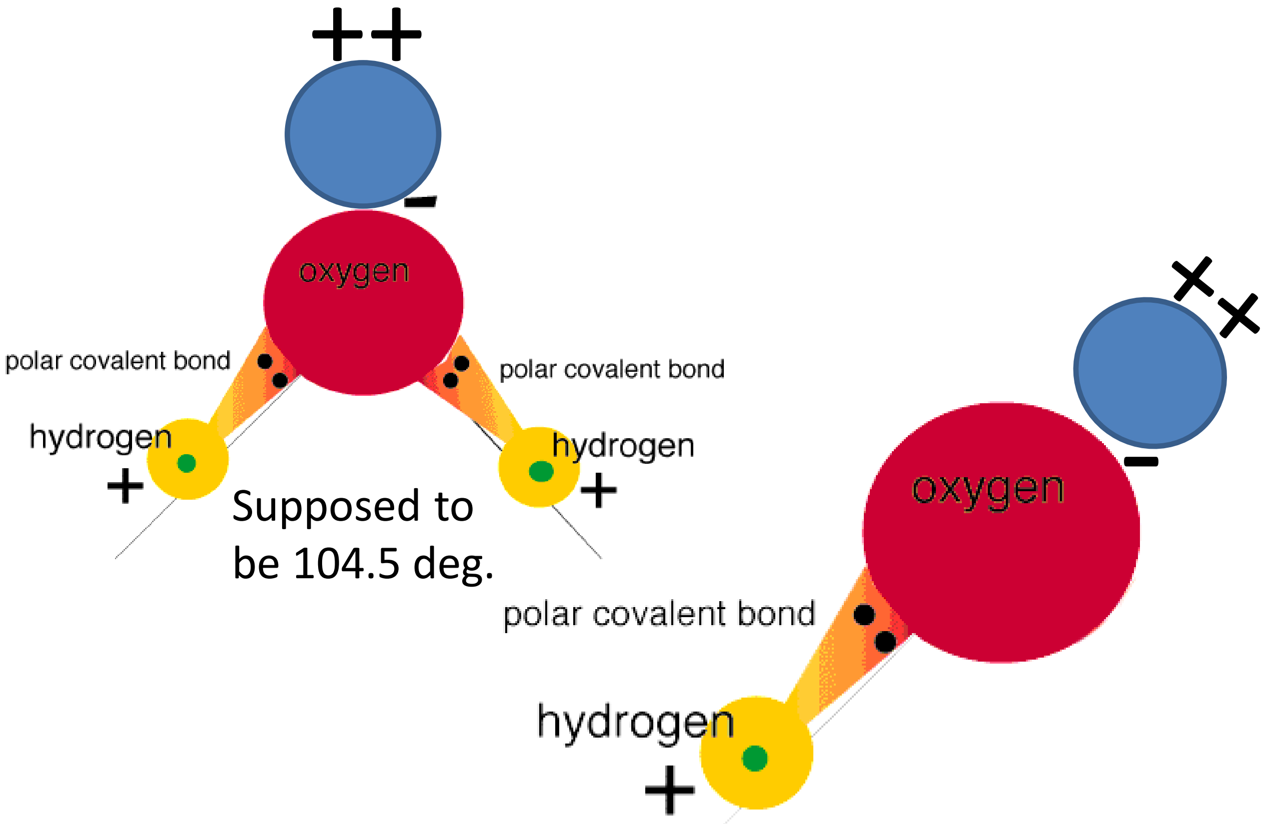
- Water has cohesivity due to a network of extensive three-dimensional hydrogen bonding and this property is strengthened both by Brucite surfaces and the strongly kosmotropic Mg^{++} ion.
- The strong polar bonding
  - Affects all wet stage properties
    - Improved rheology markedly (all formulations)
    - Dissolution of SCM's like clinker, gbfs etc.
    - High early strength
    - Greater strength
    - Reduced bleed water thereby retaining alkali
    - Reduced early age shrinkage
  - Significantly brings forward the onset of first set with high replacement mixes.
    - Increases the "wet sand effect" effect.
    - MgO goes negative
  - Reduces overall shrinkage incl. autogenous shrinkage



Ca^{++} = 114 picometres

Mg^{++} = 86 picometres

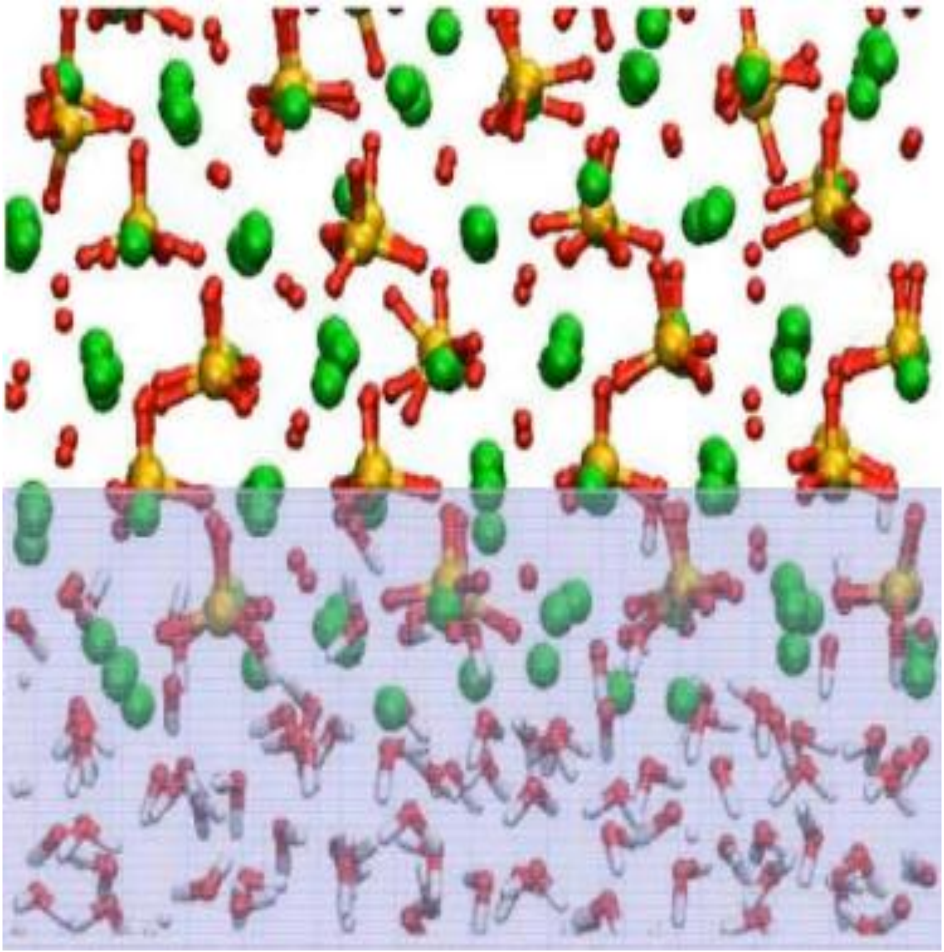
The Effect of a Strong Kosmotrope such as Mg^{++}



The polar bonding of water is supercharged by the presence of a strong cation such as Mg^{++} which has a strong affinity for the oxygen end of water.

The supercharging of the polar bonding of water and other hydrated species will propagate and may cause more rapid dissolution of clinker, GBFS and other hydraulic cements leading to earlier more complete reaction and thus early strength.

Dissolution – By Proton Wrenching?



Dissolution of alite by proton wrenching

[24] Image Source: Slide in a presentation by Prof Roland Pellenq, MIT Concrete Sustainability Hub

According to Pellenq from MIT water dissociates and the protons formed move in a Grotthus like way (i.e. by proton hopping) penetrating the crystal structure of alite and play a role in breaking it apart. Belite has a different crystal structure and this does not occur to the same extent. Pellenq suggests change Belite structure using aluminium. We mention that aluminium works in our patents at length so have the prior art however Pellenq et. al. add understanding as to possibly why. We suggest changing the nature of water by adding Mg^{++}. (See later, note both methods work well together)

Magnesium is mainly present as Mg2+ (aq) in water, but also as MgOH+ (aq) and Mg(OH)2 (aq) and other species. The strong electron pull of magnesium may also play a role in dissolution as we have noticed a much faster early setting rate and can make cements with pure gbfs for example. i.e Mg++ and associated aqueous species probably play a role in dissolution processes.

Setting – An Electrostatic Affair?

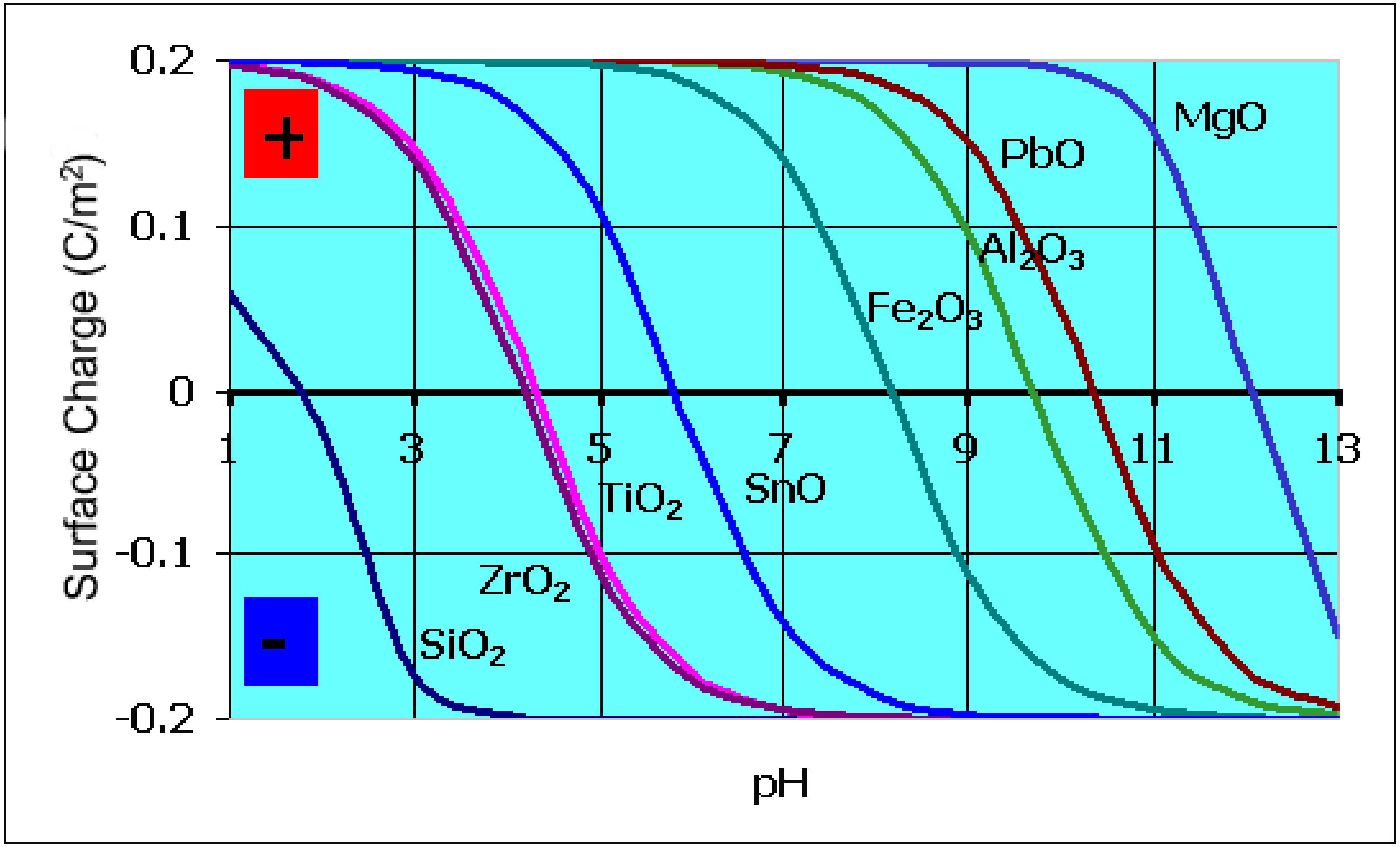
The Wet Beach affect

Sand is largely silica that has broken into small grains. At the atomic scale, silica
consists of a three-dimensional network of covalently bonded silicon and oxygen atoms.

Typically, silica surfaces contain mostly oxygen atoms, many of which are covalently bonded to hydrogen atoms.

The surface contains many polar bonds and can hydrogen-bond to water molecules. Therefore water is attracted to silica
surfaces, which are said to be hydrophilic (water loving).

MgO has a Bar Magnet Effect



The Change in the Surface Charge of Metal Oxides with pH.

[25]Source:Small, R.J. et al., 2005. Using a buffered rinse solution to minimize metal contamination after wafer cleaning. MicroMagazine.com. Available at: http://www.micromagazine.com/archive/98/01/small.html.

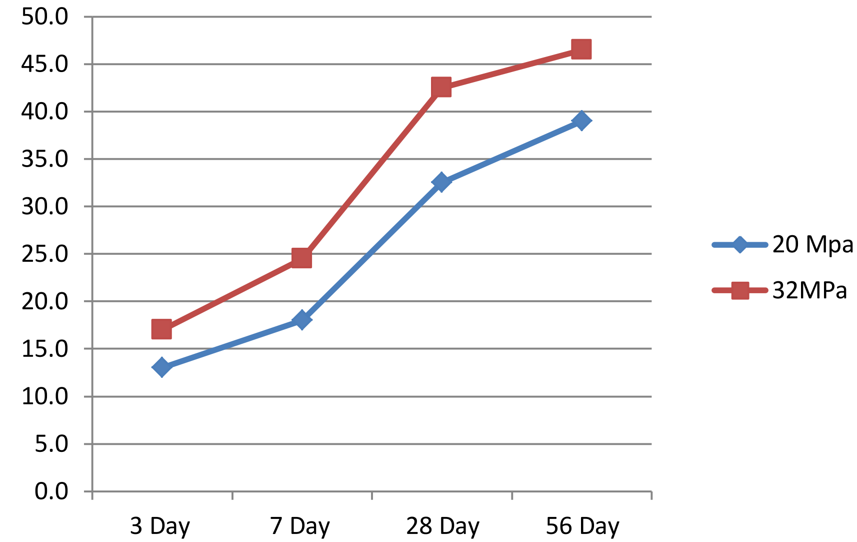
High and Total Replacement Cements

- TecEco recently announced a way forward to greater sustainability for the Portland cement industry.
- Up to 30% or more strength at all stages with high & very high replacement ternary mixes. (GBFS +- fly ash replacing PC.)
- Total replacement with class C fly ash and gbfs is possible
- Finishers can go home early using >50% replacement mixes removing the remaining barrier to their implementation.
- Brilliant rheology, low shrinkage and little or no cracking.
- Excellent durability.
- A solution to autogenous shrinkage?
- Mixes with MgO can tolerate carbon in fly ash and clays to some extent.
- Mg^{++} combines with <u>chloride or sulfate immobilising these cations</u>
- Mg^{++} neutralises humus in sands
- <u>$Mg(OH)_2$ provides long term pH control protecting steel.</u>

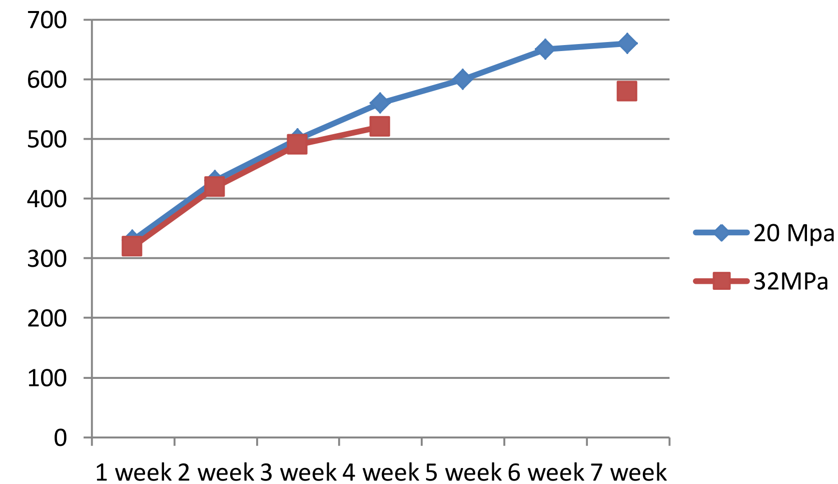
Example Results for TecEco

Date of Trial Mix	30/10/2010 20MPa		3/12/2010 32MPa	
Constituents	Kg	%	Kg	%
GP PC, kg/m3	116	47.93	155	47.78
Fly ash, kg/m3	58	23.97	78	24.04
Slag, kg/m3	58	23.97	78	24.04
Reactive Magnesia, kg/m3	10	4.13	13.4	4.13
MgO relative to PC		**8.7**		**8.7**
20mm, kg/m3	710		730	
10mm, kg/m3	275		280	
Total Coarse Aggregate	985		1010	
Manufactured Sand, kg/m3	490		440	
Fine Sand, kg/m3	390		350	
Total Fine Aggregate	880		790	
WR (WRDA PN), ml/100kg	350		400	
Water, lt/m3	185		199	
Design Slump, mm	80		100	
Actual Slump, mm	80		100	
Strength	20 Mpa		32MPa	
3 Day	13.0		17.0	
7 Day	18.0		24.5	
28 Day	32.5		42.5	
56 Day	39.0		46.5	
Shrinka	20 Mpa		32MPa	
1 week	330		320	
2 week	430		420	
3 week	500		490	
4 week	560		520	
7 week	660		580	

NB. Our patents in all countries define the minimum added % MgO as being >5% of hydraulic cement components or hydraulic cement components + MgO



Strength

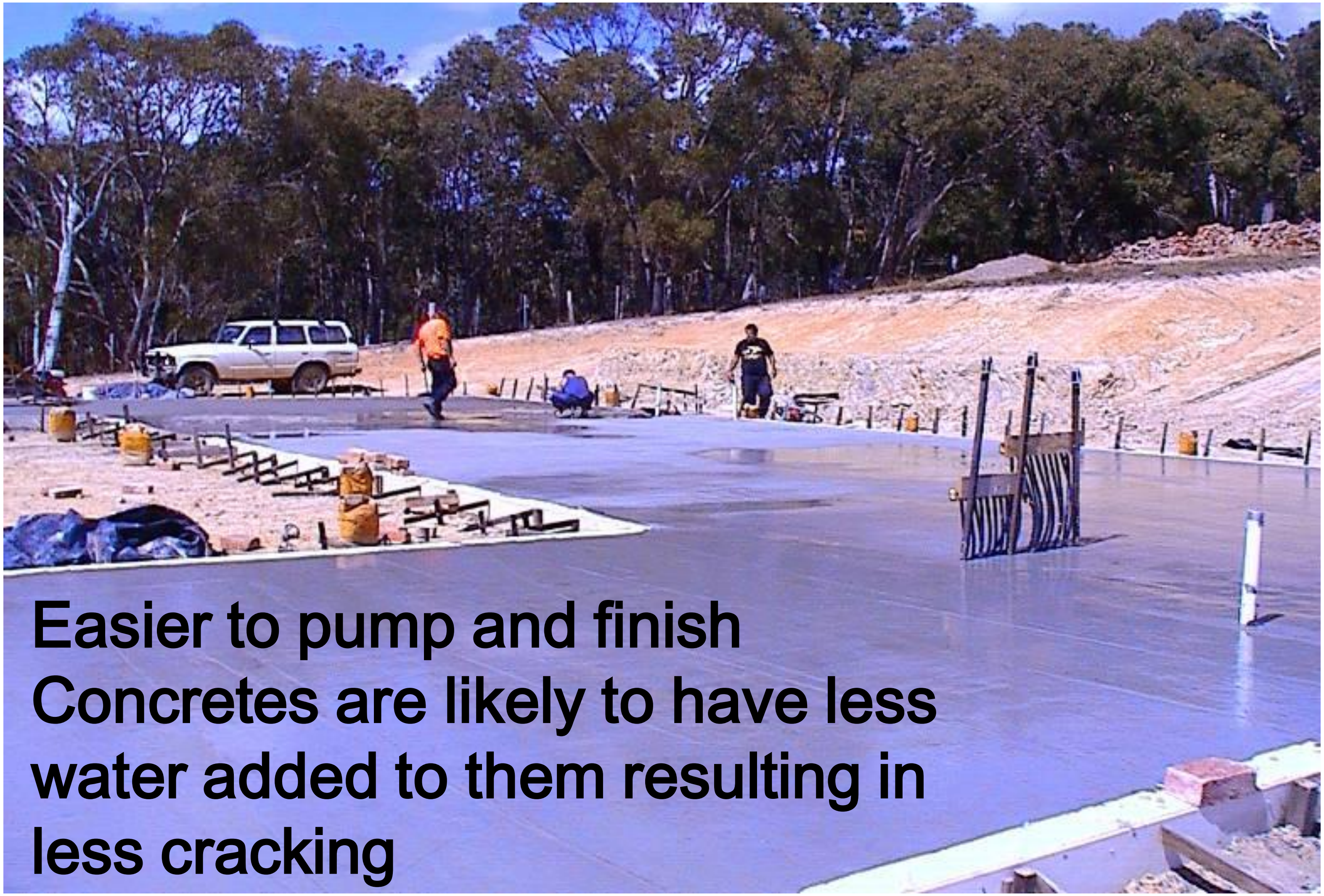


Shrinkage

TecEco Pty. Ltd. Sustainable Technologies

A Tec-Cement Modified Ternary Mix

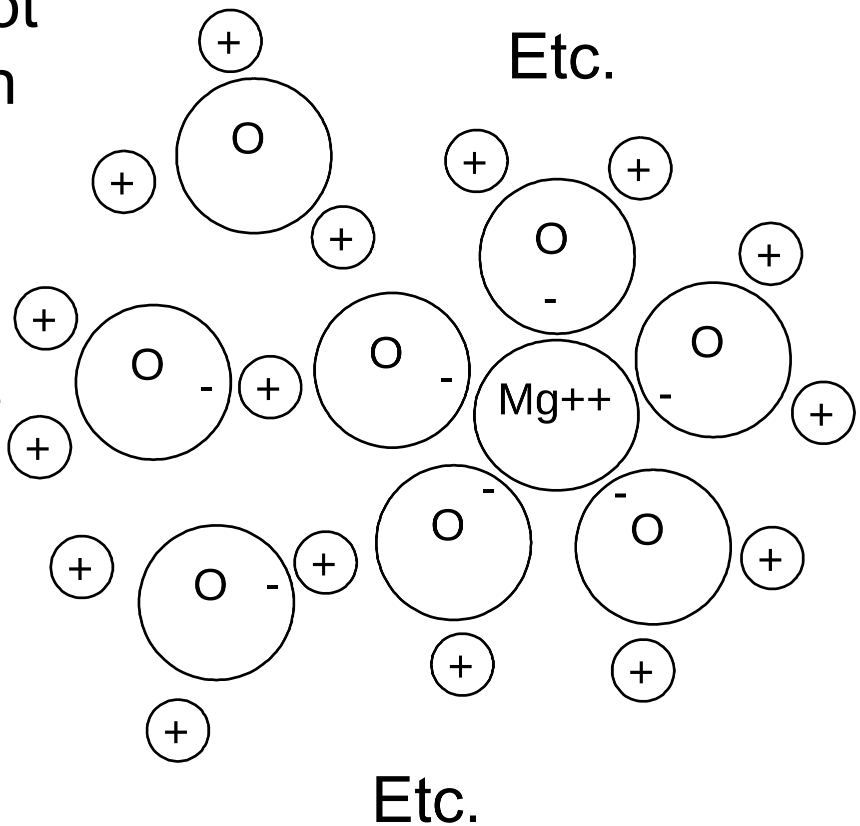
Easier to Finish Concretes



Easier to pump and finish Concretes are likely to have less water added to them resulting in less cracking

Brilliant Rheology

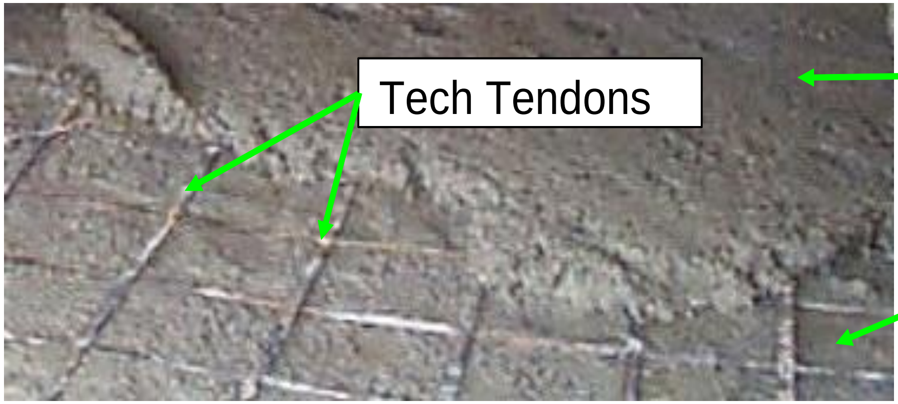
It is not known how deep these layers get



The strongly positively charged small Mg++ atoms attract water (which is polar) in deep layers introduce a <u>shear thinning property</u> affecting the rheological properties and making concretes less “sticky” with added pozzolan

Ca++ = 114, Mg++ = 86 picometres

Bingham Plastic Rheology



Second layer low slump tec-cement concrete

First layer low slump tec-cement concrete

- TecEco concretes and mortars are:
  - Very homogenous and do not segregate easily. They exhibit good adhesion and have a shear thinning property.
  - Exhibit Bingham plastic qualities and react well to energy input.
  - Have good workability.
- TecEco concretes with the same water/binder ratio have a lower slump but greater plasticity and workability.
- TecEco tec-cements are potentially suitable for mortars, renders, patch cements, colour coatings, pumpable and self compacting concretes.
- A range of pumpable composites with Bingham plastic properties will be required in the future as buildings will be "printed."

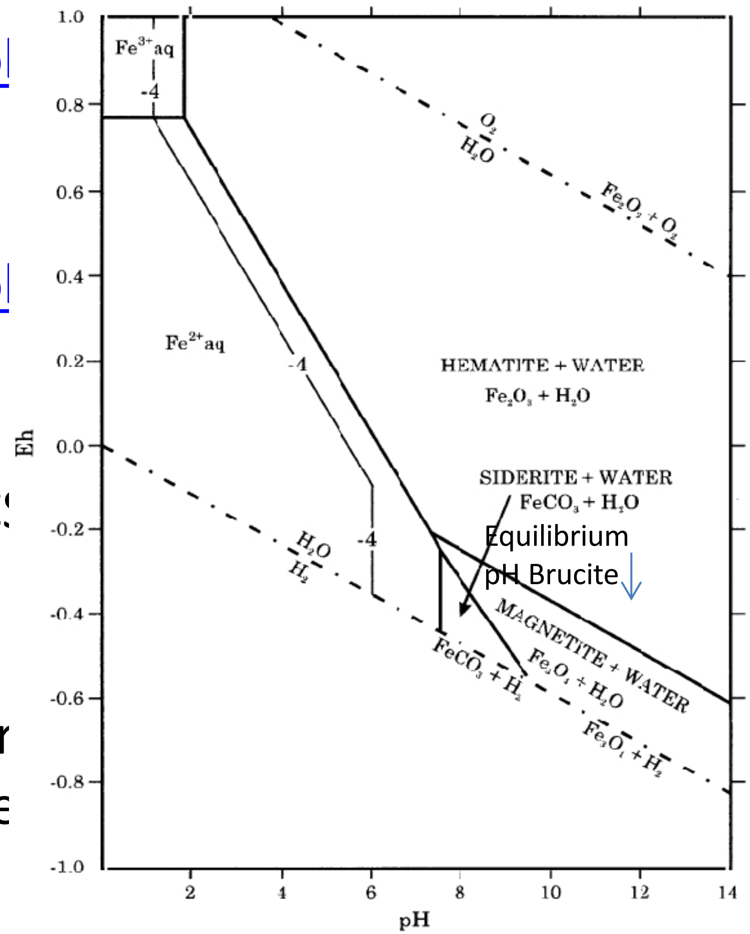
Tec-Cement Mixes

	Ordinary Mixes	TecEco Tec-Cement Mixes	Notes
Reactive MgO as defined	None	Usually 8 to 10% / PC added	1
Pozzolan (Pos)	Should be used	Recommended. } We recommend using both Pos and SCM's together	
Supplementary cementitious materials (SCM's)	Should be used	Recommended.	2
Limit on additions pozzolans + SCM's	Limited by standards that are increasingly exceeded	> 50% recommended especially if a ternary blend	
Rheology	Usually sticky, especially with fly ash. Hard to finish.	Slippery and creamy. Easy to finish.	
Setting time	Slow. Especially with fly ash only.	Much faster. Blends with a high proportion Pos. and SCM's set like ordinary PC concrete.	
Shrinkage and cracking	Significant	Much less	
Additives	Usually used	Not necessary	
Durability	Without additions of SCM's questionable.	Excellent especially with additions of SCM's	
28 day Strength (prev. 20 MPA mix)	< .20 Mpa/Kg PC/m^3	> .27 Mpa/Kg PC/m^3	
$ Cost Binder/Mpa at 28 days (prev 20 & 32 MPa mixes)	> ($2.30-$2.50)	< ($1.50-$1.90)	3

Notes
1. See http://www.tececo.com/technical.reactive_magnesia.php. % is relative to PC and in addition to amount already in PC
2. To keep our patents simple we included supplementary cementitious materials as pozzolans in our specification
3. See economics pages following

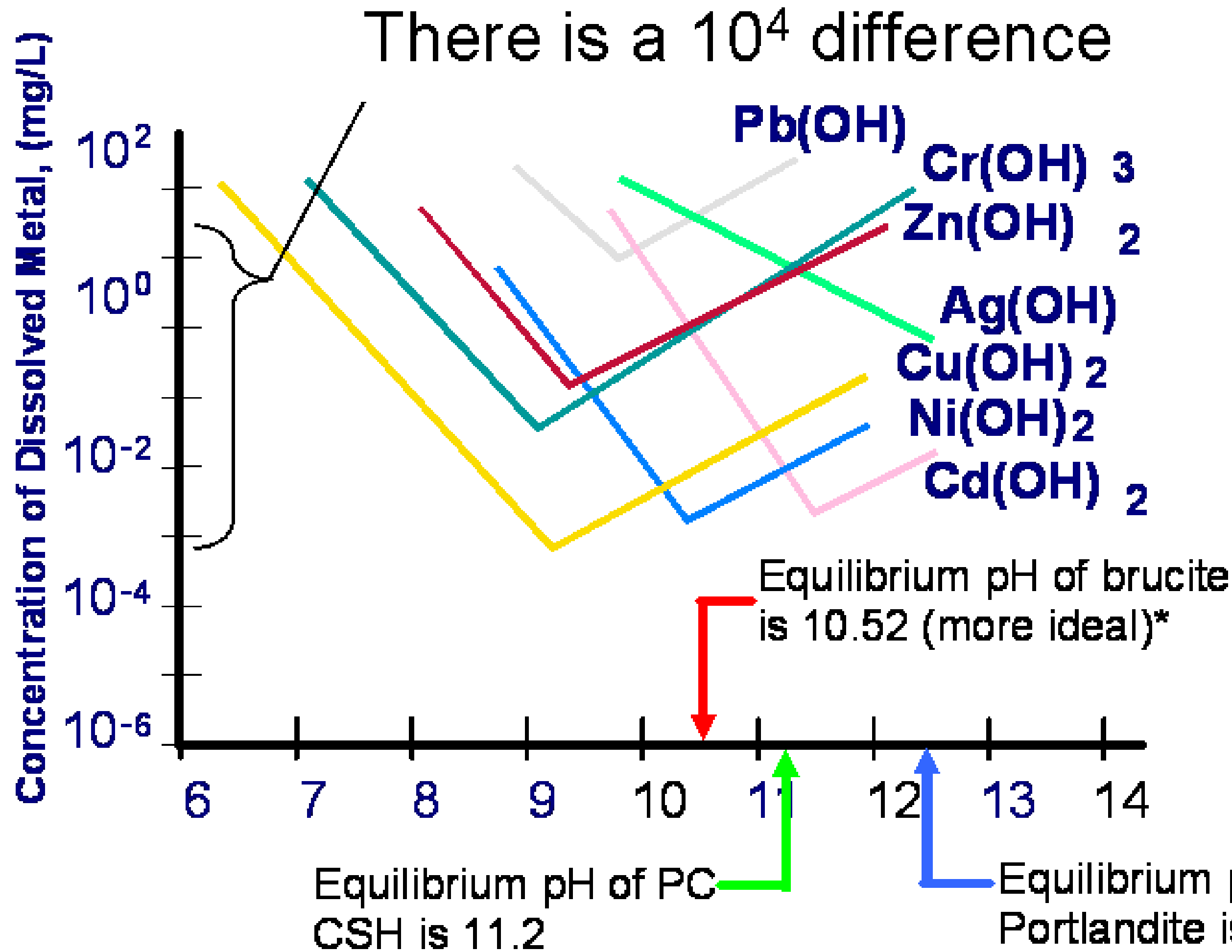
Why Put Brucite in Concretes?

- Improved rheology (see http://www.tececo.com/technical.rheol_shrinkage.php)
- Prevents shrinkage and cracking (see http://www.tececo.com/technical.rheol_shrinkage.php)
- Provides low shrinkage and pH and eH control. Reduced corrosion. Stabilises CS when Ca^{++} consumed by the pozzolanic reaction (Encouraged)
- Relinquishes polar bound water for more complete hydration of PC thereby preventing autogenous shrinkage?
- **Solves the carbon in fly ash, sulfate, chloride and clay in aggregate problems**.



Pourbaix diagram steel reinforcing

Immobilisation as Well as Encapsulation



*Equilibrium pH's in pure water, no other ions present. The solubility of toxic metal hydroxides is generally less in the range pH 10.52 - 11.2 than at higher pH's.

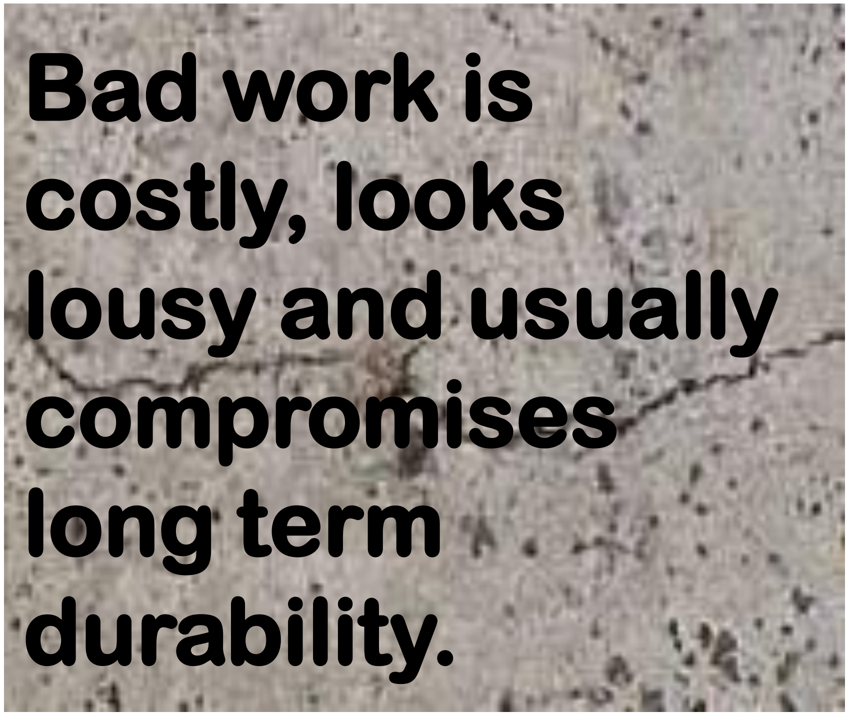
All waste streams will contain heavy metals and a strategy for long term pH control is therefore essential

Dry Stage Properties of Tec-Cement Concretes

- Significantly increased tensile strength
- Increased compressive strength (especially early strength) particularly with high replacement mixes containing significant amounts of GBFS compacting factor
- Reduced shrinkage and cracking
- Improved durability
- Higher tensile strain capacity?
- Greater creep
- Less permeable?
- Lighter albedo
- Solves autogenous shrinkage problems
- May solve other delayed reaction problems

[26]Recommended Reading: Du C. A Review of Magnesium Oxide in Concrete - A serendipitous discovery leads to new concrete for dam construction. Concrete International. 2005;(December 2005):45 - 50.

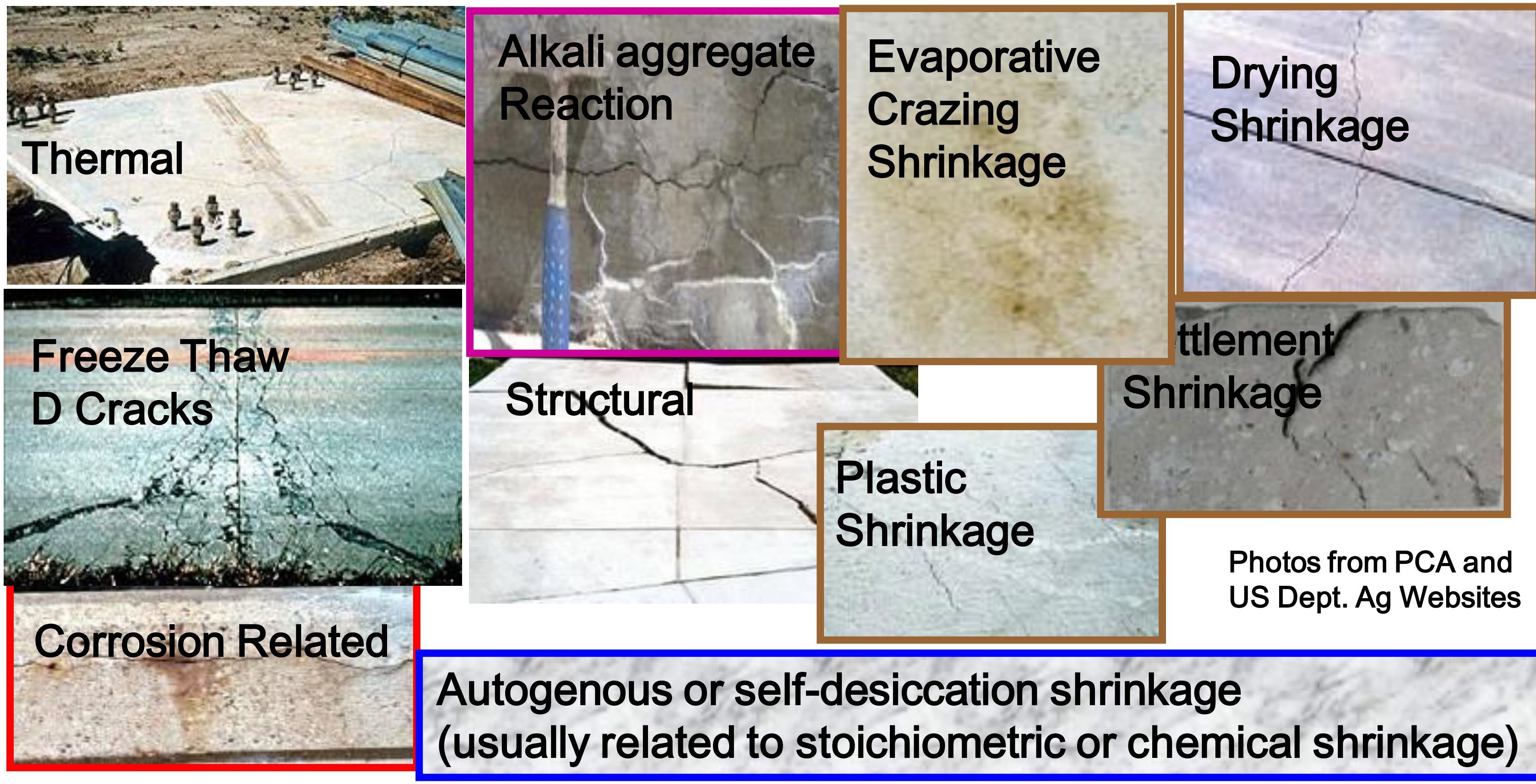
TecEco Tec-Cements – Eliminating Problems in Concrete



- There are two fundamental factors affecting durability: transport and reactivity of reactants

With TecEco Technology Much More Durable Concretes are Possible. Shrinkage, Delayed Reactions and Corrosion can be Substantially Eliminated

A Crack Collage



- TecEco technology can reduce if not solve problems of cracking:
  - Related to (shrinkage) through open system loss of water.
  - As a result of volume change caused by delayed reactions
  - As a result of corrosion.
  - Related to autogenous shrinkage

What Influences Durability?

- Concretes are said to be less durable when they are physically or chemically compromised.
- Physical factors can result in chemical reactions reducing durability
  - E.g. Cracking due to shrinkage can allow reactive gases and liquids to enter the concrete
- Chemical factors can result in physical outcomes reducing durability
  - E.g. Alkali silica reaction opening up cracks allowing other agents such as sulfate and chloride in seawater to enter.

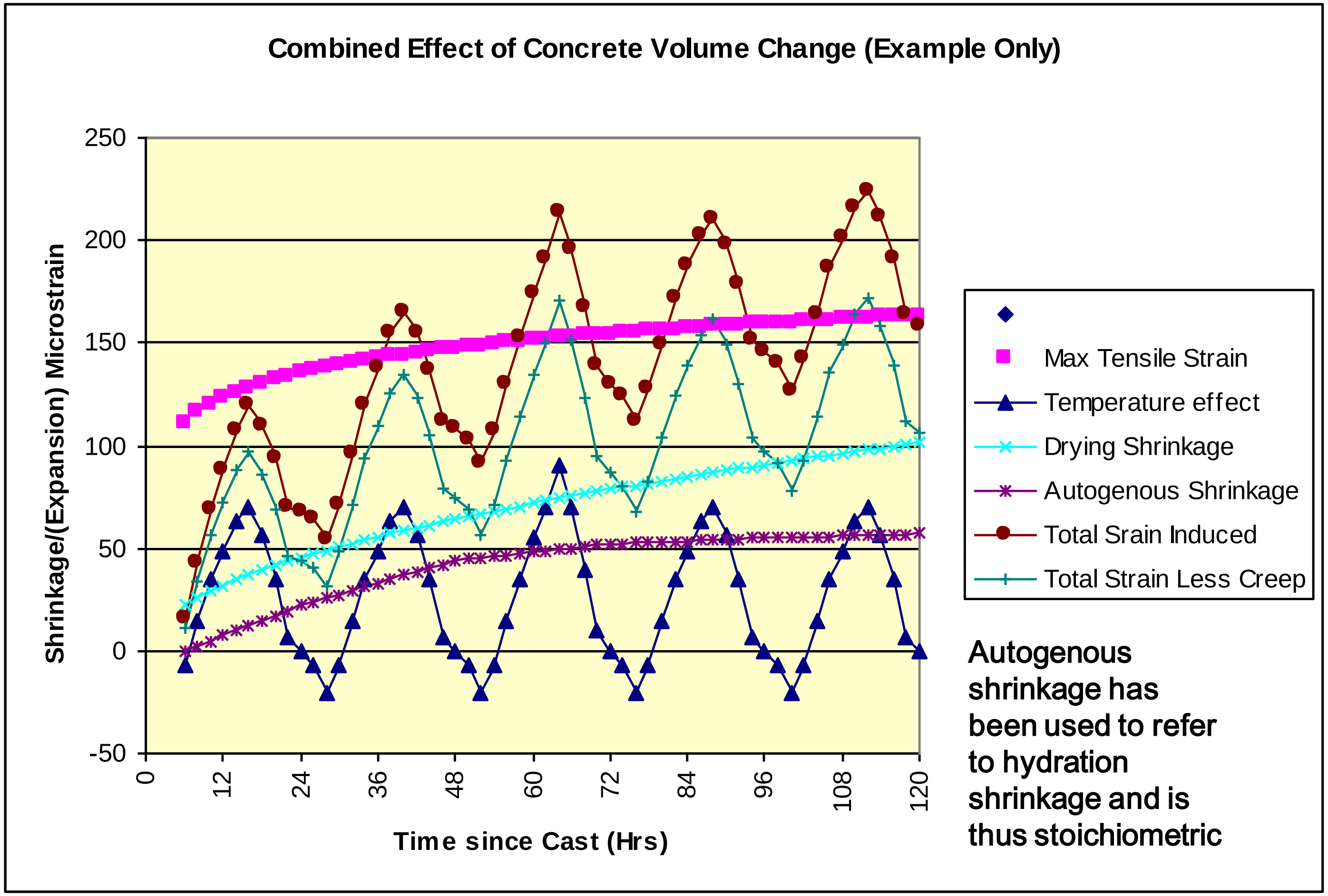
Durability (Important for Sustainability)

- Durability is related to physical and chemical factors
  - How easy is it for an aggressive agent to get into the concrete matrix
    - This depends on the density which depends on the voids and specific gravity of the minerals present.
      - The number and size of voids depends on the particle packing and water added.
      - If the number and size of voids causes percolation points to be exceeded then the material is permeable and thus not likely to be durable depending on the Eh-pH and chemical reactivity of species present.
      - Strength is not the cause of strength but a bad proxy for permeability.
  - What the aggressive agent can do once in there
    - Depends on the Eh-pH conditions inside the matrix and presence or otherwise of Portlandite
      - Ideally reducing Eh and pH above about 9.5 depending on the Eh.
      - **Brucite the hydration product of reactive MgO stabilises the pH in concrete. The equilibrium pH of Brucite is around 10.42.**
      - **Reactive MgO will also remove chloride and sulfate by reacting with them.**
      - **Consumes chloride and sulfate in the wet stage rendering them immobile.**
  - Protection of steel (pH control) and the electro coupling present
    - e.g. steel – chloride
  - Carbonation of Brucite is expansive and seals the surface.

Causes of Cracking in Concrete

- Cracking commonly occurs when the induced stress exceeds the maximum tensile stress capacity of concrete and can be caused by many factors including restraint, extrinsic loads, lack of support, poor design, volume changes over time, temperature dependent volume change, corrosion, carbonation or delayed reactions.
- Causes of induced stresses include:
  - Restrained thermal, plastic, drying and stoichiometric shrinkage, corrosion, carbonation and delayed reaction strains.
  - Slab curling.
  - Loading on concrete structures.
- Cracking is undesirable for many reasons
  - Visible cracking is unsightly
  - Cracking compromises durability because it allows entry of gases and ions that react with Portlandite.
  - Cracking can compromise structural integrity, particularly if it accelerates corrosion.

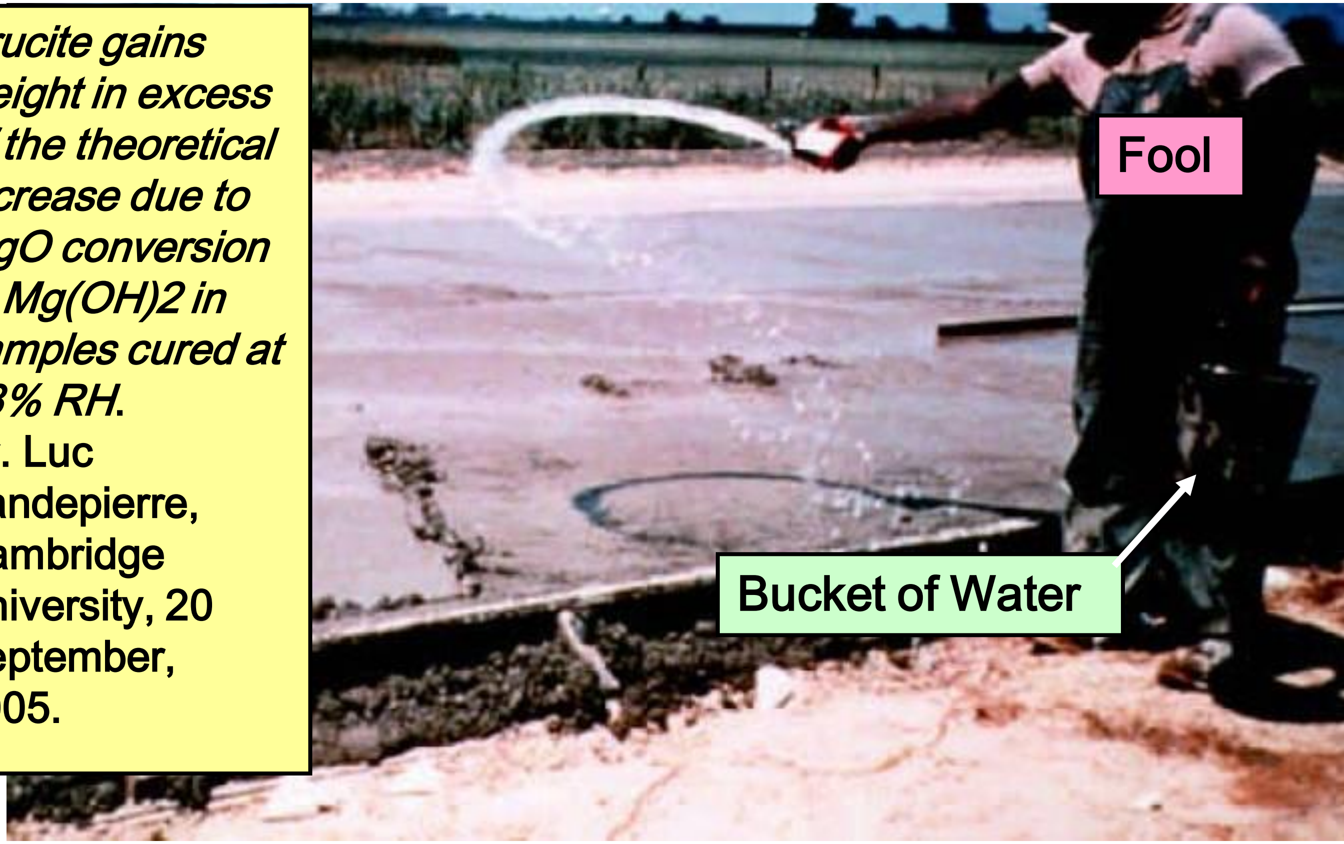
Graphic Illustration of Cracking

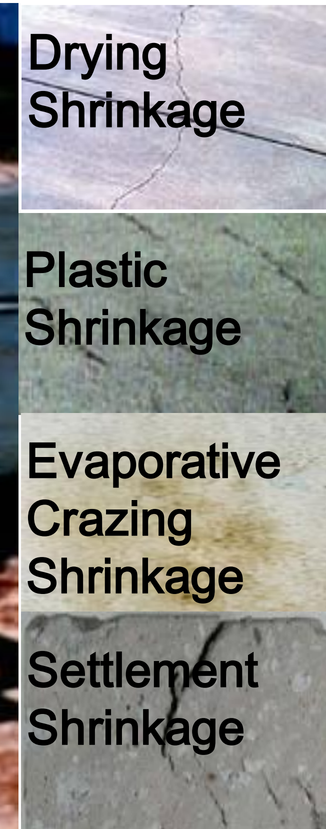


After Tony Thomas (Boral Ltd.) (Thomas 2005)

Cracking due to Loss of Water

Brucite gains weight in excess of the theoretical increase due to MgO conversion to Mg(OH)2 in samples cured at 98% RH. Dr. Luc Vandepierre, Cambridge University, 20 September, 2005.





Picture from: http://www.pavement.com/techserv/ACI-GlobalWarming.PDF

We may not be able to prevent too much water being added to concrete by fools. TecEco approach the problem in a different way by providing for the internal removal/storage of water that can provide for more complete hydration of PC.

Solving Cracking due Shrinkage from Loss of Water

- In the system water plus Portland cement powder plus aggregates shrinkage is in the order of .05 – 1.5 %.
- There are two root causes of Portland cements shrinking over time.
  - Stoichiometric (chemical) shrinkage and
  - Shrinkage through loss of water.
- The solution is to:
  - Add minerals that compensate by stoichiometrically expanding and/or to
  - Use less water, internally hold water or prevent water loss.
  - Prevent water exiting the system
- TecEco tec-cements internally hold water and prevent water loss.

$$MgO\ (s) + H_2O\ (l) \leftrightarrow Mg(OH)_2.nH_2O\ (s)$$

Preventing Shrinkage through Loss of Water

- When magnesia hydrates it consumes 18 litres of water per mole of magnesia probably more depending on the value of n in the reaction below:

  $MgO\ (s) + H_2O\ (l) \leftrightarrow Mg(OH)_{2.}nH2O\ (s)$

- The dimensional change in the system MgO + PC depends on:
  - The ratio of MgO to PC
  - Whether water required for hydration of PC and MgO is coming from stoichiometric mix water (i.e. the amount calculated as required), excess water (bleed or evaporative) or from outside the system.
  - In practice tec-cement systems are more closed and thus dimensional change is more a function of the ratio of MgO to PC
- As a result of preventing the loss of water by closing the system together with expansive stoichiometry of MgO reactions (see below).

  $MgO\ (s) + H_2O\ (l) \leftrightarrow Mg(OH)_{2.}nH2O\ (s)$

  $40.31 + 18.0 \leftrightarrow 58.3$ molar mass (at least!)

  $11.2 +$ liquid $\leftrightarrow 24.3$ molar volumes (at least!)

- It is possible to significantly reduce if not prevent (drying, plastic, evaporative and some settlement) shrinkage as a result of water losses from the system.

The molar volume (L.mol-1)is equal to the molar mass (g.mol-1) divided by the density (g.L-1).

Preventing Shrinkage through Loss of Water

- Portland cements stoichiometrically require around 23 -27% water for hydration yet we add approximately 45 to 60% at cement batching plants to fluidise the mix sufficiently for placement.
- If it were not for the enormous consumption of water by tri calcium aluminate as it hydrates forming ettringite in the presence of gypsum, concrete would remain as a weak mush and probably never set.
  - 26 moles of water are consumed per mole of tri calcium aluminate to from a mole of solid ettringite. When the ettringite later reacts with remaining tri calcium aluminate to form monosulfoaluminate hydrate a further 4 moles of water are consumed.
- The addition of reactive MgO achieves water removal internally in a closed system in a similar way.

$$MgO\ (s) + H_2O\ (l) \leftrightarrow Mg(OH)_2.nH_2O\ (s)$$

Other Benefits of Preventing Shrinkage through Loss of Water

- Internal water consumption also results in:
  - Greater strength
    - **More complete hydration** of PC .
    - Reduced in situ voids:paste ratio
  - Greater density
    - Increased durability
    - Higher short term alkalinity
    - More effective pozzolanic reactions.
- More complete hydration of PC .
  - Small substitutions of PC by MgO result in water being trapped inside concrete as Brucite and Brucite hydrates which can later **self desiccate** delivering water to hydration reactions of calcium silicates (Preventing so called "autogenous" shrinkage).

Bleeding is a Bad Thing

- Bleeding is caused by:
  - Lack of fines
  - Too much water
- Bleeding can be fixed by:
  - Reducing water or adding fines
  - Air entrainment or grading adjustments
- Bleeding causes:
  - Reduced pumpability
  - Loss of cement near the surface of concretes
  - Delays in finishing
  - Poor bond between layers of concrete
  - Interconnected pore structures that allow aggressive agents to enter later
  - Slump and plastic cracking due to loss of volume from the system
  - Loss of alkali that should remain in the system for better pozzolanic reactions
  - Loss of pollutants such as heavy metals if wastes are being incorporated.
- Concrete is better as a closed system

Better to keep concretes as closed systems

Open/Closed Systems - The Wet Sand Analogy

Wet sand or wet concrete?

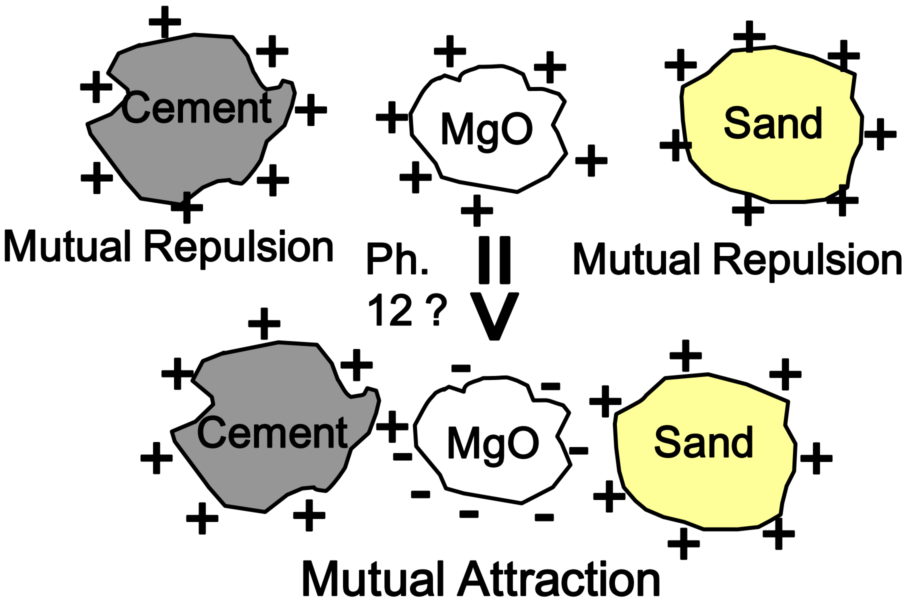
Wet concrete still in the particulate stage has much in common with wet sand

- In the particulate state wet beach sand is held together by the surface tension of water (a ramification of hydrogen bonding)
- A beach sand system emulates a closed system because water lost through evaporation or bleeding is constantly replaced by waves.
- No plastic or drying shrink cracking is observable in wet beach sands.
- To prevent plastic and drying shrink cracking in concrete the system must also be closed preventing loss of water through evaporation. To do this surface coatings such as aliphatic alcohols are used.
- The TecEco method is to internally hold water in Brucite and its hydrates that would otherwise bleed or evaporate.
- Increased surface tension in Tec-Cements reduces movement of water through capillaries and reduces evaporative loss
- Concrete can be made totally shrink proof (foolproof)
  - Adding reactive magnesia to consume and store water as it hydrates.
  - Applying surface coatings e.g. aliphatic alcohol (e.g. ethylene glycol).
- As a result joints are usually only necessary for structural reasons.

Dimensionally Control Over Concretes During Curing?

- Portland cement concretes shrink around .05%. Over the long term much more (>.1%).
  - Mainly due to plastic and drying shrinkage through **loss of water**
- The use of some wastes as aggregates also cause shrinkage e.g. wood waste in masonry units, thin panels etc.
- By adding MgO volume changes are minimised
  - <u>So far we have observed significantly less shrinkage in TecEco tec - cement concretes</u> with about (8-10% substitution OPC) with or without fly ash.
- Note that Brucite is > 44.65 mass% water and it makes sense to make binders out of water!

Greater Tensile Strength also Reduces Cracking



MgO Changes Surface Charge as the Ph. Rises. **This and a stronger "wet beach effect" could be the reason for the greater tensile strength displayed during the early plastic phase of tec-cement concretes.**

Reducing Cracking as a Result of Volume Change caused by Delayed Reactions

An Alkali Aggregate Reaction Cracked Bridge Element

Photo Courtesy Ahmad Shayan ARRB

Types of Delayed Reactions

- There are several types of delayed reactions that cause volume changes (generally expansion) and cracking.
  - Alkali silica reactions
  - Alkali carbonate reactions
  - Delayed ettringite formation
  - Delayed thaumasite formation
  - Delayed hydration or dead burned lime or periclase.
- Delayed reactions cause dimensional distress, cracking and possibly even failure.

Reducing Delayed Reactions

- Delayed reactions do not appear to occur to the same extent in TecEco cements.
  - A lower long term pH results in reduced reactivity after the plastic stage.
  - Potentially reactive ions are trapped in the structure of Brucite.
  - Ordinary Portland cement concretes can take years to dry out however the reactive magnesia in Tec-cement concretes consumes unbound water from the pores inside concrete.
  - Magnesia dries concrete out from the inside. Reactions do not occur without water.

Reduced Corrosion Related Cracking

Rusting Causes Dimensional Distress

- Steel remains protected with a passive oxide coating of Fe_3O_4 above pH 8.9.
- A pH of over 8.9 is maintained by the equilibrium $Mg(OH)_2 \leftrightarrow Mg^{++} + 2OH^-$ for much longer than the pH maintained by $Ca(OH)_2$ because:
  - Brucite does not react as readily as Portlandite resulting in reduced carbonation rates and reactions with salts.
- Concrete with Brucite in it is denser and carbonation is expansive, sealing the surface preventing further access by moisture, CO_2 and salt.

Reduced Corrosion Related Cracking

- Brucite is less soluble and traps salts as it forms resulting in less ionic transport to complete a circuit for electrolysis and less corrosion.
- Free chlorides and sulfates originally in cement and aggregates are bound by magnesium
  - Magnesium oxychlorides or oxysulfates are formed. (Compatible phases in hydraulic binders that are stable provided the concrete is dense and water kept out.)
- As a result of the above the rusting of reinforcement does not proceed to the same extent.
- Cracking or spalling due to rust does not occur

Reducing Cracking Related to Autogenous Shrinkage

- The autogenous deformation of concrete is defined as the unrestrained, bulk deformation that occurs when concrete is kept sealed and at a constant temperature.
- Main cause is stoichiometric or chemical shrinkage.
  - whereby the reaction products formed during the hydration of cement occupy less space than the corresponding reactants[1]. And/or
  - Chemical demand for water for continued hydration of PC
- A dense cement paste hydrating under sealed conditions will therefore self-desiccate creating empty pores within developing structure. If external water is not available to fill these "empty" pores, considerable shrinkage can result.

[1]Le Chatelier H. Sur les changements de volume qui accompagnent le durcissement des ciments. Bulletin de la Societe d'Encouragement pour l'Industrie Nationale 1900:54-7.

Reducing Cracking Related to Autogenous Shrinkage

- Autogenous shrinkage does not occur in high strength tec-cement concretes because:
  - The Brucite hydrates that form desiccate back to Brucite delivering water in situ for more complete hydration of Portland cement.

$$Mg(OH)_2.nH_2O\ (s) \leftrightarrow MgO\ (s) + H_2O\ (l)$$

    - As Brucite is a relatively weak mineral is compressed and densifies the microstructure.
  - The stoichiometric shrinkage of Portland cement (first observed by Le Chatelier) is compensated for by the stoichiometric expansion of magnesium oxide on hydration.

$MgO\ (s) + H_2O\ (l) \leftrightarrow Mg(OH)_{2.}nH_2O\ (s)$

40.31 + 18.0 ↔ 58.3 molar mass (at least!)

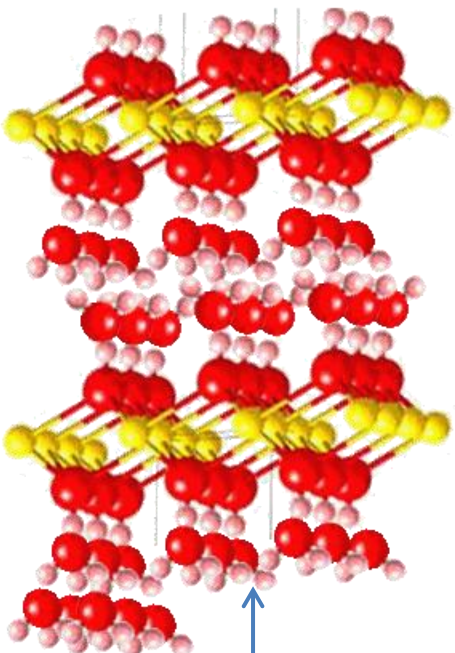
11.2 + liquid ↔ 24.3 molar volumes (at least 116% expansion, probably more initially before desiccation as above!)

More Complete Hydration of PC

In most concrete **18-23% of the PC used never hydrates**. If all the PC used could be made to hydrate less could be used saving on emissions be around 20%.

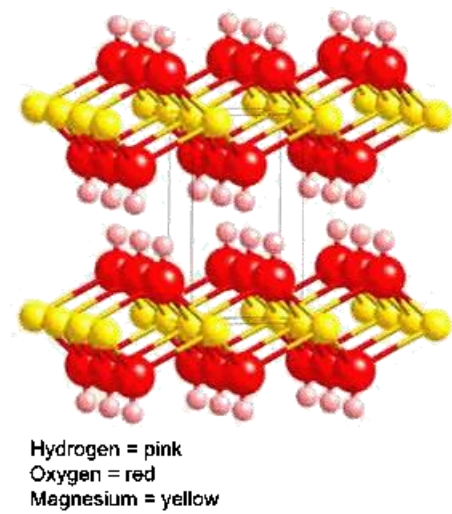
$$2C_3S+7H \Rightarrow C_3S_2H_4 + 3CH$$

$$2C_2S+5H \Rightarrow C_3S_2H_4 + CH$$



Brucite hydrates consist of polar bound layers of ionically bound atoms

NB. We think this loosely bound polar water is available for the more complete hydration of PC.



Brucite consists of polar bound layers of ionically bound atoms

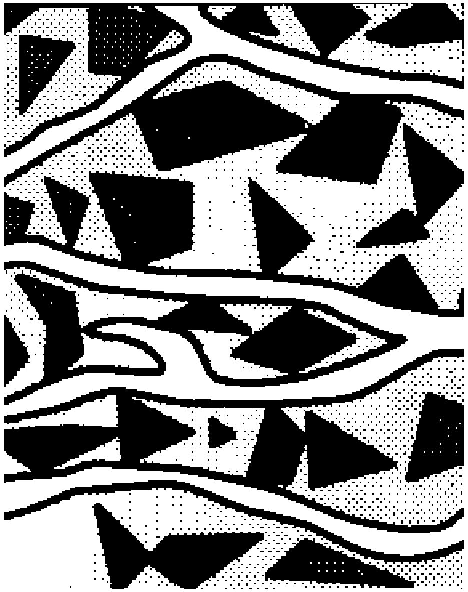
Strongly differentially charged surfaces and polar bound water account for many of the properties of Brucite

Greater Density – Lower Permeability

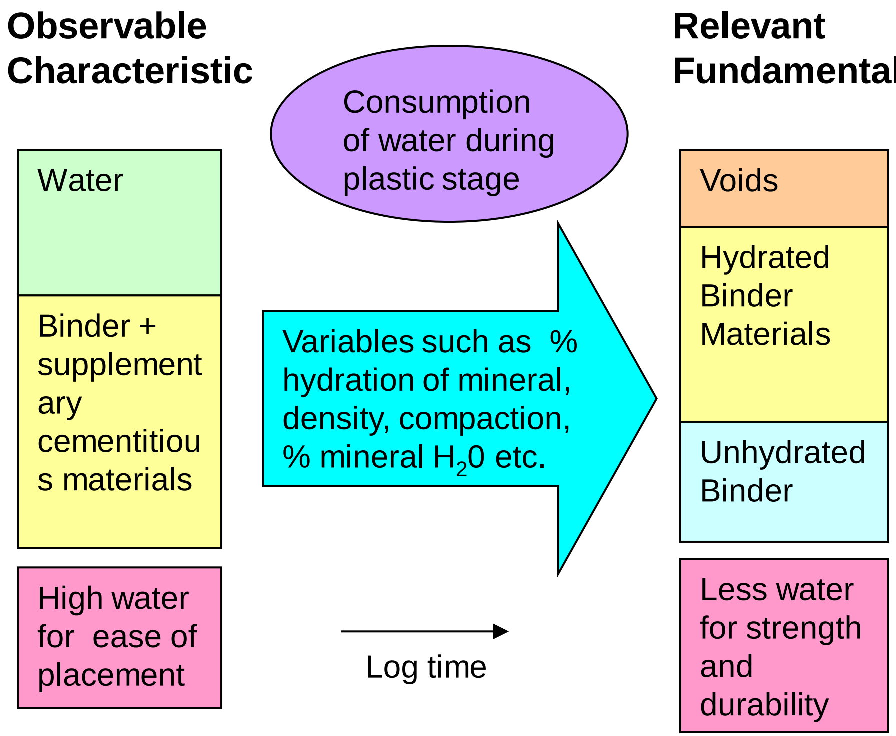
- Concretes have a high percentage (around 18% – 22%) of voids.
- On hydration magnesia expands >=116.9 % filling voids and surrounding hydrating cement grains => denser concrete.
- On carbonation to nesquehonite Brucite expands 308% sealing the surface.
- Lower voids:paste ratios than water:binder ratios result in little or no bleed water, lower permeability and greater density.

Reduced Permeability

- As bleed water exits ordinary Portland cement concretes it creates an interconnected pore structure that remains in concrete allowing the entry of aggressive agents such as SO_4^{--}, Cl^- and CO_2
- TecEco tec - cement concretes are a closed system. They do not bleed as excess water is consumed by the hydration of magnesia.
  - As a result TecEco tec - cement concretes **dry from within**, are denser and less permeable and therefore stronger **more durable** and less permeable. Cement powder is not lost near the surfaces. Tec-cements have a higher salt resistance and less corrosion of steel etc.



Densification During the Plastic Phase



Water is required to plasticise concrete for placement, however once placed, the less water over the amount required for hydration the better. Magnesia consumes water as it hydrates producing solid material.

Less water results in increased density and concentration of alkalis - less shrinkage and cracking and improved strength and durability.

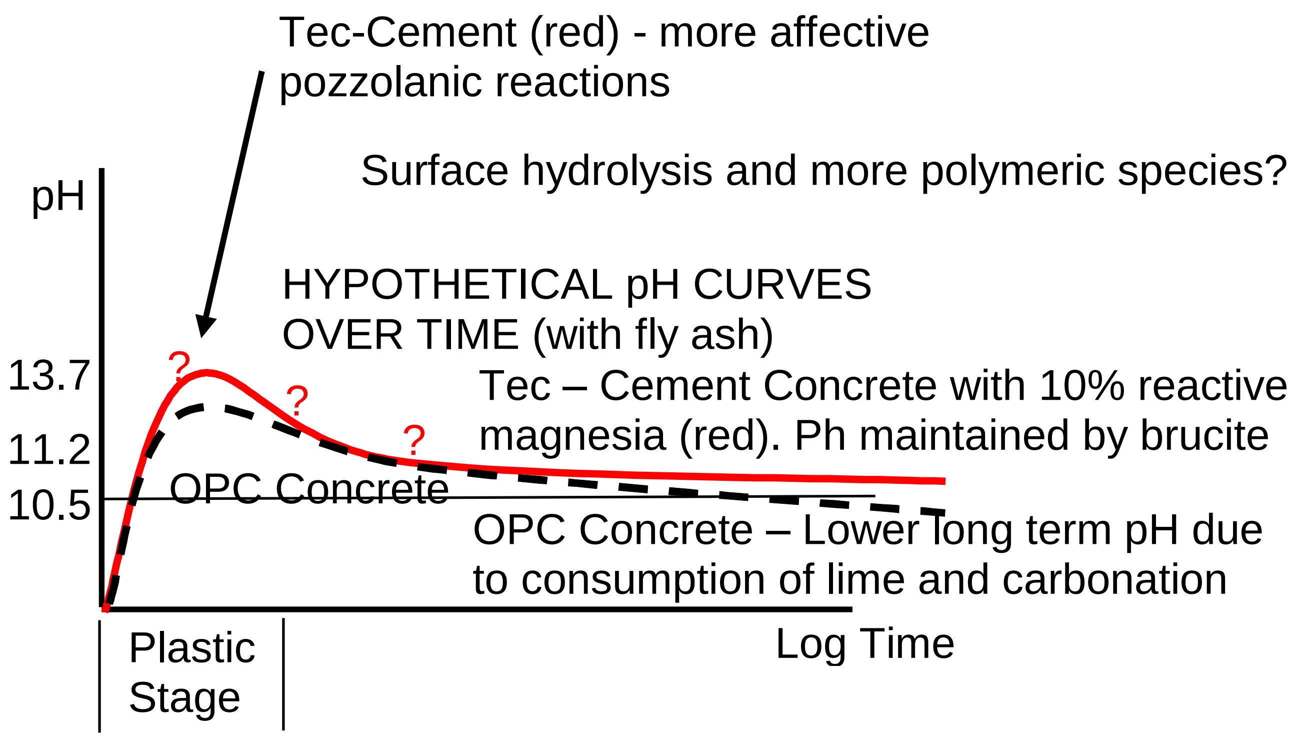
Durability - Reduced Salt & Acid Attack

- Brucite has always played a protective role during salt attack. Putting it in the matrix of concretes in the first place makes sense.
- Brucite does not react with salts once set* because it is a least 5 orders of magnitude less soluble, mobile or reactive.
  - Ksp Brucite = 1.8×10^{-11}
  - Ksp Portlandite = 5.5×10^{-6}
- TecEco cements are more acid resistant than Portland cement
  - This is because of the relatively high acid resistance (?) of Lansfordite and nesquehonite compared to calcite or aragonite

* Salts are eliminated in the wet stage by reaction with Mg++

Substitution by Brucite => Long Term pH control

- TecEco add reactive magnesia which hydrates forming Brucite which is another alkali, but much less soluble, mobile or reactive than Portlandite.
- Brucite provides long term pH control.



Carbonation is Eliminated in Tec-Cement Concretes

- Consider what happens when Portlandite carbonates:

  $Ca(OH)_2 + CO_2 \rightarrow CaCO_3$

  74.08 + 44.01 $\leftrightarrow$ 100 molar mass

  33.22 + gas $\leftrightarrow$ 28.10 molar volumes

  - 18.22% shrinkage
  - Surface shrinkage causing cracks to appear.

- In a concrete containing rMgO

  Consider nesquehonite the main phase:
  $MgO + H_2O$ <=> $Mg(OH)_2 + CO_2 + 2H_2O$ <=> $MgCO_3.3H_2O$
  40.31+ liquid <=> 58.31 + gas <=> 138.36 molar mass (at least!)
  11.2 + liquid <=> 24.29 + gas <=> 74.77 molar volumes (at least!)
- 668% expansion relative to MgO or 308 % expansion relative to $Mg(OH)_2$ (ex water or gas volume reduction)
- Significant surface tightening stopping the process

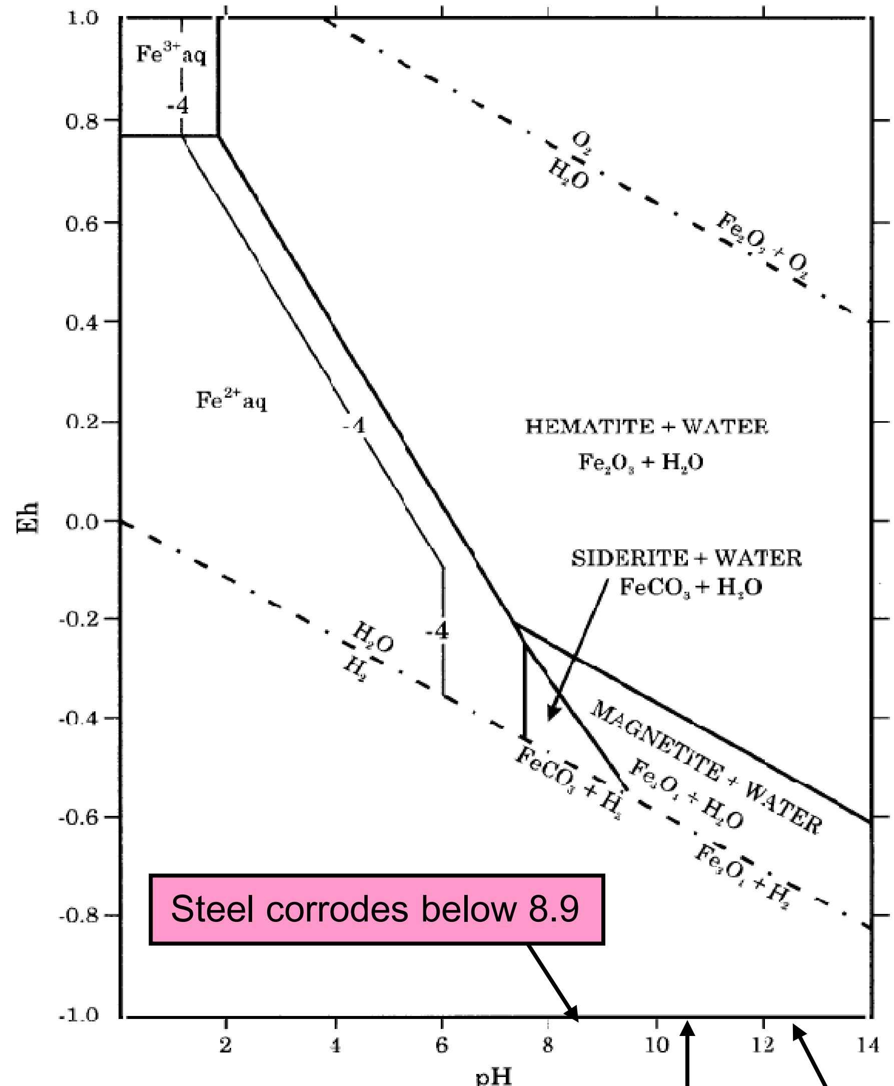
Reduced Steel Corrosion

- Steel remains protected with a passive oxide coating of Fe_3O_4 above pH 8.9.
- A pH of over 8.9 is maintained by the equilibrium $Mg(OH)_2 \leftrightarrow Mg^{++} + 2OH^-$ for much longer than the pH maintained by $Ca(OH)_2$ because:
  - Brucite does not react as readily as Portlandite resulting in reduced carbonation rates and reactions with salts.
- Concrete with Brucite in it is denser and carbonation is expansive, sealing the surface preventing further access by moisture, CO_2 and salts.
- Brucite is less soluble and traps salts as it forms resulting in less ionic transport to complete a circuit for electrolysis and less corrosion.
- Free chlorides and sulfates originally in cement and aggregates are bound by magnesium
  - Magnesium oxychlorides or oxysulfates are formed. (Compatible phases in hydraulic binders that are stable provided the concrete is dense and water kept out.)

Corrosion Reduced by a Lower More Stable Long Term pH

In TecEco cements the long term pH is governed by the low solubility and carbonation rate of Brucite and is much lower at around 10.5 -11, allowing a wider range of aggregates to be used, reducing problems such as AAR and etching. The pH is still high enough to keep Fe_3O_4 stable in reducing conditions.

Eh-pH or Pourbaix Diagram
The stability fields of hematite, magnetite and siderite in aqueous solution; total dissolved carbonate = 10^{-2} *M.*



Equilibrium pH of Brucite and of lime

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Less Freeze - Thaw Problems

- Denser concretes do not let water in.
- Brucite will to a certain extent take up internal stresses
- When magnesia hydrates it expands into the pores left around hydrating cement grains:

$$MgO\ (s) + H_2O\ (l) \leftrightarrow Mg(OH)_2\ (s)$$

$$40.31 + 18.0 \leftrightarrow 58.3 \text{ molar mass}$$

$$11.2 + 18.0 \leftrightarrow 24.3 \text{ molar volumes}$$

$$39.20 \leftrightarrow 24.3 \text{ molar volumes}$$

At least 38% air voids are created in space that was occupied by magnesia and water!

- Air entrainment can also be used as in conventional concretes
- TecEco concretes are not attacked by the salts used on roads

Rosendale Concretes - Implied Proof

- Rosendale cements contained 14 – 30% MgO
- A major structure built with Rosendale cements commenced in 1846 was Fort Jefferson near key west in Florida.
- Rosendale cements were recognized for their exceptional durability, even under severe exposure. At Fort Jefferson much of the 150 year-old Rosendale cement mortar remains in excellent condition, in spite of the severe ocean exposure and over 100 years of neglect. Fort Jefferson is nearly a half mile in circumference and has a total lack of expansion joints, yet shows no signs of cracking or stress. The first phase of a major restoration is currently in progress.

More information from http://www.rosendalecement.net/rosendale_natural_cement_.html

Many Issues with Concrete are Actually Mineralogical Issues caused by the Flawed Composition of Portland cement

- They are usually resolved by "band aid" engineering fixes. e.g.
  - Use of calcium nitrite, silanes, cathodic protection or stainless steel to prevent corrosion.
  - Use of coatings to prevent carbonation.
  - Crack control joins to mitigate the affects of shrinkage cracking.
  - Plasticisers to improve workability.

- Gypsum Portlandite and water are associated with many of the weaknesses of concrete
  - TecEco would like to replace gypsum by reactive magnesia (rMgO)
  - TecEco remove Portlandite and replace it with rMgO which hydrates to Brucite.
  - The hydration of magnesia consumes significant water, prevents loss of bleed water and provides water for the more complete hydration of PC

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Problems with Portland Cement Fixed

Strength Faster & greater strength development especially with added pozzolans	Water removal by magnesia as it hydrates in tec-cements may result in a higher short term pH and therefore more affective pozzolanic reactions. Magnesia also acts as an accelerator for Pozzolanic reactions Increased proton strength/number due to stronger polarity caused by Mg++ => faster dissolution of SCM's Brucite hydrate fills pore spaces taking up mix and bleed water as it hydrates reducing voids and shrinkage (Brucite hydrate is > 44.65 mass% water!). Greater density (lower voids:paste ratio) and lower permeability results in greater strength? Possible formation of Mg Al hydrates? Strength from self compaction

Problems with Portland Cement Fixed (1)

Durability and Performance	TecEco Tec - Cements are

Permeability and Density	• Denser and much less permeable
	  • Due mainly to the removal of water by magnesia and associated volume increases
	  • Surface tightening during carbonation of Mg phases

Sulphate and chloride resistance	• Protected by Brucite • Which is 5 times less reactive than Portlandite • Not attacked by salts,
Carbonation	• Expansive carbonation of Brucite prevents overall carbonation
Corrosion of steel and other reinforcing	• Protective of steel reinforcing which does not corrode • due to maintenance of long term pH.

Problems with Portland Cement Fixed (2)

Durability and Performance Ideal lower long term pH Delayed reactions (e.g. alkali aggregate and delayed ettringite)	As Portlandite is removed • The pH becomes governed by the pH of CSH and Brucite and • Is much lower at around 10.5 -11 • Stabilising many heavy metals and • Allowing a wider range of aggregates to be used without AAR problems. • Reactions such as carbonation are slower and • The pH remains high enough to keep Fe_3O_4 stable for much longer. Internal delayed reactions are prevented • Dry from the inside out and • Have a lower long term pH

Problems with Portland Cement Fixed (3)

Shrinkage Cracking, crack control	Net shrinkage is reduced due to: • Stoichiometric expansion of magnesium minerals, and • Reduced water loss.
Rheology Workability, time for and method of placing and finishing	The Mg++ ion adds a shear thinning making TecEco cements very workable. Hydration of magnesia rapidly adds early strength for finishing.

Problems with Portland Cement Fixed (4)

Improved Properties	TecEco cements • Can have insulating properties • High thermal mass and • Low embodied energy. Many formulations can be reprocessed and reused. Brucite bonds well and reduces efflorescence.
Properties (contd.) Fire Retardation	Brucite, hydrated magnesium carbonates are fire retardants TecEco cement products put out fires by releasing CO_2 or water at relatively low temperatures.
Cost	No new plant and equipment are required. With economies of scale TecEco cements should be cheaper

Problems with Portland Cement Fixed (5)

Sustainability issues	Tec, Eco and Enviro-Cements
Emissions and embodied energies	• Less binder is required for the same strength • Use a high proportion of recycled materials • Immobilise toxic and hazardous wastes • Can use a wider range of aggregates reducing transport emissions and • Have superior durability. Tec-Cements • Use less cement for the same strength Eco-Cements reabsorb chemically released CO_2.

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.
  - see a way forward for improvement.
- Hydraulic cements like Portland cement will survive but changes including carbon capture and reformulation are essential for humanity to survive.

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TecEco Binder Theory – Better Cements

- Tec-Cements
  - Portlandite ($Ca(OH)_2$) is too soluble, mobile and reactive.
    - It carbonates, reacts with Cl^- and SO_4^- and being soluble can act as an electrolyte.
  - TecEco add <u>reactive</u> magnesia (rMgO)
    - which hydrates, consuming significant water and concentrating alkalis forming <u>Brucite</u> which is another alkali, but much less soluble, mobile or reactive than Portlandite.
    - Brucite regulates the long term pH
    - With the use of rMgO
      - Gypsum should not be used as rMgO +/- classified SCM's will prevent flash setting (test).
        - » Too many problems associated with gypsum..
      - SCM's in particular classified SCM's should be included to consume lime in the pozzolanic reaction and densify. (Strength and durability).
      - Limestone should not be used.
  - Carbon capture and reuse as aggregate is essential
- Eco-cements
  - Require appropriate particle packing so they are gas permeable
  - Brucite and Portlandite carbonates.

TecEco Patents – The Fine Print

- Our patents cover reactive magnesia (rMgO, calcined at less than about 750 deg. C) included in a hydraulic composition with or without added pozzolans. They may or may not carbonate.
- We define in most jurisdictions hydraulic cements according to the ASTM C219-94 definition as "a cement that sets and hardens by chemical interaction with water and that is capable of doing so under water"
- In most jurisdictions we include slag cements as hydraulic and notice the American Slag Association think likewise. We therefore consider blending of slag with rMgO a blatant breach of our IP.
- It is not advisable for cements to contain more than 5% non reactive magnesia because of dimensional distress (EN197-1, ASTM C-150) . Those companies already selling unspecified magnesia into the industry to blend with PC in proportions higher than 5% are therefore also breaching our ip.
- We discuss the addition of aluminium in mixes in our patent and therefore have the prior art in relation to such additions.
- We issue a warning to the dozen or more universities and companies out there that we know about that think they will get away with it. It does not pay to steal and I believe strongly in the property rights of ip.