The science of TecEco binders is continuously changing. Since this paper was written we have determined that the carbonates formed are an amorphous phase, lansfordite and nesquehonite.

NEW CEMENTS BASED ON THE ADDITION OF REACTIVE MAGNESIA TO PORTLAND CEMENT WITH OR WITHOUT ADDED POZZOLAN

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Abstract

The built environment offers significant opportunities for improving sustainability.

TecEco Pty. Ltd. (TecEco, www.tececo.com) was incorporated to take up this challenge and have developed a new cement material based on the blending of reactive magnesia with other hydraulic cements including Portland cement that has attracted considerable interest around the world[1].

TecEco have demonstrated that reactive magnesia can be blended with other hydraulic cements such as Portland cement and usually a pozzolan in virtually any proportion and result in concretes that are theoretically more durable and in the case of porous materials such as bricks, blocks, pavers and mortars, that carbonate and therefore sequester CO_2.

This paper summarises the recently invented TecEco cements and their basic chemistry.

Keywords: Brucite, durability, reactive magnesium oxide, reactive magnesia, magnesite, hydromagnesite, fly ash, pozzolans, hydraulic cement, Portland cement

Introduction

The seven million tonnes per year of Portland cement which equates to approximately $ 900 million dollars worth produced annually in Australia[2] accounts for more embodied energy than any other material in buildings[3].

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[1] Articles have appeared in a diverse range of publications including New Scientist (Pearce, F., "The Concrete Jungle Overheats", New Scientist, vol 175 issue 2351, 19 July 2002, page 39 and Tam Dalyell, "Westminster Diary", New Scientist vol 176 issue 2368, 09 November 2002, page 55), the Toronto Star, National Report, Saturday, July 27, 2002, p. F05, the CSIRO online Sustainability Newsletter and as recently as a couple of days ago in an article by Owen Dyer appearing in The Guardian (Owen Dyer, A Rock and a Hard Place, Eco-cement yet to cover ground in the building industry, The Guardian, Wednesday May 28, 2003). A film about block making using the technology has been shown by Discovery Channel Canada and more recently in the USA. The technology won the Tasmanian Innovation of the Year Award in 2002.
[2] Email communication, Tom Glasby, Manager - Construction Solutions, Cement & Concrete Association of Australia, 02/05/2003.

Globally some 1.8 billion tonnes[4] of Portland cement are produced. Due to growing environmental concerns and the need to use less energy-intensive building products, alternatives and improvements to Portland cement (PC) and structures made from Portland cement concrete (PCC) are being actively researched worldwide. The increased interest in the concrete environment is largely due to the fact that manufacture of PC contributes significantly to greenhouse gases accounting for around 10% of global anthropogenic carbon dioxide emissions[5][6].

The built environment is our footprint on earth and offers immense potential for sequestration and this has been recognised by the Australian, British and many other governments. According to the Australian Federal Department of Industry, Science and Tourism, buildings are responsible for some 30% of the raw materials used, 42% of the energy, 25% of water, 12% of land use, 40% of atmospheric emissions, 20% of water effluents, 25% of solid waste and 13% of other releases[7][8]. In recent years, the concrete industry has recognised the need to reduce the impact[9].

Now that the Kyoto Protocol has been ratified by many nations, materials scientists around the world are examining alternatives for sequestering carbon and reducing the impact of potential CO_2 taxes as well as for encapsulating industrial wastes.

TecEco Pty. Ltd. was established in Tasmania, Australia in November 1999 to take up the challenge and develop sustainable technologies for the manufacturing and construction industries.

Focusing on reducing the environmental impacts associated with products used in the construction industry, TecEco identified the reduction of carbon dioxide emissions associated with Portland cement as being of fundamental importance and an investigation into the use of reactive magnesium oxides blended with other hydraulic cements such as Portland cement and pozzolanic wastes including fly ash resulted in a series of international patents being filed.

There are potentially two main applications for the new materials technology – carbonated eco-cements containing magnesite and a high proportion of reactive

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[3] CSIRO on line brochure at http://www.dbce.csiro.au/ind-serv/brochures/embodied/embodied.htm valid 05/08/2000.
[4] For the latest figure navigate to the USGS site.
5 Davidovits, J A Practical Way to Reduce Global Warming The Geopolymer Institute info@geopolymer.org, http://www.geopolymer.org/
[6] Pearce, F., "The Concrete Jungle Overheats", New Scientist, 19 July, No 2097, 1997, page 14.
[7] Australian Federal department of Industry Science and Tourism, "Environmental & Economic Life Cycle Costs of Construction", 1998 - Detailed Discussion Paper, (section 2 - page 8)
[8] The reference given by Industry Science and Tourism was "How Ecology and Health Concerns Are Transforming Construction" Worldwatch Paper 124 by David Malin Roodman and Nicholas Lenssen.
[9] Civil Engineers Australia, November 2002, pages 67-69

and non reactive recycled industrial materials (many of which are pozzolans) and modified hydraulic cements such as Portland cement containing brucite and preferably also a pozzolan.

Theoretically modified Portland cements have improved rheology and are more durable and limited experiments to date have confirmed this. The corrosion of reinforcing steel should also be prevented for much longer and as the pH is lower the alkali aggregate reaction problem alleviated.

TecEco eco-cements contain a much higher proportion of reactive magnesia which has been shown to carbonate in porous building materials such as bricks, blocks, pavers and mortars. With either the collection of CO_2 at source or the inclusion of carbon based fibres or both eco-cements could even be net carbon sinks. Carbonated eco-cement formulations for the built environment are also strong and resistant to the chemicals that attack Portland cement. TecEco eco-cement formulations are recyclable and can have a high proportion of recycled industrial materials such as fly ash included in their formulation.

Important uses potentially include providing a sustainable, low cost building material with high thermal capacity, low embodied energy and good insulating properties for use in construction in products such as bricks, blocks, stabilised earth blocks, pavers and mortars, wharves and airstrips and in combination with wood waste for packaging and other applications.

Much of the work to date has been theoretical and to establish properties in more detail TecEco have initiated research at a number of institutions around the world and the new cements are now the subject matter of a ₤ 165,350 R & D program with the BRE in the UK, with other possible projects at Cambridge University (UK) and the University of Technology, Sydney (Aust.)

Provided appropriate properties can be demonstrated, given economies of scale substantial savings in cost[10] will facilitate adoption of the new cements based on magnesite[11] blended with Portland cement.

The Kyoto process will also encourage development of alternative cement materials such as the TecEco cements as scientists around the world are recognizing that a multifaceted approach is necessary to reduce or even halt global warming. As the new technology will compete with alternatives such as clay bricks, the manufacture of which is being banned by many countries due to pollution, given adoption by the cement industry it is likely that the total market for cementitious products will also increase. The new TecEco cements therefore represent a market opportunity rather than a threat to the industry.

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[10] Due to the consumption of less energy.

[11] Magnesite is available in abundance in Australia and the eighth most abundant element in the crust.

The Basic Chemistry of TecEco Cements

Two main formulation groups have been defined - eco-cements containing magnesite and hydromagnesite and a high proportion of recycled pozzolanic industrial materials such as fly ash and modified hydraulic cements such as Portland cement containing brucite and preferably also a pozzolan.

Modified Hydraulic Cements

Concrete mixes incorporating modified Portland cements have demonstrated improved rheology and are theoretically more durable because brucite is so much less soluble, less reactive and less mobile than portlandite consumed by the pozzolanic reaction. TecEco cements demonstrate an increase in resistance to normally destructive salts and as the pH is lower problems associated with alkali aggregate reactions should be reduced. Advantages of using Portland cement, such as ambient temperature setting and strength gain are maintained. Unlike most other magnesium cements, expensive chemicals or potentially corrosive salts are not required.

When compared to conventional concrete mixes more industrial wastes such as fly ash can be added and as the cements are also theoretically more durable and reactive magnesia takes less energy to manufacture, they are much more sustainable.

Carbonated Eco-Cements

Eco-cements differ from modified Portland cements in that they contain higher ratios of reactive magnesia to hydraulic cement. As they are usually encouraged to carbonate they are also much more sustainable. Eco-cements are more recyclable and can have up to around 90% recycled industrial materials such as fly ash included in their formulation[12][13].

Reactions Involved

The setting and hardening of reactive magnesia in TecEco cements relies on the following reactions:

[12] 100% utilisation would reduce global CO_2 emissions in the order of 10% - 15%.
[13] With either the collection of CO_2 at source or the inclusion of carbon based fibres or both eco-cements can be net carbon sinks.

In TecEco Modified Portland Cements

Magnesia Brucite

$MgO + H_2O \rightarrow Mg(OH)_2$ → Silicates and aluminosilicates

In Eco - Cements

Magnesia Brucite Magnesite Hydromagnesite

$MgO + H_2O \rightarrow Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + Mg(OH)_2.4MgO.4CO_2.4H_2O$

Form:	Massive-Sometimes Fibrous	Often Fibrous	Acicular - Needle-like crystals
Hardness:	3.5	4	3.5
Solubility ($mol.L^{-1}$):	.00015	.0013	.0011

The combination of a hydraulic cement and reactive magnesia can be in virtually any proportion and in dense concretes, the hydration of magnesia results in the formation of brucite, which replaces portlandite deliberately consumed by pozzolans.

Brucite is much less soluble, mobile and reactive than portlandite resulting in a lower concentration of pore water hydroxide ions potentially alleviating alkali aggregate reaction problems (AAR) and introducing greater durability, resistance to carbonation and salt resistance.

TecEco consider that brucite will maintain the pH at around 10.5 – 11 for much longer periods than portlandite as for most kinetic pathways it carbonates much less readily than portlandite (ΔG_r portlandite = - 64.62 $kJ.mol^{-1}$, ΔG_r brucite = - 19.55 $kJ.mol^{-1}$). As a minimum pH of around 8.5 is required to keep the rust on steel as Fe_3O_4, the stable form, it should theoretically remain passive for much longer[14].

With high proportions of waste and reactive magnesia (relative to Portland cement), in porous or semi porous materials such as bricks, blocks, pavers, mortars and renders, as there are no kinetic barriers, the magnesia not only hydrates, but carbonates completing the thermodynamic cycle by reabsorbing the carbon dioxide produced during calcining.

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[14] As Fe_3O_4 rather than oxides such as Fe_2O_3 or FeO_2 which tend to hydrate and are dimentionally unstable.

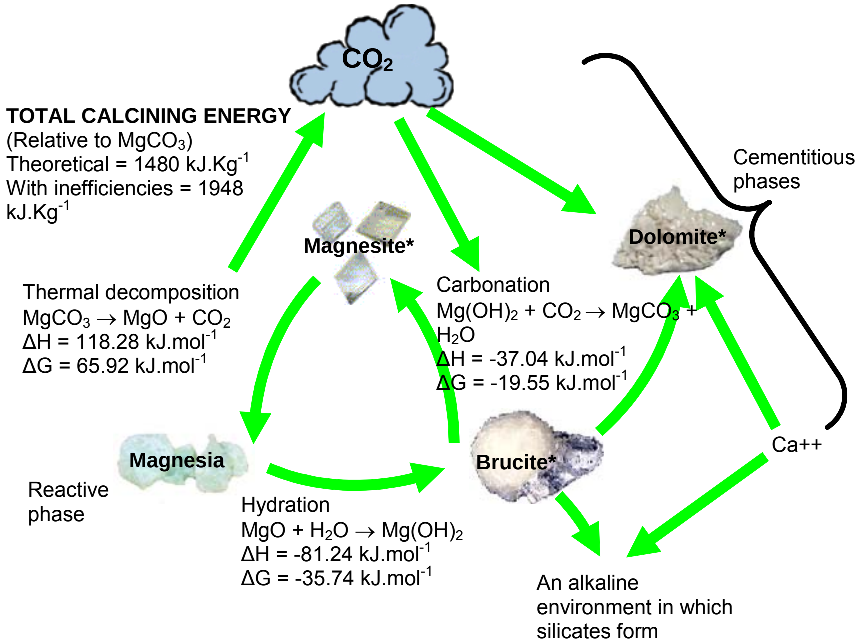

Figure 1 - The Magnesite Thermodynamic Cycle (inefficiencies estimated)

Because a full thermodynamic cycle is involved brucite, magnesite and hydromagnesite in TecEco cements can be recycled as raw materials.

If the wastes contain silica and aluminium and are at all reactive, they should also, given time, add to strength as a result of surface hydrolysis and subsequent bonding through de-hydration in the alkaline environment provided by TecEco cements.

The Difference Between Reactive and Dead Burned Magnesia

Either dead burned lime or magnesia contained in cementitious materials is potentially a problem, dead burned lime being considerably more expansive than dead burned magnesia[15]. Most Portland cement standards limit the amount of magnesia to about 4% - 6% as, if subjected to the high temperatures required for clinker manufacture, the magnesia contained in limestone becomes dead burned.

Reactivity is fundamentally a function of specific surface area and the degree of molecular disorder and TecEco have demonstrated that available commercial grades (50-60 $m^2\ g^{-1}$) of reactive magnesia can be blended with Portland cement with the addition of a pozzolan. An objective of the company is to produce much more reactive grades and totally eliminate the risk of delayed hydration and dimensional distress.

The manufacture of more reactive magnesia is a compromise between rate of calcination and reactivity of the product. For TecEco cements the objective is to completely decarbonise magnesium carbonate while avoiding at the same time sintering of the magnesium oxide produced.

The lower reactivity of mineral oxides such as MgO produced at higher temperatures is a result of a number of factors. These include denser atomic packing in larger more perfectly formed periclase crystals with fewer fissures and other surface imperfections.

Over burned or high temperature burned magnesia also contains particles coated with and to a certain extent impregnated by glasses and/or compact crystalline shells, films and granules which close any pores and hinder or prevent access of water for hydration. These films or glasses form because impurities with acidic properties[16] such as Fe_2O_3, Al_2O_3 or SiO_2 that are difficult to exclude react at high temperatures with the basic oxides being produced. The higher the level of impurities or temperature the more these compounds form.

Calcining at lower temperatures results in amorphous or less perfect atomic structure of product and less formation of the glasses and films mentioned above. Greater reactivity also enhanced by fine grinding to increase surface area.

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[15] Ramachandran V. S., Concrete Science, Heydon & Son Ltd. 1981, p 358-360.
[16] Acidic in reaction with bases such as MgO

According to M Maryska and J Blaha[17] the thermal decomposition of basic magnesium carbonate ($MgCO_3.Mg(OH)_2.4H_2O$) yields porous pseudomorphs of the original crystals. The specific surface area of the oxide decreases exponentially with increasing firing temperature. The maximum specific surface area of MgO fired at 500 ^oC amounts to 155 $m^2.g^{-1}$, falling down to 20 $m^2.g^{-1}$ when fired at 1200 ^oC. Extension of time of firing affects negligibly the specific surface area. Of the admixtures accompanying magnesium oxide in raw materials, the specific surface area of fired magnesia is mostly affected by ferric oxide. Under the same firing conditions, at a content of 2 %(m/m) of this component, the specific surface area decreases down to one tenth of that of non - doped magnesium oxide.

The molecular degree of disorder also has an effect on specific gravity. For example the specific gravity of periclase is 3.6 – 3.9 and dead burned magnesia will approach this whereas the specific gravity of reactive magnesia is in the range 3.1 – 3.4.

Highly reactive magnesia must be used in blends with hydraulic cements such as Portland cement without the use of gauging salts such as sulphates and chlorides.

The Manufacture of TecEco Cements

TecEco are currently developing a new high tech kiln that combines calcining and grinding in the one operation and will allow the capture of CO2 at source. The use of this kiln should allow manufacture of much more reactive grades of commercial magnesia from which reliable cements can be made.

Thermodynamics and Emissions

TecEco cements theoretically demonstrate sustainable properties because they use less energy and produce less lifetime CO_2 emissions when compared to Portland cement. For example a kiln used to manufacture Portland cement require a temperature in the range of 1450^oC - 1500^oC to convert limestone (and other raw materials) to Portland cement clinker. For the conversion of magnesite to magnesia, a kiln temperature in the order of 500 - 600 ^oC is required.

[17] Maryska M., Blaha J, (1997) Kinetics of Hydration of Magnesium Oxide in Aqueous Suspension, Part 2 – The Effect of Conditions of Firing Basic Magnesium Carbonate on the Specific Surface area of Magnesium Oxide Journal of Ceramics – Silikaty, Vol 41 (1) pp 21-27.

Less energy in involved in the cycle:

magnesite → magnesia → brucite → magnesite

than the cycle:

limestone → quicklime → slaked lime → limestone

↘ + clay → portland clinker

Lower temperatures correlate with savings in costs and reduced emissions and also mean less associated heat losses and low carbon output for the production of magnesia compared to either the production of lime or Portland cement. (See Figs 1,2 and 3).

In contrast the manufacture of Portland cement uses a large amounts of energy and creates CO_2 by the conversion of calcium carbonate to calcium oxide inside the kilns, and by burning large quantities of fossil fuels to raise the temperature to the 1450^oC - 1500^oC required.

Various figures are given in the literature for the intensity of carbon emissions for Portland cement production and these range from .74 tonnes carbon dioxide / tonne cement[18] to as high as 1.24[19] or 1.3[20] tonnes carbon dioxide / tonne cement.

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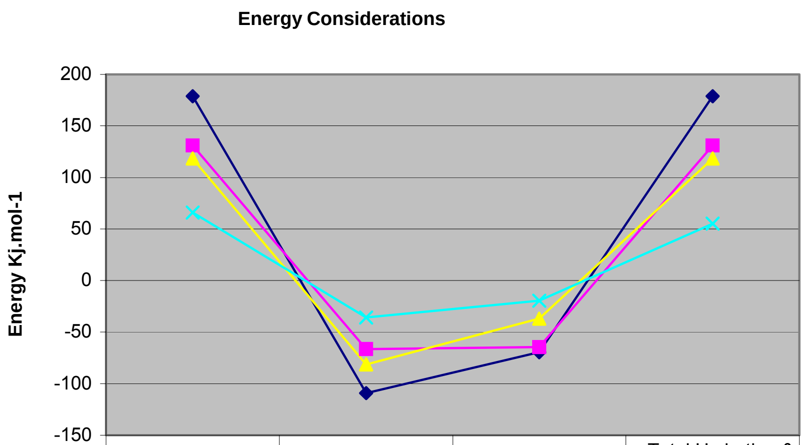
[18] New Scientist, 19 July 1997, page 14.

[19] According to the article "Cement and Concrete: Environmental Considerations" in Environmental Building News volume 2, No 2 – March/April 1993 researchers at the Oak Ridge National Laboratories (USA) put the figure at 1.24 tonnes of CO2 for every tonne of Portland cement.

[20] Tucker, Dr Selwyn, pers. comm. CSIRO Department of Building Construction and Engineering Melbourne, Australia.



	Decompostion	Hydration	Carbonation	- Total Hydration & Carbonation
ΔH Limestone	178.77	-109.19	-69.58	178.77
ΔG Limestone	130.98	-66.35	-64.62	130.97
ΔH Magnesite	118.28	-81.24	-37.04	118.28
ΔG Magnesite	65.92	-35.74	-19.55	55.29

Figure 2 - Energy Steps Magnesium and Calcium Oxides

Various figures are also given for the proportion of the world's CO_2 from anthropogenic sources that are produced by Portland cement varying from as low as 5 % (m/m)[21] to as high as 10 % (m/m)[22]. It is not the purpose of this document to argue any of the figures available, the figures are significant and theoretically much abatement can be achieved by making cements more sustainable.

The manufacturing techniques for Portland cements are nearing peak efficiencies. Within the Portland cement industry further abatement such as CO_2 capture and use of low carbon fuels is costly[23][24].

With reasonable economics of scale TecEco consider that it will cheaper to manufacture reactive magnesia (MgO) than quick lime (CaO) and Portland cement mainly due to the lower energy requirements. As a consequence TecEco

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[21] Hendriks C.A., Worrell E, de Jager D., Blok K., and Riemer P. "Emission Reductions of Greenhouse Gases from the Cement Industry." International Energy Agency Conference Paper at www.ieagreen.org.uk.

[22] Davidovits, J "A Practical Way to Reduce Global Warming" The Geopolymer Institute info@geopolymer.org, http://www.geopolymer.org/

[23] Iea Greenhouse Gas R & D Program Report No PH3/7.

[24] Hendriks C.A., Worrell E, de Jager D., Blok K., and Riemer P., "Emission Reductions of Greenhouse Gases from the Cement Industry", International Energy Agency Conference Paper,1997.

modified Portland cements and eco-cements should become cheaper to make than pure Portland cements.

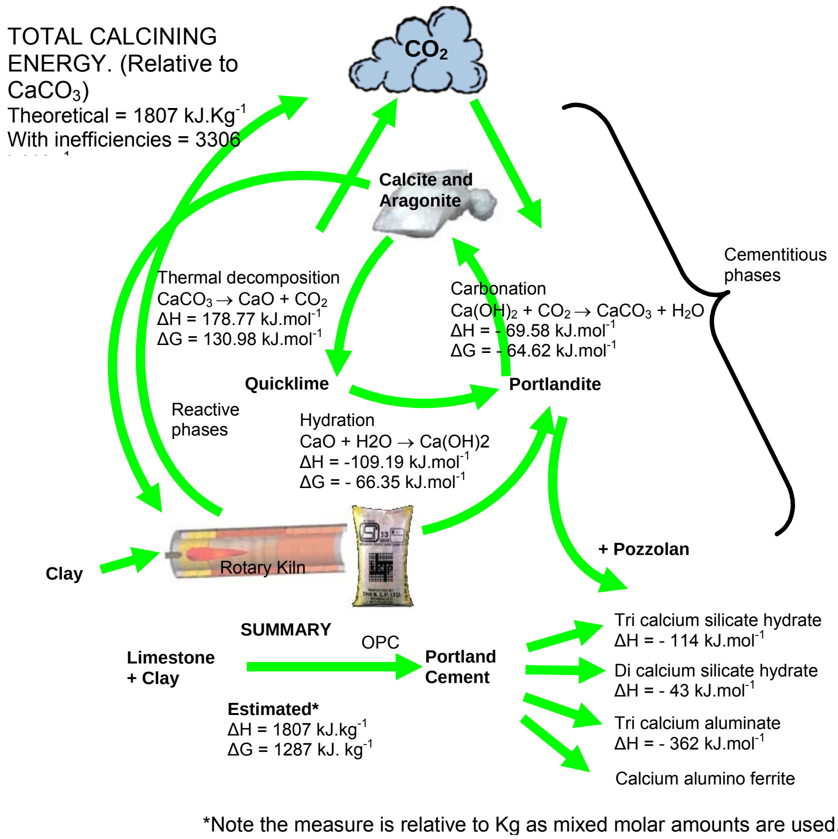

Figure 3 - The Limestone Portland Cement System (inefficiencies estimated)

Conclusion

- The built environment offers tremendous scope for improved sustainability.
- The TecEco cement technology could potentially play an important role in efforts by the construction industry to achieve greater sustainability.
- Reactive magnesia can be blended with hydraulic cements such as Portland cement.
- The problem of delayed hydration and dimensional distress with magnesium in Portland cement can be beneficially overcome.
- Portland cement concretes containing reactive magnesia and a pozzolan such as fly ash are potentially more durable.
- TecEco eco-cements could potential sequester large amounts of carbon dioxide.