The science of TecEco binders is continually evolving. Since this paper was written we have discovered that the first carbonates to form are an amorphous phase, lansfordite and nesquehonite.

# The Case for and Ramifications of Blending Reactive Magnesia with Portland Cement

*A John W Harrison, B.Sc. B.Ec. FCPA.*
*Managing Director and Chairman, TecEco Pty. Ltd.*
*497 Main Road, Glenorchy TAS 7010. Australia.*

There has been considerable publicity about TecEco cements and in particular eco-cement which is a formulation encouraged to carbonate[1].

TecEco advocate the removal of lime from Portland cement concretes using a pozzolan and replacing it with brucite by hydrating reactive magnesia. The ramifications are fundamental and far reaching. The science, technical advantages and environmental advantages are discussed from a theoretical point of view.

**Keywords:** Abatement, sequestration, $CO_2$, brucite ($Mg(OH)_2$), durability, reactive magnesium oxide, magnesia, reactive magnesia (MgO), magnesite ($MgCO_3$), hydromagnesite ($Mg_5(CO_3)4(OH)_2 \cdot 4H_2O$), fly ash, pozzolan, hydraulic cement, Portland cement, concrete, process energy, embodied energy, lifetime energy, durability, emissions.

## Potential for Change

Underlying sustainability, emissions, pollution and other environmental issues are the material flows through our society that are largely driven by economic factors.

The built environment is, in effect, our footprint on the Earth, it is the accumulation of these material flows and accounts for some 30% of the raw materials we use, 42% of the energy, 25% of water used, 12% of land use, 40% of atmospheric emissions, 20% of water effluents, 25% of solid waste, and 13% of other releases[2,3]. Include infrastructure and the figures quoted would probably double.

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[1] Articles have appeared in a diverse range of publications including New Scientist (Fred Pearce, Green Foundations, *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), Margaret Vine-Hall, The Next Generation Cement, *Clever Devils, A Mercury Supplement*, The Mercury, Thursday August 22, 2002, and more recently 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) and Climate Change Management, June 2003 issue.
Electronic Publications have included, John Harrison, *One Way to Make More Environmentally Friendly Housing*, On Line Opinion, 15/03/02, http://www.onlineopinion.com.au/2002/Mar02/Harrison.htm
Elizabeth G. Heij, Green entrepreneur in action: introducing Network member, John Harrison of TecEco, *CSIRO Online Sustainability Network Newsletter 16E*, 14 October, 2002, and many others not as yet catalogued.
A film about block making using the technology has also been shown by Discovery Channel Canada and more recently in the USA. The technology also won the Tasmanian Innovation of the Year Award in 2002 with considerable associated publicity.

[2] Australian Federal Department of Industry (1999), *Science and Tourism, Environmental and Economic Life Cycle Costs of Construction*, Detailed Discussion Paper, Section 2, p8.

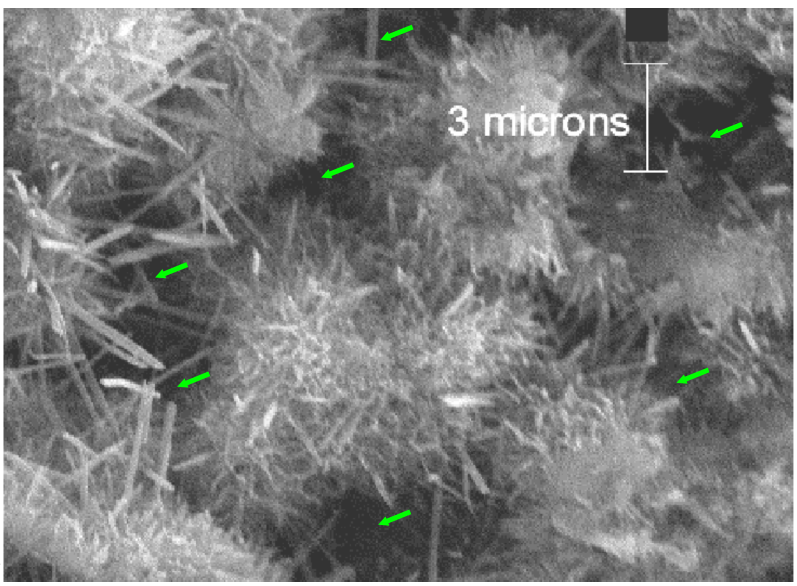
[3] The reference given by Industry Science and Tourism was David Malin Roodman and Nicholas Lenssen Worldwatch paper 124 *How Ecology and Health Concerns Are Transforming Construction.*

The importance factors in relation to the sustainability of the built environment are the embodied energies of the materials used and the lifetime energies as a result of their properties and the way they are put together. Also important in relation to the wider environment is the composition of these materials which determines the effects of extraction, how they can be reused and their effects on earth systems on wastage.

To reduce the impact of our take-make-break economic system on the environment, it is fundamental that we think about the materials we use and the molecules they are made of. The TecEco innovation is at this level and has far reaching ramifications.

# A Summary of the Chemistry of TecEco Cements

The TecEco cement chemistry is about the system of reactive magnesia - hydraulic cement – pozzolan and proposes that highly reactive magnesia can be blended with Portland cement in virtually any proportion.




The consequences of removing Portlandite (lime) with the pozzolanic reaction and filling the voids between hydrating cement grains with brucite, an insoluble alkaline mineral, need to be considered.

**Figure 1. Partially hydrated Portland cement paste (after Soroos, 1999[4]).**

So far three main formulation groups have been defined – carbonated eco-cements containing magnesite and hydromagnesite and a high proportion of pozzolanic recycled industrial materials such as fly ash, and tec and enviro cements containing brucite and preferably also a pozzolan.

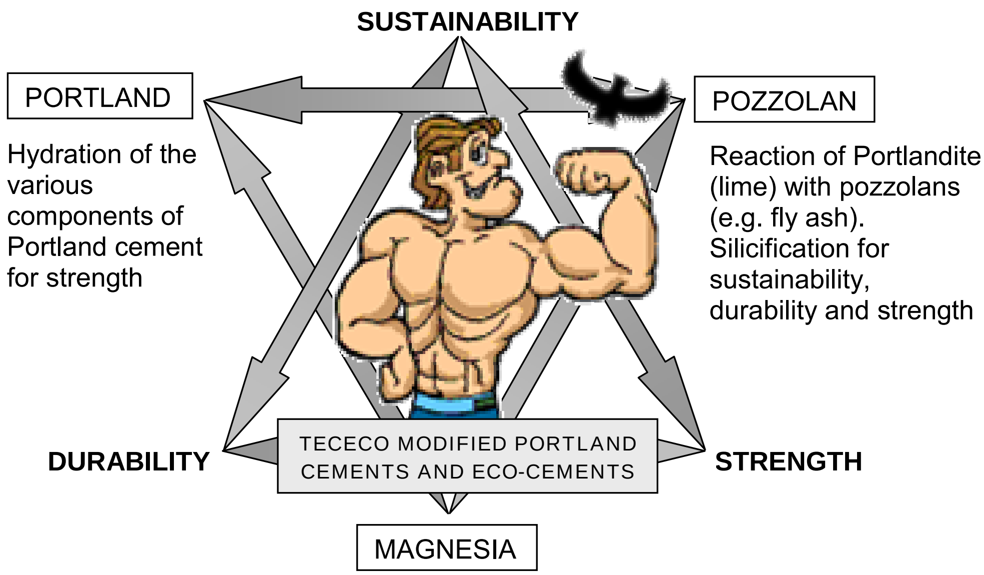
TecEco have observed that tec-cement concretes have improved rheology, have reduced shrinkage and are more durable. As the pH is lower and more stable the alkali silica reaction problem is reduced and the corrosion of reinforcing steel is prevented for much longer. Tec-cement concretes are also fire retarding as at elevated temperatures brucite releases water vapour.

As brucite is so much less soluble, less reactive and less mobile than Portlandite and consumed by the pozzolanic reaction in TecEco tec-cement concretes there is also a

[4] Soroos, E., (1999) *Scanning Electron Microscope Studies of Cement and Flyash*, Cornell University, Ithaca, New York.

dramatic increase in resistance to normally destructive salts. The advantages of using Portland cement such as setting and strength at ambient temperature are not diminished.

More flyash, gbfs and other pozzalanic industrial wastes as well a wide range of wastes that may not be pozzalanic can be added to advantage and sustainability is improved by reduced emissions ratios. In most formulations better rheology with lower water cement ratios results in denser concretes with greater strength.




<u>Modified Portland Cements</u>
Hydration of magnesia → brucite for plasticity, durability and sustainability.

<u>Eco-Cements</u>
Carbonation of brucite → hydromagnesite and magnesite for strength and abatement.

**Figure 2. TecEco cements.**

Eco-cements differ in that they contain higher ratios of magnesia to hydraulic cement and as they are usually encouraged to carbonate through use in porous materials, they are even more sustainable. They are to some extent recyclable and can have up to around 90% recycled industrial materials such as fly ash included in their formulation. Important uses will include providing a sustainable, low cost building material with high thermal capacity, low embodied energy, good acid and salt resistance[5] and insulating properties for construction in products such as bricks, blocks, stabilised earth blocks, pavers and mortars, wharves and airstrips and in combination with wood waste for packaging.

TecEco cements rely on various steps in what TecEco have called the magnesite thermodynamic cycle.

[5] Magnesite is more resistant to cold acids than limestone.

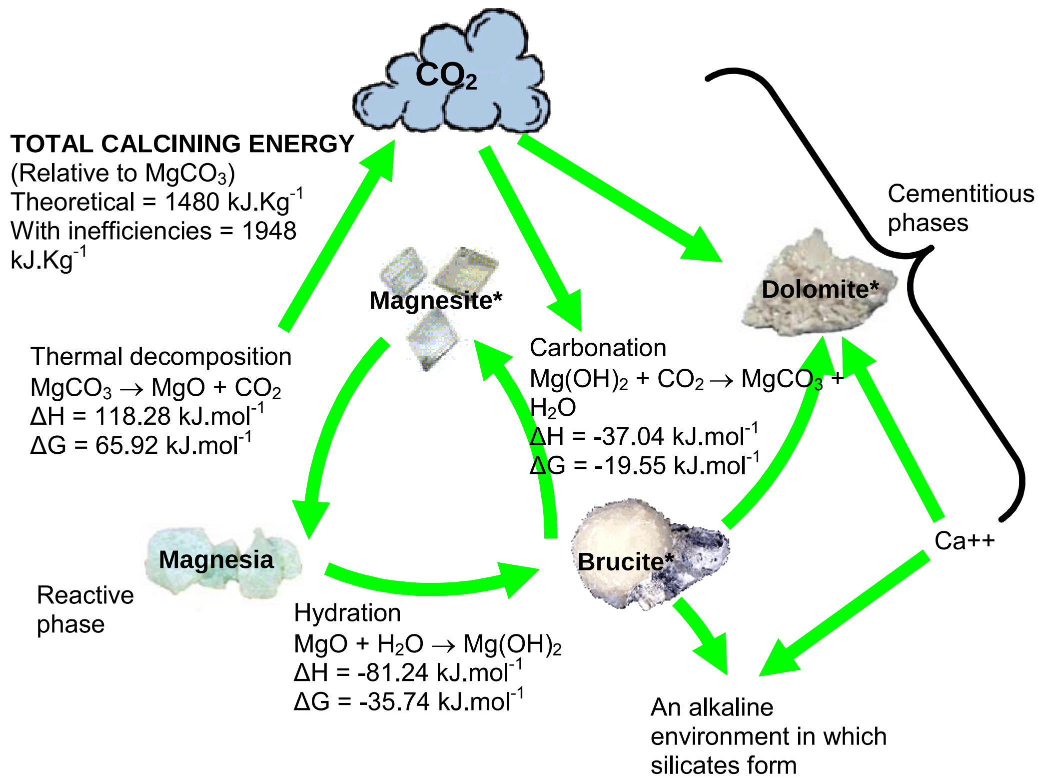



**Figure 3. The magnesite thermodynamic cycle.**

In modified Portland cements the cycle stops at brucite, whereas in eco-cements it is encouraged to complete with the formation of magnesite (and hydromagnesite).

# Reactions and the Ramifications of Reactions in TecEco Cements

Reactions for alite, belite calcium aluminate and calcium alumino ferrites proceed normally. Lime is consumed in the pozzolanic reaction or carbonates.

## The Pozzolanic Reaction

Silica + Portlandite + Water → Polymeric non- stoichiometric CSH

$SiO_2 + 1.7Ca(OH)_2 + 2.3H_20 \rightarrow 1.4\text{-}1.7Ca.SiO_2.4H_2O$

## Carbonation in Portland Cements

| | Quicklime | Portlandite | Calcite |
|---|---|---|---|
| | $CaO + H_2O \rightarrow$ | $Ca(OH)_2$ | $+ CO_2 \rightarrow CaCO_3$ |
| | | $\Delta H = -109.19$ kJ.mol$^{-1}$<br>$\Delta G = -35.74$ kJ.mol$^{-1}$ | $\Delta H = -69.58$ kJ.mol$^{-1}$<br>$\Delta G = -64.62$ kJ.mol$^{-1}$ |
| Form: | | Tabular | Massive or crystalline |
| Hardness: | | 2.5 | 3 |
| Solubility (mol.L$^{-1}$) | | .02497 | .00013 |

The combination of a hydraulic cement and reactive magnesia can be in virtually any proportion in TecEco cements and the reactive magnesia is first encouraged to hydrate under moist conditions. In dense TecEco modified Portland cement concretes, the hydration of magnesia is not encouraged to proceed to carbonation and results in the formation of brucite replacing portlandite deliberately consumed by pozzolans.

## In TecEco Modified Portland Cements

Magnesia Brucite

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

## In Eco - Cements

Magnesia Brucite Magnesite Hydromagnesite

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

| | Brucite | Magnesite | Hydromagnesite |
|---|---|---|---|
| Form: | Massive-sometimes fibrous | Often fibrous | Acicular - needle-like crystals |
| Hardness: | 2.5 - 3.0 | 4.0 | 3.5 |
| Solubility ($mol.L^{-1}$): | .00015 | .0013 | .0011 |

## Compare to Portlandite-Calcite

Portlandite Calcite

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

| | Portlandite | Calcite |
|---|---|---|
| Form: | Tabular or massive | Massive or crystalline |
| Hardness: | 2.5-3.00 | 3.0 |
| Solubility ($mol.L^{-1}$): | .024 | .00014 |

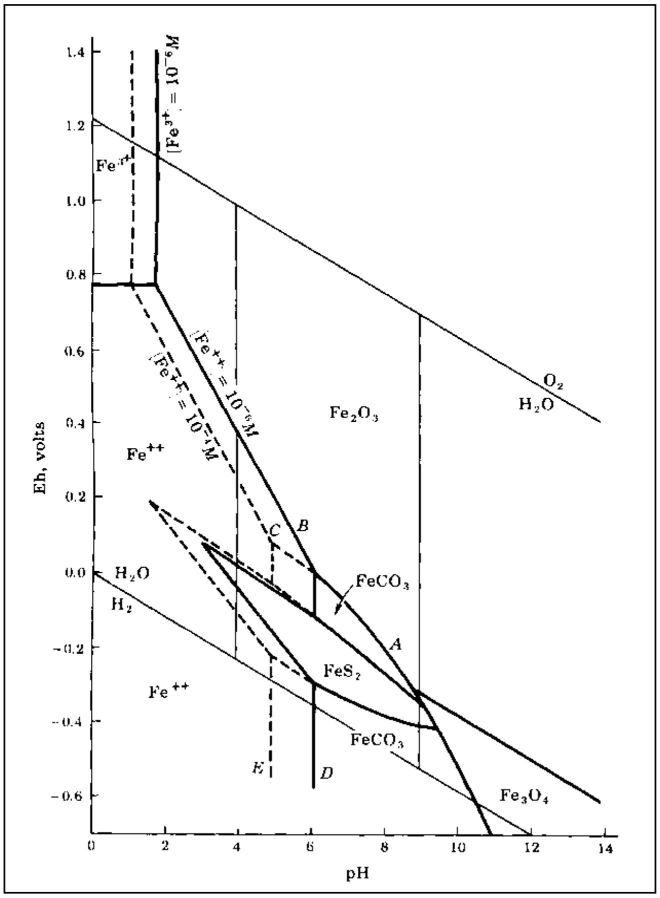
Brucite is much less soluble, mobile and reactive than Portlandite resulting in a lower concentration of pore water hydroxide ions alleviating alkali aggregate reaction problems (AAR) and introducing greater durability, passivity of steel, resistance to carbonation and salt resistance. Brucite will maintain the pH at around 11 for much longer periods than Portlandite as for most kinetic pathways it carbonates much less readily[6] ($\Delta G_r$ portlandite) = - 64.62 $kJ.mol^{-1}$, $\Delta G_r$ brucite = - 19.55 $kJ.mol^{-1}$) and in TecEco modified Portland cements, when it does carbonate it expands slightly, increasing the density of the surface (See Volume Changes as Brucite Carbonates on page 8) tending to block off further carbonation. The pourbaix diagram in Figure 4 on page 6 shows that a pH over 8.5 is sufficiently high for steel to remain passive[7]. Higher pH also favours the stability of calcium silicate hydrates.

The brucite as it hydrates fills in micropores, increasing the density of TecEco modified Portland cements. Improved rheology may also mean a lower water cement ratio and stronger concrete in some formulations.

[6] Depending on the kinetic pathway.

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

As brucite is highly insoluble and does not carbonate as readily as lime it is considered that dense concretes made using TecEco formulations would maintain reducing conditions and a high pH required for durability for many hundreds of years, although experimental work is yet to prove this.




Eco-cements have high proportions of waste and reactive magnesia relative to Portland cement and are used in porous or semi porous materials such as bricks, blocks, pavers, mortars and renders. As there are no kinetic barriers[8] the magnesia not only hydrates, but carbonates completing the thermodynamic cycle (see Figure 3. The magnesite thermodynamic cycle on page 4.) by reabsorbing the carbon dioxide produced during calcining and forming harder fibrous and acicular minerals such as magnesite and hydromagnesite that bind the matrix even with a high proportion of micro and macro aggregates.

Brucite, magnesite and hydromagnesite bond well to many different materials including wood[9] and will hold a large proportion of waste. If the wastes are at all reactive, in the alkaline environment provided by TecEco cements they also, in time, add to strength as a result of surface hydrolysis and subsequent bonding through de-hydration.

**Figure 4. Eh – pH or pourbaix diagram for iron in the presence of oxygen and carbon dioxide[10].**

Research is continuing and moving toward developing the engineering properties.

# Dogma about Magnesium in Cements

The proposition of putting magnesium compounds into hydraulic and in particular Portland cements flies in the face of existing dogma as expressed in various formula based international standards[11].

Magnesium carbonate subjected to a high temperature clinkering process results in the formation of periclase which has an ordered and stable atomic structure and therefore

[8] In porous materials the brucite has a high surface area exposed to air.
[9] Hence the contemplated use for lightweight packaging.
[10] Source: Krauskopf K. B. (1967), *Introduction to Geochemistry, McGraw Hill Book Company*, page 168, after Garrels & Christ (1965), page 224.
[11] A good reason to move to performance based standards.

takes more energy and time to hydrate than reactive magnesia which is far less ordered and has a much higher specific surface area.

In the historical context of the development of Portland cement magnesite was often an impurity in limestone and the standards dealing with magnesia content in Portland cement were introduced limiting the magnesia content to prevent the formation of periclase or "dead burned magnesia" that hydrated slowly causing dimensional distress due to expansion of some 17%[12]. During the clinker formation process high temperature reactions between magnesium and iron for example also resulted in insoluble glasses forming that further reduced reactivity[13].

Dead burned lime is far more expansive than dead burned magnesia[12], however cement chemists have largely forgotten the problem. With a little lateral thinking the problems of delayed hydration and dimensional distress have been overcome with magnesia and economic, technical and environmental advantages are the outcome.

Calcium and magnesium go together in many minerals and in theory this should also be the situation with hydraulic cements. Cement chemists have the disadvantage however that they cannot use many of the basic rock forming tools of mother earth such as time, hydrothermal fluids, pressure and heat. The answers lay in reactivity. Make a particle reactive enough and it will react with anything. For magnesia this requires low iron content, low temperature calcining and fine grinding. Provided sufficiently reactive magnesia is used it will hydrate in the same rate order as other Portland cement minerals and is not expansive.

# Volume Changes as Reactive Magnesia Hydrates

Ramachandran in the text Concrete Science quoted above[12] stated that dead burned magnesia expands some 17%. This was in the context of the slow hydration of unreactive material requiring additional water for hydration over and above the original mix water.

Volume changes with reactive magnesia as it hydrates in a cement matrix containing Portland cement can be engineered to be neutral.

Consider the volume changes that occur when magnesia hydrates:

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

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

$$11.2 + 18.0 \leftrightarrow 24.29 \text{ molar volumes14}$$

If this reaction is slow as is the case with dead burned magnesia produced as a result of high temperature thermal decomposition, it occurs after most of the free mixing water has been taken up by the hydration of other cementitious minerals, mainly comprising tricalcium silicate (alite) and di calcium silicate (belite), or vacated through bleeding or evaporation. Because the hydration of dead burned magnesia is a slow process, for it to

[12] Ramachandran V. S., (1981) *Concrete Science*; Heyden & son, Ltd., pp 356-365.
[13] Blaha, J, *Kinetics of Hydration of Magnesium Oxide in aqueous Suspension, Part1 – Method of Measurement and Evaluation of Experimental Data. Ceramics – Silikaty*, 39 (2), 1995, 41-80.
[14] The molar volume ($L.mol^{-1}$)is equal to the molar mass ($g.mol^{-1}$) divided by the density ($g.L^{-1}$).

proceed to completion some moisture is absorbed by the cement mass over and above the original mixing water (net of bleeding and drying), resulting in a volume increase of 24.3 – 11.2 = 13 molar volumes (less the volume of whatever mixing water available and used from the original mix.) Expansion and cracking occurs resulting in the bad name that dead burned magnesia contained in ground Portland clinkers has obtained.

If magnesia that is highly reactive is added after the calcining process required for the manufacture of most other cements such as Portland cement, the same hydration reactions occur much more rapidly. As a result the moisture is absorbed more rapidly, mainly from mix water reducing shrinkage due to bleeding and drying, and there is no absorption of moisture that was not contained in the original mix. In terms of molar volumes from the above equation:

$$MgO\ (s,11.2) + H_2O\ (l,18.0) \leftrightarrow Mg(OH)_2\ (s,24.3)$$

The volume of the reactants is more than the products by some 4.9 molar volumes, and this small amount is taken up from mix and pore water.

Considering only solids, brucite on hydration almost doubles in volume taking up the voids required to accommodate the excess water of convenience in concretes, densifying the whole reducing dimensional changes through bleeding and drying. There is likely to be some ratio yet to be determined whereby this net expansion of solids exactly compensates for the shrinkage of around .05% characteristic of CSH in Portland cement concretes.

TecEco observations to date are that TecEco cements made with reactive magnesia with a specific surface area of 50 – 60 m2 $g^{-1}$ and also containing a pozzolan do not bleed water and appear to be dimensionally stable with no cracking obvious even in large slabs with no crack control joints. TecEco theorise that with much more reactive grades that are currently commercially difficult to obtain, the rate of hydration would increase to the point whereby a pozzolan such as flyash is no longer required to prevent dimensional distress although it’s use is still recommended. Much more research needs to be done but the possibility of overcoming shrinkage in concretes is nonetheless exciting.

## Volume Changes as Brucite Carbonates

The volume changes as brucite carbonates need to be considered for two reasons.
The surface of a TecEco modified Portland cements will carbonate and TecEco have become known for eco-cements which have a higher proportion of reactive magnesia that in porous materials such as mortars and concrete blocks also carbonates.

The main mineral formed is magnesite and this could either form directly from brucite or from hydromagnesite with the loss of water.

Consider brucite forming magnesite as it takes up carbon dioxide:

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3$$

$$58.31 + 44.01 \leftrightarrow 84.32 \text{ molar mass}$$

$$24.29 + \text{gas} \leftrightarrow 28.10 \text{ molar volumes}$$

- Slight expansion and densification of the surface occurs reducing ingress of $CO_2$ and further carbonation.

Compared to what happens when Portlandite carbonates:

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

$74.08 + 44.01 \leftrightarrow 100$ molar mass

$33.22 + \text{gas} \leftrightarrow 28.10$ molar volume

- Surface shrinkage causing cracks to appear. The prevention of further ingress of $CO_2$ and carbonation is less effective.

# Rheological Improvements

There is a noticeable improvement in the rheology of concretes containing a percentage of reactive magnesia, particularly when a pozzolan is also present.

This is because the magnesia grains tend to act as ball bearings to the Portland cement grains and also fill the voids densifying the whole.

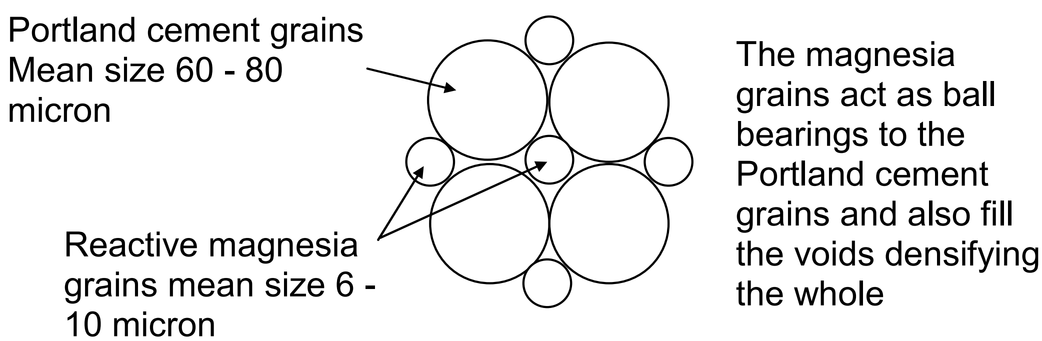



**Figure 5. Nodal particle packing in TecEco cements.** (Grains not necessarily rounded as depicted)

Ramifications include greater plasticity, a reduction in water cement ratio and possible less shrinkage.

# Durability

A study of most comprehensive texts on corrosion reveals that brucite plays a protective role during ground or salt water attack and so it is with TecEco cement concretes. Due to low solubility the brucite throughout the matrix protects steel, CSH and other minerals.

In Portland cement concretes Portlandite (lime) is responsible for a high pH in which iron or the insoluble black ($Fe_3O_4$) oxides of iron are more stable. Unfortunately lime relatively rapidly carbonates, the pH falls and other species prevail such as ferrous oxides that hydrate expansively and initiate corrosion. Portland cements also exhibit cracking from shrinkage that often exposes steel and from carbonation which tends to exacerbate the problem. The carbonation of brucite is generally less rapid ($\Delta G_r$ portlandite) = - 64.62 $kJ.mol^{-1}$, $\Delta G_r$ brucite = - 19.55 $kJ.mol^{-1}$) however this depends on the kinetic pathway[15]. It is therefore considered that the pH will remain at lower levels of around 10.5 - 11 for a much longer period of time but only research will demonstrate this. The carbonation of brucite also tends to block off further carbonation - any carbonation that does occur tending to densify the surface and seal off further access by $CO_2$. The consequences are less corrosion of steel reinforcing and less alkali aggregate and other problems associated with excessive alkalinity.

Steel is the cheapest material for reinforcing concrete and if the modification of Portland cement proposed by TecEco works and is generally adopted then it will retain favour over other more expensive but potentially superior materials such as stainless steel. Potentially much thinner architectural and other panels will be able to be constructed without fear of corrosion or shrinkage[16].

A reduction in alkali aggregate problems will mean a wider range of potentially cheaper gravels, sands and industrial wastes can be used as aggregates further reducing the cost of concrete.

# Use for Toxic and Hazardous Waste Immobilisation.

There are several basic reasons for the use of TecEco cements for toxic waste immobilisation.

The main problem with all industrial wastes is that they vary enormously and from the same source may contain heavy metals, salts, toxic volatile organic compounds or radon gas for example. The presence of most salts will cause the formation of metal oxy halide (MOX) compounds such as Sorel cements. Normally however an insoluble matrix of brucite is formed throughout the microstructure structure making the whole more dense and less soluble, preventing egress by the undesirable heavy metals, organic compounds etc.

The brucite in TecEco cements has a layered structure and is able to accommodate a wide variety of extraneous substances between the layers and cations of similar size substituting for magnesium within the layers and known to be very suitable for toxic and hazardous waste immobilisation.

Octahedrons of magnesium hydroxide are stacked in layers and composed of magnesium ions with a +2 charge bonded to six octahedrally coordinated hydroxides with a -1 charge. Each hydroxide is bonded to three magnesium atoms. The result is a neutral sheet since +2/6 = +1/3 (+2 charge on the magnesium atoms divided among six hydroxide bonds) and -1/3 = -1/3 (-1 charge on the hydroxides divided among three magnesium atoms); thus the charges cancel.

Brucite layers are found in many minerals. In chlorite and montmorillonite / smectite clays, neutral magnesium hydroxide sheets are sandwiched between silicate sheets. In Sorel type cements, neutral salt layers replace the silicate layers.

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[15] More research is required on carbonation pathways in TecEco cements.

[16] The tech tendon method of prestressing, partial prestressing and reinforcing the subject matter of another patent owned by a related company would be ideal.

The brucite in eco-cement is a fine precipitate that surrounds waste particles. Immobilisation of wastes is therefore not only by chemical incorporation but also by inclusion in a brucite matrix which is very insoluble ($K_{sp} = 1.8 \times 10^{-11}$) in all but an acid medium. Most ground waters and sea water are alkaline and so repositories are not hard to find.

TecEco cements will bind a very high proportion of waste and are likely to be cheaper given economies of scale.

# Producing Reactive Magnesia

To overcome the supply problem TecEco are currently working on a new kiln design that will not only operate some 25-30% more efficiently than current state of the art kilns, but will produce much more reactive magnesia and have the potential for capturing emitted $CO_2$ at source, with possible opportunities for re-sale into the confectionary industry for example.

# The Advantages of Including Reactive Magnesia in Hydraulic Cements such as Portland Cement.

The economic, technical and environmental advantages of TecEco cements are related and considered below under those headings.

## Economic Advantages

In the take-make-waste linear system, which underpins the majority of the world's economies, utility is added until final point of sale and from then on utility generally declines until wastage is complete. If utility can be maintained longer or increased by greater durability or reuse then the system must produce less waste, slow down and consume less.

Achieving this should be the prerogative of governments around the world. New materials are required that are more durable and that exit the linear system forming return loops eliminating wastes, reducing output and thus input (the take) from natural ecosystems. Materials with a lower embodied energy and that can use waste of themselves be recycled or reused have substantial economic advantages and TecEco cements have been designed with these desirable characteristics in mind.

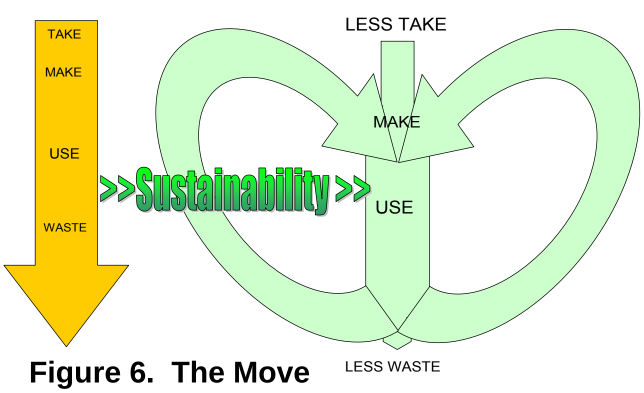


**Figure 6. The Move to a More Sustainable Society.**

### Energy

Energy is the largest cost factor in the production of mineral binders.

Whether more or less energy is required for the manufacture of reactive magnesia compared to Portland cement or lime depends on the stage in the utility adding process.

Table 1 on page 13 shows that given a take-make-waste system, on a mass for mass of natural materials consumed basis, less energy is required. TecEco argue however that the most valid point of comparison is when the utility is greatest and in the case of TecEco modified Portland cement this is when Portland cement and reactive magnesia have hydrated becoming a binders in concrete. In the case of eco-cements further utility is added when brucite carbonates completing a thermodynamic cycle and become magnesite again.

The mass comparisons in Table 1 are however also deficient in that the built environment has most utility when 3D space is created not mass. After all do we purchase 20 tonnes of bricks, timber, nails and tin for a home? The utility argument can therefore be carried further and a better basis of comparison is on a volume of binder material produced basis as in Table 2, and in this case the hydrated product, brucite, has a lower embodied energy.

## Cost

In terms of 3D space, the use of magnesia results in less embodied energy per hydrated cubic metre of building material[17] and hence potentially lower costs in terms of money spent for built environment constructed.

Given volume production and the development of TecEco cement and associated technologies even less process energy than in tables 1 and 2 should be required for the production of reactive magnesia because:

- The manufacture of reactive magnesia is a benign process occurring at relatively low temperatures and for which waste energy should be able to effectively be used.
- The manufacture of more durable building materials will mean that less energy is required over time because structures require replacing less often.
- The manufacture of reactive magnesia is suited to new TecEco kiln technology in which 25% greater efficiencies should result due to the capture of waste heat from grinding.

[17] There is a good argument for using volume comparisons as the build environment is composed of 3D space, not mass.

**Table 1. Calcining energy compared on a mass basis.**

| Relative to Raw Material Used to make Cement | From Manufacturing Process Energy Release 100% Efficient (Mj.tonne$^{-1}$) | From Manufacturing Process Energy Release with Inefficiencies (Mj.tonne$^{-1}$) | Relative Product Used in Cement | From Manufacturing Process Energy Release 100% Efficient (Mj.tonne$^{-1}$) | From Manufacturing Process Energy Release with Inefficiencies (Mj.tonne$^{-1}$) | Relative to Mineral Resulting in Cement | From Manufacturing Process Energy Release 100% Efficient (Mj.tonne$^{-1}$) | From Manufacturing Process Energy Release with Inefficiencies (Mj.tonne$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| $CaCO_3$ + Clay | 1545.73 | 2828.69 | Portland Cement | 1807 | 3306.81 | Hydrated OPC | 1264.90 | 2314.77 |
| $CaCO_3$ | 1786.09 | 2679.14 | | | | $Ca(OH)_2$ | 2413.20 | 3619.80 |
| $MgCO_3$ | 1402.75 | 1753.44 | MgO | 2934.26 | 3667.82 | $Mg(OH)_2$ | 2028.47 | 2535.59 |

**Table 2. Calcining energy compared on a volume basis.**

| Relative to Raw Material Used to make Cement | From Manufacturing Process Energy Release 100% Efficient (Mj.metre$^{-3}$) | From Manufacturing Process Energy Release with Inefficiencies (Mj.metre$^{-3}$) | Relative Product Used in Cement | From Manufacturing Process Energy Release 100% Efficient (Mj.metre$^{-3}$) | From Manufacturing Process Energy Release with Inefficiencies (Mj.metre$^{-3}$) | Relative to Mineral Resulting in Cement | From Manufacturing Process Energy Release 100% Efficient (Mj.metre$^{-3}$) | From Manufacturing Process Energy Release with Inefficiencies (Mj.metre$^{-3}$) |
|---|---|---|---|---|---|---|---|---|
| $CaCO_3$ + Clay | 4188.93 | 7665.75 | Portland Cement | 5692.05 | 10416.45 | Hydrated OPC | 3389.93 | 6203.58 |
| $CaCO_3$ | 6286.62 | 8429.93 | | | | $Ca(OH)_2$ | 5381.44 | 8072.16 |
| $MgCO_3$ | 4278.39 | 5347.99 | MgO | 9389.63 | 11734.04 | $Mg(OH)_2$ | 4838.32 | 6085.41 |

## Carbon Credits

There will potentially also be a financial bonus attached to the use of reactive magnesia in TecEco cements in the form of carbon credits:

- $CO_2$ could be captured at source (as in the TecEco kiln).
- TecEco eco-cements absorb a little less that their own weight of $CO_2$ in porous materials such as bricks, blocks, pavers, concretes and pavements.

TecEco cement concretes can also contain a large amount of waste materials such as fly ash further reducing the embodied energy per unit volume of building material. Lower embodied energy means results in reduced emissions.

The possibilities for widespread abatement and solving global climate change issues are enormous and these are discussed in detail under the heading Environmental Advantages on page 15.

## Other Cost Factors

There are other more technical factors that will contribute to the economic advantages of blending reactive magnesia with Portland cement. These include strength, durability and the ability to blend large amounts of waste materials such of fly ash, and they will be discussed below in terms of technical advantages.

Existing plant and equipment can also be used for the production of TecEco cement reducing costs of entry.

## Technical Advantages

Portlandite or as it is sometimes called, lime, has always been the weakness of Portland cement. It is more soluble than brucite, more mobile and more reactive with for example common salts in ground and seawaters. The reason is that the $Ca^{++}$ ion is much larger at 114 picometres than the $Mg^{++}$ ion at 86 picometres and the latter fits better in an atomic lattice with hydroxide anions and is therefore more stable. The essential feature of TecEco technology is replacing lime in Portland cement with brucite. Although it could of course be added directly as brucite, far more strength is gained through the process of the formation of the mineral from highly reactive magnesia in a manner that densifies Portland strength. Provided there is no delayed hydration this makes sense and technical advantages result.

Noticeable during the mixing and placing stages are a much better rheology and a marked tendency not to bleed. TecEco modified Portland cement concretes tend to resemble margarine more than traditional concretes with a low slump yet excellent workability. As the hydration of magnesia appears to take up water that would with Portland cement concretes tend to bleed, the evidence so far indicates less or no shrinkage in some formulations.

Other properties become more apparent on setting such as a usually higher strength than would be expected from the amount of Portland cement added and this is probably due to reduced water cement ratios and less cracking due to reduced shrinkage.

Over time noticeable will be the lack of “crazy” cracking due to carbonation and less corrosion, iron stains etc. as TecEco cements are much more durable.

It also takes some time for problems due to alkali aggregate reaction to emerge and with TecEco cements they will most likely never emerge.

There are many other technical advantages of TecEco cements. For example magnesite is more resistant to mild acids at low temperatures than calcite meaning eco-cement blocks will last longer than limestone or Portland cement blocks.

TecEco cements are also fire retardants as brucite breaks down releasing water vapour and magnesite breaks down releasing $CO_2$ at a relatively low temperatures cooling or putting out fires.

No doubt in time more technological improvements will emerge as the properties of the new TecEco cements are determined. What is more noticeable is the lack of problems provided appropriate grades of reactive magnesia are used. The specification sheets from vendors do not convey the full story and people interested in using reactive magnesia should talk to TecEco.

## Environmental Advantages

Apart from being much more durable, depending on the formulation and use, eco-cements used to make porous materials such as bricks, blocks, pavers, mortars and pavement re-absorb $CO_2$, are to some extent recyclable and are usually made including a high proportion of fly ash and other recycled usually pozzolanic industrial waste materials.

Around 98% of the world’s energy is derived from fossil fuels that when burnt to produce energy releases vast amounts of $CO_2$. In terms of the volume of built environment and infrastructure that results, less energy goes into making TecEco Cements for the reasons given under the heading Energy on page 11. Materials that have a lower embodied energy are more sustainable.

Lifetime energies are the energies required to heat and cool buildings over time. Building materials that have thermal capacity reduce lifetime energies and are therefore also more sustainable. TecEco cements, being mineral based, have a high thermal capacity and good insulating properties, especially with added waste organic matter such as saw dust and hence result in lower lifetime energies.

Industrial wastes are a major global problem, TecEco cements can accommodate a high proportion of many wastes reducing their impact on eco-systems.

If materials have closed loops and can substantially be recycled then their impact when they are no longer required is much less. If they can be made of materials more naturally assimilated back into the earth then nature can very quickly convert them back to its own uses. TecEco cements can be substantially recycled not only into more building materials but for other purposes as well. If wasted, they do not affect natural ecosystems as much as Portland cement because they have a lower pH.

If materials can be made that last much longer and require replacing less often, they are said to be more durable. More durable materials are therefore more sustainable. The durability of TecEco cements also results in greater sustainability.

Perhaps the most publicised formulations of TecEco cements are eco-cements which contain a much greater proportion of materials such as reactive magnesia (and thus brucite) in the cement component that carbonate to completion in porous materials, absorbing much more $CO_2$. A typical eco-cement formulation for masonry products for example would contain 50 - 85% material that will carbonate in the cement component compared to 20-25% in the cement component of concrete masonry units (CMUs) containing Portland cement only. There is therefore approximately 50 - 85 % more carbonation in an eco-cement block compared to an ordinary concrete block.

# Conclusion

The case for including reactive magnesia with Portland Cements in concretes is overwhelming and results in potential solutions to many of the problems of the material including greater sustainability.

As Fred Pearce reported in New Scientist[18] Magazine, “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”

The TecEco cement technologies therefore merit serious attention by industry and governments.

[18] Fred Pearce, *Green Foundations*, New Scientist, vol 175 issue 2351, 19 July 2002, page 39.