TECECO CEMENTS – Abatement, Sequestration and Waste Utilization.

Abstract

Around 26 billion tonnes of CO_2 are released to the atmosphere annually, around 20 billion metric tonnes of which is from the burning of fossil fuels and a significant 2 billion tonnes from the production of Portland cement. Given the huge size of the built environment, tec, eco and enviro-cements represent a novel new method of reducing emissions or sequestering large amounts of CO_2 as calcium and magnesium carbonates in bricks, blocks, pavers, mortars and other building materials.

Over two tonnes of concrete are produced per person on the planet per annum, representing an enormous opportunity to not only do mitigate global warming but to utilize solid wastes (preferably including materials made of carbon such as plastics and sawdust that would otherwise be lost to the atmosphere) for their physical property rather than chemical composition in cementitious composites with improved properties.

This paper discusses the potential impact on sustainability of the new tec and eco-cement technologies and goes into the as yet unclear chemistry of carbonation processes.

Keywords: Abatement, sustainable, sustainability, sequestration, CO_2, brucite ($Mg(OH)_2$), durability, reactive magnesium oxide, materials, nesquehonite ($MgCO_3.3H2O$), lansfordite ($MgCO_3.5H2O$), magnesian, 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, shrinkage, cracking, extract, extraction, permeability, rheology, emissions, flow, matter, materials, substances, wastes, reduce, reducing, reuse, re-using, recycle, recycling,.

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Introduction

Eco-cements became known to the world mainly through an article on them in New Scientists Magazine (Pearce 2002) and a program shown by Discovery Channel (Carbonating Eco-Cements 2003). There have been several reasons for the intense interest – the potential lower embodied energy, the ability of tec-cement and eco-cements to benignly encapsulate a wide range of wastes, the potential for reduced emissions using tec-cements and in combination with TecEco kiln technology, CO_2 sequestration by eco-cement concretes on a massive scale. The ability of tec and eco-cements to reduce net carbon dioxide emissions and utilise wastes are the main subject matter for this paper.

The built environment is our footprint on the globe and probably accounts for around 70% of all materials flows and of this "Buildings account for 40 percent of the materials and about a third of the energy consumed by the world economy. Combined with eco-city design principles, green building technologies therefore have the potential to make an enormous contribution to a required 50% reduction in the energy and material intensity of consumption in the post-modern world." (Rees 1999) Current cement production is over two billion tonnes per annum which is used to make over two tonnes of concrete per person on the planet per annum. (USGS 2004)

Global carbon dioxide flows in tonnes CO2 are (Haughton 2004 converted from tonnes C):

Atmospheric increase	=	Emissions from Fossil fuels	+	Net emissions from changes in land use	-	Oceanic uptake	-	Missing carbon sink
12.07 (±0.73)	=	20.152 (±0.1.83)	+	5.86 (±2.56)	-	7.32 (±2.93)	-	6.59 (±4.39)

Unless we want to face climate change on a massive and global scale we must sequester at least 6 billion tonnes of CO_2 per annum. As we are unlikely to give up the fossil fuel habit until we run out the need is urgent. Now Russia has joined the Kyoto treaty it has come into affect and countries that do not make an effort to sequester carbon will in due course face sanctions. As the emissions reduction is clear and definable there are significant business opportunities particularly under the clean development mechanism of the treaty. What better way to sequester carbon than in our own built environment? TecEco eco-cements mimic nature by sequestering large amounts of carbon dioxide with the added benefit of utilising wastes. TecEco tec-cements reduce net emissions because less need be used for the same strength and because they result in more durable concretes requiring replacement less often.

Basic Chemistry

TecEco cements include in their formulation reactive magnesia, a hydraulic cement such as Portland cement and usually a pozzolan. The Portlandite released during the curing of the Portland cement component is consumed by the pozzolan to produce more calcium silicate hydrate, a strength giving mineral or in eco-cements can also carbonate.

When reactive magnesia is substituted for OPC the first noticeable affect is an improvement in the rheology; blocks go through block machines with fewer failures, mortars spread more easily and stick better, concretes are easier to place. There are several reasons for this. Principal amongst them are the fineness of the reactive magnesia which affects particle packing and lubrication and the high surface charge density of the magnesium ion in solution which attracts layers of orientated water molecules adding a shear thinning affect.

Water is consumed by the hydrating brucite reducing shrinkage, and decreasing the voids paste ratio increasing strength. A higher short term pH may also contribute to more affective pozzolanic reactions. More wastes can be included mainly because of the lower long term pH.

TecEco Tec-cements generally contain less than 10% MgO and are more sustainable because they require less cement for the same strength. In concretes made using them, as for ordinary pc concretes, carbonation only proceeds to a relatively shallow depth as the formation of magnesium carbonates also results in greater density and the blockage of pores, which impedes further absorption of CO_2 into the cement. The main difference in the longer term is that the equilibrium pH controlled by brucite and CSH is much lower, reducing alkali silica reaction (ASR) problems but still sufficiently high to maintain the passive oxide layer around steel rebar deep in the substrate. Durability is improved mainly because of the pore filling affect, lower pH and lower solubility of Brucite compared to Portlandite.

In the presence of carbon dioxide and moisture inside an eco-cement block or mortar that is reasonably porous brucite ($Mg(OH)_2$ carbonates forming hydrated magnesium carbonates such as nesquehonite and lansfordite and possibly an amorphous phase at room temperatures. Although theories abound it is thought that there is a gradual desiccation with lansfordite loosing water forming nesquehonite and so on, particularly in relation to the formation of magnesite which Deelman claims to have solved (Deelman 2003). Significantly, both magnesium and calcium appear to carbonate more readily in porous concretes made using TecEco eco-cements containing magnesia that in concretes containing only Portland cement (PC) as the binder.

The silicification reactions of Portland cement are relatively well known and not discussed in this short paper. Carbonation of both Portlandite and brucite adds strength to eco-cement concretes used for blocks, mortars and renders and is encouraged for this and sequestration reasons. Calcium carbonates seem to at least obey Ostwalds law in the sequence of vaterite=>aragonite=>calcite carbonates formed however this is not the case for magnesium which forms a big range of basic and hydrated carbonates. There are a number of chemical pathways in which they can form and what favours the more important pathways is still being determined. The thermodynamics predicts hydromagnesite but more recent work has demonstrated that for kinetic reasons hydrated carbonates are formed.

Sustainability

According to the UK Hadley Center, most of the world's forests will begin to turn from sinks to sources - dying off and emitting carbon-by around 2040 (Gelbspan 2004). Recently Robin Batterham, Australia's chief scientist, said he supported the Federal Government's decision not to ratify the Kyoto Protocol on climate change because the reductions it set were not high enough. "I'm talking about enormous reductions - 80 per cent by the end of the century," Dr Batterham said. "Fifty per cent by 2050, I think, is realistic." (Batterham 2004) and in the UK, Sir David King, the government's chief scientific adviser, recently said "there is more carbon dioxide in the atmosphere than for 55 million years, enough to melt all the ice on the planet and submerge cities like London, New York and New Orleans". Dr King also said that climate change was a bigger threat than global terrorism. "We are moving from a warm period into the first hot period that man has ever experienced since he walked on the planet.....the heat wave of last summer in which 25,000 Europeans died had killed more people than terrorism, yet had not been given anything like the same level of attention.....I am sure that climate change is the biggest problem that civilisation has had to face in 5,000 years." (Brown 2004), See TecEco Newsletter 36, for details) The news from the Intergovernmental Committee on Climate Change is just as alarming.

Massive sequestration on a global scale is required. The built environment is our footprint on the planet, something like 70% of all materials flows and a patch on the planet we know well enough to change without fear of unforseen ramifications[1]. The concept of the built environment as a giant global carbon sink that utilises wastes is not only conceptually brilliant and would solve a lot of our problems. It's doable. low risk, visible and high reward for governments.

In 1999, construction activities contributed over 35% of total global CO_2 emissions - more than any other industrial activity. Mitigating and reducing the impacts contributed by these activities is a significant challenge for urban planners, designers, architects and the construction industry, especially in the context of population and urban growth, and the associated requirement for houses, offices, shops, factories and roads." (UNEP 2001)

According to the Human Settlements Theme Report, State of the Environment Australia 2001 (CSIRO 2001), "Carbon dioxide (CO_2) emissions are highly correlated with the energy consumed in manufacturing building materials. "On average, 0.098 tonnes of CO_2 are produced per gigajoule of embodied energy of materials used in construction. The energy embodied in the existing building stock in Australia is equivalent to approximately 10 years of the total energy consumption for the entire nation. Choices of materials and design principles have a significant impact on the energy required to construct a building. However, this energy content of materials has been little considered in design until recently, despite such impacts being recognized for over 20 years."

Both tec and eco-cements potentially contain significantly less embodied energy. Tec cements reduce emissions by requiring less CO_2 emitting cement and utilizing a higher proportion of pozzolans for the same strength development whilst eco-

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[1] Compare this to the dangers of dumping huge volumes of ferrous sulphate into the oceans and other much talked about schemes.

cements set by absorbing carbon dioxide from the air. Both tec and eco-cements provide a benign environment in which significant quantities of waste can be utilized. The shear thinning properties tend to prevent segregation of materials like plastics which is a problem with Portland cements and the lower pH prevents internal reactions from occurring.

Changing the Economic Paradigm – Converting Waste to Resource.

The widely held view is that sustainable strategies for construction are complex to devise and politically difficult to introduce. Currently it is more expensive to reuse and recycle than to use newly extracted resources. There would be a rapid improvement in sustainability if this hurdle could be overcome so that it was not only cheaper to reduce, reuse or recycle, but the process resulted in superior properties.

The problem is the costs involved. Sorting waste streams and then transporting sorted recyclable materials back to a location in which they can be used is expensive and tends to make recycled inputs more expensive than raw materials. Disorder is prevalent for two main reasons; things are made with mixed materials and the waste collection process tends to mix them up even more.

The current technical paradigm for the recycling process generates separate outputs based on chemical composition rather than class of property. Costs are incurred and waste generated in separating what is required from the balance of materials and then transporting to factories that can only use specific waste inputs.

The TecEco cement technologies provide an inherently more economic process as they change the technology paradigm redefining wastes as resources (Pilzer 1990). TecEco cements are benign low long term pH binders that can utilise waste more on their class of property rather than chemical composition, and therefore reduce sorting problems and costs associated with recycling.

Carbon taxes give the production of CO2 a cost. TecEco cements either reduce emissions or sequester the gas and should be eligible for credits in a fair system.

Carbonation of Eco-cement Bricks, Blocks, Pavers and Mortars

With formulations such as eco-cements, carbonation is desirable and is encouraged by the porous nature of these products. After hydration environments with a high relative humidity and wet - dry atmosphere seems best with humidity not dropping below 50-60%.

Eco-cements were the first TecEco cements to become known because they carbonate readily and therefore sequester CO_2. With the inclusion of wastes containing carbon such as sawdust or plastics they are net carbon sinks. In porous eco-cement concretes magnesia first hydrates forming brucite and this then carbonates forming hydrated magnesium carbonates including an amorphous phase, lansfordite and nesquehonite. A simplified thermodynamic cycle is depicted in Figure 1.

The high charge density of Mg^{++} explains why in water polar molecules of H_2O appear to line up in layers around the Mg^{++} ion making carbonation other than via a hydrated carbonate difficult if not impossible.

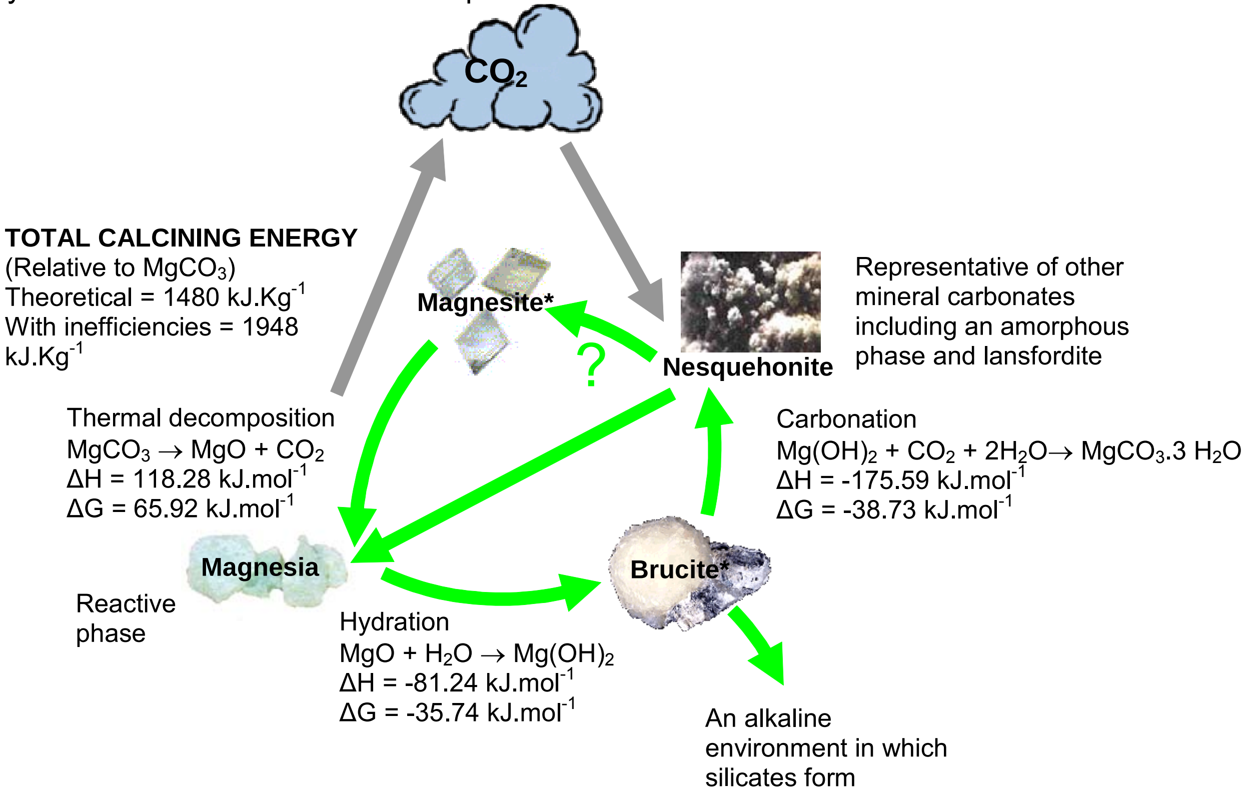

Figure 1 - The Magnesium Thermodynamic Cycle

The more important carbonates of calcium and magnesium are listed in Appendix 1 – Calcium and Magnesium Carbonates on page 23

The rate of carbonation of both calcium and magnesium compounds depends on the dissolution rate of Ca^{2+} and Mg^{2+} and partial pressure and transport of CO_2. These in turn are influenced by the mix design, affect of aggregates on porosity and setting atmospheric conditions. Dry mixes as in masonry unit formulations appear essential and wet dry cycles appear to promote carbonation providing alternatively transport and reaction media. Well graded aggregates including a coarse fraction are essential. Ideal carbonation conditions are still being considered, presently 50 – 70% relative humidity and exposure although wet dry is thought to work best.

The observed products of carbonation in eco-cement blocks are calcite, possibly vaterite, lansfordite and nesquehonite and all have strength giving properties. In the case of the magnesium carbonates this is considered to be mostly microstructural due to their shape and interactions with other matrix minerals.

Of the calcium minerals aragonite is the strongest with a hardness of 3.5 – 4. Both calcite and vaterite are relatively soft with a hardness of 3. Nesquehonite or lansfordite contribute to strength and the reason is thought to be microstructural as they are not particularly strong with a hardness of 2.5.

Of the calcium carbonates only vaterite and rarely aragonite are fibrous. On the other hand most of the carbonates and hydrated carbonates of magnesium can be fibrous or otherwise elongated. For example nesquehonite is prismatic and generally forms star like clusters thought to be a possible source of microstructural strength. Fibrous and needle like crystal growths add more microstructural strength than more rounded or tabular crystals such as calcite because of the 3D structures formed.

Calcium silicate hydrates can form elongated growths but commonly have a more granular or tabular habit. All are harder than Brucite or the carbonates of calcium or magnesium. Harder minerals that form more quickly tend to have the physical effect of forcing the growth of slower growing softer minerals into interstitial spaces. It is also possible that the more reformation processes that occur, the more crystals interlock with each other adding to strength and that the hydroxides and carbonates of magnesium are compressed adding to strength. According to CANMET, compressed brucite is, for example, as strong as CSH (Beaudoin, Ramachandran et al. 1977).

The micro tensile strength of the various carbonate minerals in the system are not generally considered and not known. It is essential this work is done as micro tensile strength is known to have a big impact on dental cement strengths. The strength development in tec-cements could well be a result of micro tensile strength in amorphous and crystalline Mg hydrated carbonates acting somewhat like a glue between stronger minerals that provide the bulk strength.

Lansfordite and nesquehonite are more soluble than magnesite and hydromagnesite which are virtually insoluble (both with a solubility of approximately .001 g L^{-1}), however both are more soluble than Brucite with a solubility of .000154 g L^{-1} (K_{sp} = 1.8×10^{-11}) which is virtually insoluble. (See Appendix 1 – Calcium and Magnesium Carbonates on page 23).

Carbonation rates depend more than anything else on porosity and gas transport. It starts at the surface of whatever surfaces are exposed to air and works inwards and can be accelerated by exposure to the weather. It is generally accepted medium to high humidity is best. Simple experiments performed by the author have also demonstrated that the presence of accelerators such as iron salts and triethanolamine may accelerate carbonation. The use of CO2 producing organics such as carbonic acid, EGDA or propylene carbonate are considered uneconomic and of academic interest only. The use of carbonated steam, carbon dioxide foam and other substance which release CO_2 is also being considered.

Masonry units are usually made hollow and due to the manufacturing process they are porous and the presence of air voids clearly speeds up carbonation. The maximum depth is less that 40 – 50 mm and averages more like 25 or 30 mm. If a porous aggregate such as bottom ash, scoria or pumice is also added an even higher internal surface area results further speeding up carbonation.

Recent work by the author has demonstrated that most commercial sands are unsuitable for the carbonation of mortars and that well graded sands including a coarser fraction up to 1/3 the thickness of a mortar joint are essential to allow the material to “breathe” thereby providing gas transport.

Other magnesium cements such as magnesium oxychloride and magnesium oxysulfate take a long time to carbonate and as reported by Cole and Demediuk (Cole and Demediuk 1955) tend to remain as unstable oxy compounds, but do eventually carbonate.

Thermodynamics

According to Deelman (Deelman 2003) "the conclusion must be drawn, that the approach based on classical thermodynamics has not provided the solution to the problem of the low-temperature syntheses of dolomite, huntite and magnesite. The reason for this failure is simple: the reactions involved are not reversible, and therefore no chemical equilibrium sets in…….. But perhaps describing how, why and when a particular reaction will be taking place, is not at all the realm of thermodynamics. And although thermodynamics have been applied to chemistry thanks to the work of Horstmann, Von Helmholtz, Planck and Gibbs, only equilibria are studied in most instances. The warning by Van der Waals (1908), that thermodynamics is not capable of describing all of the factors involved in unknown processes, and that therefore considering only the beginning and the end situation of an unknown reaction is not particularly useful, still possesses more than historic significance only. In particular the phase relations amongst the anhydrous Mg/Ca carbonates have shown how for example Gibbs' Phase Rule cannot be applied."

In multi-component alkaline concretes there is still a lot to learn, and the reader should be aware that the thermodynamic and equilibrium calculations below do not accurately predict what happens in practice. If they were followed, hydromagnesite would be the first carbonate formed and as a result of desiccation would eventually become magnesite as I first predicted. This is not the case however and the first minerals formed are lansfordite and nesquehonite possibly accompanied by an amorphous phase.

As summary of the free energy and enthalpy of formation of calcium and magnesium carbonates formed from hydroxides have been calculated and are included in Appendix 1 – Calcium and Magnesium Carbonates on page 23.

Enthalpy

Enthalpy (H) is a measure of the energy released or absorbed by a reaction at constant pressure.

Calcium Carbonates

We have not data for the enthalpy of formation of vaterite

Consider the enthalpy changes for the carbonation of Portlandite to calcite.

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

$\Delta H^o_r = [\Delta H^o_f\ (CaCO3, s) + \Delta H^o_f\ (H_2O, l)] – [\Delta H^o_f\ (Ca(OH)_2,s) + \Delta H^o_f\ (CO_2,g)]$

ΔH^o_r = (-1207.37 - 241.81) - (-986.09 - 393.51) kJ.mol^{-1}

ΔH^o_r = - 69.58 kJ.mol^{-1}

The reaction is exothermic and - 69.58 kJ.mol^{-1} of energy are released

Magnesium Minerals

We have no numbers for lansfordite.

For artinite

$2Mg(OH)_2 + CO_2 + 2H_2O \rightarrow Mg_2(CO_3)(OH)_2\cdot 3(H_2O)$

ΔH^o_r = [ΔH^o_f ($Mg_2(CO_3)(OH)_2\cdot 3H_2O$), s)] – [2 X ΔH^o_f ($Mg(OH)_2$,s) + ΔH^o_f (CO_2,g) + 2 X ΔH^o_f (H_2O,l)]

ΔH^o_r = - 2920.61 - (2 X - 924.54 - 393.51 - 2 X 241.81) kJ.mol^{-1}

ΔH^o_r = - 194.40 kJ.mol^{-1}

The reaction is exothermic with 194.40 kJ.mol^{-1} liberated.

For nesquehonite

$Mg(OH)_2 + CO_2 + 2H_2O \rightarrow Mg(HCO_3)(OH)\cdot 2(H_2O)$

ΔH^o_r = [ΔH^o_f ($Mg(HCO_3)(OH)\cdot 2H_2O$), s)] – [ΔH^o_f ($Mg(OH)_2$,s) + ΔH^o_f (CO_2,g) + 2 X ΔH^o_f (H_2O,l)]

ΔH^o_r = - 1977.26 - (- 924.54 - 393.51 - 2 X 241.81) kJ.mol^{-1}

ΔH^o_r = - 175.59 kJ.mol^{-1}.

The reaction is exothermic with 175.59 kJ.mol^{-1} liberated.

For hydromagnesite

$5Mg(OH)_2 + 4CO_2 \rightarrow Mg(OH)_2.4MgO.4CO_2.4H_2O$

ΔH^o_r = [ΔH^o_f ($Mg(OH)_2.4MgO.4CO_2.4H_2O$), s)] – [5 X ΔH^o_f ($Mg(OH)_2$,s) + 4 X ΔH^o_f (CO_2,g)]

ΔH^o_r = - 6514.86 - (- 5 X 924.54 - 4 X 393.51) kJ.mol^{-1}

ΔH^o_r = - 318.12 kJ.mol^{-1}

The reaction is exothermic with 318.12 kJ.mol^{-1} liberated.

Consider the loss of water and CO_2 by nesquehonite to give hydromagnesite

$5Mg(HCO_3)(OH)\cdot 2H_2O \rightarrow Mg(OH)_2.4MgO.4CO_2.4H_2O + 10H_2O + CO_2$

$\Delta H^o_r = [\Delta H^o_f$ (Mg(OH)$_2$.4MgO.4CO$_2$.4H$_2$O,s) + 10 X ΔH^o_f (H$_2$O,l) + ΔH^o_f (CO$_2$,g)] – [ΔH^o_f (Mg(HCO$_3$)(OH)·2H$_2$O), s)]

ΔH^o_r = (-6514.86 - 10 X 241.81 - 393.51) - (- 5 X 1977.26) kJ.mol^{-1}

ΔH^o_r = 559.83 kJ.mol^{-1}

The reaction is endothermic with 559.83 kJ.mol^{-1} absorbed.

Consider the loss of water by nesquehonite to give magnesite

$Mg(HCO_3)(OH)\cdot 2(H_2O) \rightarrow MgCO_3 + 3\ H_2O$

$\Delta H^o_r = [\Delta H^o_f$ (MgCO$_3$,s) + 3 X ΔH^o_f (H$_2$O,l)] – [ΔH^o_f (Mg(HCO$_3$)(OH)·2(H$_2$O)), s)]

ΔH^o_r = (- 1113.28 - 3 X 241.81) - (-1977.26) kJ.mol^{-1}

ΔH^o_r = 138.55 kJ.mol^{-1}

The reaction is endothermic with 8.55 kJ.mol^{-1} absorbed.

The thermodynamics predicts that neither magnesite or hydromagnesite form easily from nesquehonite

Consider the further carbonation of hydromagnesite to give magnesite

$Mg(OH)_2.4MgO.4CO_2.4H_2O + CO2 \rightarrow 5\ MgCO_3 + 5\ H_2O$

$\Delta H^o_r = [5$ X ΔH^o_f (MgCO$_3$,s) + 5 X ΔH^o_f (H$_2$O,l)] – [ΔH^o_f (Mg(OH)$_2$.4MgO.4CO$_2$.4H$_2$O), s) + ΔH^o_f CO$_2$]

ΔH^o_r = (5 X -1113.28 - 5 X 241.814) - (- 6514.86 - 393.51) kJ.mol^{-1}

ΔH^o_r = 132.9 kJ.mol^{-1}

The reaction is endothermic with 132.9 kJ.mol^{-1} being required.

For the carbonation of brucite directly to magnesite

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

$\Delta H^o_r = [\Delta H^o_f$ (MgCO3, s) + ΔH^o_f (H$_2$O, l)] – [ΔH^o_f (Mg(OH)$_2$,s) + ΔH^o_f (CO$_2$,g)]

ΔH^o_r = (-1113.28 - 241.81) - (-986.08 - 393.51) kJ.mol^{-1}

ΔH^o_r = 24.5 kJ.mol^{-1}

The reaction is endothermic 24.5 kJ.mol^{-1} of energy are absorbed.

MgO also carbonates directly to form MgCO3 as indicated by the following equation and this occurs at higher temperatures.

$MgO + CO_2 \rightarrow MgCO_3$

$\Delta H^o_r = [\Delta H^o_f (MgCO_3,s)] - [\Delta H^o_f (MgO,s) + \Delta H^o_f (CO_2,g)]$

$\Delta H^o_r = - 1113.28 - (- 601.49 - 393.51)$

$\Delta H^o_r = - 118.28$ kJ.mol^{-1}

The reaction is exothermic with 118.28 kJ.mol^{-1} liberated.

When making magnesia it is therefore important to keep the partial pressure of CO_2 low so the reaction proceeds to the left the way it is written above.

Free Energy

Calcium Minerals

Consider the free energy changes for the carbonation of Portlandite forming vaterite.

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

$\Delta G^o_r = [\Delta G^o_f (CaCO3, s) + \Delta G^o_f (H_2O, l)] - [\Delta G^o_f (Ca(OH)_2,s) + \Delta G^o_f (CO_2,g)]$

$\Delta G^o_r = -1125.54 - 228.57 - (-898.41 - 394.37)$ kJ.mol^{-1}

$\Delta G^o_r = -61.33$ kJ.mol^{-1}

The reaction is spontaneous

Consider the free energy changes for the carbonation of Portlandite forming calcite.

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

$\Delta G^o_r = [\Delta G_f (CaCO_3, s) + \Delta G^o_f (H_2O, l)] - [\Delta G_f (Ca(OH)_2,s) + [\Delta G_f (CO_2,g)]$

$\Delta G^o_r = - 1128.84 - 228.57 - (- 898.41 - 394.37)$ kJ.mol^{-1}

$\Delta G^o_r = - 64.63$ kJ.mol^{-1}

The reaction is spontaneous

Magnesium Minerals

We have no numbers for lansfordite.

For artinite:

$2Mg(OH)_2 + CO_2 + 2H_2O \rightarrow Mg_2(CO_3)(OH)_2{\cdot}3(H_2O)$ (artinite)

$\Delta G^o_r = [\Delta G^o_f (Mg_2(CO_3)(OH)_2 \cdot 3(H_2O), s)] – [2 X \Delta G^o_f (Mg(OH)_2,s) + \Delta G^o_f (CO_2,g) + 2 X \Delta G^o_f (H_2O,l)]$

$\Delta G^o_r = - 2568.35 - (2 X - 833.51 + - 394.38 + 2 X - 228.57) kJ.mol^{-1}$

$\Delta G^o_r = - 49.81 kJ.mol^{-1}$

The reaction is spontaneous

For nesquehonite:

$Mg(OH)_2 + CO_2 + 2H_2O \rightarrow Mg(HCO_3)(OH) \cdot 2(H_2O)$ (nesquehonite)

$\Delta G^o_r = [\Delta G^o_f (Mg(HCO_3)(OH) \cdot 2H_2O), s)] – [\Delta G^o_f (Mg(OH)_2,s) + \Delta G^o_f (CO_2,g) + 2 X \Delta G^o_f (H_2O,l)]$

$\Delta G^o_r = - 1723.75 - (- 833.51 - 394.37 + 2 X - 228.57) kJ.mol^{-1}$

$\Delta G^o_r = - 38.73 kJ.mol^{-1}$

The reaction is spontaneous

And for hydromagnesite:

$5Mg(OH)_2 + 4CO_2 \rightarrow Mg(OH)_{2.}4MgO.4CO_2.4H_2O$ (hydromagnesite)

$\Delta G_r = [\Delta G^o_f (Mg(OH)_{2.}4MgO.4CO_2.4H_2O), s)] – [5 X \Delta G^o_f (Mg(OH)_2,s) + 4 X \Delta G^o_f (CO_2,g)]$

$\Delta G^o_r = - 5864.17 - (- 5 X 833.51 - 4 X 394.37) kJ.mol^{-1}$

$\Delta G^o_r = - 119.14 kJ.mol^{-1}$

The reaction is spontaneous.

Consider the loss of water and CO_2 by nesquehonite to give hydromagnesite

$5Mg(HCO_3)(OH) \cdot 2H_2O \rightarrow Mg(OH)_{2.}4MgO.4CO_2.4H_2O + 10H_2O + CO_2$

$\Delta G^o_r = [\Delta G^o_r (Mg(OH)_{2.}4MgO.4CO_2.4H_2O,s) + 10 X \Delta G^o_r (H_2O,l) + \Delta G^o_r (CO_2,g)] – [\Delta G^o_r (Mg(HCO_3)(OH) \cdot 2H_2O), s)]$

$\Delta G^o_r = (-6514.86 + 10 X - 241.81 - 393.51) - (5 X - 1977.26) kJ.mol^{-1}$

$\Delta G^o_r = 559.83 kJ.mol^{-1}$

The reaction is not spontaneous and very unlikely.

Consider the loss of water by nesquehonite to give magnesite

$Mg(HCO_3)(OH) \cdot 2(H_2O) \rightarrow MgCO_3 + 3 H_2O$

$\Delta G^o_r = [\Delta G^o_f\ (MgCO_3,s) + 3\ X\ \Delta G^o_f\ (H_2O,l)] – [\Delta G^o_f\ (Mg(HCO_3)(OH)\cdot 2(H_2O)),\ s)\ ]$

$\Delta G^o_r = (-\ 1029.48 + -\ 3\ X\ 228.57) - (-1723.746)\ kJ.mol^{-1}$

$\Delta G^o_r = 8.56\ kJ.mol^{-1}$

The reaction is not spontaneous and requires energy to proceed. Note however the removal of water (evaporation) would tend to push the reaction to the right in accordance with Le Chatelier's principle.

Consider the further carbonation of hydromagnesite to give magnesite

$Mg(OH)_{2.}4MgO.4CO_2.4H_2O + CO2 \rightarrow 5\ MgCO_3 + 5\ H_2O$

$\Delta G^o_r = [5\ X\ \Delta G^o_f\ (MgCO_3,s) + 5\ X\ \Delta G^o_f\ (H_2O,l)] – [\Delta G^o_f\ (Mg(OH)_{2.}4MgO.4CO_2.4H_2O),\ s) + \Delta G^o_f\ CO_2]$

$\Delta G^o_r = (5\ X - 1029.48 + 5\ X - 228.56) - (-\ 5864.16 - 394.37)\ kJ.mol^{-1}$

$\Delta G^o_r = -\ 31.67\ kJ.mol^{-1}$

The reaction is spontaneous. Note however the removal of water (evaporation) would tend to push the reaction to the right in accordance with Le Chatelier's principle.

And for the direct carbonation of brucite to form magnesite.

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

$\Delta G^o_r = [\Delta G^o_f\ (MgCO_3,\ s) + \Delta G^o_f\ (H_2O,\ l)] – [\Delta G_f\ (Mg(OH)_2,s) + [\Delta G^o_f\ (CO_2,g)]$

$\Delta G^o_r = -\ 1012.1 -237.13 - (-\ 835.32 + -\ 394.36)\ kJ.mol^{-1}$

$\Delta G^o_r = -\ 19.55\ kJ.mol^{-1}$, the reaction is spontaneous.

MgO also carbonates directly to form MgCO3 as indicated by the following equation and this may occur in practice if magnesia is heated.

$MgO + CO_2 \rightarrow MgCO_3$

$\Delta G^o_r = [\Delta G^o_f\ (MgCO_3,s)] – [\Delta G^o_f\ (MgO,s) + \Delta G^o_f\ (CO_2,g)]$

$\Delta G^o_r = -\ 1029.48 – [-569.19 + -\ 394.37]\ kJ.mol^{-1}$

$\Delta G^o_r = -\ 65.92\ kJ.mol^{-1}$

The reaction is spontaneous, but in the presence of water the hydroxide is likely to be produced first.

Equilibrium

When considering equilibrium keep in mind that equilibrium is possibly never reached.

The equilibrium constant is related to the Gibbs free energy by the following equation.

ΔG_o =-(2.303RT)logK

And

$\log K=-\Delta G_o/2.303RT$

Calcium Minerals

The formation of calcite

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

= 64620/(2.303x8.313x298) = 11.327

Equilibrium favours carbonation.

Magnesium Minerals

The formation of nesquehonite

logK($Mg(OH)_2 + CO_2 + 2H_2O \rightarrow MgCO_3.3H_2O$)

= 38730/(2.303x8.313x298) = 6.78

Equilibrium favours carbonation.

The formation of hydromagnesite.

LogK($5Mg(OH)_2 + 4CO_2 \rightarrow Mg(OH)_{2.}4MgO.4CO_2.4H_2O$)

= 119140/(2.303x8.313x298) = 20.883

Equilibrium favours carbonation.

The formation of magnesite

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

= 19550/(2.303x8.313x298) = 3.4267

Equilibrium favours carbonation.

As may be expected intuitively, equilibrium favours carbonation products for both lime and magnesite.

Consider the loss of water of nesquehonite to give magnesite

$\log K(MgCO_3.3H_2O \rightarrow MgCO_3 + 3\ H_2O)$

$= 8560/(2.303x8.313x298) = 1.5004$

Equilibrium favours magnesite and would be pushed by desiccation.

Consider the further carbonation of hydromagnesite to give magnesite

$Mg(OH)_{2.}4MgO.4CO_2.4H_2O + CO2 \rightarrow 5\ MgCO_3 + 5\ H_2O$

$\log K(Mg(OH)_{2.}4MgO.4CO_2.4H_2O + CO2 \rightarrow 5\ MgCO_3 + 5\ H_2O)$

$= 31670/(2.303x8.313x298) = 5.55$

Equilibrium again favours magnesite

The above indirectly calculated equilibrium constant favours the formation of magnesite. With the removal of water, according to Le Chatelier’s principle the reaction should move towards products (to the right).

Practically however amorphous forms (?) lansfordite and nesquehonite seem to be favoured and further carbonation or loss of water appears slow.

Kinetics

According to Langmuir (Langmuir 1971) thermodynamics as in the above calculations make it clear that magnesite must be considered more stable than nesquehonite, which in turn is more stable than magnesium hydroxide carbonate ($MgHCO_3$). Magnesium oxide does not react with carbon dioxide gas to produce magnesite except possibly at elevated temperatures.

There may be a gradual transition with magnesite and lower water hydrates forming at the expense of nesquehonite and other hydrates over time in accordance with Ostwalds rule given the right conditions and time available.

The sequence as so far determined seems to be

$MgO \rightarrow Mg(OH)2 \rightarrow MgCO_3.5H_2O \rightarrow MgCO_3.3H_2O$? → ??????? and maybe eventually $MgCO_3$

The thermodynamics does not however accurately predict the carbonation of magnesium hydroxide as amorphous carbonate (?), lansfordite and nesquehonite prevail. The explanation is in the way magnesium tightly binds water.

The high charge density of Mg^{++} explains why in water polar molecules of H_2O appear to line up in layers around the Mg^{++} ion making direction carbonation other than via a hydrated carbonate difficult if not impossible. The mass alignment of molecules of water would also explain some of the shear thinning properties of cement made using added magnesia.

As pointed out by Deelman, why the carbonation of magnesium in solution does not appear to occur according to the thermodynamics and Ostwalds rule is because magnesium appears to more strongly than calcium hydrate forming $[Mg(H_2O)N]^{2+}$ complexes or hydroxylate forming H_3O^+ and Mg^+OH and hydrated forms of Mg^+OH. The energies associated with these complexes has to be overcome for direct combination with carbonate (which itself hydrolyses) to form magnesite. Hydrated forms, depending on the hydrate do not to the same extent have these barriers. Calcium is a bigger atom with a lower charge density and consequently lower hydration and hydroxylation energy and behaves more, but not completely normally in that Gibbs phase rule is also not obeyed.

By definition metastable phases such as lansfordite and nesquehonite have a higher rate of precipitation, and conversely a higher rate of dissolution, than magnesite and hydromagnesite which are more stable phases. Deelman (Deelman 2001) considered the mechanism for the formation of the more stable phase magnesite from nesquehonite and concluded that the mechanism was one of fluctuating conditions in which “Intervals of dissolution alternating with the intervals of precipitation are responsible for the dissolution of more and more of the metastable phase.” From this it may be concluded that given the normal pattern of weather and fluctuating pH eventually magnesite should predominate, but that this may take many years.

In TecEco tec-cements carbonation is not desirable if reinforced with steel but desirable otherwise. It is therefore generally appropriate that tec-cements are dense so carbonation is not driven by loss of water or access by CO_2. With formulations such as eco-cements, carbonation is desirable and is encouraged by the porous nature of these products. After hydration environments with a high relative humidity and wet - dry atmosphere seems best with humidity not dropping below 50-60%.

The reactions for calcium and magnesium occur in aqueous media and as a consequence rates are controlled mainly by dissolution rates, physical access to carbon dioxide and humidity.

Experimental Evidence of Carbonation to Date

Experimental work to date indicates that carbonation proceeds slowly in dense tec-cement concretes but relatively rapidly with porous materials such as eco-cement masonry units, and further work will try and improve the kinetics and include the direct foaming of concrete with carbon dioxide to create eco-cement foamed concretes.

The evidence that carbonation is complete within one and a half years in properly formulated and mixed eco-cements is simple:

Soon after eco-cement concrete samples were made they showed significant amounts of brucite. Approximately one and a half years after they were made XRD on three eco-cement samples taken from blocks showed no more brucite and instead lansfordite and/or nesquehonite in small quantities.

Further acid extraction of the carbonates demonstrated their removal and a possible discrepancy with the original amount of MgO added which may be an amorphous or very finely crystalline phase which did not show up on XRD.

The XRD traces for a simple block formulation using sand as an aggregate are shown before and after treatment with HCL used to remove carbonates in Figure 2 and are clear evidence that the binder in eco-cements is a mixture of calcite, lansfordite and nesquehonite, not calcite, hydromagnesite and magnesite as the author originally thought.

The XRD does not show an amorphous form but semi quantitative XRD indicates a possible shortfall which may be expressing as the amorphous from commented on by Deelman (Deelman 2003) or have insufficient lattice order to show up. Further work will include quantitative acid neutralisation to try and prove this.

Carbonation Volume Changes

Consider the volume changes that occur when Portlandite carbonates to calcite:

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

$74.08 + 44.01 \leftrightarrow 100$ molar mass

$33.22 + \text{gas} \leftrightarrow 36.93$ molar volumes

Slight expansion. But shrinkage from surface water loss

Consider the volume changes that occur when Brucite carbonates to nesquehonite:

$Mg(OH)_2 + CO_2 + H_2O \rightarrow MgCO_{3.}3H_2O + H_2O$

$24.3 + (g) \rightarrow 74.77 + (l)$ molar volumes[2]

Significant expansion.

The water lost by Portland cement as it shrinks is used by reactive magnesia as it hydrates negating or eliminating shrinkage.

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[2] The molar volume is equal to the molar mass of atoms or molar mass of molecules divided by the density.

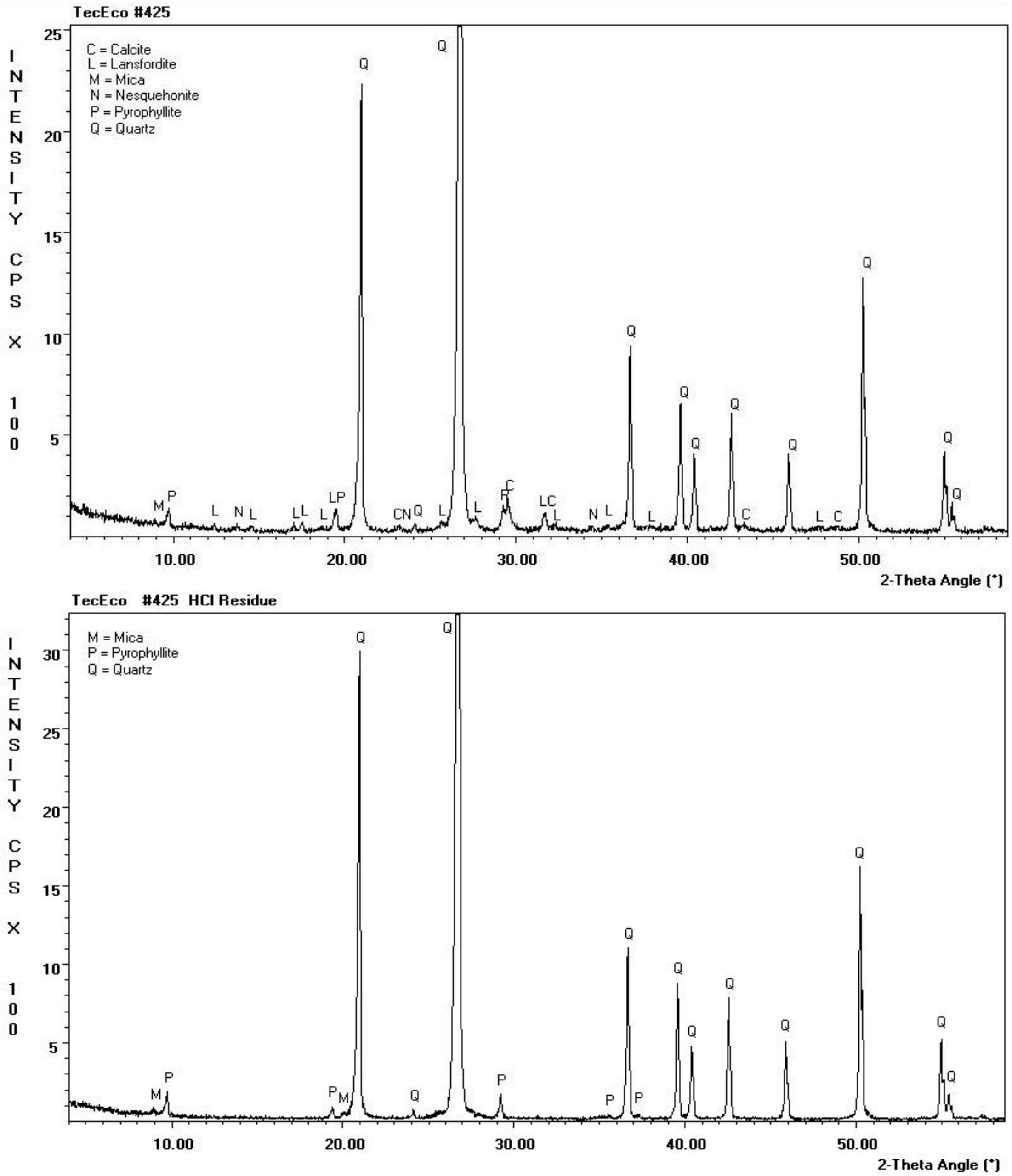


Figure 2 - XRD Showing Carbonates Before and Minerals Remaining after their Removal with HCl in a Simple Mix (70 Kg PC, 70 Kg MgO, colouring oxide .5Kg, sand unwashed 1105 Kg)

The Extent and Potential of Carbonation in Portland compared to Eco-Cement Concretes

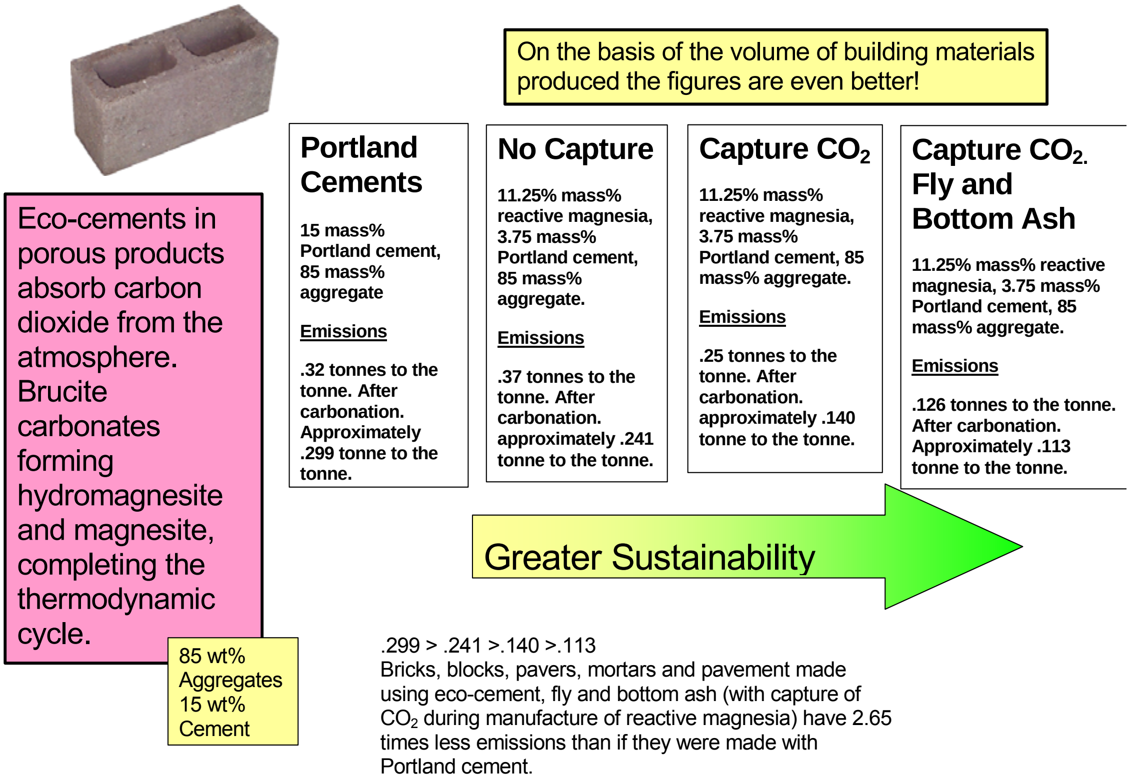
The amount of CO_2 concretes absorb is dependent on a number of factors.

Porosity is the main factor. Mortars like old fashioned lime mortars must be porous. For this a graded sand containing coarser particles is essential. Concrete masonry units tend to be more porous as they are mixed dry. It is important to note that porosity does not necessarily infer inferior quality. There is much to be said for mortars and concrete masonry units that “breathe”.

Thickness is another key factor - only the outer 35-50 mm (1 ½ to 2") of poured Portland cement and somewhat less for TecEco tec-cement concretes will absorb CO_2. Concrete masonry units and mortars are on the other hand more porous and not very thick in cross section and will generally absorb CO_2 throughout.

Eco-cements contain a high proportion of reactive magnesia. In masonry products such as mortars and blocks made using TecEco eco-cement, there are a much greater proportion of materials such as reactive magnesia (and thus Brucite) in the cement component that carbonate and carbonation proceeds to completion and much more CO_2 is reabsorbed. A typical eco-cement formulation for masonry products for example would contain 50 - 85% readily carbonated material in the cement component compared to 20-25% in the cement component of ordinary CMU’s containing Portland cement only. There is therefore approximately 50 % more carbonation in an eco-cement block compared to an ordinary concrete block.

The carbonation of a typical block formulation containing 15% cement is depicted in Figure 3 - The Carbonation of a Typical Eco-Cement Block on page 19.



On the basis of the volume of building materials produced the figures are even better!

Eco-cements in porous products absorb carbon dioxide from the atmosphere. Brucite carbonates forming hydromagnesite and magnesite, completing the thermodynamic cycle.

85 wt% Aggregates
15 wt% Cement

Portland Cements

15 mass% Portland cement, 85 mass% aggregate

Emissions

.32 tonnes to the tonne. After carbonation. Approximately .299 tonne to the tonne.

No Capture

11.25% mass% reactive magnesia, 3.75 mass% Portland cement, 85 mass% aggregate.

Emissions

.37 tonnes to the tonne. After carbonation. approximately .241 tonne to the tonne.

Capture CO_2

11.25% mass% reactive magnesia, 3.75 mass% Portland cement, 85 mass% aggregate.

Emissions

.25 tonnes to the tonne. After carbonation. approximately .140 tonne to the tonne.

Capture CO_2. Fly and Bottom Ash

11.25% mass% reactive magnesia, 3.75 mass% Portland cement, 85 mass% aggregate.

Emissions

.126 tonnes to the tonne. After carbonation. Approximately .113 tonne to the tonne.

Greater Sustainability

.299 > .241 >.140 >.113
Bricks, blocks, pavers, mortars and pavement made using eco-cement, fly and bottom ash (with capture of CO_2 during manufacture of reactive magnesia) have 2.65 times less emissions than if they were made with Portland cement.

Figure 3 - The Carbonation of a Typical Eco-Cement Block

The calculations do not take into account the use of sustainable energy to produce eco-cements or the capture of CO_2 at source as planned by TecEco.

Sustainability Other Than by Carbonation

Superior Strength Development with Less Cement and Blended Pozzolans

There are many ways in which sustainability can be improved. It has been demonstrated that tec-cements which contain a much lower proportion of reactive magnesia develop strength more rapidly from day 0 and continue to develop strength in a straight line at least for 90 days, even with a significant proportion of added pozzolans. Increased strength for the same amount of cement is no different to the same strength for less cement.

Reasons

Likely reasons for greater strength with less total binder include greater density and concentration of alkalis as magnesia removes excess water during the hydration phase.

Durability

The less often something is replaced the less energy and emissions used to replace it. TecEco cements have been demonstrated to be much more durable than their Portland cement counter parts.

Experimental Evidence of Greater Strength

An Australian company, Island Block and Paver Pty. Ltd. are now making blocks and pavers with 20% less total binders with a further 10% of OPC replaced by reactive magnesia that achieve exactly the same strength as control blocks without reduction in cement content or substitution.

TecEco have made slabs, slipways, tilt up panels and footings using the method with similar improvement in strength:binder ratios.

The British Research Establishment found a similar result with one sample in some recent tests as had student at Oxford University.

Waste Utilization

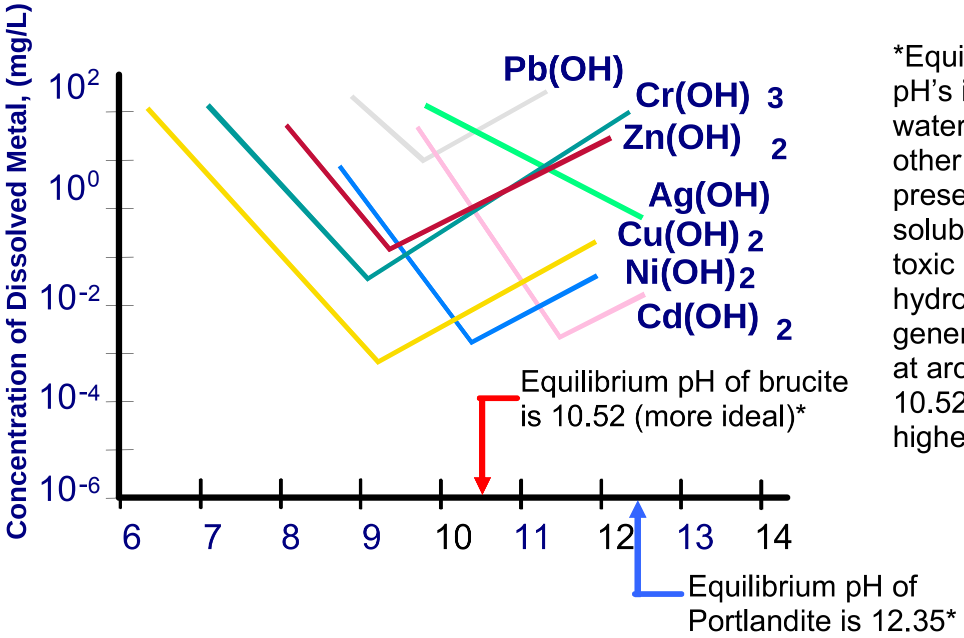
Apart from global warming, the other biggest problem on the planet today is the disposal of waste. The answer is to convert waste to resource and TecEco have developed cementitious composites that provide a benign environment suitable for waste immobilization.

Many wastes such as fly ash, sawdust, shredded plastics etc. can improve a property or properties of the cementitious composite based on their physical property rather than chemical composition. It their chemical compositions includes carbon – even better!

If wastes cannot directly be used then if they are not immobile they should be immobilized. TecEco cementitious composites represent a cost affective option for both use and immobilization.

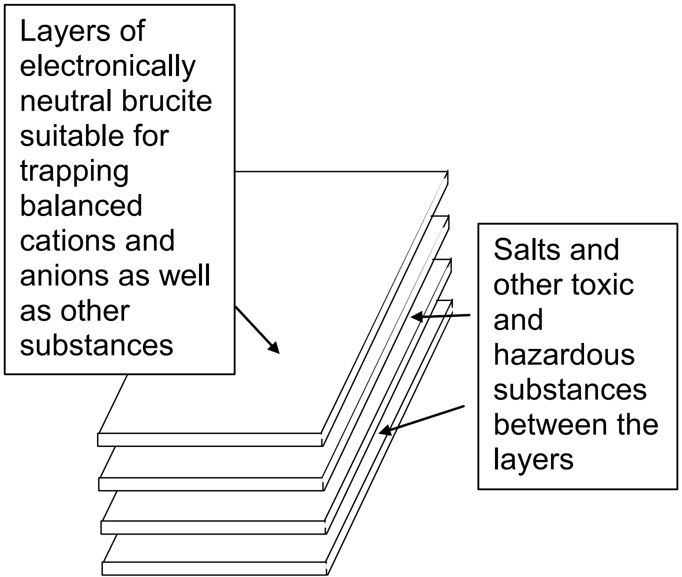
TecEco waste inclusion technology is more suitable than any other means of incorporating large volumes of wastes. Durability and many other problems are overcome. Reasons include:

- Lower reactivity (less water, lower pH)
- Reduced solubility of heavy metals (lower pH)
- Greater durability
- Dense, impermeable and
- Homogenous.
- No bleed water
- Are not attacked by salts in ground or sea water
- Are dimensionally more stable with less cracking



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

Figure 4 – The Low pH regime of TecEco cements Minimises the Solubility of Heavy Metals



Immobilisation Mechanism

In a Portland cement-brucite matrix OPC takes up lead, some zinc and germanium. The magnesium mineral is mainly brucite although hydrotalcite may form under some conditions. Both are both excellent hosts for toxic and hazardous wastes. Heavy metals not taken up in the structure of Portland cement minerals or trapped within the brucite layers end up as hydroxides with minimal solubility. The minimum solubility of most heavy metal hydroxides is in the pH range governed by brucite, not in the pH range governed by Portlandite. There is a 10^4 advantage.

Figure 5 - The Layers of Brucite Trap Toxic Wastes

The brucite in TecEco cements has a structure comprising electronically neutral layers 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 is known to be very suitable for toxic and hazardous waste immobilisation.

Summary

The late great H.F.W. Taylor, perhaps the most pre-eminent cement chemist ever, predicted a need to do something about global warming and wastes in regard to cement and concrete publicly at least as far back as 1990 in his address to a Conference on Advances in Cementitious Materials (Taylor 1990) forecast many changes not only in the way cements are made but in their composition, particularly in relation to the incorporation of wastes (See TecEco newsletter 36).

TecEco cements are a new innovation that offers sustainability in our own back yards. Tec-cements promise greater durability than ever achieved before and stronger materials with lower embodied energies and associated emissions whilst eco-cements are the first construction materials that successfully use carbon dioxide and wastes.

As stated by Fred Pearce in the article on eco-cements that was published in the New Scientist magazine (Pearce 2002)"There is a way to make our city streets as green as the Amazon Forest. 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 it change the way we make cement."

Appendix 1 – Calcium and Magnesium Carbonates

Numerous magnesium carbonates, hydrated magnesium carbonates and hydroxide carbonates exist. Mixed Mg-Ca, Mg-Fe Mg-Na etc. carbonates not shown but numerous. For a list of carbonates see http://mineral.galleries.com/minerals/carbonat/class.htm. For detail see http://webmineral.com

Basic Magnesium Carbonates

Numerous magnesium hydroxide carbonates exist.

Mineral	**Formula**	**XRD (By Intensity I/Io)**	**Molecular Weight**	**Hardness**	**Density**	**Solubility (Ml^{-1}, cold water)**	**ΔH^o reaction from hydroxide (kJ.mol^{-1})**	**ΔG^o reaction from hydroxide (kJ.mol^{-1})**	**Comment**
Artinite	$Mg_2CO_3(OH)_2.3H_2O$	2.736(1), 5.34(0.65), 3.69(0.5)	198.68	2.5	2.02		-194.4	-49.81	Hydrated basic magnesium carbonate
Hydro magnesite	$Mg_5(CO_3)_4(OH)_2.4H_2O$	5.79(1), 2.899(0.82), 9.2(0.39)	365.31	3.5	2.16	.001095	-318.12	-119.14	Hydrated basic magnesium carbonate
Dypingite	Mg5(CO3)4(OH) 2.5H2O	10.6(1), 5.86(0.9), 6.34(0.6)	485.65		2.15				Hydrated basic magnesium carbonate
Giorgiosite	Mg5(CO3)4(OH) 2.5H2O	11.8(1), 3.28(0.7), 3.38(0.7)	485.65		2.17				Hydrated basic magnesium carbonate
Nesquehonite	$Mg(HCO_3)(OH)\cdot 2(H_2O)$ or $MgCO_3\cdot 3(H_2O)$	6.5(1), 3.86(0.9), 2.61(0.7)	138.36	2.5	1.85	.012937	-175.59	-38.73	Commonly formed at room temperature and from Lansfordite
Pokrovskite	$Mg_2(CO_3)(OH)_2\cdot 0.5(H_2O)$	2.6(1), 2.17(0.9), 6.1(0.7),	151.64	3	2.51				Alteration product

Carbonates and Hydrated Carbonates

Mineral	**Formula**	**XRD**	**Molecular Weight**	**Hardness**	**Density**	**Solubility (Ml^{-1}, cold water)**	**ΔH^o reaction from hydroxide (kJ.mol^{-1})**	**ΔG^o reaction from hydroxide (kJ.mol^{-1})**	**Comment**
Vaterite	$CaCO_3$	2.73(1), 3.3(1), 3.58(1)	100.09	3	2.54			-61.33	Polymorph of calcite and aragonite
Calcite	$CaCO_3$	3.035(1), 2.095(0.18), 2.285(0.18),	100.09	3	2.71	.0001399	-69.58	-64.63	Polymorph of vaterite and aragonite
Aragonite	$CaCO_3$	3.396(1), 1.977(0.65), 3.273(0.52),	100.09	3.5-4	2.93	.00015			Polymorph of vaterite and calcite
Ikaite	$CaCO_3.6H_2O$	5.17(1), 2.64(0.9), 2.63(0.7),2.8(0.5), 2.46(0.3), 2.61(0.3), 4.16(0.3), 5.85(0.3), 4.16(0.3),	208.18		1.78				Forms in cold saline marine waters
Monohydrocalcite	$CaCO_3.H_2O$	4.33(1), 3.08(0.8), 1.931(0.6),2.17(0.6), 2.83(0.5), 2.38(0.4), 2.28(0.4), 1.945(0.3),	118.10	2-3	2.38				
Magnesite	$MgCO_3$	2.742(1), 2.102(0.45), 1.7(0.35)	84.31	4	3.009	.001257		-19.55	The most stable form but difficult to make.
Amorphous	$MgCO_3,nH_2O$	Amorphous							Exists in nature and the lab
Magnesium carbonate monohydrate	$MgCO_3 \cdot H_2O$								Does not exist in nature
Barringtonite	$MgCO_3 \cdot 2(H_2O)$	2.936(1), 3.093(1), 8.682(1)	120.34		2.83				Rare form
Lansfordite	$MgCO_3 \cdot 5(H_2O)$	3.85(1), 4.16(1), 5.8(0.8)	174.39	2.5	1.73	.01009			Commonly forms at room temperature

Mixed Carbonates and Hydrated Carbonates of Calcium and Magnesium

Mineral	**Formula**	**XRD**	**Molecular Weight**	**Hardness**	**Density**	**Solubility (Ml^{-1}, cold water)**	**ΔH^o reaction from hydroxide (kJ.mol^{-1})**	**ΔG^o reaction from hydroxide (kJ.mol^{-1})**	**Comment**
Dolomite	CaMg(CO3)2	2.883(1), 1.785(0.6), 2.191(0.5)	184.4	3.5-4	2.84	insoluble			Massive.
Huntite	CaMg3(CO3)4	2.833(1), 1.972(0.3), 2.888(0.2)	353.03	1-2	2.696	Rel. insoluble			Rare
Sergeevite	Ca2Mg11(CO3)9(HCO3)4(OH)4·6(H2O)	2.82(1), 1.965(0.3), 2.87(0.3),3.58(0.3), 7.14(0.3), 1.755(0.2), 3.37(0.2), 2.68(0.1)	1,307.78	3.5	2.27	insoluble			Very rare

Source thermodynamic data for calculation ΔH^o and ΔG^o and reaction from hydroxide: Robie, Richard A., Hemingway, Bruce S., and Fisher, James R. *Thermodynamic Properties of Minerals & Related Substances at 298.15K and 1 Bar (105 Pascals) Pressure and at Higher Temperatures.* U.S. Geological Survey Bulletin 1452. Washington: United States Government Printing Office, 1978.

Source Solubility Data: Data extracted from CRC Handbook of Chemistry and Physics, 74th Edition, 1993-1994 and from Chemistry Web Server at California State University at http://155.135.31.26/oliver/chemdata/data-ksp.htm valid 01/11/2003

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