TecEco Cement Concretes – Abatement, Sequestration and Waste Utilization in the Built Environment.

A John W Harrison, B.Sc. B.Ec. FCPA.
TecEco Pty. Ltd., Hobart, Tasmania, Australia

John Harrison has degrees in science and economics and is a qualified accountant. He is the managing director and chairman of TecEco Pty. Ltd. and is known around the world for the invention of tec, eco and enviro-cements. He is an authority on sustainable materials for the built environment, has been a speaker at many conferences and is committed to finding ways of “materially” improving the sustainability of the built environment.

Abstract

Around 26 billion tonnes of CO2 are released to the atmosphere annually, around 20 billion metric tonnes of which is from the burning of fossil fuels and close to a significant 2 billion tonnes from the production of Portland cement.

Over two tonnes of concrete are produced per person on the planet per annum, representing an enormous opportunity to not only reduce net emissions but to utilize solid wastes for their physical property rather than chemical composition in cementitious composites with improved properties.

Tec-cements reduce emissions because the same strength concretes are achievable with around 25-30% less cement than if ordinary Portland cements are used whereas eco-cements gain strength by sequestering carbon from the atmosphere in porous materials.

This paper discusses the potential impact on sustainability of the new tec and eco-cement technologies for sustainability

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), 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, recycle, recycling,.

Introduction

Tec-cements contain around 5-15% added reactive magnesia and usually a pozzolan. Eco-cements contain more magnesia and rely on carbonation for strength in more porous materials.

Eco-cements became known to the world mainly through an article on them in New Scientist Magazine (Pearce 2002) and a program shown by Discovery Channel (Gilbert 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, CO2 sequestration by eco-cement concretes on a massive scale.

The built environment probably accounts for around 70% of all materials flows. Current cement production of around two billion tonnes per annum results in concrete which comprises around 30% of these flows and is enough to make over two tonnes of concrete per person on the planet per annum (USGS 2004). The possibility of sequestering carbon dioxide and including other in this huge material flow must be considered seriously.

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

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 global scale a holistic approach to the problem is essential. Not only must we reduce output of carbon dioxide and thus consumption of fossils fuels but we should sequester at least 12-13 billion tonnes of CO_2 per annum at least until the level of carbon dioxide in the atmosphere is reduced to more acceptable levels. 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 and loose trading opportunities. Using TecEco technology emissions reduction is clear and definable and there are significant business opportunities to sequester carbon and convert waste to resource in the built environment.

The Whole Process

If we want to save ourselves from ultimate extinction we must find ways of reducing our impact on the planet. We can learn from nature and sequester massive amounts of carbon dioxide as that is what happened in previous epochs of global warming. To power processes that rectify global molecular imbalance such as the excess of CO_2 it is essential we use solar or solar derived energy which is abundant but more difficult to harness. The entire TecEco process starts with magnesite or forsterite, provides a method of scrubbing CO_2 from processes such as burning coal that produce large amounts, produces magnesite and then using a calcinations/re-scrubbing cycle removes more CO_2 from the air producing bottled CO_2 for geological sequestration and magnesia used for the production of TecEco cements.

For the purposes of this paper I will focus on just the cements and concretes made with them as most relevant to the built environment. Information on the total process is available on the TecEco web site at www.tececo.com.

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 which 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.

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 and other silicification reactions. More wastes can be included mainly because of the lower long term pH and drier internal environment as significant amounts of water are converted to solid during the hydration of magnesia to form brucite.

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, lower solubility of Brucite compared to Portlandite and drier conditions the hydration of magnesia having consumed much of the water.

In the presence of carbon dioxide and moisture inside an eco-cement block or mortar that is sufficiently 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 of lansfordite whereby nesquehonite and eventually magnesite may be formed. Significantly, both magnesium and calcium appear to carbonate more readily in porous concretes made using TecEco eco-cements containing magnesia than 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 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.

Converting Waste to Resource

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 drier internal conditions and lower long term pH prevent internal delayed destructive reactions from occurring.

The current technical paradigm for recycling 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.

TecEco cements are benign low long term pH binders that can utilize wastes more on their class of property rather than chemical composition, and therefore reduce sorting problems and costs associated with recycling and provide an inherently more economic process.

In the above manner TecEco cements change the technology paradigm redefining wastes as resources (Pilzer 1990).

Abatement

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 or more rapid strength development whilst eco-cements set by absorbing carbon dioxide from the air. This strength development has been demonstrated in several studies now including the manufacture of tec-cement blocks in Australia. Combined with TecEco kiln technology which combines calcining and grinding in a closed system whereby CO_2 can be captured there are very significant abatement opportunities.

With formulations such as eco-cements, carbonation is encouraged by the porous nature of these products. After hydration environments with a high relative humidity and wet - dry atmosphere seems best to accelerate the process.

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.

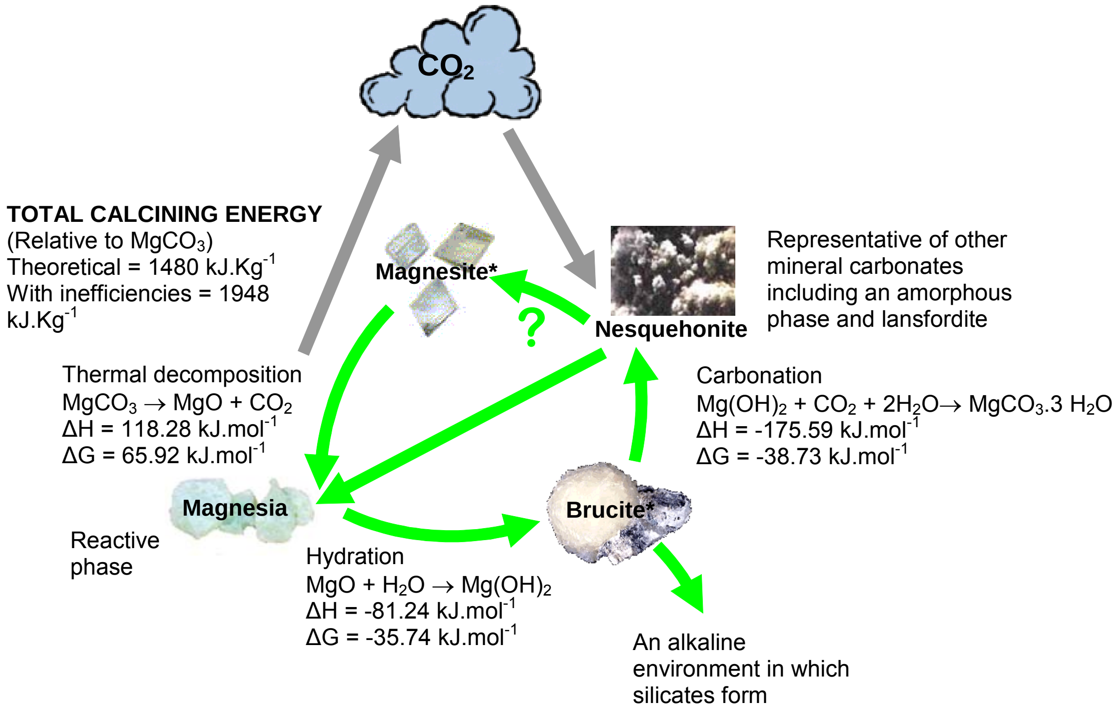


Figure 1 - The Magnesium Thermodynamic Cycle

The more important carbonates of calcium and magnesium are listed in Appendix 1 – Calcium and Magnesium Carbonates on page 12

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. Wet dry cycles appear to promote carbonation providing alternatively transport and reaction media. Well graded aggregates including a coarse fraction are essential as they are for lime mortars. Recent work by the author has demonstrated that most commercial sands specified by standards in Australia the US and Europe 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.

Fortunately block formulations are naturally porous and allow for carbonation and XRD studies in Australia using blocks that have been allowed to carbonate both before and after HCL extraction prove complete carbonation occurs within under two years.

The observed products of carbonation in eco-cement blocks are calcite, possibly vaterite, lansfordite and nesquehonite and an amorphous Mg phase 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 brucite with a solubility of .000154 g L^{-1} ($K_{sp} = 1.8 \times 10^{-11}$) which is virtually insoluble. (See Appendix 1 – Calcium and Magnesium Carbonates on page 12).

Figure 2 - John Harrison holding a 1001 fly ash bottom ash block bonded with eco-cement.

The most obvious products that could be used in the built environment are masonry blocks which are usually made hollow and due to the manufacturing process, porous.

The presence of air voids clearly speeds up carbonation. The maximum depth of concrete 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.

Figure 3 - Eco-Cement Blocks

Figure 4 - Laying Eco-Cement Blocks

Another product TecEco have been experimenting with is porous pavement which is a permeable pavement surface with a stone reservoir underneath. The reservoir temporarily stores surface runoff before infiltrating it into the subsoil or sub-surface drainage and in the process improves the water quality. Porous pavement is made without "fine" materials out of either no fines concrete or under asphalted gravel.

Porous pavements allow the earth under cities to breathe, take in water and be healthy. The stone and soil under them acts as a reservoir and cleans the water a little like the filter on a fish tank. They are safer to drive on as they do not develop "puddles", have a good surface to grip and importantly, in Australia, some parts of the US and many other places in the world subdivisions made with porous pavement that also have street trees can be several degrees cooler than surrounding suburbs without.

There are many other good reasons why councils and road authorities should switch to porous pavement and more information is available in TecEco newsletters 29 and 35. A good website about managing stormwater using porous pavement is to be found at http://www.greenworks.tv/stormwater/porouspavement.htm.

TecEco eco-cements will set in porous pavement and with their use several environmental issues would be addressed at once including water quality, replenishment of aquifers, "hot city syndrome" atmospheric carbon reduction and waste.

Figure 5 - A Porous pavement Experiment in Tasmania

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 blocks and further work will try and improve the kinetics.

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 commented on by Deelman (Deelman 2003) which did not show up on XRD. There is also Raman spectroscopic evidence of this amorphous phase.

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 6 and are clear evidence that the binder in eco-cements is a mixture of calcite, lansfordite and nesquehonite.

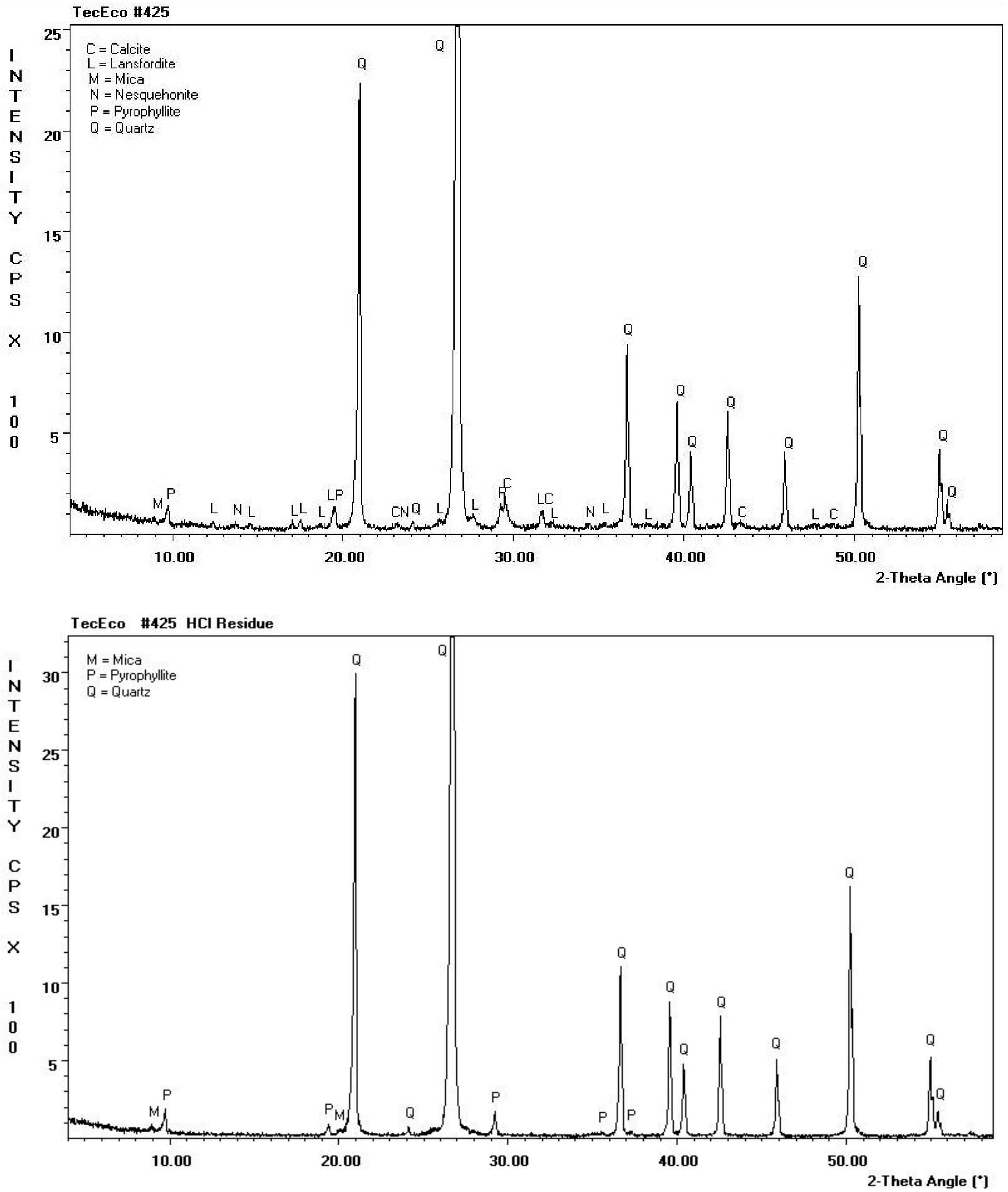


Figure 6 - XRD Showing Carbonates Before and Minerals Remaining after their Removal with HCl in a Simple Mix (70 Kg PC, 70 Kg MgO, colouring oxide .5Kg, sand unwashed 1105 Kg)

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

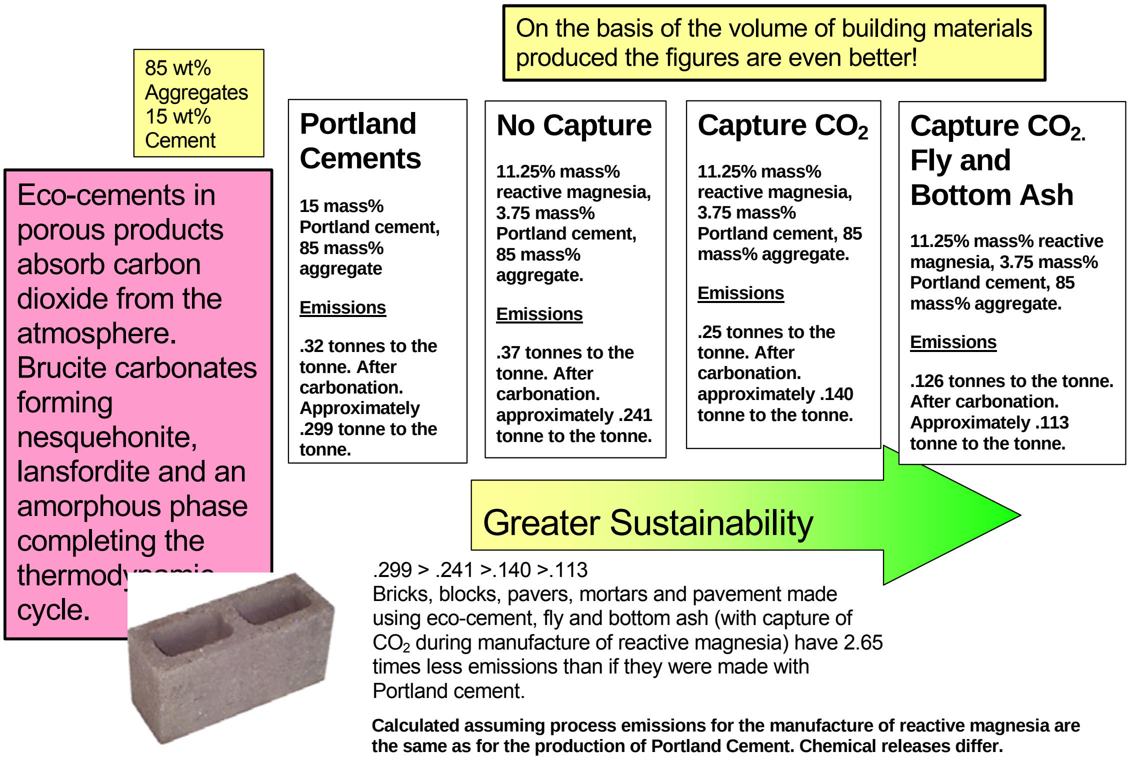
The amount of CO_2 concretes absorb is dependent on a number of factors.

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 blocks 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 blocks 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 concrete blocks 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 7 - The Carbonation of a Typical Eco-Cement Block on page 8.



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

85 wt% Aggregates
15 wt% Cement

Eco-cements in porous products absorb carbon dioxide from the atmosphere. Brucite carbonates forming nesquehonite, lansfordite and an amorphous phase completing the thermodynamic cycle.

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.

Calculated assuming process emissions for the manufacture of reactive magnesia are the same as for the production of Portland Cement. Chemical releases differ.

Figure 7 - The Carbonation of a Typical Eco-Cement Block

The calculations do not take into account the use of sustainable energy to produce eco-cements 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. As mentioned 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.

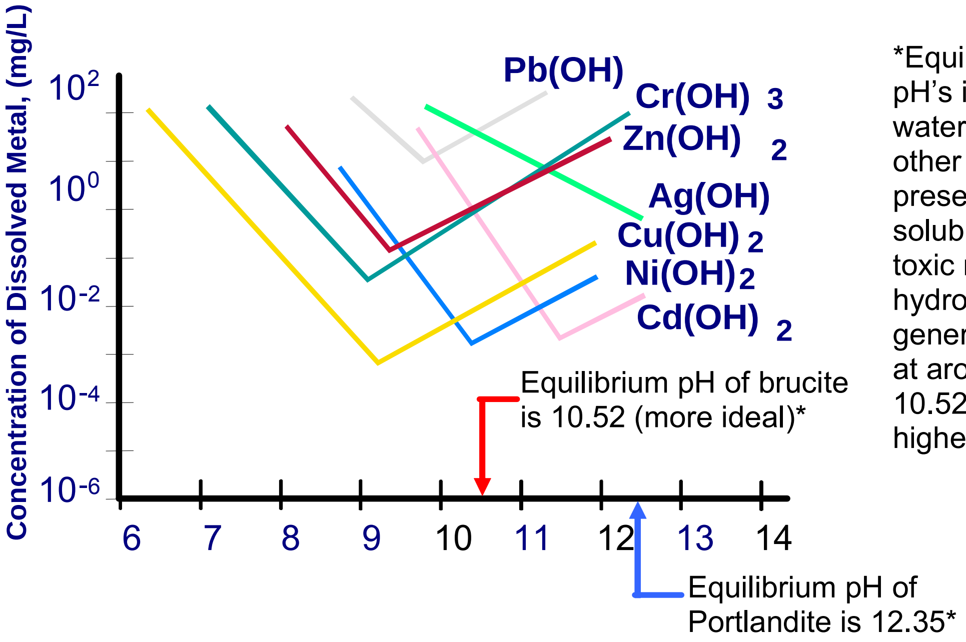
Many wastes such as fly ash, sawdust, shredded plastics etc. can improve a property or properties of the cementitious composite based on their physical property rather than chemical composition. If their chemical compositions includes carbon – even better!

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
- Internally drier

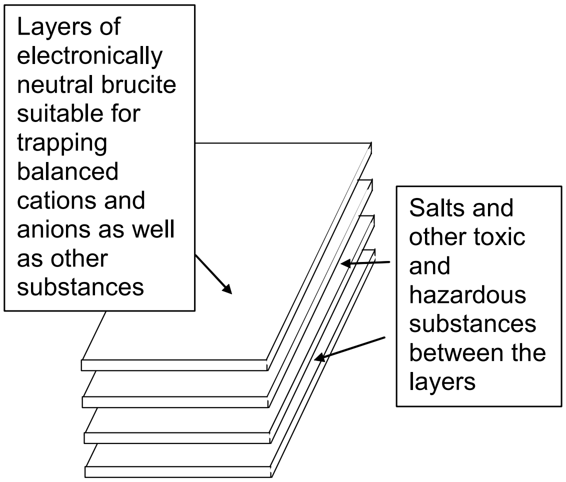
If large quantities of waste are going to be used to create building materials for the built environment it is essential to have a strategy in place for toxic and hazardous wastes which often end up contaminating more benign waste streams.



*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 8 – The Low pH regime of TecEco cements Minimises the Solubility of Heavy Metals

Immobilisation Strategy



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. There is a 10^4 advantage in the minimum solubility of most heavy metal hydroxides in the pH range governed by brucite compared to the pH range governed by Portlandite.

Figure 9 - 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 also 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

References

Beaudoin, J. J., V. S. Ramachandran, et al. (1977). American Ceramic Society Bulletin **56**: 424.

Deelman, J. C. (2003). Low-Temperature Formation of Dolomite and Magnesite, Compact Disc Publications, Geology Series.

Gilbert, J. (2003). Carbonating Eco-Cements, The Daily Planet.

Haughton, R. (2004). Understanding the Global Carbon Cycle, Woods Hole Institute.

Pearce, F. (2002). "Green Foundations." New Scientist **175**(2351): 39-40.

Pilzer, P. Z. (1990). Unlimited Wealth - The Theory and Practice of Economic Alchemy, Crown Publishers.

Taylor, H. F. W. (1990). The Environment, Cement and the Future. Conference on Advances in Cementitious Materials, Gaithersburg, Maryland, USA, The American Ceramic Society Inc.

USGS (2004). "Mineral Commodity Summary - Cement." (2004).