TECECO CEMENTS – Carbonation = Sequestration – Waste Utilization = Resource.

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 and enormous opportunity to not only do a lot about global warming but to also utilize solid wastes 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.

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 and a program shown by Discovery Channel (Pearce 2002). There have been several reasons for the intense interest – the potential lower embodied energy, the ability of the material to benignly encapsulate a wide range of wastes and the potential for reduced emissions (tec-cements) and CO_2 sequestration on a massive scale (eco-cements). 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 around 6 billion tonnes of CO_2 per annum. As we are unlikely to kick the fossil fuel habit until it kicks us 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. What better way to sequester carbon than in our own built environment? TecEco cements mimic nature by sequestering large amounts of carbon dioxide or reducing output of the gas with the added benefit of utilising wastes.

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.

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

Reducing Net Emissions and Utilizing Wastes

“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.”

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-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 utilised. The shear thinning properties tend to prevent segregation of materials like plastics which is a problem with Portland cements and the lower pH prevent internal reactions from occuring.

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

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%.

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.

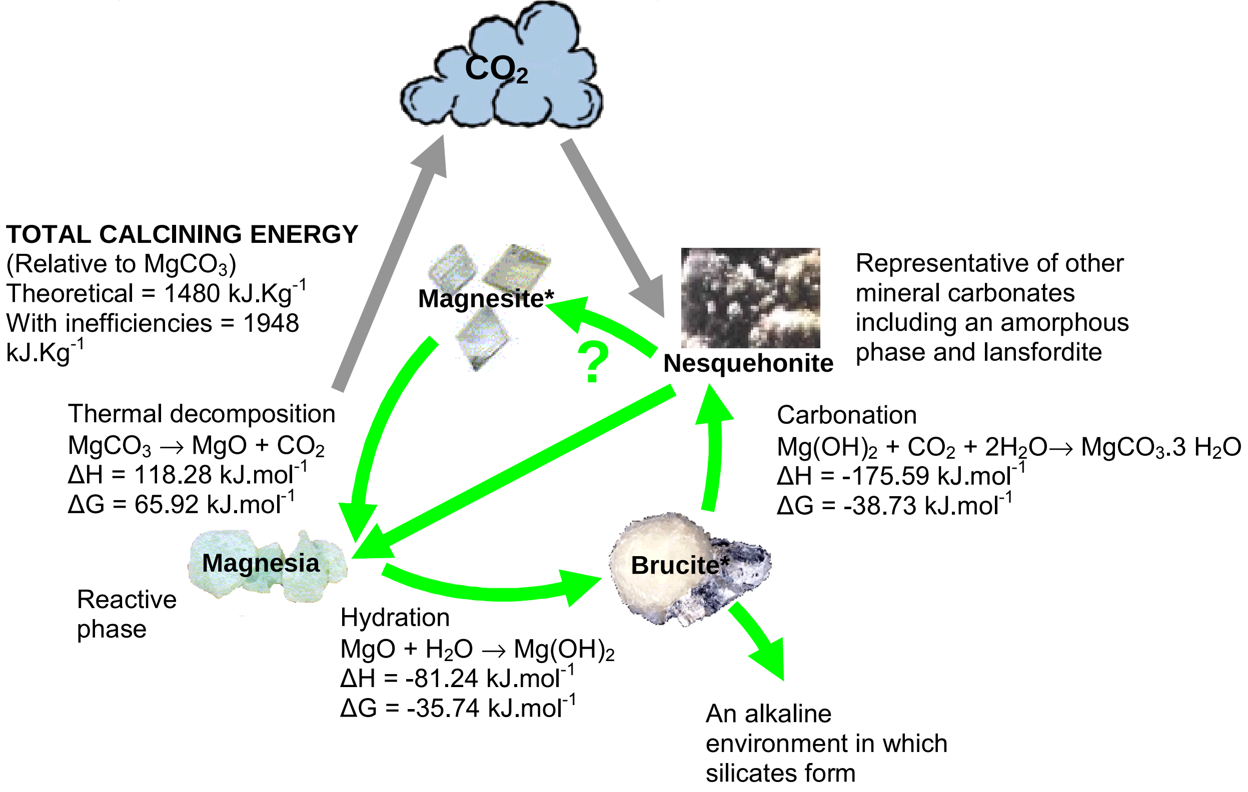

Figure 1 - The Magnesium Thermodynamic Cycle

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 but is in reality more complex.

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.

The more important carbonates of calcium and magnesium are listed in Appendix 1 – Calcium and Magnesium Carbonates on page 13

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.

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. 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 J. J. 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 13).

Carbonation starts at the surface 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.

Reactive magnesia fly ash eco-cements carbonate more rapidly than similar formulations with just Portland cement. Portland eco-cements carbonate better than Sorel cements. In all cases, carbonation occurs rapidly only in porous dry mix materials.

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.

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 + 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) → 74.77 + (l) molar volumes[1]

Significant expansion.

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

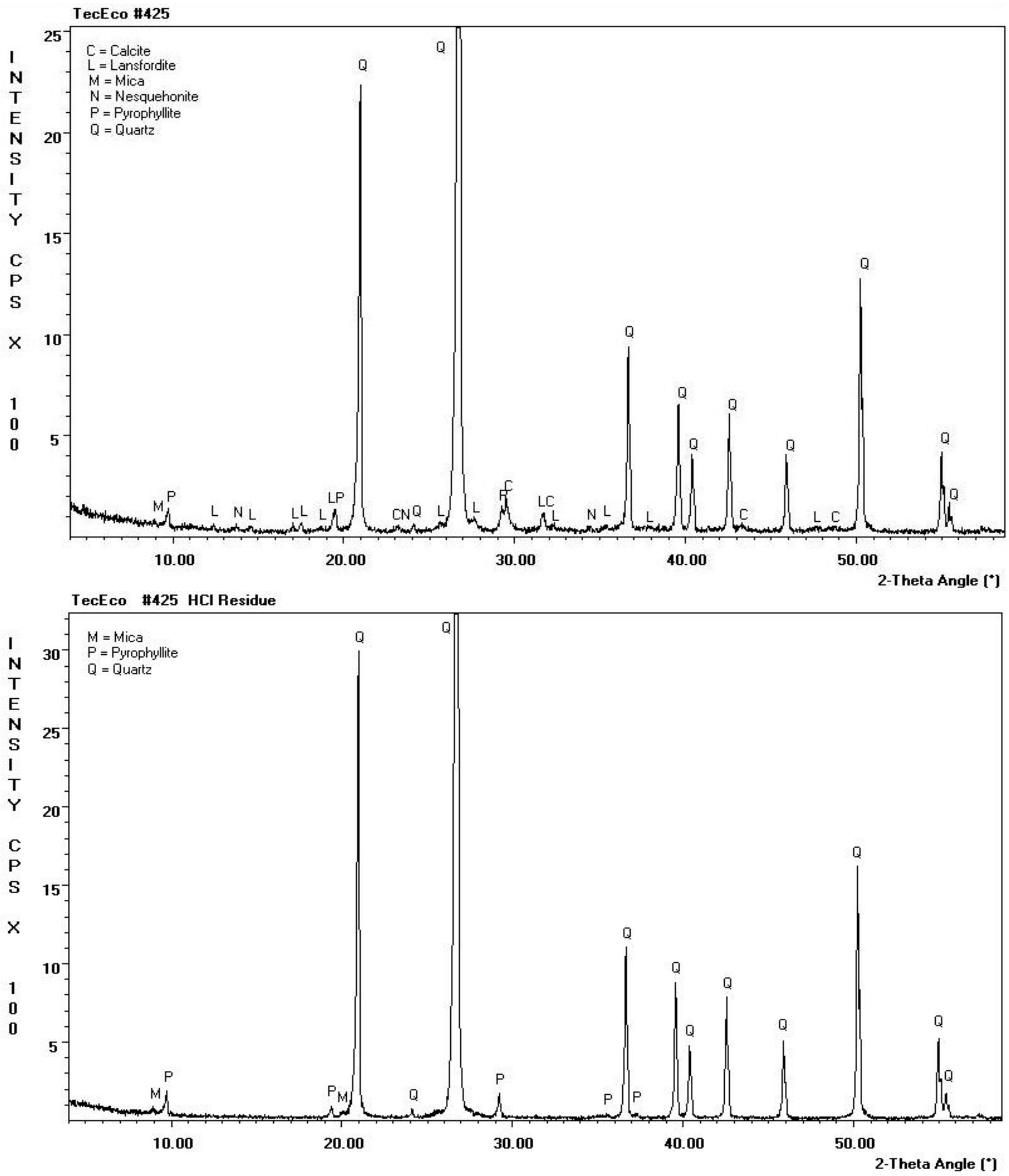

Figure 2 - XRD Showing Carbonates Before and Minerals Remaining after their Removal with HCl in a Simple Mix (70 Kg PC, 70 Kg MgO, colouring oxide .5Kg, sand unwashed 1105 Kg)

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

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

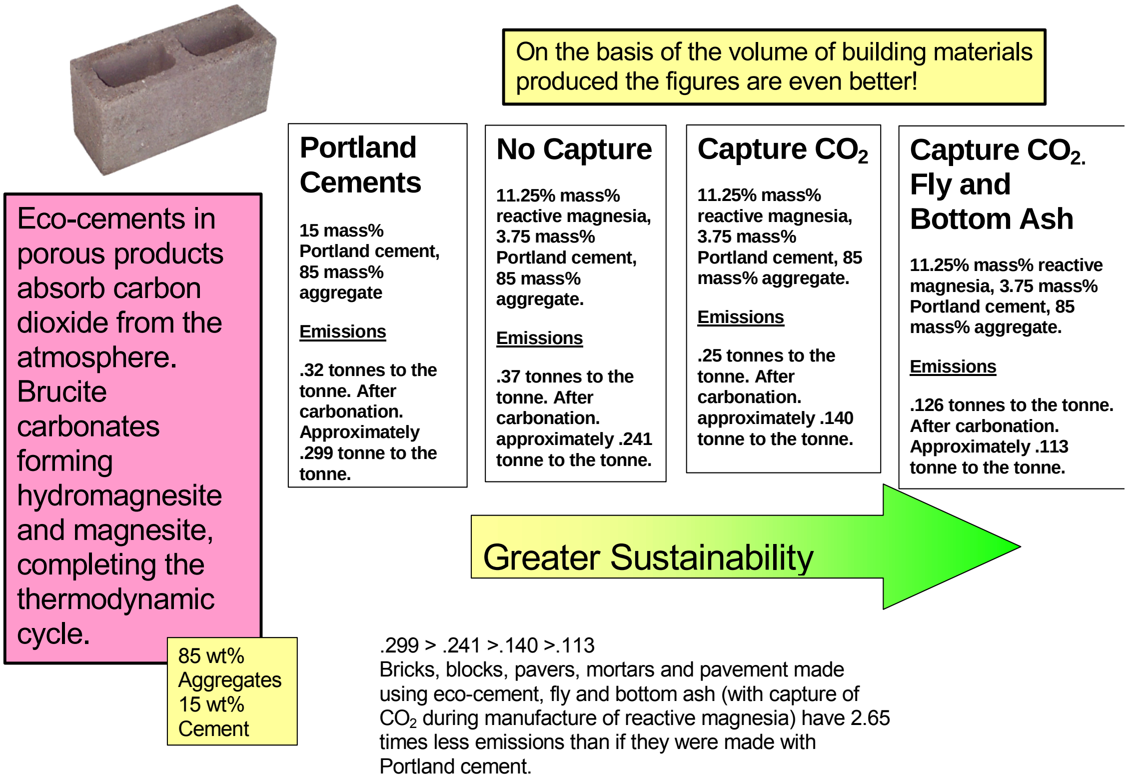
The amount of CO_2 concretes absorb is dependent on a number of factors.

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 is 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 10.



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.

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.

Waste Utilization

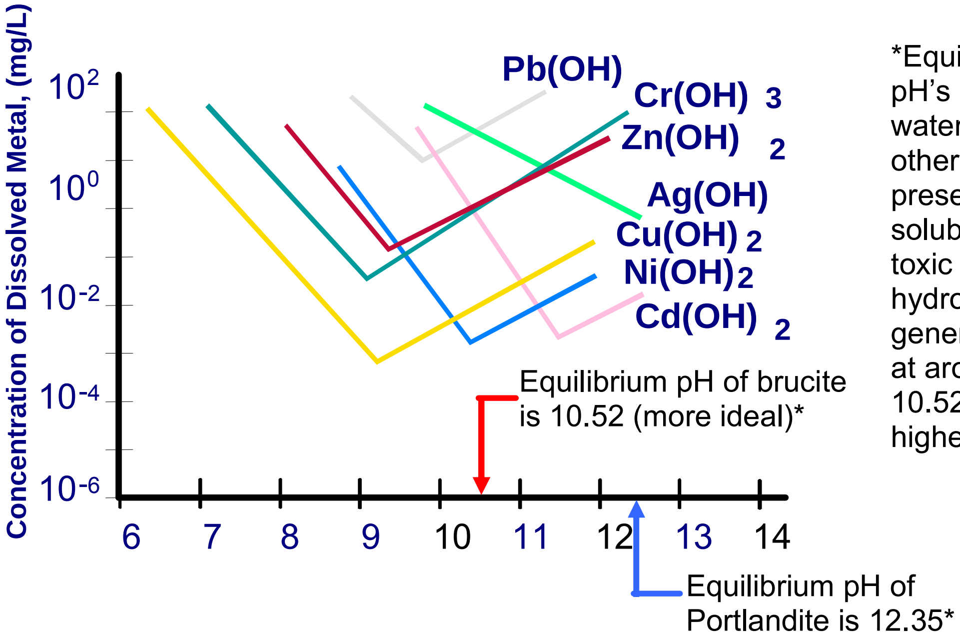
Apart from global warming, the other biggest problem on the planet today is the disposal of waste. The answer is to convert waste to resource and TecEco have developed cementitious composites that provide a benign environment suitable for waste immobilization.

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 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



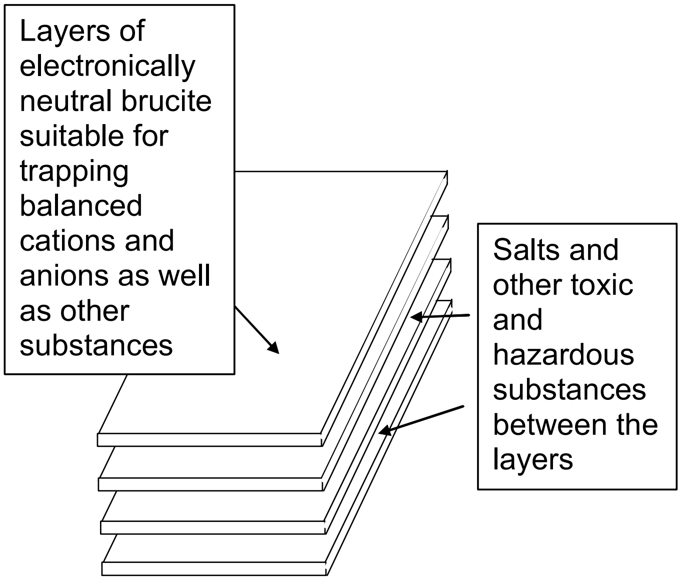
Equilibrium pH of brucite is 10.52 (more ideal)*

Equilibrium pH of Portlandite is 12.35*

*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. 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.

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 uses carbon dioxide and wastes.

As stated by Fred Pearce in the article on eco-cements that was published in the New Scientist “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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