TECECO ECO-CEMENT MASONRY PRODUCT UPDATE – Carbonation = Sequestration

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Abstract

As a consequence of global warming there is considerable interest around the world in exploiting major natural carbon sinks such as the oceans, subsurface reservoirs (such as brines or depleted oil & gas fields), or the terrestrial carbon sink to sequester carbon dioxide on a large scale.

The author is the inventor of eco-cements which, given the huge size of the built environment, represent a novel new method of sequestering large amounts of CO_2 as calcium and magnesium carbonates in bricks, blocks, pavers, mortars and other construction materials as well as a potential method of lowering embodied energies and reducing wastes.

This article goes into the as yet unclear chemistry of carbonation processes in eco-cements and corrects previous incorrect assumptions made by the author about the magnesium carbonates formed when eco-cements carbonate.

Keywords

built environment, brucite, construction, masonry units. bricks, blocks, pavers, magnesia, economic, sequestration, sustainable, sustainability, co2, concrete, waste, embodied energy, eco-cement, kyoto, magnesium carbonates, nesquehonite, lansfordite.

Introduction

Eco-cements became known to the world mainly through an article on them in New Scientists Magazine (Pearce, F., 2002) and a program shown by Discovery Channel (Gilbert, J., 2003) Since then global publicity has been huge and the most recent was a win by John Harrison in the ABC inventors program in Australia. This intense interest has been for several reasons – the potential lower embodied energy, the ability of the material to benignly encapsulate a wide range of wastes and the potential for CO_2 sequestration on a massive scale. The ability of eco-cements to utilise wastes and reabsorb carbon dioxide is the subject matter for this paper.

The built environment is our footprint on the globe and probably accounts for around 70% of all materials flows. Current cement production is over two billion tonnes per annum which is used to make 14 billion tonnes or over two tonnes of concrete per person on the planet per annum, putting concrete at around 30% of all materials flows.

According to the Woods Hole Institute global carbon dioxide flows in billions of tonnes CO2 are (Haughton, R., 2004):

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 more than 6 billion tonnes of CO_2 per annum and preferably more than 12 billion tonnes 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 eventually probably face sanctions. What better way to sequester carbon than by using TecEco eco-cement concretes in bricks, blocks, pavers, mortars and renders in our own built environment?

Both calcium and magnesium minerals in eco-cements appear to carbonate readily and to date concrete blocks and mortars in combination with a wide range of wastes have successfully been experimented with and tested to compliance with AS/NZS 4456.4, an Australian Standard for the strength of masonry units.

With the inclusion of carbon containing organic wastes such as sawdust, shredded waste plastic etc. there is an opportunity to not only sequester carbon and utilise waste but create masonry units with other new and desirable properties such as lighter weight and high R factor.

When reactive magnesia is substituted for PC 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. There are several reasons for this. Principal amongst them are the fineness of the reactive magnesia which affects particle packing and lubrication and the surface charge.

What happens inside an eco-cement block or mortar to give it durability and strength is even more fascinating. Brucite ($Mg(OH)_2$ is the stable phase in the system MgO-SiO_2-H_2O over a wide range of temperatures and pressures. In the presence of CO_2 brucite carbonates forming hydrated magnesium carbonates such as nesquehonite and lansfordite 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. 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 hydration 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 bricks, blocks pavers and mortars and is encouraged for this and sequestration reasons.

Masonry Products as a Focus for Sustainability and Utilizing Wastes

The built environment is the obvious place to focus sustainability efforts and masonry is still a major component. More than 50% of the population of the planet is housed in mud bricks or within mud walls. If clay bricks and concrete blocks are included the figure is probably well over 80%.

The dominant proportion of what we take, manipulate and make that we do not consume immediately goes into the materials with which we build the built environment. “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, W. E., 1999).

“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.” Choices of materials and design principles have a significant impact on the energy required to construct a building. However, the energy content of materials has been little considered in design until recently, despite such impacts being recognized for over 20 years.

Making Sustainability Economic

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 reuse or recycle, but the process resulted in superior properties.

The problem is the costs involved in re-using and recycling. Sorting waste streams and then transporting sorted recyclable materials back to a location in which they can be 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, P. Z., 1990). TecEco cements are benign 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.

TecEco cements also contribute to properties for example TecEco eco-cement mud bricks tested to date have resulted in a 50% improvement in strength which is significant.

As cultural shift is also shaping the demand side or market economics it follows that there is a huge opportunity to make money by providing more sustainable product.

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

Eco-cements first became 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.

The carbonation of Portlandite (free lime) in the presence of water is as below.

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

The steps of the reaction are first the dissolution of calcium hydroxide followed by reaction with dissolved carbon dioxide.

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

$$Ca^{2+} + 2OH^- + CO_2 \rightarrow CaCO_3 + H_2O$$

The mineralogical forms of calcium carbonate are vaterite, aragonite and calcite, and their precipitate follows Ostwald's rule of successive transformations in that order (Cole, W. and Kroone, B., 1960).

Magnesia is made from magnesite. In porous eco-cement concretes it first hydrates forming brucite and this then carbonates forming hydrated magnesium carbonates to lansfordite and nesquehonite. There is probably also an amorphous form that slowly changes to nesquehonite, A simplified thermodynamic cycle is depicted in Figure 1 but is in reality more complex.

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

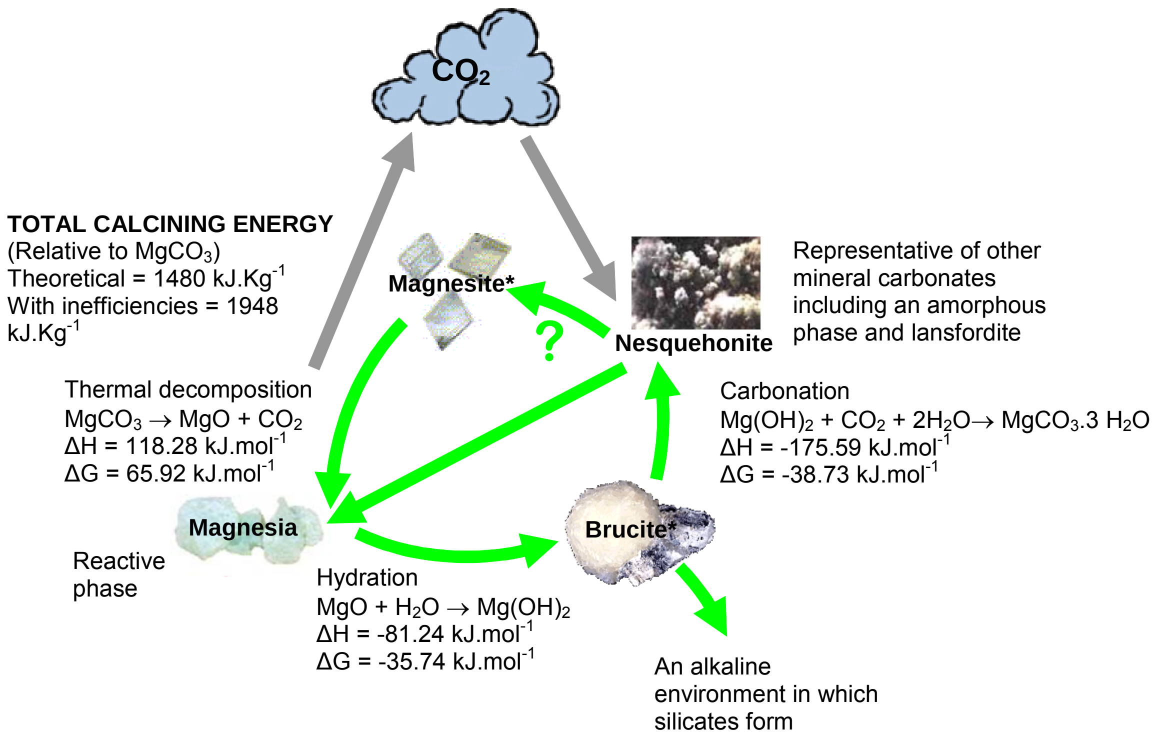


Figure 1 - The Magnesium Thermodynamic Cycle

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 originally predicted on the basis of my oversimplified thermodynamic calculations.

The rate for the 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 and setting atmospheric conditions. Wet dry cycles appear to promote carbonation providing alternatively transport and reaction media. Ideal carbonation conditions are still being considered, presently 50 – 70% relative humidity and exposure although wet dry is thought to work best.

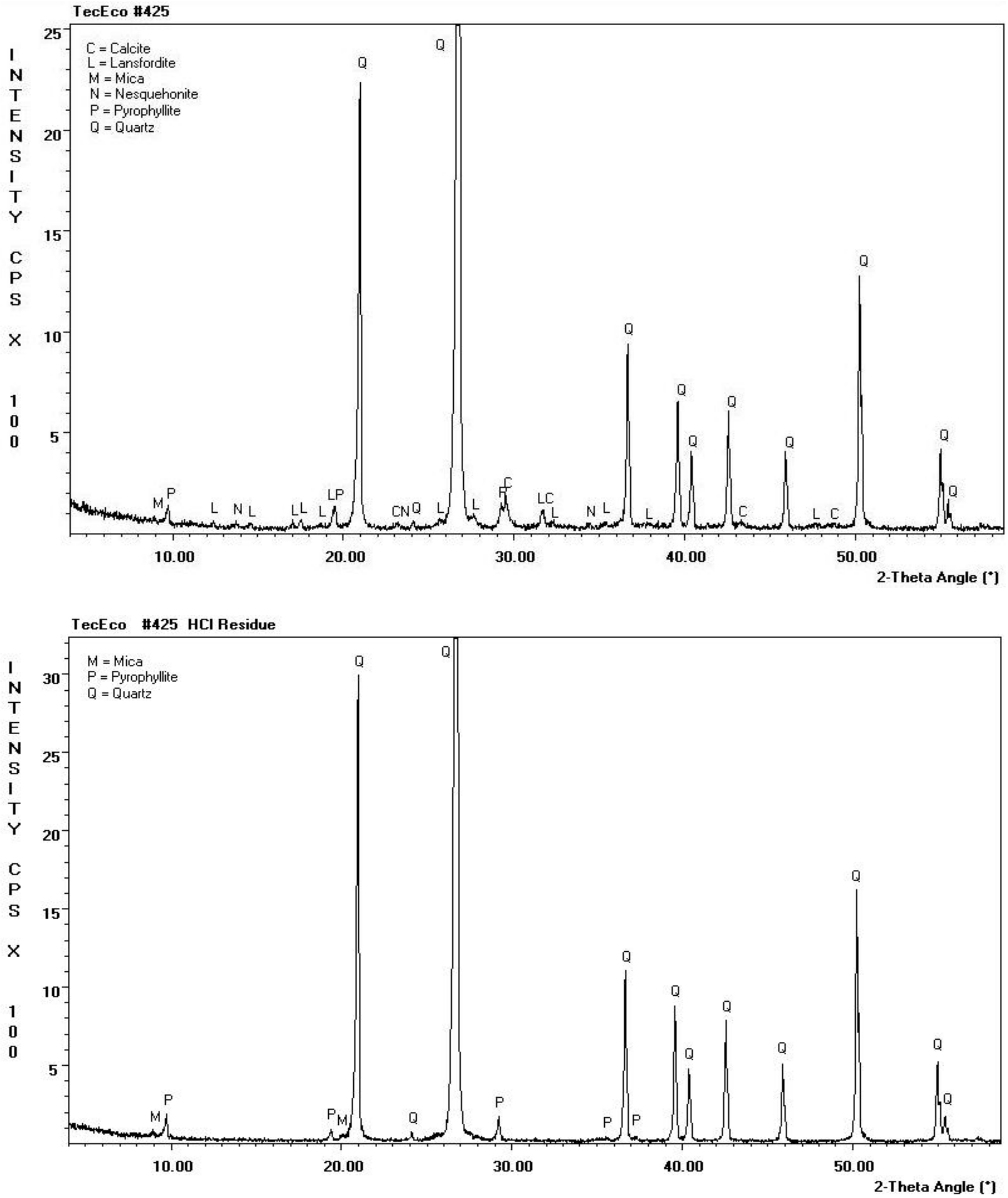


Figure 2 - XRD Showing Carbonates Before and Minerals Remaining after their Removal with HCl in a Simple Mix (70 Kg PC, 70 Kg MgO, colouring oxide .5Kg, sand unwashed 1105 Kg)

All the calcium and magnesium carbonation products have strength giving properties. 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 the 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., Ramachandran, V. S. et al., 1977).

Lansfordite and nesquehonite are more soluble than magnesite and hydromagnesite which are realtively 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} ($K_{sp} = 1.8 \times 10^{-11}$) which is virtually insoluble. (See Appendix 1 – Calcium and Magnesium Carbonates). The solubility of magnesium carbonates in mild acids seems to be generally lower.

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.

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. If a porous aggregate such as bottom ash, scoria or pumice is also added an even higher 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 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, W. F. and Demediuk, 1955) tend to remain as unstable oxy compounds, but do eventually carbonate.

Thermodynamics

In multi-component alkaline concretes there is still a lot to learn, and the reader should be aware that the thermodynamic and equilibrium calculations 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 originally first predicted by the author. This is not the case however and the first minerals formed are an lansfordite and nesquehonite possibly accompanied by an amorphous phase.

The free energy and enthalpy of formation of reactions whereby calcium and magnesium carbonates are formed from their hydroxides has been calculated and are included in Appendix 1 – Calcium and Magnesium Carbonates

Kinetics

According to Langmuir (Langmuir, D., 1971) thermodynamics make it clear that magnesite must be considered more stable than nesquehonite, which in turn is more stable than magnesium hydroxide carbonate ($MgHCO_3$). The sequence as so far determined however seems to be

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

Defying simple thermodynamics lansfordite and nesquehonite are the first minerals formed and do not readily proceed towards magnesite.

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 ↔ 100 molar mass

33.22 + gas ↔ 36.93 molar volumes

Slight expansion. But shrinkage from surface water loss

Consider the volume changes that occur when magnesia hydrates to Brucite and then carbonates to nesquehonite:

$MgO + H2O \rightarrow Mg(OH)2 + CO_2 + 2H_2O \rightarrow MgCO_{3.}3H_2O$

$11.2 + (l) \rightarrow 24.3 + (g) + (l) \rightarrow 74.77$ molar volumes.

Overall the molar volume expansion (11.2 to 74.77 molar volumes or 568%) is significant.

Portland cement shrinkage is more than compensated for by the expansion on hydration and then carbonation of magnesium oxide. What this also means is that starting with not much magnesia a lot of binder is produced. What is formed is mostly CO_2 and water and this is one of the reasons why eco-cements are potentially able to deliver high value for cost as an inorganic binder.

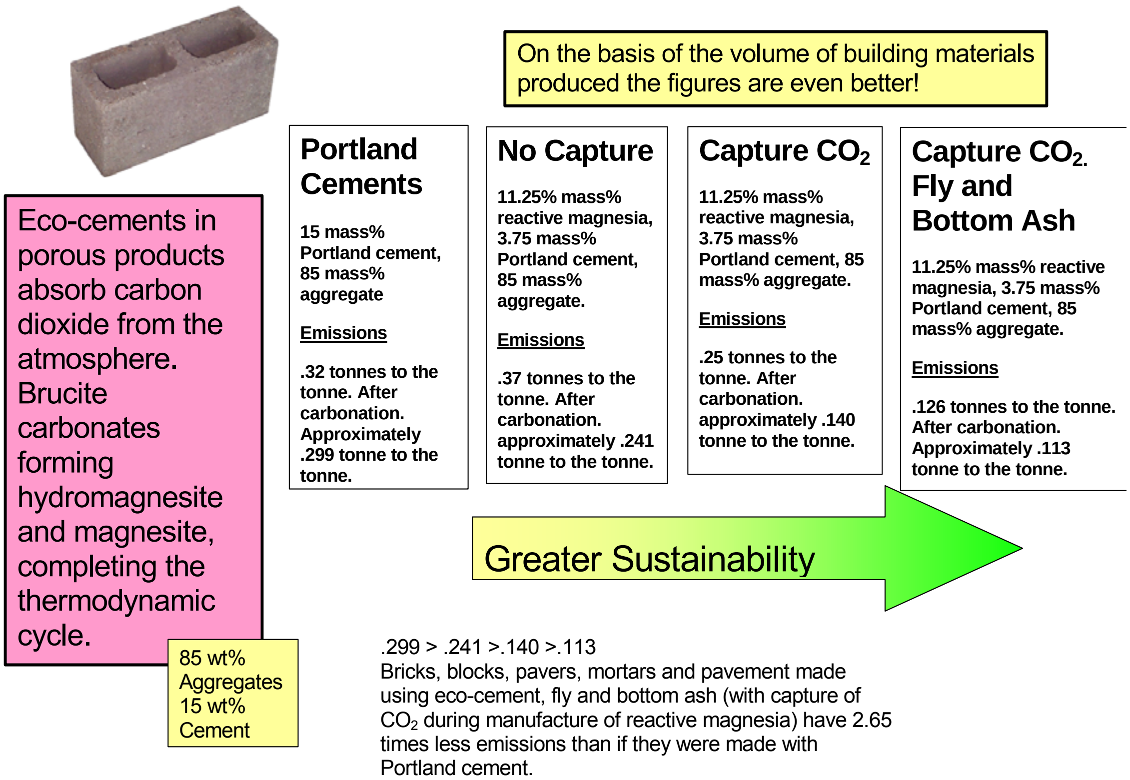
The Extent and Potential of Carbonation in Eco-Cement Concretes

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

Thickness is the 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 will generally absorb CO_2 throughout.

Eco-cements contain a relatively high proportion of reactive magnesia. In masonry products such as mortars and blocks, 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 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 - 60% 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 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.

.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

If eco-cements were adopted for 80% of concrete the potential global sequestration is over two billion tonnes, over the 10% of the global anthropogenic emissions contributed by concrete because of potential cross substitution of more emitting materials. If carbon based materials such as plastic, sawdust and bottom ash are included as aggregates the figure could be higher.

Summary and Conclusion

The built environment represents significant opportunities for sequestration on a massive scale.

The TecEco eco-cement development is the first successful method of using carbon dioxide and wastes to create construction materials such as masonry products.

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.”

There is much still to learn about carbonation processes and the carbonation of magnesium compounds has become an area of international interest because of the need for massive sequestration offered in a practical way by the TecEco eco-cement innovation.

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

Table 1 - 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	$Mg_2CO_3(OH)_2.3 H_2O$	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

Table 2 - 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

Table 3 - 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., Ramachandran, V. S., et al. (1977). "Impregnation of Magnesium Oxychloride Cement with Sulfur." American Ceramic Society Bulletin **56**: 424.

Cole, W. and Kroone, B. (1960). "Carbon dioxide in hydrated Portland cement." American Concrete Institute Journal **31**(12): 1275 - 1295.

Cole, W. F. and Demediuk (1955). "X-Ray, Thermal, and Dehydration Studies on Magnesium Oxychlorides." T Aust. J. Chem **8**: 234.

CSIRO (2001). Human Settlements Theme Report, State of the Environment Australia 2001, Australian Government Department of Environment and Heritage,

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

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

Langmuir, D. (1971). "Geochemistry of some carbonate ground waters in central Pennsylvania." Geochim. Cosmochim. Acta **35**: 1023-1045.

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.

Rees, W. E. (1999). "The Built Environment and Ecosphere: A Global Perspective." Building Research and Information **27**(4/5): 206-220.

UNEP (2001). Energy and Cities: Sustainable Building and Construction Summary of Main Issues, IETC Side Event at UNEP Governing Council, Nairobi, Kenya, UNEP.