The science of TecEco binders is continuously changing. Since this paper was written we have determined that the carbonates formed are an amorphous phase, lansfordite and nesquehonite.

Magnesian Cements – Fundamental for Sustainability in the Built Environment

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The relationship between the biosphere-geosphere (the earth an all natural things in it) and technosphere (our material world) is fundamentally affected by the way we make and use materials as they control how long they remain in the technosphere and their shape and molecular form on exit back to the biosphere-geosphere.

The built environment including buildings and infrastructure accounts for some 70% of all materials flows in the global economy. It is our footprint on earth. As such it represents an enormous opportunity for sustainability.

Of all building materials concrete, routinely made of sand cement and gravels, is the most ubiquitous. Over six cubic kilometres are poured a year[i]. There is tremendous scope to add strength and improve other properties through the addition of other substances including wastes, many of which would add tensile strength, insulating capacity or reduce weight.

Materials such as the new magnesian tec, eco and enviro-cements will have an important role in the development of these new high performance composite materials of the future as they not only absorb carbon dioxide in bricks, blocks, pavers, mortars and porous pavement, but also improve the properties of concrete, allow the incorporation of a wider range of materials including wastes, and solve workability, durability and performance, shrinkage and cracking problems.

Keywords: Abatement, sustainable, sustainability, sequestration, CO_2, brucite ($Mg(OH)_2$), durability, reactive magnesium oxide, materials, 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, permeability, rheology, emissions, flow, matter, substances.

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SUSTAINABILITY IN PERSPECTIVE

Earth System Flows

What distinguishes our planet from any other we have yet discovered is that there exists life, comprising carbon based molecules which have evolved in a delicate balance with the rest of the atoms and molecules that make up earth.

Living matter is different from dead matter in that it contains genetic coding and has the ability to take atoms and molecules from the environment to build new replicates of itself for the future. This delicate balance is characterized by the flow of substances from the dead world to living matter and in reverse and has gone on for billions of years. Since the dawn of mankind and in particular the industrial revolution our ability and willingness to manipulate everything around us has however disturbed the balance of these flows and evidence is mounting of future problems unless we can reduce our impact.

We take atoms and molecules from the dead and living matter around us, manipulate them to our uses and then when finished throw them "away". There is no such place as "away" Many of these transformed atoms and molecules return as part of the flow negatively affecting our wellbeing and that of other living matter on the planet.

Population growth and progress have had wide-ranging impacts on the environment. Atmospheric composition, land cover, marine ecosystems, coastal zones, freshwater systems and global biological diversity have all been substantially affected.

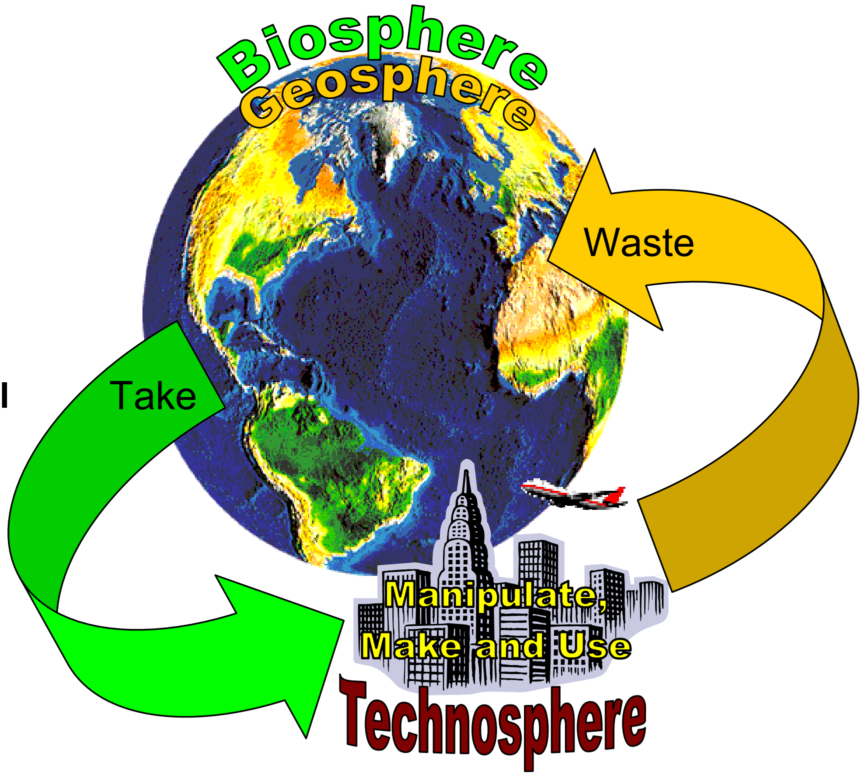


Figure 1 -We take we Manipulate, Make and Use then we Waste.

Out of Balance

According to the recent report "Global Change and the Earth System - A Planet under Pressure" IGBP SCIENCE No. 4[ii] funded largely by the Swedish Government our planet is changing quickly. In recent decades many environmental indicators have moved outside the range in which they have varied for the past half-million years. We are altering our life support system and potentially pushing the planet into a far less hospitable state.

Global population has tripled since 1930 to more than six billion and will continue to grow for several decades, and the global economy has increased more than 15-fold since 1950. This progress has however had wide-ranging impacts on the environment. Atmospheric composition, land cover, marine ecosystems, coastal zones, freshwater systems and global biological diversity have all been substantially affected.

"The world faces significant environmental problems: shortages of clean and accessible freshwater, degradation of terrestrial and aquatic ecosystems, increases in soil erosion, loss of biodiversity, changes in the chemistry of the atmosphere, declines in fisheries, and the possibility of significant changes in climate. These changes are occurring over and above the stresses imposed by the natural variability of a dynamic planet and are intersecting with the effects of past and existing patterns of conflict, poverty, disease, and malnutrition.[ii]"

The Earth is a well-connected system. Carbon dioxide emitted in one country is rapidly mixed throughout the atmosphere, and pollutants released into the ocean in one location are transported to distant parts of the planet. Local and regional emissions create global environmental problems.

Due to our pervading interference molecules are no longer produced or used in equilibrium. Of particular concern is that the carbon cycle is out of balance. Complex carbon based molecules put together by living matter over many millions of years are being used as if there was no tomorrow. The level of carbon dioxide waste from this process is rising too rapidly for conversion by photosynthesis or utilization by organisms for skeletons and shells.

Materials the Key to Sustainability

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 “technosphere”. Buildings and infrastructure probably account 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.[iii]”

“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[iv].”

Materials are the link between the biosphere-geosphere and technosphere. The use of more sustainable materials is fundamental to our survival on the planet. The choice of materials that we use to construct our physical world (the technosphere) ultimately controls emissions, lifetime and embodied energies, maintenance of utility, recyclability and the properties of wastes returned to the biosphere -geosphere.

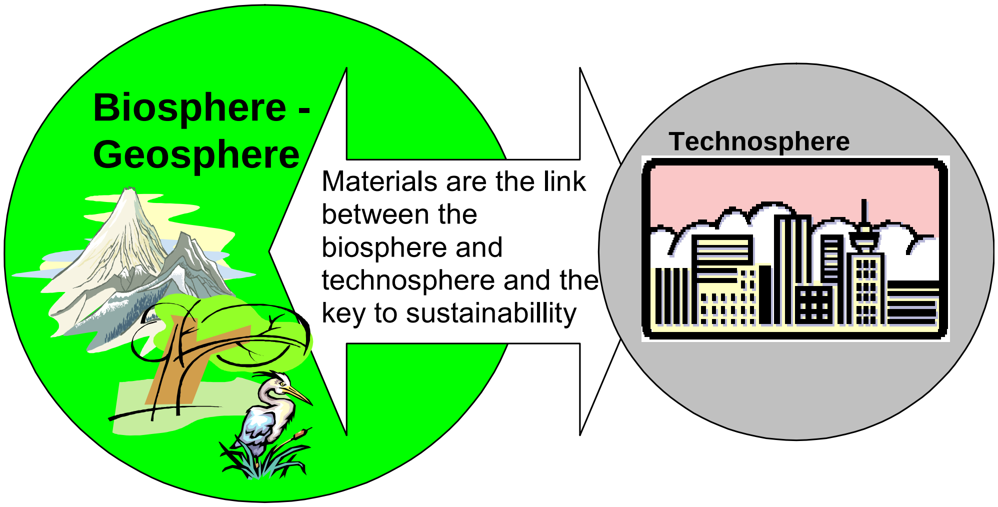


Figure 2 - Materials - The Link between the Biosphere - geosphere and Technosphere

Urbanization has serious negative implications for global sustainability^{v} yet the impact and the associated opportunities for improvement have been given little emphasis (See A direct consequence of such huge usage and growing demand is the associated enormous potential for environmental benefits and improvements in sustainability and the triple bottom line if the material could be improved.

The Role of Governments on page 7)

Given the enormous materials flows involved, the obvious place to improve sustainability is the built environment. Importance factors are embodied and lifetime energies and the properties of materials used. Also important in relation to the wider environment is the composition of materials used which determines the impact of extraction, how they can be reused and their effects on earth systems of wastage.

To reduce the impact of our take-make-break economic system it is therefore fundamental that we think about the materials we use to construct our built environment and the molecules they are made of.

Materials used to construct the built environment should have low embodied energies, low lifetime energies, and low greenhouse gas emissions when considered on a whole of life cycle basis. Many materials such as aluminium and steel have a high embodied energy and are responsible for considerable emissions. Other materials such as some plastics and metals can affect health during use and introduce toxins into the environment when wasted.

The Impact of Concrete

The main material used for buildings and infrastructure is concrete. Concrete is made by utilising a cement to bond stone and sand together. Ordinary Portland Cement (OPC) is the most common cement used and the concrete made with it is an ideal construction material, as it is generally economic, durable, easily handled and readily available.

Contrary to lay understanding Portland cement concretes have low embodied energies compared to other building materials such as aluminium and steel, have relatively high thermal capacity and are therefore relatively environmentally friendly.

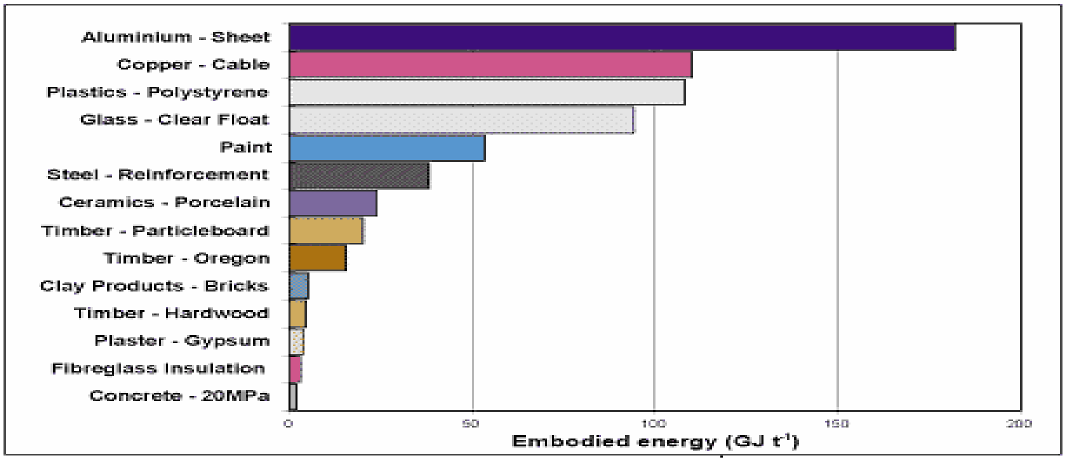


Figure 3 - Embodied Energy of Building Materials[vi]

However "Concrete, based mainly on Portland cement clinker, is the most widely used material on Earth. Current estimates of world cement manufacture are of the order of 1.7 X 10^9 tonnes/yr., enough to produce over 6 cubic km of concrete per year or about one cubic metre per person[vii]" resulting in significant global emissions.

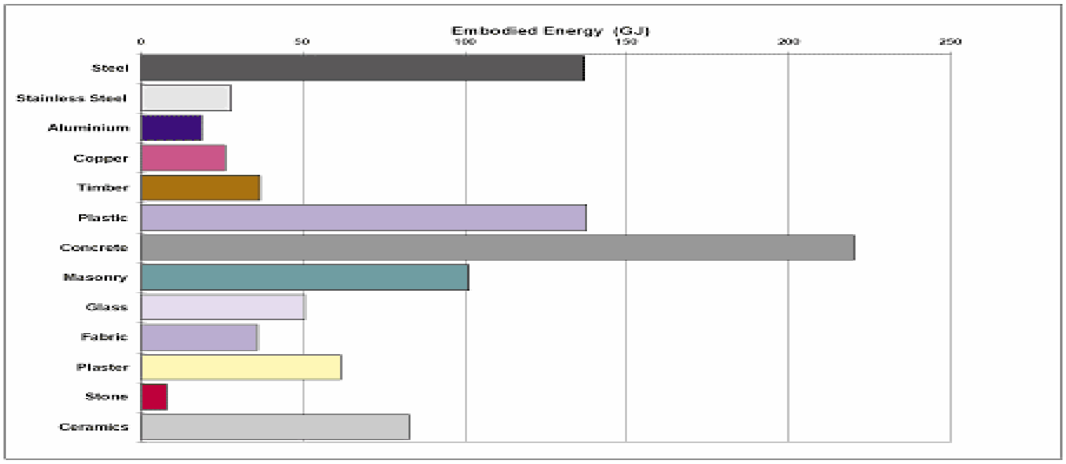


Figure 4 - Embodied Energy in Buildings[vi]

As a consequence of the huge volume of Portland cement manufactured, considerable energy is consumed (See Figure 4 - Embodied Energy in Buildings[vi] on page 6) resulting in carbon dioxide emissions. Carbon dioxide is also released chemically from the calcination of limestone used in the manufacturing process.

Various figures are given in the literature for the intensity of carbon emission with Portland cement production and these range from 0.74 tonnes coal/ tonne cement [viii] to as high as 1.24 tonne [ix] and 1.30 tonne.[x] The figure of one tonne of carbon dioxide for every tonne of Portland cement manufactured[xi] given by New Scientist Magazine is generally accepted.

These releases are due to:

- the burning of fossil fuels in the kilns used;
- emissions associated with electricity used during the manufacturing process, and;
- the chemical release of CO_2 from calcining limestone.

Globally some 1.8 billion tonnes of Portland Cement (OPC) are produced[xii] and accounts for more embodied energy than any other material in the construction sector[xiii]. The manufacture of OPC is one the biggest single contributors to the greenhouse effect, accounting for between 5%[xiv] and 10%[xv,xvi] of global anthropogenic[xvii] CO_2 emissions.

Global production of cement is likely to increase significantly over the coming decades as:

- global population grows;
- GDP grows;
- urban development continues; and,
- through increasing industrialisation.

A direct consequence of such huge usage and growing demand is the associated enormous potential for environmental benefits and improvements in sustainability and the triple bottom line if the material could be improved.

The Role of Governments

The democratic system has a fatal flaw in that the outlook of politicians and therefore governments is usually not much beyond the next election. As a consequence policy is generally extremely short sighted and too directly connected to the needs of the here and now rather than mindful of the future. Problems on a global scale are not just the concern of one or two countries but all people on the planet. World federalists believe we need a system of democratic global governance on top of (not instead of) national governments. Such a system would provide enforceable legal mechanisms for resolving conflicts and safeguarding the environment. Perhaps they have a point.

In spite of the two UN 'Habitat' conferences on urban prospects,[xviii] cities have not been given serious attention in the mainstream sustainability debate. For example the World Conservation Strategy of 1980, which first used the term "sustainable development," paid little attention to accelerating urbanization. The Brundtland report[xix] did discuss the issue, but the main emphasis was on the "urban crisis in developing countries."

The fact that the role of cities, and in particular rich cities has basically been neglected is difficult to reconcile with physical reality.

"The world population reached 6 billion in 1999.….At the current rate the world will have 7 billion people soon after the year 2010. The overwhelming share of world population growth is taking place in developing countries (…95.2% in 1990-2000; 97.6% in 2000-10; and 98.4% in 2010-20). The population of developing countries has more than doubled in 35 years, growing from 1.89 billion in 1955 to 4.13 billion in 1990.

Significant proportions of population increases in the developing countries have been and will be absorbed by urban areas (…71.8% in 1990-2000; 83.4% in 2000-10; and 93.4 in 2010-20). Urban settlements in the developing countries are, at present, growing five times as fast as those in the developed countries. Cities in the developing countries are already faced by enormous backlogs in shelter, infrastructure and services and confronted with increasingly overcrowded transportation systems, insufficient water supply, deteriorating sanitation and environmental pollution.[xx]"

Since the wealthiest 25 percent of the human population consume 80 percent of the world's economic output[xxi], approximately 64 % of the world's economic production/consumption and pollution is associated with cities in *rich* countries. Only 12 percent is tied to cities in the developing world[xxii]. In short, "half the people and three-quarters of the world's environmental problems reside in cities, and rich cities, mainly in the developed North, impose by far the greater load on the ecosphere and global commons[xxiii]".

It is time for governments to take an active role, to recognize their responsibility to seek sustainability as a cornerstone to all government expenditure and policy and facilitate economic systems that encourage sustainability such as carbon trading and deposit legislation.

Sustainable Building Technologies Must be Economically Viable to Succeed

Even though governments through policy can introduce change that brings about economies of scale it is important that building technologies that seek sustainability are also fundamentally economic otherwise they are not viable in the long run.

There is a strong need to kick the fossil fuel habit however this is unlikely to happen unless alternative sources of energy become more economical. "This may be sooner than we think as "just under half of the world's total endowment of oil and gas has been extracted already, and that output will begin to decline within the next five years, pushing prices up sharply.[xxiv]" Most geologist however concur that thirty rather than five years is more likely.

"Complementary to traditional areas of energy research, such as improving energy efficiency or shifting to renewable or nuclear energy sources, carbon sequestration will allow continued use of fossil energy, buying decades of time needed for transitioning into less carbon-intensive and more energy-efficient methods for generating energy in the future.[xxv]"

Even if we do kick the fossil fuel habit it will take centuries to bring the carbon balance back down to levels in the 50's and the need for sequestration technologies will remain.

Combined with chemical sequestration based on magnesium silicates such as forsterite or serpentinite the potential sequestration utilising TecEco technology is massive (See Sequestration on a Massive Scale on page 23). The role of governments is to facilitate economic valuation of this common good through systems such as carbon trading.

A major advantage of the TecEco technology over all other sequestration and abatement proposals it that the technology itself is viable even without a value being placed on abatement and sequestration. This paper will also demonstrate that one of the greatest advantages of the magnesian tec, eco and enviro-cement technologies is that given economies of scale they are thoroughly economic and will bring improvements in the material properties of concrete. (See Economic Advantages on page 17).

Concrete - An Imperfect Material

In spite of many years of research directed at improving properties, OPC concretes remain an imperfect material.

Our engineering and materials science libraries are full of information on problems relating to:

- Strength
- Durability and Performance
    - Permeability and Density
    - Sulphate and chloride resistance
    - Carbonation
    - Corrosion of steel and other reinforcing
    - Delayed reactions (eg alkali aggregate and delayed ettringite)
- Rheology
  Workability, time for and method of placing and finishing
- Shrinkage
  Cracking, crack control
- Bonding to brick and tiles
- Efflorescence

Problems with Portland cement concretes are usually resolved by the "band aid" application of engineering fixes. They are rarely discussed in terms of the mineralogy. For example:

- Use of calcium nitrite, silanes, cathodic protection or stainless steel to prevent corrosion.
- Use of coatings to prevent carbonation.
- Crack control joins to mitigate the affects of shrinkage cracking.
- Plasticisers to improve workability, glycols to improve finishing.

Much of the research carried out to date on cement has adopted a 'proving up' approach in order to produce materials that conform to specifications demanded on a 'top down' basis by users who are obliged to comply with existing standards and this approach has not been conducive to improvement.

The discussion should be more about how we could fix the material, overcoming rather than tolerating and mitigating these problems. To do so we need to rethink the mineralogy.

The flaw in the mineralogy of Portland cement concretes is the presence of Portlandite which is too soluble, mobile and reactive.

Concrete - The Material for the Future

There is tremendous scope to add strength and improve sustainability and other properties of concrete as a material through the addition of other substances including wastes, many of which would add tensile strength, insulating capacity or reduce weight. New composites made in this way will be the high performance materials of the future.

Materials such as the new magnesian tec, eco and enviro-cements will have a role in the development of these new materials as they not only absorb carbon dioxide in bricks, blocks, pavers, mortars and porous pavement, but also improve properties and allow the incorporation of a wider range of materials.

TECECO MAGNESIAN CEMENT TECHNOLOGY

Portlandite (or lime as it is often called) has always been the weakness of concrete as it is far too soluble, mobile and reactive. Scientists and engineers have known this for a long time but have not considered the consequences of replacement. TecEco advocate not just removal with the pozzolanic reaction but replacement with Brucite, a much less soluble and reactive hydroxide of magnesium.

TecEco have demonstrated that reactive magnesia which hydrates in a concrete forming Brucite can be advantageously blended with other hydraulic cements such as Portland cement with demonstrable improvements in properties and that previously reported dimensional distress was because the magnesia present was insufficiently reactive, having been through the high temperature process of Portland clinker production. (See Overcoming Dimensional Distress and Dogma about Magnesium in Cements on page 28)

A mineral assemblage in a concrete including brucite and carbonates of magnesium and excluding lime is ideal compared to an assemblage including a mineral as reactive as lime (Portlandite). The TecEco technology demonstrates how to achieve this assemblage. International patents[xxvi] have been applied for covering the addition of various proportions of reactive magnesia to cements used in concretes with or without added pozzolans. Lime is removed from concrete by the pozzalanic reaction and replaced with Brucite. Durability, sustainability, corrosion, carbonation, rheological, shrinkage and alkali aggregate reaction problems are substantially resolved and in some cases greater strength can even be achieved.

Many leading scientists and science organisations around the world have endorsed the technology[xxvii], publicly released on a large scale in the New Scientist Magazine of the 13th July 2002 and described variously as a “world first” and “benchmark in materials science” and having enormous medium and long term potential.

Although the capture of CO2 during the manufacture of the TecEco cements is recommended, conventional equipment can be used for all stages of manufacture reducing overheads and the capital cost of entry.

The new materials technology is applicable in a wide range of applications depending on the sustainability, durability, rheology or strength required and three main formulation strategies have so far been defined:

- Tec- cements (eg 10% MgO, 90% OPC.)

  Contain more Portland cement than reactive magnesia.

  Reactive magnesia hydrates in the same rate order as Portland cement forming Brucite which uses up water reducing the water binder ratio, increasing density and possibly raising the short term pH increasing the effectiveness of reactions with pozzolans. After all the Portlandite has been consumed Brucite controls the long term pH which is lower and due to it’s low solubility, mobility and reactivity results in greater durability.

Other benefits include improvements in density, strength and rheology, reduced permeability and shrinkage and the use of a wider range of aggregates without reaction problems.

- Enviro-cements (eg 26-75% MgO, 25-75% OPC)

  In non porous concretes Brucite does not carbonate readily.

  High proportions of magnesia are most suited to toxic and hazardous waste immobilisation and when durability is required. Strength is not developed quickly.

- Eco-cements (eg 50-75% MgO, 50-25% OPC)

  Contain more reactive magnesia than Portland cement. Brucite in porous materials eventually carbonates forming stronger fibrous mineral carbonates adding strength and presenting huge opportunities for abatement.

Tec-Cements

Tec-cements concretes have a relatively low proportion of reactive magnesia that hydrates to form Brucite. They usually also contain a pozzolan which reacts with the Portlandite released as di and tri calcium silicate hydrate and forms more calcium silicate hydrates (CSH).

As a consequence of the removal of Portlandite and replacement by Brucite tec-cement concretes have a different pH curve to Portland cement concretes and Portland cement concretes that have had pozzolans added. As the hydration of magnesia takes up a lot of water (44.65 mass% is water) it is thought that during the early plastic stage the pH may be higher. In the longer term however the pH is controlled by Brucite and is lower (See Figure 9 on page 35).

The equilibrium pH of Brucite in water is 10.38 and it maintains the pH of concretes in that range for much longer periods than portlandite as it is far less reactive. For most kinetic pathways it carbonates much less readily[xxviii] (ΔG_r Portlandite → calcite = - 64.62 $kJ.mol^{-1}$, ΔG_r Brucite → magnesite = - 19.55 $kJ.mol^{-1}$). The equilibrium pH is still however at a sufficiently high level for steel to remain passive[xxix] and for the stability of calcium silicate hydrates[xxx]. Dense concretes made using TecEco formulations should maintain reducing conditions and a pH over 8.9 required for the long term survival of steel much longer than Portland cement concretes.

Tec-cement concretes exhibit high and faster development of strength and this is probably due to:

- more silicification reactions including a more effective pozzalanic reaction during the early plastic stage whilst the pH is possibly elevated.

- a low water binder ratio as a result of improved rheology due to better particle packing and some surface charge affects.

- The removal of excess water by magnesia as it hydrates prevents bleeding and the introduction of associated weaknesses such as interconnected pore structures and also tends to dry tec-cement concretes from the inside and combined with a lower long term pH, and the low solubility and reactivity of Brucite, results in improved durability.

The advantages of using Portland cement such as ambient temperature setting and strength are not diminished however shrinkage is reduced if not eliminated due to low water loss and in appropriate proportions the expansion of magnesium minerals balancing the slight shrinkage of Portland cement concrete eliminating cracks and reducing porosity.

Low pH, low porosity, reduced shrinkage cracks, the fact that magnesia dries concrete out from the inside as it consumes water and reduced reactivity result in the virtual elimination of delayed reactions and corrosion as well as resistance to salts.

More flyash can be added to advantage and sustainability is improved by reduced binder/aggregate ratios, longer life and lower emissions ratios.

Enviro-Cements

Enviro-cements differ in that they contain higher ratios of magnesia to hydraulic cement. Chemically and physically they are more suited to toxic and hazardous waste immobilisation because they are more durable either lime, Portland cement or Portland cement lime mixes. They are also homogenous and do not bleed water, are not attacked by salts in ground or sea water and dimensionally more stable with less cracking.

In a Portland cement Brucite matrix[xxxi]

OPC takes up lead, some zinc and germanium.

Brucite and hydrotalcite are both excellent hosts for toxic and hazardous wastes. Brucite has a layered structure and traps neutral compounds between the layers.

Heavy metals not taken up in the structure of Portland cement minerals or trapped within the Brucite layers end up as hydroxides.

The pH which is controlled in the long term by Brucite is around 10.4, and is an ideal long term value at which most heavy metal hydroxides are relatively insoluble.

Eco-Cements

Eco-cements differ in that they contain higher ratios of magnesia to hydraulic cement.

In porous or semi porous materials such as bricks, blocks, pavers, mortars and renders and porous pavements, as there are no kinetic barriers, the magnesia not only hydrates, but carbonates completing the thermodynamic cycle by reabsorbing the carbon dioxide produced during calcining.

Eco-cement concretes are also to some extent recyclable and can have up to around 90% recycled industrial materials such as fly ash included in their formulation and are therefore likely to become the building material of future choice[xxxii][xxxiii]. Important uses will include providing a sustainable, low cost building material with high thermal capacity, low embodied energy and good insulating properties for construction in products such as bricks, blocks, stabilised earth blocks, pavers and mortars, wharves and airstrips and in combination with wood waste for packaging. Carbonated eco-cement formulations for the built environment are also strong and resistant to the chemicals that attack Portland cement

Brucite, magnesite and hydromagnesite bond well to many different materials including wood[xxxiv] and will hold a large proportion of waste.

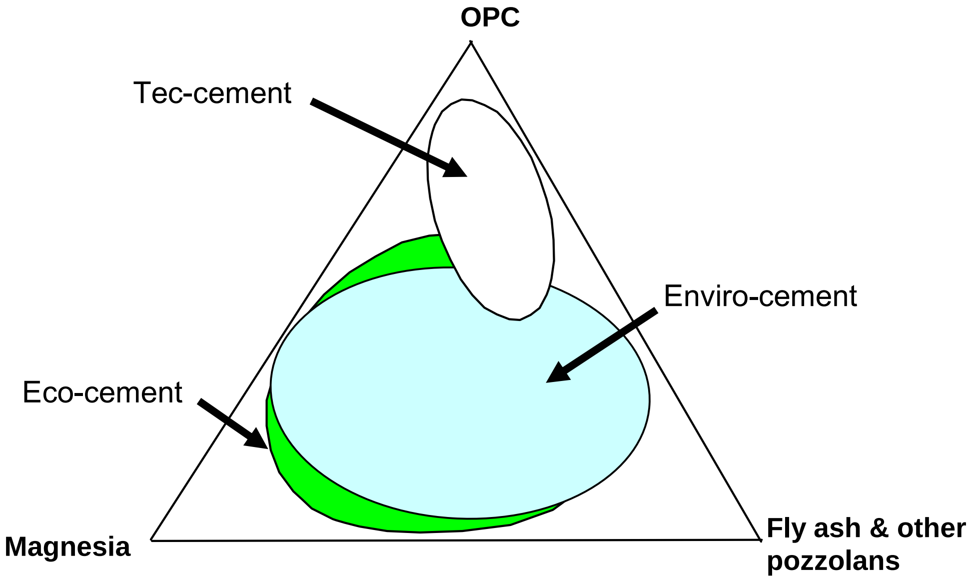


Figure 5 – TecEco Cement Formulations

Summary of the Ramifications of the TecEco Magnesian Cement Technology

The ramifications of the new binder technology are far reaching and potentially include:

Greater Strength:

Significant strength with low binder/aggregate ratios have been observed in tec-cement concretes and this is likely to be a result of low water/binder ratios, increased density and possibly more effective pozzalanic reactions caused by high early pH due to supersaturation of calcium hydroxide as the hydration of reactive magnesia takes up water.

Faster Strength Development

Tec-cement concretes exhibit more rapid strength development even with high additions of pozzolans.

Lower Long Term pH?:

As Portlandite is removed the pH becomes governed by the solubility of Brucite and is much lower at around 10.5 -11, stabilising many heavy metals and allowing a wider range of aggregates to be used without AAR problems. Carbonation is slower and the pH remains high enough to keep Fe, FeO and Fe_3O_4 stable for much longer.

Better Rheology - Easy to Use:

Better particle packing and surface charge affects enable fine magnesia to act as a lubricant for Portland cement improving homogeneity and rheology.

Durability:

TecEco Tec - cements are protected by Brucite, are not attacked by salts, do not carbonate readily and last indefinitely. As TecEco cements dry from the inside out, and have a lower long term pH internal delayed reactions are prevented.

Greater Density, reduced permeability?:

Brucite fills pore spaces taking up mix and bleed water as it hydrates reducing voids. (Brucite is 58.3 mass% water!).

Less Shrinkage?:

Internal consumption of water reduces shrinkage through loss of water. Magnesium minerals also expand on formation and take up water, whilst concrete tends to shrink. Blended in the right proportions, concretes can be made that are dimensionally neutral over time.

More Sustainable:

Tec-cements can use less binder for the same strength and all TecEco cements use a high proportion of recycled materials, a wider range of aggregates reducing transport emissions and have superior durability slowing down replacement. Eco-cements reabsorb chemically released CO_2.

Insulating Properties / High Thermal Mass / Low Embodied Energy:

Eco-cement products will be favoured for energy conserving buildings.

Recyclable:

Eco-cement products can be reprocessed and reused, making them more attractive to many users.

A Fire Retardant:

Brucite, magnesite and hydromagnesite are all fire retardants. TecEco cement products put fires out by releasing CO_2 or water vapour at relatively low temperatures.

Low Costs:

No new plant and equipment are required.

Lower materials cost. With economies of scale TecEco cements should be cheaper and less cement is required in some formulations.

Lower usage costs include easier placement and finishing, elimination of shrinkage and bleeding, faster strength gain (in some formulations), use of a wider range of aggregates reducing transport costs, less or no plasticisers, no bleeding and greater durability reducing replacement costs over time and potential carbon credits.

Potential Uses

The new cements are suitable for a wide range of uses including

- As a stabilising agent in the production of earth buildings.
- Mortars, renders, grouts & drill hole cements.
- Controlled low strength materials
- Soil stabilisation/solidification.
- Agglomeration of furnace feeds and pellet manufacture.
- Waste and toxic waste immobilisation/fixation.
- For the production of bricks, blocks and pavers utilising coal combustion by-products including waste heat.
- To manufacture lightweight disposable high thermal capacity insulated packaging
- Blended with Portland cement to improve properties such as strength and durability.
- Where rheology is important such as with gunnite or shotcrete.
- Where fire retarding properties are essential.
- Use in areas of high chloride or sulphate contamination of sand and aggregates.
- Where there are critical resource shortages such as in China.
- Where cost or environmental considerations are important.

The research and development and business plans consider priorites for research, development and deployment.

THE ADVANTAGES OF TECECO MAGNESIAN CEMENTS.

The TecEco technology represents a unique way forward for the sustainability process with no known disadvantages.

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

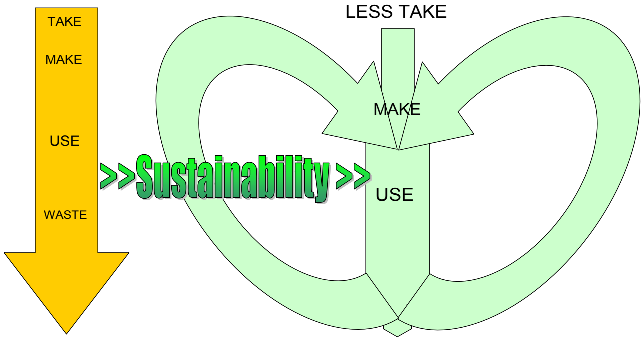


Figure 6. The Move to a More Sustainable Society.

Economic Advantages

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

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

Energy

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

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

Table 1 on page 18 shows that on a mass for mass of natural materials consumed basis, less energy is required. TecEco argue however that the most valid point of comparison is when the utility is greatest and in the case of TecEco modified Portland cement this is when Portland cement and reactive magnesia have hydrated becoming a binders in concrete. In the case of eco-cements further utility is added when brucite carbonates completing a thermodynamic cycle and become magnesite again.

The mass comparisons in Table 1 are also deficient in that the built environment has most utility when 3D space is created not mass. After all do we purchase 20 tonnes of bricks, timber, nails and tin for a home? The utility argument can therefore be carried further and a better basis of comparison is on a volume of binder material produced basis as in Table 2on page 18. In this case the hydrated product, Brucite, has a lower embodied energy.

Table 1. Calcining energy compared on a mass basis.

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

Table 2. Calcining energy compared on a volume basis.

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

Cost

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

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

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

Carbon Credits

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

- CO_2 could be captured at source (as in the TecEco kiln).
- TecEco eco-cements absorb considerable CO_2 in porous materials such as bricks, blocks, pavers, concretes and pavements.

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

The potential for widespread abatement and solving global climate change issues is enormous and is discussed in detail under the heading Sequestration on a Massive Scale on page 23.

Other Cost Factors

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

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

Technical Advantages

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

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

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

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

It also takes time for problems due to alkali aggregate reaction to emerge, and with TecEco cements they will most likely occur.

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

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

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

Environmental Advantages

The TecEco cement technology is far more sustainable than either the production of lime or Portland cement and would significantly reduce the impact of these materials. There are many reasons for this.

- The manufacture of reactive magnesia is a benign process that can be achieved with waste or intermittently available energy. The new TecEco kiln technology will result in around 25% less energy being required and the capture of chemically released CO_2 during production resulting in lower costs and carbon credits.

- A high proportion of Brucite compared to Portlandite is water and of magnesite compared to calcite is CO_2. Every mass unit of TecEco cements (containing MgO) therefore produces a greater volume of built environment than Portland and other calcium based cements. Less need therefore be used reducing costs/energy/emissions.

- Energy and emissions are lower, particularly on a volume of built environment created basis (See Table 1. Calcining energy compared on a mass basis. and Table 2. Calcining energy compared on a volume basis. on page 18).

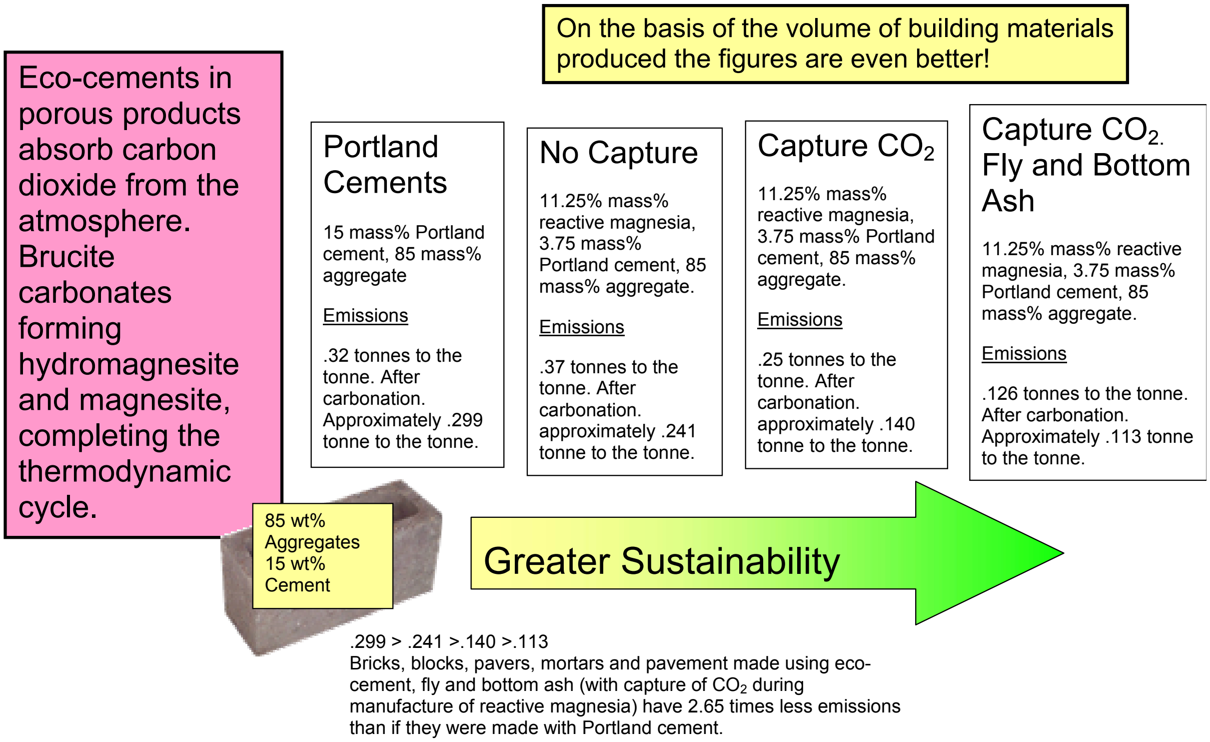
- Improved durability and other properties will result in lower long run costs/energies/emissions due to less frequent replacement. Brucite is less soluble, mobile or reactive than Portlandite and not attacked by salts or carbon dioxide to the same extent. The drier internal environment and lower long term pH results in greater stability resulting in less delayed reactions, salt attack, etching and other problems. The pH is still however high enough to maintain the passivity of steel.

- A wider range of aggregates can be utilised effectively, including many wastes reducing transport and other costs/energies/emissions.

- Because of the higher pH during the early plastic stage of tec-cements many marginally pozzolanic materials, many of which are wastes, become reactive and add strength.

- Lower binder/strength ratios are achievable in some tech-cement formulations resulting in less net emissions.

- In porous materials such as bricks, blocks, pavers and mortars that utilise eco-cement CO_2 is reabsorbed as brucite carbonates forming strong binding minerals such as magnesite and hydromagnesite. With capture of CO_2 during manufacture enormous amounts of carbon dioxide could be sequestered (See Figure 5 on page 22 for an example of sequestration in eco-cement blocks). What distinguishes the TecEco technology is that utility (value in products) is added at the same time.



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.

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 7 - CO2 Abatement in TecEco Eco-Cements

In tec-cements lower binder : aggregate ratios are required and this is probably because of the higher early pH initiating more affective pozzolanic reactions and because reactive magnesia removes water as it hydrates increasing the density by reducing the voids:paste ratio. The use of less cement to achieve the same result improves the sustainability of concrete as a material considerably.

Depending on the formulation and use, eco-cements used to make porous materials such as bricks, blocks, pavers, mortars and pavement re-absorb CO_2, are to some extent recyclable. They can also be made including a high proportion of fly ash and other recycled usually pozzolanic industrial waste materials.

Around 98% of the world's energy is derived from fossil fuels that when burnt to produce energy releases vast amounts of CO_2. In terms of the volume of built environment and infrastructure that results, less energy goes into making TecEco Cements for the reasons given under the heading Economic Advantages on page 17. Materials that have a lower embodied energy are more sustainable.

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

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

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

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

The most publicised formulations of TecEco cements are eco-cements which contain a much greater proportion of materials such as reactive magnesia (and thus brucite) in the cement component that carbonates to completion in porous materials thus absorbing considerable chemically released CO_2

The use of Calcium sulfoaluminate compound together with belite (C_2S) and reactive magnesia is to be investigated by TecEco at a future date.

Combined with chemical sequestration based on forsterite or serpentinite the potential sequestration utilising TecEco technology is potentially massive and will go a long way toward solving the problem of global warming.

Sequestration on a Massive Scale

The Built Environment is potentially a repository for sequestration on a massive scale. Starting with either forsterite or serpentine to produce eco-cements the total sequestration is potentially much more than any other method, and the solid output a useful product for constructing the built environment saving on alternative production and disposal costs. Mineral and geological sequestration are combined resulting in a solution to the carbon balance problem with positive economic outcomes.

“Complementary to traditional areas of energy research, such as improving energy efficiency or shifting to renewable or nuclear energy sources, carbon sequestration will allow continued use of fossil energy, buying decades of time needed for transitioning into less carbon-intensive and more energy-efficient methods for generating energy in the future.[xxxvi]”

Carbonate sequestration has been the mechanism through which previous atmospheric global carbon imbalances have been corrected and still represents the best opportunity for permanent immobilization of atmospheric carbon.

The deposition of carbonate sediments is a slow process and involves long periods of time. Ways of accelerating sequestration using carbonates include geological sequestration and mineral carbonation. “there are significant fundamental research needs that must be addressed before geologic formations can be widely used for carbon sequestration.[xxxvii]” “Mineral carbonation, the reaction of CO_2 with non-carbonated minerals to form stable, benign mineral carbonates, has been identified as a possible safe, long-term option for storing carbon dioxide by many authors[xxxviii][xxxix][xl][xli][xlii][xliii][xliv][xlv]”

The TecEco eco-cement technology involves mineral carbonation with the added benefit of an end product of the process that is of value and made of eco-cement concrete. Products manufactured using the TecEco eco-cement technology to date include include bricks, blocks, pavers, mortars, renders and potentially porous pavement and are distinguished in that they can sequester carbon dioxide whilst providing the fabric for the built environment.

Combined with chemical sequestration based on forsterite or serpentinite which is carbonated in accordance with the following reactions the potential sequestration utilising TecEco technology is massive:

$\frac{1}{2}Mg_2SiO_4 + CO_2 \rightarrow MgCO_3 + \frac{1}{2}SiO_2 + 95\ kJ.mol^{-1}$

$^{1}/_{3}Mg_3Si_2O_5(OH)_4 + CO_2 \rightarrow MgCO_3 + 2/_{3}SiO_2 + 2/_{3}H_2O + 64\ kJ.mol^{-1}$

The first reaction with forsterite appears to occur more readily and results in greater abatement. The second reaction with chrysotile or serpentine as it is sometimes called is favoured as the mineral is abundant although problems remain to be solved with the kinetics.

At low partial pressures of CO_2 and relatively low temperatures, $MgCO_3$ will break down yielding MgO and CO_2[xlvi].

$MgCO_3 \rightarrow MgO + CO_2 - 118.28\ kJ.mol^{-1}$

Utilising a closed system such as with TecEco Kiln technology the CO2 re-emitted can be captured for industrial use (replacing alternative production) or direct sequestration.

The MgO can then either be re carbonated for further capture for as many cycles as required or used to make eco-cement products.

$MgO + H_2O \rightarrow Mg(OH)_2 + 109.19\ kJ.mol^{-1}$

$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O + 37.04\ kJ.mol^{-1}$

Sequestering even more CO2

Total sequestration is two, three or many times that possible with direct mineral sequestration of forsterite or serpentinite alone, depending on whether the CO_2 produced during calcination replaces or abates other production or not and how many cycles of calcination are rolled over. Sequestration possible with one one, five or ten calcination cycles is shown in Table 3 - Silicate Molar Tonne Equivalents on page 24.

Table 3 - Silicate Molar Tonne Equivalents

	Chrysotile (Serpentinite)	Forsterite (Mg Olivine)
Tonnes CO2 sequestered by 1 tonne of mineral mined directly	.4769	.6255
Tonnes CO2 captured during calcining	.4769	.6255
Tonnes CO2 captured by eco-cement	.4769	.6255

Total tonnes CO2 sequestered or abated per tonne mineral mined (Single calcination cycle).	**1.431**	**1.876**
Total tonnes CO2 sequestered or abated (Five calcination cycles.)	**3.339**	**4.378**
Total tonnes CO2 sequestered or abated (Ten calcination cycles).	**5.723**	**7.506**

Sequestration from Making Eco-Cement

The following graphs (Table 5, Table 6 and Table 7) illustrate the massive sequestration available[xlvii] even with only one cycle of calcination. More cycles would result in greater calcination.

It can be seen from the graphs that starting with either magnesite, forsterite or serpentine the amount of eco-cement or eco-cement concrete that can be produced is about the same, in that around 10 million tonnes will give a similar amount of eco-cement of around 6.6 to 8.7 million tonnes – roughly the capacity of the Australian cement industry.

The total sequestration however is very different depending on the starting mineral. For one cycle of calcination only for each 10 million tonnes mined, forsterite gives the best result at 18,766,257 tonnes of CO_2 sequestered, starting with serpentine the figure is 14,307,916 tonnes of CO_2 sequestered and with magnesite 10,438,805 tonnes CO_2 are sequestered. At $ 15- 30 dollars per tonne for carbon credits the values are respectively $ 313, 563 and 429 million dollars, an incentive worth considering by the concrete industry.

Summary totals presented by the Wood's Hole Institute for carbon in the carbon cycle during the decade ending 1990 (in billion metric tonnes or petograms) are as in Table 4 below:

Table 4 - Summary totals presented by the Wood's Hole Institute for carbon in the carbon cycle during the decade ending 1990 (in billion metric tonnes or petograms)

Atmospheric increase	= Emissions from Fossil fuels	+ Net emissions from changes in land use	- Oceanic uptake	- Missing carbon sink
3.3(±0.2)	=5.5(±0.5)	+1.6(±0.7)	-2.0(±0.8)	-1.8(±1.2)

Converting to tonnes CO_2 this is:

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)

In general agreement with other research there appears to be a discrepancy which is believed to be because there has been a greater than measurable amounts taken up by living plant sinks[xlviii].

By extrapolation, and without taking into account process emissions, given only one cycle of calcination it would roughly take the mining and processing of 12.2 billion tonnes of magnesite, 6.8 billion tonnes of forsterite or 8.9 billion tonnes of serpentine to sequester 12.7 billion tonnes of extra CO_2 put into the atmosphere every year. With more cycles of calcination using TecEco kiln technology less cycles. This would also involve the production of 8.8, 5.9 and 5.5 billion tonnes of eco-cement containing 66.6% magnesia. As the global demand would not exceed say 1 billion tonnes an economic maximum of sequestration with only one cycle of calcination would be in the order of 2 – 2.5 billion tonnes. A very significant figure. The combined method presented by TecEco is by far the best solution on the planet so far enunciated.

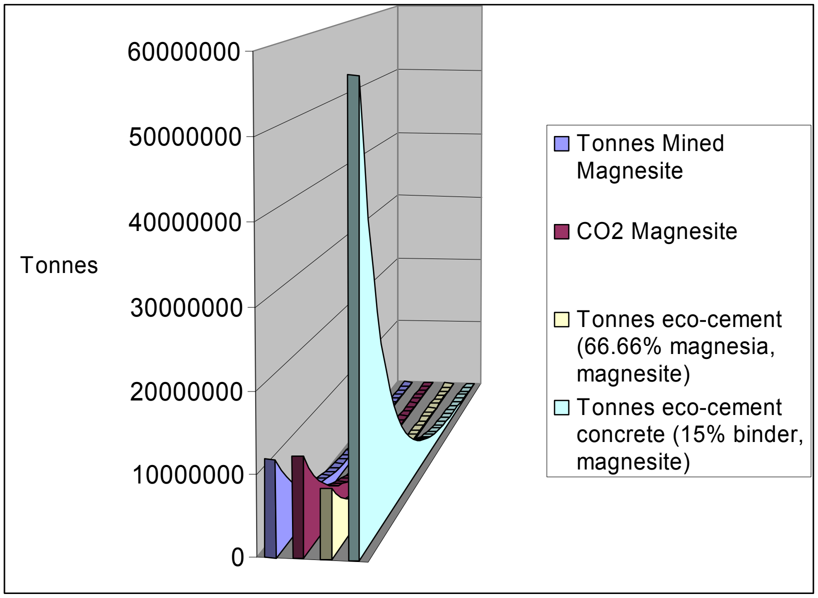


Table 5 – Graph Showing Sequestration and Output Eco-Cement (66.66% Magnesia)and Eco-Cement Concrete (15% Eco-Cement) per Tonne of Magnesite Mined and Processed.

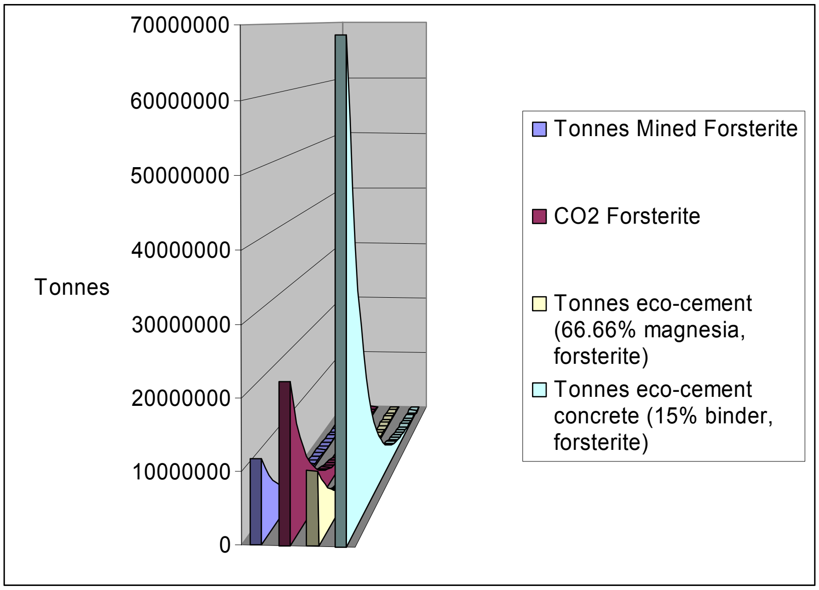


Table 6 – Graph Showing Sequestration and Output Eco-Cement (66.66% Magnesia)and Eco-Cement Concrete (15% Eco-Cement) per Tonne of Forsterite Mined and Processed.

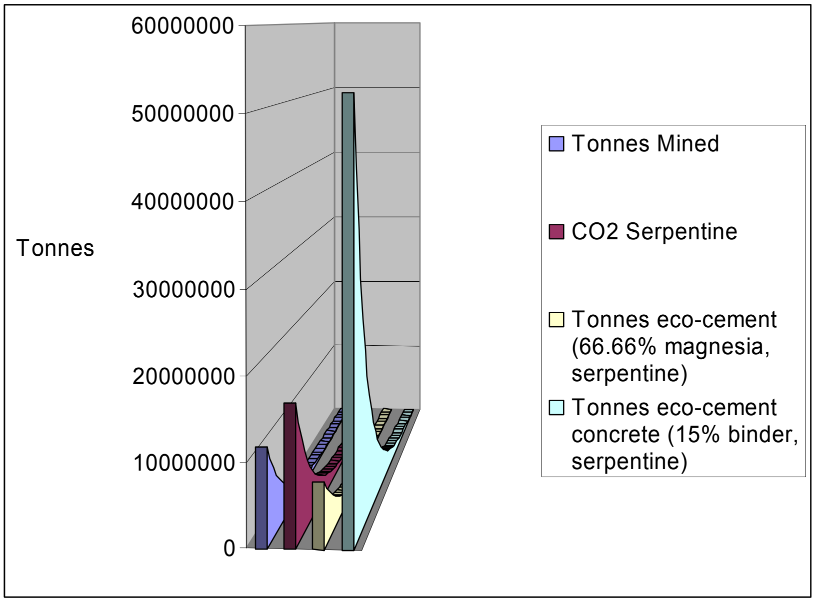


Table 7 – Graph Showing Sequestration and Output Eco-Cement (66.66% Magnesia)and Eco-Cement Concrete (15% Eco-Cement) per Tonne of Serpentine Mined and Processed.

SUMMARY OF THE CHEMISTRY AND ENGINEERING OF TECECO CEMENTS

Overcoming Dimensional Distress and Dogma about Magnesium in Cements

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

Magnesium carbonate subjected to a high temperature clinkering process results in the formation of periclase which has an ordered and stable atomic structure and therefore takes more energy and time to hydrate than reactive magnesia which is far less ordered and has a much higher specific surface area.

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

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

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

What is important about the TecEco technology is that is demonstrates that magnesia, provided it is reactive rather than "dead burned" (or high density, periclase type), can be beneficially added to cements in excess of the amount of 5% w/w generally considered as the maximum allowable in cements[lii].

As Neville mentions in his comprehensive text on concretes, "only periclase, that is, "dead burned" crystalline MgO, is deleteriously reactive, and MgO present in glass is harmless.[liii][liv]"

A fear of dead burned lime and magnesia until the development of TecEco cements has prevented useful additions or magnesia but not slaked lime ($Ca(OH)_2$) which was either added to aid plasticity or in its own right.

According to Taylor, H. F. W.[lv] "The content of MgO is usually limited to 4-5%, because quantities of this component in excess of about 2% can occur as periclase (magnesium oxide), which through slow reaction with water can cause destructive expansion of hardened concrete. Free lime (calcium oxide) can behave similarly."

Taylor further states that "Portland cement raw materials contain small proportions of MgO…they must be limited to avoid formation of more than a minor amount of periclase[lvi]."

Unfortunately most standard do not distinguish between the varying forms of magnesium occurring in cements.

Such forms include:

- Periclase (which is a problem in cements.)
- In the structure of all four major components of Portland cement[lvii]
- In many other cementitous phases in the $CaO-MgO-Al_2O_3-SiO_2$. (See table below)
- Reactive magnesia.

Table 8 - Magnesium Minerals in the System $CaO-MgO-Al_2O_3-SiO_2$[lviii]

Periclase	MgO
Forsterite	M_2S
Monticellite	CMA
Merwinite	C_3MS_2
Bredigite	C_7MS_4
Akerminite	C_2MS_2
Enstatite	C_2MS_2
Enstatite	MS
Akerminite	C_2MS_2
Enstatite	C_2MS_2
Diopside	CMS_2
Spinel	MA
Phase Q	C_3A_2M C_7A_5M $C_{20}A_{13}MsS_3$

If not limited to the $CaO-MgO-Al_2O_3-SiO_2$ system Table 8 would be considerably larger with minerals such as Brucite, sepiolite, "MSH", calcium and magnesium oxy chlorides and sulphates.

International and national standards measure magnesium as the oxide regardless of form or consequence and many national and international standards have limits of around 5%. According to Jackson P. J.[lix] "In addition to having requirements in respect of the secondary components which are permitted to be incorporated into the cement, there are also chemical constraints on the cements themselves. ENV 197-1 limits the amount of magnesia (MgO) in the Portland cement clinker to 5.0 %, whilst ASTM C 150, which deals only with cements comprising 100 per cent Portland cement clinker and gypsum rock (apart, that is, from small amounts of processing additions and air-entraining agents, etc.), limits the amount to 6.0 % (with an autoclave soundness test in addition), as does ASTM C 595M for the pozzolan-containing cements and just the autoclave test for the slag containing blended cements. The reason for this restriction is the danger of having an excessive amount of magnesia in the form of periclase, the presence of which may lead to long-term expansions."

The Role of Magnesia

Reactive magnesia in hydraulic cements hydrates relatively quickly to form Brucite and the advantages of Brucite in concretes has been noted by many authors. Biczok E.[lx] for example in an early text on corrosion notes that magnesium hydroxide "has a sealing affect and delays thus the migration of aggressive ions" and "magnesium hydroxide….decreases the permeability of concrete"[lxi], Richardson comments that "…insoluble magnesium hydroxide can provide protection below low water level but higher up it is lost through wave action.[lxii]" Furthermore, Ramachandran et. al. observed that compacted Brucite can be as strong as Portland cement of the same porosity[lxiii].

The use of reactive magnesia may well solve the problem of dead burned metal oxides in cements such as found in India where dead burned lime is a problem. Early cements contained considerable un-reactive or dead burned lime, however as setting rates were slower this was not such a problem as it would be today[lxiv].The problem of dead burned lime has been largely forgotten by cement technologists, even though dead burned lime is much more expansive than dead burned magnesia[lxv]. Portland and other hydraulic cement concretes can take many years to dry out depending on their mass and shape and much water may remain in a bound state (suface adsorbed or trapped in the structure of CSH). Free water is required for most delayed reactions to occur[lxvi]. Because magnesia as it hydrates has a high water demand TecEco cement concretes tend to dry from the inside out more quickly making it more difficult for delayed reactions to occur as diffusive processes are much slower.

Not only does Brucite present in a tec or enviro-cement matrix add to durability, it may well add to strength in some tec-cement formulations due to forced lower voids/paste ratios, compaction by the surrounding CSH and perhaps higher pH during the plastic stage which may result in more affective pozzalanic reactions.

The formation of Brucite as a mineral does not appear to detract much from other chemical processes going on in cements although detailed research is still required to confirm this for the more common hydraulic cements. There are some questions also remaining as to the fate of the sulphate in gypsum.

There have been two very divergent objectives in concretes over the past twenty years or so. Because more progressive strength development has been required the material has become more reactive, with higher alite/belite ratios and finer grinds. For other reasons such as cost, improved properties and sustainability objectives more and more supplementary cementitous materials are being used that delay strength development. Research will most likely prove that Tec-cements make it possible to use high ratios of supplementary materials without delaying strength development, thus converging what were divergent objectives.

The main reason for the addition of Brucite to Portland cement is not however strength but durability. Lime has always been the problem with Portland cement concretes, it is far too soluble (1.85 g L^{-1}), mobile and reactive. It combines with salts, especially common anions such as sulfates and chlorides, carbonates or just leaches out resulting in a drop in the Ca/Si ratio of CSH and brittleness. Portlandite goes into solution readily, producing a high a concentration of calcium and hydroxide ions that can act as an electrolyte during the electrolytic phase of rusting. Although carbonation adds strength, it results in a lowering of the pH reducing the passivity of steel. The weakness of Portland cement is Portlandite.

In TecEco cements Portlandite is removed using the pozzalanic reaction and replaced by magnesium hydroxide, improving rheology in the manner that lime added to concretes did in the days before the discovery of plasticizers.

Durability whether expressed in terms of carbonation, corrosion of steel, salt attack or delayed reactions is a major problem and is basically a ramification of the reactivity of the Portlandite and other reactive alkalis in Portland cement concretes and the presence of moisture for reactions to occur. TecEco cement concretes are much more durable as they eliminate Portlandite, dry out internally much earlier and have a lower long term pH.

Shrinkage is yet another problem that may well be overcome using TecEco technology and this is because magnesium mineral volumetric stoichiometry is expansive compared to calcium chemical shrinkage and because moisture is consumed expansively internally without bleeding resulting in less plastic and drying shrinkage. With appropriate blending dimensionally neutral over time concretes should be possible.

Enviro-cements are likely to have more specialised usages such as the immobilisation of toxic and hazardous wastes and research is continuing in this area.

Eco-cements are the first building material of high thermal capacity with a low embodied energy that are recyclable, carbon dioxide neutral or even a net sink[lxvii]. They usually contain a high proportion[lxviii] of wastes such as fly ash, silica fume, sewerage ash, ground vitrified iron blast furnace slag, rice husk ash etc. that are often also pozzolanic or marginally pozzolanic as well. Other wastes such as sawdust, other organic wastes or even red mud can also be added, can add insulative capacity and other properties and stick well to brucite and magnesite[lxix].

Lower embodied energies, greater durability and high thermal capacity make eco-cements and eco-cement composites very sustainable and extremely useful as a potentially low cost building material compared to materials containing only Portland cement.

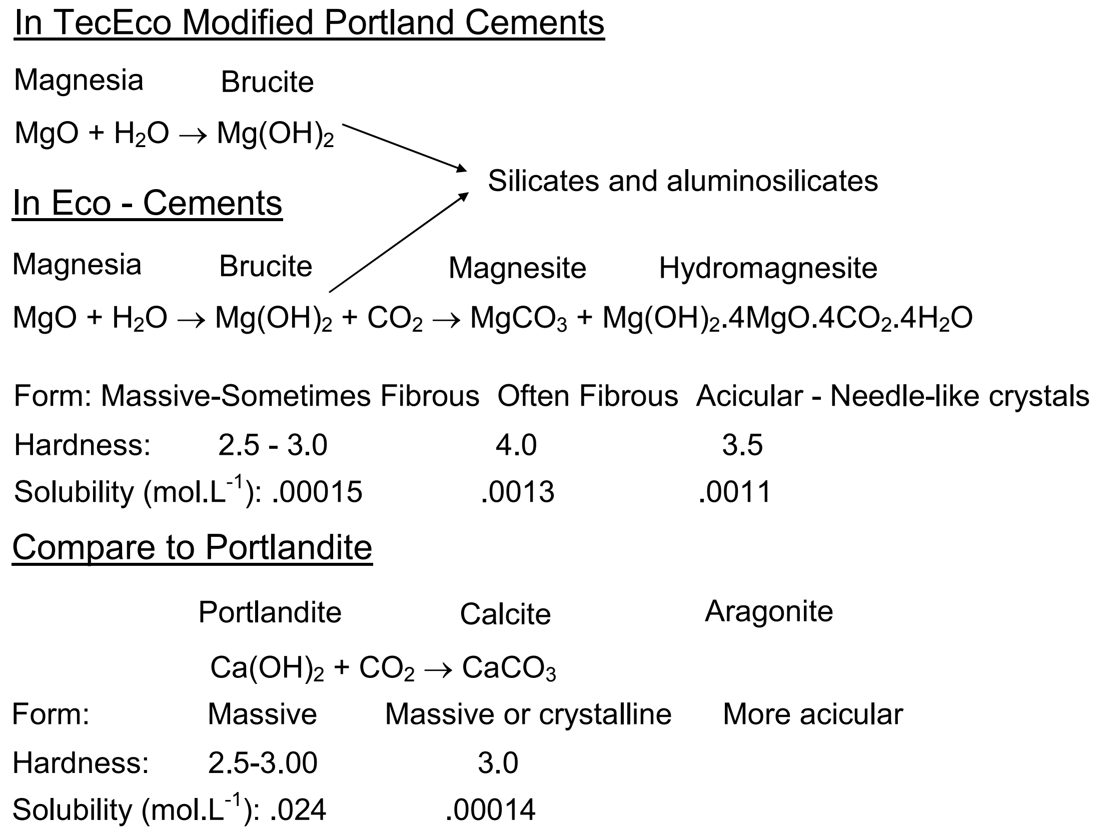
TecEco cements will become more economic in the long run and better for some purposes, better than Portland cements. The project is well advanced and various trials of TecEco-cements for the built environment are also now in progress.

Magnesium is the sixth most abundant element in the earth's crust and occurs in concentrated form as the mineral brucite, magnesite, forsterite, enstatite or serpentinite which are abundant in many parts of the world and in particular China and Australia and in most cases the supply of raw materials will not be an issue.

For many product areas such as toxic and hazardous waste immobilisation and block manufacture the chemistry of TecEco cements is sufficiently well defined. All that is required for more widespread adoption by technical umpires such as engineers and architects for construction generally is more engineering research to quantify properties and the development of case histories in which the technology has been used.

Reactions

The TecEco cement system principally involves the addition of reactive magnesia in virtually any ratio to other hydraulic cements such as Portland cement. Reactions vary depending on the local fugacity of CO_2 and are as follows



In TecEco Modified Portland Cements

Magnesia Brucite

$MgO + H_2O \rightarrow Mg(OH)_2$

Silicates and aluminosilicates

In Eco - Cements

Magnesia Brucite Magnesite Hydromagnesite

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

Form:	Massive-Sometimes Fibrous	Often Fibrous	Acicular - Needle-like crystals
Hardness:	2.5 - 3.0	4.0	3.5
Solubility (mol.L^{-1}):	.00015	.0013	.0011

Compare to Portlandite

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

	Portlandite	Calcite	Aragonite
Form:	Massive	Massive or crystalline	More acicular
Hardness:	2.5-3.00	3.0	
Solubility (mol.L^{-1}):	.024	.00014	

Figure 8 - Reactions of Reactive Magnesia and Portlandite in Concretes.

Chemistry

The main factor controlling the chemistry of TecEco cement blends is the differences and similarities between magnesium and calcium. Both metals are reactive and therefore do not exist in nature as metals and both form ionic 2^+ bonds. They exhibit only one valency in which they give up two electrons. Ionic size and valency control stacking and substitution in mineral structures substantially affecting many other properties. Mg^{++} has an ionic size of 86 pico metres (pm) whilst Ca^{++} has an ionic size of 114 pm. As a result magnesium stacks more closely in an ionic lattice than calcium in oxides and hydroxides and this is what reduces solubility and reactivity.

Brucite, the hydroxide of magnesium has a solubility of around .009 g.L^{-1} compared to 1.850 g.L^{-1} for Portlandite in cold water and .04 g.L^{-1} compared to .770 g.L^{-1} in hot water.

Brucite is therefore between 205 and 20 times less soluble than Portlandite which is the hydroxide of calcium and a major component of Portland cement.

In tec and enviro – cement concretes Brucite maintains the pH of the cement at between 10.5 and 11[lxx] for much longer than Portlandite does for Portland cement concretes, reducing alkali aggregate reaction problems and steel corrosion.

Although the Gibbs Free Energy for the carbonation of Brucite resulting in the formation of both magnesite is much less negative than that of Portlandite forming either calcite or aragonite (See Table 9 – Properties of Portlandite and Brucite, there are no kinetic barriers in porous materials such as bricks, blocks, pavers, mortars and roof tiles the process still occurs sufficiently readily for it to be useful providing tremendous potential for CO_2 abatement.

The formation of magnesite and various hydrated magnesium carbonates such as hydro magnesite adds tremendous strength as magnesium carbonates are stronger than calcium carbonates. Not only are magnesium carbonates innately stronger, they are also fibrous or acicular and form microscopic 3D shapes adding microscopic structural strength. In masonry blocks for example carbonation of the magnesia phase takes a few months to complete and is a good source of strength.

The properties of Portlandite and Brucite are compared in Table 9 below.

Table 9 – Properties of Portlandite and Brucite

Property	**Portlandite (Lime)**	**Brucite**
Density	2.23	2.9
Hardness	2.5 – 3	2.5 – 3
Solubility (cold)	1.85 g L^{-1} in H_2O at 0 ^oC	0.009 g L^{-1} in H_2O at 18 ^oC.
Solubility (hot)	.77 g L^{-1} in H_2O at 100 ^oC	.004 g L^{-1} H_2O at 100 ^oC
Solubility (moles cold)	0.000154321 M L^{-1}	0.024969632 M L^{-1}
Solubility (moles hot)	0.000685871 M L^{-1}	0.010392766 M L^{-1}
Solubility Product (K_{sp})	$5.5 X 10^{-6}$	$1.8 X 10^{-11}$
Reactivity	High	Low
Form	Massive, sometime fibrous	Usually fibrous
Free Energy of Formation of Carbonate $\Delta G_o f$	- 64.62 kJ.mol^{-1}	- 19.55 kJ.mol^{-1}

Pozzolans, many of which are reactive siliceous and aluminous wastes, are also added to TecEco cements and strength gains result particularly if the hydraulic cement used releases calcium and hydroxide ions as does the setting of Portland cement whereby around 24 % (m/m) Portlandite is produced as part of the stoichiometry of hydration. The calcium alkali mobilises and reacts with the silica in pozzolans which is moderately soluble at higher pH's in a reaction known as the pozzolanic reaction. Not only are more CSH minerals produced in this reaction but surface hydrolysis followed by dehydration tends to bind grains of pozzolan together especially in tec-cements where higher pH's are likely during the early stages of hydration. Combined with the micro aggregate affect, it is advantageous to add pozzolans such as fly ash and more appears to be able to be added than with ordinary Portland cement concretes.

The use of heat, such as steam with or without additional pressure, is potentially useful for accelerated setting. Methods other than using steam for acceleration of a given mix include the use of alkalis, salts of strong acids and organic substances and many of these have also been investigated.

A body of work dating from the early thirties suggests that sulfates accelerate the reaction of free lime with pozzolans such as fly ash[lxxi,lxxii,lxxiii]. As the presence of sulfate is an advantage as a set regulator for the Portland cement component, accelerator for the magnesium oxide component, accelerator for silicification reactions and flocculation agent, commercial Portland cement containing a small percentage of ground gypsum is very suitable for blending in eco-cements.

The addition of sulfate as is generally the practice with Portland cements is preferable as the early formation of ettringite provides initial early setting strength but then retards the hydration of tri calcium aluminate, spreading the liberation of heat over a longer period. At this point in time it is considered that sulphates do not end up forming magnesium oxy sulphates and that they initially form ettringite and eventually end up in monosulfoaluminate hydrates. Further research will either confirm of reject this proposition.

Ph Changes

Important ramifications of the TecEco technology are the changes to the pH of concretes over time as a result of the concentration of water by magnesia as it hydrates, the consumption of alkalis like Portlandite by the pozzalanic reaction and the long term contribution to OH^- ion concentration (pH) by the enduring Brucite alkali.

Short Term Plastic Phase pH

A typical analysis of Portland cement shows total alkalis in the range .5 -1.5 mass%. Because of the presence of these alkalis the short term pH of ordinary Portland cement concretes (during the plastic and early hydration period) is higher than would be caused by lime produced as part of the hydration reaction and is usually around 12.7 -13.4 depending on the other alkalis and their concentration on the surface of the cement grains.

Magnesia as it hydrates has a strong water demand and is pulling water out of the system cement powders – water at the same time as reactions are producing hydroxide ions which as a result are concentrated or perhaps even supersaturated. As a consequence of this the short term pH during the plastic and early stages of tec-cement concretes is thought to be higher. Further evidence is the fact that tec-cement concretes exhibit significant early strength gain and this is likely to be another result of reducing the voids/paste ratios and possibly a more efficient pozzalanic reaction.

Long Term pH

In the long term long term the pH of Portland cement concretes still containing lime is controlled by it and the equilibria between it and CSH[lxxiv]. Portlandite or lime has an equilibrium pH of around 12.35 as determined in the calculation below:

$$Ca(OH)_2(s) \leftrightarrow \underset{x}{Ca^{2+}} + \underset{2x}{2OH^-}$$

$$K_{sp} = 5.8 \times 10^{-6} = [Ca^{2+}][PH^-]^2 = [x][2x]^2$$

Solving for x:

$4x^3 = 5.8/1000000$
$x^3 = (5.8/1000000)/4$
$x^3 = .0000014$
$x = 0.01118688942081397$
$[OH\text{-}] = 2x = 0.022374$
$pOH = -\log[.022374] = 1.650256$
$pH = 12.34974$

One problem with Portland cement concretes is that although the addition of pozzolans has many beneficial consequences, lime is removed by the pozzalanic reaction resulting in a drop in pH, drop in the Ca/Si ratio and potential destabilization of CSH. As long as there is CSH present the pH probably does not however fall below 11[lxxv]

In tec-cement concretes Brucite replaces Portlandite or lime and contributes to the maintenance of pH without necessarily a significant drop in the Ca:Si ratio in CSH. The pH controlled by Brucite is calculated below.

$Mg(OH)_2(s) \leftrightarrow \underset{x}{Mg^{2+}} + \underset{2x}{2\ OH^-}$
$K_{sp} = 1.8 \times 10^{-11} = [x][2x]^2$
Solving for x:
$4x^3 = 1.8/100000000000$
$x^3 = (1.8/100000000000)/4$
$x^3 = .0000000000045$
$x = 0.00016509636244473142$
$[OH\text{-}] = 2x = .000330193$
$pOH = -\log[.000330193] = 3.4812325$
$pH = 10.51876$

In tec-cement concretes, with the consumption of Portlandite, Brucite becomes the major contributor to pore water OH^-. Chemical and physical barriers are introduced preventing change and the Ca/Si ratio in CSH minerals is maintained. The pH becomes strongly influenced by the presence of $Mg(OH)_2$

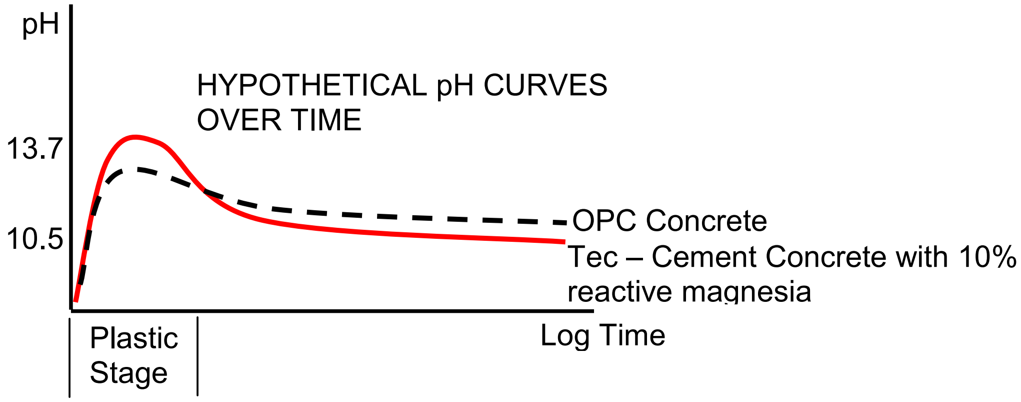


Figure 9 - Tec-Cement Concrete - Hypothetical pH Curves over Time.

A hypothetical pH over time plot for TecEco tec-cements is shown in Figure 9. The main outcomes are that reinforcing steel is kept passive and that delayed reactions such as the alkali aggregate reaction problem are alleviated[lxxvi] by reduced alkalinity.

Strength Development

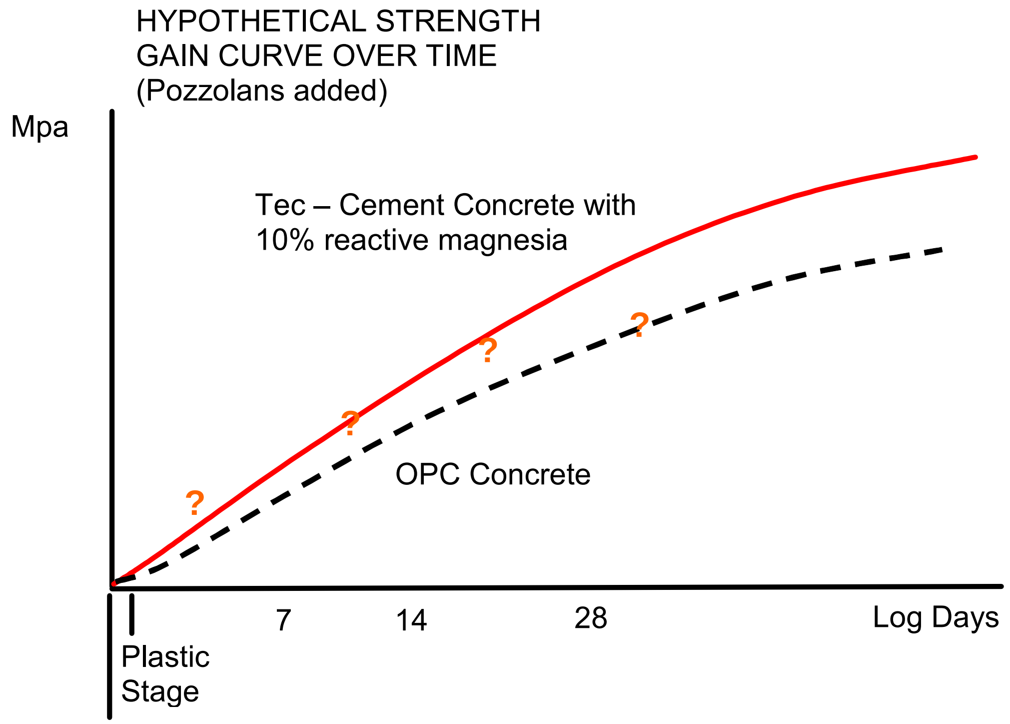


Figure 10 - Strength Development in TecEco Tec-Cement Concretes

TecEco tec-cements use less cement for the same strength development or conversely reach greater strengths with the same amount of cement. More importantly they appear to gain strength more rapidly even with added pozzolan due to the higher short term pH initiating what appear to be more affective pozzolanic reactions (See Short Term Plastic Phase pH on page 34) and lower voids paste ratios due due to the consumption of water by magnesia (See Figure 11 – Greater Density and Reduced Permeability due to the Consumption of Water in Tec-Cement Concretes on page 38).

As brucite is not as strong as CSH, the strength development in enviro-cements will depend on the proportion of brucite which in turn depends on the amount of reacative magnesia in the mix.

Eco-cements only gain strength as brucite absorbs CO_2 forming magnesite and other carbonates of magnesium such as hydromagnesite. Fortunately magnesium carbonates are generally stronger than calcium carbonates. They are harder and add microstructural strength due to their generally acicular shape.

As at the date of writing block formulations have been developed that easily reach the Australian standards of 8 mpa for lightweight walling and 15 mpa for ordinary blocks.

According to the building code AS/N25 4455:1997 a building material used in for example mud bricks must reach a standard of 2 mpa to be considered suitable for a load bearing structure. Virtually any eco-cement formulation will meet this standard.

Volume Changes

Volume Changes in Portland Cement

Portland cements change dimensionally over time. Stoichiometric (chemical[lxxvii]) and plastic shrinkage occur during the early stages of hydration. In the system water plus cement powder this is in the order of .05 – 1.5 %. Once rigidity develops drying shrinkage becomes more important.

Plastic shrinkage occurs through loss of water from the system water plus cement when and drying shrinkage occurs with the withdrawal of water from concrete in unsaturated air, whether this is due to loss of adsorbed water or intracrystalline water or both is not certain.

Creep occurs when concrete moves to relieve stress over time and is usually less than shrinkage.

Cracking, the symptomatic result of shrinkage, is undesirable for many reasons, but mainly because it allows entry of gases and ions reducing durability. Cracking can be avoided only if the stress induced by the free shrinkage strain, reduced by creep, is at all times less than the tensile strength of the concrete.

The amount and rate of shrinkage is reduced by a low water binder ratio and the resulting voids paste ratio.

Volume Changes in TecEco-Cements.

Chemical and Plastic Shrinkage

Magnesia as it hydrates increases in volume 116.96% forming Brucite which 44.65 % water. With the right proportions of magnesia to OPC the increase in volume is at the expense of volume lost through the chemical shrinkage, plastic shrinkage and loss of bleed water of the OPC component.

Water is required to plasticise concrete for placement, however once placed, the less water over the amount required for hydration the better. Magnesia rapidly removes water as it hydrates.

Less water results in greater density, less shrinkage and cracking and improved durability.

Concentration of alkalis and increased density result in greater strength.

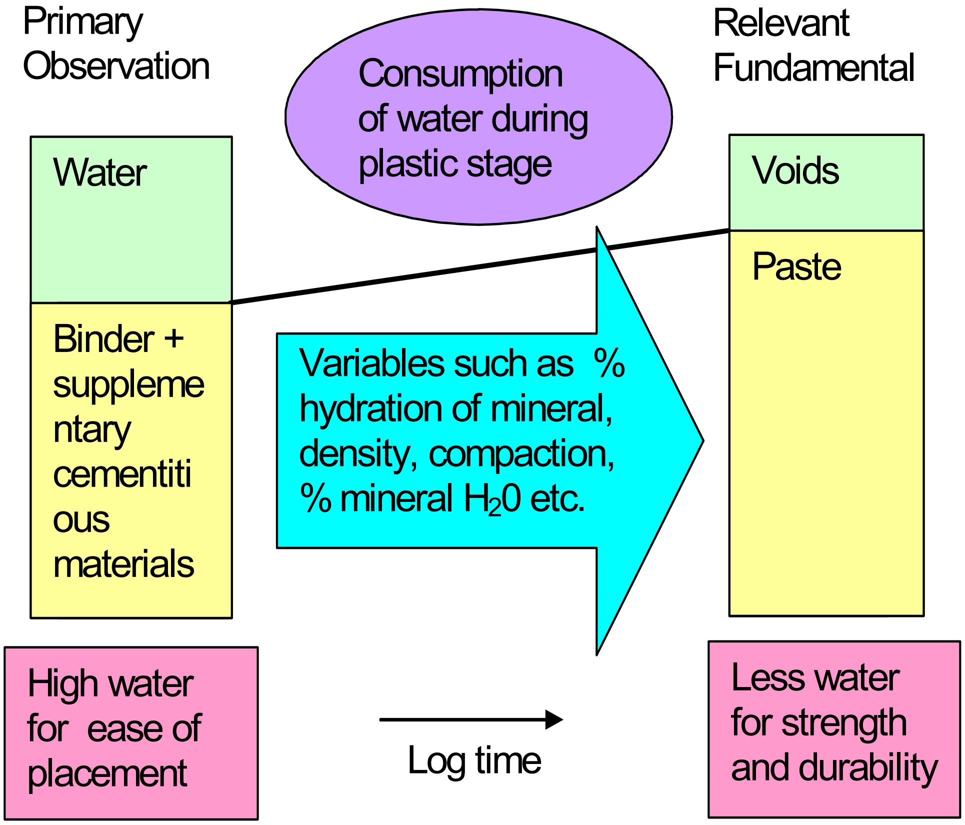


Figure 11 – Greater Density and Reduced Permeability due to the Consumption of Water in Tec-Cement Concretes

Hydration Changes

Consider the volume changes that occur when magnesia hydrates:

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

40.31 + 18.0 ↔ 58.3 molar mass

11.2 + 18 (l) molar volumes ↔ 24.3 (s) molar volumes[lxxviii]

Up to 116.96% solidus expansion depending on whether the water is coming from stoichiometric mix water, bleed water or from outside the system. In practice much less as the water comes from mix and bleed water.

To understand the possible volume changes consider two cases – the hydration of periclase or dead burned magnesia and the hydration of reactive magnesia in the context of open, closed and partially closed systems.

Hydration of Periclase or "Dead Burned Magnesia"

Although periclase is not used by TecEco and to be avoided, the volume change consequences are considered for comparative purposes.

If the hydration reaction for magnesia is slow as is the case with periclase or dead-burned magnesia produced as a result of high temperature thermal decomposition, it occurs after most of the free mixing water has been taken up by hydration of other cementitious minerals. For example, during the manufacture of ground Portland clinkers, the main minerals produced are tricalcium silicate (alite) and di calcium silicate (belite). Alite hydrates much more rapidly than belite but for both hydration proceeds much more rapidly than for the periclase component. As a result of this much of the free moisture is used up before hydration of periclase can proceed to completion. For the hydration reaction to proceed then some moisture must be made available from outside the system such as in a wet environment and absorbed by the cement mass over and above the original mixing water resulting in a net volume increase of 24.3 – 11.2 = 13 molar volumes (less the volume of whatever mixing water is still available from the original mix). A net expansion and cracking can occur.

Hydration of Highly Reactive Magnesia

If magnesia that is highly reactive is added after the calcining process required for the manufacture of most other cements such as Portland cement, the same hydration reactions occur much more rapidly. As a result the moisture is absorbed more rapidly, mainly from mix water and the excess water of convenience that would normally bleed from Portland cement concretes.

The system cement powders - water in affect closed as water is used by hydrating magnesia and no longer bleeds. Less plastic shrinkage due to water loss occurs. Less water results in densification.

The Chemically Determined Water Cement Ratio

$2\ C_3S + 7H \rightarrow C_3S_2H_4 + 3CH$

$428.48 + 126 = 332.24 + 74.08$ Water:cement ratio = .294

$2\ C_2S + 5H \rightarrow C_3S_2H_4 + CH$

$316.32 + 90 = 332.24 + 74.08$ Water:cement ratio = .284

MgO + H2O → Mg(OH)2

$40.31 + 18 \rightarrow 58.31$ Water:cement ratio = .45

Because different molar proportions of water are required for the hydration of di and tri calcium silicate, the water required for complete hydration will depend on the proportion of C_3S to C_2S and other ingredients. In the case of TecEco cements this will include the proportion of magnesia.

The amount of water in a mix will depend on the proportion of hydrating cement paste to the total mix. With 10% cement and 90% aggregates of various kinds this ratio is in the order of .25-30%. Practically cements are made with a larger content in the order of 10 – 15% water otherwise, even with plasticisers they would be too difficult to place.

Summary

Depending on where the water is coming from and proportion of magnesia to Portland cement it is possible to achieve no net chemical or plastic shrinkage or volume change.

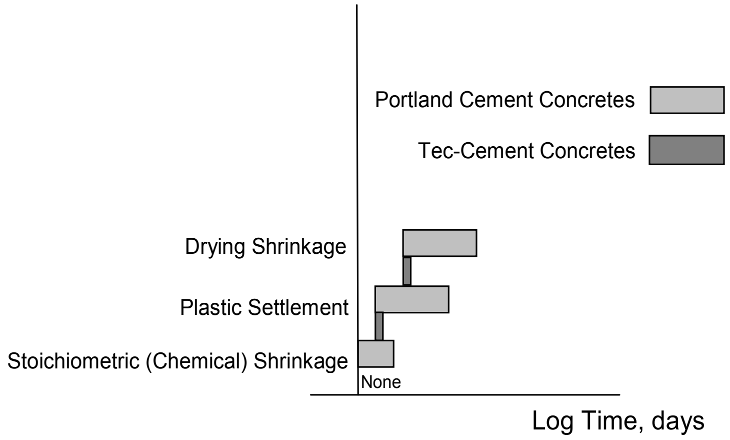


Figure 12 – Hypothetical Reduced Shrinkage in TecEco Cement Concretes

So far drying shrinkage has not been observed in tec-cement concretes.

Volume Changes on Carbonation

Carbonation of Portlandite proceeds relatively readily. Most texts maintain the carbonation reaction is one between ions in solution yet carbonation is observable in very dry conditions such as inside building in concrete that does not have an outside face. The transport of carbon dioxide is 10^6 times more rapid in air than in water and adherence to Le Chatelier's principal would also indicate dry conditions as the removal or water as a product would help the reaction

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \ (\Delta G_o f - 64.62 \ kJ.mol^{-1})$$

to proceed towards products (the right). The highly negative Gibbs free energy of the reaction indicates this should occur spontaneously.

Consider the molar volumes of the above reaction in dry air.

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

$$74.08 + 44.01 \leftrightarrow 100 \text{ molar mass}$$

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

18.22% shrinkage. Cracks may appear allowing further carbonation.

The Gibbs free energy for the reaction

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O \ (\Delta G_o f – 19.55 \ kJ.mol^{-1})$$

is also negative but nearly as much so and our observation is that carbonation is slower but that it mainly proceed by this route.

Consider the molar volumes of the above reaction in dry air.

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

58.31 + 44.01 ↔ 84.32 molar mass

24.29 + gas ↔ 28.10 molar volumes

15.68% expansion and densification of the surface preventing further ingress of CO_2 and carbonation.

Dimensionally Neutral Concretes over Time?

TecEco tec-cements do not bleed water as any excess is taken up by magnesia as it hydrates. From the above it can be concluded that with proper proportioning of a reactive magnesia OPC blend it is possible to minimise dimensional change due to chemical and plastic shrinkage (loss of water)

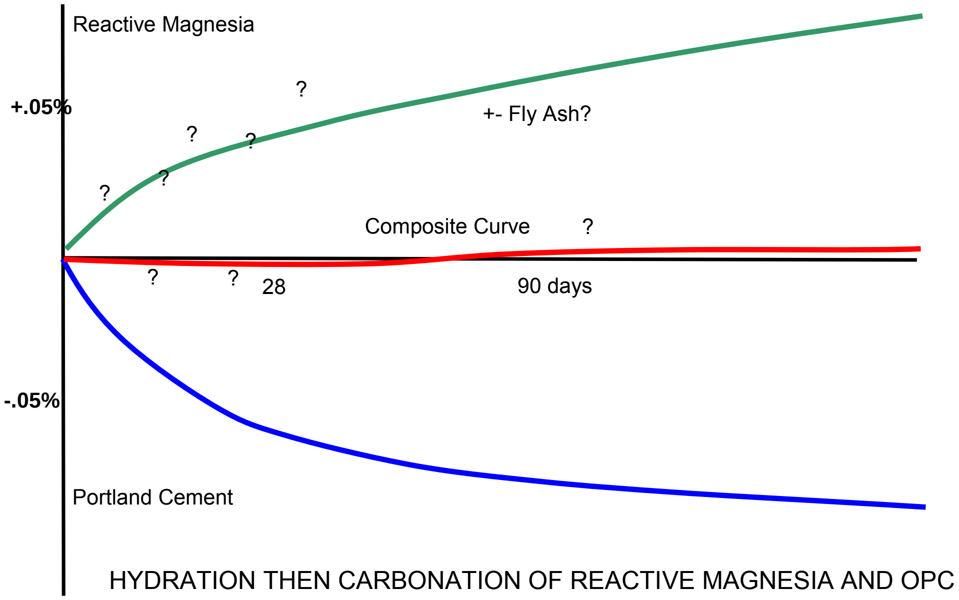


Figure 13 - Dimensionally Neutral Concretes?

At some ratio, thought to be around 90 mass% OPC and 10 mass% reactive magnesia volume changes cancel each other out.

Rheological Improvements

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

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

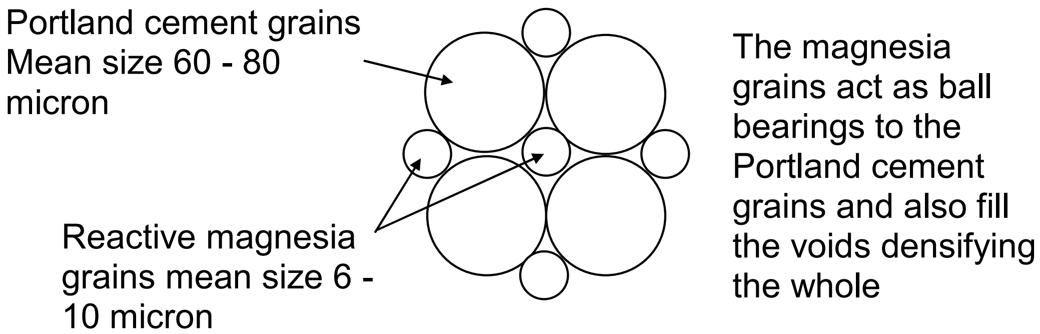


Figure 14. Nodal particle packing in TecEco cements. (Grains not necessarily rounded as depicted)

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

Durability

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

In Portland cement concretes Portlandite (lime) is responsible for a high pH in which iron or the insoluble black (Fe_3O_4) oxides of iron are more stable. Unfortunately lime relatively rapidly carbonates, the pH falls and other species prevail such as ferrous oxides that hydrate expansively and initiate corrosion. Portland cements also exhibit cracking from shrinkage that often exposes steel and from carbonation which tends to exacerbate the problem. The carbonation of brucite is generally less rapid (ΔG_r portlandite) = - 64.62 $kJ.mol^{-1}$, ΔG_r brucite = - 19.55 $kJ.mol^{-1}$) however this depends on the kinetic pathway[lxxix]. It is therefore considered that the pH will remain at lower levels of around 10.5 - 11 for a much longer period of time but only research will demonstrate this. The carbonation of brucite also tends to block off further carbonation - any carbonation that does occur tending to densify the surface and seal off further access by CO_2. The consequences are less corrosion of steel reinforcing due to maintenance of a relatively high pH (See Figure 15 on page 43) and less alkali aggregate and other problems associated with excessive alkalinity.

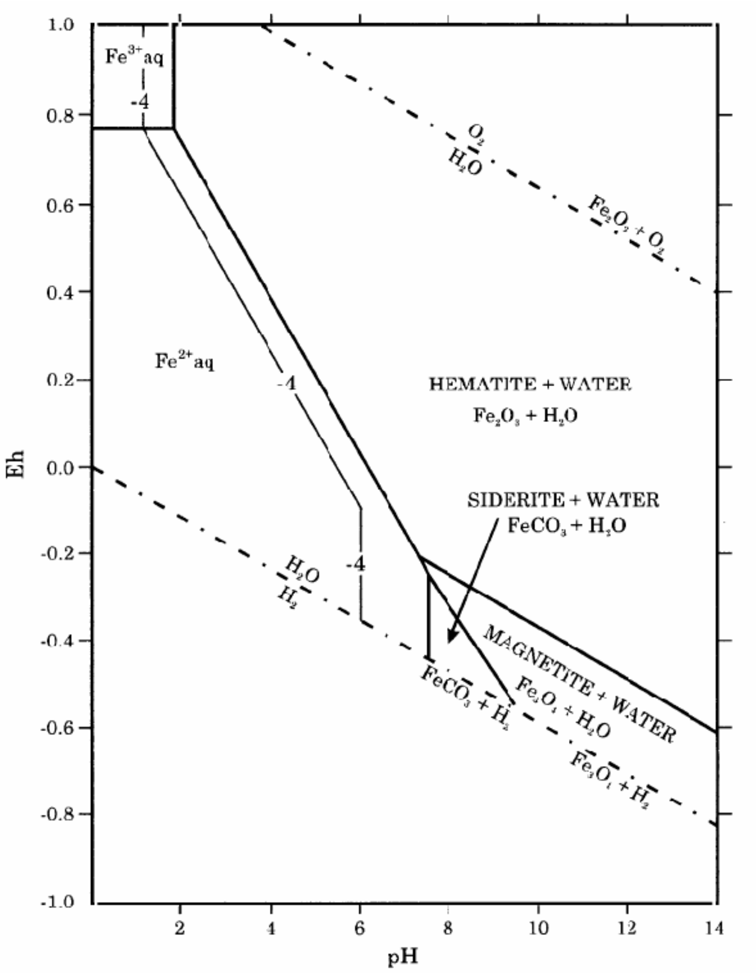


Figure 15. Eh-pH or Porbaix Diagram. The Stability Fields of Hematite, Magnetite and Siderite in Aqueous Solution; total dissolved carbonate = 10^2 M.

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

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

MATERIALS AVAILABILITY

The basic ingredients of TecEco cements are:

- Magnesium oxide
- Portland cement
- Pulverised fuel ash or similar pozzolanic material.

Magnesium is the eighth most abundant element in the earth's crust and the availability of magnesium ores to make magnesium oxide is not an issue in Australia and in most other parts of the world. Furthermore it is not necessary to use pure magnesite in all applications. Starting from magnesium silicates the sequestration potential is significant. (See Sequestration on a Massive Scale on page 23.)

Producing Reactive Magnesia

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

CONCLUSION

The built environment deserves far more attention in the debate on sustainability and is very important because of the huge materials flows involved.

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

As Fred Pearce reported in New Scientist[lxxxi] Magazine, “There is a way to make our city streets as green as the Amazon rainforest. Almost every aspect of the built environment, from bridges to factories to tower blocks, and from roads to sea walls, could be turned into structures that soak up carbon dioxide - the main greenhouse gas behind global warming. All we need to do is change the way we make cement”

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[ii] http://www.igbp.kva.se/cgi-bin/php/publications_books.show.php?section_id=48&article_id=105&onearticle=, download the summary from http://www.igbp.kva.se/cgi-bin/php/frameset.php)

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[viii] New Scientist, 19 July 1997, page 14.

[ix] According to the article *Cement and Concrete: Environmental Considerations* in Environmental Building News volume 2, No 2 – March/April 1993 researchers at the Oak Ridge National Laboratories (USA) put the figure at 1.24 tonnes of CO2 for every tonne of Portland cement.

[x] Pers comm. Dr Selwyn Tucker, CSIRO Department of Building Construction and Engineering, Melbourne

[xi] Pearce, F., "The Concrete Jungle Overheats", New Scientist, 19 July, No 2097, 1997 (page 14).

[xii] USGS figures extrapolated to 2004

[xiii] Dr Selwyn Tucker, CSIRO on line brochure at http://www.dbce.csiro.au/ind-serv/brochures/embodied/embodied.htm valid 05/08/2000

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[xvii] Anthropogenic – human produced

[xviii] Vancouver in 1976 and Istanbul in 1996.

[xix] In 1983 the United Nations appointed an international commission to propose strategies for "sustainable development" - ways to improve human well-being in the short term without threatening the local and global environment in the long term.The Commission was chaired by Norwegian Prime-Minister Gro Harlem Brundtland, and it's report "Our Common Future", published in 1987 was widely known as "The Brundtland Report."

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[xxvi] International patent number PCT/AU01/00077

[xxvii] Independent appraisals are downloadable from our website at www.tececo.com

[xxviii] Depending on the kinetic pathway.

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

[xxx] The neutralisation of Lime by pozzolans results in a drop in the Ca/Si ratio in CSH and potential brittleness (pers com Prof. Fred Glasser, University of Aberdeen)

[xxxi] Portland cement minerals and Brucite are the main binder minerals. A host of minor species also form and are also present.

[xxxii] 100% utilisation would reduce global CO_2 emissions in the order of 10% - 15%.

[xxxiii] With either the collection of CO_2 at source or the inclusion of carbon based fibres or both eco-cements can be net carbon sinks

[xxxiv] Hence the contemplated use for lightweight packaging.

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

[xxxvi] Chemical And Geologic Sequestration Of Carbon Dioxide, at http://www.netl.doe.gov/products/r&d/annual_reports/2001/cgscdfy01.pdf , page 7 valid 28/12/03.

[xxxvii] Chemical And Geologic Sequestration Of Carbon Dioxide, at http://www.netl.doe.gov/products/r&d/annual_reports/2001/cgscdfy01.pdf , page 1 valid 28/12/03.

[xxxviii] Chemical And Geologic Sequestration Of Carbon Dioxide, http://www.netl.doe.gov/products/r&d/annual_reports/2001/cgscdfy01.pdf at page 8 valid 28/12/03.

[xxxix] Seifritz, W. (1990). Nature, 345, 486.

[xl] Lackner, K., Wendt, C., Butt, D., Joyce Jr., E., and Sharp, D. (1995). Energy, 20, 1153-1170.

[xli] Walters, R. P., Chen, Z. Y., Goldberg, P. M., Lackner, K. S., McKelvy, M. J., and Ziock, H. (1999). Mineral carbonation: A viable method for CO2 sequestration.

[xlii] Morgantown, WV: National Energy Technology Laboratory, US DOE: http://www.fetc.doe.gov/products/ggc

[xliii] Dahlin, D. C., O’Connor, W. K., Nilsen, D. N., Rush, G. E., Walters, R. P., and Turner, P. C. (2000). A method for permanent CO2 sequestration: Supercritical CO2 mineral carbonation. 17th Annual International Pittsburgh Coal Conference.

[xliv] O’Connor, W. K., Dahlin, D. C., Nilsen, D. N., Walters, R. P., and Turner, P. C. (2000). Proceedings of the 25th International Technical Conference on Coal Utilization & Fuel Systems, 153-164.

[xlv] Fauth, D. J., Baltrus, J. P., Knoer, J. P., Soong, Y., Howard, B. H., Graham, W. J., Maroto-Valer, M. M., and Andrésen, J. M. (2001). Prepr. Symp. Am. Chem. Soc., Div. Fuel Chem., 46(1), 278.

[xlvi] Equilbrium at one atmosphere is 540 oC. Waste heat could be used.

[xlvii] Note that as yet a full life cycle analysis has not done. As a result CO_2 process emissions have not been taken into account.

[xlviii] We may also be increasing the overall size of our atmosphere!

[xlix] A good reason to move to performance based standards.

[l] Ramachandran V. S., (1981) *Concrete Science*; Heyden & son, Ltd., pp 356-365.

[li] Blaha, J, *Kinetics of Hydration of Magnesium Oxide in aqueous Suspension, Part1 – Method of Measurement and Evaluation of Experimental Data. Ceramics – Silikaty*, 39 (2), 1995, 41-80.

[lii] Reactive magnesia is essentially amorphous magnesia produced at low temperatures and finely ground.

[liii] Neville, A. M. *Properties of Concrete*, 4th Ed. Pearson Prentice Hall, England, 2003, page 52.

[liv] Glassy MgO is amorphos and very reactive.

[lv] Taylor H.F.W, *Cement Chemistry*, 2nd Edition, Thomas Telford, 1998 p2, paragraph 4.

[lvi] Taylor, H. F. W., *Cement Chemistry*, 2nd Edition, Thomas Telford, 1998, p42, paragraph 3.

[lvii] Taylor, H. F. W., *Cement Chemistry*, 2nd Edition, Thomas Telford, 1998 p42, paragraph 4.

[lviii] After table 2.3 Taylor, H. F. W., *Cement Chemistry*, 2nd Edition, Thomas Telford, 1998 p43

[lix] Jackson, Peter J, *Portland Cement: Classification and Manufacture*. Lea's Chemistry of Cement and Concrete, fourth edition ed. Peter C Hewlett. Arnold, 1988
, Chapter 2, page 31

[lx] Biczok Imre, *Concrete Corrosion and Concrete Protection*, Chemical Publishing Company, Inc. N.Y. 1967 at page 69.

[lxi] Biczok Imre, *Concrete Corrosion and Concrete Protection*, Chemical Publishing Company, Inc. N.Y. 1967 at page 150.

[lxii] Richardson, Mark G. *Fundamentals of Durable Reinforced Concrete* Spon Press, 2002. page 198.

[lxiii] Beaudoin J. J. Ramachandran and V.S Feldman R. F. *Impregnation of Magnesium Oxychloride Cement with Sulfur*, Am. Ceram. Soc. Bull. 56 424 (1977) at page 424.

[lxiv] See Blezard, Robert G. *The History of Calcareous cements*, Lea's Chemistry of Cement and Concrete, fourth edition ed. Peter C Hewlett. Arnold, 1988.

[lxv] Ramachandran V. S., Concrete Science, Heydon & Son Ltd. 1981, p 358-360.

[lxvi] Much water in concretes is arguable not "free"

[lxvii] If CO_2 is collected at source and/or waste carbon based materials such as fibres are included.

[lxviii] Blocks have been made with up to 90% fly and bottom ash.

[lxix] In 1867 a French engineer Stanislas Sorel who invented magnesium oxychloride cement realised that the new materials had an excellent bonding capacity, enabling the binding of various organic and inorganic aggregates.

[lxx] The equilibrium pH of finely ground Brucite in water is 10.52.

[lxxi] Steopoe, A (1935b) *Uber die Einwirkung von Magnesiumhydroxyd auf erharteten Zement*, Tonindustric Ztg. No. 64

[lxxii] Malquori G, Spadana A., *Azione combinata del gesso e dela calce sui materials pozzolanici*, La Ricerca Scientifica 1936; 185 – 91

[lxxiii] Gani, M.S.J., Cement and Concrete, Chapman Hall 1997, p92.

[lxxiv] Glasser F. P. *Chemistry of Cement Solidified Waste Forms* in Chemistry and Microstructure of Solidified Waste Forms, ed Spence Roger D.Lewis Publishers. 1992, Page 17.

[lxxv] Glasser F. P. *Chemistry of Cement Solidified Waste Forms* in Chemistry and Microstructure of Solidified Waste Forms, ed Spence Roger D.Lewis Publishers. 1992, Page 18.

[lxxvi] Brucite also absorbs some of the more mobile alkalis.

[lxxvii] The author is still looking for a good analysis of chemical shrinkage in Portland cement.

[lxxviii] The molar volume ($L.mol^{-1}$)is equal to the molar mass ($g.mol^{-1}$) divided by the density ($g.L^{-1}$).

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

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

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