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.

The Properties of Reactive Magnesia - Portland Cement - Pozzolan Blends

A John W Harrison, B.Sc. B.Ec. FCPA.
Managing Director and Chairman, TecEco Pty. Ltd.
497 Main Road, Glenorchy TAS 7010. Australia.

TecEco Pty Ltd have demonstrated that reactive magnesium oxide, a hydraulic cement such as Portland cement and usually a pozzolan can successfully be blended together and result in improvements in sustainability, strength and many other properties of concretes.

This article summarises what is know so far about concretes made using the new cement.

Keywords: Abatement, tec-cement, eco-cement, sustainability, sequestration, CO_2, brucite ($Mg(OH)_2$), durability, reactive magnesium oxide, 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, emissions.

Introduction

Sustainability

Vitrified and calcined minerals and their derivatives are the main materials used to construct the built environment which is our footprint on earth.

Globally around 2 billion tonnes of calcined minerals (cement, lime and magnesia) are produced annually[1]. Portland cement is by far the biggest proportion and production is in the order of 1.85 billion tonnes[2]. The largest producers are China at over 500 million tonnes[1] followed by India at over 111[3] million tonnes. The figures for vitrified clays are substantial but unknown.

TecEco estimate that buildings and infrastructure account for over 70% of anthropogenic materials flows and the built environment therefore represents a huge opportunity for sustainability[4].

Apart from wood, steel and aluminium, the main materials used in construction are concretes and vitrified clays. Concretes are by far the largest component and in Australia for example contribute more embodied energy than any other material to buildings[5].

The manufacture of vitirifed clays and concretes both release process emissions and in the case of calcined materials used in concretes, chemically bound CO_2.

$$\mathbf{MCO_3 \underset{\Delta}{\rightarrow} MO + CO_2}$$

Fuel oil, coal and natural gas are mainly directly or indirectly burned to produce the energy required for vitrification of clays and calcining of metal carbonates responsible for around 12% -15% of global anthropogenic CO_2. Portland cement alone is generally agreed to contribute around 10%[6].

---

[1] USGS Mineral Year Books 2002. 116 million tonnes lime, 10.9 million tonnes magnesia, 1,900 million tonnes Portland cement (extrapolated from 2001 figure)

[2] G. M Sabnis, *Concrete Constituent Materials*, Proceedings Indian Concrete Institute, International Symposium on Innovative World of Concrete, Pune India 19-21 September, 2003.

[3] A K Jain, *Status of Cement Industry and Future Changes*, Proceedings Indian Concrete Institute, International Symposium on Innovative World of Concrete, Pune India 19-21 September, 2003.

[4] According to the Australian Federal department of Industry Science and Tourism buildings alone account for some 30 % of the raw materials we use. Australian Federal department of Industry Science and Tourism, *Environmental & Economic Life Cycle Costs of Construction, 1998 - Detailed Discussion Paper*, (section 2 - page 8)

[5] Pers communication Dr Selwyn Tucker, CSIRO.

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

Concretes already have high thermal capacity and can supply essential thermal mass to buildings. With the use of TecEco technology, concretes will offer greater opportunities for sustainability with:

- Lower binder aggregate ratios
- Greater durability
- Lower embodied and lifetime energies
- Waste utilisation and recycling
- Abatement and sequestration

The TecEco 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 pozzalanic 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.

International patents[7] 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[8], 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[9], 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 two main formulation strategies have so far been defined:

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

  Contain more Portland cement than reactive magnesia which hydrates in the same rate order as Portland cement forming brucite which densifies, using up water

---

[7] International patent number PCT/AU01/00077
[8] Independent appraisals are downloadable from our website at www.tececo.com
[9] Using a new kiln that combines calcining and grinding at the same time patented by TecEco.

reducing the water binder ratio 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.

- 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.

Ramifications of the Technology and Potential Uses.

The new cements are applicable to a wide range of uses including

- As a stabilising agent in the production of earth buildings.
- Mortars, 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 mortars, renders, tile cements, 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.

Properties

Improvements in the properties of concretes will 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.

Lower Long Term pH?:

As Portlandite is removed the pH becomes governed by the solubility of brucite which has an equilibrium pH of around 12.38, allowing the stabilization of many heavy metals and a wider range of aggregates to be used without AAR problems. Carbonation is slower and the pH remains over high enough to keep Fe FeO and Fe_3O_4 stable for much longer.

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 slightly and take up water, whilst calcium minerals tend to shrink. Blended in the right proportions, concretes can be made that are dimensionally neutral over time.

More Sustainable:

Tec-cements generally 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 reducing replacement energy/emissions/costs. Eco-cements reabsorb chemically released CO_2.

Insulating Properties / High Thermal Mass / Low Embodied Energy:

Eco-cement products also containing materials that improve insulation will be favored for energy conserving buildings.

Recyclable:

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

A Fire Retardant:

Brucite and magnesite are both fire retardants. TecEco cement products put fires out by releasing CO2 at relatively low temperatures.

Low Capital Cost:

No new plant and equipment is required. With economies of scale TecEco cements should also be cheaper.

Lower Construction Costs:

Greater durability, lower water/binder ratio resulting in less binder for the same strength, no plasticiser, lower in the bag costs, reduced crack control costs, reduced costs of controlling bleed water, no under plastic necessary, easier placement and better finishing, use of a wider range of aggregates reducing transport costs, lower or no carbon taxes.

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 more ideal pH curve to Portland cement concretes. As the hydration of magnesia takes up a lot of water (58.3% 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 the equilibrium pH of brucite in water which is 10.38.

Brucite maintains the pH of concretes for much longer periods than Portlandite as it is far less reactive. For most kinetic pathways it carbonates much less readily[10] (ΔG_r portlandite) = - 64.62 $kJ.mol^{-1}$, ΔG_r brucite = - 19.55 $kJ.mol^{-1}$), 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 more rapid strength development and this is probably due to a lower water/binder ratio, greater density and more effective silicification reactions including the pozzalanic reaction during the early plastic stage whilst the pH is elevated.

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 hence reactivity of brucite, results in greatly reduced reactivity. Reduced reactivity results in the virtual elimination of delayed reactions and corrosion as well as resistance to salts.

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 less water loss and in appropriate proportions the expansion of magnesium minerals balancing the slight shrinkage of Portland cement concrete.

More flyash ground blast furnace slag and other supplementary materials can be added to advantage and sustainability is improved by reduced binder/aggregate ratios, longer life and lower emissions.

Eco-Cements

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

[10] Depending on the kinetic pathway.

In porous or semi porous materials such as bricks, blocks, pavers, mortars and renders, 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-cements 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[11][12]. 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[13] and will hold a large proportion of waste.

The Importance Of The Technology

The TecEco technology offers tremendous scope for the development of a new class of durable, environmentally friendly mineral binders. The low net CO_2 emissions, low temperature setting, lower pH, ability to be formulated as an all-in-the-bag mix, salt and corrosion resistance, excellent rheology, prevention of delayed reactions, dimensional stability, superior bonding to most materials and adjustable setting times will favour more widespread use.

It took a long period for the impact of Smeaton's experiments in 1759 to occur and lime pozzolan mixtures continued to predominate for many years. Joseph Aspidin only did his experiments in the 1820's and it was not until the 1840's that Portland cement started to be used in quantity.

TecEco cements were conceived at the end of the last century and have taken only four years to evolve to the formulations now being tested. Most developed are eco-cement formulations for fly ash bricks, blocks and pavers and to date both the 8 and 15 mpa Australian standards have been met. Blocks are already being test marketed and have less than half the emissions that would come from the equivalent Portland cement product.

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[14]. They can contain a high proportion[15] of wastes such as fly ash, silica fume, sewerage ash, ground vitrified iron blast furnace slag, rice husk ash or even red mud. Lower embodied energies, greater durability and high thermal capacity make eco-cements very sustainable and extremely useful as a potentially low cost building material compared to materials containing only Portland cement.

The built environment including infrastructure offers tremendous potential for sequestration as it is our footprint on the earth. Now that more and more nations are ratifying the Kyoto

---

[11] 100% utilisation would reduce global CO_2 emissions in the order of 10% - 15%.
[12] 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
[13] Hence the contemplated use for lightweight packaging.
[14] If CO_2 is collected at source and/or waste carbon based materials such as fibres are included.
[15] Blocks have been made with up to 90% fly and bottom ash.

Protocol laboratories around the world are examining alternative building materials and looking for ways to improve existing materials as a means of sequestering carbon and reducing the impact of potential CO_2 taxes and for incorporating or encapsulating waste. TecEco cements are a major contender and will be more economic in the long run and better for some purposes than Portland cements. The project is well advanced and various trials of tec-cements are also now in progress.

During the period of development of Portland cements the material has become progressively more reactive, requiring the addition of set regulators such as gypsum. Early forms 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[16]. 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[17]. It is possible the use of small substitutions of reactive magnesia for Portland cement will eliminate the problem of dead burned metal oxides in cements as hydration of concretes is terminated within a year or so by the removal of water and the long term pH is lower.

The most noticeable trend in concretes in the last twenty years or so has been the inclusion of supplementary cementitious materials such as flyash and ground blast furnace slag. Such materials tend to delay early strength development however which is also a requirement with the result that not as much is used that could be for greater sustainability. TecEco tec-cements have exhibited higher early strength and address this major issue.

Durability whether expressed in terms of carbonation, corrosion of steel, salt attack or delayed reactions is another 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 dry out internally much earlier and have a lower long term pH.

Shrinkage is another problem that may well be overcome using the technology and this is because moisture is expansively internally consumed and with appropriate blending, concretes, dimensionally neutral over time, can be formulated.

For many product areas such as toxic and hazardous waste immobilisation the chemistry of TecEco cements is sufficiently well defined. All that is required for more widespread adoption by technical umpites such as engineers and architects for construction generally is more engineering research to quantify properties.

---

[16] Blezard, Robert G. *The History of Calcareous cements*, Lea's Chemistry of Cement and Concrete, fourth edition ed. Peter C Hewlett. Arnold, 1988.
[17] Ramachandran V. S., Concrete Science, Heydon & Son Ltd. 1981, p 358-360.