TecEco Short Form Technical Summary

TecEco have established that low lattice energy MgO will hydrate in the same time frame as other components of modern hydraulic binders and has a wide and important role blended with them. The most common hydraulic cement is Portland cement (PC) and TecEco call its formulations with Portland cement tec-cements eco-cements or enviro-cements according to the degree of replacement of PC by magnesia and the type of concrete produced. Readers should consult the TecEco website www.tececo.com for voluminous details of his work as only a brief summary is possible here.

Magnesite is a naturally occurring magnesium carbonate ore and needs to be calcined to provide MgO (magnesia or magnesium oxide) in the same way as lime is calcined to make OPC, but at a much lower temperature and therefore more efficiently. Magnesia also has to be ground, but is softer and easier to grind than OPC clinker.

TecEco theorised that Portlandite and water are responsible for most of the problems of pre-mix concrete, In his view Portlandite is too soluble, mobile and reactive. It carbonates, reacts with Cl^- (chlorine) and SO_4^{--} (sulfate) and being soluble can act as an electrolyte. He also considered that if some way could be found to internally consume the significant amounts of water added to concrete in excess of that required for hydration, such as by pump operators and finishers, the material would be not only stronger but much more durable.

According to his invention Portlandite is generally removed using the pozzolanic reaction and replaced with magnesia which hydrates to Brucite and hydrates of Brucite, consuming significant water, adding strength for up to about 10% addition and increasing durability.

TecEco demonstrated that the hydration reactions of magnesia are not only independent of other reactions in Portland cement but that they occur sufficiently rapidly to not cause dimensional distress.

Brucite and Brucite hydrates are much more stable alkalis than Portlandite, which is produced by the hydration of di and tri calcium silicate in Portland cement. They therefore provide long term pH control, essential for the durability of concretes and the immobilisation of heavy metals that occur in waste streams.

One ramification of the technology that has received considerable publicity around the world is that the Brucite in eco-cements is encouraged to further carbonate in porous materials which results in the sequestering of CO_2.

Portland cement concretes are already a relatively sustainable material. With low cost and high thermal capacity they supply essential thermal mass to buildings. With the advent of the TecEco technology, concretes will become even more sustainable with lower binder to strength ratios, greater durability, waste utilisation and sequestration in the case of eco-cements.

The magnesia used should be as reactive as is commercially feasible to prevent risk of delayed hydration. Suitable pozzolans include industrial wastes such as fly ash and ground granulated iron blast furnace slag as well as a large range of less well known industrial wastes.

The affect of composition and porosity on strength is shown in Figure 1.

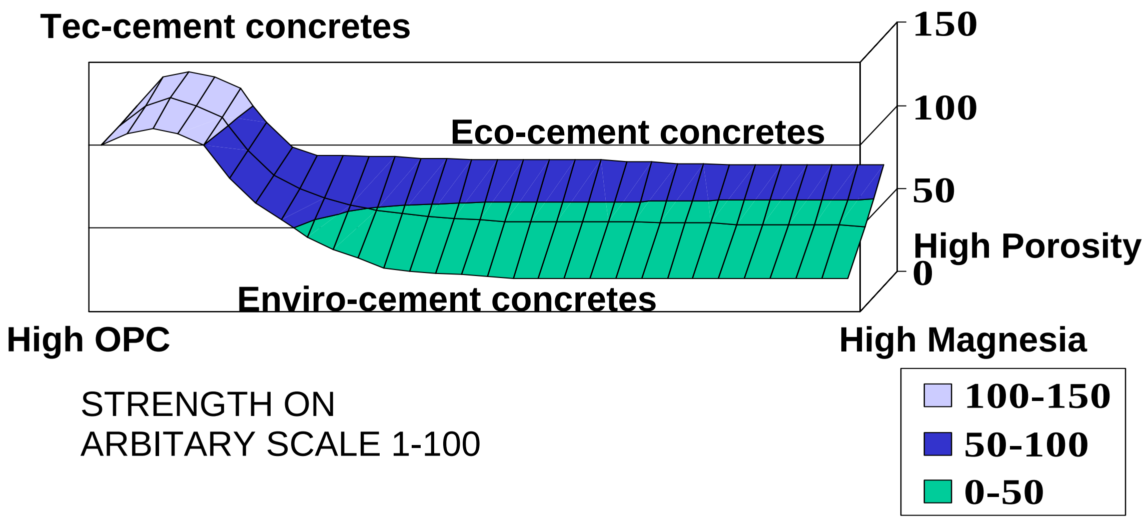


Figure 1 –TecEco Cement Concrete Types Relative to Porosity and Magnesia Content

Three main formulation strategies have so far been defined:

Tec-cements (5-15% MgO, 85-95% OPC)

Tec-cements contain more Portland cement than reactive magnesia. Reactive magnesia hydrates in the same rate order as Portland cement forming Brucite and Brucite hydrates which use up water reducing the voids:paste ratio, increasing density and possibly raising the short term pH resulting in more effective reactions with pozzolans. After all the Portlandite has been consumed Brucite controls the long term pH which is lower and due to its low solubility, mobility and reactivity results in greater durability.

Other benefits include improvements in density, strength and the introduction of a shear thinning property to rheology, reduced permeability and shrinkage and the use of a wider range of aggregates many of which are potentially wastes without reaction problems.

Eco-cements (15-95% MgO, 85-5% OPC)

Eco-cements contain more reactive magnesia than in tec-cements. Brucite in porous materials carbonates forming stronger fibrous mineral carbonates and therefore presenting huge opportunities for waste utilisation and sequestration.

Enviro-cements (5-15% MgO, 85-95% OPC)

Enviro-cements contain similar ratios of MgO and OPC to eco-cements, but in non porous concretes Brucite does not carbonate readily. Higher proportions of magnesia are possibly most suited to toxic and hazardous waste immobilisation and when durability is required. Strength is not developed quickly or to the same extent.

The new cements are suitable for a wide range of uses including any purpose for which lime or Portland cement are currently used.

Some TecEco tec-cement formulations will result in less cement being required, easier placement and finishing, elimination of shrinkage and bleeding, faster strength gain and the use of a wider range of aggregates reducing transport costs. Greater strength, less shrinkage and cracking and greater durability given adequate engineering back up should result in widespread use. Eco-cements will also become more important with the introduction of carbon trading and rise in the real price of carbon.

No new plant and equipment is required to manufacture the new cements although John Harrison, the inventor says he would prefer to use a new kiln he has designed that captures CO_2. With the resulting improvement in efficiency, he expects the cost of magnesia to fall below that of PC.

There are obvious advantages of including more stable alkalis or carbonates in cements so perhaps it is time to bury the dogma regarding magnesia and rewrite all cement standards so that they only contain a performance based test such as in ASTM C 150 and ASTM C 595M where autoclaving is required. No special comment should be necessary regarding reactive magnesia which would then be classed as a supplementary cementitious material.

Tec-Cement Concretes

Tec-cements concretes have a relatively low proportion (5-15%) of reactive magnesia added and this hydrates internally, consuming water and adding strength in according to Duff Abrams law when blended for example with Portland cement.

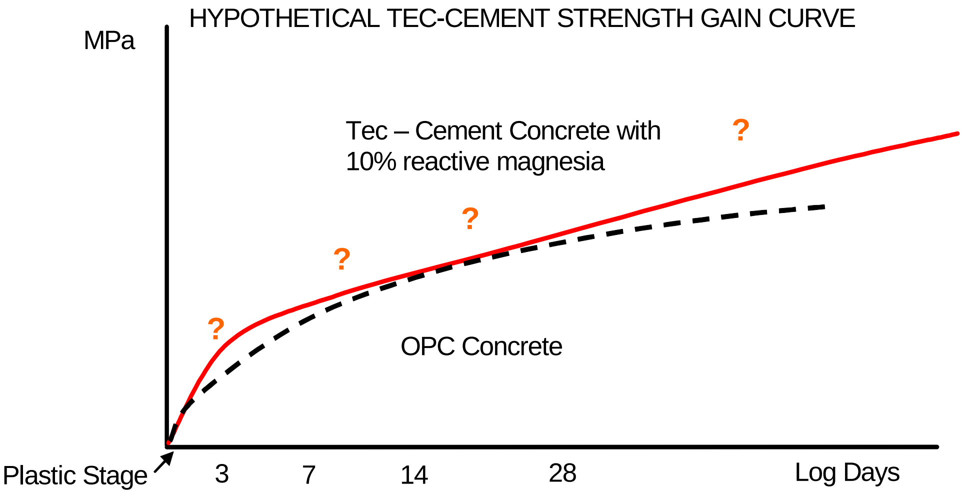


Figure 2 - Representative Strength Development Curve for Tec-Cement Concretes

The water consumption stoichiometry is variable but involves the formation of still to be characterised Brucite hydrates:

$$MgO\ (s) + H_2O\ (l) \leftrightarrow Mg(OH)_2.nH_2O\ (s)$$

One consequence of water removal is less bleeding.

The comparatively high and fast strength development is probably due the interaction of a number of factors. Most likely are:

- More and stronger silicification reactions including a more effective pozzolanic reaction during the early plastic stage whilst the pH is possibly elevated.
- A lower voids: paste ratio as a result of improved rheology due to better particle packing, some surface charge affects and high consumption of water by reactive magnesia as it hydrates.
- Slow release of water by hydrated Brucite gels ($Mg(OH)_2.nH_2O \rightarrow Mg(OH)_2$) resulting in more complete hydration reactions of PC.
- The formation of magnesium aluminium hydrates analogous to the hydrogarnets sometimes formed in Portland cement concretes with insufficient gypsum.

Tensile strength is also improved in the first 15-25 days and this is probably the result of both more rapid early strength development and a change in the surface charge of the magnesia added from positive to negative at pH 12

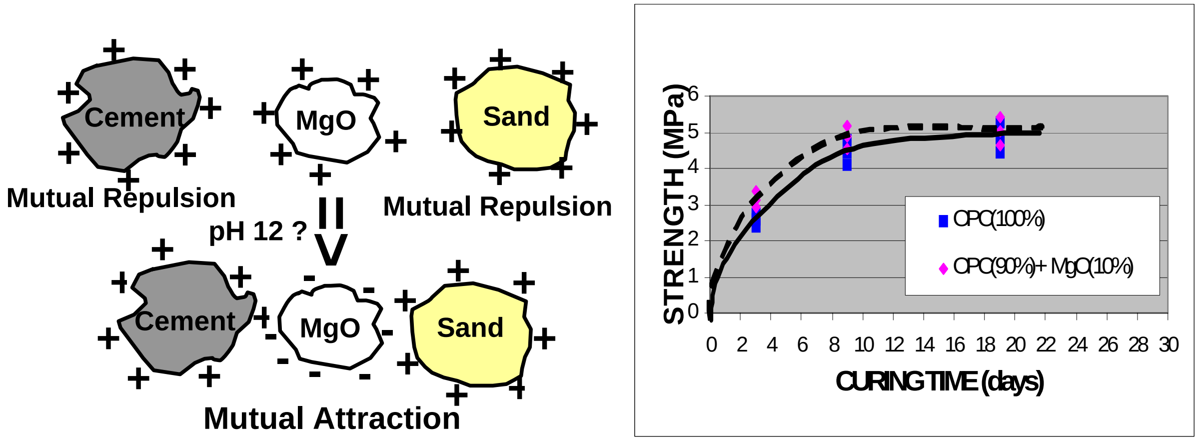


Figure 3 - The Affect of pH on the Surface Charge of Magnesia

There is also calorimetric evidence of earlier strength development (See Figure 4 - Calorimetric Evidence of Early Strength Gain).

Removal of Portlandite and replacement with a more stable alkali is central to the theory of tec-cements and they therefore usually also contain a pozzolan which reacts with the Portlandite released as di and tri calcium silicate hydrate and forms more Pozzolanic calcium silicate hydrates (PCSH).

Noticeable from the moment water is added is the improved rheology. This is due to the lubricating affect of the smaller magnesia particles and their packing with other components as well as the introduction of a shear thinning effect. The shear thinning effect is due to the influence of the negative magnesium ion in solution on water which is a polar molecule (See Figure 3).

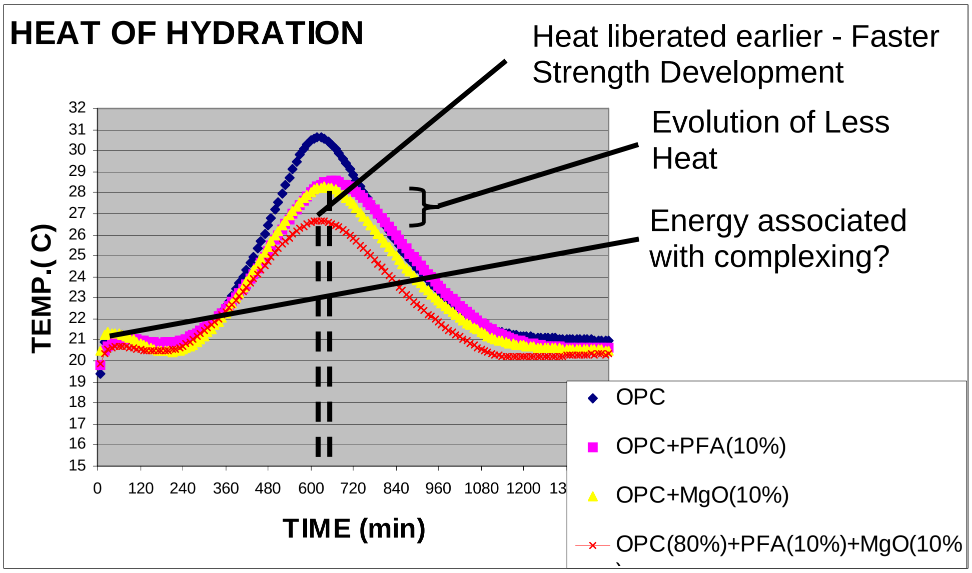


Figure 4 - Calorimetric Evidence of Early Strength Gain

As a consequence of the removal of Portlandite using the pozzolanic reaction and replacement by Brucite, tec-cement concretes have a different pH curve to Portland cement concretes with or without added pozzolan. As the hydration of magnesia takes up a lot of water (Brucite is 44.65 mass% water; Brucite hydrate gels contain even more water) and because tec-cement concretes do not bleed as much, 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 which has an equilibrium pH of 10.52 and CSH which has an equilibrium pH of 11.2 and remains somewhere between.

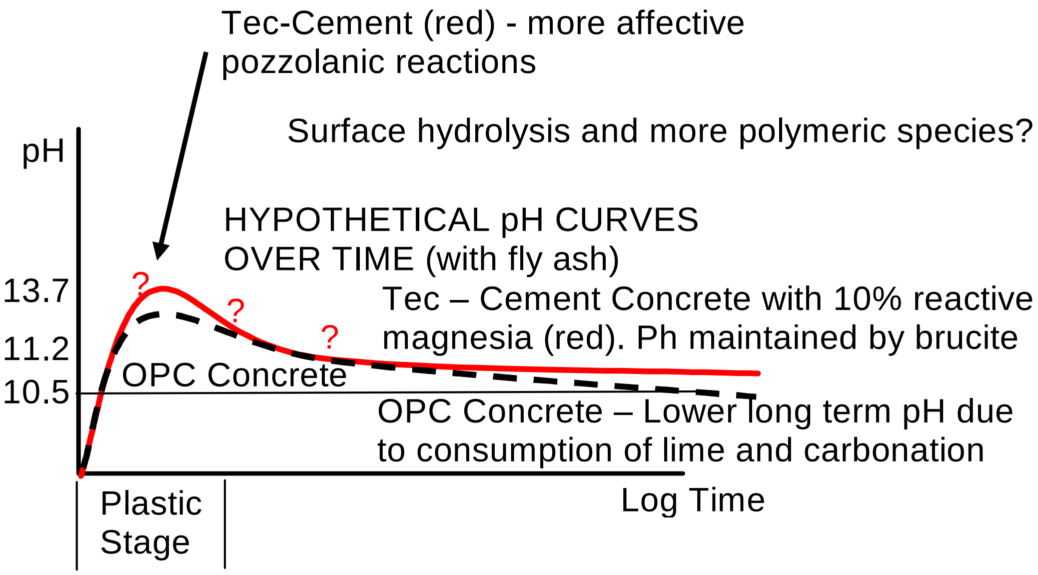
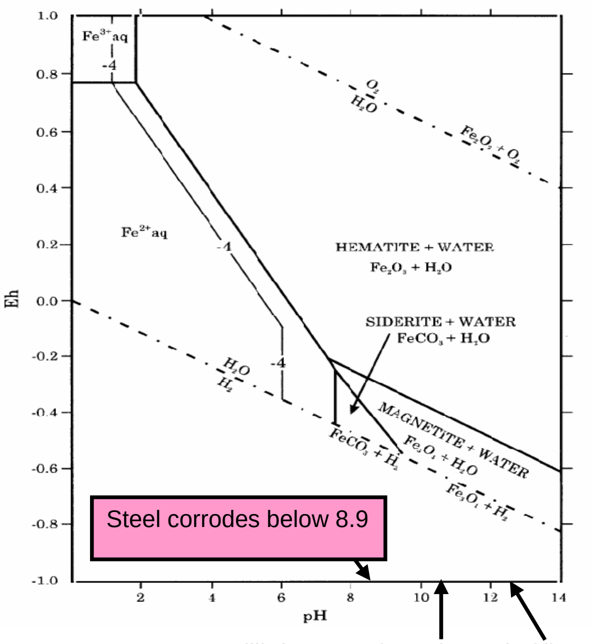


Figure 5 - Theoretical pH Curve for a Tec-Cement Concrete

For most kinetic pathways Brucite carbonates much less readily (ΔG_r Portlandite → calcite = - 64.62 kJ.mol^{-1}, ΔG_r Brucite → nesquehonite = - 38.73 kJ.mol^{-1}). The equilibrium pH is still however at a sufficiently high level for steel to remain passive[1] and for the stability of calcium silicate hydrates[2]. It is thought that dense concretes made using TecEco formulations should maintain reducing ion free conditions and a pH over around 8.9 required for the long term survival of steel indefinitely.

In TecEco cements the long term pH is governed by the low solubility and carbonation rate of Brucite and is much lower at around 10.5 -11, allowing a wider range of aggregates to be used, reducing problems such as AAR and etching. The pH is still high enough to keep Fe_3O_4 stable in reducing conditions.



Steel corrodes below 8.9

Equilibrium pH of Brucite and of lime

Eh-pH or Pourbaix Diagram
The stability fields of hematite, magnetite and siderite in aqueous solution; total dissolved carbonate = 10^{-2}*M.*

Figure 6 - Pourbaix Diagram Showing pH Stability Introduced by Brucite

The removal of excess water by magnesia as it hydrates has a number of other consequences. Bleeding and the introduction of associated problems such as efflorescence due to lime, freezing of bleed water and weaknesses such as interconnected pore structures and high permeability do not appear to occur as much.

Tec-cement concretes tend to dry out from the inside due to the water demand of magnesia as it hydrates and combined with a lower long term pH, density and the low solubility and reactivity of Brucite, improved durability results.

Brucite does not react with salts because it is a least 5 orders of magnitude less soluble, mobile or reactive than Portlandite. Sulfates, chlorides and other aggressive salts have no effect and delayed reactions do not occur. The Ksp of Brucite = 1.8 X 10^{-11} is much less that that of Portlandite is at 5.5 X 10^{-6}.

The advantages of using quick setting and convenient Portland cement such as ambient temperature setting, easy placement and strength are not diminished however shrinkage is reduced, if not eliminated, due to low water loss. In appropriate proportions the expansion of magnesium minerals balances the slight stoichiometric shrinkage of Portland cement concrete eliminating cracks and reducing porosity. Blended in the right proportions, concretes can be made that are dimensionally neutral over time.

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[1] As Fe_3O_4 rather than oxides such as Fe_2O_3 or FeO_2 which tend to hydrate and are dimensionally unstable.
[2] The neutralisation of Lime by pozzolans results in a drop in the Ca/Si ratio in CSH and potential brittleness

Autogenous shrinkage does not occur in high strength tec-cement concretes because the Brucite hydrates that form self desiccate back to Brucite delivering water in situ for more complete hydration of Portland cement.

$$Mg(OH)_2.nH_2O\ (s) \leftrightarrow MgO\ (s) + H_2O\ (l)$$

As Brucite is a relatively weak mineral it is compressed and densifies the microstructure.

As the propensity of Brucite to carbonate measured by the Gibbs free energy is less than that of lime and when it does carbonate it expands tending to block of the process, Brucite will remain as such under most conditions for much longer in a protective and pH regulatory role.

Delayed reactions do not appear to occur to the same extent in Tec Cement Concretes because a lower long term pH results in reduced reactivity after the plastic stage and potentially reactive ions are trapped in the structure of Brucite. Ordinary Portland cement concretes can take years to dry out however the reactive magnesia in Tec-cement concretes consumes unbound water from the pores inside concrete, drying concrete from the inside. Reactions do not occur without water. Brucite and its carbonates are also well known fire retardants.

There are also likely to be less problems with freeze thaw as denser concretes do not let water in and Brucite will, to a certain extent, take up internal stresses. When magnesia hydrates it expands into the pores left around hydrating cement grains, creating air voids in space that was occupied by magnesia and water, increasing the freeze thaw resistance.

Enviro-Cements

Enviro-cements are similar to tec-cements but differ from eco-cements in that they have higher ratios of magnesia to hydraulic cement. Chemically and physically they are more suited to toxic waste immobilisation because they are more durable than either lime, Portland cement or Portland cement lime mixes. Unlike geopolymers they do not suffer from the same nano-porosity problems, on the contrary – they are relatively dense and very durable. They 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[3] OPC takes up lead, some zinc and germanium.

Brucite in enviro cements is an excellent host for toxic wastes as it has a layered structure and traps electronically balanced ions and 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 require porous substrates to carbonate and differ in that they contain higher ratios of magnesia to hydraulic cement.

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

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-cement concretes are also to some extent recyclable and can have up to around 90% recycled industrial materials such as fly and bottom ash included in their formulation and are therefore likely to become more important in the future[4][5]. 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 (mud bricks), pavers and mortars, porous pavements 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.

The use of eco-cements for block manufacture, particularly in conjunction with the kiln also invented by TecEco (The Tec-Kiln) would result in sequestration on a massive scale.

Eco-cements gain early strength from the hydration of PC. Later strength comes from the carbonation of Brucite forming an amorphous phase, lansfordite and nesquehonite. Strength gain in eco-cements is mainly micro structural because of more ideal particle packing (Brucite particles at 4-5 micron are under half the size of cement grains) and the natural fibrous and acicular shape of magnesium carbonate minerals which tend to lock together.

Magnesium is a small lightweight atom and the carbonates that form contain proportionally a lot of CO_2 and water. Total volumetric expansion from magnesium oxide to lansfordite is 811%, meaning that a little binder goes a long way:

$$\mathbf{Mg(OH)2 + CO2 \rightarrow MgCO3.5H2O}$$

Magnesium carbonates and hydrated magnesium carbonates are also fire retardants. Eco-cement concretes put fires out by releasing CO_2 or water vapour or both at relatively low temperatures.

Waste and On Site Excavation Waste Utilization by TecEco Cement Concretes

As the price of fuel rises, the use of on-site low embodied energy materials, rather than carted aggregates, will have to be considered. The new hydraulic calcium magnesium binders invented by John Harrison provide benign environments allowing the use of many local materials and wastes without delayed reactions.

Wastes are only wastes because nobody wants them. The key is to find uses and convert them to resources. Uses can be based on chemical composition or physical property. As many materials have common physical properties, but are chemically very different, utilization on the basis of physical property has huge potential, especially on a geographically distributed basis.

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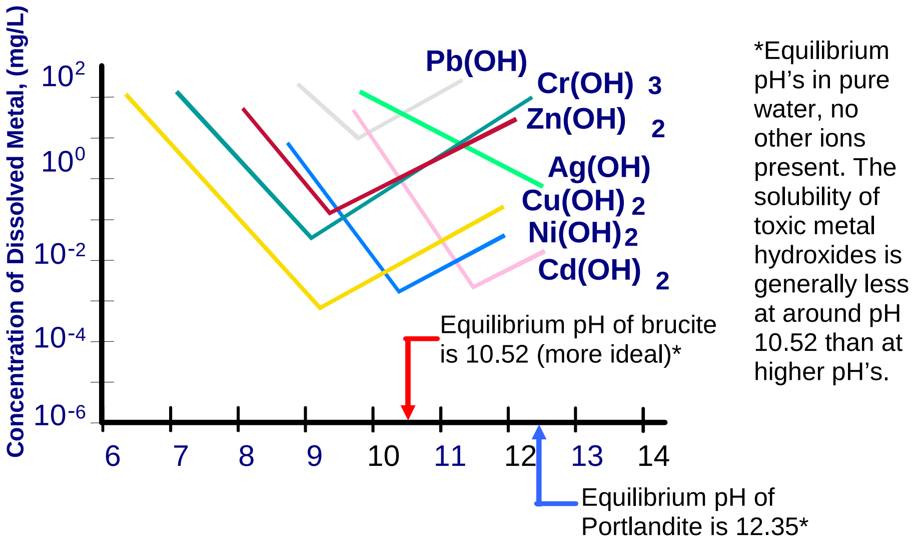
[4] 100% utilisation would reduce global CO_2 emissions in the order of 10% - 15%.

[5] 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

The benign chemical environment of tec, eco and enviro-cements will allow a wide range of wastes and non traditional aggregates to be used regardless of their chemical composition and Brucite and magnesium carbonates bond well to many different materials including wood[6] and will hold a large proportion of waste. Many wastes such as fly ash, sawdust, shredded plastics etc. can improve a property or properties of the cementitious composite.

If wastes of any kind are to be incorporated in a cementitious matrix, such as Portland cement, it is essential that the long term pH is regulated in the region of the minium solubility of heavy metals, as is the case in TecEco cement concretes.



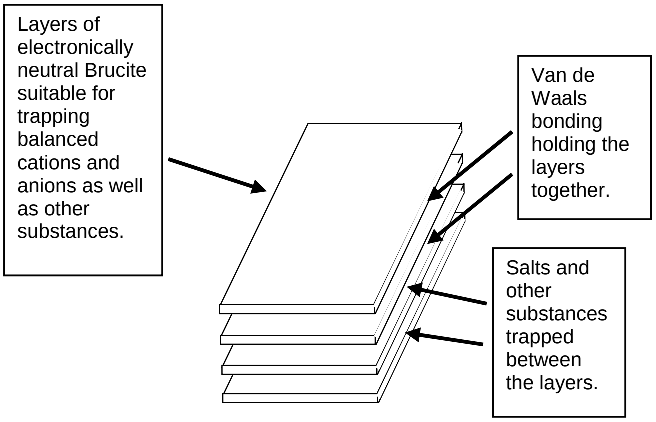
Equilibrium pH of brucite is 10.52 (more ideal)*

Equilibrium pH of Portlandite is 12.35*

*Equilibrium pH's in pure water, no other ions present. The solubility of toxic metal hydroxides is generally less at around pH 10.52 than at higher pH's.

Figure 7 - Low Solubility of Metal Hydroxides at the Equilibrium PH of Brucite

In a Portland cement and Brucite matrix the calcium silicate hydrates take up lead, some zinc and germanium. Heavy metals not taken up in the structure of Portland cement minerals or trapped within the Brucite layers end up as hydroxides with minimal solubility.



Layers of electronically neutral Brucite suitable for trapping balanced cations and anions as well as other substances.

Van de Waals bonding holding the layers together.

Salts and other substances trapped between the layers.

The Brucite in TecEco cements has a structure comprising electronically neutral layers and is able to accommodate a wide variety of extraneous substances between the layers and cations of similar size substituting for magnesium within the layers and is known to be very suitable for toxic and hazardous waste immobilisation.

Figure 8 - Layered Structure of Brucite

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[6] Hence the contemplated use for lightweight packaging.

For robotic construction of the future (Lemley 2005) a wide range of self setting solid composites will be required. Many materials currently considered as wastes can provide the properties necessary. For example plastics have in common low weight, low conductance and tensile strength. Why waste them? They can impart these properties to concretes.

References

Lemley, B. (2005). The Whole-House Machine, Discover Magazine.