Tec-Cement Reactions
Can Hydraulic Cements and Geopolymers Merge?

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Abstract

The reactions of tec-cements containing reactive magnesia are discussed and compared to geopolymers.

Keywords

Geopolymer, tec-cement, magnesia, brucite, Portland cement, hydration, silicification

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John Harrison has degrees in science and economics, is the managing director and chairman of TecEco Pty. Ltd. and is known around the world for the invention of tec, eco and enviro-cements. He is an authority on sustainable materials for the built environment, has been a speaker at many conferences and is committed to finding ways of “materially” improving the sustainability of the built environment.

Background

The first author to seriously point out the ramifications of continued high use of Portland cement and global warming was probably Prof. Joseph Davidovits in his paper published in World Resources Review in 1994 (Davidovits, J., 1994). His work attracted the attention of Fred Pearce, a renowned writer with New Scientist Magazine who wrote an article in New Scientist with the attention grabbing title of “The Concrete Jungle Overheats”(Pearce, F., 1997). Fred’s article caught the attention of the world and was one of the influences that inspired me to research magnesium cement systems. Later Fred was to publish the article “Green Foundations” about the ramifications of our eco-cement concretes for global warming (Pearce, F., 2002).

The chemistry of TecEco binder systems has progressed. We have several research students and some exemplars on the ground. In TecEco’s arsenal of more sustainable binders we now not only have eco-cements, which set by absorbing CO_2, but tec-cements which require less binder for the same total strength and are more sustainable because of this and their superior durability due to the presence of brucite through the matrix.

Tec-cements are essentially hydraulic but we suspect silicification reactions also play a role and in that sense they may be a bridging material, retaining the benefits of hydraulic cements such as ease of use and placement but with the advantage of good strength gain. They do not unfortunately have the fire resistance of true geopolymers, on the contrary – they tend to extinguish fires.

In this paper I will in a summary way relate tec-cement chemistry to geopolymers in the hope of stimulating greater research interest.

Starting by describing the various reaction systems I will then move on into ramifications for properties and suggest where the addition of magnesium oxide may solve some viscosity problems with geopolymers.

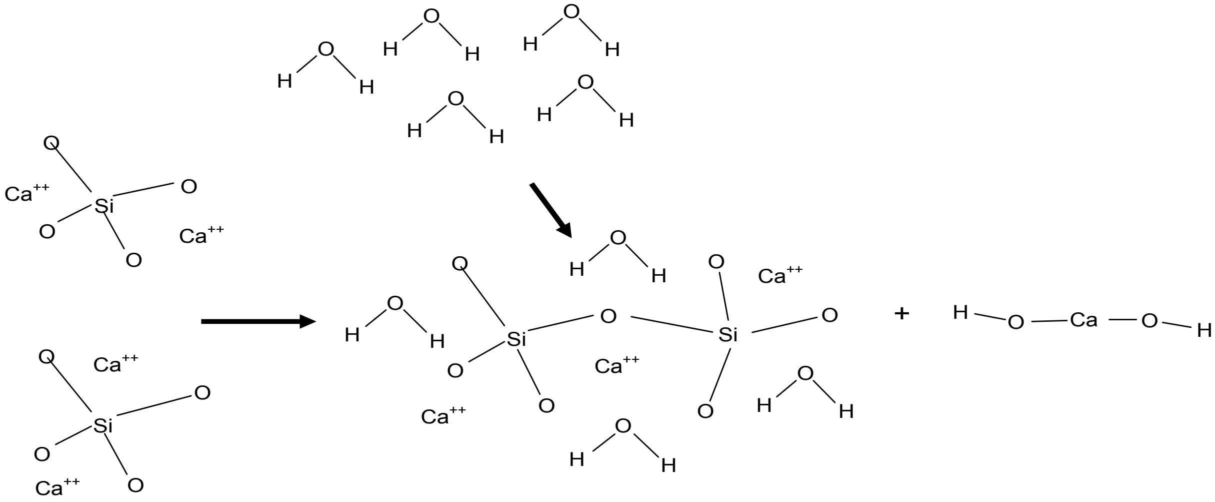
Comparing Reactions[1]

Hydration Reactions

Hydration reactions are semi stoichoimetric[2] – for example two moles of di calcium silicate (a monomer) take on water releasing calcium (which then combines with hydroxides from water) to form a mole of di calcium silicate hydrate (a dimer)[3]

$2Ca_2SiO_4 + 5H_2O ==> Ca_3Si_2.O_7.4H_2O + Ca(OH)_2$

Using "atom and stick" nomenclature



The pozzolanic reaction is similar to the hydration reaction for di and tri calcium silicate; the difference is that the components all come together to form compounds that are hydrated silicates with less calcium and bound water.

$1.1Ca(OH)_2 + SiO_2 + .67H_2O ==> Ca_{1.1}SiO_{3.1}.2.1H_2O$

Atoms don't come in fractions so the formula suggest that larger molecules are formed that are probably oligopolymers – and with the pozzolanic reaction they are.

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[1] I have not used cement nomenclature as I prefer to think about molecules and find cement nomenclature confusing to say the least.

[2] Not always stoichiometric in that the Ca:Si ratio can and does vary

[3] Since this discussion is about monomers, dimers, (geo)polymers etc. it is appropriate to explain that these terms are borrowed from plastics chemistry. Plastics are composed of long chains (sometimes with cross linking) made up of repeating units called monomers. Thus a substance that has these singular units as the main composition is called a monomer. Where substances are made up of compounds in which two of these units are joined together they are called dimers. Where 3 of these units are joined together the ensuing compounds are referred to as trimers. Where a number greater than 3 monomer units are linked together but less than 100, oligomers are formed. With more than 100 monomer units linked together, polymers are the result and for silicon they are referred to as geopolymers. In minerals including geopolymers the monomer units are basically silicon or aluminium tetrahedra.

Silicification Reactions

Hydrolysis and Recombination

As portlandite is formed in reactions like the one depicted above the pH of the mix rises to around 12.5 at equilibrium[4].

At high pH the surfaces of silica and alumina containing compounds tend to hydrolyze. Strength giving reactions occur when the hydrolyzed surfaces then bind back together losing water as depicted in the “atom and stick” diagram below.

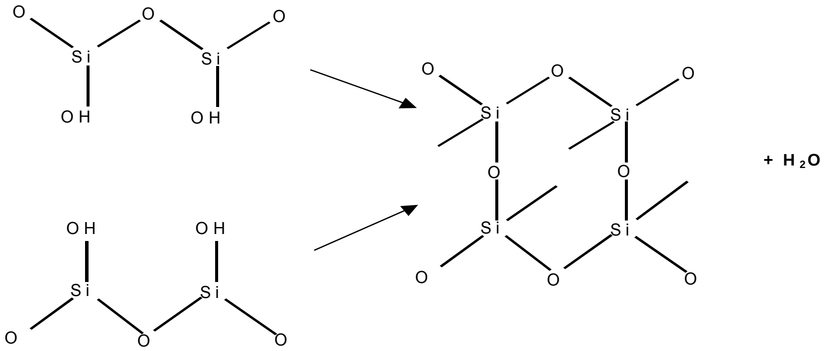

Figure 1 - Surface Bonding of Silicates through Hydrolysis.

In tec-cement concrete formulations many wastes containing silica and alumina such as fly ash and ground granulated blast furnace slag[5] can be added in high proportion and tend to recombine in the above manner as well as becoming involved in the pozzolanic reaction.

Geopolymeric reactions

According to Davidovits (Davidovits, J. A., 1994) the sialate[6] network in “geopolymers” consists of SiO_4 and AlO_4 tetrahedra linked alternately by sharing all the oxygens. Positive ions (Na^+, K^+, Li^+, Ca^{++}, Ba^{++}, NH_4^+, H_3O^+) must be present in the framework cavities to balance the negative charge of Al_3^+ in IV fold coordination.

Geopolymers have the empirical formula:

$$M_{n}(-(SiO_2)_z-AlO_2)_n, wH_2O$$

wherein M is a cation such as potassium, sodium or calcium etc. (see above), and «n» is the degree of polycondensation; «z» is 1, 2, 3.

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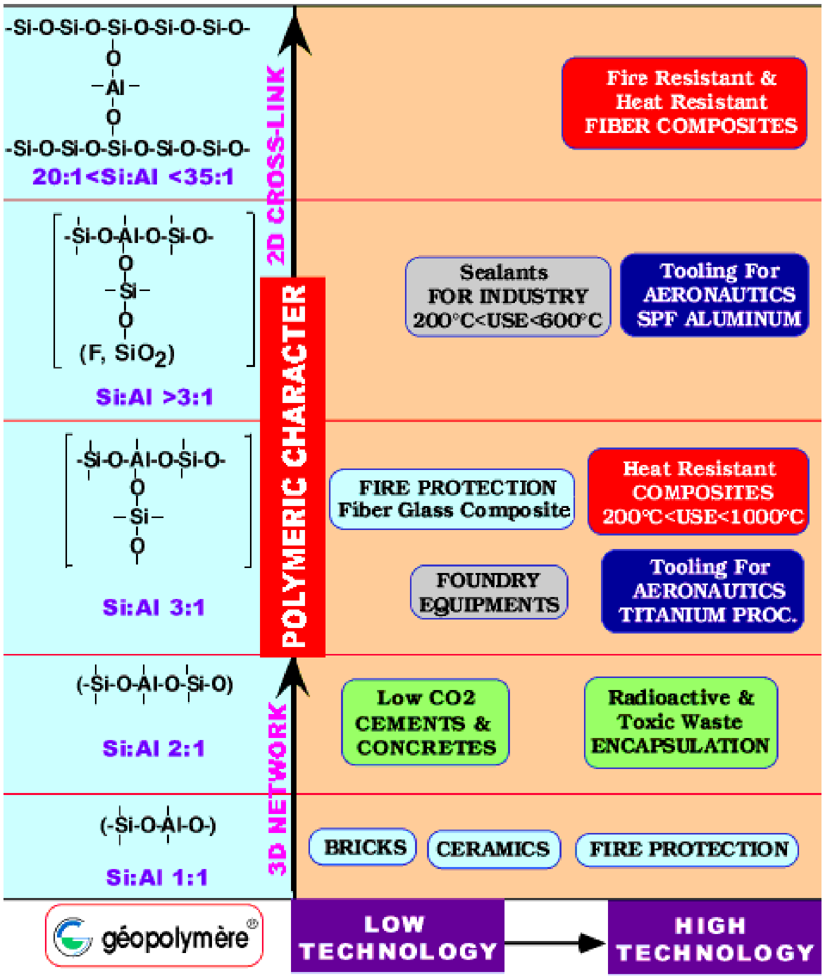
[4] It is the surface alkalis, K+ and Na+ on cement grains that tend to push the pH higher to over 13 in high alkali Portland cements

[5] pozzolans

[6] Sialate is a term coined by Davidovits and an abbreviation for silicon-oxo-aluminate

Many chain and ring polymers with Si_4^+ and Al_3^+ in IV fold coordination with oxygen and that are often cross linked are formed. These amorphous to semi-crystalline three dimensional silico-aluminate structures were given the name “geopolymer” by Davidovits because they resembled plastics which are polymers based on carbon rather than silicon.

Davidovits further classified geopolymers into the following types depending on the Si:Al ratio:



Crystalline Polysialate M_n-(-Si-O-Al-O-)$_n$
Poly(sialate-siloxo) M_n-(Si-O-Al-O-Si-O-)$_n$
Poly (sialate-disiloxo) M_n-(Si-O-Al-O-Si-O-Si-O)$_n$

In reality geopolymer materials consist of mixtures of these structures with the predominating form being controlled by the Si:Al ratio.

According to Davidovits The atomic ratio Si:Al in the poly(sialate) structure determines the properties and application fields. A low ratio Si:Al (1,2,3) initiates a 3D-Network that is very rigid. A high ratio Si:Al, higher than 15, causes greater polymerisation.

Figure 2 - Geopolymer Types Depending on Si:Al Ratio (from Davidovits, J. A., 1994)

Not all the materials in a geopolymer formulation react completely.

As in plastics, geopolymers generally also contain some smaller monomer, dimer, trimer and oligomer units.

Depending on the level of alkalinity reached, many of them do not react at all and the particles of fly ash or dehydrated clay (Kandoxi) used to make them remain as micro-aggregates. This does not matter as the minerals in fly ash such as mullite and gibbsite are themselves strong.

To form a good strength geopolymer the basic requirement is that enough of the mix reacts and reforms to create sufficient solid phase to hold what does not react together.

To get enough of a geopolymer mix to react high alkalinity is required. Unfortunately the use of concentrated alkalis results in viscous mixes and therein lies the nub. To achieve high alkalinity it is necessary to keep the pH up and not add too much water and the result is high viscosity. To place liquid materials that set in complex moulds low viscosity is required. One alternative is to pre-dissolve silica in sodium or potassium hydroxide, however these fluids are still viscous and do not get over the process problem.

The dichotomy between viscosity and ease of placement defines much of the current research on geopolymers and magnesium oxide as used in tec-cements may provide part of the solution (See Viscosity and Placement Issues below).

Comparing Bonds with Aggregates

In PC concretes there is no chemical bond with aggregates – they are physically held in place. Portlandite also tends to form around larger aggregates weakening the bond to them. A further source of weakness is the reaction between alkali and silica

Geopolymers are different in that the geopolymeric paste tends to bond with silica in the micro aggregates and aggregates and this together with cross linking are reasons for high strength, .

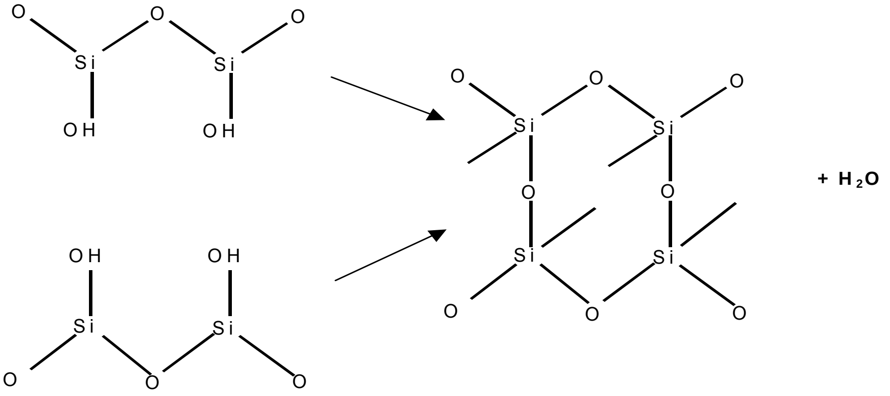


Figure 3 - Surface Bonding of Silicates through Hydrolysis.

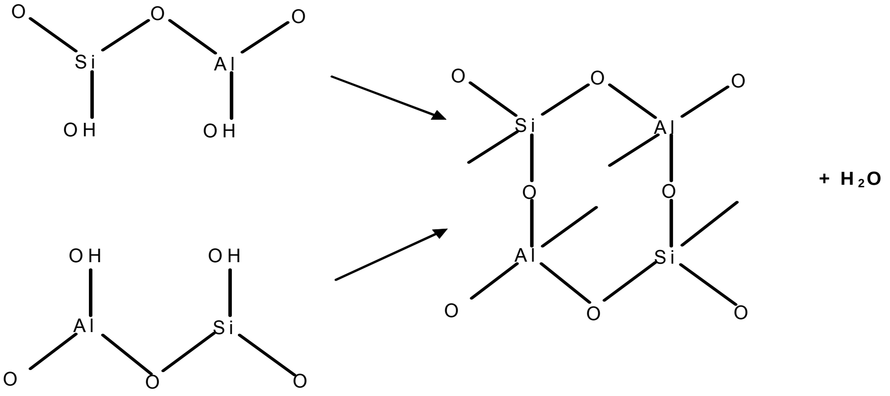


Figure 4 - Surface Bonding of Silicates/Aluminates through Hydrolysis (or any other surface combination of Si and Al) (after Van Jaarsveld, J. G. S. and Van Deventer, J. S. J., 1996) similar diagrams have been used by Davidovits (Davidovits, J. A., 1994)

Viscosity and Placement Issues

Portland Cement Concretes

Portland cements stoichiometrically require around 23 -25% water for hydration yet we add approximately 45 to 50% at cement batching plants to fluidise the mix sufficiently for placement.

If it were not for the enormous consumption of water by tri calcium aluminate as it hydrates forming ettringite in the presence of gypsum, concrete would remain as a weak mush and probably never set.

Consider the first part of the reaction:
Tricalcium aluminate + gypsum + water ==> ettringite.

In cement nomenclature:

C_3A+3CSbarH_2 + 26H ==> C_6ASbar3H_{32} (Cement chemist talk)

Or in what I think is a more understandable form:

$Ca_3Al_2O_6$ + 3$CaSO_4$.2H_2O + 26 H_2O ==> $Ca_6Al_2(SO_4)3(OH)_{12}\cdot 26(H_2O)$

Consider the molar volumes:
89.1 + 3 X 74.2 + 26 X 18.01 ==> 715 (molar volumes)
89.1 + 222.6 + 470.6 ==> 715 (molar volumes)
782.3 ==> 715 (8.6% reduction in total molar volumes)
311.70 ==> 715 (403.3% increase in total solid volumes)

26 moles of water are consumed per mole of tri calcium aluminate to from a mole of solid ettringite. When the ettringite later reacts with remaining tri calcium aluminate to form monsulfoaluminate hydrate a further 4 moles of water are consumed.

Yet water still usually bleeds from freshly poured concretes even with plasticisers added meaning that even more water than can be consumed in the production of ettringite and by other hydration reactions has been added.

The Romans did not add too much water, on the contrary unlike modern finishing crews they were disciplined and tamped their concrete into place and achieved much higher quality. The question arises as to how we can achieve similar benefits whilst at the same time making the mix so fluid that finishers, who are a lazy lot, have little or no work to do placing concrete?

Geopolymers

It is not possible to add water to geopolymers. If water were add the alkalis would be diluted, the pH would fall and the mix would not set as unlike the setting of Portland cement concretes there is no reaction that consumes water. On the contrary – water is expelled.

Before considering how the addition of magnesium oxide may be able to help with this problem it is necessary to consider what happens in a tec-cement concrete.

Tec-Cement Concretes

Summary

Tec-cements concretes have a relatively low proportion (5-15%) of reactive magnesia added and this 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).

Noticeable from the moment water is added is the improved rheology[7] (See Magnesia as a Plasticiser on page 12 below). Workability is much better than Portland cement concretes and this is due to the lubricating affect of the smaller magnesia particles and possibly some charge affects.

As a consequence of the removal of Portlandite 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 (44.65 mass% is 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 and is lower.

The equilibrium pH of Brucite in water is 10.52 and it maintains the longer term pH of concretes in that range for much longer periods than Portlandite as it is far less soluble, mobile or reactive. The solubility product of brucite at 1.8×10^{-11} is much lower than that of Portlandite at 5.5×10^{-6}. The equilibrium pH is still however at a sufficiently high level for steel to remain passive[8] and for the stability of calcium silicate hydrates[9]. Dense concretes made using TecEco formulations should maintain reducing conditions and a pH over around 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 the interaction of a number of factors (See the discussion on Strength and Figure 5 below). Most likely are:

- More silicification reactions including a more effective pozzalanic 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.

The removal of excess water by magnesia as it hydrates has a number of 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.

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[7] This may not be the case if microsilica is also added. More work is required in this area.

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

[9] The neutralisation of Lime by pozzolans results in a drop in the Ca/Si ratio in CSH and potential brittleness

Tec- cements 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. Protection against sulfates, chlorides and other aggressive salts and delayed reactions do not occur.

The advantages of using 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 and in appropriate proportions the expansion of magnesium minerals balancing the slight 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.

As the propensity of Brucite to carbonate measured by the Gibbs free energy is also less 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. (e.g. ΔG_r Portlandite → calcite = - 64.62 $kJ.mol^{-1}$, ΔG_r Brucite → nesquehonite = - 38.73 $kJ.mol^{-1}$).

Brucite is a fire retardant and tec-cement concretes are drier because of the water consumption of magnesia meaning that fires tend to be cooled and heat induced spalling does not incur to the same extent.

A concrete with around 25 – 30% less binder for the same strength is less expensive to make. The manufacture of reactive magnesia is a low temperature process that is also therefore inherently more efficient. As energy and money are the same given economies of scale, and for all of the reasons given above, concretes should not only get better and use more marginally pozzolanic wastes, they should become less expensive!

Stability of CSH

Cement chemists should beware as the use of fly ash and other pozzolans introduces another problem. The stability of calcium silicate hydrates is related to the equilibrium they maintain with surrounding alkali. Remove the lime and they are destabilized, loose calcium and eventually become brittle.

TecEco replace the lime consumed in the pozzolanic reaction with brucite, a far less soluble and reactive alkali. Given the addition of a pozzolan, long term pH is controlled by a much more stable brucite – CSH – H_2O equilibrium system not CSH – H_2O alone at somewhere between the equilibrium pH of CSH (11.2) and that of brucite (10.48).

Strength

In Tec-cement concretes reactive magnesia added to a Portland cement concrete mix in low proportions of around 5 - 10% internally consumes water during the plastic stage reducing the voids paste ratio and resulting in greater density and strength.

$MgO + H_2O \Longrightarrow Mg(OH)_2$
13.98 + 18.01 ==> 24.63 (molar volumes)
31.99 ==> 24.63 (23% reduction in molar volumes)

To the extent that $Mg(OH)$ forms a gel including complex ions such as $[Mg(H_2O)_6]^{2+}$ - much more water (see Magnesium Complexes below)

Strength is also probably also increased because alkalis are concentrated as the volume of water reduces and because they do not bleed out of the mix as much. The result is a higher pH during at least the early plastic stage resulting in more affective silicification reactions (See above).

As to whether pozzolanic reactions occurs more readily, there is little experimental evidence but empirically, the higher the pH, the more mobile silica and the more likely it is to react. It is doubtful however that geopolymeric reactions as such occur in tec-cement concretes.

It has been claimed that magnesium silicate hydrates form and they have certainly been observed in corrosion scenarios. It is the author's opinion that they are not important or strength giving in tec-cement concretes. When they do occur at low temperatures, the MSH formed is most likely essentially a gelatinous sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6(H_2O)$) type compound of low strength.

There may well be other strength affects. It is likely that the brucite formed is initially gel like because of the hydration complexes formed by magnesium and as these desiccate they would slow release water for other hydration reactions possibly resulting in more crystalline phases of CSH and greater strength (See Magnesium Complexes below).

Brucite itself is not a strong mineral unless compacted and Ramachandran et. al. observed that compacted Brucite can be as strong as Portland cement of the same porosity (Beaudoin, J. J., Ramachandran, V. S. et al., 1977). It may be that Brucite is to some extent compacted by its own hydration in tec-cement concretes.

There are a combination of strength giving and weakening affects that are yet to be optimised in tec-cement concretes. Figure 5 below is an attempt to graphically illustrate this.

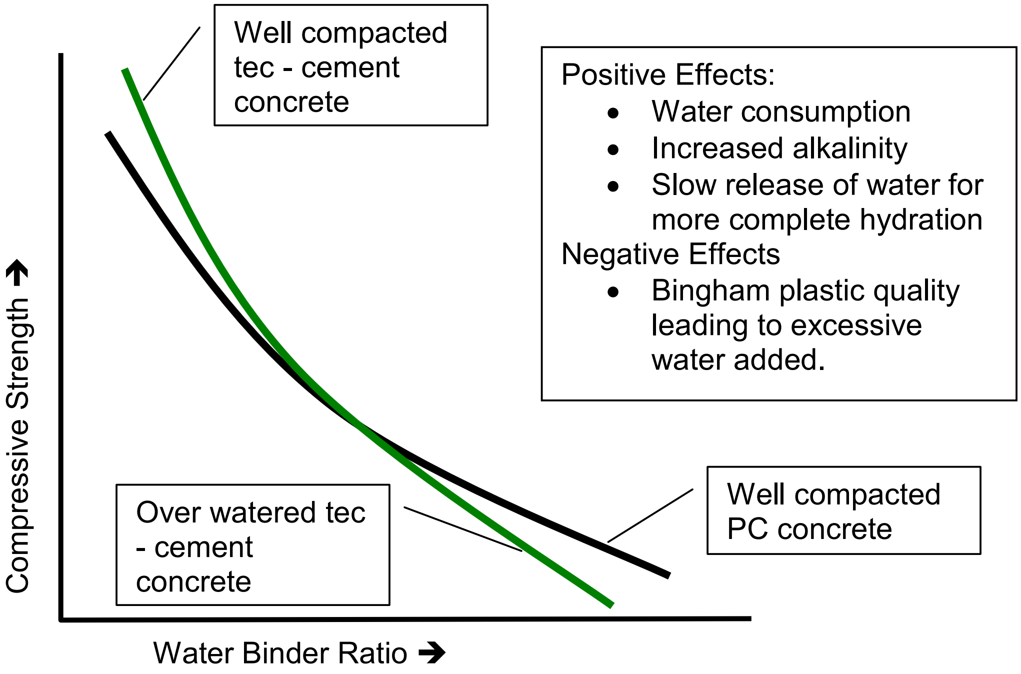

Figure 5 - Interactions between Strength Giving and Weakening Effects in Tec-Cement Concretes and their Possible Relationship to the Water/Binder Ratio.

Summary Reactions Mechanisms of MgO in Tec-Cement Concretes

Many reactions of magnesium oxide in a cement mix are still being worked out and the less obvious reactions not discussed in this paper are included below for the sake of completeness.

The extent to which metastable magnesium hydroxide [$Mg(OH)_2 \bullet nH_2 0$] is formed is not known and at this stage is still lost in the literature as it is unreferenced by Skalmowski. (Skalmowski 1957). More literature searches and experimental work are required.

Table 1 - Summary Reactions Mechanisms of Mg in Tec-Cement Concretes

	Reaction	**Mechanism**	**Condition change**	**Result**
1	$MgO + H_2O \Rightarrow Mg(OH)_2.nH_2O$	Internal water consumption	Greater density and higher alkalinity	Greater density => strength Higher alkalinity => more reactions involving silica & alumina
2	$Mg(OH)_2.nH_2O \Rightarrow Mg(OH)_2 + nH_2O$	Slow release of water	Water intimately available for hydration other components	More complete hydration of CSH?
3	$MgO + Al + H_2O \Rightarrow 3MgO.Al.6H_2O$???	Mg equivalent to flash set reaction of PC ?	Different to hydrogarnet reaction in PC.	Three day peak in strength?
4	$MgO + SO_4^{--} \Rightarrow$ various Magnesium oxysulfates ??	Possible	None?	Does not seem to happen as ettringite formation consumes SO_4^{--}
5	$MgO + SiO_2 \Rightarrow$ MSH ??	Can happen in highly alkaline conditions	Strength MSH variable	An analogous material to CSH could form but may not be important.

Tensile Strength

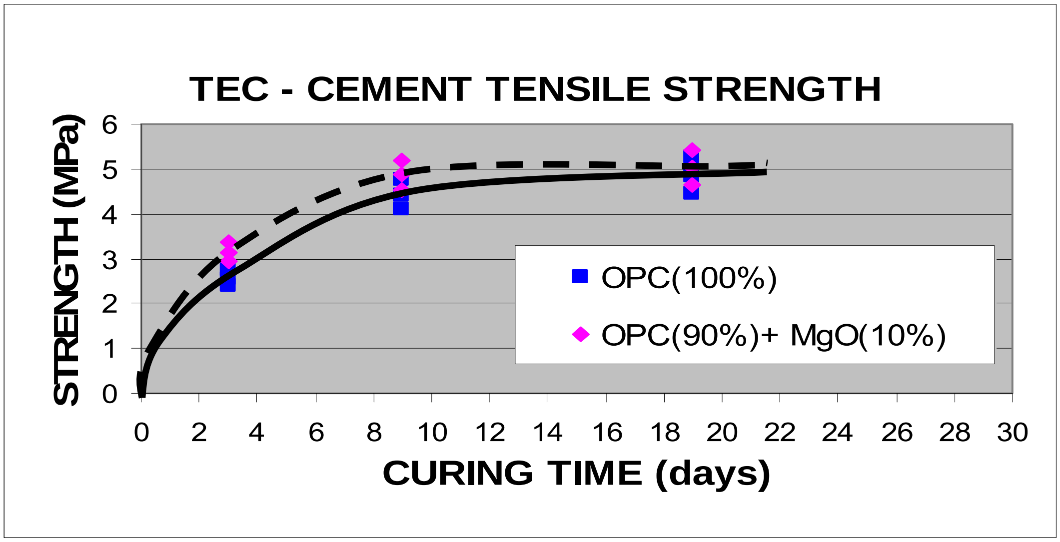

Figure 6 - Tensile Strength (Plot by Oxford Student)

Tec-cements develop very interesting early tensile strength which help to reduce cracking and this property is thought to be caused by a change in the surface charge on MgO particles from net positive to negative above around pH 12 – 12.4 and the resulting change in electrostatic attractive forces (See Figure 7). As Portlandite is produced by the hydration of C_3S and C_2S and has an equilibrium pH of around 12.48 and there are also other alkalis in and on cement grains (Na^+, K^+) which raise the pH even more, MgO would go negative possibly during the late plastic stage depending on conditions.

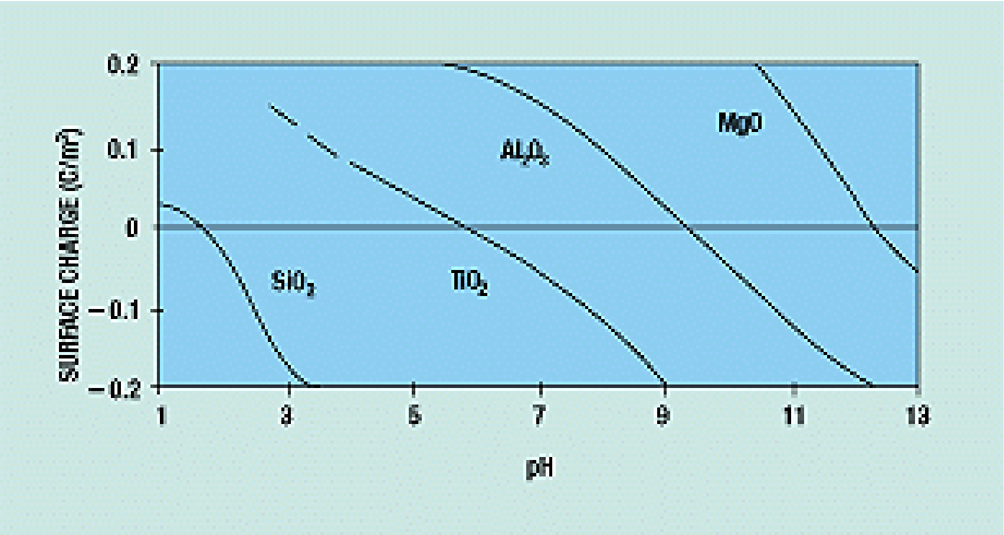

Figure 7 - Effect of Solution pH on the surface charge of various oxides (Small, Peterson et al. 2005)

Cement grains are known to have a net positive charge. Sand, being silicon dioxide on the other hand has a net negative surface charge given the pH conditions in concrete (See Figure 7). The use of some plasticizers such as ligno sulphonate induce a net negative charge to both cement and aggregate causing mutual repulsion however a preliminary observation is that some plasticizers do not work effectively in the presence of MgO including ligno sulphonate.

It would be speculation to guess the exact mechanisms whereby the change in surface charge on MgO causes an observed rapid “gelling” up and increased tensile strength and even more speculative to factor in the effect of various additives. More work is required (See also A Possible Role of Magnesia to get over the Viscosity Problem with Geopolymers on page 14)

Magnesia as a Plasticiser

As one of the problems of geopolymers is their viscosity a detailed discussion of magnesia as a plasticizer follows.

Particle Size and Charge Effects

The reactive magnesia TecEco have been using (Causmag XLM) is around 4-5 microns in size and may act as a lubricant to the larger Portland cement (18-26 micron) and fly ash particles (A flat peak from 10 to 100 micron) however there is a water demand associated with fineness. See Figure 8 and Figure 9 below.

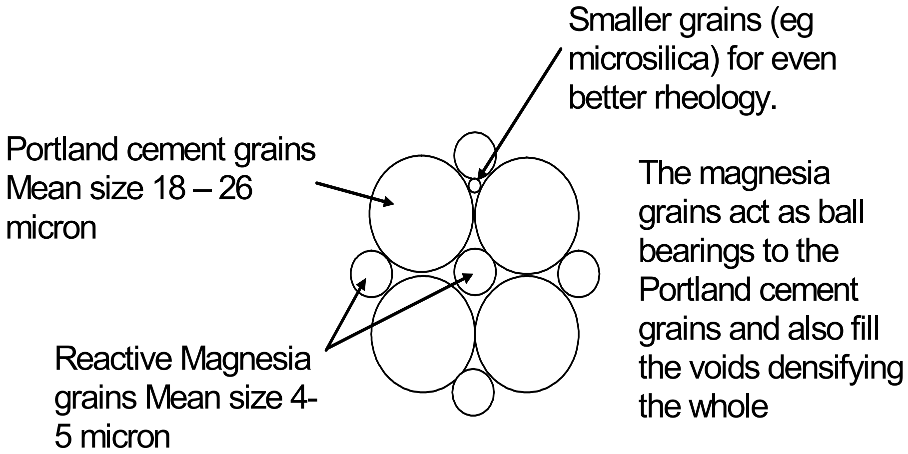

Figure 8 - Particle Packing Effect on Rheology

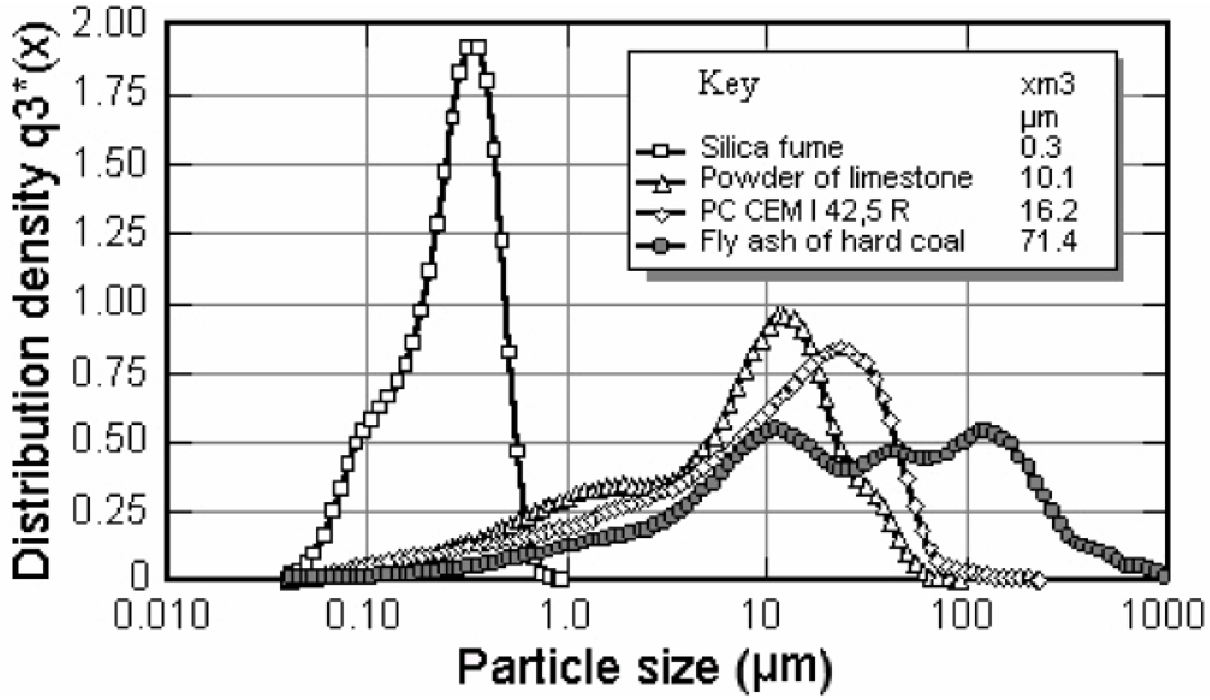

Figure 9 - Particle Size Distribution of Ordinary Portland Cement and Various Mineral Admixtures (after Stark, U. and Mueller, A.)

Water tends to disassociate onto the surface of metal oxides and with magnesia there is a net residual positive surface charge up to pH 12 – 12.4 in water. As cements grains also have a net residual positive charge in water, magnesia mutually repels Portland cement grains and therefore tends to plasticise them.

Interactions with plasticisers and pozzolans, magnesia and sands have not yet been worked out and are a subject of ongoing research.

As mentioned, we have observed that tec-cement concrete mixes containing MgO tend to gel up quickly, although this effect could also be due to the removal of water, there are other possible reasons including ionic affects and the formation of magnesium complexes.

Ionic Effects

Mg^{++} is a small ion with a large surface charge and much more than the larger Ca^{++} ion, tends to cause water which is a polar molecule to line up around tending to introduce a thixotropic property to the rheology of tec-cement concretes.

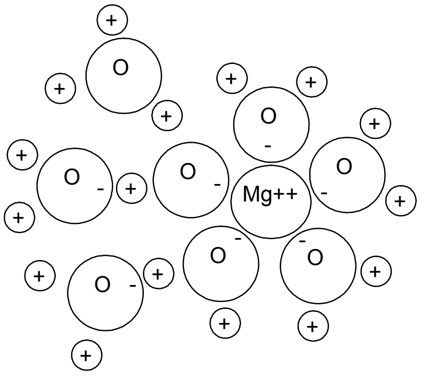

Figure 10 - Thixotrophic or Bingham Plastic Rheology of Tec-Cement Concretes

Magnesium Complexes

Both magnesium and calcium show an ability to form complexes with water.

Magnesium appears to more strongly than calcium hydrate forming $[Mg(H_2O)N]^{2+}$ complexes or hydroxylate forming H_3O^+ and Mg^+OH and hydrated forms of

Mg^+OH. As $[Mg(H_2O)_6]^{2+}$ for example is not acidic, the water in it can be removed by dehydration and may well be how the suspected supply of water to hydration reactions of clinker minerals in Portland cement - magnesia tec-cement formulations occurs.

A Possible Role of Magnesia to get over the Viscosity Problem with Geopolymers

Magnesium is not a Network Former

In the presence of water magnesium is not a network former in silicate structures including geopolymers and this is probably because of it's high affinity for water which it retains even when it carbonates.

Getting Over the Viscosity Problem

Magnesium may however be useful as an adjunct to assist with the viscosity problem.

Most people researching geopolymers seem to be trying various super, duper, hyper, blah blah plasticiser molecules to see if they can be used to fluidise the mix sufficiently. Jannie Van Deveneteer and his co-workers at Melbourne university claim to have got over the viscosity issue without the use of plasticisers but until I understand what they have done I remain sceptical. Coming to an understanding will be difficult because of the secrecy surrounding their work.

The water removal mechanism of magnesia and its plasticising properties may be useful as a totally different approach to get over the viscosity issue. There is obviously more work to do pending funding but could it be that the best features of geo polymeric and hydraulic cements can be combined?

Conclusion

Reactive magnesia is a new tool that can reduce water and adjust if not control the pH of binders that rely on the presence of water for reaction and/or placement. Many other properties including rheology and durability are also affected.

There are tantalizing properties that may be useful in getting over the viscosity problem with geopolymers.

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