

Tec-Cement Update

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Abstract

Tec-cements are hydraulic cements containing 5-15% reactive magnesia. Reasons for adding reactive magnesia including improvements in durability, rheology and strength are discussed.

Keywords

Tec-cement, magnesia (M,MgO), Brucite (MH,Mg(OH)₂), Portland cement (PC), hydration, silicification, magnesium complexes, pozzolan, di calcium silicate (C₂S, Ca₂SiO₄), tri calcium silicate (C₃S, Ca₃SiO₃), tri calcium aluminate (C₃A, Ca₃Al₂O₆), tetra calcium alumino ferrite (C₄AF, 4CaO.Al₂O₃.Fe₂O₃), gypsum (C\$H₂, CaSO₄.2H₂O), rheology, durability, strength, magnesium complexes.

Why Tec-Cements?

The weakness of Portland cement is the lime produced during the hydration of di and tri calcium silicates. One of the foundations of TecEco cement theory is that for durability it is essential to remove this lime and the pozzolanic reaction is conveniently available to do so. Unlike others, we also surmised that it is also important to replace the lime removed with another alkali for a number of reasons including maintaining CSH equilibrium with hydroxide ions. In tec-cement concretes this alkali is Brucite.

Brucite forms in a concrete matrix by the hydration of magnesium oxide. It is much less soluble, mobile or reactive, is slightly more acid resistant, and an ideal mineral to accompany CSH keeping it stable. It is dispersed right through a tec-cement and has a prominent protective role.

Given that we have now poured in excess of 300 cubic metres of tec-cement concrete containing between 5 and 10% of added MgO relative to Portland cement and had much less cracking problems than with associated Portland cement only controls we can now say categorically that provided that the reactive magnesia is reactive enough there are no problems with delayed hydration. Amorphous magnesia can be added to hydraulic cements and it will hydrate in the same time frame as other minerals, without substantial interference in their hydration in most hydraulic binder systems and certainly in calcium based hydraulic systems.

The resulting tec-cements retain the benefits of hydraulic cements such as ease of use and placement, have the advantage of good durability strength and rheology. There is still however a lot to be understood.

The differences between Portlandite which TecEco remove and Brucite are in Table 1 below.

Table 1 - Properties of Brucite Compared to Portlandite.

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 ₂ O at 0 °C	0.009 g l ⁻¹ in H ₂ O at 18 °C.
Solubility (hot)	.77 g l ⁻¹ in H ₂ O at 100 °C	.004 g l ⁻¹ H ₂ O at 100 °C

Solubility (moles, cold)	0.024969632 mol.l ⁻¹	0.000154321 mol.l ⁻¹
Solubility (moles, hot)	0.010392766 mol.l ⁻¹	0.000685871 mol.l ⁻¹
Solubility Product (Ksp)	5.5 X 10 ⁻⁶	1.8 X 10 ⁻¹¹
Reactivity	High	Low
Form	Massive, sometime fibrous	Usually fibrous

Note that Brucite is of similar hardness and strength, usually fibrous and much less soluble including in mild acids.

Tec-Cement Summary

Tec-cement 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).

So far we think that reactions of magnesium oxide do not interfere with those of Portland cement (PC). There is a question mark over competition for sulfate as magnesium oxide will readily form magnesium oxy sulfate. It is a case of competition for ionic species and we suspect the reactions of tri-calcium aluminate (C₃A) forming ettringite occur more readily and are more successful. More research is required.

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. TecEco formulations concretes are denser because they do not bleed as much and because of the internal expansion of Brucite.

After all the Portlandite has been consumed Brucite, which is less soluble, mobile or reactive controls the long term pH.

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

Noticeable from the moment water is added is the improved rheology. Workability is better than Portland cement concretes and this is due to the lubricating affect of the smaller magnesia particles, the formation of magnesium complexes in water 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 (Brucite is 44.65 mass% is water, and 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 and is lower.

The equilibrium pH of Brucite in water is 10.52 and once this equilibrium has a role in controlling the pH it does so indefinitely as Brucite is far less mobile or reactive than Portlandite. For most kinetic pathways Brucite carbonates much less readily (ΔG_f Portlandite \rightarrow calcite = - 64.62 kJ.mol⁻¹, ΔG_f Brucite \rightarrow nesquehonite = - 38.73 kJ.mol⁻¹). At between 10.52 and 11.2 (the equilibrium pH of CSH) the long term pH of tec-cement concretes is still at a sufficiently high level for steel to remain passive¹ and for the stability of calcium silicate hydrates².

Apart from increased strength (see below) the removal of excess water by magnesia as it hydrates has a number of consequences.

¹ As Fe₃O₄ rather than oxides such as Fe₂O₃ or FeO₂ 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

Bleeding and the introduction of associated problems such as freezing of bleed water and weaknesses such as interconnected pore structures and high permeability do not appear to occur.

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. The main reason for improved durability however is the insolubility of Brucite which having developed right through the matrix tends to protect CSH and other hydration products of Portland cement (PC). Delayed reactions do not occur in such a stable low alkali environment and protection against sulfates, chlorides and other aggressive salts is provided.

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.

Brucite is also 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.

More fly ash can be added to advantage due to early strength gain and sustainability is improved by reduced binder:aggregate ratios, longer life and lower emissions ratios.

Durability

Modern concretes are not durable. We need to consider why not and what can be done to make them durable. The use of reactive magnesia which hydrates to brucite is a solution.

Durability and the 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 alkalis. Remove the lime and they are destabilized, loose calcium and eventually become brittle (Glasser 1992).

TecEco replace the lime consumed in the pozzolanic reaction with Brucite, a far less soluble and reactive alkali. Given the addition of sufficient pozzolan, long term pH is controlled by a much more stable Brucite – CSH – H₂O equilibrium system not CSH – H₂O alone at somewhere between the equilibrium pH of CSH (11.2) (Glasser 1992) and that of Brucite (10.48).

Durability and pH

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 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 as well as CSH it maintains the longer term pH of tec-cement concretes in the range 10.5 - 11.2 for much longer periods than Portlandite does in equilibrium with SCH. Brucite is also far less soluble³, mobile or reactive. In the range 10-5 – 11.2 the equilibrium pH is sufficiently high level for steel to remain passive⁴ and for the stability of calcium silicate hydrates⁵. Less internal reactions occur than at higher pH values delivered by lime and heavy metals in included wastes have lower solubility.

³ The Ksp or solubility product of Brucite at 1.8×10^{-11} is much lower than that of Portlandite at 5.5×10^{-6}

⁴ As Fe₃O₄ rather than oxides such as Fe₂O₃ or FeO₂ which tend to hydrate and are dimensionally unstable.

⁵ The neutralisation of Lime by pozzolans results in a drop in the Ca/Si ratio in CSH and potential brittleness – see earlier.

Durability and Carbonation

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 \rightarrow calcite = - 64.62 kJ.mol⁻¹, ΔG_r Brucite \rightarrow nesquehonite = - 38.73 kJ.mol⁻¹).

Historical Proof of Durability

Many Roman hydraulic cement concretes have a high percentage of MgO and in recent times some interesting rock cement concretes made from dolomitic limestones (Powers 2005) have been examined partly because of their extreme durability and found to contain significant quantities of brucite. I suggest that this is a major reason for the durability.

Interactions with Aggregates

Apart from alkali reactions during the plastic phase similar to the hydrolysis reactions described above there is not much chemical reaction with aggregates in tec-cement concretes.

They mostly are physically held in place and reactions with paste reduced because of lower reactivity of the matrix and immobility of aggressive ions. Note that another reason why TecEco theorise that Portlandite should be removed is that it also tends to form around larger aggregates weakening the bond of CSH "paste" to them.

Water Consumption by Magnesia

One characteristic we are very interested in with MgO is the extent to which, when it reacts with water, it actually forms a "gel" containing hydrated complexes – as by doing so it would use a lot more water than calculated in a simple hydration reaction from magnesia to Brucite.

Magnesium Complexes

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

Magnesium as a hydroxide or carbonate appears to have a very strong affinity for water. In solution Mg⁺⁺ complexes with water more readily than Ca⁺⁺ forming complexes of the general form [Mg(H₂O)_N]²⁺. Mg⁺⁺ can also hydroxylate forming H₃O⁺ and Mg⁺OH and hydrated forms of Mg⁺OH.

According to Skalmowski, in the first stage of magnesium oxide hydration Brucite is not formed; instead metastable magnesium hydroxide [Mg(OH)₂·nH₂O] is formed and only after some time does it recrystallizes to Brucite which is the stable. (Skalmowski 1957).

Investigations done in Japan proved that the structure of metastable magnesium hydroxide unlike aluminium hydroxide "gel" becomes crystalline. It differs from Brucite in that it holds monomolecular layers of water between neighbouring Mg(OH)₂ packets. Intra packet water is removed during re-crystallisation and Brucite is formed as hexagonal lamellae. Increasing the temperature increases the rate of transformation. According to Skalmowski the properties of metastable Mg(OH)₂ are different from Brucite. It is four times more soluble in water, but still less soluble than Portlandite.

We suspect that the hydrate complexes form what amounts to a metastable "gel" or microcrystalline substrate holding water for slow release right through the matrix of the concrete resulting in more complete hydration of PC. In ordinary PC concrete up to 15 - 20% PC may remain un-hydrated. The hydration of more of this fraction would add to efficiency of PC as a binder and result in greater strength.

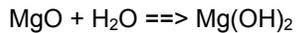
Unfortunately as scientists without much money we only easily see the end results. Furthermore we would have to make a lot of guesses as to the extent of complex formation.

Water Consumed without Taking Complexes into Consideration

Without taking the as yet unknown amount of water in hydrated magnesium hydroxide gels into account and using the cement produced in Tasmania by Australian cement of the following composition:

C₃S (Ca₃SiO₃) - 68%, C₂S (Ca₂SiO₄) - 6%, C₃A (3CaO.Al₂O₃) - 6%, C₄AF (4CaO.Al₂O₃.Fe₂O₃) - 10%, C_SH₂ (CaSO₄) - 3.6%, (CaCO₃) - 5.4%, M (MgO) - 2%, C (CaO) <1%, Na₂SO₄, K₂SO₄ <.6%

The hydration stoichiometry is as follows:

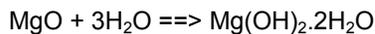


40.31 (MgO) + 18.02 (H₂O) ==> 58.33 Mg(OH)₂ – molar mass

11.26 (MgO) + 18.02 (H₂O) ==> 24.61 Mg(OH)₂ – molar volume

An increase of over two molar volumes of solid

Taking into account the formation of a gel of composition Mg(OH)₂.2H₂O (assuming .2 H₂O) the stoichiometry is:



40.31 (MgO) + 54.05 (H₂O) ==> 94.36 Mg(OH)₂.2H₂O – molar mass

11.26 (MgO) + 54.05 (H₂O) ==> 39.81 Mg(OH)₂ – molar volume⁶

An increase in over three molar volumes of solid produced and significant consumption of water. Our experience is that this consumption is more than the additional water required to plasticise the mix. Further very detailed work may determine how much water and under water conditions is taken up.

The stoichiometric water demand of the mix with 10% added magnesia using Tasmanian cement rises by observation and we think this is mostly due to complex. Assuming Mg(OH)₂.2H₂O is formed by calculation the additional water required for hydration is a minimum of 4-5%. Less than 4-5% appears to be required however for plasticity and so there is a net benefit in terms of reduced water.

As magnesia does not hydrate all that quickly in at least the first half hour or so this water consumption is a potentially a very useful property. There are a number of potential 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. Denser concretes without interconnected pour structures are more durable.
- 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. Brucite protects against sulfates, chlorides and other aggressive salts and delayed reactions do not occur.
- Drying shrinkage does not occur as the water consumed is converted expansively to solidus⁷.
- There is no loss of alkalis in bleed water and the early pH is forced up by water removal.

The advantages of using Portland cement such as ambient temperature setting, easy placement and strength are not diminished

Dimensional Change

Shrinkage is reduced if not eliminated depending on the MgO content 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.

⁶ No data is available for the density of these hydrated gels and the figure for molar volume is a best a guesstimate.

⁷ The molar volume relationships in concrete will be worked out in a new paper one day when I get the time

Strength

Provided excess water is not added tec-cement concretes exhibit high and faster development of strength and this is probably due to the interaction of a number of factors. Most likely are:

- A lower voids:paste ratio as a result of improved rheology due to better particle packing, some surface charge effects and high consumption of water by reactive magnesia as it hydrates and compaction of Brucite once formed.
- More silicification reactions including a more effective pozzolanic reactions during the early plastic stage whilst the pH is possibly elevated.
- Slow release of water by hydrated Brucite gels ($\text{Mg}(\text{OH})_2 \cdot n\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2$) resulting in more complete hydration reactions of PC.

Strength is probably 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.

As to whether pozzolanic reactions occur 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 my 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 hydrated gelatinous sepiolite ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6(\text{H}_2\text{O})$) type compound of low strength.

There may well be other strength affects. As mentioned, 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, Ramachandran et al. 1977). It may be that Brucite is to some extent compacted by its own hydration in tec-cement concretes.

There is however an issue with water as the industry, as everybody and especially finishers, work to slump and because tec-cement mixes are very thixotropic exhibiting Bingham plastic qualities this is leading to the addition of too much water and loss of strength (See ???? on page 7). Until a lot more work is done on rheology, this remains a problem.

Compressive Strength

Unless too much water has been added compressive strength development appears to occur early and more rapidly than PC controls and continues in more or less a straight line right through until ninety days as a minimum.

The interesting feature is the almost straight line strength development after day 3. Even with lower strength concretes that have had too much water added this appears to be characteristic and continues into more than 60 days.

Our best approximation of how the strength curves look is given in Figure 1 as follows.

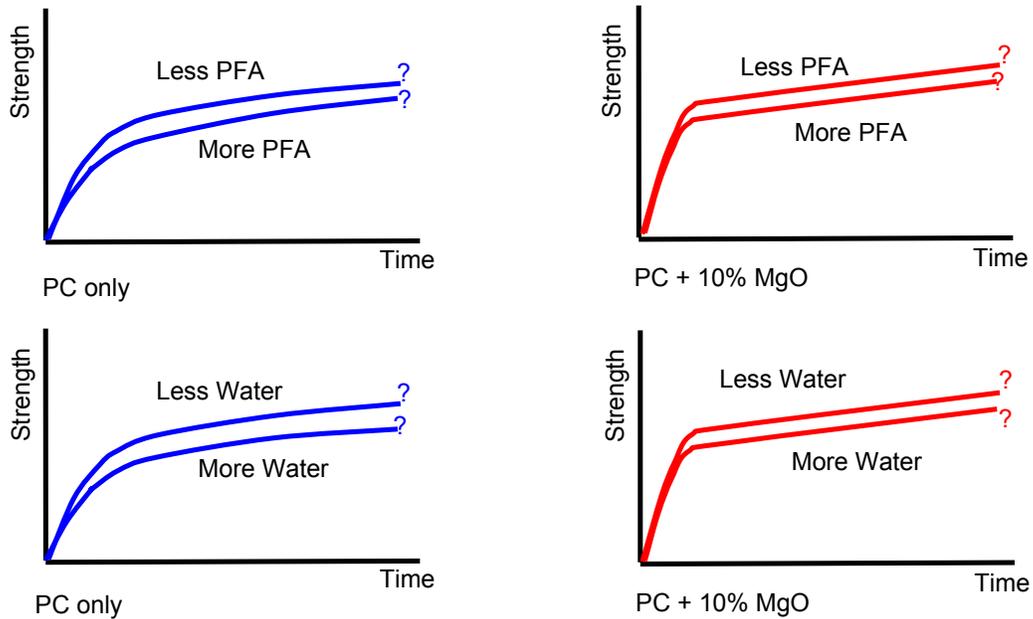


Figure 1 – Indicative Effects of Adding Water, MgO and Fly ash (PFA)

Tensile Strength

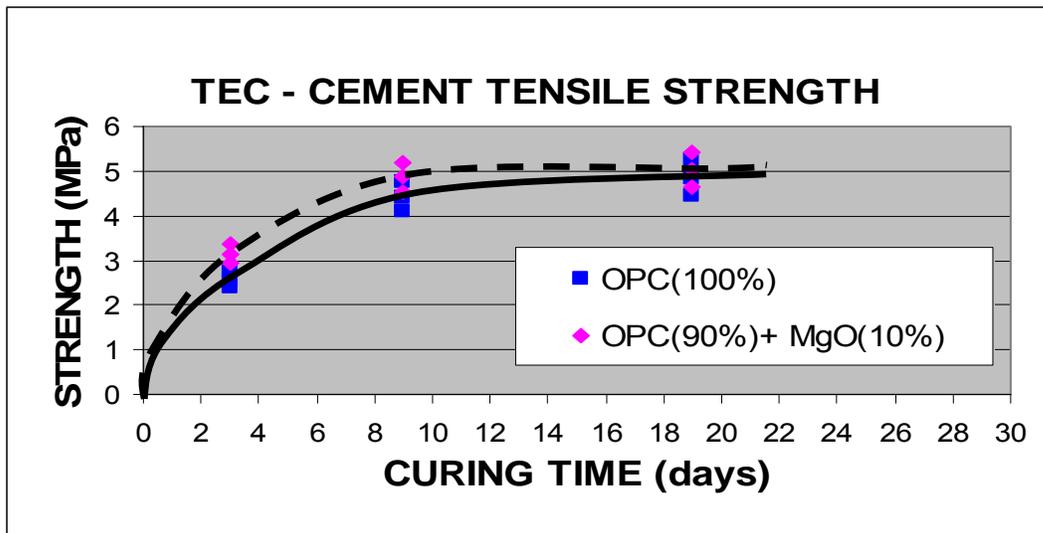


Figure 2 - Tensile Strength (Plot by Oxford Student)

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 3). 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.

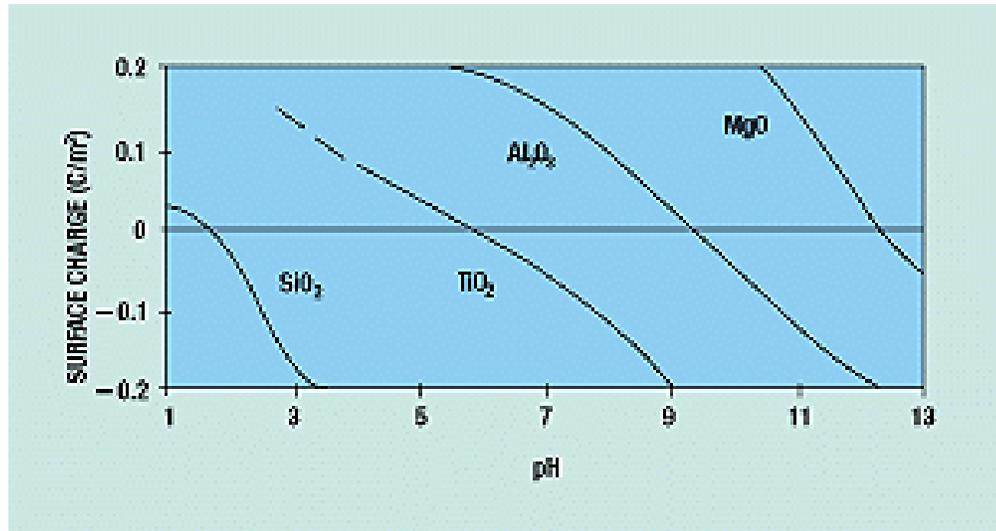


Figure 3 - Effect of Solution pH on the surface charge of various oxides (Small, Peterson et al. 2005)

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 3). 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.

The Rheology of Tec-Cements

This is a complex area and where a lot of work will be required. We have seen some very positive effects, unfortunately however the standard industry practice of working to slump has, because of the thixotropic – Bingham plastic nature of the mixes, resulted in some strength issues through the addition of too much water.

Mineralogical ways of improving the plasticity of mixes are better than using complex organic chemicals for no other reason other than that the behavior of the latter can be unpredictable and many large complex unnatural organic molecules are potentially carcinogens.

Magnesia may potentially be useful as a rheology modifier, but we still have a lot of work to do to optimize usage.

Water as a Plasticizer

Water is the best plasticizer in many ways and what is generally added to concrete by finishers for this purpose. As a minimum of between 4 and 5% more water is consumed in a tec-cement concrete (maybe more – see Magnesium Complexes above) with 10% magnesia substituted for PC, if less water than required is added, greater strength is the result because during the plastic stage there is still a net reduction in water. If more – less strength.

Particle Size and Charge Effects

The reactive magnesia TecEco have been using is around 4-5 microns in size and tends to act as a lubricant to the larger Portland cement (18-26 micron) and fly ash particles (A flat peak from 10 to 100 micron) reducing for example the “stickyness” of fly ash mixes.. See Figure 4 and Figure 5 below.

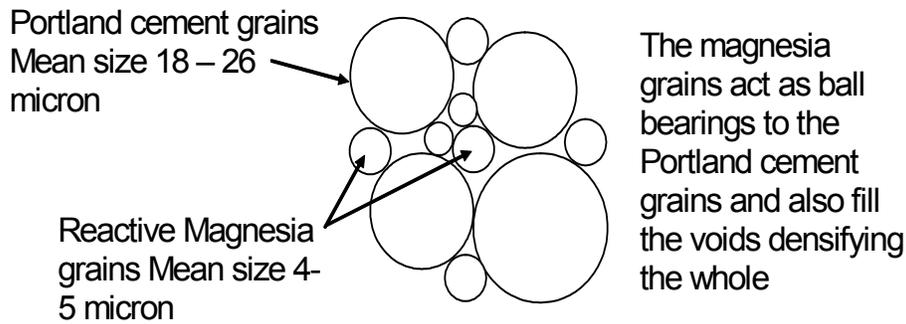


Figure 4 - Particle Packing Effect on Rheology

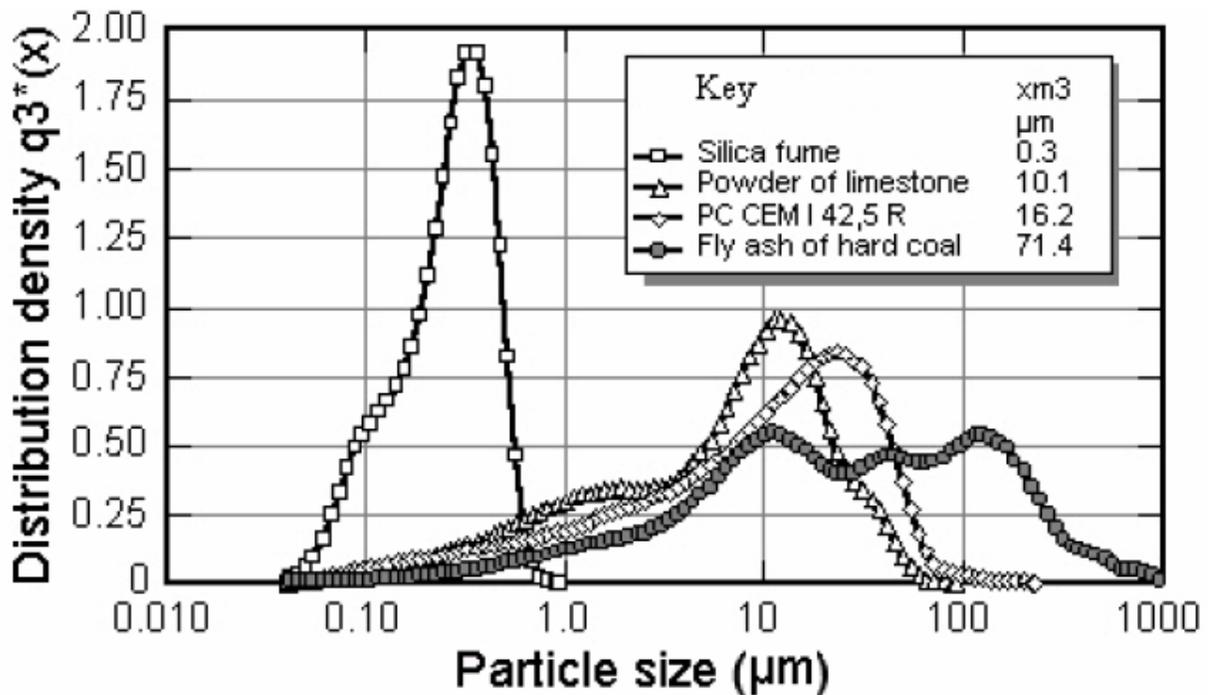
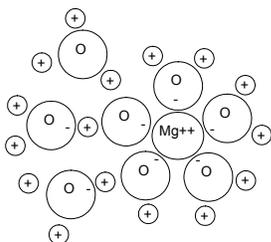


Figure 5 - Particle Size Distribution of Ordinary Portland Cement and Various Mineral Admixtures (after Stark and Mueller)

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 in water. As cements grains also have a net residual positive charge in water, magnesia should mutually repel Portland cement grains.

The consequence of a shift to a negative surface charge on the surface of magnesia as the pH rises as a result of the hydration of di and tri calcium silicates and release of Portlandite have not been determined, neither have the interactions with plasticisers and pozzolans, magnesia and sands been worked out.

What is observable is that tec-cement concrete mixes containing MgO tend to “gel up” quickly, imparting a thixotropic – Bingham plastic quality to the mix. Although this effect could also be due to the removal of water, there are other likely 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 – Bingham plastic property to the rheology of tec-cement concretes. Hence the observation of workability with relatively low slumps

Figure 6 - Thixotropic or Bingham Plastic Rheology of Tec-Cement Concretes

It has also been observed that the "stickyness" associated with the use of fly ash does not appear to be so noticeable and this could be a slipperiness introduced by ionic factors.

Doing Without Plasticisers?

From the above it follows that magnesia may be useful as an adjunct to assist with the viscosity problem of concretes. Because it has other beneficial effects it may be useful as an additive with or instead of plasticisers. Much more work is however required.

Problems to Overcome Using Tec-Cements

There are problems to overcome and much more work to do.

Requiring attention are the following.

1. The habit in the industry of working to slump and lack of training in relation to handling thixotropic – Bingham plastic type mixes is leading to some problems with loss of strength due to too much water being added
2. A possible loss of plasticity when micro silica has also been added due to particle interactions.
3. As yet unknown interactions with additives.

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. The most important improvement is however the extreme durability due to the insolubility of its hydrate. Many other properties of concrete including strength and rheology are also positively impacted.

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