Towards Making Pre-Mix Concrete Foolproof

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Abstract

Most problems with concretes occur during delivery, placement and early life and the addition of too much water is often to blame. Remediation or litigation is not the only solution. Internal removal of water is another option.

Modern concretes are also not very durable because of the high Portlandite content. Removal and replacement by Brucite is suggested.

This paper demonstrates using stoichiometric math that the addition of reactive magnesia to concretes provides additional internal water consumption.

Benefits of water removal and replacement of Portlandite by brucite include strength, less shrinkage and cracking and enhanced durability.

Keywords

Tec-cement, magnesia (M,MgO), Brucite (MH,$Mg(OH)_2$), Portland cement (PC), hydration, silicification, magnesium complexes, pozzolan, di calcium silicate (C_2S, Ca_2SiO_4), tri calcium silicate (C_3S, Ca_3SiO_3), tri calcium aluminate (C_3A, $Ca_3Al_2O_6$), tetra calcium alumino ferrite (C_4AF, $4CaO.Al_2O_3.Fe_2O_3$), gypsum ($C§H_2$, $CaSO_4.2H_2O$), rheology, durability, strength, magnesium complexes.
committed to finding ways of “materially” improving the sustainability of the built environment.

Background

Our observation is that there are less visible problems with concrete such as shrinkage and cracking when reactive MgO has been added to the mix. The reason is that when MgO is added more water than is required by water demand due to the fineness effect is stoichiometrically consumed by it. i.e there is a net water reduction as a result of adding MgO. As the presence of too much water is at the root of most problems with Portland cement concretes, the result is potentially more foolproof concrete and should be investigated further.

There are also many other good reasons to add reactive MgO, notably durability and shrinkage.

To prove the above hypothesis mathematically I have developed a complex spreadsheet that accurately calculates mass and volume relationships.

The variables are the actual formulas of some of the products like CSH, pozzolanic CSH and the degree to which some of the reactions occur. The model is however flexible as the formulae can be changed and reactions changed. The rate and degree of reaction modeling is yet to be improved.

The spreadsheet is a useful tool and fortunately for my company, TecEco Pty. Ltd. confirms the hypothesis that less additional water is required when MgO is added than is stoichiometrical consumed by it mathematically. What is now needed is a lot more work on site to confirm this hypothesis empirically.

Our suspicions about water consumption all started when on a number of occasions we observed that tec-cement concretes do not appear to bleed as much and had much lower shrinkage than ordinary PC concretes.

As at the time of writing this paper our most recent experiment was a 80 cubic metre slab on the Whittlesea Wallan road in Victoria, Australia. Approximately 8% PC was substituted by reactive MgO. The concrete also contained 36% fly ash to PC and its composition was as in Table 1.

Table 1 – 20MPa High Fly Ash Mix

EXPERIMENT NO =>	**A30**
PURPOSE	TecEco 20 MPa high fly ash mix
Date of Experiment	18-03-05
CEMENT	
OPC (grey or off white)	180.00
Magnesia	15.00
TOTAL CEMENT	195.00
OTHER PASTE POZZOLANS	
Fly Ash	65.00
SUB TOTAL POZZOLANS	65.00
TOTAL PASTE	260.00
MIXED PASTE AND SAND/AGGREGATE	
Quarry Dust 5 mm all in	100.00
TOTAL MIXED PASTE	100.00
SANDS	
Course Sand	850.00
TOTAL SANDS	850.00
AGGREGATE	
Aggregate 14 mm	500.00
Aggregate 20 mm	500.00
TOTAL AGGREGATE	1000.00
SUB-TOTAL	2210.00
AEA	25ml/m3
Water Cement Ratio	84.62%
Water Binder Ratio	63.46%
Fly ash/PC ratio	36.11%
Pozzolan/PC ratio	36.11%
Magnesia/PC ratio	8.33%
Paste aggregates ratio	26.00%

Strength development, and in particular early strength development was good. Also noticeable was the fact that the concrete was not as "sticky" as it normally is with a fly ash mix exhibiting a shear thinning property. Furthermore less bleeding was noticed.

Most importantly we did some shrinkage tests and were please to see that at 7 days shrinkage was 133 micro strains, at 14 days, 240 micro strains, 28 days, 316 micros strains and at 56 days 470 micro strains - much less than normal. The slab was also inspected a couple of weeks after it was poured and in spite of the fact that no crack control was installed there were only a few very small micro cracks that were visible from a position of being on hands and knees. 80 cubic metres is a large slab for no crack control.

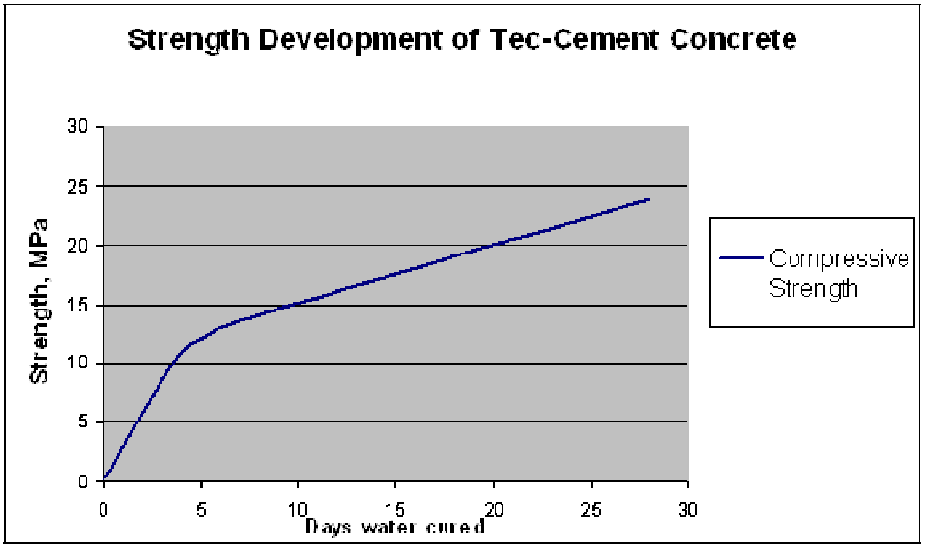

Figure 1 - Strength Development of Tec-Cement Concrete

The curve for strength development was quite different to that of ordinary Portland cement concretes as can be seen from the plot above. Noticeable was the high early strength gain even with added fly ash and the straight line development thereafter which from our work so far appears to continue for a considerable period.

As at the date of writing (three months later) the concrete from the pour is continuing to gain strength at the rate of 5 MPa a month.

Volume Changes in Concrete

Concrete is an inherently challenging material. Apart from the reactivity of Portlandite the biggest problem is shrinkage and cracking brought about by volume changes.

Strength and durability are directly related to density and porosity. More durable and stronger concretes have less capillary pore volume and cracks.

The most important addition other than cement is water to plasticise the mix. The lowest amount that still results in a workable plastic mix should be used as too much will result in more voids and cracking.

The objective should be to make dense concretes with high early strength gain, hydrating as much of the binder as possible, minimising pores and capillary and crack voids as well as bleed water. The addition of reactive magnesia goes a long way towards achieving this mainly because it internally consumes significant water.

The difference between the observable characteristic – the water binder ratio, and what matters – the voids paste ratio or density of the concrete is shown in Figure 2.

Engineers talk about bleed water being a good thing. What they really mean is that surface shrinkage is a bad thing and having a film of bleed water present long enough for tensile strength to develop tends to prevent this. The converse is actually true. Concrete should be a closed system as alkalis exit in bleed water. The key is to prevent surface shrinkage and this occurs in tec-cement concretes to some extent because the mix is more homogenous, holding more water through the formation of Brucite gels.

Problems with freshly made concrete such as loss of workability at or before placement resulting in on site addition of water, segregation or too much bleeding during consolidation or an unusually slow rate of strength gain because of too much water or insufficient binder or hydration of binder present increase porosity and cracking and impair and reduce service life.

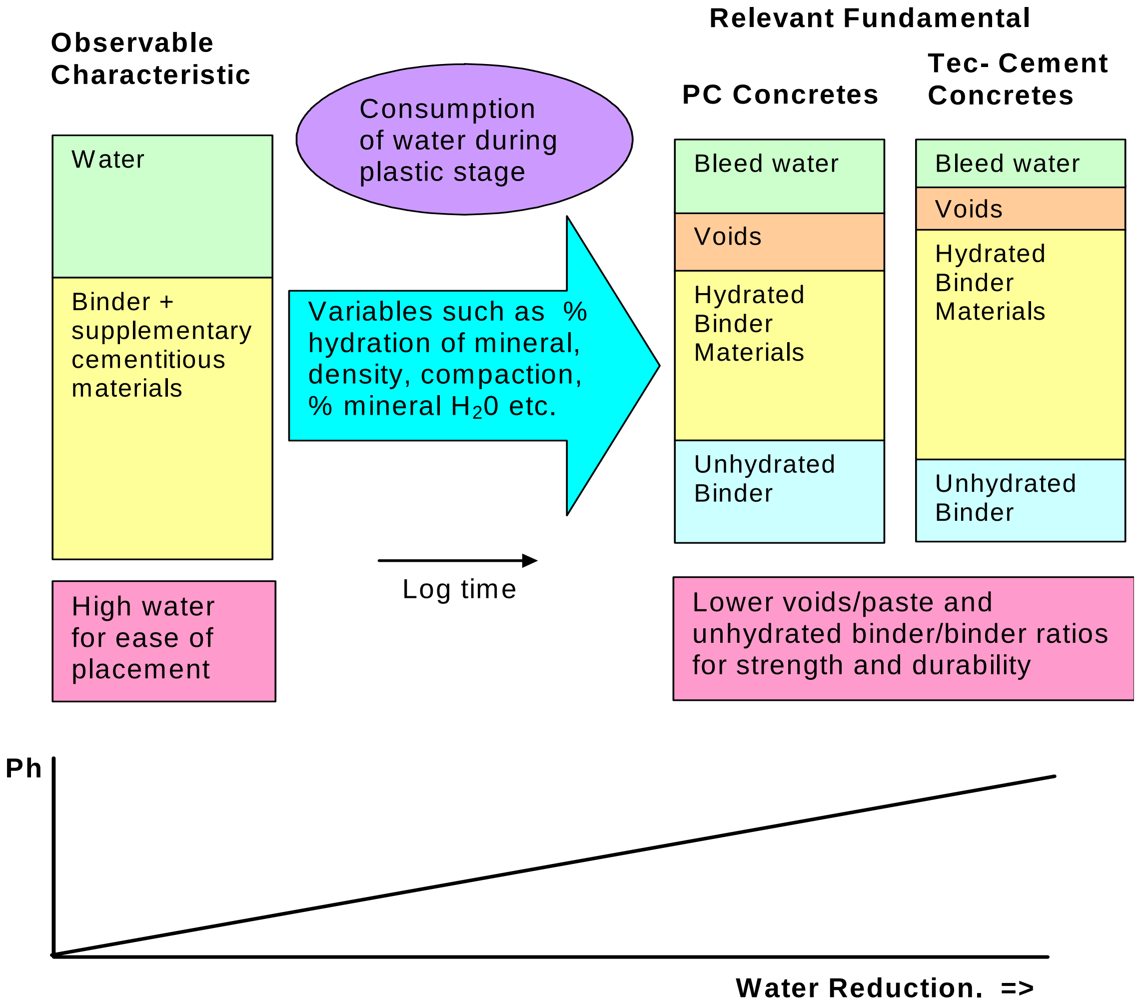

Figure 2 - The Relationship between the Water Binder Ratio, Voids Paste Ratio, PH Durability and Strength.

Increased permeability and especially cracking allows the ingress of aggressive chemicals which eventually leads to premature corrosion of reinforcing steel, spalling and deterioration of concrete. The result is increased maintenance costs and reduced service life.

These problems are confounded by early age treatment on site by finishers who generally add too much water and the use of incompatible admixtures as concrete mix designs become more complex[1].

The Impact of TecEco Technology on Shrinkage and Cracking.

One of the reasons for adding reactive magnesia to concrete mixes is that significant additional water is consumed as the magnesia hydrates forming Brucite gels.

To explain this a discussion on hydration reactions in ordinary Portland cement and tec-cement concretes thought to be representative of the complicated and poorly understood processes that actually take place in real concretes follows and is presented in summary form under the heading Summary Reactions Mechanisms of MgO in Tec-Cement Concretes on page 15.

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[1] The likelihood of incompatibility among materials increases with the number of ingredients added to the mix. The problem is compounded because not much is known about the factors that lead to incompatibility, and tests are lacking to determine the susceptibility of materials combinations to distress mechanisms.

Hydration Reactions of Portland Cement

The composition of the cement particles is conventionally broken down into several pure phases. It is however to be remembered that this is at best idealization. The reactions given are only representative or real reactions and real particles vary in composition, have regions which are not pure or that are hybrids of different proportions of silicate, ferrite and aluminate. Concrete chemistry is still not totally resolved and varying clinkers and conditions add to the complexity of the products produced.

Concretes are complex systems and there is still considerable controversy in the literature about what reactions are actually occurring and what the spatial consequences are, what is the rate of these reactions, what the mechanisms are and even the exact chemical composition of the species that may exist during hydration.

The first to identify major cement minerals was Le Chatelier in his doctoral thesis in 1905 (Bogue and Steinour 1961). Bogue predicted phase compositions starting from oxide analyses of clinker (Bogue 1929). Although these predictions are still widely used they can as previously mentioned only be considered as approximations. The amorphous gels and crystalline products produced during hydration actually have a wide variety of chemical forms (Taylor 1990) and the analysis is deficient to that extent.

At best the idealized cement hydration reactions calculated presented are only approximations.

Mass and volume of Water Consumed in Hydration Reactions

Cracking is the result of shrinkage and high permeability is the result of excess water. As shrinkage is substantially caused by loss of water both are related.

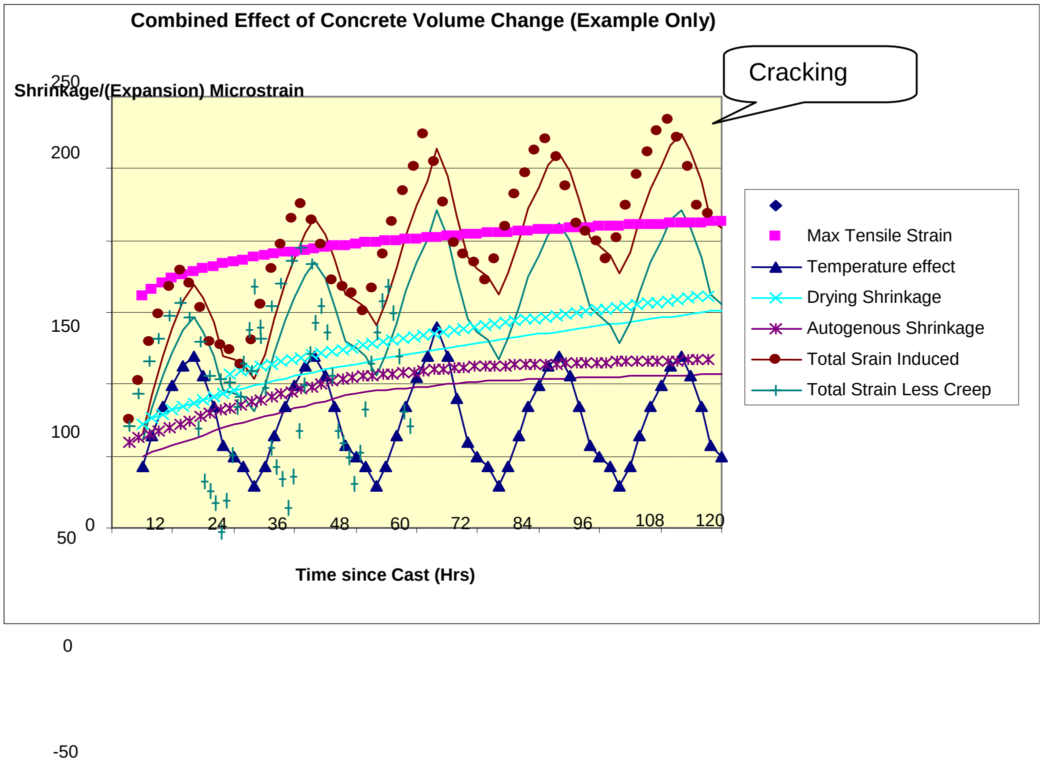

Figure 3 - Combined Effect of Concrete Volume Change. Example after Tony Thomas (Boral Ltd.) (Thomas 2005)

Visible evidence of an undesirably high voids:paste ratio (see Figure 2) and high permeability and shrinkage is cracking. Concrete that is badly cracked is not acceptable as the phenomena is obvious and detracts from appearance. Both high permeability and cracking reduce durability.

Portland cement concretes generally shrink, however cracking only occurs if total strain less creep exceeds the maximum tensile strain of the concrete as shown in the example plots in Figure 3.

It follows that an understanding of the volumetrics of concretes is essential if the strength and durability related to permeability of concrete is to be improved and cracking reduced

Mehodology

A complex mathematical model was created in a spreadsheet of the mass and volume changes in relation to reactions going on in a concrete with or without the addition of reactive magnesia and silica as in fly ash. The stoichiometry, mix ratios, water and a number of other variables can be changed in the model.

As the exact composition of CSH, pozzolanic CSH as well as the ferrite reactions are still being debated the best approximations available to us have been used for the stoichiometry and provided by Bentz et. al. (Bentz, Coveney et al.). The reader should be cautious as the model is only as only as good as the inputs and we welcome corrections.

The model was confirmed as correct as mass balance was present at all times. The methodology used was to work out the mass and volume relationships of all major known reactions and to then using the composition of a particular cement available readily in Australia, with or without the addition of reactive magnesia and silica as in fly ash to determine the overall mass, volume and water changes. Unknown but suspected reactions such as a reaction analogous to the formation of Mg hydrogarnet were not included.

The complex mathematical model of the hydration of Portland cement and tec-cement is available for a small fee from TecEco Pty Ltd. Using the spreadsheet makes it much easier to analyse the mass and volume stoichiometry of reactions.

Finally reference is made to some properties such as strength and durability as a result of the volume changes consequential to changes in proportions and composition of reactants and products.

Data

Data was assembled as in Table 2 and the molar stoichiometry of Bentz et. al. (Bentz, Coveney et al.) was used for Portland cement clinker components as it is probably the most up to date and accurate[2].

Densities from the cement literature (Lu, Sun et al. 1993) (Mindess and Young 1981) (Young and Hansen 1986), summarised in Table 2 were used to calculate molar volumes.

Table 2 - Densities and molar volume stoichiometries of cementitious materials

Compound Name	**Cement Nomenclature**	**Compound Formula**	**Density (g cm^{-3})**	**Molecular Weight**	**Molar Volume (cm^{-3} mol^{-1})**
Tricalcium silicate	C_3S	Ca_3SiO_3	3.21	228.33	71.13
Dicalcium silicate	C_2S	Ca_2SiO_4	3.28	172.25	52.51
Tricalcium aluminate	C_3A	$Ca_3Al_2O_6$	3.03	270.2	89.17
Tetracalcium aluminoferrite	C_4AF	$CaO.Al_2O_3.Fe_2O_3$	3.73	485.98	130.28
Gypsum	C§H$_2$	$CaSO_4.2H_2O$	2.32	188.18	81.11
Calcium silicate hydrate	$C_3S_2H_4$	$C_{1.7}SH_4$, (sometimes approximated as $Ca_3Si_2.O_7.4H_2O$)	1.85	227.49	122.97
Pozzolanic C-S-H	$C_{1.1}SH_{2.1}$	$C_{1.1}Si.H_{2.1}$	1.97	159.61	81.02
Calcium hydroxide	CH	$Ca(OH)_2$	2.24	74.08	33.07

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[2] If readers have more accurate date please contact the author.

Ettringite	$C_6A§_3H_{32}$	$Ca_6Al_2(SO_4)3(OH)_{12}\cdot 26H_2O$	1.75	1303.14	744.65
Monosulfoaluminate hydrate	$C_4A§H_{12}$	$3CaO\cdot Al_2O_3\cdot CaSO_4\cdot 12H_2O$	1.99	638.54	320.87
Hydrogarnet	C_3AH_6	$Ca_3Al_2(O_4H_4)_3$	2.52	429.30	170.35
Iron hydroxide	FH_3	$Fe(OH)_3$	2.2 (Estimated (Bentz, Coveney et al.))	106.85	48.57
Magnesia	M	MgO	3.6	40.31	11.20
Brucite	MH	$Mg(OH)_2$	2.39(Robie, Hemingway et al. 1979)	58.31	24.40
Brucite gel		$Mg(OH)_2.2H_2O$ (?)	2.39 (?)	91.36 (?)	39.81 (?)
Water	H	H_2O	1	18.02	18.02
Magnesia	MgO	MgO	1.738	40.31	23.19
Silica	S	SiO_2	2.21 (fused silica)	60.09	27.14

Cement Nomenclature: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, § = SO_3, CH = $Ca(OH)_2$, and H = H_2O (§ is a representation of $\bar{S}$ which is actually used

Reaction Stoichiometry

The four major clinker phases present in Portland cement (which is the most widely used) are tricalcium silicate (C_3S , Ca_3SiO_3), dicalcium silicate (C_2S ,Ca_2SiO_4), tricalcium aluminate (C_3A, $Ca_3Al_2O_6$), and tetracalcium aluminoferrite (C_4AF, $4CaO.Al_2O_3.Fe_2O_3$.

The model assumes 100% hydrates for the purposes of this paper however this can be varied and the consequences of doing so will later be considered.

The reactions of di and tri calcium silicate are simpler than those of the aluminate and ferrite phases of Portland cement.

C_3S (Tri Calcium Silicate)

The hydration product of tri calcium silicate (C_3S) is referred to as calcium silicate hydrate and when C_3S reacts with water, a nanoporous, amorphous calcium silicate hydrate (CSH) gel is deposited on the surfaces of the original C_3S and on previously deposited CSH , while calcium hydroxide (CH) crystals nucleate and grow in the available capillary pore space. As time proceeds, the CSH gel polymerizes to some extent and may even crystallize.

$C_3S + 5.3H ==> C_{1.7}SH_4 + 1.3CH$

$228.33 + 95.51 ==> 227.49 + 96.30$ Molar masses

$1 + 1.34 ==> 1.73 + .60$ Molar volumes (relative to C_3S)

Tri calcium silicate is the major component of Portland cement because of its more rapid reaction rates and 50-70% is generally present in modern clinkers. Clinkers from twenty or thirty years ago contained significantly less.

Tri calcium silicate is responsible for controlling many of the ultimate properties of concrete including rate of strength gain and strength properties.

Di Calcium Silicate (C_2S)

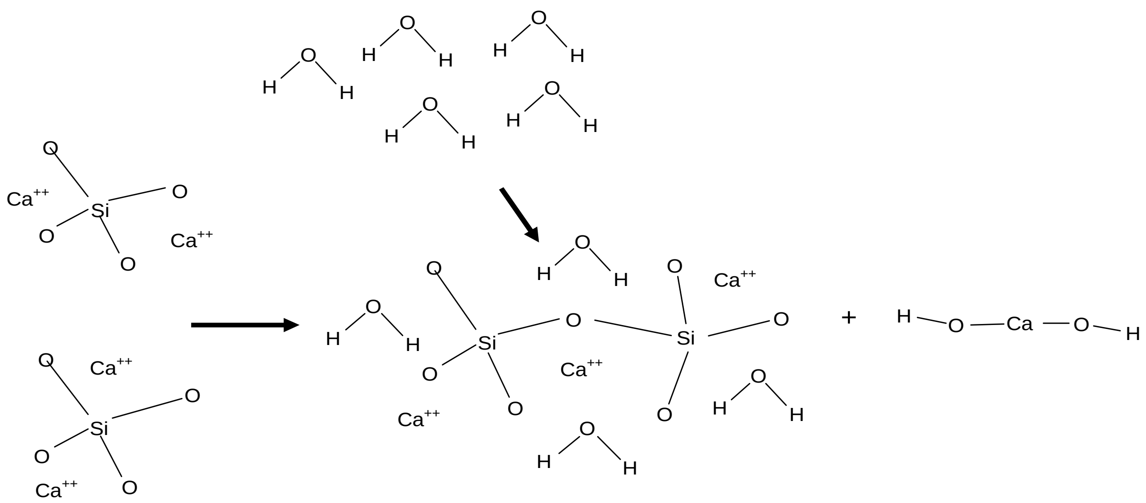
The hydration reactions for di calcium silicate (C_2S) are similar but slower and less CH is formed because C_2S has a lower Ca/Si molar ratio. High C_2S concretes do not develop strength as quickly but are more durable due to the lower lime content.

C_2S + 4.3H ==> $C_{1.7}SH_4$ + .3CH

172.25 + 77.47 ==> 227.49 + 22.23 Molar masses

1 + 1.48 ==> 2.34 + .19 Molar volume (relative to C_2S as 1)

An approximation using “atom and stick” nomenclature follows:



The Pozzolanic Reaction

Pozzolanic materials such as silica fume and fly ash are these days extensively used in concretes and recommended for tec-cement concretes. The stoichiometry for the pozzolanic reaction is based on recently published data (Lu, Sun et al. 1993) and is an approximation as it is likely to vary with water-to-cement (w/c) ratio and silica fume content. The pozzolanic reaction is similar to the hydration reaction for C_2S and C_3S; the difference is that the components all come together to form compounds that are hydrated silicates with less calcium and bound water.

The extent of pozzolanic reactions depends on the quantity of silica (S) added and the amount of calcium hydroxide (CH) produced as a result of the hydration reactions of PC.

1.1CH + S + H ==> $C_{1.1}SH_{2.1}$

81.51 + 60.09 + 18.02 ==> 159.61 Molar masses

1.34 + 1 + .66 ==> 2.98 Molar volume (relative to S as 1)

1 + .75 + .50 ==> 2.23 Molar volume (relative to CH as 1)

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.

The CH (Portlandite) that reacts in the pozzolanic reaction is mainly supplied from the hydration reactions of C_3S and C_2S in Portland cement (see above). C_3S produces approximately three times as much CH (Portlandite) as C_2S on a volume and molar basis.CH is also produced during the hydration of C_3A and C_4AF

Modern cements have less and less C_2S. For example the local plant where I live in Tasmania, run by Australian cement, produces cement of the following approximate composition.

C_3S (Ca_3SiO_3) - 68%, C_2S (Ca_2SiO_4) - 6%, C_3A ($3CaO.Al_2O_3$) - 6%, C_4AF ($4CaO.Al_2O_3.Fe_2O_3$) - 10%, $C\S H_2$ ($CaSO_4$) - 3.6%, ($CaCO_3$) - 5.4%, M (MgO) - 2%, C (CaO) <1%, Na_2SO_4, K_2SO_4 <.6%

Like the Goliath general purpose cement described above, the C_2S content of cements around the world has been falling because people are demanding faster setting mixes and C_3S hydrates much more quickly than C_2S. As a consequence, if the objective is to remove lime, more silica is required to react with the higher proportion of CH produced from C_3S in the pozzolanic reaction today than say a decade ago.

Often not considered is that fact that fly ash is never pure silica and not all of it will react in the pozzolanic reaction. Unfortunately fly ashes vary and it is impossible to give an average composition. Reactive silica is however usually only 50 – 70 mass% of the total.

As the theory behind TecEco cements is to consume all the CH (Portlandite) it is recommended that excess fly ash is added and 30 – 40 mass% is a good figure to aim for.

Note that some of the other compounds in fly ash will also participate in other silicification reactions (see later)

Tri Calcium Aluminate

When gypsum ($C§H_2$) is not present in the system, C_3A reacts rapidly with water to form a variety of crystalline hydration products, with hydrogarnet, (C_3AH_6), being the ultimately stable mineral formed.

Reactions are slower and much more complex in the presence of $C\bar{S}H_2$ which is specifically added to Portland cement to avoid 'flash set.'

The first product of the reaction of C_3A with $C§H_2$ is needle like ettringite, $C_6A_3§H_{32}$ crystals which are thought to be more sensitive to additives such as sucrose retarders and variations in temperature (Bentz, Coveney et al.) than other components of PC.

When all of the $C§H_2$ is consumed, the ettringite mostly decompose, reacting with more C_3A to form monosulfoaluminate hydrate, ($C_4A§H_{12}$). Sulfate ions are generally more mobile than aluminate ions so that ettringite forms either in solution or at the surfaces of the aluminate phases in cement paste. Because ettringite is unstable above 60 ºC, care needs to be taken with autoclaved concrete that it does not form later.

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.

In the absence of or insufficient gypsum:

$C_3A + 6H ==> C_3AH_6$

$270.2 + 108.12 ==> 429.30$ Molar masses

$1 + 1.21 ==> 1.68$ Molar volumes (relative to C_3A as 1)

In the presence of gypsum:

$C_3A+3C§H_2 + 26H ==> C_6A§_3H_{32}$

$270.2 + 564.53 + 468.52 ==> 1314.94$ Molar masses

$.37 + 1 + 1.93 ==> 3.09$ Molar volumes (relative to $C§H_2$ as 1)

$1 + 2.73 + 5.25 ==> 8.43$ Molar volumes (relative to C_3A as 1)

26 moles of water are consumed per mole of tri calcium aluminate to from a mole of solid ettringite. Note the significant volume of water consumed.

Ettringite then reacts slowly with the remaining tri calcium aluminate to form monsulfoaluminate hydrate consuming a further 4 moles of water relative to tri calcium aluminate.

$2C_3A+ C_6A§_3H_{32}+ 4H ==> 3C_4A§H_{12}$

540.4 + 1314.94 + 72.06 ==> 1915.61 Molar masses

.24 + 1 + 0 10 ==> 1.28 Molar volume (relative to $C_6A\S_3H_{32}$ as 1)

1 + 4.21 + .40 ==> 5.40 Molar volume (relative to C_3A as 1)

Tetra Calcium Alumino Ferrite

The reactions of the ferrite phase, tetracalcium aluminoferrite (C_4AF), are the least well understood and the slowest. They are most like those of C_3A, with the production of additional CH and FH3 to account for the extra calcium and iron present in the C_4AF phase (Brown 1987).

$C_4AF + 3C\S H_2 + 30H \Longrightarrow C_6A\S_3H_{32} + CH + FH3$

485.98 + 564.53 + 540.48 ==> 1314.94 + 74.10 + 213.75 Molar masses

.54 + 1 + 2.22 ==> 3.09 + .14 + .40 Molar volumes (relative to $C\S H_2$ as 1)

1 + 1.87 + 4.15 ==> 5.77 + .25 + .75 Molar volumes (relative to C_4AF as 1)

$2C_4AF + C_6A\S_3H_{32} + 12H \Longrightarrow 3C_4A\S H_{12} + 2CH + 2FH_3$

971.96 + 1314.94 + 216.19 ==> 1915.61 + 148.19 + 427.50 Molar masses

.350 + 1 + .29 ==> .43 + .089 + .26 Molar volumes (relative to $C_6A\bar{S}_3H_{32}$ as 1)

$C_4AF + 10H \Longrightarrow C_3AH_6 + CH + FH_3$

485.98 + 180.16 ==> 378.30 + 74.10 + 213.75 Molar masses

1 + 1.38 ==> 1.31 + .25 + 37

1 + 1.38 ==> 1.15 + .25 + .75 Molar volumes (relative to C_4AF as 1)

Obviously assumptions need to be made and care taken in balancing $C\S H_2$ to the amounts of C3A and C4AF present.

Silicification Reactions

Hydrolysis and Recombination

As Portlandite is formed as a consequence of the hydration of PC minerals the pH of the mix rises to around 12.5 -13 or more at equilibrium depending on soluble alkalis also present[3] and whether reactive magnesia has been added.

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.

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[3] 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

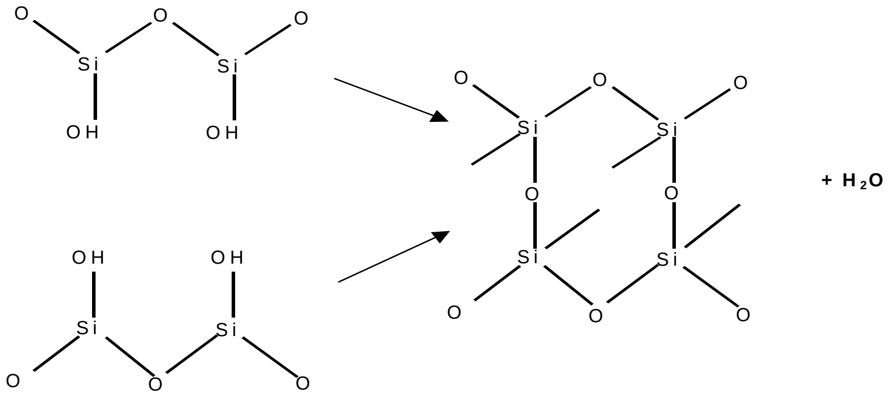

Figure 4 - Surface Bonding of Silicates through Hydrolysis.

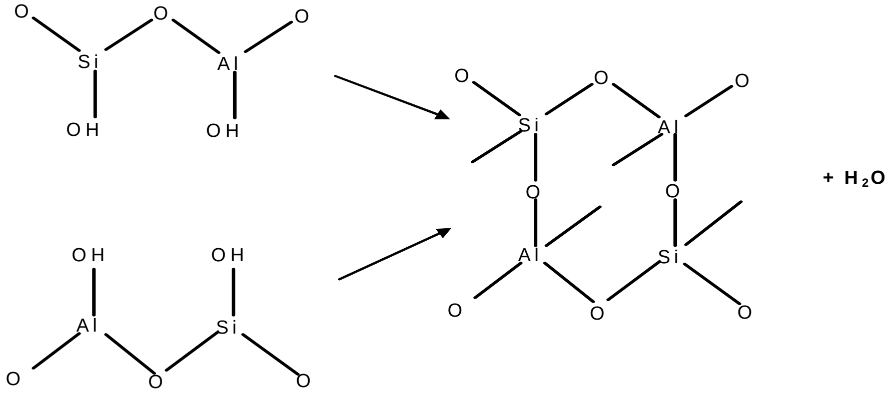

Figure 5 - Surface Bonding of Silicates/Aluminates through Hydrolysis (or any other surface combination of Si and Al) (after Van Jaarsveld and Van Deventer 1996) similar diagrams have been used by Davidovits (Davidovits 1994)

In tec-cement concrete formulations many wastes containing silica and alumina such as fly ash and ground granulated blast furnace slag[4] that are added tend to recombine in the above manner as well as becoming involved in the pozzolanic reaction.

Calculating Volume stoichiometries of Water Consumed

Overall water consumption can be calculated using a complex spreadsheet developed by TecEco.

Commonly 40-65% water is added at pre-mix plants which is more than required. Even with water reducing agents and other chemicals added water still usually bleeds from freshly poured concretes. Much more water than can be consumed in the production of ettringite and by other hydration reactions is usually added causing significant problems.

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 have little or no work to do placing concrete?

Water Consumption by Magnesia in Tec-Cements

It would seem that we will not be able to change the practice of finishers – on the contrary, the author has not seen a rake or vibrator on a slab for some years.

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[4] pozzolans

The only alternative is to make concrete more forgiving of bas practice and this involves the removal of excessive water. Magnesia added in a tec-cement concrete has the important function of consuming water. We are very interested in the extent to which MgO, when it reacts with water forms a "gel" containing hydrated complexes of the general form $Mg(OH)_2.nH_2O$ – as by doing so it would use a lot more water than the amount calculated for a simple hydration reaction from magnesia to Brucite.

According to Skalmowski, in the first stage of magnesium oxide hydration Brucite is not formed; instead metastable magnesium hydroxide [$Mg(OH)_2$•nH_20] is formed and only after some time does it recrystallizes to Brucite which is the stable. (Skalmowski 1957).

Investigations done in Japan but not detailed by Skalmowski proved that the structure of metastable magnesium hydroxide is 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” 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% may remain unhydrated. 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 the hydration stoichiometry is as follows:

$MgO + H_2O ==> Mg(OH)_2$

40.31 (MgO) + 18.02 (H_2O) ==> 58.33 $Mg(OH)_2$ – molar mass

11.26 (MgO) + 18.02 (H_2O) ==> 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 $Mg(OH)_2.2H_2O$ (assuming .2 H_2O) the stoichiometry is:

$MgO + 3H_2O ==> Mg(OH)_2.2H_2O$

40.31 (MgO) + 54.05 (H_2O) ==> 94.36 $Mg(OH)_2.2H_2O$ – molar mass

11.26 (MgO) + 54.05 (H_2O) ==> 39.81 $Mg(OH)_2$ – molar volume[5]

An increase in over three molar volumes of solid produced and significant consumption of water. Our experience is that water consumption is more than the additional water required to plasticise the mix.

The affects of adding MgO (M) and silica (S) to a standard formulation is calculated by our model as shown below in Table 3.

Table 3 – Affect of Addition of MgO (M) and Pozzolanic Silica (S) on Water Binder Ratios and Excess Water

	Scenario	

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[5] No data is available for the density of these hydrated gels and the figure for molar volume is a best a guestimate.

Parameters	No M or S	10% M	$Mg(OH)_2.H_2O$ 10%M	10%M 30%S	$Mg(OH)_2.H_2O$ 10%M 30%S
Total binder	251.539	251.540	251.540	251.54	251.54
Desired Water binder ratio	0.500	0.500	0.500	0.500	0.500
Calculated water from water binder ratio	125.769	125.770	125.770	125.770	125.770
Actual stoichiometric water binder ratio	0.409	0.407	0.424	0.397	0.414
Actual water from stoichiometry	102.943	102.387	106.711	99.867	104.122
Excess water (or deficiency in H)	22.826	23.383	19.059	25.903	21.648
Volume difference solid products to reactants	97.925	97.690	99.515	95.349	97.14
(increase means more product, less water)					

The affect of adding MgO (M) is to raise the water binder ratio for complete hydration as could be expected.

As magnesia does not hydrate all that quickly in at least the first half hour or so the additional water consumption by it is a potentially a very useful property. There are 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 as much. Denser concretes without interconnected pour structures are more durable.

Tec- cements concretes tend to dry 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. Some proof is provided by concretes such as in the Harlem high bridge in New York, which has a very durable concrete in which the matrix is full of Brucite.

Drying shrinkage does not occur as the water consumed is converted expansively to solidus. There is less loss of alkalis in bleed water and the early pH is forced up by water removal.

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

Strength

The most considered property of concrete is 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 (See Figure 8 below). Most likely are:

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

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 our 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 ($Mg_4Si_6O_{15}(OH)_2 \cdot 6(H_2O)$) 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.

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.

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 $[Mg(OH)_2 \bullet nH_20]$ 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 4 - 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	$MgO + SO_4^{--}$ => 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

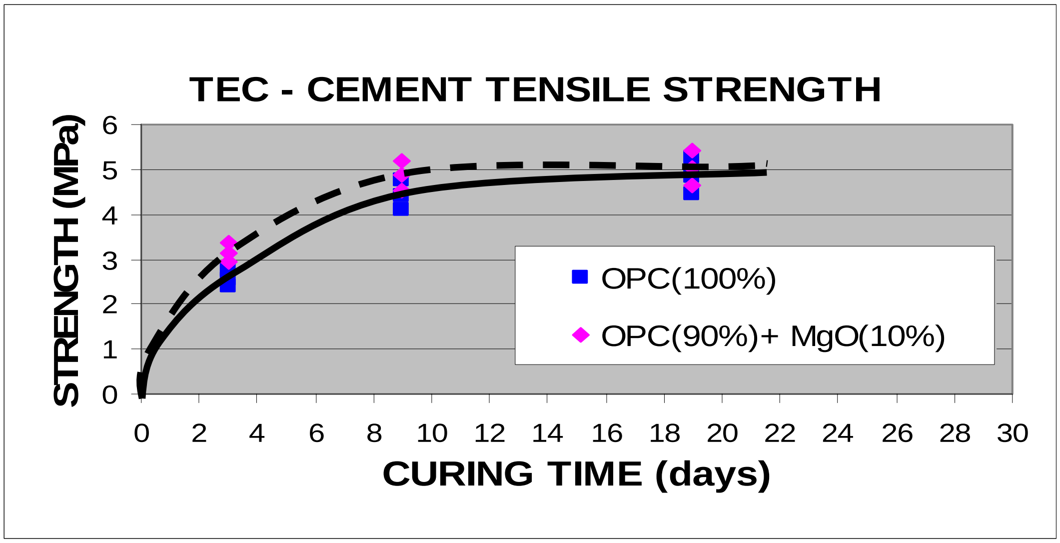

Figure 6 - Tensile Strength (Plot by Oxford Student)

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.

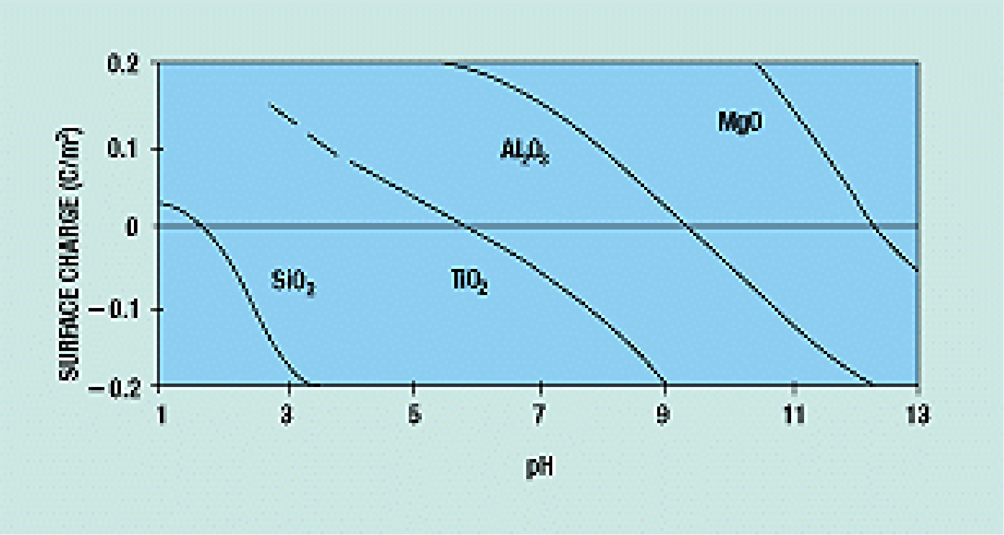

Figure 7 - Effect of Solution pH on the surface charge of various oxides (Small, Peterson et al. 2005)

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.

Adding the Right Amount of Water - Problems Relating to Slump as a Measure of Workability

Problems have been experienced with the addition of water in tec-cements as the industry and especially finishers, work to slump. Because tec-cement mixes are very thixotropic exhibiting shear thinning Bingham plastic qualities this is leading to the addition of too much water and loss of strength. Finishers and others in the industry should use workability as a measure rather than slump and a lot more work is done on rheology and additives with respect to using tec-cement concretes.

We have had some conflicting results and water seems to be causal factor. As with other concretes such as ordinary PC concrete the addition of too much reduces strength. Figure 8 below is an attempt to graphically illustrate this given our current state of knowledge.

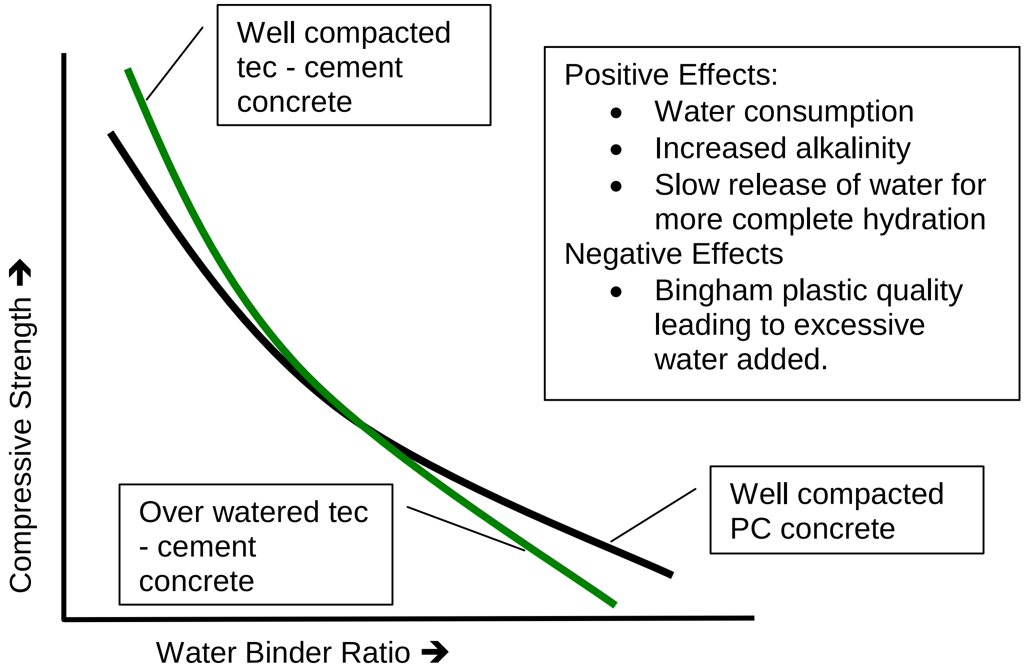

Figure 8 - Interactions between Strength Giving and Weakening Effects in Tec-Cement Concretes and their Possible Relationship to the Water/Binder Ratio.

The problem is that the industry and especially finishers, work to slump. Because tec-cement mixes are very thixotropic exhibiting shear thinning Bingham plastic like qualities and this is leading to the addition of too much water and loss of strength. Finishers and others in the industry should use workability as a measure rather than slump and until a lot more work is done on rheology and additives, this will remain a problem with tec-cement concretes which are workable even with low slump.

Conclusion

The addition of reactive magnesia to control water reducing shrinkage and cracking is a new tool available to cement chemists. It may be possible by adding reactive magnesia to mixes to reduce shrinkage and cracking to negligible amounts and work so far gives support to this contention.

By adding reactive magnesia 7 day plus shrinkage in accordance with AS 1012.13 is reduced. As most shrinkage appears to occur before 7 days, with this new technology there is a strong case to measure shrinkage from day 0.

References

Beaudoin, J. J., V. S. Ramachandran, et al. (1977). "Impregnation of Magnesium Oxychloride Cement with Sulfur." American Ceramic Society Bulletin **56**: 424.

Bentz, D. P., P. V. Coveney, et al. "Cellular Automaton Simulations of Cement Hydration and Microstructure Development." Retrieved 8 May 2005, 2005, from http://ciks.cbt.nist.gov/~garbocz/cell1994/cellauto.htm.

Bogue, R. H. (1929). "Calculation of the compounds in Portland cement." Ind. Eng. Chem. Anal. Ed. **1**: 192-7.

Bogue, R. H. and H. H. Steinour (1961). "Origin of the Special Chemical Symbols Used by Cement Chemists." Journal of the PCA Research & Development Laboratories **3**(3): 20-21.

Brown, P. W. (1987). "Early hydration of tetracalcium aluminoferrite in gypsum and lime-gypsum solutions." J. Am. Ceram. Soc. **70**: 493-6.

Davidovits, J. A. (1994). "GEOPOLYMERS: Inorganic polymeric new materials." J. Materials Education **16**(2 & 3): 91-139.

Lu, P., G. K. Sun, et al. (1993). "Phase composition of hydrated DSP cement pastes." J. Am. Ceram. Soc. **76**(4): 1003-1007.

Mindess, S. and J. F. Young (1981). Concrete. Englewood, NJ, Prentice Hall.

Robie, R. A., B. S. Hemingway, et al. (1979). "Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (105 pascals) pressure and at higher temperatures." Geol. Surv. Bulletin: 1452.

Skalmowski, W. (1957). Chemistry of Building Materials. Warszawa, Budownictwo I Architectura.

Small, R. J., M. L. Peterson, et al. (2005). "Using a buffered rinse solution to minimize metal contamination after wafer cleaning." MicroMagazine.com Retrieved 15 April 2005, from http://www.micromagazine.com/archive/98/01/small.html.

Thomas, W. A. (2005). Early Age Protection of Concrete. Sepcifying for Commercial Reality, Hobart, Boral.

Van Jaarsveld, J. G. S. and J. S. J. Van Deventer (1996). "The Potential Use of Geopolymeric Materials to Immobilise Toxic Metals. Part 1 Theory and Applications." Minerals Engineering **10**(7): 659-669.

Young, J. F. and W. Hansen (1986). Volume relationship for C-S-H formation based on hydration stoichiometry. Microstructural Development During Hydration of Cement, Boston MA, Mater. Res. Soc. Symp. Proc.