An update on Recent Advances in Carbonating and PC-GBFS-Flyash Concretes with Added Reactive Magnesia

John Harrison, TecEco Pty. Ltd.

Abstract

Although a large number of almost fully carbonating products containing reactive magnesia (TecEco (1)) such as concrete blocks have been made the high price of the raw material and absence of a sensible carbon trading scheme have made it difficult to commercialize the technology in Australia where it was invented. In the UK, in spite of a carbon trading regime and much greater financial backing from the government, variants are still not on sale.

Faced with this dilemma the author and inventor has had to seek out niche products for which price is not a determining factor and so more recently has been testing other aspects of the theory which is the basis of his patents and that is that reactive magnesia (TecEco (1)) can usefully be included in any hydraulic composition in any proportion.

Going beyond the lab the author was pleasantly surprised when a large cement company added MgO to a mix containing both fly ash and GBFS. The results achieved were stunning and are described in the paper along with the results of a large number of other Tec-Cement formulations.

Theories are suggested for the excellent results achieved to date that are in accord with mainstream chemistry and physical properties effected are discussed from a practical point of view. The story of reactive magnesia (TecEco (1)) in hydraulic binders and Sorel type cements (also patented in Europe) continues. Soon the author and inventor will be further testing additions in non Portland hydraulic cements such as Calcium sulfoaluminate cements & belite calcium sulfoaluminate cements and the results are eagerly awaited by many as these cements have inherently low embodied energies and emissions.

The Technology

TecEco uniquely discovered that reactive magnesia (TecEco (1)) can be blended in any proportion with any hydraulic or Sorel cement formulation.

This powerful new tool in cement chemistry has not been fully tested yet alone understood however all properties are affected, usually favourably depending on the proportion added, other components, particle packing and the chemistry of the mix.

Eco-Cements have relatively high proportions of reactive magnesia (TecEco (1)) which in permeable materials carbonates adding strength and durability. Eco-Cement formulations are generally used for bricks, blocks, pavers, pervious pavements and other permeable cement based products (TecEco (2)).

Enviro-Cements are made using large quantities of reactive magnesia (TecEco (1)) which reacts to form Brucite which is unique in TecEco Cements and is an ideal mineral for trapping toxic and hazardous wastes due to its layered structure, equilibrium pH level, durability and low solubility (TecEco (3)).

Tec-Cements are cement blends that comprise a hydraulic cement such as Portland cement mixed with a relatively small proportion of reactive magnesia (TecEco (1)) and optionally pozzolans and/or supplementary cementitious materials which react with Portlandite reducing its concentration and making more cement or are activated by Portland cement. They offer a solution to many of the technical problems that plague traditional cement formulations caused by the reactivity of lime (Portlandite) and have significant advantages including faster setting even with a high proportion of non PC additions (TecEco (4)).

What is Reactive Mangnesia and Why it can be added in Hydraulic Compositions?

One of the most significant contributions to the science of binders by the author has been the profound statement in his patents around the world that “The key for the successful blending of magnesia and other cements and in particular Portland type cements is that the hydration rates of all components in the cement must be matched. In order to achieve this the magnesia component must be separately calcined at lower temperatures and in conditions that are suitable for the manufacture of reactive magnesia (TecEco (1)), ground to a fine size depending on the reactivity required and only then blended with other cementitious components, pozzolans or both" Why low temperatures are required is essentially a matter of lattice physics and requires an understanding beyond the scope of this paper and the reader is directed to the authors web site at www.tececo.com.

Figure 1 – Eco-Cement Mud Bricks and Mortar

Figure 2 – Eco-Cement Floor using locally dug chalk as Aggregate

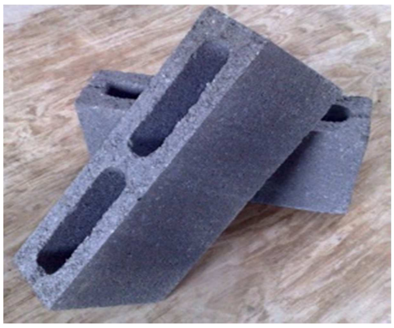

Figure 3 – Eco-Cement Blocks made by ADBRI

Eco-Cements

Carbonating magnesium based binders such as TecEco Eco-Cements only carbonate in gas permeable substrates[1] forming strong fibrous minerals[2]. Water vapour and CO2 must be available for carbonation to ensue. In the TecEco system Portland cement provides nucleation and the right pH conditions for a preponderance of $CO3^{2-}$ ions that are required for the formation of nesquehonite, our preferred mineral because of the contribution of its shape to microstructure.

Eco - Cement Products

Eco-Cements can be used in a wide range of products from foamed concretes to bricks, blocks and pavers, mortars renders and grouts Somewhere in the vicinity of the Pareto proportion (80%) of conventional concretes could be replaced by Eco-Cement.

Over 10,000 Eco-cement blocks have now been made and have found their way into buildings around Australia. No problems have been experienced and the users have not been able to distinguish the blocks from other similar blocks made with Portland cement.

Eco-Cement is also ideal for making Earthcrete Blocks, walling, breathing floors, mortars etc. and several houses have been built using this technology. The most successful promotion of Eco-Cements has been the now famous low carbon network Earthship Brighton building in the UK (TecEco (5)).

More recently our carbonating Eco-Cement blocks were made by ADBRI for a job in Newcastle (TecEco (6)).

Eco-Cement Permeacocrete Pervious Pavements

The key to making successful Eco-Cement formulations is an understanding of particle packing which does not appear to be similarly appreciated by other researchers working with carbonating magnesium binders. See the discussion under the heading Particle Packing.

For pervious concretes is essential to mono grade the dominant stone and then gap grade particle size down to paste.

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[1] This was not understood by researchers for some years in the UK.
[2] Such as lansfordite and nesquehonite.

Figure 4 - A Permeacocrete

Figure 5 - A composite Close Up of a Permeacocrete Showing Carbonate Bridging

Figure 6 - A Permeacocrete Showing Water Passing Through

Concrete cannot get much more sustainable than TecEco Eco-Cement water capturing permeacocretes which set by absorbing CO2. Our Permeacocretes can be made with recycled or man-made carbonate aggregates and have the potential to sequester significant carbon. Used in cities permeacocretes will result in stormwater harvesting as well as cleansing. Other benefits include a reduction in hot city syndrome, subsoil movement and coastal pollution.

TecEco have an ongoing project with the WA Conservation trust, Canning council and Main Roads Western Australia and the author's objective with this project has been to reduce the cost and risk of laying pervious pavements.

The use of MgO gives an ideal rheology which should make it possible to make permeacocrete pervious pavements using conventional road laying equipment therefore substantially reducing labour costs. There are many other advantages of pervious pavements well documented elsewhere (TecEco (7)).

Because of high molar volume growth less reactive magnesia (TecEco (1)) based Eco-Cement can be used than conventional Portland cement in some products but Eco-Cements have still not permeated the market to any great extent because of the lack of carbon trading and issues including availability and cost especially in the UK. We are working to address the high price of reactive magnesia (TecEco (1)) using a low temperature route to magnesium oxide via nesquehonite. This technology was suggested in the 1940's by DOE scientists and has recently been promoted by the University of Rome – La Sapienza. At the authors suggestion Cambridge University also appear to have taken up working on the technology.

Tec-Cement Niche Technologies

Tec-Cements contain more Portland cement than reactive magnesia (TecEco (1)). (5-20% MgO, 80-95% OPC, SCM or pozzolan) Reactive magnesia (TecEco (1)) hydrates in the same rate order as Portland cement forming Brucite which, provided the particle packing is right (See Particle Packing), uses up excess water reducing the voids:paste ratio, increasing density and possibly raising the short term pH.

Reactions with pozzolans are more effective with less water as the pH rises and there may even be some reactions with CSM's like GBFS. After much of the Portlandite has been consumed Brucite tends to control the long term pH which is lower and due to its low solubility, mobility and reactivity, contributes to greater durability[3].

Other benefits include improvements in density, strength and rheology, reduced permeability and shrinkage (which also contribute to durability) and the use of a wider range of aggregates many of which are potentially wastes without reaction problems. Of interest to the industry we are currently undertaking tests to hopefully demonstrate that the problem of autogenous shrinkage has been solved as a result of the polar bound water attached to Brucite becoming available for more complete hydration of PC.

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[3] In the authors view Eh-pH conditions within the matrix of a concrete are fundamental to durability and should be included with low permeability and reduced cracking as most important.

From our earlier work we knew that the addition of reactive magnesia (TecEco (1)) had a profound effect on hydraulic mixes and we have recently mainly been working in this area because, with the low proportion of reactive magnesia (TecEco (1)) added, cost will not be a key factor on the decision to use the technology. Recently we conducted trials of MgO-PC-GBFS-Flyash mixes in Brisbane and were very pleased with the results (TecEco (8)). Most importantly they demonstrated significant improvements in performance for dollars and gave the company new direction.

A mix design with 50% replacement of PC by ground granulated blast furnace slag (GBFS) and flyash in equal proportions, substituted 8.5% reactive MgO for PC was used. The compression results were 30% above target strength for both 20MPa and 32 MPa (nominal) mixes and more recent testing has indicated the development of very high tensile strength for similar mixes. Overall the mixes performed very well in the "wet" stage with positive comment from the placers. The rheology was almost warm margarine like, placement was easy and there was little or no bleeding that would have resulting in capillary pores that compromise the durability of concrete. Amazingly for a 50% replacement mix the finishers were able to leave much earlier than expected. On a 32MPa (nominal) slab the last concrete truck arrived at 8:30 am and the finishers had gone home by 11:30 am. There were no early age shrinkage cracks and the long term drying shrinkage results were low.

Figure 7 - Bill Ennals Brisbane 32MPa (Nominal) Pour. Note the Warm Margarine Like Rheology

Details about the two record breaking pours are included in Table 1 – Modified 20 and 32 MPa (nominal) mixes. Bill Ennals Brisbane, Figure 9 - Compressive Strength - Modified Mixes Bill Ennals Brisbane and Figure 10 - Shrinkage - Modified Mixes Bill Ennals Brisbane. These mixes are number T19 and T20 in the comprehensive results shown in Figure 13 through to Figure 19.

Theoretical Considerations

Why did these mixes and many other mixes like them perform so well particularly in the wet phase?

An understanding of granular or sand pile physics which describes how grains when wet or dry flow, rearrange, segregate or slump gives some insight into the behaviour of wet concrete. Add to this the complex overlays of particle packing considerations and particle charge phenomena and we have very complex fluids indeed.

In water magnesium also forms a bicarbonate ion which like sodium and calcium bicarbonate has strong buffering capability. In time we will learn how this property also influences early chemical reactions and setting but for the purposes of this paper we will go no further into sand pile physics or buffers.

The properties imparted to a wet mix are predominantly due to the remarkable properties of the magnesium ion. It is known that electrostatics is very important for the setting and strength development of concretes (Labbetz and Nonat (9)) and reactive magnesia (TecEco (1)) is a powerful new tool in hydraulic compositions because it will go into solution reasonably rapidly forming the strongly charged yet small magnesium ion which is a strong kosmotroph and influences the early age properties of Portland cement and other hydraulic concretes.

Effects of the strongly Kosmotropic Mg^{2+} Cation

The small highly charged magnesium ion has a strong influence on the rheological and other properties of TecEco magnesium cements including the pseudoplastic thixotropic nature, low bleed, low sag, high stick and low shrinkage. Water, being a polar molecule with a differential charge density and one of the main ingredients of hydraulic cement concretes when freshly mixed, is strongly affected. Once set strong polar bonding results as the highly charged magnesium ion causes strong differential surface charge densities in the compounds it forms. This tendency for strong polar bonding expresses in the structure of Brucite, nesquehonite and other magnesium carbonates and is the reason for their ability to form a wide range of nanocomposites as well as form strong bonds to other surfaces thus increasing the range of waste materials that can be added to concrete composites to advantage.

The viscosity of a liquid is determined by the ease with which molecules can move relative to each other. It depends on the forces holding the molecules together and in water this force is referred to as hydrogen bonding which is a special case of polar or dipole bonding. Hydrogen bonding describes the attraction between the hydrogen on one polarised water molecule and oxygen on another and is described more fully below because of its importance to rheology, early age setting and other properties.

Ions in water are either kosmotropic or chaotropic based on their "water structuring" or "water disrupting" nature. Ions, such as Mg2+, Na+, K+, can disorder or order water structure thereby strongly modifying the properties. Mg2+ and Na+ are known as ionic kosmotropes (order-makers), exhibiting stronger interactions with water molecules than water itself and therefore capable of breaking water-water hydrogen bonds. While K+ is known as an ionic chaotrope (disorder-maker), exhibiting weaker interactions with water than water itself and thus interfering little in the hydrogen bonding of the surrounding water (Chaplin (10)).

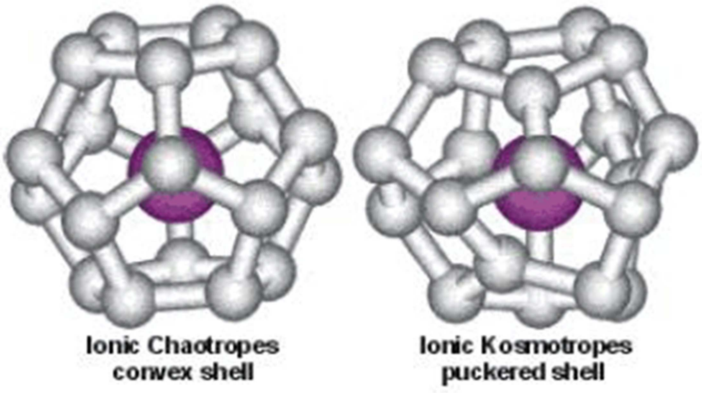
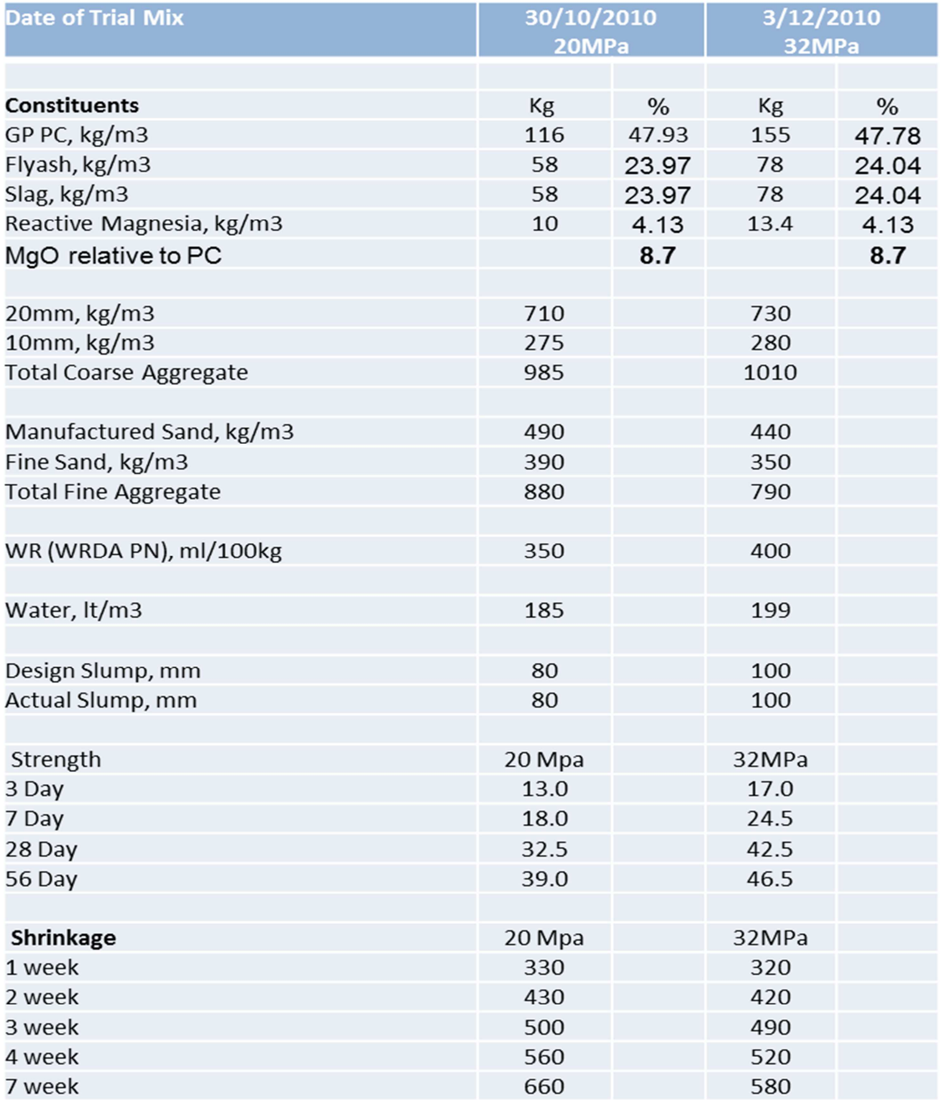


Figure 8 - Chaotropic and kosmotropic Ions (Chaplin (10))

Water has cohesivity due to a network of extensive three-dimensional hydrogen bonding and this property is strengthened both by Brucite surfaces and the strongly kosmotropic magnesium ion in solution.

Table 1 – Modified 20 and 32 MPa (nominal) mixes. Bill Ennals Brisbane



Date of Trial Mix	30/10/2010 20MPa		3/12/2010 32MPa	
Constituents	Kg	%	Kg	%
GP PC, kg/m3	116	47.93	155	47.78
Flyash, kg/m3	58	23.97	78	24.04
Slag, kg/m3	58	23.97	78	24.04
Reactive Magnesia, kg/m3	10	4.13	13.4	4.13
MgO relative to PC		8.7		8.7
20mm, kg/m3	710		730	
10mm, kg/m3	275		280	
Total Coarse Aggregate	985		1010	
Manufactured Sand, kg/m3	490		440	
Fine Sand, kg/m3	390		350	
Total Fine Aggregate	880		790	
WR (WRDA PN), ml/100kg	350		400	
Water, lt/m3	185		199	
Design Slump, mm	80		100	
Actual Slump, mm	80		100	
Strength	20 Mpa		32MPa	
3 Day	13.0		17.0	
7 Day	18.0		24.5	
28 Day	32.5		42.5	
56 Day	39.0		46.5	
Shrinkage	20 Mpa		32MPa	
1 week	330		320	
2 week	430		420	
3 week	500		490	
4 week	560		520	
7 week	660		580	

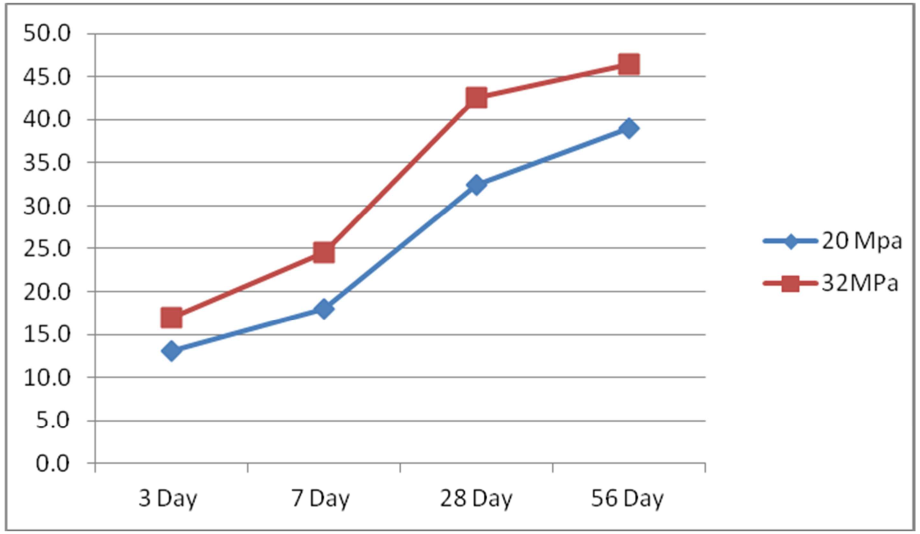


Figure 9 - Compressive Strength - Modified Mixes Bill Ennals Brisbane

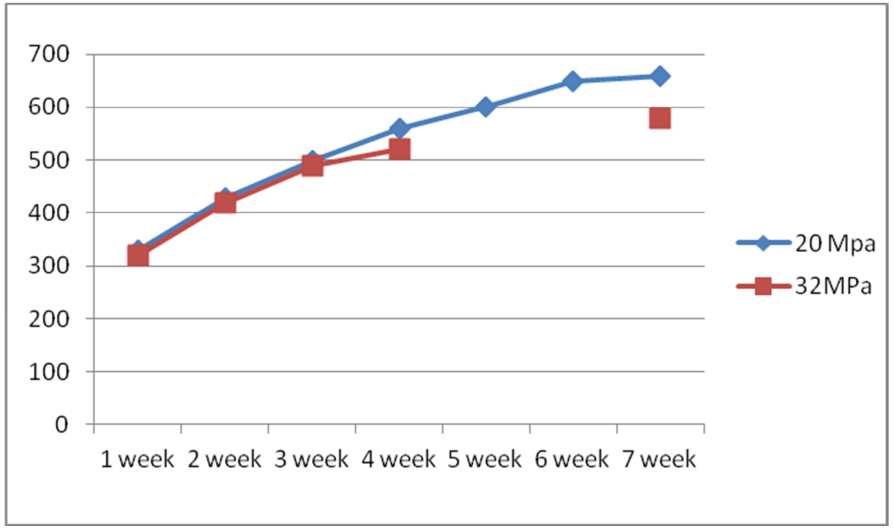


Figure 10 - Shrinkage - Modified Mixes Bill Ennals Brisbane

In a recent written personal communication Prof Chris Cuff[4] (Cuff, (11)) said “Dynamic models of the transient structural effects of magnesium ions in solution, indicate that it and its hydration sheaths are relatively large and also contain extensive arrays of oxygen and hydrogen dipoles and associated networks of hydrogen bonding. The relatively large size of a transient cluster of water molecules around a magnesium ion (the hydration sheath) imparts a degree of structure not only to itself but also, by conventional electrostatic considerations, to the associated anions in solution. This ‘structural ordering’ of the solution phase may also lead to drastic effects on the thermal vacancies present in the water. This in turn will lead to major effects on the internal transport processes of the fluid phase. Additionally, due to these constraints, these interactions may lead to the formation of thermodynamically metastable phases many of which may have very strong but metastable internal chemical bonding.”

In relation to the influence of Brucite surfaces on proximate water Wang (12) and others concluded that "The oxygen and hydrogen atomic densities and H_2O dipole orientations vary significantly with distance from the surface and deviate from the corresponding structural properties of bulk water to distances as large as 15 A° (~5 molecular water layers) from the surface."

According to Lippmann (13) and conventional crystallographic electrostatic theory, the ion dipole bond energy, decreases proportionally to the square of the bond length:

$E = - e.\mu / r2 .\cos(\mu, r)$

Where e is the ion charge, µ the dipole moment, r the distance between cation centre of the negative charge of the dipole (the oxygen centre for H_2O), and (µ, r) the angle formed by the dipole direction µ and the join cation-oxygen r. The values obtained are 44.9 kcal/mol for Ca^{2+} and 57.7 kcal/mol for Mg^{2+}. The dipole bond energy of Mg^{2+} is 28.5 % greater than that of calcium and together with the effect of the surface chemistry of Brucite is probably sufficient to explain the higher viscosity at low stress (when no "work" is applied as during placement).

According to Wikipedia (14) “A hydrogen bond is a special type of attractive interaction (a variation of a dipole-dipole bond) that exists between an electronegative atom and a hydrogen atom bonded to another electronegative atom”. This type of bond always involves a hydrogen atom, thus the name. Hydrogen bonds can occur between molecules (intermolecularly), or within different parts of a single molecule (intramolecularly. The typical hydrogen bond is stronger than van der Waals forces, but weaker than covalent, ionic and metallic bonds.

In the presence of magnesium ions another type of dipole or polar bond develops between strongly positively charged magnesium ions (Mg++) and the negatively charged oxygen atoms in water molecules which are attracted to them. In solution weakly bonded "hydration shells" many layers deep form around magnesium ions which have a much stronger influence in solution on water than calcium ions and for that matter many dispersants. These sheaths are in addition to the more common primary and secondary hydration shells so important in the kinetics of surface-controlled reactions.

Mg-O dipole bonds are very strong and they distort the electron cloud on the water molecule further towards the oxygen end strongly enhancing hydrogen bonding. The increased strength of hydrogen bonds then propagates (all charges must be statistically equal and opposite) through water and between water and sand or cement as well as additives such as dispersants.

Another way of considering the above is that the strong positive charge density on magnesium ions distorts the electron cloud around water, increasing the density of electrons around an associated oxygen atom in a dipole pair, exposing the hydrogen atoms in water molecules with even less electrons and thus rendering them more positively charged to more strongly hydrogen bond with other oxygen atoms.

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[4] Professor Chris Cuff PhD has worked as a consultant to TecEco and is currently a private consultant in chemical mineralogy and crystallography. Prior to this he was Dean of Science at James Cook University where his tenured appointment was in Geochemistry and Mineral Chemistry. Prior to his appointment at James Cook he was employed by then Process Technology Division of the United Kingdom Atomic Energy Commission working on the crystallisation of phases from high concentration aqueous solutions. Over the last 30 years Prof. Cuff has served on numerous national and international committees including the Australian Council of Nuclear Science and Engineering and on Committees of the International Mineralogical Association. He has served as assessor for various research councils including ARC and NSF and has acted as peer reviewer for numerous publications in the refereed professional literature.

Although a relatively large ion in solution due to hydration effects, crystallochemically Mg++ is a small ion with a diameter, although dependent on site co-ordination and symmetry, of around 86 picometres compared to calcium for example of around 114 picometres. It also has a high bond energy of 57.7 kcal/mol. Compared to other alkali earth metal ions. Mg++ has a very high charge density and attaches to oxygen in a similar way to the way hydrogens attach to the oxygen of water.

The development of hydration sheaths around magnesium coupled with the interactions with Brucite surfaces with water increase the thixotropic pseudo-plastic property of what amounts to a highly electrostatic fluid that is most importantly very slippery to the bull trowel and float and thus easy to finish.

Although very difficult to determine, the strength of the dipole bonding system described above could be, statistically double that in normal water as a result of the presence of magnesium ions and this strong molecular charge interaction between the magnesium ion and oxygen significantly affects the rheology of the mix.

Still concretes, freshly made with either Tec or Eco-Cements show first set quickly due to the propagation of stronger than normal dipole bonding and interactions with Brucite surfaces with water. When stress (such as during placing) is applied, the electrostatic influence of magnesium ions de-propagates and the weak dipole bonds break up leaving very small balls of water surrounding magnesium ions that are positively charged on the surface and thus repel each other, sand and cement sufficiently to increase fluidity. The better particle packing achieved by using smaller magnesia particles also starts to show influence.

By way of caution, the slump test is somewhat irrelevant for pseudo plastic mixes and should not be used with reactive magnesia (TecEco (1)). A test for the response of a mix to work is required.

Dimensional Stability

A further advantage of adding reactive magnesia (TecEco (1)) is a reduction in shrinkage. As concrete sets plastic shrinkage is caused by the loss of water through bleeding followed by evaporation or by seepage if the substrate is porous Gani (15). Neville (16) describes drying shrinkage as being the losses of adsorbed water. He stresses that "the loss of free water, which takes place first, causes little or no shrinkage. As drying continues, adsorbed water is removed and the change of volume is in the order of 10000 × 10^6." Both have in common loss of water.

Our original theory to explain the reduced shrinkage of Tec-Cement concretes was that the main cause was the volumetric expansion of magnesium oxide using up free water preventing bleeding by consumption and greater density. Whether this is so and to what extent depends on where the water is coming from during setting and curing. We think that in non porous concretes containing magnesium it comes from water that would most likely bleed or evaporate out of concrete if it were not for the presence of magnesium increasing surface tension markedly and introducing a thixotropic pseudo plastic behaviour property to water reducing its mobility inside concrete (and thus reducing bleeding).

When magnesia hydrates it may or may not be expansive depending on whether the water used comes from within or from outside the system cement + aggregates + water in accordance with the following equations:

MgO (s) + H2O (l) = Mg(OH)2 (s)
40.31 + 18.0 => 58.3 molar mass
11.2 + liquid => 24.3 molar volumes

The presence of magnesium ions and Brucite also have other effects that act together to reduce plastic and drying shrinkage.

Water has an abnormally high surface tension. Water molecules at the liquid-gas surface have lost potential hydrogen bonds directed at the gas phase and are pulled towards the underlying bulk liquid water by the remaining stronger hydrogen bonds. The addition of the strongly charged kosmotropic magnesium ion in sufficient concentration increases this effect and increases surface tension thereby reducing evaporation.

Bleed water does not so readily exit TecEco cement concretes and this must be explained. Water in fresh ordinary Portland cement concretes bleeds through capillary pores and shortly after it is placed "percolates" through it to the surface where it evaporates or forms bleed water. If concrete is not sufficiently covered or protected by surface coatings of for example aliphatic alcohol, to some extent, depending on the weather it is also pulled by transpiration tension (evaporation). In such circumstances strong cohesive properties hold the water column in the capillary pores together, preventing tension rupture. The addition of magnesium ions sufficiently increase the viscosity of water reducing transport through such capillary pores, rendering the capillary water to exposed surface transport system in Tec-Cement concrete, less effective. According to Wang et. al. there are also significant amounts of adsorbed water on the surfaces of Brucite, propagated off the differentially charged surfaces many layers deep (Wang et al. (12)). Charge propagation increased the dipole bonding effect of water, increasing cohesion and further reducing the flow through capillary pores

Water also has an anomalously high enthalpy (44.8 kJ mol^{-1}) and entropy of vaporisation (109 kJ mol^{-1}) due to its strong dipole bonding (Discussed earlier under the heading Effects of the strongly Kosmotropic Mg^{2+} Cation). The presence of kosmotropic magnesium ions increase the enthalpy and entropy of vaporisation of water, meaning that less would evaporate at the surface thereby reducing the capillary suction and volume loss. i.e. the polar bonds between water and the less volatile magnesium atoms prevents loss of water from the setting mix.

As less water exits concrete containing magnesium ions and Brucite in the above manner the internal relative humidity is maintained at a higher level also reducing later autogenous shrinkage. Longer term drying and autogenous shrinkage may also be reduced because of the surface tightening affect as Brucite carbonates further reduce the loss of internal water. Probably the strongest influence reducing autogenous shrinkage is the interest phenomenon whereby water is "stored" in Brucite hydrates ($Mg(OH)_2.nH_2O$ species) and available for later more complete hydration of PC

In summary, shrinkage, and therefore cracking is curtailed partly as a function of the fact that the water used for the hydration of magnesia whereby Brucite is formed comes from mix water which does not exit the mix resulting in volume loss and partly, as for many other properties, as a result of the extremely kosmotropic nature of the magnesium ion.

Dissolution Processes

During the hydration process, reactive magnesia (TecEco (1)), MgO, is converted to Brucite hydrates, $Mg(OH)_2.nH_2O$ and an equilibrium establishes between the solid and the liquid phases. Even though Brucite is far less soluble than other compounds such as Portlandite, magnesium ions are present in the water pore solution in accordance with the equilibrium established.

$MgO + H_2O \rightarrow Mg(OH)_2$

$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2\ OH-$ $\quad$ $Ksp = [Mg^{2+}]*[OH-]_2 = 1,8*10-11$

If $[Mg^{2+}] = s$ (solubility)

$Ksp = 4s\text{^}3 = 1,8*10^{-11}$

$s = 1,65*10^{-4}$ mol.L-1

According to theoretical physical chemistry “Interactions between particles dissolved in aqueous solutions are sometimes significantly affected by the presence of different electrolytes. The nature of the different salts, even those having identical charge characteristics, specifically affects the interaction pair potential between surfaces. This is a phenomenon experimentally known a long time ago, although a satisfactory theoretical interpretation is still missing.” (Lo´pez-Leo´n (17)).

Specific ionic effects on numerous solid-aqueous solution interfaces have usually been ranked in the so called Hofmeister series. Ion specificity has experimentally been manifested in many ways. Mg^{2+} is a strong kosmotroph and not only affects the surface tension of water but has DLVO theory[5] effects in solution.

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[5] DLVO theory is named after Derjaguin and Landau, Verwey and Overbeek. The theory describes the force between charged surfaces interacting through a liquid medium. It combines the effects of the van der Waals attraction and the electrostatic repulsion due to the so called double layer of counterions.(Wikipedia (18))

Without digressing too much into theoretical physical chemistry is can be seen that the process of dissolution of a cement particle will be strongly affected. To put this as simplistically as I can within the level of my own understanding, the electrostatic properties of water are strongly strengthened in the presence of kosmotrophs and it would seem likely that the proton wrenching mechanism for the dissolution of MgO and possibly clinker is strengthened. Proton wrenching is suggested by Stumm (19) however according to Fruhwith (20) there are other mechanisms at higher pH for the dissolution of MgO.

There are also likely to be buffer effects we do not as yet fully understand. For the purposes of this paper it will have to suffice to say that if clinker goes into solution more rapidly than hydration products will form more quickly and this could be the basis of a partial explanation of more rapid setting and high early strength.

Charged Surface Effects

This leads me to what sells pre-mix concrete which is the rate of setting and finishability. The kosmotropic magnesium ion has a big effect on the rheology of concretes and early strength development. Concretes containing magnesia have a silky feel to them and are easy to finish even with added pozzolans such as fly ash which tends to make mixes sticky.

In Tec-Cement concretes early strength is improved particularly with mixes containing GBFS so finishers can go home early. There are two main factors involved: The kosmotropic effect of the highly charged magnesium ion and also because the surface charge of the magnesium oxide added changes as lime is being produced by the hydration mainly of alite. The result is electro statically induced earlier strength.

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. The use of some plasticizers such as ligno sulphonates induce a net negative charge to cement, sand and aggregate causing mutual repulsion. This is probably also the case with MgO, at least I have been told so by people who work in this field.

Another important factor that affects early tensile strength gain and helps reduce cracking is that the average surface charge of metal oxides changes with pH and in the case of magnesium oxide goes negative at around pH 12 to 12.4 so without additives it becomes strongly attracted to both sand and cement particles rather than mutually repulsive. As Portlandite is produced by the hydration of C3S and C2S 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.

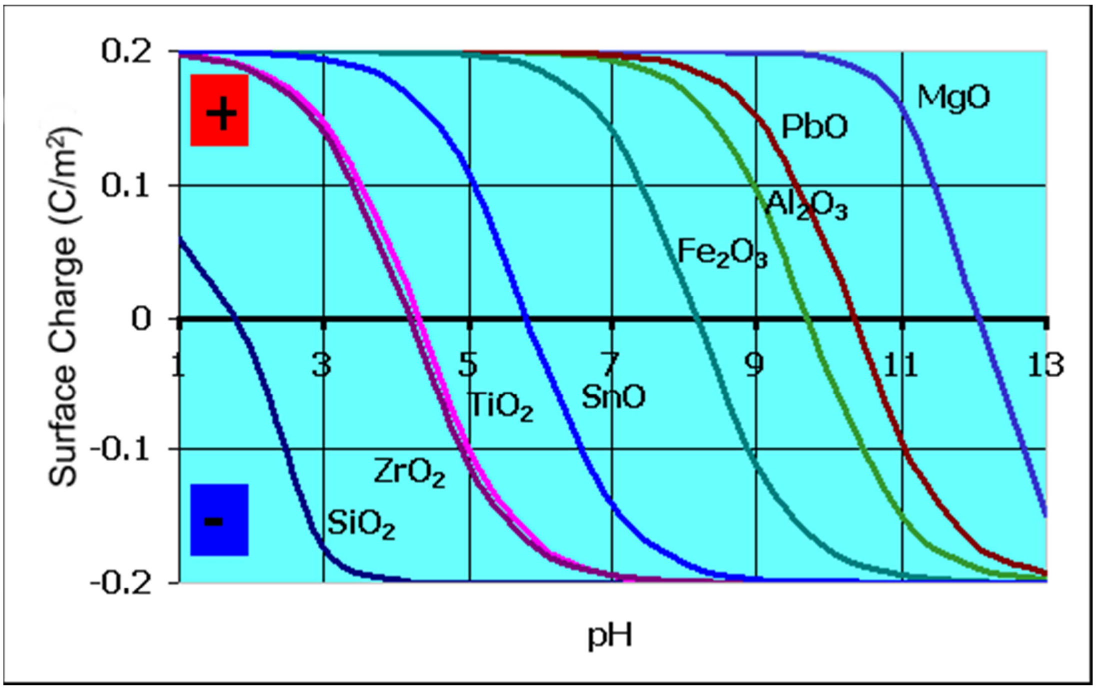

Figure 11 The Change in the Surface Charge of Metal Oxides with pH. (Small (21)

The effect is obviously dramatic and helps explain the early onset of first set and final setting (Vicat apparatus, see also Figure 17) as well as high early (day 0 - 4) tensile and compressive strengths of TecEco cements. Early setting is important because finishers push this requirement in the market place mainly so they can go home earlier. Besides time is money to builders. They want to strip boxing as soon as they can.

Particle Packing

Not all the effects are electrostatic as the physical size of the magnesia added also affects rheology. The mean particle size of the reactive magnesia (TecEco (1)) TecEco generally use is around 5-8 micron. Experimental work backed up by the mathematical theory of de Larrard (22) indicates that this is not far off the right size for ideal packing with Portland cement which in Australia has a mean particle size of around 15 - 20 micron (Gani (15)). Assuming spheres de Larrard (22) calculates a ratio of 1:2.41.

Magnesia is finer than most grinds of Portland cement (PC) and therefore, if attention is not paid to particle packing i.e fitting magnesia between cement grains, it will add to the fineness demand for water. Operators using the material should be careful adding water however as this fineness demand is compensated for by a much greater response to work including pumping. A formulation that may have a nominal slump of around 60 in a barrel mixer characterised by relatively low shear will end up being more like 140 nominal slump after passing through a pump. Hi shear mixers such as ribbon or paddle mixers are possibly more suitable for TecEco cements and the plasticity induced by work will last for at least 5 - 10 minutes to allow placement. If a barrel mixer is all that is available then the user should make sure it is spun up regularly to high revs before checking slump. As rheology is very work sensitive with MgO containing mixes, static tests such as slump are not so suitable and we are looking for a better test. For more information on particle packing, see (TecEco (23)).

Property Outcomes of Hydraulic Mixes containing 5 – 20% Reactive magnesia (TecEco (1))

Above under the heading **What is Reactive Mangnesia and Why it can be added in Hydraulic Compositions?** we explain how reactive magnesia (TecEco (1)) is a particular kind of magnesia with low total lattice energy prepared at low temperatures (TecEco (1)). We explain how it dissolves and reacts in the same rate order as other hydraulic cement components forming strongly charged kosmotropic ions. There are many consequences of these electrostatic phenomena. In the short term a marked reduction in water related shrinkage and a substantially different thixotropic rheology that results in easy to finish concretes. In the medium and longer term properties such as compressive and tensile strength, durability, modulus of elasticity and creep are improved.

We call hydraulic cements containing reactive magnesia (TecEco (1)) “Tec-Cements” and they have low sag and high stick yet are slippery and easy to finish. They do not bleed much and have low shrinkage. They set quickly and develop significant early age compressive and tensile strength particularly if GBFS is used[6].

Rheology

Mixes containing reactive magnesia (TecEco (1)) exhibit what is probably best described as a non Newtonian pseudoplastic fluid property with viscosity decreasing as shear rate increases in accordance with a Herschel-Bulkley or similar model. Simply put they are very thixotropic exhibiting strong shear thinning. They work up with pumps and stay fluid for about 10 minutes before gelling up again taking on the consistency of a warm margarine.

Shrinkage and Cracking

A significant advantage of adding reactive magnesia (TecEco (1)) is a reduction in shrinkage. As concrete sets plastic shrinkage is caused by losses of water through bleeding followed by evaporation or by seepage if the substrate is porous. Under the heading Dimensional Stability we go into the physics and chemistry of why less shrinkage occurs with the addition of reactive magnesia (TecEco (1)).

Shrinkage is a problem with Portland cement concretes and the use of magnesia has been known for some time as a solution. The Chinese have used much less reactive magnesia (TecEco (1)) than we do for some time to control shrinkage through delayed autogenous expansion (Du C (24), TecEco (25)). And early

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[6] We hope to get similar results with other variant hydraulic binders.

Rosendale cements containing up to 30% MgO were known for the same characteristic as well as durability (TecEco (26)).

Bleed Water

Water has an abnormally high surface tension. Water molecules at the liquid-gas surface have less hydrogen bonds and more easily move into the gas phase and thus evaporate if they statistically achieve enough energy. Raising the temperature increases this energy and at the boiling point all water molecules have enough energy to escape at the surface. To evaporate water molecules must have sufficient energy to overcome the hydrogen bonds of water molecules further to the interior of a liquid and the addition of the strongly charged kosmotropic magnesium ion in sufficient concentration increases the strength of these bonds. The increase affects the retentive force increasing the surface tension, boiling point and reducing evaporation at lower temperatures.

Some engineers view bleed water as essential. This is basically nonsense as less dimensional change and loss of alkali with damage to lower completed sections of a building is a good thing. The author could develop this argument significantly further.

Early Strength Development

As mentioned in the introduction to the theoretical section above (see **Theoretical Considerations**) early strength development is one of the key properties associated with the use of reactive magnesia (TecEco (1)) and hydraulic cements and that apart from the reactions that occur, there are a number of theoretical influences including sand pile or granular physics, particle packing and particle charge. We think the strongest of these to be particle charge in relation to Portland cement. In the case of GBFS there are other factors as play as we mention in the theoretical section and this is likely with other hydraulic binders.

The results below from Figure 13 on, even with fly ash rather than GBFS for fly ash show good early age strength development. Up to a third in the case of blends with GBFS and significantly greater tensile strength in all cases.

Later Age Properties

An excellent paper by Du (24) sets our many of the later age properties of blends containing up to about 5% caustic magnesia not nearly as reactive as the magnesia we use to Portland Cement compositions and as they are similar to the later age properties we have observed we invite readers to obtain this paper. We conclude that later age properties are similar and differ only to the extent that early age property changes have modified them and that our formulations may be more plastic and elastic[7].

The Chinese rely on the slower and delayed hydration of much less reactive magnesia (TecEco (1)) to counter the normal shrinkage of Portland cement concretes (TecEco (TecEco (25)) and a substantial difference between our technology and theirs is the early presence of the highly kosmotropic Mg^{++} ion. Magnesia in our system dissolves then hydrates when there is plenty of water in the mix and forms Brucite hydrates ($(Mg(OH)_2.nH_2O$) The early presence of the Mg^{++} ion and Brucite hydrates tends to electrostatically trap water for later more complete hydration of PC. Mixes containing reactive magnesia are much more closed.

Later Strength and How the Problem of Autogenous Shrinkage is Solved

As less water exits concrete containing magnesium ions and Brucite in the above manner the internal relative humidity is maintained at a higher level increasing the rate of hydration of PC and reducing later autogenous shrinkage. Longer term drying and autogenous shrinkage may also be reduced because of the surface tightening affect as Brucite carbonates further reduce the loss of internal water and because water is "stored" in Brucite hydrates ($Mg(OH)_2.nH_2O$ species) and is available for later hydration of clinker partices.

There are a few definitions of autogenous shrinkage but essentially it is associated with a deficit of water for the hydration of cement. Because of the polar nature of water a nano - layer is adsorbed on to many surfaces including minerals which if drawn away by chemical reaction will cause shrinkage. Neville (16)

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[7] Yet to be demonstrated conclusively

describes this rather too simply as a "withdrawal of water from the capillary pores" referring to a concrete matrix that has become a closed system.

Any compound with a surface charge (positive, negative or both of appropriate spacing) will attract water that will stick to it as a result of what are called Van der Waals or polar bonds which are of an electrostatic nature. This adsorbed water layering, often referred to as hydration shelling or Van der Waals shelling can be one to many layers deep and has been shown by Wang (12) to be very deep around Brucite the mineral that forms as a result of the hydration of magnesia. Reduce the amount of this adsorbed water by consuming water as a result of chemical reaction and shrinkage occurs as the nano layers disappear on a compounding basis.

The Gibbs free energy describes how readily reactions proceed on a molar basis however does not describe the demand/transport of water molecules or whether this propensity to react is greater than the propensity to merely stick to charged surfaces as a result of hydrogen bonding reduced by distance. We have asked several eminent geochemists and at this point in time nobody has developed suitable models or math. For bright young people it would be an interesting and challenging project because then we could predict the amount of autogenous shrinkage and mitigation using for example Brucite hydrates to supply an alternative source of water for the later more complete hydration of PC.

The setting and hardening of concrete is far from a rapid process and it takes years for ultimate strength to develop. Conventionally we add water only at the beginning or during the early life of a concrete and are limited in how much can be added if strength is not to be compromised as result of increased voids as this water is consumed. As concretes dry out and hydration proceeds a shortage of water available at reaction sites for more complete hydration of PC becomes manifest.

Few people are aware that around 18-20% of the Portland cement in most concretes does not hydrate anyway as the concrete dries out first and there is insufficient water left. It follows that virtually all concretes have chemical shrinkage as a result of latent water demand for more complete hydration and for practical purposes this is often not separated from drying shrinkage.

Hydration is a slow process and the key to solving chemical or autogenous shrinkage is to have water available for the duration and Brucite hydrates perform this role because they contain polar bound water between the layers of Brucite which is available for the more complete hydration of PC.

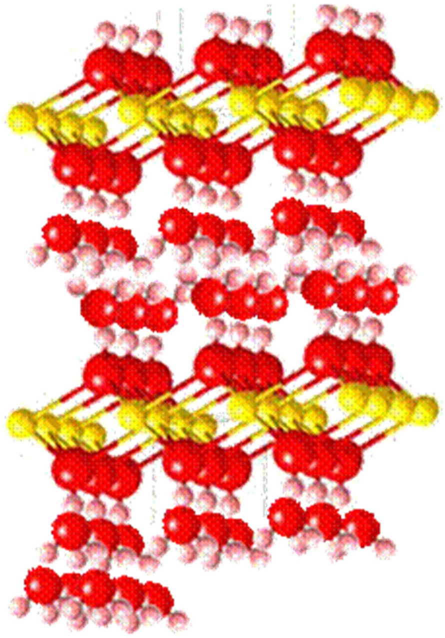

Figure 12 - A Structural Model of Brucite Hydrate (Yellow = Mg, White=Hydrogen, Red = Oxygen

The more complete hydration of PC means that less can be used reducing costs and saving the environment. With reduced dimensional distress as a result of less autogenous shrinkage concretes are much more durable and for this reason also more sustainable (Hawken (27))

A Note to the Figures Depicting Tests to Date

Figure 14 through to Figure 19 show results of various tests to date and are strong evidence that, to quote a senior concrete engineer, “there is something to adding reactive magnesia (TecEco (1))”.

Most of the tests depicted have been done by students to whom I am grateful for the way they have pushed the boundaries of our knowledge. Only three of the mixes tested used additives of any kind and they were done by major commercial operators.

All the results are positive. Because magnesia seems to work best with GBFS one wonders if it is a silicate network former like calcium. Some recent work at Cambridge university indicates it may be (personal communication, Martin Liska PhD (28).

With the success of mixes containing GBFS, questions surrounding use with other hydraulic cements need to be answered. It may be that the addition of magnesia solves the outstanding issues relating to for example aluminate or sulphated formulations. There is a good chance it will.

The results are supporting evidence for the attributes discussed from a theoretical and practical point of view in relation to TecEco Tec-Cement formulations.

Conclusions

Most of the properties of hydraulic cement mixes to which reactive magnesia (TecEco (1)) has been added are profoundly positively affected as shown by the results in Figure 13 through to Figure 19. The improvements are associated with the fact that the magnesium ion is small yet has a big charge and is strongly kosmotropic. Theories are put forward to explain them the properties and as indirect evidence results presented. It is early days however and they may yet be proven to be wrong.

The results presented are enticing and from them emerges an urgent need to understand more about this powerful new tool for modifying the chemistry and physics of cement and hopefully soon the opportunity will arise to test the mixes with slag-lime or PC cements, supersulfated cements, calcium aluminate cements, calcium sulfoaluminate cements and belite Calcium sulfoaluminate cements and belite Cements.

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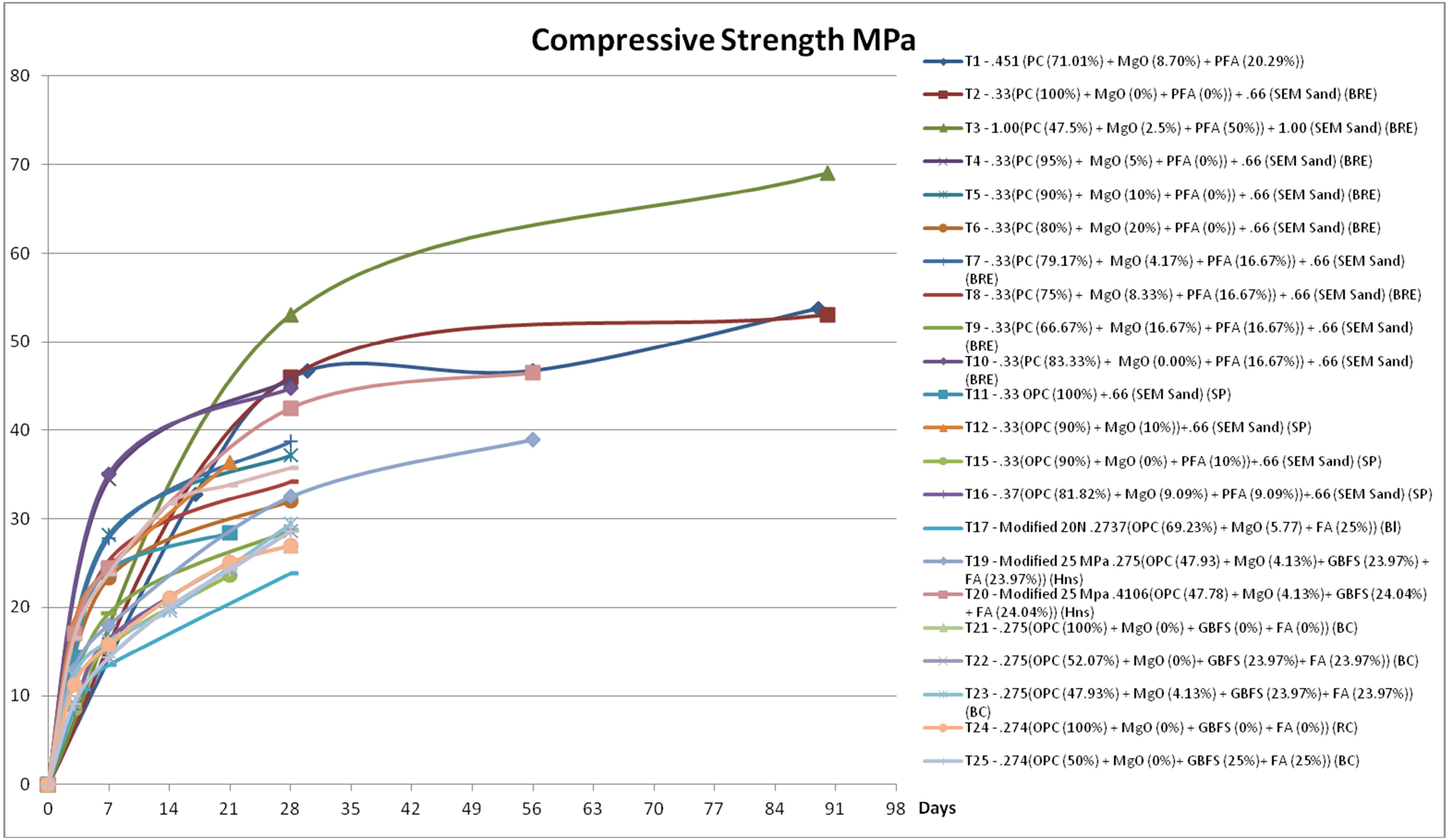

Figure 13 - Compressive Strength Results (Note that no additives were used except for T17, 19 &20)

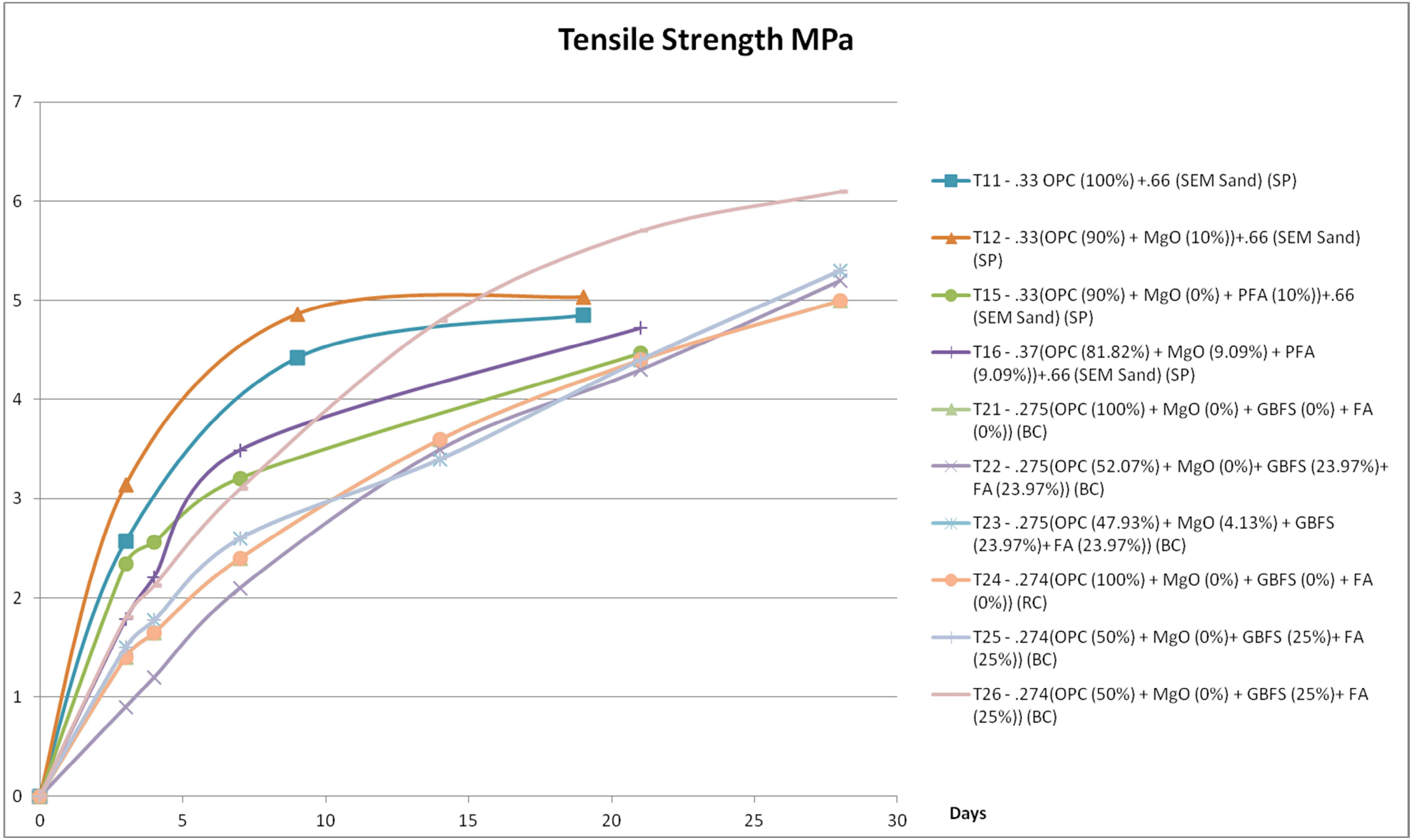

Figure 14 - Tensile Strength Results (Note that no additives were used except for T17,19 &20)

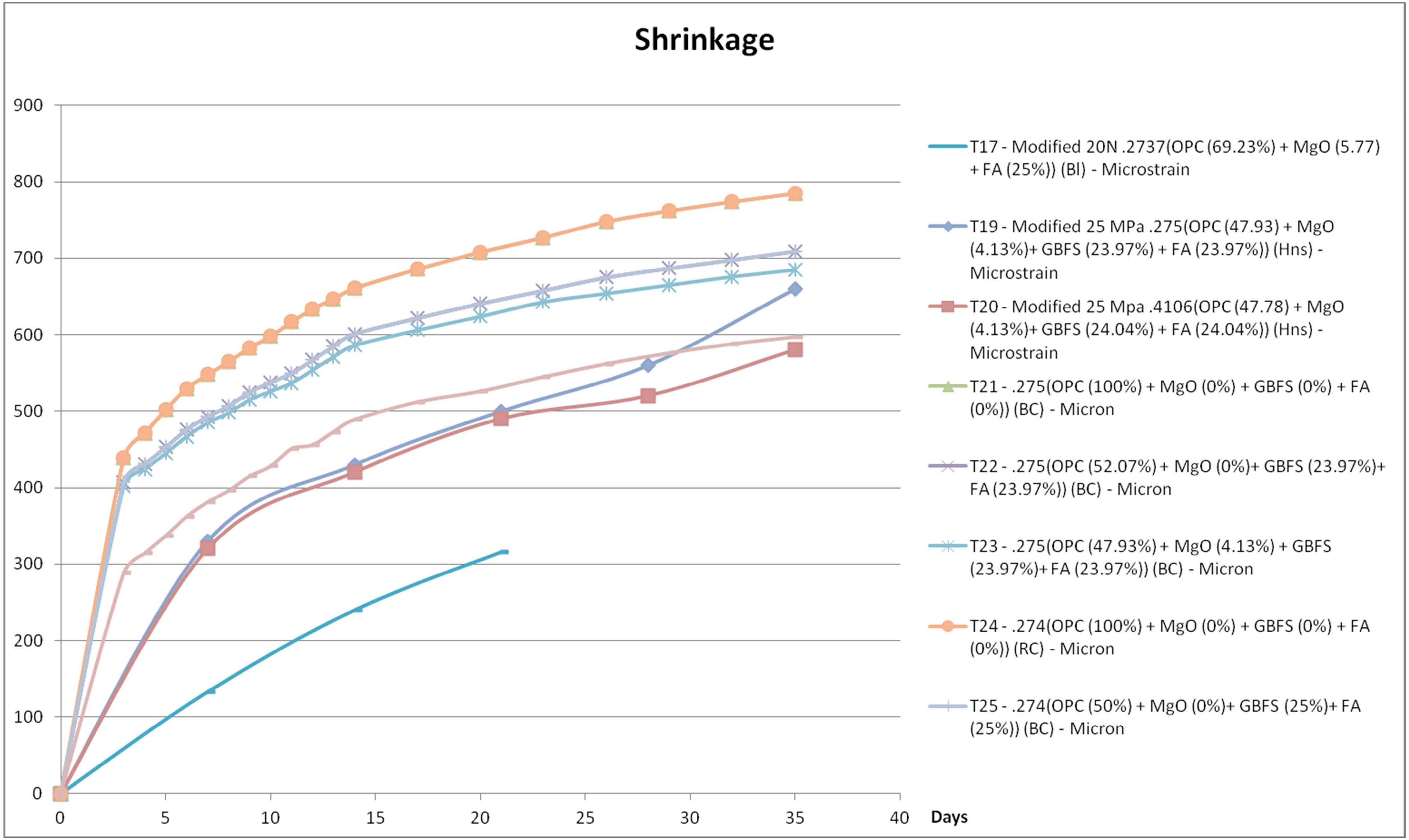

Figure 15 - Shrinkage Results (Note that no additives were used except for T17,19 &20. Units are Microstrain and Micron – See Legend)

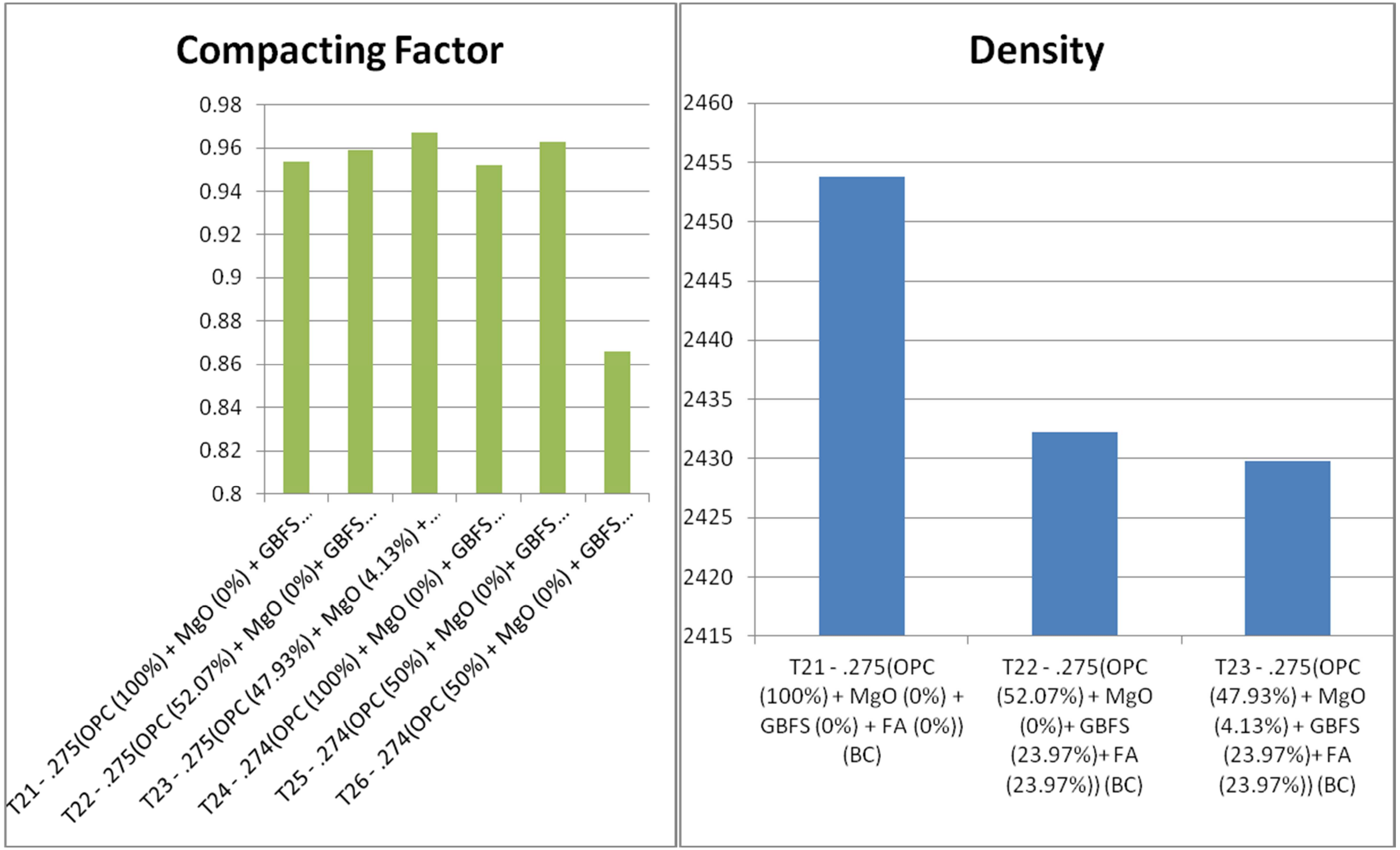

Figure 16 - Compacting Factor and Density (Note that no additives were used except for T17, 19 & 20).

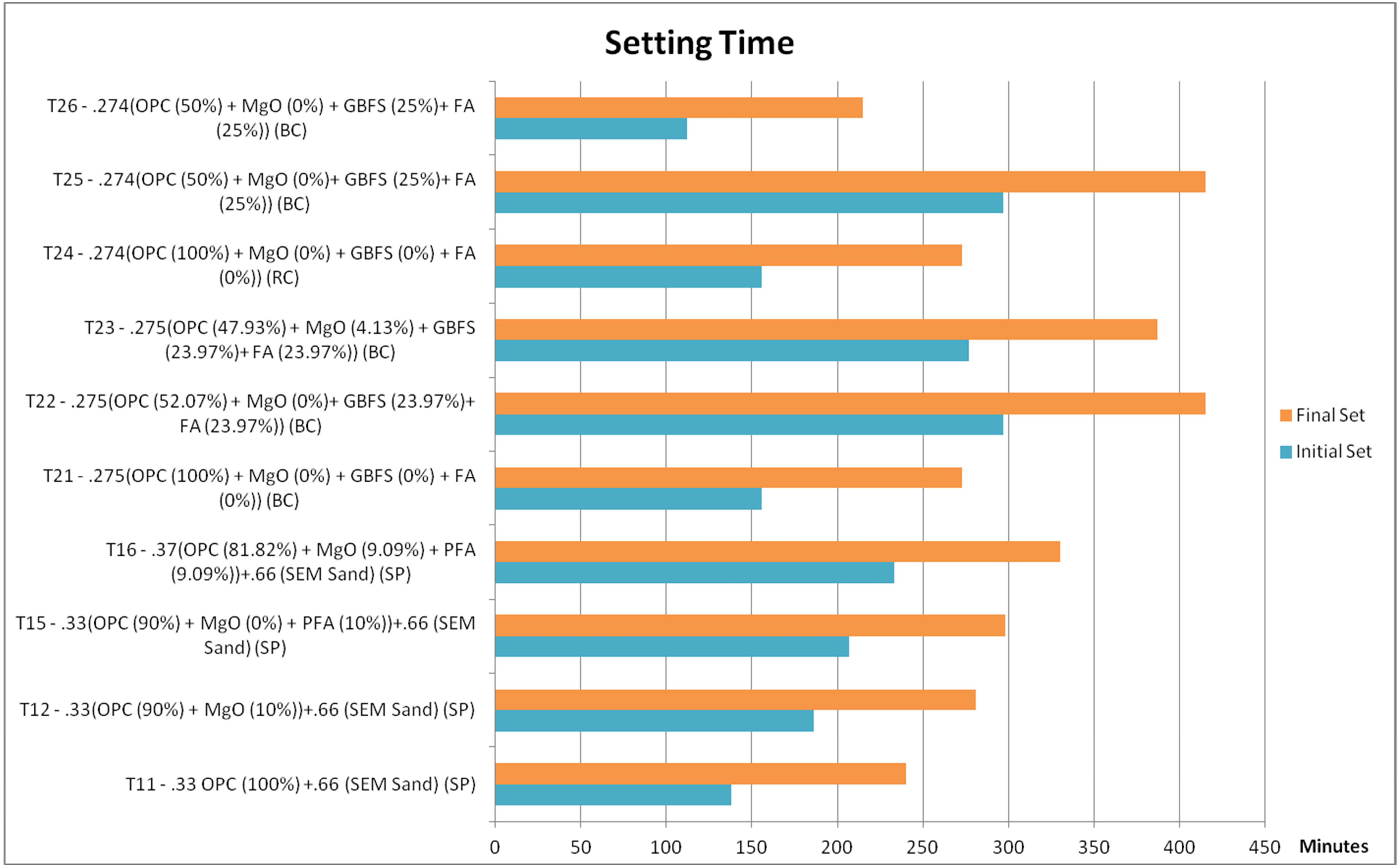

Figure 17 - Setting Time (Vicat - Note that no additives were used except for T17, 19 & 20. Units are Microstrain and Micron – See Legend)

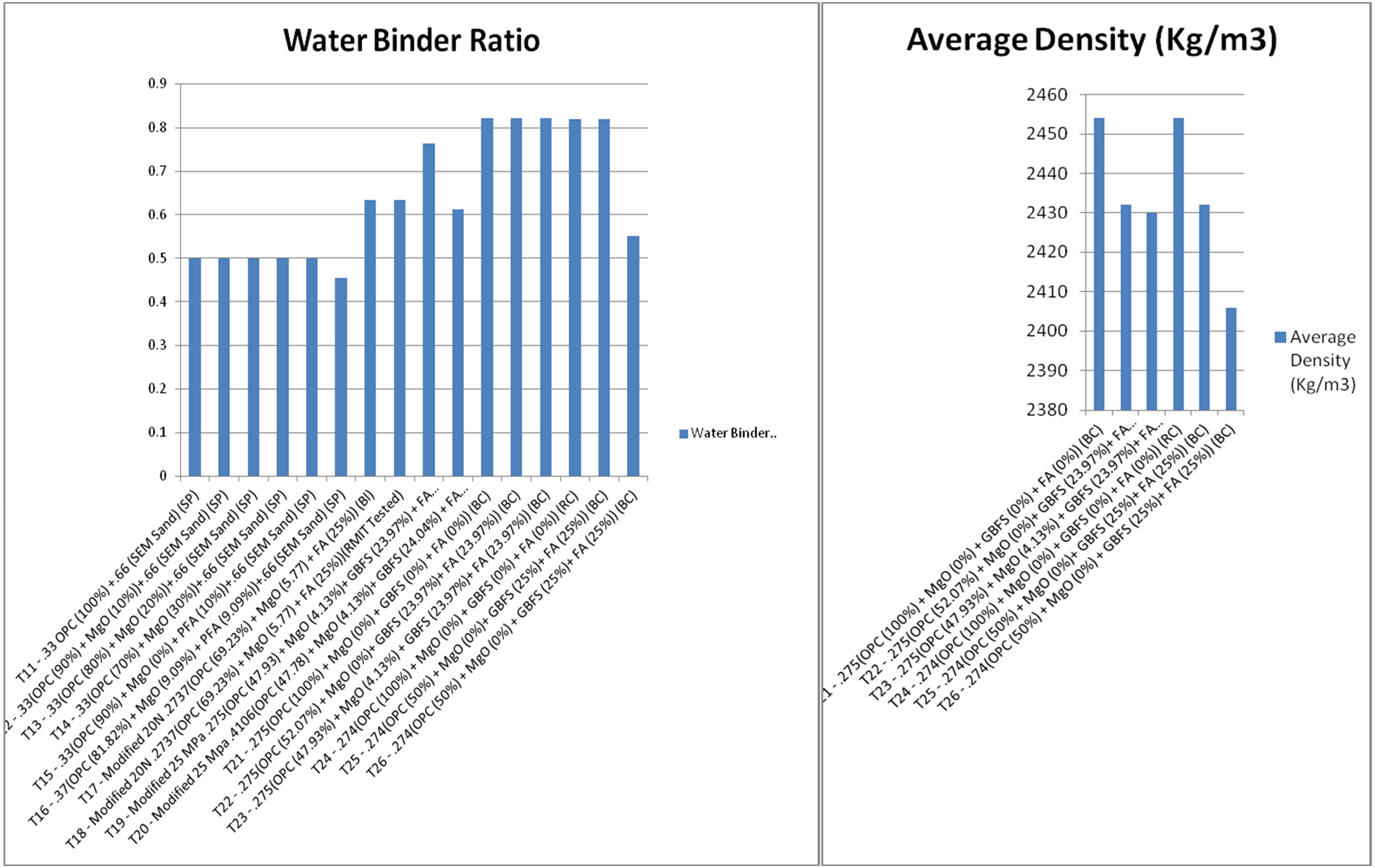

Figure 18 - Water Binder Ratio and Average Density (Note that no additives were used except for T17,19 &20)

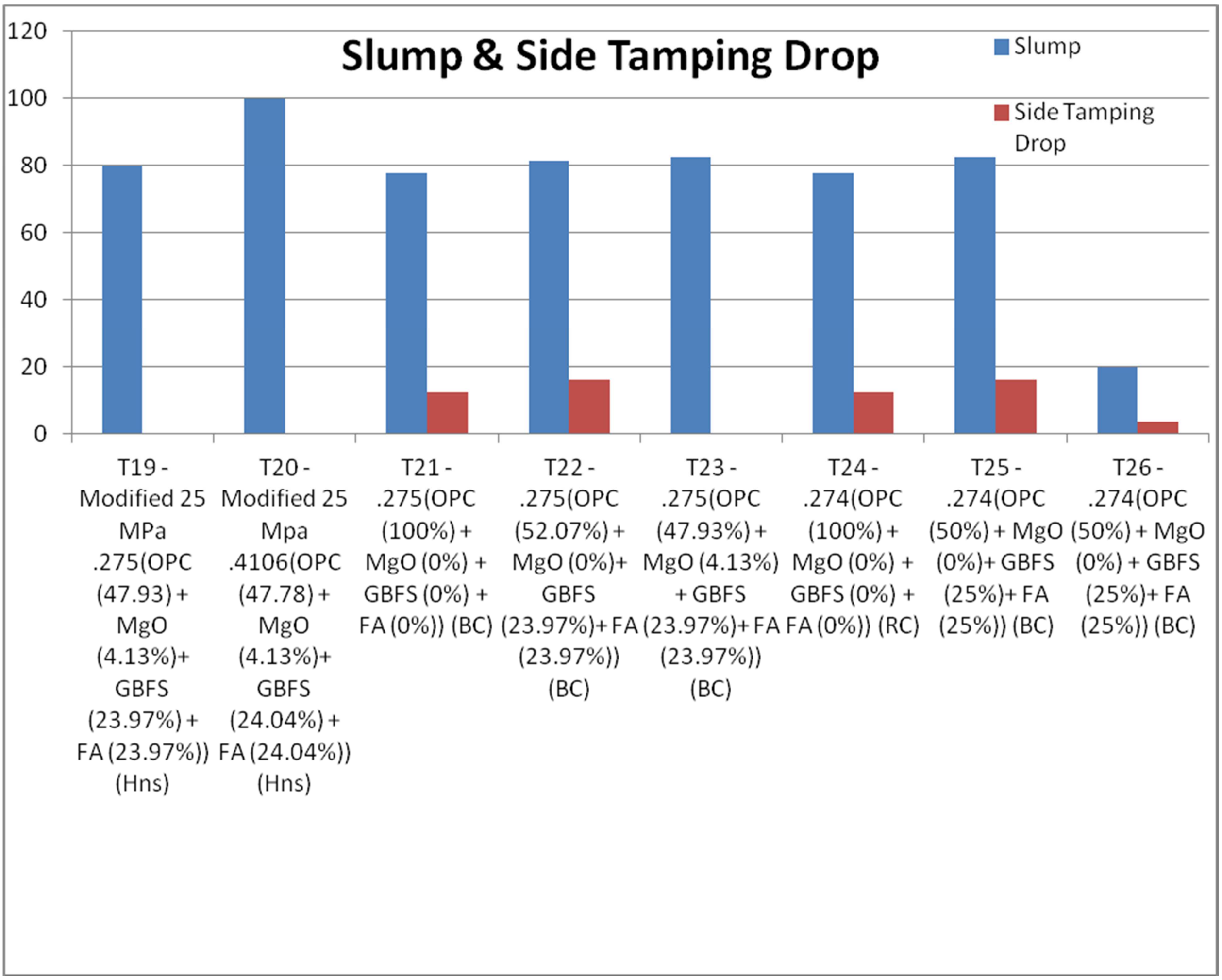

Figure 19 - Slump and Side Tamping Drop