TESTING TECECO CEMENTS

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At the time Spiros conducted his experiments he was a 4th year engineering student at Oxford university. His tutor was Nick Eden.

Spiros made a number of standard mixes using 1 part cement to three parts sand in accordance with BS-EN-196-1. He then substituted the cement with various proportions of fly ash and reactive magnesia supplied by TecEco sourced from Causmag International in Australia. We now think these mixes were probably not optimal as they may have contained a little too much MgO, nonetheless, Spiros contribution is important.

I have edited Spiros English to make it a easier to read but not changed his meaning. Where warranted or I believe Spiros is wrong I have made comment in italics.

John Harrison

Heat of Hydration

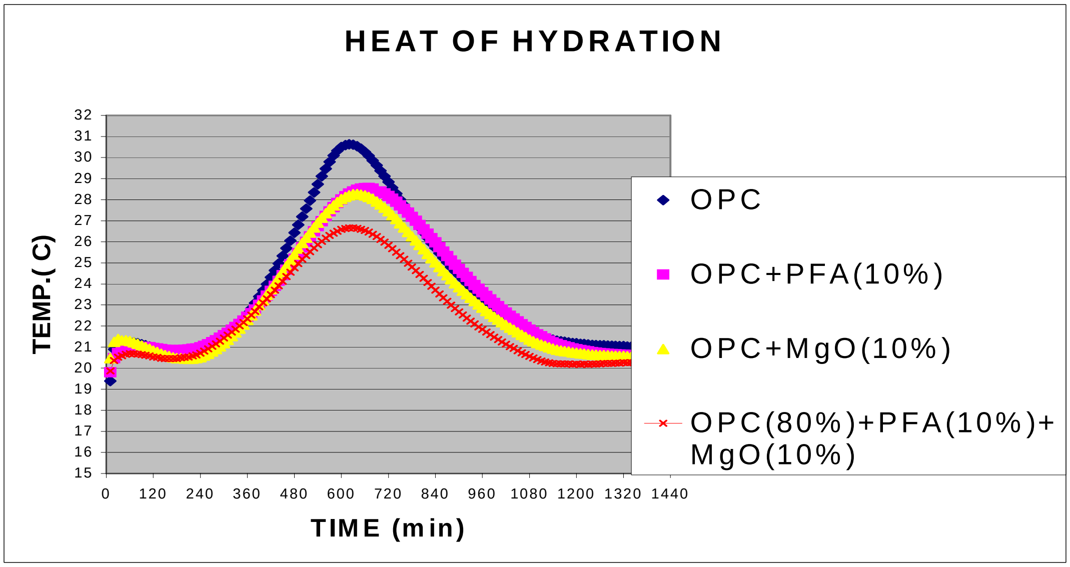

Figure 1 -Temperature of various cement mixes versus time during hydration

The heat evolution during the hydration process was measured for the different mixes and is presented in Figure 1.

Setting Time

The setting time of the different mixes was measured by using the VICAT apparatus. The results of the initial and final set are tabulated in the table below:

Table 1 - The Setting Time of the Different Mixes

	INITIAL SET (min)	FINAL SET (min)
OPC(100%)	138	240
OPC(90%):PFA(10%)	186	281
OPC(90%):MgO(10%)	207	298
OPC(80%):MgO(10%):PFA(10%)	233	330

Comments on Heat of Hydration and Setting Time

After initial contact of cement with water and for about 30 min afterwards a rapid dissolution of ionic species into the liquid phase is taking place. This early fast hydration is accompanied by heat release observable in the graph of heat of hydration (Figure 1) that shows a small increase in the initial temperature immediately after mixing. This period is called the pre-induction period and was observed to be the same for all the mixes.

After this short initial period the temperature becomes steady for about 3.5 hrs during what is referred to as the induction or dormant period and can be explained by the formation of Van der Waals and electrostatic forces. These forces act as a layer around the cement grains preventing the progress of hydration (*This is one of several theories*). From the heat of hydration experiment it is observed that the duration of the dormant period is about the same for all the mixes.

From the results of the VICAT experiment (See Table 1), it is concluded that the initial set of all the mixes is completed during the induction or dormant period. The OPC and OPC:PFA have an earlier initial set in comparison to the initial set of the mixes that MgO is used as a replacement.

The dormant period ends when the protective layer around the cement grains is broken down either by osmosis, which builds up an internal pressure or by the formation of calcium hydroxide crystals (*Again, mostly theory, somewhat in contradiction to the "Van der Waals forces" theory commented on above*). During this period the hydration rate is rapidly progressing and the bonds between the solid particles are getting stronger resulting in the increased strength of the paste. The acceleration period started for all the mixes about 4hrs after the start of the hydration and a rapid increase in the temperature was observed. Six hours after the start of acceleration period (i.e.10 hours after the start of hydration) the peaks of the temperature increase occur for the various mixes simultaneously.

The graph of the released heat during hydration (Figure 1) indicates that the rate of acceleration and the peak of the hydration temperature are smaller for the mixes that a replacement is used. The effect of MgO on OPC is similar to that of PFA, reducing the rate and the peak temperature of the hydration, which means that the enthalpy of the reaction is quite low (*it is*) The addition of 10% replacement (either PFA or MgO) to OPC produced a reduction of about 6.5% in the peak temperature (from 31^{0}C to 29^{0}C). The addition of

20% replacement produced a reduction of 13 % in the peak temperature (from 31^{0}C to 27^{0}C) respectively. This would be expected because the hydration of OPC includes powerful exothermic reactions resulting in undesirable high temperatures, the more OPC is in the mix the higher the peak temperature.

From the results of the VICAT experiment (Table 1) it is concluded that the final setting of all the mixes, except for OPC, is completed during the acceleration period. The OPC has an earlier final set about 4 hrs after the mixing in comparison to OPC:PFA:MgO that has a later final set 4.5 hrs after the mixing.

After reaching the maximum temperature the rate of hydration starts to slow down gradually, as the amount of still non-reacted material declines and the hydration process becomes more diffusion-controlled. The movement of water through the hydration products to the un-hydrated cement becomes slower. For this reason complete hydration is not possible for cement grains of more than around 50 µm in diameter and even after many years there is residual un-hydrated cement. (This period is called the post-acceleration period and it can be observed from the graph that the slowing down of hydration is faster for OPC and has similar gradients for the other three mixes (OPC with replacements).

Compression Tests

OPC - MgO

The graph below shows the influence of MgO on the strength development of OPC standard mortars when it is used as a replacement in different percentages. From the graph it is concluded that a 10% substitution is the most promising of the formulations tested when compared with the OPC control.

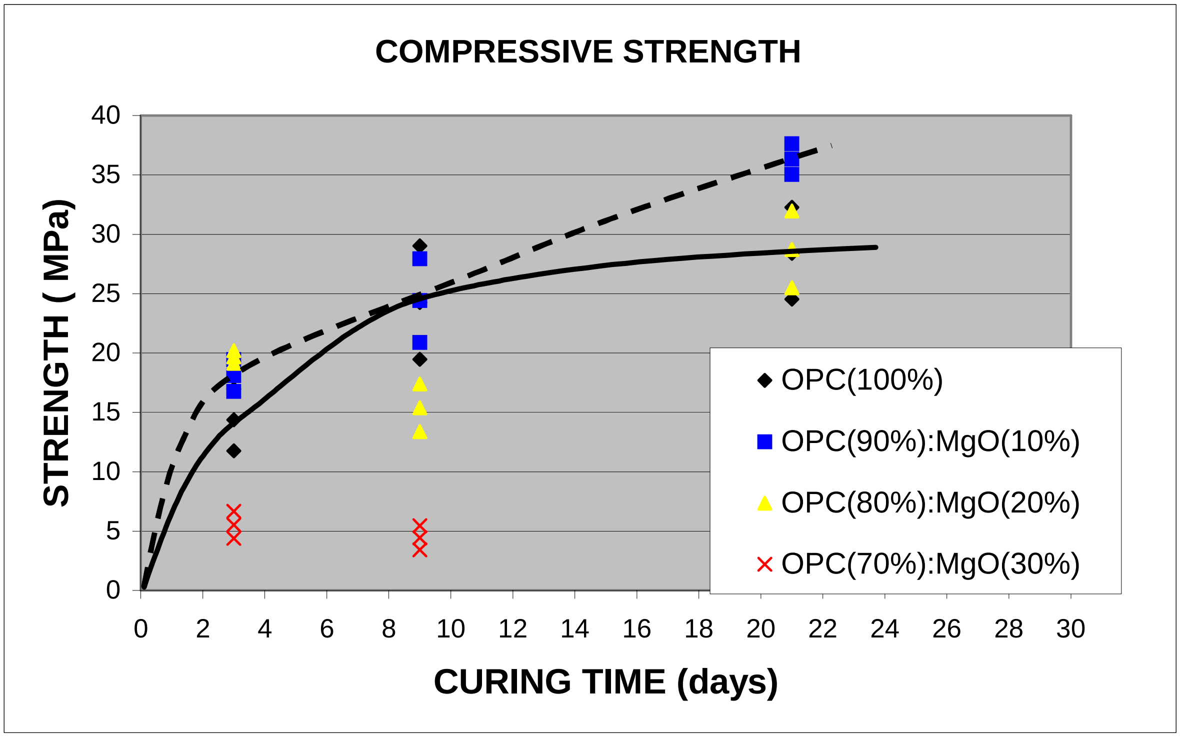

Figure 2 - Compressive Strength of OPC:MgO Mixes (No PFA) Versus Curing Time

The 3-day results give a mean compressive strength of 14.4 N/mm^2 for OPC and a mean of 18.1 N/mm^2 for OPC(90%):MgO(10%).

Statistics

t-test: $t_{stat.}=3.27 \succ t_{crit.}=1.812$ thus accept H_1

Mann-Whitney test: $U=1 \prec T_{crit.}=6$, thus accept H_1

It can therefore be concluded from both tests that the use of 10% MgO as a replacement improves the 3-day mean compressive strength of OPC.

The 9-day results give a mean compressive strength of 24.2 N/mm^2 for OPC and a mean of 24.4 N/mm^2 for OPC(90%):MgO(10%).

t-test: $t_{stat.}=0.7 \prec t_{crit.}=1.812$ thus accept H_0

Mann-Whitney test: $U=17 \succ T_{crit.}=6$, thus accept H_0

It can therefore be concluded from both tests that the use of 10% MgO as a replacement in OPC although it gives a small increase in the mean strength the tests showed that we cannot be confident that it improves the 9-day mean compressive strength of OPC.

The 21-day results give a mean compressive strength of 27.6 N/mm^2 for OPC and a mean of 36.3 N/mm^2 for OPC(90%):MgO(10%).

t-test: $t_{stat.}=5.0 \succ t_{crit.}=1.812$ thus accept H_1

Mann-Whitney test: $U=0 \prec T_{crit.}=6$, thus accept H_1

Conclusions

From the above strength tests it can be concluded that the use of 10% MgO as a replacement improves the 21-day mean compressive strength of OPC used without MgO.

The statistical tests showed significant increase in the early and later mean compressive strength of 25% and 31% respectively.

Spiros goes on to say that the increase in strength can be explained as a result of the activity of the additional alite and belite forms that are formed.

This can be explained as a result of the activity of the additional alite and belite forms that are formed.

Spiros explanation is not supported by research into the hydration phases and even though it may yet be proved to be correct or partially correct, on the basis of his experiments it is supposition. The gain in strength is more likely to be as a result of consumption of water by MgO as it hydrates reducing the water binder ratio and thus the voids paste ratio. The consumption of water internally and prevention of bleeding is also likely to increase the alkalinity and thus the effectiveness of silicification reactions such as surface hydrolysis and the pozzolanic reaction.

MgO – OPC – Fly ash

Spiros further investigated the effect of the replacement of a blended mix of OPC with fly ash substituted by MgO and drew the graph below.

Although we believe Spiros's proportions were not optimal, the results were still encouraging. Since Spiros's experiments we have managed to outperform an OPC control with .45 OPC .5 fly ash .05 MgO binder mix.

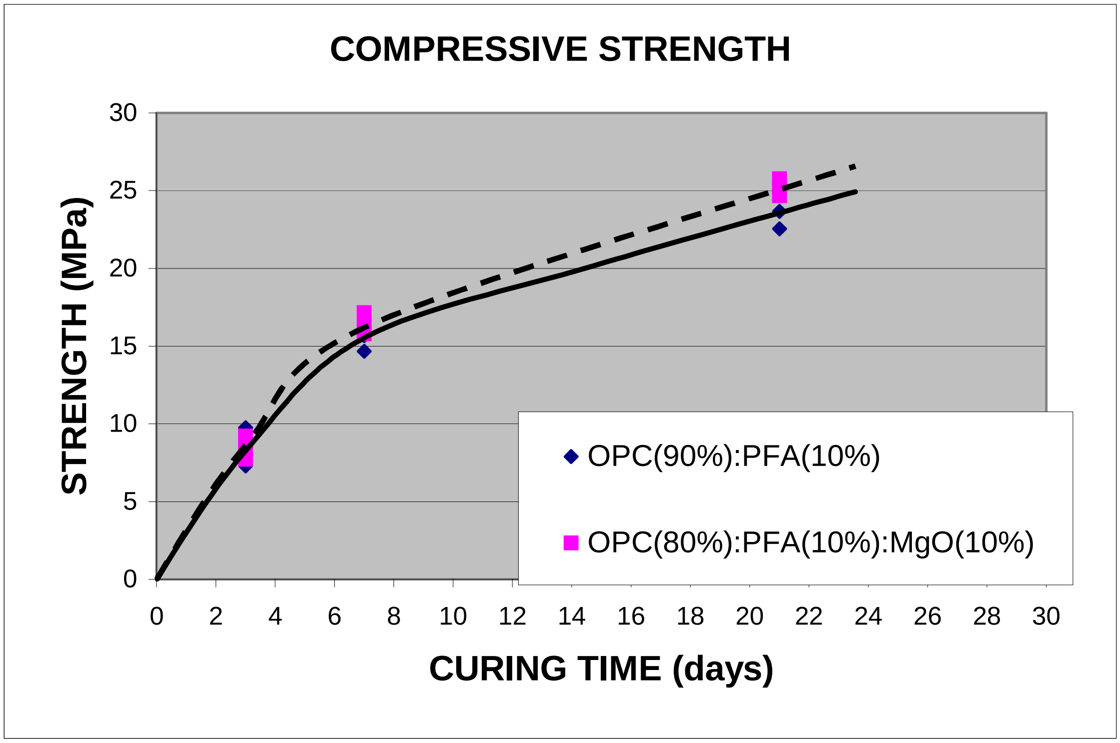

Figure 3 - Compressive Strength of OPC:MgO:PFA Mixes Versus Curing Time

Spiros's data in Figures 2 and 3 has been combined to produce Figure 4 below.

Usually the replacement of OPC by PFA gives a lower early strength and a higher later strength. The 3-day results of OPC:PFA gave an early mean compressive strength of 8.5 N/mm^2 which is lower than the 14.4 N/mm^2 strength achieved by the OPC control as expected. The 21-day results give a compressive strength of 23.7 N/mm^2 for OPC:PFA and 27.6 N/mm^2 for OPC. However from the two graphs (Figure 2 and Figure 3) it is observed that the rate of increase in strength is much higher for OPC:PFA so it can be assumed that this difference would be eliminated in the next few days.

The graph (Figure 3) shows the effect of the replacement of OPC(90%):PFA(10%) by MgO(10%). The 3-day results give a mean compressive strength of 8.5 N/mm^2 for OPC (90%): PFA(10%) and a mean strength of 8.4 N/mm^2 for OPC(80%): PFA(10%) :MgO(10%).

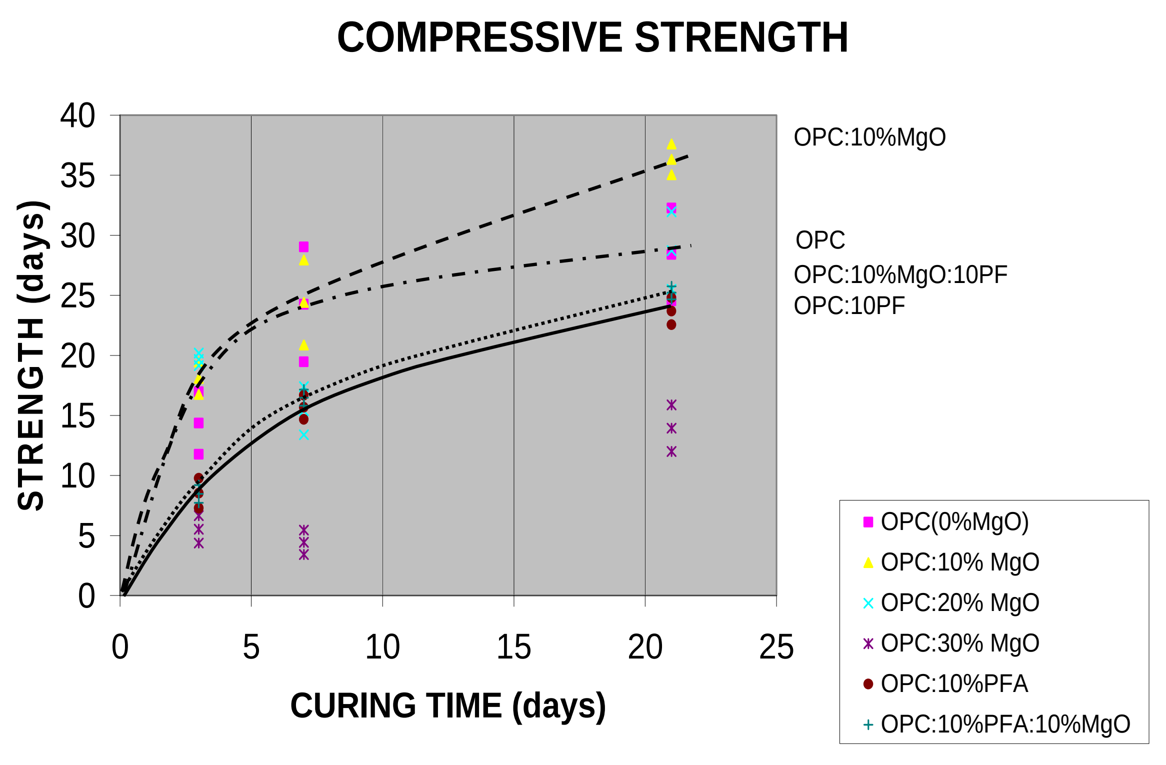

Figure 4 - Compressive Strength of OPC:MgO:PFA Mixes Versus Curing Time Showing Relative Strength Gain

Statistics

t-test: $t_{stat.}=0.11 \prec t_{crit.}=1.812$ thus accept H_0

Mann-Whitney test: $U=16 \succ T_{crit.}=6$, thus accept H_0

It can therefore be concluded from both tests that the use of 10% MgO as a replacement statistically does not improve the 3-day mean compressive strength of OPC(90%):PFA(10%).

The 9-day results give a mean compressive strength of 15.67 N/mm^2 for OPC(90%):PFA(10%) and a mean compressive strength of 16.48 N/mm^2 for OPC(80%):PFA(10%):MgO(10%).

t-test: $t_{stat.}=1.7 \prec t_{crit.}=1.812$ thus accept H_0

Mann-Whitney test: $U=7.5 \succ T_{crit.}=6$, thus accept H_0

The addition of 10% MgO as a replacement although it gives a small increase in the compressive strength, it is not enough to pass the statistical tests.

The 21-day results gives a mean compressive strength of 23.6 N/mm^2 for OPC(90%):PFA(10%) and a mean of 25.2 N/mm^2 for OPC(80%):PFA(10%):MgO(10%).

t-test: $t_{stat.}=3.2 \succ t_{crit.}=1.812$ thus accept H_1

Mann-Whitney test: $U=3.5 \prec T_{crit.}=6$, thus accept H_1

Spiros does however conclude that:

From both tests that the use of 10% MgO as a replacement improves the 21-day mean compressive strength of OPC:PFA.

From the above it is concluded that the overall effect of the replacement is positive.

The addition of MgO significantly improves the later compressive strength of the blended mix (OPC:PFA). However although the replacement gives a small increase in the early mean compressive strength that cannot be considered to be significant according to the statistical analysis.

Tensile Strength Test Results

The mixes produced for compression test were also tested in tension. The effect of the replacement OPC by MgO in different percentages is investigated and gives the graph below (Figure 5).

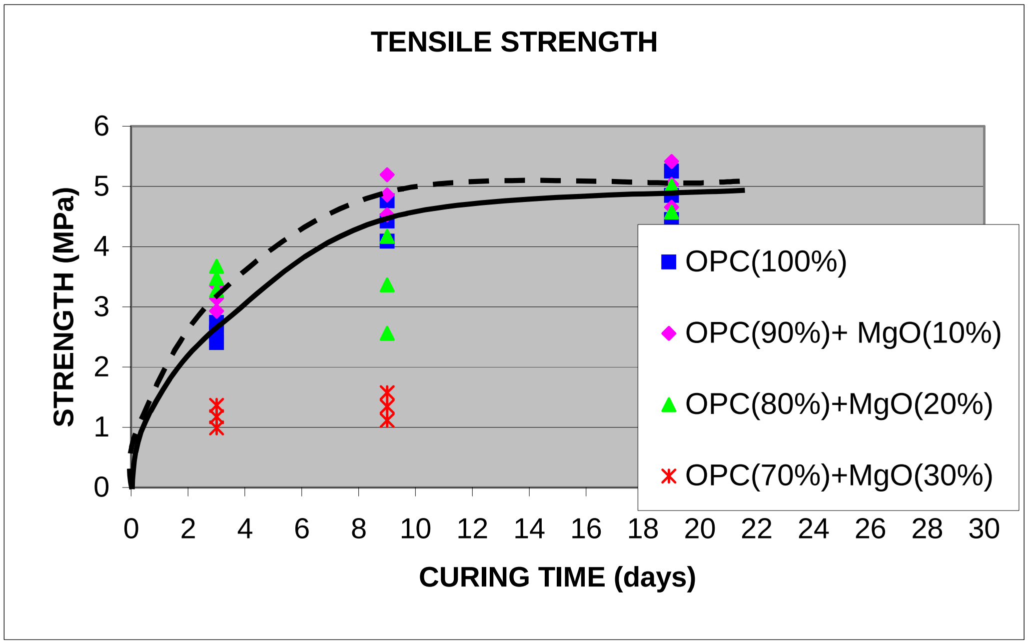

Figure 5 –Tensile Strength of Various Cement Mixes Versus Curing Time

The graph shows that the replacement of OPC with 10% MgO increases the tensile strength during the curing period. However the statistical tests give a positive indication only for 3-day and 9-day results but failed in the 21-day result. It is concluded that replacement by MgO gives an early development of tensile strength, but the later behaviour of the mix becomes similar with OPC.

The effect on the tensile strength of using MgO (10%) as a replacement in a blended mix of OPC with PFA was further investigated and gives the graph below ()

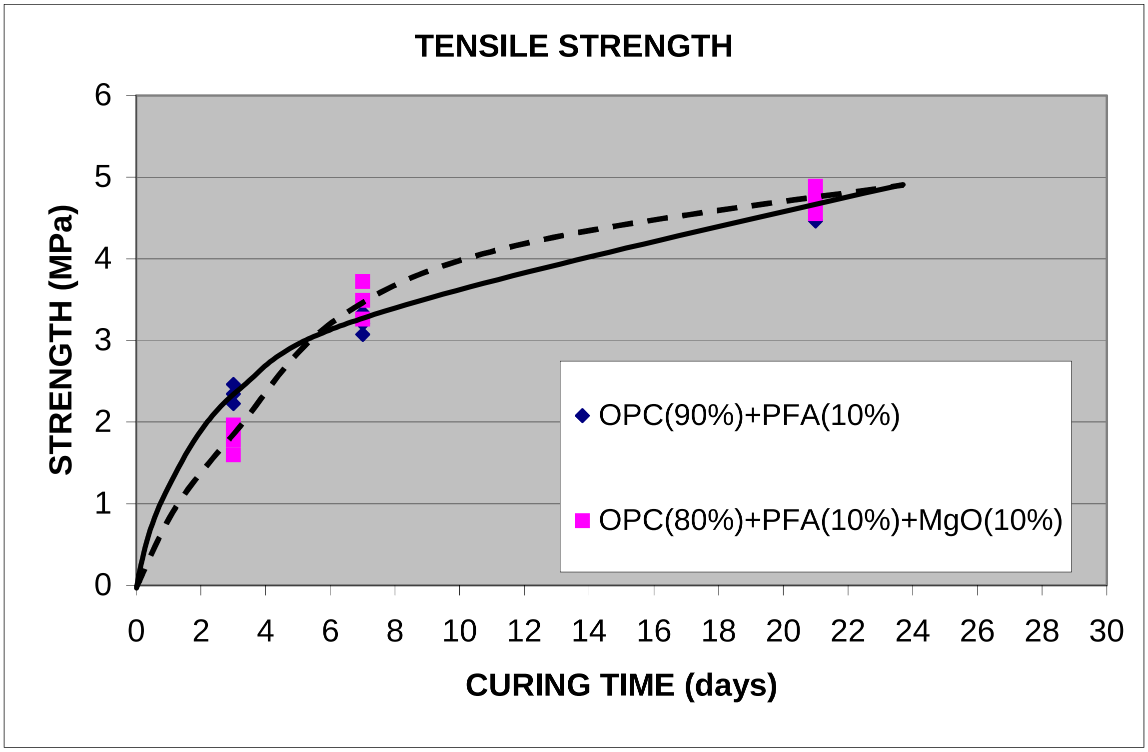

Figure 6 -Tensile Strength of Different Cement Mixes Versus Curing Time)

The statistical analysis tests give a negative influence in the 3-day strength (95% confidence) and a neutral influence in the 7-day and 21-day (fail to pass the tests).

From the above it can be concluded that the overall effect of MgO on the tension strength of cement cannot be considered significant, it has a neutral influence.

I disagree with Spiros conclusion because Figure 5 did show early development of tensile strength. TecEco now consider this affect to be a function of the small size and high charge of the Mg^{++} *ion and the way this affects water which is a polar molecule.*

Conclusions

It is claimed by John Harrison of TecEco that the use of MgO as a replacement of OPC in a high percentage (more than 10%, expressed as mass fraction) is not only environmental beneficial but moreover improves the properties of the cement. (*This is only partially correct in that the statement misunderstands the reasons for the greater sustainability of TecEco cements. There are two main formulation types: tec-cements and eco-cements. I have no recollection of having made the comments Spiros has attributed to me such as" high percentage (*more than 10%, expressed as mass fraction)" *as both tec and eco-cements are more sustainable. Tec-cements are more sustainable because they develop more strength for the same amount of binder (as shown by Spiros tests), conversely, less binder can be used to produce the same strength. Eco-cements are more sustainable because in porous materials they go the full thermodynamic cycle reabsorbing* CO_2 *out of the air to gain strength. In all formulations the properties of cement are improved.*) In this study this solution is checked and from the quantitative and qualitative investigation the conclusions reached are listed below:

1. The replacement of ordinary Portland cement (OPC) by the magnesium oxide (MgO) is environmental beneficial because it decreases the operation temperature of the kiln, saving a lot of energy, emissions and cost. The magnesium carbonate is converted to magnesium oxide at 700^0C (*the equilibrium temperature is around* 540^0*C*) in comparison with the 1400^0C needed for the conversion of calcium carbonate to calcium oxide. (*This is not correct as the equilibrium temperature for this reaction is lower. Perhaps what Spiros meant was “*1450^0*C needed for the manufacture of Portland cement clinker.”*) Although the majority of MgO is produced from the naturally occurring mineral magnesite ($MgCO_3$), there is also an alternative way to produce it from brine (saturated salt solution). So magnesia can be easily produced by known methods and with lower energy.

2. The investigation of the replacement on the hydration process shows that:

   - The replacement does not have an influence on the duration of the hydration periods (pre-induction, induction, acceleration, post-acceleration periods).

   - The use of MgO as a replacement has similar effects to that of PFA. During the acceleration period the replacement reduces the rate and the peak temperature of the OPC(100%) hydration. That means that the enthalpy of the reaction is quite low. The slowing down of the OPC(100%) hydration is proportional to the replaced percentage. The replacement of 10% OPC, either by MgO or PFA, decreases the released heat about 7%. The replacement of 20% of OPC gives a reduction of 14% of the hydration temperature respectively.

     So from the above it can be concluded that the effect of the replacement on the evolution of hydration is beneficial because it prevents rapid hydration ‘flash set’ of the cement paste with the associated negative consequences.

3. The evolution of hydration is reflected in the VICAT experiment’s results. The replacement delays the initial and final set of the mixes, so it has positive effect on preventing the formation of early stage cracks and allowing the development of gradual compressive strength. (*There are other tensile strength and volumetrically related reasons for the prevention of cracking in tec-cements. The development of greater tensile strength and matched expansion and contraction are the two main ones.*)

4. From the analysis of the compression tests results it can be concluded that:

   - The replacement of OPC(100%) by magnesium oxide is most effective when 10% magnesium oxide is used. The statistical analysis indicates (with 95% confidence) that the replacement increases significantly not only the later compressive strength of the cement paste by about 30% but also the early compressive strength by about 25%.

   - The effect of replacing 10% of the blended mix OPC(90%):PFA(10%) by magnesium oxide is also significant and increases the later strength about 7%. The statistical analysis shows (with 95% confidence) that there is no effect of the replacement on the development of early compressive strength. (*More work has since shown that it probably does*)

From the above it is concluded that the overall effect of the replacement on the compressive strength is positive particular on the developed later strength. The increase of the later compressive strength can be explained as a result of the additional belite forms that are formed. Moreover the strength development is achieved without causing bleeding and segregation of the cement paste. (*The comments about additional belite forms are conjecture but may yet turn out to be correct. The important and most relevant observation by Spiros is in relation to the lack of bleeding. Unfortunately he did not deduce that alkalis would therefore be retained and the water binder ratio would reduce over time as MgO consumed water forming* $Mg(OH)_2$)

5. From the analysis of the tension test results it is concluded that the replacement does not have significant influence on the developed tension strength. The long-term influence is considered as neutral. (*From the graphs yes, statistically however no - but then statistics and the truth are not the same thing!*)

6. The main drawback in the use of MgO as a replacement is the long-term unsoundness that arises from the slow hydration rate of MgO. The hydration of MgO to $Mg(OH)_2$ is expansive and its formation in a cement that has already been hardened can cause cracking. However the qualitative study shows that there are several ways to prevent unsoundness in the cement. (*Unsoundness is related to the rate of strength gain and volume change of the various components of a cement. Periclase hydrates very slowly and incompletely compared to amorphous reactive magnesia, the use of which eliminates the problem. Spiros did not detect unsoundness so his "conclusion" is not a conclusion. It is a statement based on erroneous preconditioning common in the cement industry amongst engineers.*)

   - The use of small grains MgO, smaller than 0.005 mm, increases the percentage of periclase that causes cracking. (*Yes in the sense that obviously a few large lumps of periclase will have less affect than a large number of smaller well distributed particles. This is purely a function of the greater surface area of the latter compared to the former. The conclusion is however, as previously, a function of Spiros's conditioning during his training and not based on the experiments. The important factor is the degree of order of the crystal lattice*)

   - The use of rapid cooling rate clinker is beneficial because it reduces the average size of the periclase crystals and distributes them widely within the mixture. (*This may be true but is not a conclusion of the experiment. It is a repetition of the lack of understanding in the literature as to the importance of lattice energy. Periclase has a high lattice energy, reactive magnesia a relatively low lattice energy to overcome. Spiros was supplied reactive magnesia not finely ground periclase! Compare diamonds to carbon from toast – they are very different*)

   - The addition of fly ash and gypsum stabilises effectively high percentage of MgO. (*Again this is not a conclusion - it is a statement of Spiros's understanding of the literature*.)

   - Portland cement produced from raw materials with high percentage of iron oxide produce a smaller percentage of periclase. (*Again this is not a conclusion - it is a statement of Spiros's understanding of the literature. It may also not be correct as iron oxide has deleterious affects during the low temperature calcination of magnesium carbonate to produce reactive magnesia*.)

> Summarising the above it can be concluded that the use of MgO as a replacement in the cement industry will have beneficial environmental impacts and will reduce the cost of production of cement. The replacement not only improves the main properties of OPC but also it can be positively combined with other pozzolanic materials (fly ash) and gypsum. The drawbacks of its use can be effectively eliminated in various ways.

CRITICAL APPRAISAL

The aim of the study undertaken was to investigate the effects of the replacement of OPC by MgO on the main properties of Portland cement. This was achieved by producing various mixes and subjected them to different tests. The final results achieved to give valuable information about the behaviour of MgO when it is used as a replacement and to draw valuable conclusions.

In this investigation it would be useful if further tested were carried out between the critical intervals of 10-20 % of the replaced material. (*TecEco believe the ideal addition rate for tec-cements as tested by Spiros to be in the range 5-15%*) These experiments may find out whether there is a higher percentage of MgO more promising to be used in the cement industry. Further investigation could also be carried out to check the behaviour of blended mixes with much higher percentage of fly ash ($\approx$20%, expressed as mass fraction).

Future investigation is essential to check the unsoundness of cements, when reactive magnesia ($\geq$10%) (*the figure used here of 10% is arbitrary, most standards specify 5%*) is used as a replacement of OPC and of blended mixes (OPC:PFA). There are two methods that are used to test the soundness of cement, the Autoclave test and the Le Chatelier test. Whilst the Autoclave test detects the unsoundness due to free CaO and MgO, the Le Chatelier test fully accounts only for the unsoundness due to free CaO. It has been reported that cements with more than 5% MgO passed the Le Chatelier test provided their free CaO was low, while they failed in the Autoclave test. (*This last comment by Spiros is as are many others preconditioned by his training and not a valid conclusion to any of the work done by him. Spiros work is important and useful. It also makes it clear that one of the main hurdles for TecEco to overcome will the lack of understanding about the causes of unsoundness and how it can be overcome by using low lattice energy reactive MgO.*)