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Comments on Papers from Cambridge University and Imperial College London

This document contains a detailed summary of the work by Cambridge University and Imperial College London Students under the supervision of Dr Al Tabaa (Cambridge University) and Dr Chris Cheeseman (Imperial College London).

First however we examine whether there was another agenda.

Was there Another Agenda?

Our Eco-Cement Technology must be good because after their collaborators at Cambridge did their best to show our technology in bad light, Dr Cheesman, a lecturer and supervisor of some of the authors, some of whom are now at Imperial College London, claimed he invented it![1] To say the least we were stunned. Not only did John Harrison our MD invent carbonating magnesium cements some years ago, there is overwhelming evidence including granted patents and much publicity to prove it (See media[2]). What is particularly disturbing is that John Harrison also explained to Dr Cheeseman and his collaborators at Cambridge university including Dr Al Tabbaa how to make Eco - Cements concretes. We therefore question whether these researchers did not, at least at first, understand Mr Harrison's directions or whether there was a deliberate attempt to discredit Mr. Harrison, TecEco and the technology before claiming it for themselves.

The only positive to this charlatan like behaviour is that it possibly demonstrates that some researchers to whom we have shown our technology are at last starting to realise the importance and potential of carbonating magnesium cement systems so much that they would now like to steal the credit for them. Plagiarism and other bad behaviour by academics seems live and well as others as well the authors from Cambridge and Imperial College whose contributions are discussed below have used all Mr Harrison's quotes and even paraphrased him without reference when setting out their findings.

The story about Dr Cheeseman came to our attention in an article in CNPlus, the on line newsletter of Construction news in the UK which announced that Dr Cheeseman of Imperial College London had just invented a carbonating magnesium oxide cement [1] According to the report "while carrying out research on one such compound the Imperial team stumbled upon the fact that the resulting cement also absorbed further CO2 from the atmosphere as it hardened." The only thing the researchers at Imperial College have

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[1] See http://www.cnplus.co.uk/News/2008/05/green_cement_sucks_up_co2.html and http://www.aggregateresearch.com/article.aspx?id=13823. These files as downloaded on the 8th May 2008 are available from the TecEco web site

[2] http://www.tececo.com/media.php

stumbled on is the truth as we demonstrated how to make Eco-Cement concretes to them some years ago.

We went to some trouble to telephone Alasdair Reisner the author of the report, and he stands by what he wrote. Although Dr Cheeseman of Imperial College has now in a letter to us denied that he invented our cements he has not done so publicly.

This fact together with the fact that Dr Cheeseman has set up a company to develop “his” technology leads us to believe that there was all along a plot to steal our intellectual property.

I have not doubt that this plot will continue to unfold and I am keen to be persuaded otherwise.

John Harrison

Reactive Magnesium Oxide Cements: Properties and Applications

Vandeperre, L.J.[#], Liska*, M., Al-Tabbaa, A.*, 2007. 'Reactive magnesium oxide cements: properties and applications'. In: Y.M. Chun, P. Claisse, T.R. Naik, E. Ganjian, ed. Proc. Int. Conf: Sustainable construction materials and technologies, 11-13 June 2007 Coventry. Taylor and Francis, London, ISBN 13: 978-0-415-44689-1, p397-410.

*[#]Imperial College London; *Department of Engineering, University of Cambridge, UK*

The title, abstract and text in this paper make seriously wrong inferences as to the properties including carbonation and strength of TecEco cements generally. As the formulations tested were out of spec for most of TecEco’s formulations this is not valid.

For the information of the authors carbonation requires a permeable matrix that will allow gas transport and the formulations chosen are not graded properly and relatively impermeable.

A formulation containing just MgO PC and pfa in various proportions essentially consists of fine powders and optionally aggregates and sands designed for hydraulic binders cannot possibly carbonate. The mistake made by the authors of this paper is as bad as that made by the BRE where sands in accordance with BS EN 196-1 which refers to CEN references sands designed for hydraulic cements were used. The point being that CEN sands have particle size distributions optimised to minimise voids, reducing the water binder ratio and porosity for maximum strength in a hydraulic rather than carbonation context.

The failure to understand particle packing and inclusion of fly ash or other fines and exclusion of coarse gritty sands and aggregates is a serious mistake if natural carbonation is to ensue and of great concern to me as I have specifically made it clear how to make an Eco-Cement in numerous publications. We even warn people about particle packing on the labels of Eco-Cement we were selling.

It would also have been more appropriate to adjust water based on workability rather than standard consistence as in BS En 196-3 which is a static test as our magnesium cements are much more thixotropic and respond to the input of energy (working). They can thus be made with a lower nominal slump.

In spite of these two major criticisms there are nevertheless some useful finding in this paper which concur with our experience. For example the paper confirms that the hydration of the magnesia supplied was relatively rapid (See figure 7) and that mixes with reactive MgO do not display unsoundness thereby resoundly dispelling the myths attached to all forms of MgO and confirming that reactivity matters.

I further congratulate the authors for their conclusion that "in mixtures containing both PC and MgO, the normal hydration products for PC were found in addition to brucite, suggesting that the hydration reactions occur in parallel." The observation that a more reactive magnesia that is courser may be more useful is in line with our thinking as there were some obvious issues in relation to the fineness demand for water that the industry will find it hard to understand and compensate for. We are currently doing work with cement companies to blend grades to see if we can achieve better particle packing.

In this paper the tests undertaken would have been suitable for Tec or Eco-Cements however the proportions chosen were in neither category. The fact that Tec and Eco-Cements set by entirely different mechanisms was clearly not recognised or understood. There is far to much MgO in all formulations for a Tec-Cement. Much less would have been appropriate given the particle packing. The team could have then tested for shrinkage and durability which are the properties Tec-Cements have that excel.

Given the formulations and low permeability that resulted any attempt to achieve efficient carbonation was doomed to fail from the start and even though the authors achieved some carbonation under forced conditions it would have been much more efficient and greater strength would have been achieved if the particle packing was more appropriate.

I note that an attempt is made to promote carbonation by using wet dry conditions however the lack of permeable passageways for air transport due to the over abundance of fines would not allow carbonation to proceed efficiently right through the material.

The use of aggregates was considered and commented on towards the end of the paper. We have not run the sieve analyses through our formulation software, however a perusal indicates that the aggregates used were designed for hydraulic rather than carbonating concretes. Reasonably or well grading (the words used by the authors whatever this means to them) for carbonating Eco-Cements must mean to some extent mono grading the dominant or largest particle and gap grading the fines end of the size range and TecEco have gone to some trouble to explain this at http://www.tececo.com/technical.importance_particle_packing.php.

The Cambridge researchers have done the exact opposite and there are far too many fines in the mixes for carbonation and far to much MgO given their formulation for hydraulic strength. The particle packing is for Tec-Cement concretes, the proportions for neither Tec or Eco-Cement concretes.

In the conclusions the important point is stated but perhaps not appreciated when the authors say "Upon carbonation of samples made out of 80 wt% pfa and 20 wt% MgO the strength increased significantly from 1 to 6 Mpa" They then in the second last paragraph note "strengthening is somewhat slower for mixes with Lytag aggregates than for mixes with gravel, sharp sand and pfa."

TecEco are prepared to disclose under confidentiality how to make Eco-Cement concretes with high fly ash[3]

We are more impressed when the authors noticed (after fig 19) that "the improvements in strength were even more pronounced for aggregate based systems than for systems without aggregates. Where before the strength increased to close to but below what could be achieved by 28 days hydration of Portland cement, the strengths here are higher than what is obtained at 28 days of Portland cement hydration. This is probably due to easier transport of CO_2 towards the interior of the aggregate based materials than towards the centre of the materials made with 80 wt% pfa (my underlining) as indicated by the difference in capillary absorption. The fact that the strength is significantly higher than the strength range for typical masonry units (4.2-10 MPa), suggest that it might be possible to reduce the cement content further while achieve useful properties."

These findings point the way forward for future research using more appropriately graded permeable mixes with proper proportioning and reduced fines suitable for natural carbonation of high MgO Eco-Cements as specified by us. It is saddening to know that this did not happen.

There is some comment that pfa changes the nature of the carbonation products. Although we have also noticed the presence of aluminium seems to speed setting we think that the changes in carbonation products is more likely a function of the availability of CO_2 and water as a result of the matrix structure.

We note the authors attribute later strength gain should MgO, pfa and PC all be present to the pozzolanic reaction. This requires water which we believe is provided by dehydrating brucite as the hydration of magnesia actually forms brucite hydrates. We are currently exploring the possibility with other researchers that the polar bound water in brucite hydrates is available for later more complete hydration of PC thereby reducing autogenous shrinkage. Unfortunately the formulations used by the authors have far too much MgO for Tec-Cements and shrinkage was not tested.

Finally in their conclusion the authors point out that "PC can be omitted from the composition entirely if it is feasible to include a carbonation step in the production process." In a real world production situation we have demonstrated that a small proportion of PC (e.g 20 -30%) will promote sufficiently rapid curing for practical use given proper formulation and use of aggregates. Hence the use of a small amount.

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[3] Patent matters are pending

Performance of magnesia cements in pressed masonry units with natural aggregates: Production parameters optimisation

Liska, M*. and Al-Tabbaa, A.*, (2007) Performance of magnesia cements in pressed masonry units with natural aggregates. Construction and Building Materials . ISSN 0950-0618 (In Press)

**Department of Engineering, University of Cambridge, Trumpington Road, Cambridge CB2 1PZ, United Kingdom*

In the first sentence the authors say that their “concrete mixes are characterised by low paste content, high aggregate content, and the inability to be self-consolidated.” I was enthused to read on as such mixes properly used should result in masonry units that are sufficiently permeable for carbonation to ensue provided not too much water is added.

The next few lines when the authors said “it has been found that magnesia-based pressed masonry units can increase in strength substantially provided they are subjected to accelerated carbonation” soon dampened my enthusiasm for their work as it is simple to demonstrate that improving permeability has twice the affect of forced carbonation (See http://www.tececo.com/technical.importance_particle_packing.php).

It is obvious the researchers had no experience in the manufacture of concrete masonry units and no idea how to make them properly, indeed they admit the problem when they refer to operators (of masonry unit factories) finding it difficult to part with their “trade secrets” having significant impact on the methodology adopted in the experimental work.

Without proper equipment for making concrete bricks blocks and pavers the authors would have had little chance of getting it right anyway. Making good blocks is about using the right materials, adding just the right amount of water and applying just the right amount of vibration and compression and any good block maker knows how to make blocks that carbonate because by doing so they can save a lot of cement. A shareholder of TecEco makes masonry units and would admit this and further add that it takes some time for full strength to develop using a magnesium system however the strength attained can exceed that in a PC only system. It follows that the conclusion that forced carbonation is necessary is not very useful for no other reason than the cost.

In spite of their opening remarks about mix design the authors have included pfa in substantial proportions in a mix that they then try and set by carbonation. Carbonation did not ensue readily because the presence of too many fines reduced the porosity well beyond the point of permeability percolation (See http://www.tececo.com/technical.importance_particle_packing.php.)

Without so much pfa the MP mix in table 1 in the paper probably would have carbonated properly using the methods and techniques of the authors however with high proportions of pfa a different approach is required which we will disclose under confidentiality[4].

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[4] Patent matters are pending

The grading required to make masonry units effectively in many brick block and paver making machines will allow carbonation and such grading is illustrated in Figure 1 in relation to our comments on the paper “Influence of carbonation on the properties of reactive magnesia cement-based pressed masonry units” on page 6. One of TecEco’s shareholders have been making carbonating Eco-Cement blocks now for some years and have not had to resort to forced carbonation.

It is interesting to note that strength development in figure 8b (PC/MgO) is very much a straight line whereas in 8c with PC only the normal log type curve is presented. There is no comment on the straight line characteristic of figure 8b however it is an important indicator of the reaction process. In figure 9b the curves are also straighter and continue indicating that strength through increases in mass and microstructure are occurring by carbonation. Note that because of the obvious rate differences comparison on a 28 day basis as in the paper is not appropriate. It is like comparing apples to oranges with a citric acid test.

Nesquehonite is known as the star mineral by many and there is a good chance that the radiating needle like growths in figure 10b are nesquehonite not ettringite as suggested in the paper and that the mineral formed subsequent to fracture.

I am concerned about the emphasis on forced carbonation in this paper and think that more research on optimal formulations and conditions for natural carbonation would yield information about how to more economically make the product.

We suggest to proponents of forced carbonation that they try adding up the cost and emissions associated with building carbonation rooms and transporting product to them when merely doubling the pore size will quadruple carbonation rates as we mathematically demonstrate at http://www.tececo.com/technical.importance_particle_packing.php.

Influence of carbonation on the properties of reactive magnesia cement-based pressed masonry units

Liska, M.* Vandeperre L.J.# and Al-Tabbaa, A.*, Influence of carbonation on the properties of reactive magnesia cement-based pressed masonry units, Advances in Cement Research, 2008, vol. 20, no. 2, pages 53-64

**University of Cambridge; #Imperial College London*

In spite of the numerous naturally carbonated block samples we have provided to researchers in the UK along with the formulations we used to make them researchers in that country and in particular the Cambridge – Imperial college team seem intent on using their own formulations, not ours. These formulations are illogical given the objectives, technically stupid given the plethora of papers confirming the conditions for natural carbonation I have cited in paper 25 on the TecEco web site (Harrison 2005) and just cannot carbonate for a host of reasons including the overabundance of fines, excess sand over gravel or excess water! The authors have demonstrated this very well and little else.

Table 2 sets out the composition by percentage weight of the cement mixes tested reported by this paper.

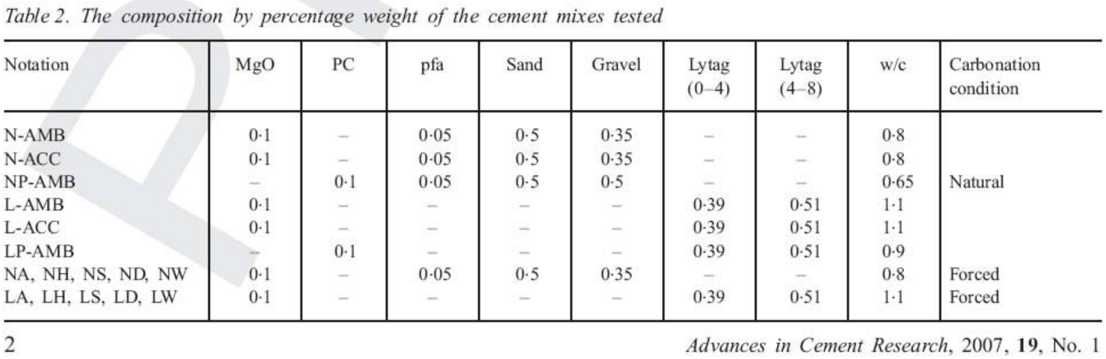

Table 2. The composition by percentage weight of the cement mixes tested

Notation	MgO	PC	pfa	Sand	Gravel	Lytag (0–4)	Lytag (4–8)	w/c	Carbonation condition
N-AMB	0·1	–	0·05	0·5	0·35	–	–	0·8	Natural
N-ACC	0·1	–	0·05	0·5	0·35	–	–	0·8	
NP-AMB	–	0·1	0·05	0·5	0·5	–	–	0·65	
L-AMB	0·1	–	–	–	–	0·39	0·51	1·1	
L-ACC	0·1	–	–	–	–	0·39	0·51	1·1	
LP-AMB	–	0·1	–	–	–	0·39	0·51	0·9	
NA, NH, NS, ND, NW	0·1	–	0·05	0·5	0·35	–	–	0·8	Forced
LA, LH, LS, LD, LW	0·1	–	–	–	–	0·39	0·51	1·1	Forced

2 *Advances in Cement Research*, 2007, **19**, No. 1

A perusal of Table 2 indicates no formulation that contains MgO and PC as specified by us, let alone a composition that contains MgO and PC without pfa. In all formulations the ratio of sand to coarser gavels is 10:7 whereas the Columbia manual would have this ratio as 9:8. It does not really matter so much as long as the matrix is permeable.

On the basis of the above mixes it is not possible to assess our technology and it needs to be said that the numerous conclusions this paper arrives at are thus totally misleading and unfair to us and a disservice to science.

The UK research has become incestuous. Mistakes are feeding on mistakes to back them up. This and other papers from the current rash emanating from the Cambridge – Imperial college team often refer to their own findings or those of the BRE with whom they have shared confidences to confirm a statement in a different paper. As none of the experiments in this and the other papers from the team or BRE use formulations that are anything like those of TecEco they are substantially irrelevant.

For example a comment appears on the first page of this paper thus “Despite potential sustainability advantages, in terms of lower manufacturing temperatures, substantial use of by-products and significant potential for sequestering CO_2, these MgO-based cements have been shown to be substantially weaker in comparison with identical mixes made of PC resulting in much lower strengths and stiffness values” This is a generalisation that is a good example of the incestuous nature of the research so far in the UK as the comment refers to their own work which is as we have pointed out limited and doomed to failure in many areas in any event. Nothing in the Cambridge work and especially this paper should be taken without thorough analysis as generally applying to TecEco cements.

TecEco have shown naturally carbonated Eco-Cement concrete blocks to be at least as strong by testing them according to Australian standards which is every respect are not dissimilar to the European standards. For that matter in an earlier paper (L.J. Vandeperre, M. Liska & A. Al-Tabbaa , Reactive Magnesium Oxide Cements: Properties and Applications) , even the Cambridge group made the following comment “Where before the strength increased to close to but below what could be achieved by 28 days hydration of

Portland cement, the strengths here are higher than what is obtained at 28 days of Portland cement hydration." This earlier statement is contradicted in this paper

There then follow some correct statements about the carbonation process recognising that it depends on the factors "drying, concentration of CO_2 and transport of CO_2 into the sample." At least the main carbonate formed is correctly identified as nesquehonite and the fact that water is required recognised. That this is so should have then also given the researchers a clue as to how to efficiently carbonate as should have the work by Vandeperre et al (Vandeperre L. J. and Al-Tabbaa A. in the paper Forced carbonation of reactive MgO cements. Advances in Cement Research, 2006 discussed in this document) which examined small plates. The problem is obviously the mixes. They are not allowing carbonation as they all have in them far too much fine pfa or if no pfa no MgO. Fine materials like pfa reduce porosity and hence carbonation.

None of the tests applied to the formulations and carbonation conditions (AMB, ACC A, S, D, H and W and various combinations of aggregate, PC, pfa and MgO) recreate the conditions we have stated on many occasions are necessary for efficient natural carbonation which are damp or wet alternating dry. Wet for the provision of water required for nesquehonite to form and dry for optimal gas transport. These conditions are to some extent a necessary but not sufficient condition for carbonation. Permeability is the other necessary condition for carbonation at a reasonable rate (2 – 6 months to approach completion)

There is no dispute with the authors that carbonation results in significant strength as they note this in other papers. They just do not seem to know how to achieve it. Under normal outside conditions in temperate climates we have demonstrated time and time again with the production of literally thousands of blocks that natural carbonation proceeds reasonably rapidly and our own XRD studies indicate completion within 12 months and close to completion within much less time.

Given the formulations in this paper readers will be relieved to know I consider it a waste of time to further analyse it. This is a damning but deserved statement. The discussion on forced carbonation is interesting but the process likely to be uneconomic. Natural carbonation was not successfully achieved because the samples were not correctly formulated as explained and they were not permeable. The fine pfa content when present is totally unnecessary and will reduce access by $Mg(OH)_2$ and $Ca(OH)_2$ to air and thus in most circumstances reduce rather than increase strength. TecEco will divulge under confidentiality to power companies and others how to make Eco-Cement concretes using pfa however at the moment cannot disclose this technology as it is still subject to patent application.

Although many of the formulations do not contain PC as specified by us it should be noted that in a macro porous carbonating formulation Portlandite will gain strength by carbonation (usually in the sequence vaterite => aragonite => calcite?).

Another example of an incestuous but incorrect statement is that found on page 3 where it is claimed that the mix ratios used in both sets of aggregates, as shown in Table 2, resulted in an aggregate particle size distribution that is commonly employed in the production of semi-dry masonry units. The reference given is once again their own group. Although a good block maker can make a masonry unit out of just about anything I have had considerable experience making blocks and would not use any of the mixes given.

Our previous comments in relation to the paper “Reactive Magnesium Oxide Cements: Properties and Applications” by L.J. Vandeperre, M. Liska & A. Al-Tabbaa about using standard consistence which according to BS EN 196-3 is a static test also apply in the case of this paper. Besides these comments are irrelevant as block formulations are supposed to be dry mixes! It should not therefore be possible to add too much water as has clearly been the case according to the table in relation to the MgO only mixes. Our contrary experience is that it is easier to make MgO containing blocks because of the plasticity they develop during intense vibration.

The fact that natural aggregates resulted in almost twice as much carbonation as Lytag aggregates (See the bottom of page 4) indicate there are factors at play that the Cambridge Imperial team did not take on board or probably understand. The Cambridge – Imperial authors blamed the strength of Lytag yet the particle distribution is quite different to that of the natural aggregates used. This is not a scientific conclusion but a most likely incorrect guess.

The statement at the top of page 5 that “It is evident that the influence of natural carbonation on strength and stiffness of magnesia-based pressed masonry units is very limited is a generalization irrelevant to properly formulated blocks based on misleading science.

Using forced carbonation is like applying fertilizer in agriculture, expensive and usually not as good as properly managed natural nutrition. (carbonation in the context of our discussion) The statement on page 7 that “They also show the much increased UCS and E_{50} following forced carbonation of the magnesia cement mixes (NA and LA), where values close to those of the PC mixes were achieved and in most cases were even higher.” And on page 9, column 2 that “In comparison with the UCS of the PC systems, it can be seen that the MgO cement systems can produce much higher UCS values, up to twice the PC system values, under forced carbonation at the appropriate saturation levels” gives me encouragement that when the team learn how to properly make block formulations that can naturally carbonate they will really achieve something.

I then may accept that some forced carbonation in for example flue gas or bag house air streams may actually increase production efficiencies but at this stage with most block makers it would represent considerably extra expense.

It is true that the reaction

MgO + water => $Mg(OH)_2 + CO_2$ => $MgCO_3.3H_2O$ Nesquehonite

11.20 + liquid => 24.30 + Gas = 74.79 Molar volumes (Assuming density MgO is 3.6, $Mg(OH)_2$ is 2.4 and $MgCO_3.3H_2O$ is 1.7 g/l)

===> Expansion of (74.59-11.2)/11.2 = 565.98 %

Results in a molar volume increase of around 307% from the hydroxide and 566% overall and densification does occur however it is no good guessing that densification is the only reason for strength gain as suggested on the top of column 2 on page 8 as the interlocking microstructure provided by nesquehonite is probably the main reason and TecEco have demonstrated that considerable strength can be achieved in more porous naturally carbonated mixes.

There are enough clues in this paper to confirm that alternating wet then dry conditions are what are necessary for proper natural carbonation but nowhere do the authors arrive at this important realisation[5]. The comment that wet then dry in one cycle worked well (Page 7 column 1) and that reducing the humidity from saturation improved carbonation (Page 8 column 2) should have got them there.

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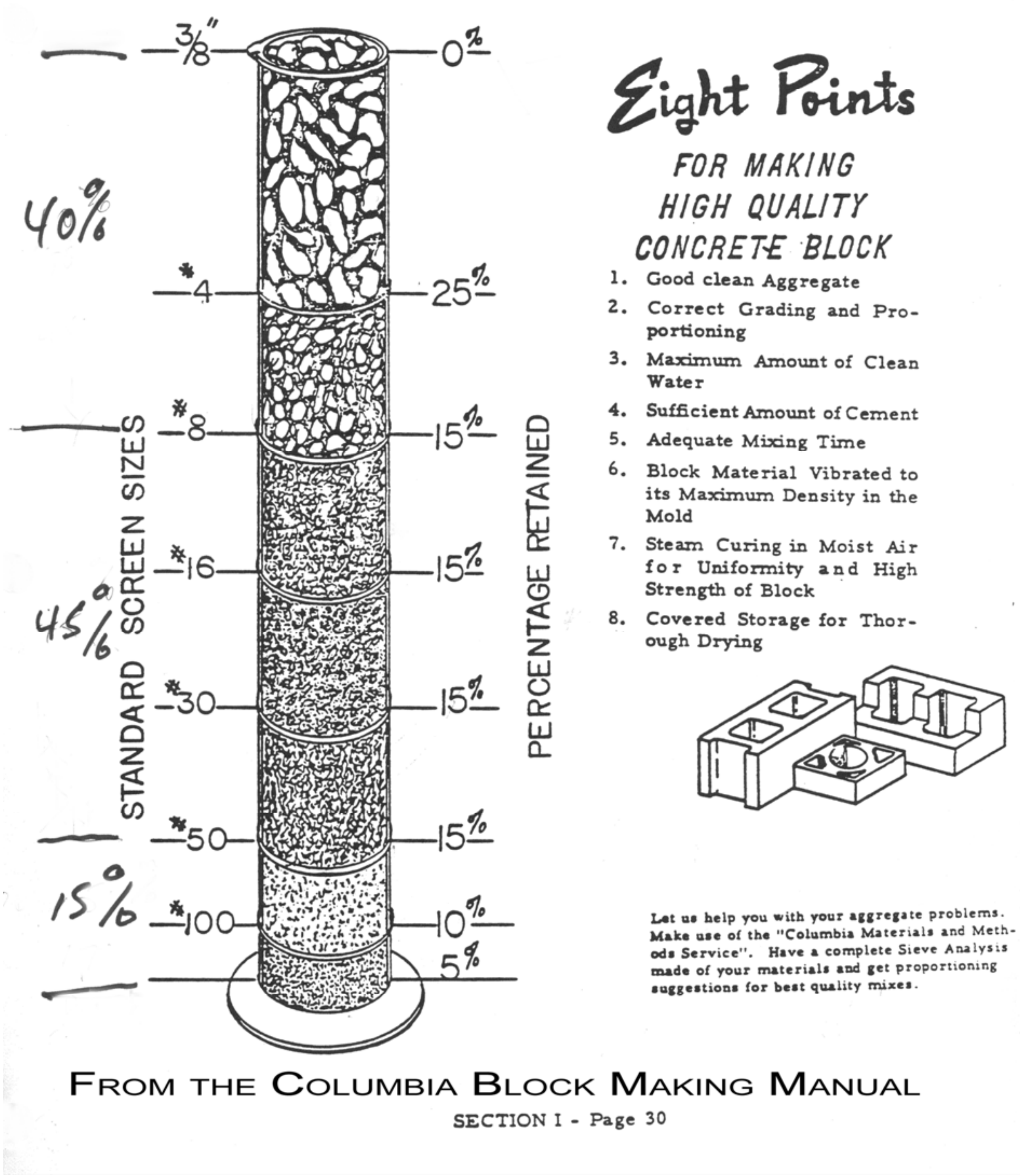
[5] Fortunately they do in other papers I have reviewed



Eight Points

FOR MAKING HIGH QUALITY CONCRETE BLOCK

1. Good clean Aggregate
2. Correct Grading and Proportioning
3. Maximum Amount of Clean Water
4. Sufficient Amount of Cement
5. Adequate Mixing Time
6. Block Material Vibrated to its Maximum Density in the Mold
7. Steam Curing in Moist Air for Uniformity and High Strength of Block
8. Covered Storage for Thorough Drying

Let us help you with your aggregate problems. Make use of the "Columbia Materials and Methods Service". Have a complete Sieve Analysis made of your materials and get proportioning suggestions for best quality mixes.

FROM THE COLUMBIA BLOCK MAKING MANUAL

SECTION I - Page 30

Figure 1 - Correct Mixes for Block Making from the Columbia Manual

Hydration and Mechanical Properties of Magnesia, Pulverised Fuel Ash and Portland Cement Blends

Vandeperre L.J. [#], Liska M.*, Al-Tabbaa A.* (Unknown where published. If as a reader you know – please advise us)

[#]*Imperial College London, *University of Cambridge*

My overall comment is that this is a much better paper. It is more objective and less inclined to jump to conclusions.

In the introduction to the paper it is claimed that our TecEco cements are “blends of a normal hydraulic cement, such as PC, reactive magnesium oxide, and often also a pozzolan such as pulverised fuel ash (pfa) or fly ash. The word often is correct and we are please the authors noted that we use it. They should have however been put on notice that pfa is not mandatory and there that there were circumstances in which it should be used and should not be used. In recent years we have used the term “optionally” in relation to pozzolans when referring to Eco-Cements and for some time have been suggesting they are counter productive in relation to carbonation. Even our patents are being issued using the wording “optionally”. Readers should note however that the restriction in relation to pfa is not a result of its chemical composition, only and outcome of the bad particle packing that results.

As for all the other papers from Cambridge and Imperial college insufficient notice of our formulation specifications has been taken and the mixes are therefore sub-optimal but at least more logically determined than in many of the other papers I have had to read.

On the top of page 7 I note the comment that the slight mass increase was probably due to the take up of water from the air. The researcher does not appear to have canvassed the fact that it is more likely as a result of carbonation that involves the take up of even more water as well as CO_2.

The peak at $2\theta = 11°$ is of interest and I query if it could be attributed to a magnesium form of a hydro garnet sometimes found in PC concretes. The comment on page 12 regarding packing densities is also interesting as other workers have remarked on a more open structure for similar formulations.

In relation to the fineness demand for water TecEco will, funds permitting, make more reactive MgO with a much coarser grind using its new kiln design. In the meantime the author of this paper correctly points out that this could be a characteristic of the mix type or alternatively could be a function of the addition water consumed by the fineness of magnesia.

This paper makes some useful contributions and so far is the best I have read. Plagiarism and incestuous cross referencing are however a problem. When reading this and other papers I am always conscious of my own words coming back to me. There is some unreferenced paraphrasing of our patent applications and other documents I have written and I would have preferred credit when it is due.

Mixtures of pulverised fuel ash, Portland cement and Magnesium oxide: characterisation of pastes and setting behaviour

Vandeperre L.J.[#], Liska M. *, Al-Tabbaa A.* Science and Technology Raw and Rest Materials in Building Products, WASCON 2006 Conference, Belgrade, Serbia & Montenegro, 30 May, 2 June 2006

[#]*Imperial College London, *University of Cambridge*

This paper is much fairer, better written and much more objective. The problem is that the formulations used are very badly scoped. The proportions used indicated by table 2 have either too much MgO for a Tec-Cement and far too much pfa for an Eco-Cement to carbonate properly.

The conclusion in the abstract that MgO and PC interact when mixed together by means of retardation of the setting time of the mix is not necessarily correct as there are many other intertwined factors. In other words it is not very scientific to arrive at such a conclusion given all the other variables. For example the fineness demand for water of magnesia is high should it be present but in most cases compensated for by the thixotropic nature of the mixes so working to standard consistency which is a static test that does not measure the result of the input of energy into the system is invalid and obviously leads to too much water being added and a number of other consequential outcomes. I note however that the authors state that reduction in water leads to more expansion and give an interactive mechanism for this.

The mechanism for the lubrication of mixes by highly kosmotropic magnesium ions is discussed at http://www.tececo.com/technical.rheological_shrinkage.php and I therefore make it clear that a workability test is the only one that is valid, particularly now we all know that the reactive magnesia currently being used has a high water demand. There are several different "rheometers" available and one should be consistently used in any given project. In relation to the fineness demand TecEco would be interested in supplying a magnesia calcined at the same low temperature but not ground as finely to see if that overcomes some of the fineness water demand issues. Work in Australia is underway to more properly grade magnesia.

The temperature data presented in this paper is useful and further supports the case for a coarser grind.

The calculated figure for the enthalpy of the reaction

$MgO + H_2O = Mg(OH)_2$

Is

$\Delta H^{o}_{r} = - 81.24 \text{ kJ.mol}^{-1}$

The molar mass of MgO is 40.31 gm so 81240 Joules per 40.3 gm equates to 2015 Joules per gram which is in broad agreement with the figure obtained in the paper by experiment.

The theory about the poisoning by silica ions is interesting and the results of the Le Chatelier test for expansion useful even thought the formulations would never be used in the proportions given.

Mixtures of pulverized fuel ash, Portland cement and Magnesium oxide : strength evolution and hydration products

Vandeperre L.J.[#], Liska M. *, Al-Tabbaa A.* Science and Technology Raw and Rest Materials in Building Products, WASCON 2006 Conference, Belgrade, Serbia & Montenegro, 30 May, 2 June 2006

[#]*Imperial College London, *University of Cambridge*

This paper is not badly written, explores theories without jumping to conclusions and if it analysed our cements instead of the totally inappropriate formulations listed below then it would have been a useful contribution.

Table 2 below shows the formulations examined and as can be seen they are all high pfa. Our formulation specification would dictate low MgO and high PC given the level of PFA. If the rationale was carbonation then our specification would have been high MgO and no fines like pfa. Nowhere in this any other the papers I have reviewed is the objective of immobilising toxic and hazardous wastes given so using Enviro-Cement type formulations is given the test undertaken is not good science or practice.

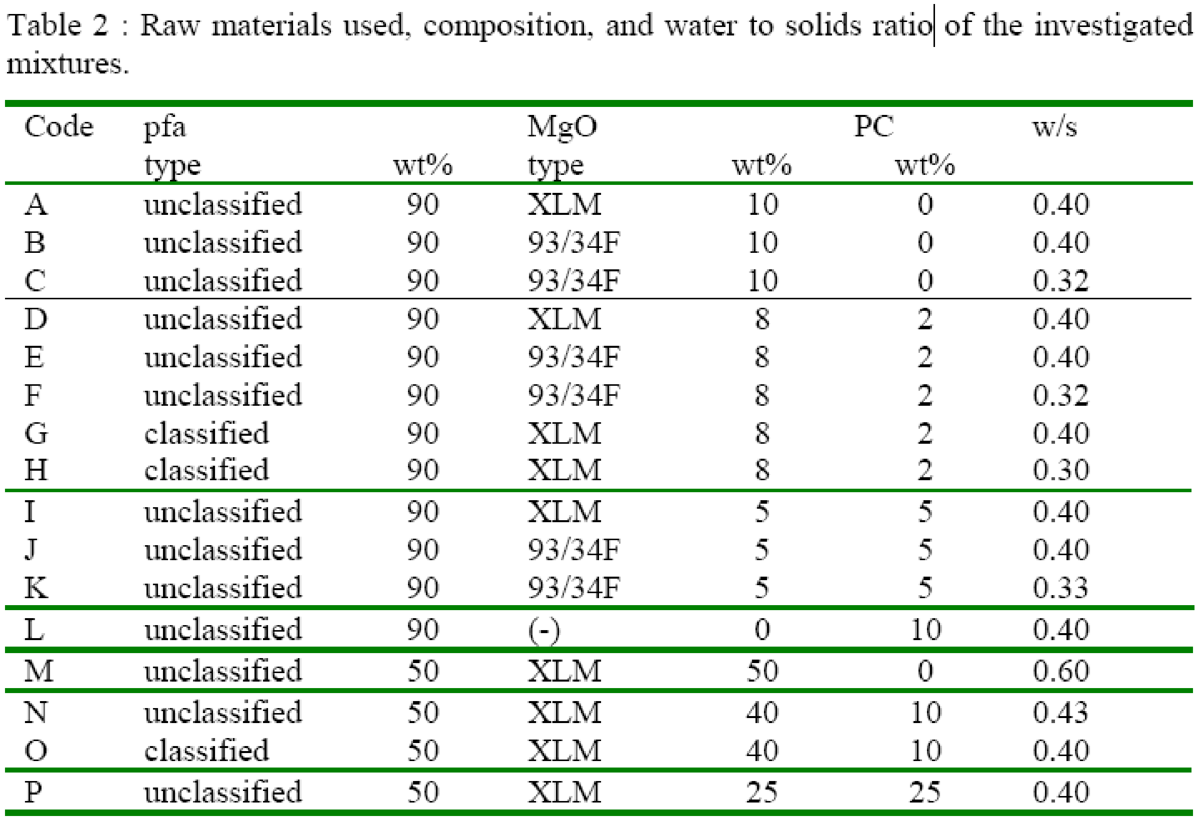


Table 2 : Raw materials used, composition, and water to solids ratio of the investigated mixtures.

Code	pfa		MgO		PC	w/s
	type	wt%	type	wt%	wt%	
A	unclassified	90	XLM	10	0	0.40
B	unclassified	90	93/34F	10	0	0.40
C	unclassified	90	93/34F	10	0	0.32
D	unclassified	90	XLM	8	2	0.40
E	unclassified	90	93/34F	8	2	0.40
F	unclassified	90	93/34F	8	2	0.32
G	classified	90	XLM	8	2	0.40
H	classified	90	XLM	8	2	0.30
I	unclassified	90	XLM	5	5	0.40
J	unclassified	90	93/34F	5	5	0.40
K	unclassified	90	93/34F	5	5	0.33
L	unclassified	90	(-)	0	10	0.40
M	unclassified	50	XLM	50	0	0.60
N	unclassified	50	XLM	40	10	0.43
O	classified	50	XLM	40	10	0.40
P	unclassified	50	XLM	25	25	0.40

Unfortunately Brucite is not a strong mineral and neither does it have shape that assists with the development of microstructure that adds strength[6]. The researchers need to understand that Brucite plays and entirely different role relating to pH control and durability in our cement system.

There is some discussion about using pfa because it is a waste but the team would have been far better off with a whole host of other wastes including material from tunnel digging, demolition etc. that were not fine. As before pfa is a fine material and should not be used if carbonation is required as it densifies the mix preventing the free passage of air.

It is possible to use pfa to make Eco-Cement Concrete and TecEco will disclose how this is done under confidentiality[7]

It is interesting that the 93/34F from CJC Chemicals, UK has produced a better result and we believe this is because the material packs better with PC and the pfa used.

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[6] See http://www.tececo.com/technical.importance_particle_packing.php

[7] Patents are pending

Microstructures of reactive magnesia cement blends

Vandeperre L.J. [#], Liska M.*, Al-Tabbaa A.* (Unknown where published. If as a reader you know – please advise us)

[#]*Imperial College London, *University of Cambridge*

This paper like all the rest would have been useful if it had examined our cements. As for the other papers reviewed the authors have incorrectly decided to mix high percentages of pfa with MgO and expected carbonation.

The point is that there is no value in mixing MgO with pfa and a small amount of PC for what you appear to be trying to achieve. Brucite is a relatively weak mineral with no microstructural advantages and does not react readily with pfa to form M-S-H. Your references are however useful. For information on how M-S-H is formed in a concrete rather than an artificial environment see (Glasser 1991).

About all I have been able to glean from this and the other papers is that XLM may be too fine although it should be possible to make a paste without excess water due to the kosmotropic affect of the Mg++ ion. I agree however a coarser grind is the way to go. It may also be that with slightly slower early hydration the formation of OH ions from the dissolution of Mg will not interfere so much with the claimed initial hydration of PC based on the theories in another paper from the same researchers.

The fact that PC and MgO hydrate rather independently was usefully confirmed in this and other papers by the same authors.

I also found the discussion on volume product per gram of constituent (under Discussion) interesting as I have a volume stoichiometry model and we are currently working on a complex particle packing program.

The authors of this paper have shown some simplistic understanding of particle packing and microstructure in this paper so why are they trying to glue pfa together with brucite? It just does not make sense. The role of brucite in our system is as a pH regulator, potential toxic and hazardous waste host and shrinkage reducer. Our binders are mainly nesquehonite and lansfordite and it is only in Eco-Cements that MgO performs this role. In Tec-Cements rheology, durability, ph regulation, shrinkage and self desiccation are mainly what are addressed.

The theory of agglomeration of MgO is very interesting and supports the case for a coarser grind. We would be concerned about reducing reactivity and our patent specifies grinds up to 120 micron which is much coarser. The theory requires further work. Note that what many do not understand is that reactivity is mostly related to lattice energy, not so much grind size.

If only the team had bothered to read a little more before embarking on research that is interesting, but no very useful. Their work is very wide of the target.

A comparison between two types of pfa in the performance of blends of MgO, PC and pfa

#Vandeperre, L.J., Liska, M.*, and Al-Tabbaa, A*. (2006). A comparison between two types of pfa in the performance of blends of MgO, PC and pfa, AshTech2006 conference, May, Coventry, UK, D.05, pp 1-17.

*#Imperial College London, *University of Cambridge*

This paper is an interesting study of very inappropriate mixes with a high pfa and MgO content as in all the other papers. The ratio of MgO to PC in the hydraulic binder was fixed to 4:1 and the water to solids ratio was fixed at 0.4, whereas the ratio of hydraulic binder to pfa was varied between 1:9 to 1:1. All formulations are again outside the scope of our specifications for Tec and Eco-Cements and not fit for the purpose of the tests scoped.

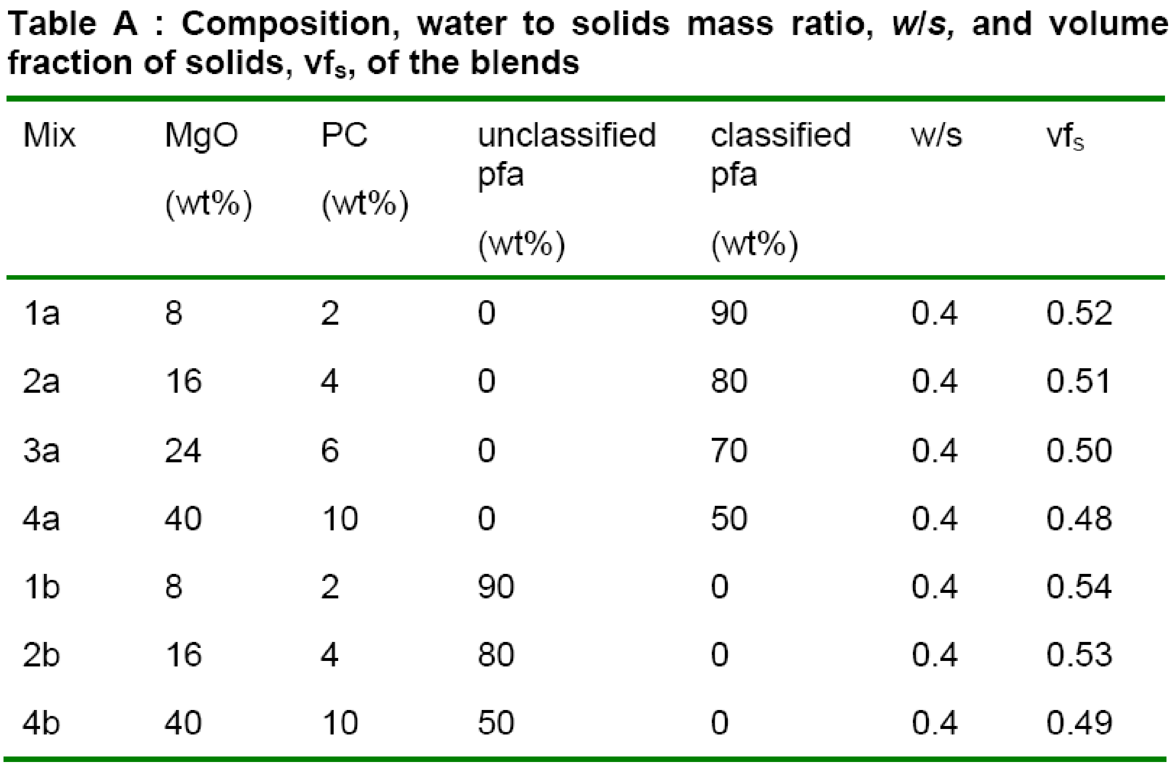

Table A : Composition, water to solids mass ratio, *w/s,* and volume fraction of solids, vf_s, of the blends

Mix	MgO (wt%)	PC (wt%)	unclassified pfa (wt%)	classified pfa (wt%)	w/s	vf_S
1a	8	2	0	90	0.4	0.52
2a	16	4	0	80	0.4	0.51
3a	24	6	0	70	0.4	0.50
4a	40	10	0	50	0.4	0.48
1b	8	2	90	0	0.4	0.54
2b	16	4	80	0	0.4	0.53
4b	40	10	50	0	0.4	0.49

The stated aim of the study “was to determine whether the processing of mixtures of MgO, PC and pfa and the resulting strength is affected by the type of pfa used.”
Although interesting the paper serves no purpose, the point being pfa should not have been used at all given the ratio of MgO to PC or at least using the methods of the authors[8].

Let me explain further

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[8] It is possible to make high fly ash Eco-Cements which was the objective of the Cambridge-Imperial college team however not using the methods described. De to patent matters we are unable to disclose how this is done except under confidentiality.

In the introduction the authors state "The rationale for including pfa in the composition of reactive MgO cements is to encourage any calcium hydroxide (Portlandite, $Ca(OH)_2$) formed during hydration of Portland cement to be converted in an hydrated calcium silicate gel (C-S-H)." Around 30% of clinker hydration products is Ca(OH)2. So why are the authors adding much more pfa than could possibly react with the lime that is formed given this rationale? The problem is not the chemical composition of pfa or the reactivity. The problem is the particle packing that results.

Given the further and following comment in the introduction (there are no page numbers) in relation to our concrete systems that "These are blends of a normal hydraulic cement, such as PC, and reactive magnesium oxide, which sometimes also include a pozzolan such as pulverised fuel ash (pfa)" and the reference is our patent application, the word "sometimes" should have put the team on notice that pfa is not mandatory. Even if members did not bother to read the technical information on the official web site for the cements (www.tececo.com) or any other paper by me this at least should have put them on notice that pfa and other pozzolan was optional. Unfortunately throughout this research project our input has been avoided. This has been a disaster as on the official web site for the cements (www.tececo.com) and in many papers we make it clear that Eco-Cements should not include too many fines. We have been saying this for a number of years and at least before the students involves started. Yet in every experiment undertaken by the Cambridge team so far too much pfa (which is fine) is used given the ratio of MgO to PC which is far to high. For high pfa the ratio of MgO to PC should be low. The authors know that pfa is fine. In this paper they say under the caption to figure 1 "pfa contains larger particles, it is still much finer than e.g. sand used as fine aggregates in concrete." Unfortunately they have not studied the conditions for carbonation generally or our mechanisms for strength gain in Eco-Cements. See for example papers 14 (2004), 19 (2005) and 25 (2005) on the TecEco web site (www.tececo.com).

The Cambridge team have realised that sometimes pfa is not suitable as they have read our original patent specification. Besides they note this in the introduction to this paper. We cannot understand why they are so serious about binding pfa together with brucite. The team should have realised by the time this and many of the other papers were written that doing so is a very sub-optimal use of reactive MgO in most circumstances[9]. As explained in many of our technical documents and papers for many years now the only way real strength achieved with the addition of MgO is through carbonation. We have also pointed out at length that MgO has a totally different role in dense concretes.

Given the irrelevance of this and other papers to our cement system I hardly feel like continuing but have read this rest of this paper just in case there was something useful to glean.

This paper does provide an interesting geometrical analysis assuming spheres which fortunately for the authors is a reasonable assumption for many fly ashes including the rather spherical looking ones used. In the real world of real concretes the spherical models are too simplistic and as mentioned we are developing software based on the maths of de Larrard and others. The basics of the mathematical models in the new software will be open source and the Cambridge team, if they can pass our moderation are welcome to

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[9] In another patent specification we are working on we will disclose how this also can be done satisfactorily.

contribute. Other people other than de Larrard we know of working on modelling include Karen Scrivener in France and the people at NIST in the USA.

This paper also plagiarise my work reiterating what I have said about reactive MgO viz a viz dead burned MgO (without reference) and a much more precise scientific discussion is on the TecEco web site.

As in other work standard consistence is used and this is just not relevant to highly thixotropic mixes.

Accelerated carbonation of reactive MgO cements

L. J. Vandeperre* and A. Al-Tabbaa†, (2007). Accelerated carbonation of reactive magnesia cements. ICE Journal of Advances in Cement Research, vol. 19, Issue 2 pages 67-69

**Imperial College, London; †University of Cambridge*

In this paper our cements are redefined for us as in many of the other papers as always containing a pozzolan viz in the introduction, “Reactive MgO cements are recently proposed mixtures of reactive magnesium oxide (MgO), a hydraulic cement, such as Portland cement (PC), and a pozzolan, such as pulverised fuel ash (pfa). We note that at least in one other paper “L.J. Vandeperre, M. Liska, A. Al-Tabbaa, Hydration and Mechanical Properties of Magnesia, Pulverised Fuel Ash and Portland Cement Blends the team got it right by using the word often in relation to pozzolans. Readers please note. Pozzolans are not mandatory. We did not even mention pozzolans until claim 5 in our original PCT application and they have never been mandatory.

In this paper The Cambridge - Imperial team seem determined to reinvent our cements in a form that is obviously very sub optimal from the poor results and totally out of our specification given the test involved and obvious objectives. If they are interested in Enviro-Cements then they are closer to spec but unfortunately all the findings they make they damagingly speak of as though they apply to more appropriate compositions formulated by us.

This like the other Cambridge papers is incestuous in that the authors constantly refer to their own findings in other papers they have written as though it is accepted fact. For example in this paper “reactive MgO powders have a high water demand and this leads to highly porous and weak products”

This comment in very concerning as it is totally unscientific. The statement may be true for the totally sub-optimal and off spec formulations used in all the work by the authors but as they are so sub-optimal and way off our widely publicized specification by us their findings cannot be properly extrapolated and generalized. There are also many other variables.

Besides, the authors should be aware that water demand is totally related to particle packing and the surface characteristics of powders, not so much to their chemical composition. The particular MgO used by the team was finely ground and the water demand is a result of this and not as the authors rather naively suggest to the fact that the powders are reactive MgO. TecEco have been selling coarser grades of magnesia for some time and in due coarse plan to calcine at lower temperatures but grind to a larger size.

I am pleased to see that the strong affinity MgO has to oxygen which is explained as affinity to water (of which oxygen is a major part) is noted. This helps explains why nesquehonite and lansfordite are formed rather than magnesite. Indeed this affinity for oxygen (not so much water) defines the chemistry.

In spite of the recognition on page one that “the rate of transport of CO_2 through water is orders of magnitude slower than transport via the gas phase” none of the formulations in this paper as shown in the table below or for that matter any of the work form this team provided a suitable matrix for gas transport. There is, as in all the other papers from the same authors an overwhelming amount of fly ash that swamps the matrix making it impermeable to CO_2. It is possible to include high proportions of fly ash but not by using the methods of the authors[10].

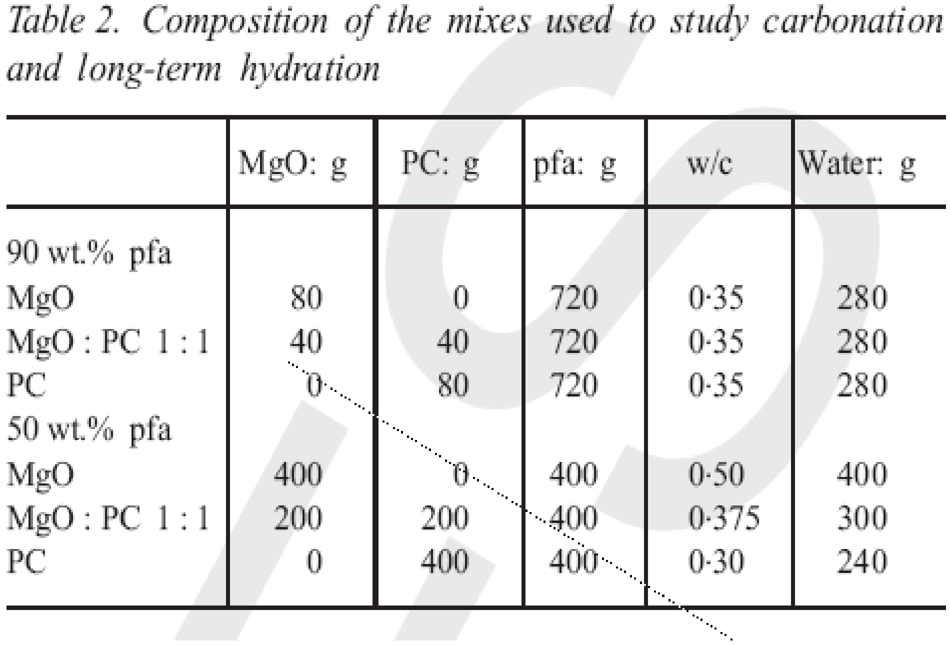

Table 2. Composition of the mixes used to study carbonation and long-term hydration

	MgO: g	PC: g	pfa: g	w/c	Water: g
90 wt.% pfa					
MgO	80	0	720	0·35	280
MgO : PC 1 : 1	40	40	720	0·35	280
PC	0	80	720	0·35	280
50 wt.% pfa					
MgO	400	0	400	0·50	400
MgO : PC 1 : 1	200	200	400	0·375	300
PC	0	400	400	0·30	240

The authors in this paper repeat what we have said for some years on our web site as though it were a momentous discovery. On page 3 “No evidence was found for the formation of new hydration products due to interaction between PC and MgO when both were present in the same blend.” I would have thought some understanding of chemistry including the preference of magnesium for oxygen would have got them there.

Contrary to the statements on page 3 nesquehonite forms readily in many conditions and higher temperatures than lansfordite which will revert to it. Even though the authors mention “the elongated needle-like habit of these crystals (form) was consistent with the expected morphology of nesquehonite” (page 4), in all the work from these authors the preferred model for strength is density not microstructure. For example in the conclusion “The properties improve because the solid volume increases substantially when brucite is converted into nesquehonite, and this additional solid reduces the initial high porosity in high MgO materials due to the high water demand of reactive MgO powders.” Obviously density is important but strength is more related to microstructure and the crystal structure of nesquehonite adds considerably to strength in this way. Unfortunately this obsession comes from reading to much and accepting without thinking.

The discussion relating to pH equilibria is interesting and it is a pity more detail is not given. Fortunately it is referenced.

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[10] TecEco will only disclose this to large players under confidentiality due to pressing patent matters.

I had always thought of toughness as the ability to withstand a shock loading, i.e. to have a meaning the opposite of brittleness which carries the implication of sudden failure. A brittle material has little resistance to failure once the elastic limit has been reached. As a major conclusions of the authors is that “Accelerated carbonation of reactive MgO cements with high MgO contents has been found to increase toughness and stiffness so that compositions high in MgO can achieve similar properties to those achieved when using Portland cement.” it would have been helpful if they had provided more information as to what is meant by the word toughness. Portland cement concretes are hard but brittle. The word tough should be used carefully.

I note the words in the conclusion “the carbonation of brucite requires a sufficient supply of water and CO_2 so that full carbonation is more easily and more rapidly achieved in highly porous materials.” Eureka! Does this mean the team have woken up at last? Does this footnote like yet profound statement retract much of the nonsense in the paper and in others from the same team? Have the team finally realized the proper basis for formulating carbonating mixes?

It would be exciting if this is the case as there is much misinformation they have created to be corrected.

References

de Larrard, F. (1999). Concrete Mixture Proportioning: A Scientific Approach, E & FN Spon.

de Larrard, F. and T. Sedran (2002). "Mixture-proportioning of high-performance concrete." Cement and Concrete Research **32**(11): 1699.

Glasser, F. P. (1991). Chemical mineralogical and microstructural changes occurring in hydrated slag-cement blends. Materials Science of Concrete II. J. Skalny and S. Mindess, The American Ceramic Society**:** 41-82.

Harrison, J. (2005). Carbonating and Hydraulic Mortars - the difference is not only in the binder. Aggregates are also important. Concrete 05, Melbourne, Concrete Institute of Australia.