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# Comments on Research Papers and Progress

A large number of research project have been initiated around the world and we are concerned that as at the date this document was posted on the web they have all been totally off course. As many of the errors could have been avoided merely by consulting the TecEco web site[1] or us we will not supply magnesia or sign off on future research grant applications without a written assurance that there will be genuine collaboration and consultation

There have been serious failures by a number of researchers including an inability to understand our basic formulations types and the differing requirements they have particularly in relation to the proportion of reactive magnesia added and particle packing.

Many researchers not working directly with TecEco are about where the company was in 1999 before we lodged our patents and much has changed since then. The scoping of the BRE, UTS and Cambridge - Imperial experimental work all has little focus given what we now know about the cements and the mistakes that were made in the beginning by the BRE are slavishly been followed.

The problem started with totally incorrect statements by Ellis Gartner from Lafarge in his paper “Scientific and Societal Issues Involved in Developing Sustainable Cements“ presented at the 2003 Dundee “Role of Cement Science in Sustainable Development” Conference (Gartner 2003). These Comments are dealt with on page 3 below under the heading Ellis Gartner’s Comments.

Gartner’s comments were followed by a study by Keith Quillin and Richard Nixon of the BRE dealt with in summary form below under the heading The BRE Report (Quillin and Nixon 2006) on page 4 and a paper that even used John Harrison, our managing directors name without authority from the University of Technology in Sydney (See Abhi Ray UTS on page 4).

We hoped that Cambridge University under Dr Al Tabbaa would put the record straight and in one or two respects they did but generally their work and in particular the incorrect conclusions about our cements that they arrived at were a disaster. Where Dr Tabbaa and her students went wrong is summarised below under the heading Cambridge University and Imperial College London on page 10 and in a separate document[2].

TecEco recognised the fundamental failure of researchers to understand proper formulation of our magnesium cements some years ago when the BRE published the

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[1] www.tececo.com

[2] See http://localhost/TecEco/document.technical.php

results of their work. The lack of understanding is most pronounced in the area of carbonation and in an attempt to overcome the pervading ignorance about the subject:

- An associated company of TecEco is writing software that will predict properties including porosity and thus permeability based on particle packing.

  TecEco and an associated company TecSoft[3] are developing software that will properly pack particles based on the maths of Francois de Larrard (de Larrard 1999), some of the NIST work[4] and our own ideas.

  Using this software it will be possible to graphically demonstrate the importance of particle packing in relation to many fundamental properties of concretes and it is an early target to predict porosity and from that property determine percolation thresholds for permeability.

- TecEco have prepared a web page summarising the basics of particle packing, porosity and permeability[5] and we also refer readers to the NIST web site[4].

- A summary of carbonation and errors being made by researchers in relation to carbonation follows under the heading Carbonation Issues follows on page 12

Some of the papers, reports and summaries have been so seriously in error that we have prepared separate documents with comments on what the researchers involved have written.

The failure of the research so far has caused John Harrison our MD considerable stress. TecEco ask what is it about researchers that preclude them from learning from those who precede them? We have never refused to help anybody who has had the courtesy to ask for assistance and do not enjoy taking the role of the devils advocate in relation to their work. We had hoped to mostly learn from the research done by others. This has not been so to the extent we would have liked and our role has reversed and we have been forced to teach and rebut work by others due to the obvious errors.

The debacle we have found ourselves in has made TecEco more vigilant and to keep researchers on the ball we will make comment on their work without fear or favour. If we think they have gone wrong we will point out why. If they can convince us that we are wrong we will thank them. We will give credit where it is due and admonishment when it is not. Such praise, criticisms and comments are part of what we hope will be a much freer exchange of ideas. Because this has not occurred in the past we have to criticise the work of others and it is important to note that this does not necessarily reflect on their ability, integrity or good intent.

On the positive side there are several useful findings that have come out of the work to date and on occasions we have read statements that give us some encouragement. We are concerned however that on the whole many opportunities to move the state of the art in relation to magnesium cements forward have been squandered. The work so far has

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[3] www.tecsoft.com.au
[4] http://ciks.cbt.nist.gov/garbocz/
[5] http://www.tececo.com/technical.importance_particle_packing.php

been so bad that we are concerned that there may be another agenda as many of the mistakes that have been made should have been obvious.[2] [6]

TecEco cements can work for the environment but some in the industry may feel threatened and have made what we believe are very unfair and misleading statements which unfortunately are getting about the same PC industry we would prefer to make friends with. We ask why are all the researchers testing for strength and little else? Why were they deliberately using aggregates that obviously would result in impermeable mixes? For carbonation to ensue there obviously must be sufficient permeability ofr gas transport.

Fortunately most people recognise our contribution for what it is and evidence of this are the 250 thousand people who go to our web site every month and the many emails we receive that we cannot possibly answer encouraging us to continue.

## Ellis Gartner's Comments

Ellis Gartner is or was the principal Scientist at the Lafarge Central Research Laboratory in France. In 2003 he spoke before John Harrison at a conference in Dundee Scotland and John Harrison was forced to get up and correct him.

According to Gartner in his paper "Scientific and Societal Issues Involved in Developing Sustainable Cements" (Gartner 2003) "A third possibility for the activation of pozzolans is by reaction with magnesium hydroxide (or oxide) following the same type of chemistry as given in Eq. (3) but substituting Mg for Ca[7].

It has been claimed recently that such chemistry is feasible for the manufacture of concrete products(Pearce 2002). However, it seems unlikely to be of widespread value as a low-$CO_2$ cementing system due to:

(a) the very low solubility of magnesium hydroxide, which will render its reaction with pozzolans very slow;

(b) the very high RMC ("raw materials" $CO_2$) and FDC ("fuel derived" $CO_2$) values associated with the manufacture of MgO from magnesite, and

(c) the relative global scarcity of good magnesite deposits."

Point (a) is interesting as first of all Pearce made no reference to a pozzolanic reaction with magnesium. Although MSH does form, particularly in high Mg slag cement concretes (Glasser 1991) we have stressed and again note here that the reaction is unimportant[7].

Gartner has a point at (b) but on deeper analysis the LCA data for the calcination of magnesium carbonates is not so bad as fuel derived emissions are about the same as for PC depending on the efficiencies assumed for what is a lower temperature process. Although the chemical release from the calcination of magnesium carbonate to produce magnesia is more, so also is the chemical recapture on carbonation. In the context of Gaia

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[6] http://localhost/TecEco/files/newsletters/Newsletter78.htm

[7] In equation (3) Garnet describes the pozzolanic reaction – which we have never claimed occurs and we do not believe important

Engineering, our proposed process, there will of course be no releases and the technology comes into its own with massive sequestration.

Mention of Gaia Engineering takes us to Gartner's point (c) above. Magnesium is the 8th most abundant element on the crust and in the context of Gaia Engineering will be extracted from seawater, bitterns or brines and there is and will be no shortage.

Gartner then went on to say "Claims that MgO-based cements carbonate more rapidly than Portland cements have yet to be verified publicly, but both lime-based and magnesia-based hydrates will fully carbonate in air (equivalent to the reversing reaction (1) if exposed for a long enough time, giving calcium or magnesium carbonate plus silica and alumina gels, and absorbing all of the RMC emitted during their manufacture. The main limitation of this reaction is that it is diffusion-controlled, so that, in large concrete pours, it may take many thousands or even millions of years."

TecEco see no point whatsoever in carbonating silicates as they are strong minerals and can in the right matrices be reasonably durable. Carbonation of lime and in the case of Eco-Cements, brucite formed by the hydration of magnesia is beneficial however and depending on the permeability can occur in very short periods of time – not the many thousands or even millions of years mentioned by Gartner

## Abhi Ray UTS

Abhi Ray from the University of Technology Sydney (UTS) published a paper (Lawry, Ray et al.) bearing John Harrison's name as an author titled "Thermal Characterization of Portland Cement-Magnesia Blends".

John Harrison's permission was not sought for the use of his name and he should at least have had the opportunity to go through the procedures and results with Prof Ray or his students prior to publication however this opportunity was not afforded to him.

Although there are some useful contribution such as the SEM work and the hydration analysis which was interesting, there were however serious problems as follows:

1) Reactive magnesia is magnesia with low lattice energy and TecEco advocate much lower temperatures than suggested in the paper. We have written at length about the requirements for the manufacture of reactive magnesia for use in our cements. See "The Importance of Temperature for the Manufacture of Reactive Magnesia" under technical web pages on the TecEco web site[8].

2) The aggregate used (Type 200G ground silica supplied by Unimin Australia) has a specific surface area of 360 $m^2\ kg^{-1}$ which is very similar to the Portland cement used at 350 $m^2\ kg^{-1}$[9].

   Figure 1 below shows the particle distribution for 200G ground silica and as can be seen the "aggregate" is actually a silicious filler/reactant of the same size range as Portland cement. The only difference appears to be that the distribution is perhaps

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[8] http://www.tececo.com.au/technical.reactive_magnesia.php

[9] The specific surface area of ordinary Portland cement typically ranges between 280 and 350 $m^2\ kg^{-1}$ Odler, I. (2000). Special Inorganic Cements, E & F N Spon, Taylor and Francis.

wider.

There are several serious detrimental consequences which Prof Ray should have realised:

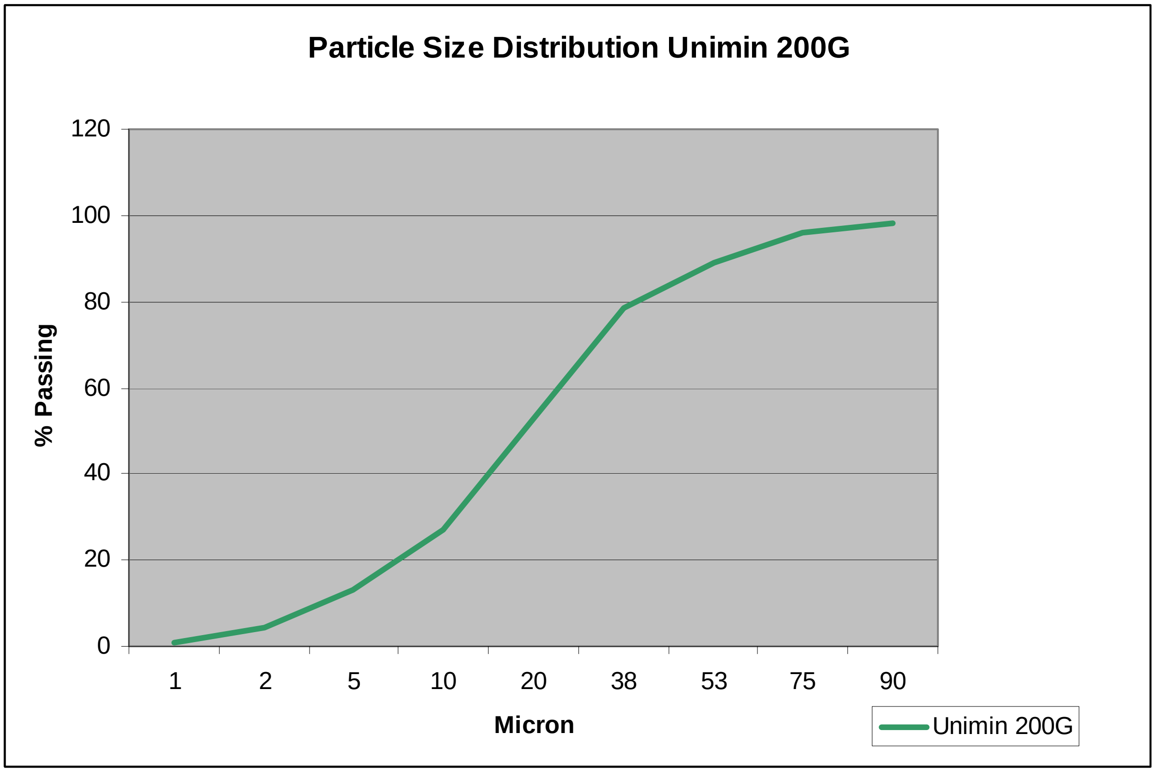

**Figure 1 - Particle Distribution of 200G Ground Silica.**

a) The particle packing will lead to significant voids in the microstructure as there is only one grain size range. The optimum ratio between grain sizes is a ratio of in the order of 2.5 to 3 to 1 (F. de Larrard, 1999, Concrete Mixture Proportioning, Modern Concrete Technology).

b) As a result of the high voids as in (a) above there is a very high water requirement leading to extremely high water cement ratio of almost three times normal. In the examples 1.5 whereas ASTM C105 for example suggests a water/cement ratio of 0.46.

c) The competition between similar size grain sizes will result in the cement matrix not being able to develop around the aggregate leading to an absence of significant strength giving structure.

This “aggregate” appears to be material left over from Prof Ray’s testing of fibre board cements and is totally inappropriate for the purpose of TecEco’s formulations in the proportions used. The result was that the mixes are far from the characteristic optimal that would have obtained with a well designed mix.

Because water and strength are so strongly correlated [10] the strength and the porosity of the samples have little in common with what is normal or optimal.

The rate of hydration of MgO is interesting, but probably very different to a more normal mix containing at least 3 times less water.

The remark in the conclusions that "The experimental results using a combination of analytical methods suggested that MgO did not behave as a pozzolan when used alone as a supplementary material in cement mortar production" makes me wonder whether these authors knew what they were talking about at all! MgO could not possibly be characterised as a pozzolan. Silicification reactions do occur as we noted in our patent. But they are very slow.

The paper is wrong for the reasons given above and many others and will have a damaging effect on TecEco and on Mr Harrison's good name.

## The BRE Report (Quillin and Nixon 2006)

The BRE report we refer to was penned by Keith Quillin and Richard Nixon of the BRE and we have been told that a representative of Lafarge, the same Ellis Gartner mentioned above, was very negative at meetings guiding its progress. Considering this same manufacturer funds significant BRE research we are concerned that the report on our technology may have been deliberately misguided.

We are yet to make detailed comments on the final BRE report but make it clear that in our view the main findings are totally misleading. For example statements like "On the basis of the same slump or the same water TecEco Tec-Cement concretes are weaker than PC concretes" or "a simple understanding of the thermodynamics would confirm that lime carbonates more rapidly than Brucite" standing on their own may be technically correct but they are also totally misleading in context and a deeper understanding is required. A detailed report will be posted soon without fear or favour and summary comments follow

### Strength Issues

Testing in relation to the main benefits of adding MgO such as durability and shrinkage in low MgO mixes was deliberately avoided. There was an obsession with strength testing pursuant to BS EN 196-1: 2005 and we note that this standard requires the use of CEN standard sands.

Higher strength for low magnesia additions, given the water demand of the MgO used was not expected although we note did occur in at least one sample although why this occurred was not investigated.

In low magnesia mixes or Tec-Cement concretes as we call them the main reason TecEco add magnesia which hydrates to Brucite is for durability and to reduce shrinkage which it does very well. Brucite, unless highly compressed, is weaker than CSH found in PC concretes. On the basis of slump or equivalent water added Tec-cement concretes may also be weaker. Strong Tec-Cement concretes with less shrinkage and cracking can

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[10] Abrams law linearly relates the logarithm of strength to the water to cement ratio.

however be made by adding magnesia in small quantities (5-10%) if advantage is taken of the strongly thixotropic plastic properties it introduces to concrete. The use of small quantities of magnesia also makes it easier to use fly ash.

Subsequent to the BRE work we are trying to pay more attention to particle packing using a blend of magnesia that is both finer and coarser and calcined at a lower temperature and thus more reactive. The objective of this more recent research is to improve packing with PC and thus reduce the "fineness" water demand. In this manner and taking advantage of the additional plasticity provided by the Mg++ ion in solution we are achieving better results particularly with added pozzolan. We are however limited to commercial supply chains not having the funds to build our own kiln.

These days most concrete is pumped and therefore "worked" and we have noticed that Tec-Cement concretes under these conditions perform very well. We have made detailed reference to the rheology of our mixes[11] for a number of years and this message should be understood by now. We note however there is still much research required in relation to the use of plasticising and other additives.

The rheology delivered by magnesia should not be all that hard to understand as the properties contributed are not significantly different to those provided by calcium in a PC-lime mortar in which plasticity is induced by the Ca++ ion from the lime as it dissolves. The Mg++ ion not only introduces plasticity but a stronger thixotropic property to mortars and concretes than lime because of its smaller size and consequently high charge density. To use MgO correctly this must be understood and taken advantage of.

## Carbonation Issues

For high MgO mixes carbonation was not achieved and as a consequence lower strengths were found than should have developed with more appropriate particle packing.

The CEN standard sands used are designed for minimum cement in hydraulic mixes and totally unsuited for carbonation as a glance at Figure 2 on page 8 should have indicated to the BRE. As a consequence the comments on strength in relation to high magnesia mixes are totally irrelevant as carbonation could not and did not ensue properly as the BRE indicator testing with phenolphthalein confirmed.

We explain in our web page on the importance of particle packing[12] that for proper carbonation a somewhat mono graded dominant particle size and a gap grading of fines is required.

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[11] See Technical/Web Pages/ Rheological and Shrinkage Reduction Affects of Adding Reactive Magnesia to Concretes at http://www.tececo.com/technical.rheological_shrinkage.php

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

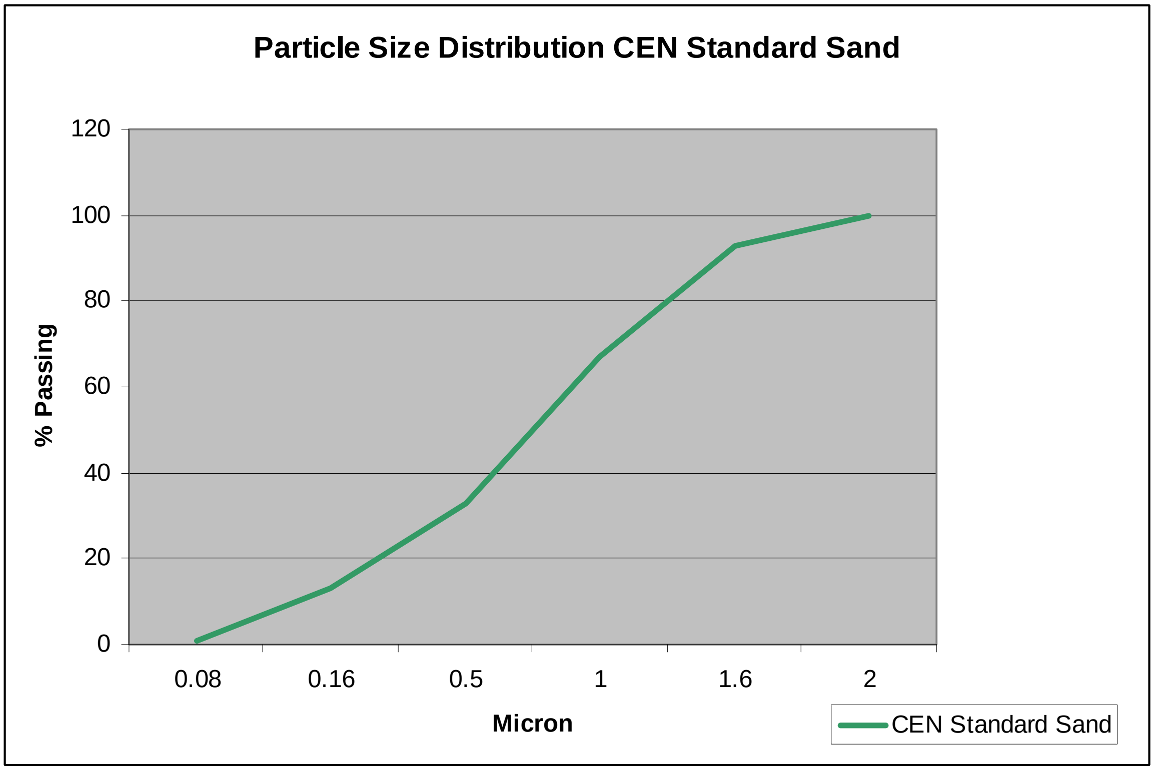

**Figure 2 - % Retained Each Sieve CEN Standard Sand for Strength Determination in Accordance with EN 196-1:2005.**

CEN standard sands are totally unsuitable for high MgO mixes as they are designed for minimum porosity certainly well below the threshold of percolation and thus result in impermeable concretes that cannot possibly carbonate. More information on the requirements for carbonation and errors researchers have made follows under the heading Carbonation Issues on page 7 and is to be found on the TecEco web site[13].

The BRE also claim that magnesium hydroxide does not carbonate as well as calcium and requires moisture. Both these assertions are true but it does not follow that PC or Portlandite (lime) are more appropriate for deliberate carbonation than Brucite.

Nobody except a cement chemist who is totally biased would consider for more than a passing moment leaving calcium hydroxide as a component in a mineral binder system except for carbonation reasons. Neither should anybody in their right mind be seriously suggesting making a strong calcium silicate hydrate just to carbonate it as the BRE seem to think is appropriate. With magnesium hydroxide both durability and carbonation can be enjoyed whilst the strength property of calcium silicate hydrate can remain as we have clearly demonstrated.

## The BRE Figure 3

The BRE generated a figure 3 in their final report showing PC magnesia mixes to be inferior on carbonation which is nonsense for several reasons and demonstrates their lack of understanding of the kinetics of carbonation.

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

On the first of August 2006 we published a correction in which we stated “The main problem with the BRE spreadsheet … is that it assumes that all PC carbonates.

This is not a valid assumption. Although calcium silicate hydrate (CSH) does carbonate it does so very slowly depending on permeability. The literature also suggests that there are limits to the loss of calcium by CSH and not all carbonates. On the other hand the CH (Portlandite or $Ca(OH)_2$) component of PC carbonates readily and in materials permeable to air (and water in the case of drier concretes) within 50 years as does MH (Brucite or $Mg(OH)_2$).”

This was only one of the problems with their spreadsheet. Whilst writing this summary another has come to our attention which is far more serious.

Imagine two substrates: A dense Portland cement pre-mix concrete and a permeable Eco-Cement Concrete matrix. It is nonsense to assume the same rate model for carbonation applies to both which is exactly what the BRE have done.

In a permeable concrete as is supposed to the case with Eco-Cement Concretes the rate is much faster because the surface area presented for carbonation is much greater. In these circumstances a different rate model must be used for MgO and probably also for calcium hydroxide (CH).

As we have done insufficient work to determine the validity of a new rate model for MgO and we doubt if one that has been rigorously established exists for properly formulated non hydraulic lime mortars we will publish a new diagram 3 with an estimated rate model in due course. In the meantime we have removed our previously “corrected” model because it was invalid to use the BRE rate model for Eco-Cement concretes represented by the 2 MgO : 1 PC mix in it.

The new graph when available will be under tools[14] on the TecEco web site. The TecEco kiln produces MgO without release of $CO_2$ to the atmosphere and the user will have the choice of whether it is used or not in the spreadsheet.

## Summary

John Harrison, TecEco’s principal scientist and managing director has in the past made mistakes in assumptions and predictions and in the interests of good science freely admits this. After all this is how new sciences evolve. It is unfair however to refer to something we may have said some years ago and no longer ourselves support as the British Research Establishment (BRE) consistently did in their 2006 report. We also think it unfair to compare two different materials with the same tests without understanding the properties, advantages and disadvantages of the materials being tested as was the case with the BRE who relied on strength testing without considering the advantages of concretes containing magnesia such as durability, better rheology for finishing and reduced cracking as is the case with Eco-Cement Concretes.

The BRE report, like most other research to date appears to have deliberately overlooked the positive aspects of adding small quantities of reactive magnesia to cements for making

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[14] http://www.tececo.com/downloads.tools.php

pre-mix type concretes. The report is very one sided and shows a lack of appreciation of how the system we are developing works in spite of all our attempts to enlighten the authors involved. Some excellent results were achieved but ignored and we wonder why this is so as bad science will not in the long run stand up in spite of a pecuniary disadvantage perceived to be attached to better science.

The worst about the BRE report is that they demonstrated their total lack of understanding of porosity and its relationship with and gas permeability which is very important in Eco-Cement concretes for carbonation and we suggest they study the work of Garboczi Bentz and Hampton (Garboczi 1990) (Garboczi and Bentz 1996) (Garboczi and Bentz 1999) (Bentz 2006) (Bentz, Coveney et al.) (Bentz, Garboczi et al. 1999) (Hampton D. 1993) to cite a few and the NIST web site[15]

Unfortunately much public money could have been better spent. The opinions of the BRE reflect their funding sources and in the interests of a fairer assessment of our work we will soon be publishing a much more detailed and critical analysis of their draft final report.

## Cambridge University and Imperial College London

After the initial overtures to us to obtain our signature on funding applications we were rarely consulted by a team at Cambridge University headed by Dr Al Tabaa working in collaboration with Dr Chris Cheeseman and other researchers at Imperial College London.

Formulation guidance for our cements has been on our web site for a number of years and our advice was never sought yet these researchers had the gall to intimate in several of the papers that ensued that there is a lack of information. For example in the paper L. J. Vandeperre, M. Liska, A. Al-Tabbaa “A comparison between two types of pfa in the performance of blends of MgO, PC and pfa” they said in the second paragraph that “little technical data is available which makes it difficult to define relevant areas of application.”

TecEco take exception to this because it is utter nonsense. On more than one occasion our Managing Director personally approached Dr Tabbaa and was fobbed off. Apart from initial meetings where our Managing Director explained the basics at no stage did she or any member of her team make any attempt to seek our guidance yet all they needed to know to prevent them making the serious mistakes they have made is on the TecEco web site. Although their formulations are within the specification of our patents they obviously did not study the technical information we have freely provided on our web site because they are totally inappropriate.

The team displayed a total lack of understanding of the science behind our formulation types and as a consequence the concretes examined are not fit for the purposes for which they were examined such as strength or degree of carbonation. The formulations are nothing like what is recommended except for a few in one paper. The inferences and parallels drawn are irrelevant yet damaging and we are forced to totally rebut them. We have little choice but to point out where the team went wrong in detail. As we are very busy we would have preferred to allocate time to more positive activities. A detailed report is available in relation to all the papers published by the Cambridge – Imperial team from the R & D section of the TecEco web site[16]. More general comments follow.

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[15] http://ciks.cbt.nist.gov/garbocz/

[16] http://www.tececo.com/technical.php

It is possible to train somebody to look into a telescope or microscope and describe what they see. Good scientists however have a cognitive ability to determine what to look for and why. The point is that the Cambridge team have pointed their microscopes in entirely the wrong direction and not properly understood or researched our cements which for many years now have been described by us in detail in words similar to what follow:

## "Tec-Cements (5-20% MgO substitution)

Tec-Cements contain more Portland cement than reactive magnesia. As noted, reactive magnesia hydrates in the same rate order as Portland cement forming Brucite and Brucite hydrates which use up water reducing the voids: paste ratio. Durability is improved particularly if pozzolans are also added and there is a marked decrease in shrinkage and cracking. Suitable pozzolans include fly ash and ground granulated iron blast furnace slag as well as a large range of other material such as quarry wastes.

## Eco-Cement and Enviro-Cement concretes (20-95% MgO substitution)

Higher proportions of magnesia are used in Eco-Cements and Enviro-Cements. The difference between Eco-Cement and Enviro-Cement concretes is that Eco-Cement concretes carbonate in permeable concretes such as masonry blocks and tend not to have too much pozzolan added and depending on the formulation objectives, usually none at all as pozzolans reduce porosity and permeability and will slow down carbonation. Pozzolans also react with lime in the pozzolanic reaction preventing its carbonation.

Enviro-Cement concretes are not very porous or permeable[17] and do not contain other than surface carbonates and the use of pozzolans is optional but encouraged to reduce free lime. Enviro-Cements contain similar percentages of MgO to Eco-Cements, but in non-permeable concretes, Brucite does not carbonate readily. Higher proportions of magnesia are more suited to toxic and hazardous waste immobilisation and when durability is required mainly because of the lower pH regime."

No doubt the Cambridge – Imperial team did not know it but most of their mix designs fall into the category of badly designed Enviro-Cement concretes. Their comments in all of the papers we have reviewed regarding the ability of magnesia concretes generally to carbonate, or about strength and many other properties are totally misleading and irrelevant as Enviro-cements are not designed for strength and cannot carbonate due to their density (and thus lack of permeability). They are potentially more suitable along with Tec-Cements for toxic and hazardous waste immobilisation which is what we thought the Cambridge – Imperial team were working on given their claimed area of knowledge and from comments Dr Al Tabbaa had made to John Harrison our managing Director.

If the team were working with toxic and hazardous waste immobilisation in mind why did they not say that the formulations they were using were not designed for strength or carbonation and undertake more relevant tests that would have indicated their suitability

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[17] Permeability is related to porosity See The Importance of Particle Packing at http://www.tececo.com/technical.importance_particle_packing.php

for the purpose of toxic and hazardous waste immobilisation. From the work we have read we doubt if any of the team knew or understood the difference!

Whilst in the UK John Harrison our managing director provided both the BRE and the Cambridge – Imperial team with samples of Eco-Cement blocks made in Australia and that should have put both on notice that not only are calcium-magnesium cements that carbonate easy to make but that they can set by carbonation in natural conditions – outside, in the weather.

Apart from his initial visits to the UK John Harrison our MD has on several occasions attempted to communicate with Dr Al Tabbaa and her students about the work they have been doing and have been told little. This included a further visit and several phone calls in which little was divulged and nothing asked. More recently Mr Harrison had to press the team for copies of papers and although they were eventually provided this took a long time. Basically TecEco have been "kept in the dark" until the requirement for a report from "participants" named as collaborators in the original funding application came about. Although this requirement is now no longer relevant, now we have read the published work we have little choice but to strongly and publicly rebut them for the sake of Mr Harrison's reputation as a scientist and that of TecEco.

In all the Cambridge - Imperial work not only are the proportions in ranges totally unsuitable for Eco-Cements or Tec-Cements and badly designed for Enviro-Cements but they slavishly use pfa because it is as they state "a waste" and they want to use it with no understanding of what they are trying to achieve or the steps required to do so. The team try and carbonate mixes that cannot possibly carbonate. Pfa is only useful in the context of the pozzolanic reaction which Dr Tabbaa's students comment in at least one paper and not important insofar as magnesia is concerned[18]. That pfa is of no value in a carbonating formulation we would have thought obvious however pfa turns up in all the formulations including all those in which the stated as well as obvious objective of the experimental work is to achieve carbonation.

With Tec-Cement concrete formulations the opposite of what we say above applies - it is useful to use pozzolans in them. We note however that low magnesia formulations, in spite of their sustainability through durability, and thus potential use for toxic and hazardous waste immobilisation, appear not to have been canvassed by any of the papers except by the paper "Mixtures of pulverized fuel ash, Portland cement and Magnesium oxide : strength evolution and hydration products" by L.J. Vandeperre, M. Liska, A. Al-Tabbaa, where the rationale for the inclusion of pozzolans was cited thus: "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 to hydrated calcium silicate gel (C-S-H), which is expected to increase the resistance to chemical attack of the cement" It is a pity this profound statement is not acted on generally and pfa added only for this purpose!

More detailed comments on the papers published by the Cambridge – Imperial college group of researchers are to be found on the TecEco web site under Third Party Research[19]

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[18] Magnesia is not readily a reactant in either the pozzolanic or geopolymeric reactions.

[19] http://localhost/TecEco/rdandd.thirdparty.php

Because the formulations used were so different to what is recommended the Cambridge – Imperial team were totally unjustified in making general statements about the strength, ability to carbonate or otherwise of our cements.

## The Requirements for Carbonation

As all researchers so far have failed to understand the requirements for gas permeability and carbonation we discuss the subject briefly here and ask readers to go to the TecEco web site and read the web page the importance of particle packing under our technical section[20].

The use of fines in a matrix that must be permeable enough to allow the passage of air for proper carbonation is not recommended by us and warnings about the need for porosity => permeability for proper carbonation have been on the web site for some years. The use of sands designed for hydraulic cements or and fine materials like pfa is very counter productive when trying to make a concrete in which the binder carbonates as the particles pack too well and are not gas permeable. Given the formulations there are just too many particles in the finer size ranges severely reducing porosity (and thus permeability) for carbonation to occur and adding to the fineness demand for water. This is not to say that pfa and other fine wastes cannot be used and when patent applications are completed we will publish how this can be achieved.

Where this notion that fine pozzolans are in some way is useful in a carbonating magnesium system came from is unknown to us and a real issue because it is not directly so. The example in our patent was actually an Enviro-Cement and within patent spec. No claim was made that it would carbonate as it is very obviously too tightly packed. We are amazed researchers have not quickly arrived at the same conclusion and sought guidance on more appropriate formulations. That the use of fines reduces porosity and mixes containing excessive fines do not exceed the percolation threshold and are thus not permeable and cannot carbonate is well enough documented in the literature. Pfa or sands designed for hydraulic cement concretes strongly inhibit carbonation.

The historical record confirms everything we say about the requirements for proper carbonation. In Mr Harrison's paper "Carbonating and Hydraulic Mortars - the difference is not only in the binder. Aggregates are also important." presented at Concrete 05 (Harrison 2005) and freely available on our web site and in a similar paper presented in Canada (Harrison 2005) Mr. Harrison noted.

"Carbonating mortars require somewhat mono graded aggregates with no fine fraction to carbonate properly. The sort of building sand commonly available from hardware or sand and gravel suppliers today is generally just not suitable. In the past rough sand would have been cut from a local source and grits were often obtained from rivers in which case the particles were of a rounded form, however sharp grits were also used which are a waste product from stone quarrying (Nicholson 2004)

Mr Harrison then said further

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

“For proper carbonation of Eco-Cement and lime mortars, the sand must result in the mortar being sufficiently porous to "breathe". Coarser rather than fine sand fractions are required in the aggregates used and this is unfortunately poorly understood except by some in the restoration industry. “Generally specify washed sharp sand with 3-4 mm grit (where the joints allow) and not too high a proportion of fines” is suitable.(Farey 2004). A masonry sand that is lacking in fines is best. The coarsest grains should be no more than 1/3 the depth of the mortar between bricks for easy laying. Although logical as a ramification of the chemistry this seems to be poorly understood except by a few within the restoration fraternity.”

I then further said in the above quoted paper in relation to the historical context

“According to Benjamin Herring, editor in chief of constructor magazine “The Romans had two distinct types of concrete mortar: One was made with simple lime and river sand, mixed at a ratio of three parts sand to one part lime. The other type used pozzolan instead of river sand and was mixed at a ratio of two parts pozzolan to one part lime.” (Herring 2002).

The oldest record we have come across addressing the issue of appropriate sands for carbonating and hydraulic cements is book II, chapter IV of the Ten Books of Architecture by Vitruvius Pollio (Pollio 27 - 23 BC). According to Vitruvius “the best (sand) will be found to be that which crackles when rubbed in the hand, while that which has much dirt in it will not be sharp enough. Again: throw some sand upon a white garment and then shake it out; if the garment is not soiled and no dirt adheres to it, the sand is suitable” Vitruvious was talking about gritty sand with no fines.

There is no doubt that grading is one of the most important parameters for properly carbonating mortars. As a further example of older literature supporting our view that coarse sands and a lack of fines are required for carbonating mortars are the comments by the 16th century architect Andrea Palladio, renowned for "The Four Books of Architecture" which were translated into English in the early 18th century and used as a principal reference for building for almost two centuries (Palladio 1738).

In the first book Palladio says, inter alia, "the best river sand is that which is found in rapid streams, and under water-falls, because it is most purged". In other words, it is coarse. Compare this with most sand for use in mortar today (Jordan 2004).

Alf Waldum of the Norwegian Building Research Institute states at page 4. “in the "good quality" ancient mortars relatively coarse sand is often found. Grains up to 6 - 8 mm were often used for renders 20 - 30 mm in thickness and for masonry mortars." (Waldum).

We are stunned given that the UK is full of old buildings with carbonating lime mortars that nobody in the Cambridge team or for that matter at the BRE bothered to find out the requirements for their proper setting as the conditions are very similar to those required for our formulations. These old carbonating mortars do not contain pozzolans[21] or fines. The formulations from the BRE, Abhi Ray and Dr Al Tabbaa consist mostly of fines.

TecEco’s carbonating Eco-Cement formulations for mortars and concrete are substantially the same as for non hydraulic lime mortars except that reactive magnesia is substituted for

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[21] Note that we have no problem with the addition of a small amount of pozzolan to improve rheology.

lime. In the UK as least pfa is not added to carbonating mortars except perhaps in small quantities[21] by some to improve the “muddiness.” All the researchers so far should have known this.

The Cambridge team in particular did not seek our advice in relation to any of our formulation types in spite of Mr Harrison’s repeated offers to assist and we would have thought it essential that they did so before completing their experimental program given the abject failure to achieve carbonation other than by raising the partial pressure of $CO_2$.

Carbonation research has gone and is going very wrong in the UK and elsewhere around the world and the concept of using forced carbonation should be dispensed with. We are now in crisis with the $CO_2$ content of the atmosphere and many researchers want to build carbonation rooms. Both the construction of these facilities and the transportation of product to them for forced carbonation will consume even more $CO_2$! In relation to this we point out that on our web site under Technical/Web Page List/The Importance of Particle Packing (http://www.tececo.com/technical.importance_particle_packing.php) that the relationship between concentration and carbonation rate is linear whereas a doubling in dimensions of the size of pores for the transport of gas leads to a quadrupling of the amount of $CO_2$ that can diffuse to the reaction front. Obviously appropriate particle packing is more effective.

TecEco plan to make magnesia production part of the Gaia Engineering process which involves the capture of $CO_2$ which is inherently easy to do as the process is simple, runs at a low temperature and is ideal for non fossil fuel energy input. The production of PC or lime is unfortunately not so adaptable.

Provided carbon dioxide can be captured during the manufacture of magnesia, then the mere fact that the low molecular weight magnesium atom can attach proportionally more is a distinct advantage as more will be reabsorbed in a permeable material such as found in concrete blocks, mortars, renders, pervious pavements etc.

Critics claim that water is a limiting factor for carbonation as TecEco Eco-Cements require moisture as the formula of nesquehonite would dictate. In all but the driest of atmospheres our experience is that there is sufficient in the air, although wet dry conditions would be expected to and in fact do deliver the best result the most quickly.

A major advantage of carbonating magnesia rather than lime is this same water because it adds mass and volume at low cost allowing less total binder to be used. Using a good plasterer’s sand which is somewhat coarser and more mono-graded and thus porous to air it is possible to use mixes that have around half the total binder in them compared to PC. On a molar volume basis much more nesquehonite is produced per mole of MgO than calcite per mole of Portlandite.

There is a significant quantity of binding phase produced as hereunder.

$MgO$ + 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 %

$MgO$ + water => $Mg(OH)_2$ + $CO_2$ => $MgCO_3.5H_2O$ Nesquehonite

11.20 + liquid => 24.30 + Gas = 102.59 Molar volumes (Assuming density MgO is 3.6, $Mg(OH)_2$ is 2.4 and $MgCO_3.5H_2O$ is 1.85 g/l)

===> Expansion of (102.59-11.2)/11.2 = 815.98%

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