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Progress with CEM-Zero

Peter Claisse¹, David Gore¹, Seema Karami², Homayoon Pouya¹ and Esmaiel Ganjian¹

¹Coventry University. Construction Materials Applied Research Group
Priory Street, Coventry, CV1 5FB, UK.
²Mott Macdonald PLC, Perth Australia

Corresponding Author: Peter Claisse: p.claisse@coventry.ac.uk
David Gore ab0647@coventry.ac.uk; Seema Karami cma_ka@yahoo.com
Homayoon Sadeghi Pouya aa0490@coventry.ac.uk; Eshmaiel Ganjian cbx111@coventry.ac.uk

ABSTRACT

Almost half of the papers presented at the 2010 SCMT conference in Ancona described replacement materials for cement in concrete. The ultimate aim of such research must eventually be to replace all of the cement in concrete with environmentally friendly alternatives. The term CEM0 is derived from the European cement types such as CEM1 and is used to describe a cementitious powder without cement. This paper will present results for types of CEM0 that have been made and also discuss problems which affected the models that were used to predict strength. These were caused by the variability of the secondary materials that are used to replace the cement. New models are being developed which rely solely on the observed properties of the materials such as their oxide contents. The paper will present initial findings from this new study and show how it could be used in a CEM0 production process.

KEYWORDS

Cement replacement, CEM0, Slag, Gypsum

INTRODUCTION

We use the term “Cem-Zero” (CEM0) in research programmes at Coventry University to describe the powders that we are developing to replace all of the Portland cement (PC) in concrete. These powders are made entirely of secondary minerals which are dried and ground as necessary and then pre-blended so the user may add them to a concrete mix using existing plant. The name is intended to correspond to the various other cement types such as CEM1, CEM2 etc. which are currently used in EN197-1 (2011). It is hoped that, as the work progresses, this extra category could be considered for inclusion in this standard. CEM0 is not intended for use in combination with PC, it should just be mixed with water and aggregate to make concrete.
The idea of making concrete without PC is not new; indeed it was universal for thousands of years. The Romans built many concrete structures which survive today, and the technology was also developed independently in Central America and some of their structures also survive.

The key benefits obtained from the use of PC since it was invented almost 200 years ago have been high strength and rapid strength gain. The theory behind the development of CEM0 is to maximise these properties as far as possible and then to target applications where they are not critical. Thus CEM0 is typically intended for use in soil stabilisation, controlled low strength materials, unreinforced concrete, paving and building blocks and footings rather than beams and columns.

THE BENEFITS OF CEM0

The environmental benefits of reducing the use of PC will be well known to readers of this paper. The focus of our research programmes is to use secondary materials which have no current market value and are being sent to landfill. This brings an additional environmental benefit of reducing the need for landfill sites. It also brings an economic benefit and, if the saving on disposal costs is maximised, it is possible to produce “negative cost concrete”.

CURRENT ALTERNATIVES TO CEM0

The usual methods used to produce low-strength concrete are either to use normal PC with a high water to cement ratio or, for very low strength applications, to use foam in a mortar mix. We maintain that PC is too valuable a resource to be used in these ways.

Some hydraulically bound materials for road construction contain no PC, however we are not aware of any pre-blended powders being produced for this.

We understand that Cenin (2012) is a CEM0 which is made by re-processing steel slags and could be used without PC, however it is normally used in combination with PC.

THE MATERIALS

Most of the material combinations used in our programmes depend for their hydraulic properties on one of two basic reactions:

- The pozzolan-alkali reaction which was exploited by the Romans by burning limestone and mixing the resulting lime with either volcanic ash or ground clay tiles or bricks. In current use in concrete Pulverised Fuel Ash (PFA) reacts with the lime produced by the hydration of PC. In our research programmes PFA is generally minimised because it already has a market. Run of station ash (ROSA) is used because it is often freely available as it is not suitable for use in structural mixes. Waste industrial alkalis such as kiln dusts are used as activators.

- The sulphate-slag reaction. This has been known about for a long time. Super-sulphated cement made from Ground Granulated Blastfurnace Slag (GGBS) and gypsum was popular during much of the 20th century, only disappearing from used in the UK due to a relatively poor shelf life. In our research programmes the use of GGBS is minimised due to its existing market. Many of the mixes contain ground Basic Oxygen Slag (BOS) from steel production. Waste gypsum is freely available.
from a number of sources (Claisse and Ganjian 2006). A CEM0 produced in this way could cause unwanted sulphate reactions if blended with PC, so it would be necessary to make sure that users did not confuse a CEM0 with a traditional cement replacement material such as PFA.

TEST METHODS

There is an abundance of published literature about the use of different secondary materials in concrete, including many papers from SCMT2 (Claisse et.al. 2010). In this literature it is generally agreed that compressive strength is an important property to measure but, beyond that, a considerable range of different tests are used. The strategy for our CEM0 programme is to target specific applications and select the tests to suit. Thus, for example, in our work on waste containment the tests focussed on transport properties, but expansive reactions such as sulphate attack were not considered because they would not reduce the effectiveness of the containment (Claisse et.al. 2006).

Larger scale site trials yield very useful information. For example, our trials have shown very clearly that using pre-blending powders is the only method which will make most secondary materials acceptable for use in industry. Concrete batching plants do not have enough silos to store the individual components.

OPTIMISING BY MATERIAL

In this work (Karami et.al. 2012) different proportions of a range of secondary materials were used to make types of CEM0. Methods were then used to optimise the strength based on the proportions of the different materials. The following materials were used:

BOS was obtained from Corus UK (now Tata) Scunthorpe plant. When this material is used for applications such as road embankments it is weathered to hydrate the calcium oxide. The material used in this project was not weathered but it was ground to pass a 600µm sieve.

Ground waste plasterboard gypsum (PG) was obtained from Lafarge Plasterboard in Bristol UK. This material comes from off-cuts from site and production rejects from the manufacturing plant. It is processed at a recycling plant where 99% of the paper is removed; however, it still contained minor amounts of glass and paper. The plasterboard was also ground to pass a 600µm sieve.

ROSA was obtained from Ratcliffe-on-Soar Power Station, UK. It is understood that this ash came from burning a conventional UK bituminous coal. It was not classified and was therefore not a designated PFA.

Red Gypsum (RG) was obtained from Huntsman Tioxide, UK. This is a titanogypsum from titanium dioxide production. This process produces both pure white gypsum and the red gypsum which acquires its colour from iron oxide impurities. The white gypsum is sold for plasterboard production but the red gypsum is normally landfilled.

The mixes were optimised in two steps: In step 1 binary (2 component) mixes were tested and optimised for compressive strength. In step 2 a third material was added to the optimised mix and the ternary blend was then optimised. The results are shown in figures 1 and 2.
Contour plots of this type can be used to give an indication of strengths to be expected with different blends but could not be used in a systematic way to predict strengths of mixes. There are a number of mathematical methods available to optimise the strength obtained with combinations of different materials. Artificial Neural Networks based on material proportions have been used by many authors and were used in this programme. The limitation with these methods is, however, that they can be used to develop optimised mixes for particular samples of materials but the models they produce will then fail when new batches are obtained if they are not identical, and this happened with this data.

Figure 1. Compressive Strength (MPa) of BOS- ROSA-RG mixes (7days) and (28days)
Figure 2  Compressive Strength (MPa) of BOS- ROSA-PG mixes (7days) and (28days)

OPTIMISING BY OXIDE CONTENT

Figure 3. Relationship between total calcium and 7 day strength.

Our more recent programmes have focussed on measured properties of the materials, specifically the oxide percentages from X-ray fluorescence (XRF), to see if these can be used as predictors for strength. We are starting by using the oxide data in published papers to
build a model to predict strength. The initial results are shown in figure 3 and table 1.

Table 1. Values of the correlation coefficient $r^2$. Ca/Si is the calcium/Silicon ratio.

<table>
<thead>
<tr>
<th></th>
<th>28 day strength</th>
<th>7 day strength</th>
<th>Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/Si</td>
<td>0.0333</td>
<td>0.0786</td>
<td>positive</td>
</tr>
<tr>
<td>Ca/Al</td>
<td>0.0608</td>
<td>0.1321</td>
<td>positive</td>
</tr>
<tr>
<td>Ca</td>
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<td>0.107</td>
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</tr>
<tr>
<td>Si</td>
<td>0.0185</td>
<td>0.0396</td>
<td>negative</td>
</tr>
<tr>
<td>Al</td>
<td>0.0323</td>
<td>0.0987</td>
<td>negative</td>
</tr>
</tbody>
</table>

Using a large number of papers from the literature, 250 different mixes were studied. For each one the oxide analyses and the proportions of the different materials in the cementitious blends were obtained. From these the total percentages of the different oxides in the blends were calculated. The strengths were then corrected to a water/cementitious ratio of 0.5 using standard mix design charts (Teychenne 1998). Figure 3 shown one of the relationships obtained and table 1 shows the correlation coefficients from a selection of them. For a sample size of 250 the critical value of $r^2$ for 5% significance is 0.014, for 1% it is 0.029 and for 0.1% it is 0.04. It can be seen that many of these are significant at the 0.1% level and almost all at 5%. However the graph shows that this method is not yet near the accuracy needed for effective strength prediction.

As a next step we plan to use this data to train an Artificial Neural Network. If this proves inadequate, we shall include other measurements such as infra-red spectroscopy.

PRODUCTION OF CEM0

A CEM0 production plant would basically consist of facilities to receive secondary materials from local sources, dry and grind them as necessary and blend them in optimised proportions. However, to overcome variations in the materials it would be necessary to use in-line analysis such as XRF on them and then to adjust the blending proportions to compensate. The aim of our research is to provide a model to calculate the adjustment and ensure that the blend is continually optimised.
EXAMPLE OF A CEM0

In a recent research programme (Ganjian et.al. 2008) we produced 100 tonnes of a CEM0 which contained 15% plasterboard-derived recycled gypsum, 5% bypass dust and 80% basic oxygen slag. Two site trials were carried out with this material. It was used without aggregate (fig. 4) achieving a strength of 30MPa. Given that the CEM0 was produced entirely from materials that would otherwise have gone to landfill, the use of a mix without aggregate was economically justified. In the second trial crushed concrete aggregate was used and a semi-dry mix was made. The cores (fig 5) gave strengths of 10MPa.

CONCLUSIONS

1. The term CEM0 is used to designate a blended powder which can be used to make concrete with no Portland Cement.

2. Optimising by material is difficult due to changes in successive batches. Optimising by oxide content is not yet working but may work in future.

3. We have demonstrated that strengths of up to 30MPa can be achieved with CEM0 mixes.

REFERENCES


