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Durability studies of a non-hydraulic CO₂ sequestering cement for use in pre-casting applications

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ABSTRACT

This paper describes durability studies of a calcium silicate cement containing non-hydraulic phases which is produced in existing cement kilns using the same raw materials as Portland cement (PC). The key difference is that this type of cement is produced using less limestone and at lower kiln burning temperatures. This translates into reduced CO₂ emissions during cement manufacturing. The concrete production process involves mixing cement, aggregates, sand, and water that is then cured in CO₂ to form a hardened matrix. The Solid Life project (granted by the EU under the LIFE program) is intended to demonstrate the CO₂ and energy savings and demonstrate fitness of this concrete for various applications. This paper briefly describes the process for manufacturing the cement clinker and concrete products and presents early performance test results (including creep, frost scaling and resistance to abrasion) for a Solidia ConcreteTM and Portland cement reference concrete. Acceptance of any new non-Portland based cements (such as Solidia Cement), will require demonstrating compliance with standards (including durability); hence, the paper will introduce potential route of CE Marking/European Assessment documents as a means towards getting end user acceptance of new cements that are not covered by existing European standards. Outcomes from full scale concrete production trials (by a UK pre-caster) are also described.

1. INTRODUCTION

Portland clinker is produced via a combustion process that sees limestone (calcium carbonate) from the quarry calcined to lime, which then combines with clay to produce the clinker. This process requires thermal energy, e.g. 2.9 GJ/t clinker with the best available technology. The CO_2 emission related to both calcination and combustion is ~ 810 kg CO_2 /t clinker produced.

The SOLID LIFE project focuses on some particular novel low-CO₂ products named Solidia CementTM and Solidia ConcreteTM which are offered by Solidia Technologies. These new products are a breakthrough for the Portland cement (PC) industry. The composition of Solidia Cement differs from CEM I Portland cement as the raw meal contains less limestone. Also, it sets and hardens through a carbonation process and not via hydration. As a result, CO₂ emissions related to the burning process are reduced by 30 per cent,

and it recaptures additional CO_2 during the curing of the concrete, ie 250 kg CO_2/t cement. Altogether, the emissions per tonne of binder in the concrete are expected to be reduced at least by a factor of two, i.e., below ~400 kg CO_2/t for Solidia Cement instead of 810 kg CO_2/t for PC.

Solidia Cement develops high early strength and can already address several market segments, such as precast blocks and roof tiles.

The Solidia Cement clinker can be manufactured using conventional technology to form monocalcium and dicalcium silicates in existing PC clinker kilns. The curing process (in the presence of water), involves the following reactions:

 $CaO \cdot SiO_{2} + CO_{2} \rightarrow CaCO_{3} + SiO_{2}$ $3CaO \cdot 2SiO_{2} + 3CO_{2} \rightarrow 3CaCO_{3} + 2SiO_{2}$ $2CaO \cdot SiO_{2} + 2CO_{2} \rightarrow 2CaCO_{3} + SiO_{2}$

Curing of the Solidia Concrete begins only when Cement, CO_2 and H_2O (I) are Solidia simultaneously present in the system. The Solidia Cement clinker composition is lower in calcium than that of CEM I PC. Solidia Cement falls outside the scope of EN 197, the European Standard for common cements (BSI). The SOLID LIFE project seeks to show the industrial feasibility of manufacturing Solidia Cement and producing Solidia Concrete products from it within the EU (at pilot and industrial scale). It also aims to establish the CO_2 savings and demonstrate performance/durability. This paper focuses on some early performance test results (from work conducted at BRE) and on potential routes to standardization of new cements.

2. Experimental details

BRE was provided with concrete test specimens made from the two concrete mixes shown in Table 1. Due to the requirement for a special carbonation curing chamber for making the Solidia Concrete, the specimens were manufactured in the US by Solidia Technologies and shipped to BRE for testing. The BRE testing compared a Solidia Cement-based concrete mix to a PC based control concrete mix. Both mixes had the same cement content, aggregate type + grading and w/c ratio.

Table 1. Concrete mix designs for durability tests		
Mix constituent	PC reference specimens (reference concrete mix)	Solidia Cement- based specimens (test concrete mix)
SC PECS (Solidia Cement) (kg/m ³)	-	350
PC (kg/m ³)	350	
Construction. Sand (kg/m ³)	821	821
3/8" Coarse aggregate (kg/m ³)	414	414
3/4" Coarse aggregate (kg/m³)	737	737
Water (kg/m ³)	136	136
w/c	0.39	0.39
Glenium 7500, (cm³/kg cementitious)	5	5
MBAE 90 air entraining agent, (cm ³ /kg cementitious)	3	3
Sika Plastiment, (cm ³ /kg cementitious)	2	5

Plasticizing admixtures, (Glenium 7500 and Sika Plastiment), were used to reduce water demand and improve rheological properties in both the mixes, with an air entraining agent also included to improve frost resistance. The PC reference exceeded the minimum cement content and maximum w/c requirements of XF3 (freezing and thawing without de-icing salts). Both concretes were designed to a minimum of C40 grade.

The PC concrete specimens were all moist cured in the form and were not submerged in water at any time. The Solidia Concrete specimens were cured in a CO₂ atmosphere with an exposure time of typically <72 hours.

The test methods applied by BRE were:

- a) Taber abrasion (Annex A of BSI, 2009a) (on slices, 100 x 100 x 11 mm, sawn from the interior of 100 mm concrete cubes)
- b) Creep in compression of concrete cylinders (BSI, 2009b).
- c) Freeze-thaw resistance without de-icing salt (BSI, 2016), (on sawn slices from 150 mm concrete cubes).

In the Taber abrasion test, four different specimens from each mix design were assessed, with the abraded material being collected and weighed at intervals up to 500 cycles. The Taber Wear Index of each type of concrete, (also, an expression of the abrasion resistance), was calculated (BSI, 2009a). The Taber Wear Index was calculated after 500 cycles as follows:

For creep, nine cylinder specimens (200 mm x 100 mm diam.) per mix design were held under compressive load for 3 months at 20% of their compressive strength (as determined at the start of the creep test). The 18 cylinders were contained in six test rigs, whilst three further cylinders of each mix design were sealed with wax at the top and kept next to the test rigs to assess drying shrinkage. Deformation of the central 100 mm of each cylinder was measured with a dial gauge across measurement points before the start of loading, immediately after loading, once a day for a week, once a week for a month and once a month for a total of 3 months. The resulting strain data was used to calculate the Specific Creep, Creep Coefficient and Creep Rate according to BSI ISO 1920-9 (BSI, 2009b).

For assessment of freeze thaw resistance, Solidia Concrete and PC-based concrete specimens were exposed to accelerated freeze-thaw cycles (1 cycle per 24 hours) whilst ponded with potable water (i.e. without de-icing salt). The loose (scaled material) was collected at intervals over 56 freezethaw cycles and an average cumulative scaled mass was calculated.

3. Results

Figure 1 shows the Taber results. The average weight loss after 500 cycles was 970 mg for the PC-based concrete reference and 1,064 mg for the Solidia Concrete sample the corresponding average Taber Wear Index values were 797 and 858 for the PC-based concrete reference and Solidia Concrete, respectively. Each point in Figure 1 is a mean of four different test specimens.



Figure 1. Taber abrasion results (PC-based concrete reference and Solidia Concrete)

Figure 2 shows the Creep Coefficient results (maximum, minimum and average), from the creep testing for the two types of concrete. This shows that the Solidia concrete maintains an almost zero creep in comparison to the PC-based concrete. Strains due to drying shrinkage alone over the period of the test have been taken into account in calculating the Creep Coefficient values. Specific Creep and Creep Rate values are not shown here.

The elastic modulus (determined from the measurements made during the creep test) was 44% higher for the Solidia Concrete than for the equivalent strength PC-based concrete (51.4 GPa for the Solidia Concrete against 35.6 GPa for the PC-based concrete).



Figure 2. Creep coefficient results (PC-based concrete reference and Solidia Concrete)

Figure 3 shows the frost scaling results for 56 cycles. Each curve is a mean of four specimens.



Figure 3. Freeze-thaw (scaling) results

Scaling over 56 cycles was approx. 0.4 g (scaled weight) for PC-based concrete and 0.12 g for Solidia Concrete, (corresponding to 0.02 kg/m² and 0.01 kg/m² respectively). Most of the scaling occurred within the first 12 cycles in both cases.

4. Discussion

The Taber test gave very similar results for both concretes. This implies a similar abrasion resistance for the paste phase in both cases (if the aggregates are, as here, the same in both cases - aggregates and sand are likely to dominate the abrasion performance and these are not trowelled surfaces, hence surface finishing is not an influence).

The creep testing showed that the Solidia Concrete had much lower values of Specific Creep, Creep Coefficient and Creep Rate than the PC-based concrete for all measurements taken during the 3 months of the creep test. The data collected also showed that the drying shrinkage of the Solidia Concrete was almost zero during the 3month test period and it was much stiffer (higher modulus). These differences elastic are presumably associated at least in part to the different mineralogy of the cement paste phases of the Solidia Concrete.

The Solidia Concrete has shown significantly better performance than the PC-based concrete reference in freeze thaw exposure. Nevertheless, performance of both mixes is also significantly better than a BRE reference PC-based concrete with mix proportions and compressive strength deemed to resist XF3 conditions (freezing and thawing without de-icing salts) assessed previously by BRE.

5. Standards and CE marking

The main European standards relating to cement, concrete and concrete products in the UK are as follows:

- BS EN 197-1, the European Standard for cement (BSI 2011, BSI, 2014).
- BS EN 206:2013, the European standard for concrete, (BSI, 2013)
- Various performance-based standards for concrete products, such as BS EN 1339:2003 (BSI, 2003a) for concrete paving flags or BS EN 1338 for paving blocks (BSI, 2003b).

The above European Standards define various technical parameters and criteria needed to meet the requirements of the Construction Products Regulation (European Union, 2011) of the European Union. Where there is a harmonised European Standard (such as EN 197), this can provide the means for applying a CE mark for a new product such as a cement or binder. BS EN 206 by implication only apply to BS EN 197 cements as the prescriptive approach based on minimum strength grade, maximum water/cement ratio (w/c), minimum binder content and restrictions on the cement type permitted in particular exposure environments are all focused on cements and concretes containing PC in conjunction with other binder materials such as ground granulated blast furnace slag (ggbs) or fly ash.

Pre-cast concrete products made from new binders may be suitable for testing against existing performance-based standards such as BS EN 1338. New types of binder (such as Solidia cement) that are not within the scope of EN 197 require a different approach. These approaches can include development of a new European Standard for the binder, or completion of a European Technical Assessment (ETA) against a European Assessment document (EAD). Durability and performance data such as that being generated as part of the Solid Life project (of which this paper provides some examples), may be usable, as determined by the Technical Assessment Body (TAB), to underpin the development of such new standards or assessment documents.

6. Industrial pilot trials

Several tonnes of Solidia Concrete pavers were produced in industrial scale trials by a UK precast concrete manufacturer. The pavers passed the relevant performance tests for tensile splitting strength, freeze-thaw resistance and abrasion (BSI, 2003b). A pallet of pavers from the trial (approx. 1.7 tonnes) was shipped to BRE together with a similar number of reference pavers made using the same aggregates and PC. Test specimens were randomly selected and placed in a variety of exposure conditions. This provides the potential to gather data on the long-term performance of Solidia Concrete. The exposure conditions include aggressive sulfate or acid solutions, seawater, coastal and inland exposure sites and air or water at different temperatures. Limited early age exposure data are currently available. However, these results are expected to inform the development of standards/assessment documents as they become available in the future.

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