Properties of Solidia Cement and Concrete

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ABSTRACT

Solidia Cement containing non-hydraulic phases is produced in existing cement kilns using 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 to reduced CO_2 emissions during cement manufacturing (30% reduction). The concrete production process involves mixing cement, aggregates, sand, and water. The wet concrete is then exposed to gaseous CO_2, which reacts with the cement to form a durable matrix. The curing process can capture up to 300 kg of CO_2 per tonne of cement used. Together, Solidia Cement and Concrete production reduce the CO_2 footprint by 70% when compared to conventional cement and concrete products.

The Solid Life project (granted by EU under the LIFE program) intends to demonstrate the CO_2 and energy savings that can be realized in industrial applications and to increase the robustness of the technology. Moreover, a dedicated part of the project was to develop underpinning data for a European Assessment Document (EAD) to enable a European Technical Approval (ETA) and hence a potential route to CE marking for this new cement. To this end, concrete specimens produced by the project partners and pavers produced by commercial concrete manufacturers have been tested internally by the industrial partners and by the Building Research Establishment in terms of their durability.

This paper describes the knowledge acquired on the production of Solidia Cement to its use in precast plants and early durability results obtained from concrete specimens. Short and long term experiments were performed to assess the behaviour of this new type of concrete.

Keywords: Mineral carbonation; Low carbon cement & Concrete; Durability; European Technical Approval
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1| INTRODUCTION

Concrete is the most consumed man-made material in the world. A typical concrete is made by mixing Portland cement (PC), water, and aggregate (e.g., sand and crushed stone). PC is a synthetic material made by burning a finely ground mixture of limestone, clay and correction materials, or materials of similar composition, in a rotary kiln at a sintering temperature of 1450°C. PC manufacturing releases considerable quantities of greenhouse gas (CO_2). The cement industry accounts for approximately 8% of the global anthropogenic carbon dioxide (CO_2) emissions [1].

Solidia Cement™, a new calcium silicate-based cement (CSC) product developed by Solidia Technologies®, is a reduced-lime, non-hydraulic calcium silicate cement capable of significantly reducing the energy requirement and CO_2 emissions at the cement plant. The Solidia Cement manufacturing process is adaptable and flexible, allowing it to be produced under a variety of raw materials formulations and production methods across the globe. It offers cement manufacturers considerable savings in CO_2 emissions and energy consumption. Additionally, Solidia Cement cures via a reaction with gaseous CO_2, thus offering the ability to permanently and safely sequester CO_2.

The CO_2 savings obtained in the cement production and precast applications are presented in this paper.

2| Energy requirements and CO_2 emissions during cement manufacturing

Both PC and Solidia Cement manufacturing require significant amounts of energy and emit significant quantities of CO_2. Heat energy is needed to dry the raw meal, calcine the limestone, react the oxide components, and form the cement clinker. The electrical energy needed to crush and grind the raw materials, to operate the clinkering process, to comminute the clinker, and to transport materials throughout the process will not be considered in this analysis. To illustrate the benefits associated with the production of Solidia Cement, the differences in energy consumption and CO_2 emissions are discussed below.

2.1 Energy requirements

In modern cement plants, the production of one tonne of PC clinker requires heat energy totalling 3.2 GJ [2]. From a theoretical perspective, the thermal energy consumed in producing one tonne of PC clinker is about 1.757 GJ [3]. The difference between the actual and theoretical heat requirements is due to heat retained in clinker, heat losses from kiln dust and exit gases, and heat losses from radiation. The pyro-processing step that consumes the most heat energy is the endothermic decomposition of calcium carbonate (calcination) therefore Solidia Clinker thermal energy is expected to be lower than OPC.

The total lime content of Solidia Clinker is in the range of 45-50 wt.%, representing approximately a 30% reduction from that required for PC. This reduction in lime concentration translates directly into a 30% reduction in the major component of the theoretical enthalpy, i.e., the calcination step. Solidia as well as PC raw meals require roughly equivalent amounts of enthalpy to decompose the clay component and the exothermic reaction associated with the formation of the cement phases. Dominated by the large difference in calcination step, the total theoretical enthalpy of formation of Solidia Clinker is expected to be about 1.051 GJ/t, almost 40% lower than that of PC clinker.
From a practical perspective, Solidia Clinker is burned at temperatures approximately 200°C lower than those used in PC manufacturing, and with the potential for significantly reduced system-wide heat losses than that experienced in PC manufacturing. This is expected to translate into a reduction in fossil fuel consumption by as much as 30%.

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2.2 CO_2 emissions

EPA's historical estimates indicate that 900 to 1,100 kg of CO_2 are emitted for every tonne of PC clinker produced in the US. The exact quantity depends on the raw ingredients, fuel type, and the energy efficiency of the cement plant [4]. Even the most efficient Portland cement facilities report CO_2 emission ~810 kg/tonne of clinker [5].
The CO_2 emissions from chemical decomposition of calcium carbonate depend on the lime content of the clinker product (~70% for PC). The CO_2 emissions from pyro-processing depend on the fossil fuel type (for example, ~3.0 tonnes of CO_2 per tonne of coal consumed). The carbon footprint from electricity consumption for cement production is about 90 kg/tonne in the US but as stated earlier, this CO_2 is not considered here. Table 1 compares the sources of CO_2 emission in the production of cement clinker.

The low-lime content of Solidia Clinker enables two separate opportunities to reduce the CO_2 emissions associated with cement production:
Reduction in the lime content of the cement from approximately 70% (for PC) to approximately 50% (for Solidia Clinker) enables a proportionate reduction in CO_2 emission (540 kg/t for PC clinker vs. 375kg/t for Solidia Clinker),
Reduction of 200°C in the clinkerization temperature of 1450°C vs.1250°C, enables CO_2 emissions reduction coming from fossil fuels (270 kg per tonne for PC clinker vs. 190 kg per tonne for Solidia Clinker),
The total CO_2 emissions associated with PC and Solidia Clinker manufacturing are compared in Table 1. Note that Solidia Clinker production offers the potential to reduce CO_2 release associated with cement manufacturing by as much as 30%.

Table 1: CO_2 emissions during the production of PC and Solidia Clinker (Note: The CO_2 associated with the electrical energy usage in the cement making process is not considered.)

CO_2 emissions from:	Per tonne of PC clinker	Per tonne of Solidia Clinker
Limestone decomposition	540 kg	375 kg
Fossil fuel combustion	270 kg	190 kg
Total CO_2 emissions	810 kg	565 kg

2.3 Energy requirements and CO_2 emissions during production of Solidia Clinker

Recently, the first, industrial Solidia Cement production campaign was performed in a North American plant of the LafargeHolcim group. This campaign sought to prove the production feasibility in a modern industrial kiln with 4-stage preheater. Approximately 5000 tonnes of Solidia Clinker was produced. The raw mix was adapted to meet the chemical specifications and the wollastonite (CS) and rankinite (C_3S_2) clinker phases of Solidia Cement.
During the production campaign, CO_2 emissions and energy consumption (specific heat consumption) were tracked in order to assess the relevance of the theoretical numbers indicated above. In order to adequately compare the production of PC and Solidia Clinker, stable production periods were taken into account for each clinker type, not only in the same plant, but also in the same kiln. The measurements, highlighted in Table 2, confirm the predicted energy and CO_2 savings.

Table 2: Industrial Solidia Clinker trial measurements

		PC clinker	Solidia Clinker
Period		Normal production	Stable production period
Specific heat consumption (SHC)	GJ/t ck	3.89	3.16
Stack CO_2	%	24.4	14.2
CO_2 emissions	Nm^3/t ck	474	334

In terms of energy, a 20% savings was measured for the specific heat consumption (SHC). This SHC savings is slightly lower than expected because the production rate of Solidia Clinker in the kiln was not fully optimized. It was noted that the Solidia Clinker behaviour in the kiln is different than that of PC clinker. Room for considerable improvement in Solidia Clinker production remains.
It should also be noted that the typical plant fuel utilization was modified for the Solidia Clinker production. Only the main burner, fed with petcoke, coal and recycled plastics. PC production used the main burner in the same manner, but tires were also fed into the back end of the kiln.
The reduction in CO_2 emissions during Solidia Clinker production is in accordance with expected values. Measurements at the stack of the plant confirmed that conversion from PC production to Solidia Cement production resulted in CO_2 emission savings of about 30%.
In conclusion, measured reductions in the SHC and CO_2 emissions during the first industrial Solidia Clinker production campaign matched predictions. Further improvements of these parameters are expected as clinker production is further optimized.

3| Concrete mixing, forming and curing processes

PC- and Solidia Cement-based concretes are manufactured using the same basic mixing and forming processes. Concrete production typically begins by mixing the dry (cement, sand and crushed stone) and the liquid (water and chemical additives) components of the concrete. The water and chemical additive control the flow behaviour of the concrete mix while it is in the plastic stage.
Both PC- and Solidia Cement-based concretes can be mixed in standard concrete mixers. Similarly, they can be formed into the final concrete part shapes by the same processes and equipment. These processes include casting, extrusion, rolling and pressing.
PC and Solidia Cement-based concrete differ in the chemical process by which they set and harden. These processes are collectively referred to as "curing."

3.1 PC-based concrete curing

When PC is exposed to water, a series of hydration reactions initiate which are responsible for the setting and hardening of PC-based concrete: CSH, $Ca(OH)_2$ and ettringite are basically formed. The complex calcium silicate hydrate (CSH) is an amorphous phase wherein the Ca:Si ratio can vary during the hydration period. The hydration of the calcium silicate components of PC begins as soon as it is exposed to water, but proceeds at a relatively slow kinetic. The maturity of PC-based concrete is only reached after up to 28 days, when the required performance is achieved. Under normal curing conditions, and without chemical accelerators, roughly 70% of the cement particles are hydrated.

3.2 Solidia Cement-based concrete curing

The low-lime, CS and C_3S_2 components of Solidia Cement do not hydrate when exposed to water during the concrete mixing and forming processes. Cast Solidia Cement-based concrete parts will not cure until they are simultaneously exposed to water and gaseous CO_2. Solidia Cement-based concrete curing is a mildly exothermic reaction in which the low-lime calcium silicates in the Solidia Cement react with CO_2 in the presence of water to produce calcite ($CaCO_3$) and silica (SiO_2) as follows:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$$

The above reaction process requires a CO_2-rich atmosphere. However, the process can be conducted at ambient gas pressures and at moderate temperatures (~ 60°C). These parameters are well within the capabilities of most precast concrete manufacturers.

Unlike the hydration reaction in PC-based concrete, the carbonation reaction in Solidia Cement-based concrete is a relatively speedy process. Full curing of Solidia Cement-based concrete is limited only by the ability of gaseous CO_2 to diffuse throughout the part. Thin concrete products such as roof tiles (~10 mm thick) can be cured in less than 6 hours. Larger concrete parts, such as those in railroad sleepers (~250 mm thick) can be cured within a 24-hour period. This rapid curing process can potentially enhance the productivity of an existing precast operation.

A microstructural evaluation of Solidia Cement-based concrete shows the reaction products calcite ($CaCO_3$) and amorphous silica (SiO_2) as well as un-carbonated cement particles. A typical microstructure of CO_2-cured Solidia Cement-based concrete is illustrated in Figure 1. The calcite fills the pore space within the concrete, creating a dense microstructure. As the silica is relatively insoluble in the prevailing conditions of the carbonation process, it forms at the outer surface of the reacting cement particle.

Unlike PC-based systems, concrete products hardened with CO_2-cured Solidia Cement do not consume water. In fact, up to 90% of the water used in the Solidia Cement-based concrete formulation can be recovered during the CO_2-curing process. The remaining water is retained in the cured concrete.

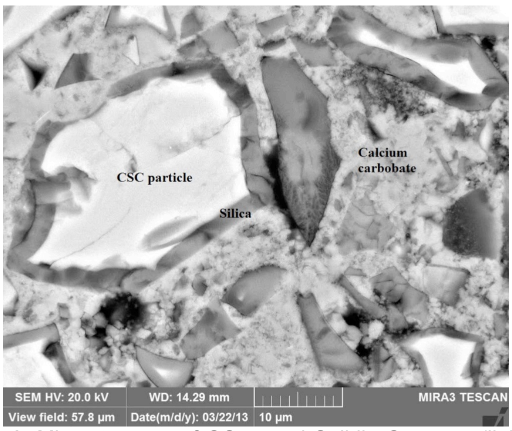

Figure 1: Microstructure of CO_2-cured Solidia Concrete (light grey area is calcite ($CaCO_3$), dark grey area is amorphous silica (SiO_2), and white area is unreacted cement particle ($CaO \cdot SiO_2$).)

3.3 CO_2 sequestration in Solidia Cement-based concrete

The unique ability of Solidia Cement to avoid hydration and cure via a reaction with gaseous CO_2 opens the possibility for the permanent sequestration of CO_2 in cured concrete structures. The curing processes, described in Section 2.2, enables Solidia Cement-based concrete to sequester up to 300 kg of CO_2 per tonne of Solidia Cement used in the concrete formulation. The CO_2 used in the curing process of Solidia Concrete is industrial-grade CO_2 sourced from waste flue gas streams.

Within the framework of Solid Life European project, the Solidia technology was tested in an industrial pilot at a UK precast site. Solidia Cement-based block pavers were produced following the same production protocols and equivalent mix design of OPC block pavers. The only variation was the curing part in contact with gaseous CO_2 during 30h in the case of the Solidia pavers in a curing chamber designed and installed by Solidia Technologies.

This curing chamber consists in a container equipped with a gas conditioning system dealing with flow introduction during the production run in order to maintain a 98%v CO_2 concentration at atmospheric pressure and around 60 to 70°C. A production run represents roughly 110 production boards, an equivalent of 15 tonnes of concrete.

Figure 2: Solidia Technologies' curing chamber installed at a UK precast site

CO_2 curing and sequestration was studied on pavers by thermal analyses method and determined to sequester 240kg of CO_2 per tonne of cement. Added to the 245kg saved per tonne of cement produced, these numbers lead to 60% reduction in the CO_2 footprint associated with the production and use of Solidia Cement if a direct flue gas is used for concrete curing.

It should be noted that paver production during the Solid Life European project utilized CO_2 acquired from an industrial gas supplier. The energy cost associated with the collection, purification, condensation and transportation of the CO_2 from the emitter to the user is equivalent to 15% of the CO_2 used during the concrete curing process. Combined with the fact that the pilot curing equipment had a CO_2 yield of about 80%, the CO_2 footprint reduction measured in this specific case was about 54%.

4| Durability assessment to ETA route

The Solid Life project aimed at starting the process to get an European Technical Approval for Solidia Cement and Concrete. Cement and concrete characterizations are therefore necessary.

Before getting some industrial pavers specimens, BRE performed some durability experiments on concrete elements reported in the following article [6]. Creep, Taber abrasion and freeze-thaw results were already obtained on lab scale concrete specimens and showed equivalent and/or better results for Solidia specimens than for PC ones.

Then several tonnes of Solidia Concrete pavers were produced in industrial scale trials (more than 20 runs).

Adjustments of the mix design, paver production and curing processes parameters led to pavers passing the relevant performance tests for tensile splitting strength and freeze-thaw resistance.

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:

- Specimens (> 120 per mix type) have been placed in various conditions with potential for future durability monitoring both during and after completion of the Solid Life project
- Solidia product showed better dimensional stability under dry conditions and when subjected to wet dry cycling than the PC concrete
- Evidence of deterioration in citric acid but no evidence of deterioration to date (91 days) in sulfate solutions or seawater in either mix type
- Taber (wide-wheel) abrasion, similar results for both product types

However, these results are expected to inform the development of standards/assessment documents as they become available in the future. In parallel to this long-term concrete durability database acquisition, LafargeHolcim's Austrian entities (Solid Life partners) are developing an EAD document to get a CE marking for the Solidia Cement to be able to commercialize the Solidia solution.

5| CONCLUSIONS

The low-lime content of Solidia Clinker enables two separate opportunities to reduce the CO_2 emissions at the cement plant:

- The CO_2 released from the chemical decomposition of limestone: 540 kg per tonne of PC clinker to about 375 kg of CO_2 per tonne of Solidia Clinker.
- The clinkering temperatures reduction of about 200°C: 270 to 190 kg CO_2 per tonne clinker.

This makes it possible to reduce the CO_2 emissions from ~810 kg/tonne of PC clinker to ~565 kg/tonne of Solidia Clinker. A 30% CO_2 emissions saving was measured during a first worldwide industrial Solidia Clinker production, as predicted. Energy savings of 20% were measured (with only SHC taken into account).

The unique ability of Solidia Cement to avoid hydration and cure via a reaction with gaseous CO_2 opens the possibility for the permanent sequestration of CO_2 in cured concrete structure. It has been demonstrated that the curing process enables Solidia Concrete to sequester about 240 kg of CO_2 per tonne of cement used in the concrete formulation.

The combined effects of CO_2 savings at cement plant and the ones measured at a pilot installation in a UK precast plant, offers the ability to reduce the CO_2 footprint associated with the production and use of Solidia Cement by 54%. Upscaling this pilot to industrial level and utilizing a direct stream of flue gas would increase this number to 60%. First promising durability assessment on industrial cement and concrete specimens are performed and are on-going in order to develop an European Technical Approval the help the Solidia solution development within Europe.

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