Low-energy, low-emissions

As part of the drive to reduce CO_2 emissions, cement companies are developing novel cement types with reduced lime contents and based on non-hydraulic calcium silicates that require less energy during production and absorb CO_2 once poured as concrete.

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Ordinary Portland cement (OPC) production is one of the most energy-intensive processes. OPC clinker is a synthetic material made by burning a finely-ground mixture of limestone, clay and correction materials in a kiln at a sintering temperature of 1450˚C. In modern cement plants, the average energy consumption is 3.2GJ/t of clinker as fuel[1] and about 110kWh/t of cement as electrical energy. In addition to CO_2 emissions from fuel and electricity use, OPC manufacturing also releases considerable quantities of chemically-bound CO_2 through calcination in the clinkerisation process. The cement industry accounts for approximately eight per cent of global anthropogenic CO_2 emissions.[2]

Solidia Cement™, a new calcium silicate cement (CSC) developed by Solidia Technologies®, is a reduced-lime, non-hydraulic calcium silicate cement capable of significantly reducing the energy consumption and CO_2 emissions at a cement plant. It offers cement manufacturers considerable savings in terms of energy consumption and CO_2 emissions. Additionally, Solidia Cement cures via a reaction with gaseous CO_2 and is therefore, able to permanently and safely consume CO_2.

Solidia Concrete™ manufactured by EP Henry in a residential setting, New Jersey, USA

Energy savings and emissions reductions in Solidia Cement production

Cement manufacturing requires significant amounts of heat energy 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, operate the clinkering process, comminute the clinker and transport materials throughout the production process will not be considered in this analysis.

From a theoretical perspective, the thermal energy consumed in producing 1t of OPC clinker is about 1.8GJ.[3] The difference between the actual (3.2GJ/t) and theoretical heat requirement is due to heat retained in clinker, heat loss from kiln dust and exit gases, and heat loss from radiation. The pyroprocessing step that consumes the most heat energy is the endothermic decomposition of calcium carbonate (calcination).

The total lime content of Solidia Clinker is in the range of 45-50 weight per cent, representing approximately a 30 per cent reduction from that required for OPC. This reduction in lime content translates directly to a 30 per cent reduction in the major component of the theoretical enthalpy, ie, the calcination step. Solidia and OPC raw meals require roughly equivalent amounts of enthalpy to decompose the clay component and carry out the exothermic reaction associated with the formation of the cement phases. Dominated by the large difference in the calcination step, the total theoretical enthalpy of formation of Solidia Clinker is expected to be about 1.1GJ/t, almost 40 per cent lower than that of OPC clinker. From a practical perspective, Solidia Clinker is burnt at temperatures ~200˚C lower than OPC clinker, leading to significantly reduced system-wide heat losses. This is expected to translate into a reduction in fossil fuel consumption by as much as 30 per cent.

The low-lime content of Solidia Clinker enables two separate opportunities to reduce the CO_2 emissions associated with cement production:

1. reduction in the lime content of the cement from ~70 per cent (for OPC) to ~50 per cent (for Solidia Clinker) enables a proportionate reduction in CO_2 emission (540kg/t for OPC clinker vs 375kg/t for Solidia Clinker)
2. reduction of 200˚C in the clinkerisation temperature of 1450˚C (OPC) to 1250˚C (Solidia Clinker) enables CO_2 emissions reduction due to decreased fossil fuel use (270kg/t for OPC clinker vs 190kg/t for Solidia Clinker).[4]

Industrial Solidia Cement production trials were performed at a North American plant of the LafargeHolcim group on two separate occasions. These sought to prove

Table 1: industrial Solidia Clinker trial measurements and comparison to OPC production during steady-state operation		
Ranking	**OPC clinker**	**Solidia Clinker**
Specific heat consumption (GJ/t clinker)	3.89	3.16
Stack CO_2 (%)	24.4	14.2
CO_2 emissions (Nm³/t clinker)	474	334

the production feasibility in a modern industrial kiln with a four-stage preheater. Approximately 5000t of Solidia Clinker was produced in both trials. 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 to assess the relevance of the previously-mentioned theoretical numbers. To adequately compare the production of OPC 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 1, confirm the predicted energy and CO_2 savings.

In terms of energy, a 20 per cent saving was measured for the specific heat consumption (SHC). This SHC saving is slightly lower than expected because the production rate of Solidia Clinker in the kiln was not fully optimised. Room for considerable improvement in Solidia Clinker production remains. Measurements at the stack of the plant confirmed that conversion from OPC production to Solidia Cement production resulted in CO_2 emissions savings of about 30 per cent. Measured reductions in the SHC and CO_2 emissions during the industrial Solidia Clinker production campaign matched predictions. Further improvements are expected as Solidia Clinker production is further optimised.

CO_2 curing of Solidia Concrete

The low-lime, CS and C_3S_2 phases 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:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \quad \text{[Eq 1]}$$

$$Ca_2Si_3O8 + 2CO_2 \rightarrow 2CaCO_3 + 3SiO_2 \quad \text{[Eq 2]}$$

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), parameters well within the capabilities of most precast concrete manufacturers.

Unlike the hydration reaction in OPC-based concrete, the carbonation reaction in Solidia Cement-based concrete is a relatively-rapid process. For example, Solidia Cement-based pavers can be cured to their full potential within 24h.

A microstructural evaluation of a Solidia Cement-based paver shows the reaction products calcite ($CaCO_3$) and amorphous silica (SiO_2) as well as uncarbonated cement particles (see 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 OPC-based systems, concrete products hardened with CO_2-cured Solidia Cement do not consume water. In fact, up to 90 per cent 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.

Application and performance in pavers

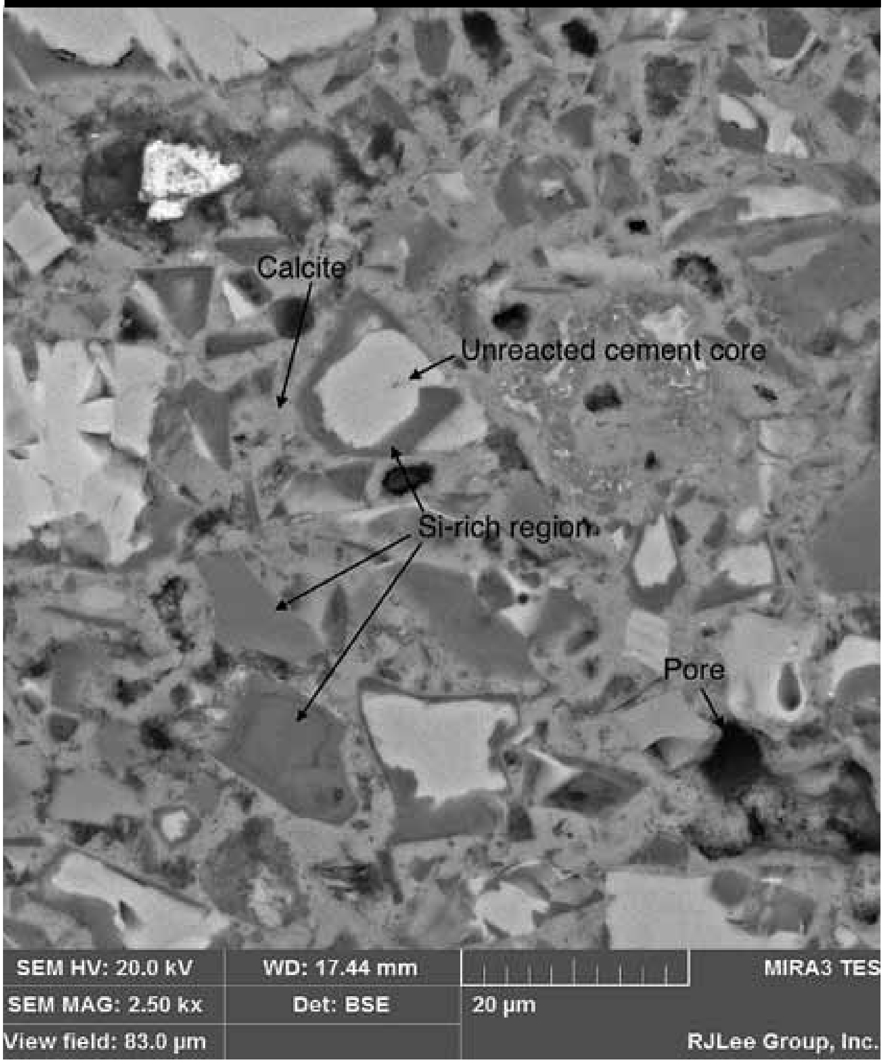
The application of Solidia Cement was demonstrated at an industrial scale. This was carried out at a commercial OPC-paver manufacturing facility. Solidia Cement was added to the existing production line, using all of the existing standard equipment for storage, mixing, pressing and material handling. The only change to the plant process equipment was the modification of the curing chamber to allow for the introduction of CO_2 for Solidia Cement carbonation as well as conditioning of the gas – the process where Solidia Cement is cured and CO_2 is consumed (typically a 24h process). The mix design for the OPC-paver was slightly

Low-energy Solidia Cement[TM] is naturally white in colour

Table 2: paver compressive strength and porosity results

Sample ID	Compressive strength (psi)	Average compressive strength (psi)	Standard deviation	Porosity (%)	Average porosity (%)
SC#1	10,027			NA	
SC#2	8049	8730	918	15.0	15.9
SC#3	8113			16.7	
OPC#1	10,978			12.8	
OPC#2	11,883	11,522	391	12.0	11.5
OPC#3	11,705			9.6	

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 the white area is an unreacted cement particle ($CaO.SiO_2$)



modified by changing admixtures and included a one-to-one replacement of OPC with Solidia Cement.

Solidia pavers (6 x 9 x 2.5in) as well as commercially-available OPC pavers of similar dimension were tested for compressive strength, porosity and freeze-thaw durability in salt water. These tests were independently carried out by the New York State Department of Transportation (NYSDOT). The compressive strength and porosity results are shown in Table 2. The Solidia paver results presented here are from one of the early trials. Since, significant improvements have been made producing average compressive strength of 10,000 psi consistently.

The freeze-thaw tests were carried out following a test procedure developed by NYSDOT with 10 per cent NaCl and up to 25 cycles. Both Solidia and OPC pavers passed this severe test with minimum mass loss.

Conclusion

Solidia Cement is a non-hydraulic cement that is being produced on a commercial scale at an existing OPC cement plant in North America, using the same raw materials as OPC production. When compared to OPC, Solidia Cement requires 20-30 per cent less energy to produce, emits as much as 30 per cent less CO_2 during calcination and consumes CO_2 during the curing process. Together, this leads to an overall reduction in the carbon footprint of up to 70 per cent when compared to OPC.

Concrete pavers using Solidia Cement are presently being commercially produced in an existing commercial OPC paver manufacturing facility. Production occurs side-by-side with OPC concrete pavers, using existing equipment together with a modified curing chamber to introduce CO_2 during curing. Solidia pavers, evaluated by a certified third party, have strength and durability performance similar to OPC pavers. ■

REFERENCES

[1] MADLOOL, N A, SAIDUR, R, HOSSAIN, M S AND RAHIM, N A (2011) 'A critical review on energy use and savings in the cement industries' in: *Renewable and Sustainable Energy Reviews,* 15 (4), p2042-2060.

[2] *Carbonbrief.com*. Accessed: 2019-05-07.

[3] TAYLOR, HFW (1997) *Cement Chemistry, 2nd Edition*. London, UK: Thomas Telford, p58-59.

[4] MEYER, V, SAHU, S AND DUSTNER, A (2020) 'Solid properties' in: International Cement Review, March, p45-47.

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