

## Solidia Cement an example of Carbon Capture and Utilization

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### Abstract

Solidia Cement is a non-hydraulic binder that is produced in existing cement kilns using the same raw material as Portland cement (PC). The key difference is that the Solidia binder is produced using less limestone and at lower kiln burning temperatures. This translates into reduced CO<sub>2</sub> emissions during cement manufacturing (30% reduction). The Solidia concrete solution consists in a mix between the binder, aggregates, sand, water that is reacted with CO<sub>2</sub> to form a durable matrix. The curing process captures up to 300 kg of CO<sub>2</sub> per ton of cement used. Together, the Solidia cement and concrete reduce the CO<sub>2</sub> footprint by down to 70% when compared to conventional cement and concrete products.

The advantages to precasters are multiple also:

- Full strength in concrete parts achieved within 24 hours thus allowing just-in-time manufacturing and a significant reduction in inventory cost.
- Concrete waste from forming process is almost eliminated and equipment cleanup time is significantly reduced because the concrete does not harden until it is exposed to CO<sub>2</sub>.
- The final precast products present better aesthetics than PC-based concretes (no efflorescence, better pigmentation, and better color grading).

The first industrial demonstrations (cement production and precast applications) were achieved and confirm the CO<sub>2</sub> and energy savings announced.

**Keywords:** CO<sub>2</sub> emissions reduction, cement, concrete, precast

## 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 mixture of ground limestone, clay and corrections 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<sub>2</sub>). The cement industry accounts for approximately 5% of global anthropogenic carbon dioxide (CO<sub>2</sub>) emissions.

A modern cement plant releases ~810 kg of CO<sub>2</sub> per tonne of cement clinker produced. More than 60% of this CO<sub>2</sub> comes from the chemical decomposition, or calcination, of limestone (CaCO<sub>3</sub> → CaO + CO<sub>2</sub>). The balance comes from the combustion of fossil fuel to heat the kiln.

The International Energy Agency (IEA) has created a roadmap to guide the long-term sustainability efforts of the cement industry. As per this roadmap, the cement industry must reduce its total CO<sub>2</sub> emissions from 2.0 Gt in 2007 to 1.55 Gt by 2050. Nevertheless, over this same period, cement production is projected to grow from 2.6 Gt to 4.4 Gt [1].

With the implementation of energy-efficient production technologies, the use of alternative fuels, the development of new, low-lime cement chemistries, and the reduction of clinker factor in cement through addition of supplementary cementitious materials, the cement industry has tried to attain the IEA objective. However, even the combined effect of these initiatives is likely to fall far short of the IEA goals.

LafargeHolcim has long been working on many options for CO<sub>2</sub> emissions reduction in the cement industry. The common levers are related to performance: SHC, waste fuels (biomass), reduction in clinker factor. This presentation deals with breakthrough levers i.e. CCUS & New Low-CO<sub>2</sub> products development.

In order to get a good feeling of the maturity on different technologies, LafargeHolcim investigated and has already been involved in many projects related to CCUS: from CO<sub>2</sub> capture to storage and/or reuse. In order to reduce the costs associated to all these solutions, LafargeHolcim decided to focus on low-CO<sub>2</sub> products based on mineral carbonation.

Since 2013, LafargeHolcim signed a joint development and commercial agreement with Solidia Technologies<sup>®</sup> in order to develop mineral carbonation in precast industry mainly.

Solidia Cement<sup>™</sup>, a new calcium silicate-based cement (CSC) product developed by Solidia Technologies<sup>®</sup>, is a reduced-lime, non-hydraulic calcium silicate cement capable of significantly reducing the energy requirement and CO<sub>2</sub> 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<sub>2</sub> emissions and energy consumption. Additionally, this CSC cures via a reaction with gaseous CO<sub>2</sub>, thus offering the ability to permanently and safely sequester CO<sub>2</sub>.

The CO<sub>2</sub> savings obtained in the whole chain and two precast applications are presented in this paper.

## **1. Energy requirements and CO<sub>2</sub> emissions during cement manufacturing**

Both PC and CSC manufacturing require significant amounts of energy and emit significant quantities of CO<sub>2</sub>. 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 processing of CSC, the differences in energy consumption and CO<sub>2</sub> emissions are discussed below.

### **1.1 Portland cement**

#### **1.1.1 Energy requirements**

In modern cement plants, the production of one tonne of PC clinker requires heat energy totaling 3.2 GJ [4]. From a theoretical perspective, the thermal energy consumed in producing one ton of PC clinker is about 1.757 GJ [5]. 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 the CSC clinker thermal energy is expected to be lower than for OPC.

#### **1.1.2 CO<sub>2</sub> emissions**

EPA's historical estimates indicate that 900 to 1,100 kg of CO<sub>2</sub> is emitted for every ton 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 [6]. Even the most efficient Portland cement facilities report CO<sub>2</sub> emission ~810 kg/ton of clinker [7].

The CO<sub>2</sub> emissions from chemical decomposition of calcium carbonate depend on the lime content of the clinker product (~70% for PC). The CO<sub>2</sub> emissions from pyro-processing depend on the fossil fuel type (for example, ~3.0 tonnes of CO<sub>2</sub> 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<sub>2</sub> is not considered here. Table 1 compares the sources of CO<sub>2</sub> emission in the production of cement clinker.

## 1.2 Calcium silicate cement

### 1.2.1 Energy requirements

The total lime content of CSC 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. CSC and PC are roughly equivalent in terms of the enthalpy required to decompose the clay component of the raw meal 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 CSC clinker is expected to be about 1.051 GJ/t, almost 40% lower than that of PC clinker.

From a practical perspective, CSC 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%.

### 1.2.2 CO<sub>2</sub> emissions

The low-lime content of CSC clinker enables two separate opportunities to reduce the CO<sub>2</sub> emissions associated with cement production:

- Reduction in the lime content of the cement from approximately 70% (for PC) to approximately 50% (for CSC) enables a proportionate reduction in CO<sub>2</sub> emission (540 kg/t PC clinker vs. 375kg/t for CSC clinker),
- Reduction of 200°C in the clinker temperature of 1450°C vs.1250°C, enables CO<sub>2</sub> emissions reduction coming from fossil fuels (270 kg per ton for PC clinker vs. 190 kg per ton of CSC clinker),

The total CO<sub>2</sub> emissions associated with PC and CSC manufacturing are compared in Table 1. Note that CSC clinker production offers the potential to reduce CO<sub>2</sub> release associated with cement manufacturing by as much as 30%.

Table 1: CO<sub>2</sub> emissions during the production of PC and CSC clinker (Note: The CO<sub>2</sub> associated with the electrical energy usage in the cement making process is not considered.)

CO <sub>2</sub> emissions from:	Per ton of PC clinker	Per ton of CSC clinker
Limestone decomposition	540 kg	375 kg
Fossil fuel combustion	270 kg	190 kg
Total CO <sub>2</sub> emissions	810 kg	565 kg

### 1.2.3 Energy requirements and CO<sub>2</sub> emissions during production of Solidia Cement 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 preheated kiln. Approximately 5000 tons of Solidia Cement clinker was produced. The raw mix was adapted to meet the chemical specifications and the wollastonite (CS) and rankinite (C<sub>3</sub>S<sub>2</sub>) clinker phases of Solidia Cement.

During the production campaign, CO<sub>2</sub> 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 Cement clinker, stable production periods were taken into account for each cement type, not only in the same plant, but in the same kiln. The measurements, highlighted in Table 2, confirm the predicted energy and CO<sub>2</sub> savings.

Table 2: Industrial Solidia Cement 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 <sub>2</sub>	%	24.4	14.2
CO <sub>2</sub> emissions	Nm <sup>3</sup> /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 Cement clinker in the kiln was not yet equal to that of PC clinker. It was noted that the Solidia Cement clinker behavior in the kiln is different than that of PC clinker. Room for considerable improvement in Solidia Cement clinker production remains.

It should also be noted that the typical plant fuel utilization was modified for the Solidia Cement clinker production. Only the main burner, fed with petcoke, coal and recycled plastic, was used. 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<sub>2</sub> emissions during Solidia Cement 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<sub>2</sub> emission savings of about 30%. In conclusion, measured reductions in the SHC and CO<sub>2</sub> emissions during the first industrial Solidia Cement clinker production campaign match predictions. Further improvements of these parameters are expected as clinker production is optimized.

## 2 CONCRETE MIXING, FORMING AND CURING PROCESSES

PC- and CSC-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 behavior of the concrete mix while it is in the plastic stage.

Both PC- and CSC-based concretes can be mixed in standard concrete mixers. Similarly, they

can be formed into the final concrete part shape by the same processes and equipment. These processes include casting, extrusion, rolling and pressing.

PC- and CSC-based concrete differ in the chemical process by which they set and harden. These processes are collectively referred to as “curing.”

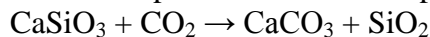
## 2.1 PC-based concrete curing

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)<sub>2</sub> 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.

The microstructure of hydrated PC paste shows that two distinct types of calcium silicate hydrate form in the system: an “inner product” and an “outer product.” The outer product forms early in the curing process, is highly porous, and precipitates in the open spaces within the concrete structure. The inner product forms late in the curing process, is denser than the outer product, and forms near the original cement particles.

## 2.2 Calcium silicate cement-based concrete curing

The low-lime, CS and C<sub>3</sub>S<sub>2</sub> components of CSC do not hydrate when exposed to water during the concrete mixing and forming processes. Formed CSC-based concrete parts will not cure until they are simultaneously exposed to water and gaseous CO<sub>2</sub>. CSC-based concrete curing is a mildly exothermic reaction in which the low-lime calcium silicates in the CSC react with CO<sub>2</sub> in the presence of water to produce calcite (CaCO<sub>3</sub>) and silica (SiO<sub>2</sub>) as follows:



The above reaction processes require a CO<sub>2</sub>-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 CSC-based concrete is a relatively speedy process. Full curing of CSC-based concrete is limited only by the ability of gaseous CO<sub>2</sub> 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 CSC-based concrete shows the reaction products calcite (CaCO<sub>3</sub>) and amorphous silica (SiO<sub>2</sub>) as well as un-carbonated cement particles. A typical microstructure of CO<sub>2</sub>-cured CSC-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<sub>2</sub>-cured CSC do not consume water. In fact, up to 90% of the water used in the CSC-based concrete formulation can be recovered during the CO<sub>2</sub>-curing process. The remaining water is retained in the cured concrete.

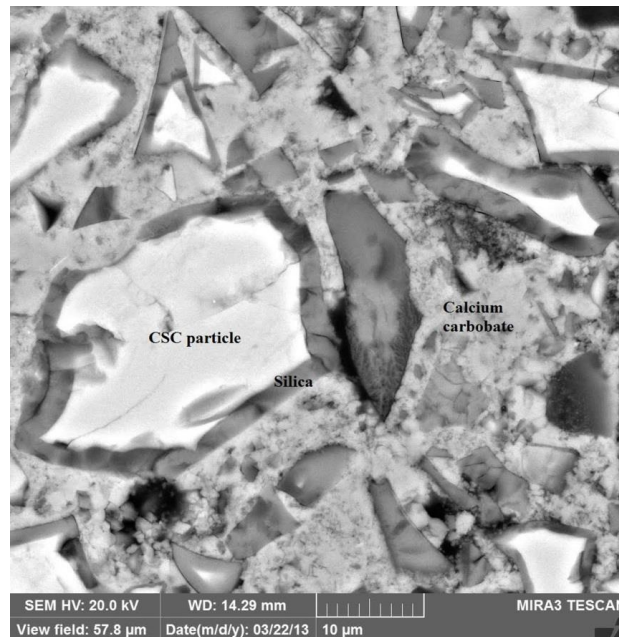


Figure 1: Microstructure of CO<sub>2</sub>-cured CSC (light grey area is calcite (CaCO<sub>3</sub>), dark grey area is amorphous silica (SiO<sub>2</sub>), and white area is unreacted CSC (CaO·SiO<sub>2</sub>).)

### 2.3 CO<sub>2</sub> sequestration in calcium silicate cement-based concrete

The unique ability of CSC to avoid hydration and cure via a reaction with gaseous CO<sub>2</sub> opens the possibility for the permanent sequestration of CO<sub>2</sub> in cured concrete structures. The curing processes, described in Section 2.2, enables CSC-based concrete to sequester up to 300 kg of CO<sub>2</sub> per ton of CSC used in the concrete formulation. The CO<sub>2</sub> used in the curing process and captured within CSC-C is industrial-grade CO<sub>2</sub> sourced from waste flue gas streams.

CO<sub>2</sub> sequestration in two fully-cured, CSC-based concrete forms was studied:

1. Pavers of dimensions 6 cm thick x 15 cm wide x 23 cm long paver, with a dry concrete formulation of 14.7 wt. % CSC, 41.6 wt. % aggregate, 0.2 wt. % pigment, and 43.5 wt. % sand; and,
2. A hollow core slab of dimensions 20 cm thick x 115 cm wide x 10 m long, with a dry concrete formulation of 15 wt. % CSC, 44 wt. % aggregate, and 41 wt. % sand.

Small core specimens, representative of the overall concrete microstructure, were drilled from the concrete forms and exposed to a high temperature protocol to determine the CO<sub>2</sub> and H<sub>2</sub>O amounts sequestered. The mass difference after water removal is assimilated to captured CO<sub>2</sub>. The specimens taken from the CSC-based concrete paver exhibited an average mass gain of ~3.4% due to CO<sub>2</sub> sequestration. This translates to 236 kg of CO<sub>2</sub> sequestered per ton of CSC in the paver concrete formulation. The specimens from the concrete hollow core slab exhibited an average mass gain of ~3.3%. This translated to 220 kg of CO<sub>2</sub> sequestered per ton of CSC in the slab concrete formulation.

## 4 Conclusions

1. The low-lime content of CSC clinker enables two separate opportunities to reduce the CO<sub>2</sub> emissions at the cement plant:
  - The CO<sub>2</sub> released from the chemical decomposition of limestone: 540 kg per ton of PC clinker to about 375 kg of CO<sub>2</sub> per ton of CSC clinker.

- The clinkering temperatures reduction of about 200°C: 270 to 190 kg CO<sub>2</sub> per ton clinker.

This makes it possible to reduce the CO<sub>2</sub> emissions from ~810 kg/ton of PC clinker to ~565 kg/ton of CSC clinker. A 30% CO<sub>2</sub> 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).

2. The unique ability of CSC to avoid hydration and cure via a reaction with gaseous CO<sub>2</sub> opens the possibility for the permanent sequestration of CO<sub>2</sub> in cured concrete structure. It has been demonstrated that the curing process enables CSC-C to sequester over 230 kg of CO<sub>2</sub> per ton used in the concrete formulation.
3. Depending on the specific ratios of sand, aggregate and CSC used in the concrete mix, the final CSC-based concrete part may contain in excess of 3 wt.% of sequestered CO<sub>2</sub>.
4. The combined effects of 1, 2, and 3 above, replacement of PC by CSC offers the potential to reduce the carbon footprint associated with the production and use of cement by up to 60%.
5. Unlike PC-based, concrete products hardened with CO<sub>2</sub>-cured CSC do not consume water. Thus, if necessary, the process water used in the CSC-based concrete formulation can be recovered during the CO<sub>2</sub>-curing process.

### Acknowledgements

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Additional data will be available with the actions foreseen in Solid LIFE project, to continue to prove the environmental benefits reached by the technology.

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