

Environmental Impact of Carbonated Calcium Silicate Cement-Based Concrete

N. DeCristofaro¹, V. Meyer², S. Sahu³, J. Bryant⁴ and F.Moro⁵

^{1,3,4} Solidia Technologies,
11 Colonial Drive, Piscataway, NJ-08854, USA
e-mail: ndecristofaro@solidiatech.com

^{2,5} LafargeHolcim Research Centre
95, rue du Montmurier, BP 15, 38291 Saint-Quentin Fallavier, France
e-mail: vincent.meyer@lafargeholcim.com

SUMMARY: Solidia Technologies and LafargeHolcim have collaborated on the development and commercialization of an innovative process allowing mineral sequestration of CO₂ through the carbonation of calcium silicate-based cement (CSC). In advancing international efforts to meet CO₂ emissions reduction goals, the success of this technology is predicated on three major components: (1) the extent of CO₂ emission reductions in cement manufacturing; (2) the capacity of CSC materials to efficiently store CO₂ during concrete curing; and (3) wide-scale adoption of this technology within the concrete industry.

The potential for emissions reductions and CO₂ storage have already been demonstrated. The production of CSC, as a replacement for Portland cement (PC), can reduce CO₂ emissions at a cement plant by decreasing energy and limestone consumption. Reductions in CO₂ emission up to 30% (~250 kg per tonne of cement clinker) have been predicted and measured.

CSC carbonation during the curing of concrete occurs extremely rapidly. Full hardness in CSC-based concretes can be achieved within 24 hours, during which CO₂ is permanently and safely sequestered in the form of calcium carbonate. Sequestration of up to 300 kg of CO₂ per tonne of CSC in the concrete has been predicted while values in excess of 230 kg of CO₂ per tonne of CSC have been measured.

Taken together, these two factors enable the CO₂ footprint associated with the production and use of cement by up to 70%.

KEY WORDS: cement, concrete, CO₂, mineral carbonation

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 (CO₂). The cement industry accounts for approximately 5% of global anthropogenic carbon dioxide (CO₂) emissions.

A modern cement plant releases ~810 kg of CO₂ per tonne of cement clinker produced. More than 60% of this CO₂ comes from the chemical decomposition, or calcination, of limestone ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$). The balance comes from the combustion of fossil fuel to heat the kiln. A small amount of additional CO₂, approximately 90 kg per tonne of cement, is associated with the electricity required to operate the clinkering process, to grind and transport materials throughout the process, and is not considered in this paper.

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 CO₂ 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.

Solidia Cement™, a new calcium silicate-based cement (CSC) product developed by Solidia Technologies®, is poised to address this unanswered challenge [2,3]. Solidia Cement is a reduced-lime, non-hydraulic calcium silicate cement capable of significantly reducing the energy requirement and CO₂ 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 CO₂ emissions and energy consumption. Additionally, this CSC cures via a reaction with gaseous CO₂, thus offering the ability to permanently and safely sequester CO₂.

2 ENERGY REQUIREMENTS AND CO₂ EMISSIONS DURING CEMENT MANUFACTURING

Both PC and CSC manufacturing require significant amounts of energy and emit significant quantities of CO₂. 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 CO₂ emissions are discussed below.

2.1 Portland cement

2.1.1 Energy requirements

In modern cement plants, the production of one tonne of PC clinker requires heat energy totalling 3.2 GJ [4]. From a theoretical perspective, the thermal energy consumed in producing one tonne of PC clinker is about 1.757 GJ. The breakdown of that enthalpy into the various pyro-processing steps is provided in Table 1 [5]. While the overall process is endothermic, note that the process step in which the cement phases are formed is exothermic. 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. As can be seen from Table 1, the pyro-processing step that consumes the most heat energy is the endothermic decomposition of calcium carbonate (calcination).

Table 1: Theoretical enthalpy of formation of 1 tonne of clinker. PC clinker values are from [5]; CSC clinker values are based on a model clinker and may vary slightly depending on the phase composition.

Reaction	PC Clinker ΔH (GJ)	CSC Clinker ΔH (GJ)
Calcination	+2.138	+1.514
Decomposition of clay	+0.063	+0.075
Formation of cement phases	-0.377	-0.538
Total	1.757	1.051

2.1.2 CO₂ emissions

EPA's historical estimates indicate that 900 to 1,100 kg of CO₂ is 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 [6]. Even the most efficient Portland cement facilities report CO₂ emission ~810 kg/tonne of clinker [7].

There are three sources of CO₂ emission in cement production:

1. the chemical decomposition of the calcium carbonate within the limestone
 $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$;
2. the combustion of fossil fuel to heat the kiln for pyro-processing the raw meal; and,
3. the generation of electricity needed to drive the kiln, the grinding mills and materials transportation systems.

As stated earlier, the CO₂ associated with the generation of electricity are not considered here.

The CO₂ emissions from chemical decomposition of calcium carbonate depend on the lime content of the clinker product (~70% for PC). The CO₂ emissions from pyro-processing depend on the fossil fuel type (for example, ~3.0 tonnes of CO₂ per tonne of coal consumed). The carbon footprint from electricity consumption for cement production is about 90 kg/tonne in the US. Table 2 compares the sources of CO₂ emission in the production of cement clinker.

2.2 Calcium silicate cement

2.2.1 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 enthalpy of formation of CSC clinker is expected to be about 1.051 GJ/t, almost 40% lower than that of PC clinker (see Table 1).

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%. This may translate into additional savings in the electrical energy required for clinker grinding.

2.2.2 CO₂ emissions

The unique, low-lime content of CSC clinker enables two separate opportunities to reduce the CO₂ emissions associated with cement production.

The first opportunity can be traced to the chemical decomposition of the calcium carbonate in limestone. Reduction in the lime content of the cement from approximately 70% (for PC) to approximately 50% (for CSC) enables a proportionate reduction in this form of CO₂ emission. Thus, the CO₂ released from the chemical decomposition of limestone will be reduced from 540 kg per tonne of PC clinker to about 375 kg of CO₂ per tonne of CSC clinker.

The second opportunity, also enabled by the low-lime chemistry of CSC, allows the reaction between lime and silica to occur at a clinker temperature of 1250°C, which is 200°C lower than the temperature required for PC clinker formation. During the production of CSC, the CO₂ emissions associated with the burning of fossil fuel to heat the kiln are expected to be 190 kg per tonne of clinker, compared to 270 kg per tonne for PC clinker.

The total CO₂ emissions associated with PC and CSC manufacturing are compared in Table 2. Note that CSC clinker production offers the potential to reduce CO₂ release associated with cement manufacturing by as much as 30%.

Table 2: CO₂ emissions during the production of PC and CSC clinker (Note: The CO₂ 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 CSC clinker
Limestone decomposition	540 kg	375 kg
Fossil fuel combustion	270 kg	190 kg
Total CO ₂ emissions	810 kg	565 kg

2.2.3 Energy requirements and CO₂ 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 tonnes of Solidia Cement clinker were produced based on raw materials available in the quarry of the plant. The raw mix was adapted to meet the chemical specifications and the wollastonite (CS) and rankinite (C₃S₂) clinker phases of Solidia Cement. This was accomplished by reducing the limestone content and favouring the silica source

During the production campaign, CO₂ 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 3, confirm the predicted energy and CO₂ savings.

Table 3: 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 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 Cement clinker in the kiln was not yet equal to that of PC clinker. It was noted that the Solidia Cement clinker behaviour 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 during Solidia Cement production. 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 CO₂ 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 CO₂ emission savings of more than 30%.

In conclusion, measured reductions in the SHC and CO₂ emissions during the first industrial Solidia Cement clinker production campaign match predictions. Further improvements of these parameters are expected as clinker production is optimized.

3 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."

3.1 PC-based concrete curing

When PC is exposed to water, a series of hydration reactions initiate with a release of a significant amount of heat. These hydration reactions are responsible for the setting and hardening of PC-based concrete. In

a very simplistic way, the curing process involves reactions between:

- C_3A , gypsum and water, to produce ettringite;
- C_3S and water, to produce a complex calcium silicate hydrate and calcium hydroxide; and,
- C_2S and water, which also yields calcium silicate hydrate and calcium hydroxide.

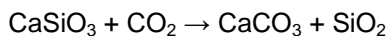
The complex calcium silicate hydrate is an amorphous phase wherein the Ca:Si ratio can vary during the hydration period.

The hydration of the calcium silicate components of Portland cement begins as soon as the PC is exposed to water, but proceeds at a relatively slow pace. 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.

3.2 Calcium silicate cement-based concrete curing

The low-lime, CS and C_3S_2 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_2 . CSC-based concrete curing is a mildly exothermic reaction in which the low-lime calcium silicates in the CSC react with CO_2 in the presence of water to produce calcite ($CaCO_3$) and silica (SiO_2) as follows:



The above reaction processes require a CO_2 -rich atmosphere. However, the process can be conducted at ambient gas pressures and at moderate temperatures ($\sim 60^\circ C$). 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_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 CSC-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 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 CO₂-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 CO₂-curing process. The remaining water is retained in the cured concrete and may be additionally recovered, if necessary. Assuming a water to cement ratio of 0.4, this implies that, if the 30 billion tons of concrete that was produced in 2011 was cured using CSC in place of PC, then the amount of water consumed or lost during the production of concrete could be reduced from an estimated 2.6 billion tons [8] to 0.45 billion tons.

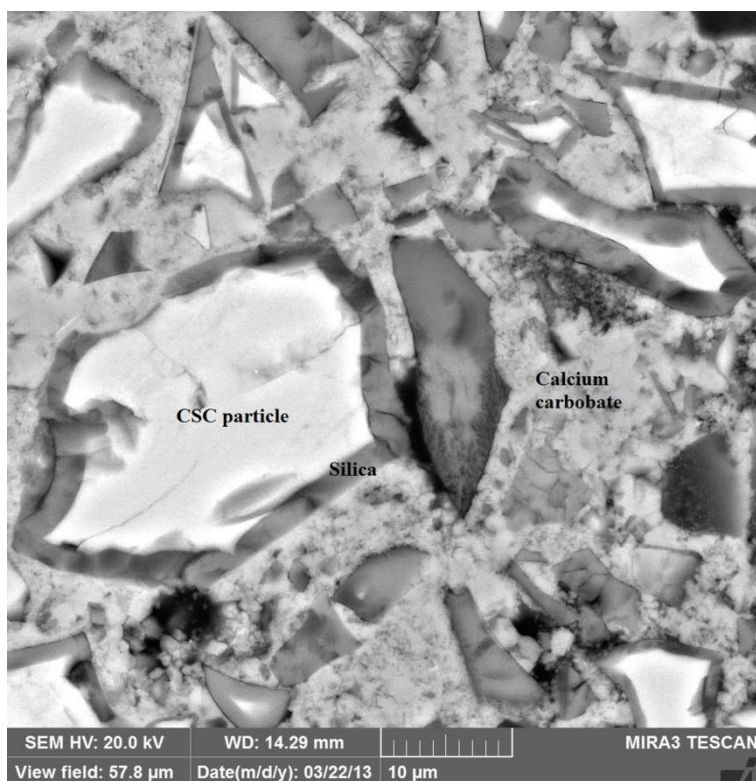


Figure 1: Microstructure of CO₂-cured CSC (light grey area is calcite (CaCO₃), dark grey area is amorphous silica (SiO₂), and white area is unreacted CSC (CaO·SiO₂.)

3.3 CO₂ sequestration in calcium silicate cement-based concrete

The unique ability of CSC to avoid hydration and cure via a reaction with gaseous CO₂ opens the possibility for the permanent sequestration of CO₂ in cured concrete structures. The curing processes, described in Section 3.2, enables CSC-based concrete to sequester up to 300 kg of CO₂ per tonne of CSC used in the concrete formulation. The CO₂ used in the curing process and captured within CSC-C is industrial-grade CO₂ sourced from waste flue gas streams.

CO₂ 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 the procedure described below.

To calculate the amount of CO₂ sequestered within a CSC-based concrete sample, the test specimen is oven dried at 105°C for 72 hours to remove any residual moisture and placed in a furnace at 550°C for 4 hours to remove any remaining bound water or organic material. Once fully dried, the specimen is heated to 950°C at a ramp up rate of 10°C/min. After 3 hours at 950°C, the specimen is returned to 105°C and mass loss was recorded. This mass loss was then corrected to account for mass loss from the sand and aggregate, exposed to the same procedure. The remaining mass difference represents the amount of CO₂ sequestered during the curing process and is attributed to the thermal decomposition of CaCO₃, which is the primary reaction product of CSC carbonation.

The specimens taken from the CSC-based concrete paver exhibited an average mass gain of ~3.4% due to CO₂ sequestration. This translates to 236 kg of CO₂ sequestered per tonne 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 CO₂ sequestered per tonne of CSC in the slab concrete formulation.

4 CONCLUSIONS

1. The unique, low-lime content of CSC clinker enables two separate opportunities to reduce the CO₂ emissions at the cement plant. The CO₂ released from the chemical decomposition of limestone will be reduced from 540 kg per tonne of PC clinker to about 375 kg of CO₂ per tonne of CSC clinker. Additionally, the low-lime chemistry of CSC allows the reaction between lime and silica to occur at temperatures 200°C lower than that required for PC clinker formation, reducing the CO₂ emissions associated with the burning of fossil fuel from 270 to 190 kg per tonne. This makes it possible to reduce the CO₂ emissions from ~810 kg/tonne of PC clinker to ~565 kg/tonne of CSC clinker. A 30% CO₂ 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). Production improvements remain to be done to reach the value assessed theoretically (30%). Nevertheless for a first industrial trial, these values remain extremely promising.
2. The unique ability of CSC to avoid hydration and cure via a reaction with gaseous CO₂ opens the possibility for the permanent sequestration of CO₂ in cured concrete structure. It has been demonstrated that the curing process enables CSC-C to sequester over 230 kg of CO₂ per tonne of CSC used in the concrete formulation. The CO₂ used in the curing process and captured within CSC-based concrete is industrial-grade CO₂ sourced from waste flue gas streams.
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 CO₂.
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 70%.

5. Unlike PC-based, concrete products hardened with CO₂-cured CSC do not consume water. Thus, if necessary, the process water used in the CSC-based concrete formulation can be recovered during the CO₂-curing process.

ACKNOWLEDGMENTS

This paper deals with cement and concrete production done in North America.

In June 2016, the European LIFE program provided the award grant N° LIFE15 CCM/FR/000116 to the Solid LIFE project. This grant will fund the Solid LIFE partners (LafargeHolcim, Solidia Technologies® and Building Research Establishment) efforts to develop and deploy this technology within Europe. The authors acknowledge the European Union for this funding.

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

REFERENCES

- [1] Barcelo, L. et al : Cement and Carbon Emission, *Materials and Structures* 47 (2013) 6, pp. 1055-1065, 1871-6873
- [2] Riman R.E. & Atakan V.: Systems and methods for carbon capture and sequestration and compositions derived therefrom. *US Patent* 8,114,367 (2012)
- [3] Riman R.E. et al : Bonding element, bonding matrix and composite material having the bonding element, and method of manufacturing thereof. *US Patent Application* Publication US 2013/0122267., May 16 (2013).
- [4] Madlool, N.A. et al : A critical review on energy use and savings in the cement industries, *Renewable and Sustainable Energy Reviews* 15 (2011) 4, pp. 2042-2060, ISSN 1364-0321
- [5] Taylor H.F.W.: *Cement Chemistry*, 2nd Edition, Thomas Telford, ISBN 978-0727725929, (1997)
- [6] Environmental Protection Agency, Washington, DC : AP42 - Compilation of air pollutant emission factors, Vol. 1; Stationary point and area sources (2005). Available from <https://nepis.epa.gov/> Accessed: 2017-03-24
- [7] Marceau M.L. et al : Life Cycle Inventory of Portland Cement Manufacture, PCA R&D Serial No. 2095b, Available from <https://www.nrmca.org/> Accessed: 2017-03-24
- [8] U.S. Geological Survey (2012) USGS Mineral commodity summaries 2012, ISBN 978-1-4113-33499.