CO_2-Reducing Cement

Nick DeCristofaro and Sada Sahu, Solidia Technologies®, USA, discuss a low CO_2 alternative to Portland cement.

Abstract

Solidia Cement™ is a non-hydraulic cement composed primarily of low lime-containing silicate phases such as wollastonite/pseudowollastonite ($CaO{\cdot}SiO_2$) and rankinite ($3CaO{\cdot}2SiO_2$). This is in contrast to Portland cement clinker, which is composed of lime-rich phases such as alite ($3CaO{\cdot}SiO_2$), belite ($2CaO{\cdot}SiO_2$), tricalcium aluminate ($3CaO{\cdot}Al_2O_3$) and tetracalcium aluminoferrite ($4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$). Solidia cement clinker is produced at a temperature of approximately 1200 ˚C, which is roughly 250 ˚C lower than the firing temperature used in the manufacture of Portland cement clinker. These two features – low lime content and low firing temperature – allow Solidia cement clinker to be produced while emitting around 30% less carbon dioxide than its Portland cement counterpart.

When incorporated into a concrete product, Solidia cement undergoes a curing process that substitutes gaseous CO_2 for the large quantities of water used as a reactive hydration hardening agent in Portland cement-based concrete. Incorporated into concrete, 1 t of Solidia

cement will sequester up to 300 kg of CO_2 during the curing process.

Together, the reduced CO_2 emissions associated with Solidia cement manufacturing and the CO_2 sequestered during the curing of Solidia cement in concrete products, offer the opportunity to reduce the CO_2 footprint of finished concrete by as much as 70% when compared to Portland cement-based concrete.

Introduction

Each year an estimated 17 – 25 Gt of concrete is manufactured worldwide, making it one of the most utilised substances on earth. According to a study published by the US Department of Energy in 2010, the production of Portland cement accounts for more than 2.4 Gt, or ~5%, of global anthropogenic CO_2 emissions on an annual basis. This translates to about 810 kg of CO_2 emissions for each tonne of Portland cement clinker produced.

Figure 1. Ternary diagram showing the region of oxide mineral composition of Portland cement (PC) and Solidia cement (SC).

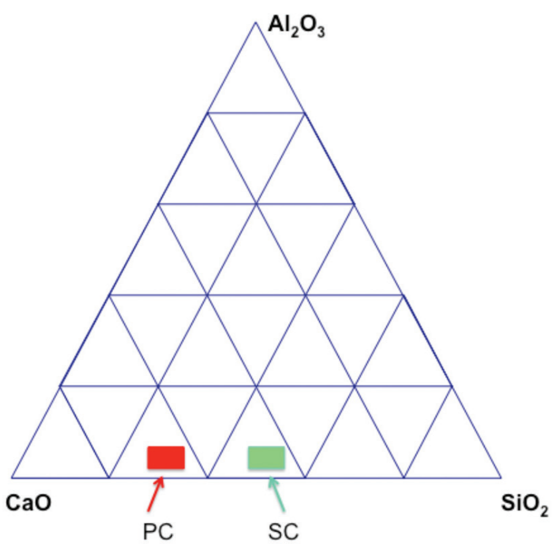
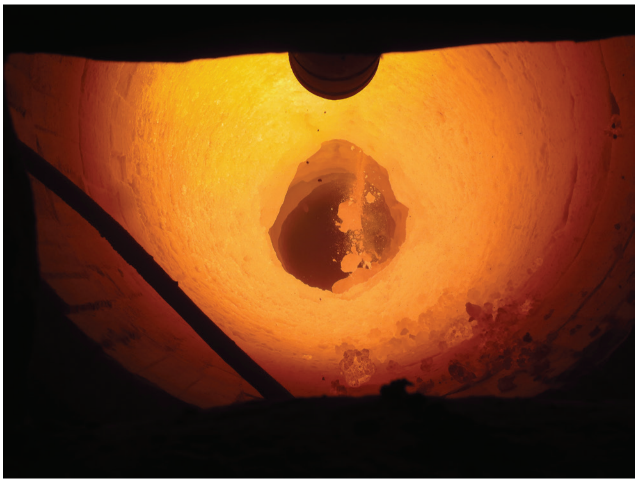


Figure 2. Formation of Solidia clinker nodules in a rotary kiln heated to 1200 °C.



Recognising the need to lower both its CO_2 and energy footprints, the cement industry actively participates in the World Business Council for Sustainable Development's Cement Sustainability Initiative. Characterised by a comprehensive CO_2 emissions reduction strategy – including the use of alternative fuels, supplementary cementitious materials and sequestration technologies – the initiative has made significant progress. However, there is still work to be done.

In recent years a number of new cement chemistries have been introduced in attempts to reduce the CO_2 footprint of Portland cement. These new cements have come from both within and outside of the traditional cement industry. They include products such as:

- Aether cement from Lafarge, which contains primarily belite (C_2S) and calcium sulfoaluminate (C_4A_3S).
- Celitement cement from Celitement GmbH, which is composed of calcium hydrosilicate.
- Novacem cement from Novacem Ltd, which is based on magnesium oxide extracted from naturally occurring magnesium silicates.
- E-Crete from Zeobond Pty Ltd, a concrete product that contains a geopolymer derived from the activation of flyash.

While these products all have unique attributes, their acceptance by the concrete industry and penetration into the concrete marketplace has been slow.

The keys to further "greening" cement and concrete industry operations include:

- Modification of cement production practices to reduce the emission of toxic substances and greenhouse gases, including CO_2.
- Access to a viable and efficacious CO_2 sequestration technology that will further alleviate the industry's undesirable environmental impact.
- Demonstration of an improved concrete end product that can serve as an alternative to traditional Portland cement concrete.
- Accomplishing the above while remaining compatible with the industry's existing infrastructure and operations.

Solidia cement offers an innovative approach to reducing CO_2 emissions arising from the production and use of a cement product, while addressing the four environmental challenges outlined above.

Solidia cement chemistry and synthesis

Solidia cement is composed primarily of low lime-containing silicate phases such as wollastonite/pseudowollastonite ($CaO{\cdot}SiO_2$) and rankinite ($3CaO{\cdot}2SiO_2$). In total, Solidia cement clinker contains between 42 and 48 wt% lime (CaO). This is in contrast to Portland cement, which is composed of lime-rich phases such as alite ($3CaO\cdot SiO_2$), belite ($2CaO\cdot SiO_2$), tricalcium aluminate ($3CaO\cdot Al_2O_3$) and tetracalcium aluminoferrite ($4CaO\cdot Al_2O_3\cdot Fe_2O_3$). Portland cement clinker typically contains approximately 65 – 70% lime. The general chemistries of the two cements, in terms of the CaO, SiO_2 and Al_2O_3 mineral concentrations, are compared in Figure 1.

The similarities and differences between the Solidia cement and Portland cement chemistries are significant. The two are similar in the fact that Solidia cement is made from the same raw materials, in the same manufacturing facilities and with the same unit operations as those used to manufacture Portland cement. Compatibility with the existing cement industry infrastructure is mandatory for the quick and efficient implementation of a new product.

The chemistry of Solidia cement differs from that of Portland cement as it allows for the reduction of CO_2 emissions associated with cement manufacturing and provides the basis for CO_2 sequestration during cement curing.

The manufacturing processes for both cements start by creating ground mixtures of limestone as a source of lime (CaO) and sand, clay or shale as a source of silica (SiO_2). These materials are present in the quarries located at or near virtually every cement plant worldwide. Lime-rich Portland cement typically requires a mixture that consists of more than 70% limestone. Low-lime Solidia cement requires only around 50% limestone. This difference offers two significant opportunities to reduce the CO_2 footprint of the cement clinker.

As the raw materials are heated in a cement manufacturing operation, the first significant chemical reaction begins at a temperature of about 800 ˚C. At this temperature the limestone decomposes, or calcines, to create lime and gaseous carbon dioxide according to this reaction:

- $CaCO_3$ --> CaO + CO_2 (g).

With the raw materials mixture for lime-rich Portland cement chemistry, the calcination reaction releases about 540 kg of CO_2/t of Portland cement clinker produced. The low-lime raw materials mixture used to make Solidia cement will emit approximately 375 kg of CO_2/t of Solidia cement clinker, representing a 30% reduction.

The next significant chemical reaction in cement production occurs at temperatures where the raw materials sinter, react and partially fuse together to form clinker nodules. For the Portland cement chemistry, this reaction occurs at approximately 1450 ˚C and results in the formation of the requisite alite, belite, tricalcium aluminate and tetracalcium aluminoferrite compounds. These compounds are produced in the following reactions:

- 3CaO + SiO_2 --> $3CaO\cdot SiO_2$ (alite).
- 2CaO + SiO_2 --> $2CaO\cdot SiO_2$ (belite).
- 3CaO + Al_2O_3 --> $3CaO\cdot Al_2O_3$ (tricalcium aluminate).
- 4CaO + Al_2O_3 + Fe_2O_3 --> $4CaO\cdot Al_2O_3\cdot Fe_2O_3$ (tetracalcium aluminoferrite).

The low-lime chemistry of Solidia cement allows raw materials to sinter, fuse and form clinker at approximately 1200 ˚C (Figures 2 and 3). The resulting wollastonite/pseudowollastonite and rankinite phases, which comprise Solidia cement clinker, occur according to the formulas:

- CaO + SiO_2 --> $CaO\cdot SiO_2$ (wollastonite/pseudowollastonite).
- 3CaO + $2SiO_2$ --> $3CaO\cdot 2SiO_2$ (rankinite).

The ability to produce Solidia cement clinker at a lower peak temperature than that required for Portland

Figure 3. Examples of Solidia clinker nodules produced in a rotary kiln heated to 1200 ˚C.

Table 1. **CO_2 emissions during the production of Portland cement and Solidia cement clinker**

CO_2 emissions	Per t of Portland cement clinker	Per t of Solidia cement clinker
Limestone decomposition	540 kg	375 kg
Fossil fuel combustion	270 kg	190 kg
Total CO_2 emissions	810 kg	565 kg
		(~30% reduction)

cement directly translates into reduced fossil fuel consumption. The fuel combustion required to produce 1 t of Portland cement clinker at a 1450 ˚C peak temperature will create approximately 270 kg of CO_2. One tonne of Solidia cement clinker formed at 1200 ˚C will emit as little as 190 kg of CO_2 from fuel combustion.

Table 1 compares the CO_2 emissions associated with limestone decomposition and fossil fuel combustion during the production of Portland cement and Solidia cement. In total, Solidia cement production can be accomplished with CO_2 emissions up to 30% less than that for Portland cement.

Carbon dioxide curing

Cements are typically classified as being hydraulic or non-hydraulic in nature. Portland cement falls into the hydraulic category; that is, it sets and hardens by hydration, a chemical reaction between the cement powder and water. When Portland cement comes into contact with water, the lime-rich alite and belite phases are converted into amorphous calcium silicate hydrate gel and calcium hydroxide. The hydration process proceeds relatively slowly. Portland cement-based concretes can take up to 28 days to reach the target hardness.

Solidia cement is a non-hydraulic cement. The low lime wollastonite/pseudowollastonite and rankinite phases react minimally with water. However, in the presence of liquid water and CO_2, the cement will react with CO_2 according to the general formulae:

- $CaO{\cdot}SiO_2 + CO_2 + H_2O \text{ --> } CaCO_3 + SiO_2 + H_2O$.
- $3CaO{\cdot}2SiO_2 + 3CO_2 + H_2O \text{ --> } 3CaCO_3 + 2SiO_2 + H_2O$. (Note that no water is consumed in this reaction).

The reaction products, namely calcite ($CaCO_3$) and amorphous silica (SiO_2), and the typical microstructure of the CO_2-cured cement are illustrated in Figure 4. The calcite and silica phases are thermodynamically stable to temperatures in excess of 500 ˚C, thereby offering an effective way to safely and permanently sequester CO_2. One tonne of Solidia cement, used as a bonding agent to set and harden concrete, can sequester up to 300 kg of CO_2 during the curing process. Unlike Portland cement-based concretes, concrete products that are hardened with CO_2-cured cement do not consume water.

Figure 4. Microstructure of CO_2-cured Solidia cement: the green area is calcite ($CaCO_3$), the red area is amorphous silica (SiO_2) and the yellow area is unreacted wollastonite ($CaO{\cdot}SiO_2$).

The reaction products and microstructure of CO_2-cured cement are able to effectively bond discrete aggregate particles, such as sand and crushed stone, into strong, durable concrete products. Concrete mixtures consisting of 50% aggregate, 33% sand and 17% Solidia cement can reach ASTM C39 compressive strengths in excess of 10 000 psi (69 MPa) and ASTM C78 flexural strengths in excess of 1100 psi (7.5 MPa). These strengths can be achieved in relatively short curing times compared to those of Portland cement-based concretes. For example, thin concrete products such as roof tiles (thickness ~10 mm) can reach target hardness within 10 hours. Thicker concrete products such as railroad sleepers/ties (thickness ~250 mm) can reach target hardness within 24 hours. Fast curing times offer the concrete manufacturer greater flexibility in equipment utilisation, inventory management and production planning.

Conclusion

The introduction of Solidia cement as a non-hydraulic, cementitious binder used to produce concrete products offers the potential to significantly reduce the CO_2 footprint of the cement and concrete industries. By manufacturing this new type of cement, the industry will be able to reduce its CO_2 emissions by consuming less limestone and fossil fuels. By setting and hardening their products with this cement, the concrete industry will be able to produce strong and durable products and reduce its manufacturing cycle time while permanently sequestering CO_2 in its products. The cement and concrete industries can realise these benefits while preserving both their raw materials supply chains and their capital investment in plants and equipment.

Solidia cement provides the cement and concrete industries with an alternative to traditional Portland cement that offers important sustainability and performance benefits:

- Cement production with 30% reduction in CO_2 emissions.
- A concrete curing process that safely and permanently sequesters CO_2 in quantities equal to 30% of the mass of cement used.
- Production of concrete products that will effectively reduce the CO_2 footprint associated with cement manufacturing and use by up to 70%.
- CO_2-cured concrete products that equal or exceed the performance of conventional water-cured Portland cement-based concretes.
- Accomplishing all of the above in a manner that is compatible with the raw materials supply chains, manufacturing equipment and unit processes of the cement and concrete industries.