Characterization of carbonated calcium silicate cement-based concrete

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INTRODUCTION

Concrete is the single most utilized man-made material in the world. A typical concrete is made by mixing ordinary Portland cement (OPC), water, and aggregates. OPC is a synthetic material made by burning a finely ground mixture of limestone, clay and correction materials in a rotary kiln at a sintering temperature of 1450°C. OPC manufacturing releases considerable amounts of CO_2.

Solidia Cement™, a new calcium silicate-based cement (CSC) 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. Additionally, this CSC cures via a reaction with gaseous CO_2, thus offering the ability to permanently and safely sequester CO_2.

The carbonation products of this cement is characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), and optical microscopy.

CO_2 EMISSIONS

EPA's historical estimates indicate that 900 to 1,100 kg of CO_2 are emitted for a ton of OPC clinker produced in the US. The exact amount depends on the type of raw materials, fuel type, and the energy efficiency of the cement plant [1]. Even the most efficient Portland cement facilities report CO_2 emissions of ~810 kg/ton of clinker.

The CO_2 emissions from chemical decomposition of calcium carbonate depend on the lime content of the clinker product (~70% for OPC). The CO_2 emissions from pyro-processing depend on the type of fossil fuel used. The CO_2-footprint from electricity consumption for cement production is about 90 kg/ton. In this calculation this CO_2 is not considered. The comparison of CO_2 emissions in the production of OPC and CSC clinker is provided in Table 1. Note that CSC clinker production offers the potential to reduce CO_2 release associated with cement manufacturing by as much as 30% [2].

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

CO_2 emissions from:	Per ton of OPC clinker	Per ton of CSC clinker
Limestone decomposition	540 kg	375 kg
Fossil fuel combustion	270 kg	190 kg
Total CO_2 emissions	810 kg	565 kg

INDUSTRIAL PRODUCTION OF CEMENT

Recently, a second industrial production of Solidia Cement was carried out in Europe after a successful production trial in USA by LafargeHolcim [3]. This production was carried out in a modern cement plant with preheater and precalciner. The raw mix was adapted to meet the chemical specifications and the wollastonite (CS) and rankinite (C_3S_2) clinker phases of Solidia Cement. The average phase composition of the clinker as determined by quantitative X-ray diffraction with Reitveld refinement is shown in Table 2

Table 2: The average phase composition of CSC clinker as measured by X-ray diffraction.

Phases	Formula	Conc. (wt. %)
Pseudowollastonite	$CaSiO_3$	51.0
Wollastonite	$CaSiO_3$	0.2
Rankinite	$Ca_3Si_2O_7$	13.1
Belite	Ca_2SiO_4	2.7
Amorphous	--	24.4
Melilite	$(Ca,Na,K)_2(Al,Mg,Fe^{2+})[(Al,Si)SiO_7]$	5.9
Brownmillerite	$Ca_2(Fe,Al)_2O_5$	0.6
Silica	SiO_2	1.9
Lime	CaO	0.4

CONCRETE FORMULATION AND CURING

A batch of pavers was made using the same mix design as OPC pavers but replacing OPC with CSC. After vibro-pressing the green pavers were cured in 100% CO_2 environment for 40h at elevated temperatures (< 100 °C). Post curing, the pavers were tested for compressive strength and resistance to freeze-thaw in salt solution. The average compressive strength was 10,380 psi (72 MPa). The pavers passed the freeze-thaw resistance test without any mass loss. It has been demonstrated that industrial production of pavers sequesters about 240 kg of CO_2 per ton of CSC cement [4].

CHARACTERIZATION

Phenolphthalein pH indicator is often used to determine the depth of carbonation in OPC concrete. When applied to a freshly cut/fractured surface of a field concrete the interior of the concrete creates a magenta color (pH = 12-13) and the surface zone is colorless (pH = 8.5-9). The colorless zone is the carbonated zone created due to atmospheric carbonation (left image, Figure 1). Using similar technique, the uniformity of carbonation of CSC-pavers is checked (right image, Figure 1). A freshly mixed CSC concrete has a pH of about 12; however, after carbonation the pH drops to about 9. The phenolphthalein pH indicator for the carbonated CSC concrete shows uniformly colorless throughout the cross section of the paver. This indicates that the binder is uniformly carbonated throughout the paver.

A thin section of the CSC-paver was made and examined under an optical microscope in various light modes such as plain-polarized light, cross-polarized light. An examination using transmitted cross-polarized light mode indicates the paste is composed of calcite and residual cement particles, Figure 2.

SEM examination of the polished surface shows that void spaces left from the mix water is filled with calcite ($CaCO_3$), a layer of silica-rich region is present surrounding the core, un-carbonated cement grains and silica-rich regions showing the imprint of original cement grains, Figure 3.

A CSC-paste sample was cured under the same CO_2 environment as the above-mentioned CSC-paver for powder X-ray diffraction (XRD) analysis. The main crystalline phases detected in the carbonated sample are calcite and residual cement phases.

CONCLUSIONS

The production of CSC typically emits about 30% less CO_2 than the production of Portland cement, and the total energy consumption is also about 30% less. Concretes made by carbonating CSC can achieve a reduction in the CO_2-footprint by 50-70% compared to conventional OPC-based concretes. This is achieved a) by reducing the CO_2 emitted during cement production from 810 kg per ton of OPC clinker to 565 kg per ton of CSC clinker and b) by consuming up to 300 kg of CO_2 per ton of this cement during the CO_2-curing.

The carbonation of the cement produces calcite ($CaCO_3$) and amorphous silica (SiO_2). The silica is present as a layer surrounding the partially reacted cement grain or maintains the structure of a completely reacted cement particle.

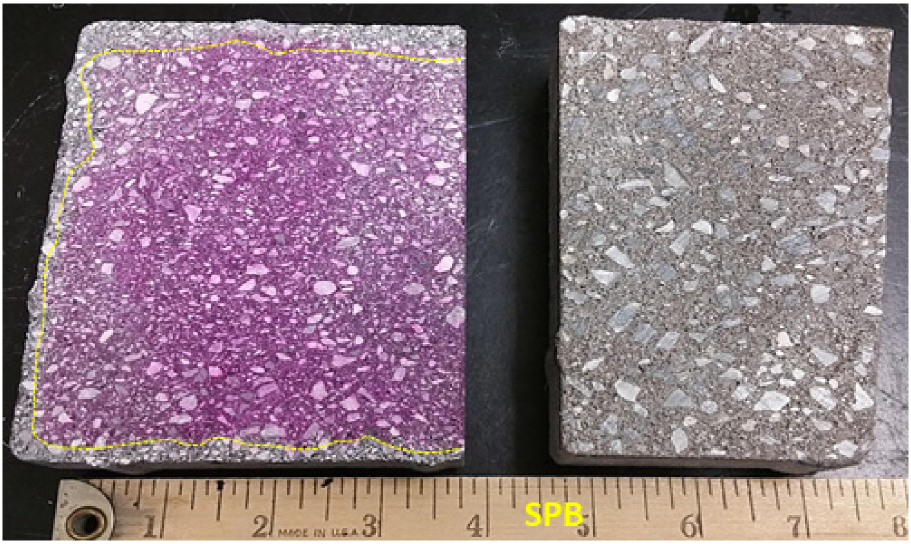

Figure 1: Cut surface of OPC-paver (left) and CSC-paver (right) subjected to phenolphthalein pH indicator.

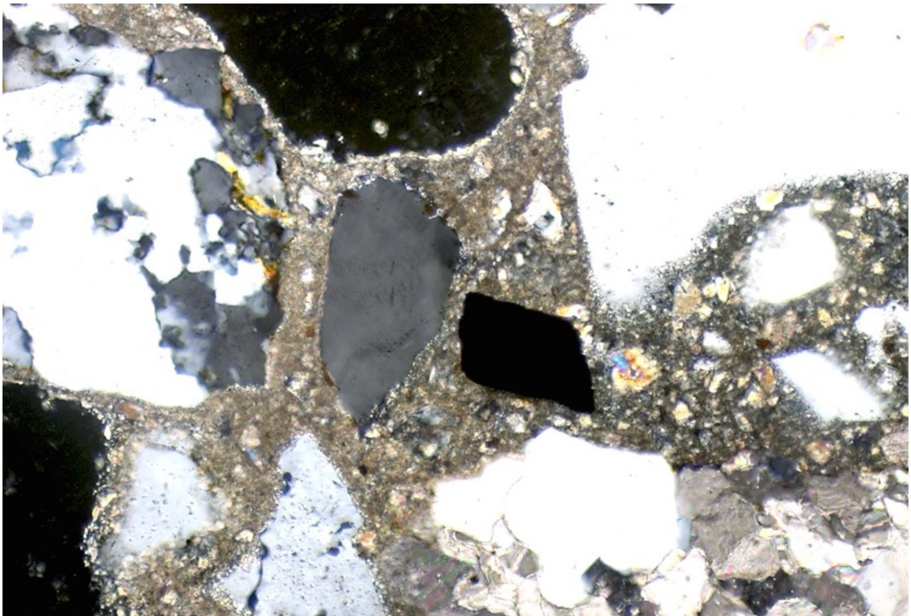

Figure 2: Thin section Photomicrograph showing formation of calcite in the paste of CSC-paver (transmitted cross-polarized light).

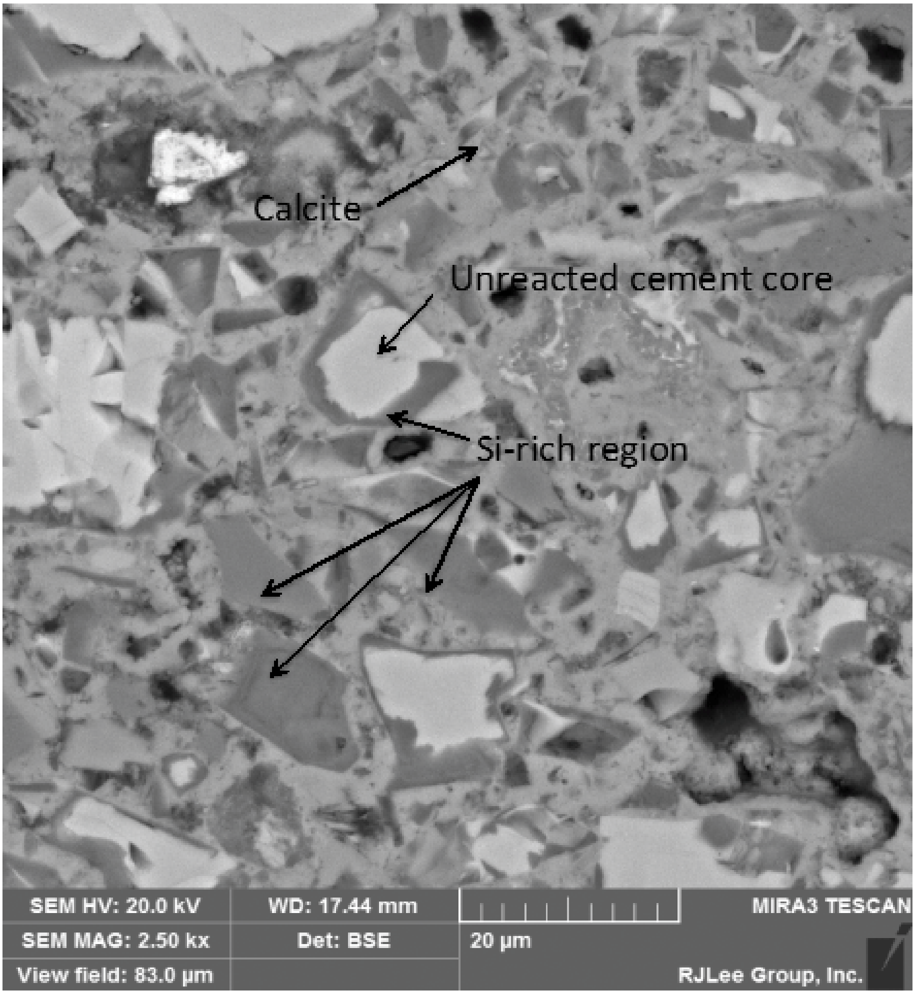

Figure 3: FESEM-BSE image showing the microstructure of the carbonated paste area.

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