Low-CO_2 synthetic SCMs

With the cement sector seeking technologies and practices to reduce its environmental footprint, synthetic supplementary cementitious materials (SCMs) are the next frontier in sustainable innovation. Solidia Technologies' latest focus is an alternative SCM developed by carbonating Solidia Cement™. As the company explains, use of this SCM has the potential to significantly reduce the CO_2 footprint of concrete.

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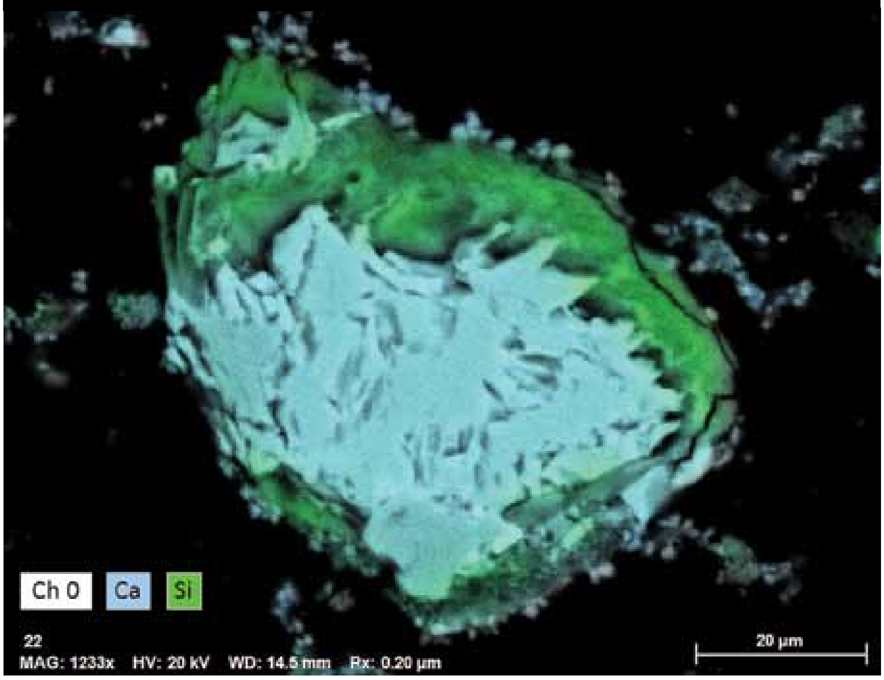
For some time, cement industry leaders have sought technologies and practices designed to reduce their environmental footprint. Increasingly, concrete companies are joining the quest. Both precast and ready-mix manufacturers are reaching out to industry innovators for solutions that will help them survive as sustainability up and down the value chain is considered as a key element of risk management.

Current and developing approaches to achieve this goal include reductions in the clinker factor using supplementary cementitious materials (SCMs) and other innovative new technologies. The cement industry must invest and innovate not only in CO_2 emissions reduction strategies but also in technologies for direct carbon capture, utilisation and storage (CCUS) in cement and concrete production. Solidia Technologies® is at the forefront of developing technologies that both reduce CO_2 emissions during production and utilise CO_2 during the curing process.

About SCMs

SCMs are added to concrete mixtures for a wide variety of reasons including improving rheology, pumpability, finishability, durability and alkali-silica reaction (ASR). SCMs improve the overall hardened properties of concrete through hydraulic or pozzolanic reaction, or both. They are added to the concrete as a partial replacement of ordinary Portland cement (OPC) or directly used in blended cements. They are typically industrial byproducts and their use contributes to environmental and energy conservation goals. Most commonly used SCMs are fly ash – a byproduct of pulverised coal-fired power plants, ground granulated blastfurnace slag (GGBS) – a byproduct of the iron industry, and silica fume from the silicon or ferrosilicon industry. In addition to these, small quantities of natural pozzolans are also used, such as calcined clays (metakaolin), volcanic ash and pumice.

Figure 1: EDS map of SEM-BSE image showing formation of calcite on the surface as well as away from cement particles and silica rim around the cement particle



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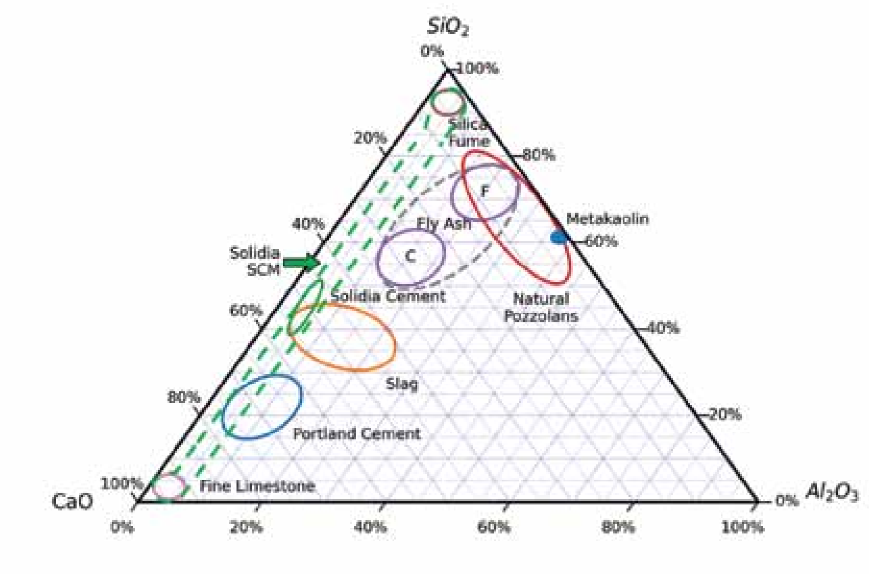
SCMs to reduce CO_2 emissions

World cement production reached 4.1Gt in 2019[1] and is estimated to contribute about eight per cent of total anthropogenic CO_2 emissions.[2,3] During the 21st Conference of the Parties (COP-21) within the United Nations Framework Convention on Climate Change (UNFCC) 2015 in Paris, member nations adopted by consensus the resolution to keep the global temperature rise within 2°C of the preindustrial era by the end of the 21st century by reducing GHG emissions (The Paris Agreement).[4] To meet this 2 Degree Celsius Scenario (2DS), in its publication, Energy Technology Perspectives 2020, the International Energy Agency (IEA) identified and projected pathways towards net-zero emissions from 2019 until 2070 for the cement and concrete industries.[5] Reduction of clinker-to-cement ratio or clinker factor (CF) is identified as a key lever.

The current estimated clinker-to-cement ratio or CF of OPC-based binder in concrete is 70 per cent. The goal is to reduce this ratio to 60 per cent by

Figure 2: composition of various SCMs in the system $CaO-SiO_2-Al_2O_3$



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2050 to meet the 2DS goals. Beyond 2050, further reduction in clinker factor is anticipated but at a slower pace. To reduce the CF, the use of SCMs is important. They are primarily amorphous silicate, aluminosilicate or calcium aluminosilicate powders used as partial replacements of clinker in cements or as partial replacements of OPC in concrete formulations.

However, the most widely-used SCMs such as fly ash and GGBS are industrial byproducts and their consistency in quality is not guaranteed. In addition, supplies of both fly ash and GGBS are diminishing as coal-fired power plants are closing, and steel production is modernising. There is a short supply of SCMs in some markets and prices have risen. Therefore, there is a need for a synthetic product with consistent quality and comparable performance.

In general, SCMs have a very low CO_2 footprint compared to OPC, as the CO_2 footprint associated with industrial byproducts are allocated to the primary industry. Natural pozzolans typically have low CO_2 footprints, as there are no decarbonation processes involved: most natural pozzolans only require hydroxylation during the calcination process, which is a relatively low-energy expenditure. However, supply of natural pozzolans is localised and limited.

As a direct extension of its CO_2-cured precast concrete application, Solidia Technologies has developed a new technology to produce a synthetic, low-CO_2 SCM that can serve as a substitute for traditional SCMs.

Production of Solidia SCM

Solidia SCM™ is created by directly reacting Solidia Cement™ with CO_2 in a wet (slurry) or semi-wet condition. This carbonation can be carried out at the cement plant utilising the flue gas, creating an opportunity for direct utilisation of CO_2 and permanent consumption of carbon. In an initial study, industrial-grade CO_2 was used in experiments to carbonate Solidia Cement for the production of Solidia SCM in a slurry form. The carbonation products of Solidia Cement are described below in Equations 1 and 2 – the main carbonation products are calcite and amorphous silica.

$$CaSiO_3 + CO_2 \xrightarrow{H_2O} CaCO_3 + SiO_2 \qquad \text{Eq 1}$$

$$Ca_3Si_2O_7 + 3CO_2 \xrightarrow{H_2O} 3CaCO_3 + 2SiO_2 \qquad \text{Eq 2}$$

An energy dispersive spectroscopic (EDS) map of a scanning electron micrograph (SEM) in the backscattered electron (BSE) mode is shown in Figure 1. This sample was prepared by mounting in epoxy and polishing. The images show formation of calcite crystals on the surface of the cement particles and silica rim around the core cement particle.

The bulk chemistry of Solidia SCM with respect to other SCMs used in concrete is shown in the $CaO-SiO_2-Al_2O_3$ ternary diagram (see Figure 2). Although the bulk chemical composition of Solidia SCM is similar to Solidia Cement, it has similar functionality to slag, silica fume and fine

Figure 3: compressive strength and Strength Activity Index of Solidia SCM at 20% replacement

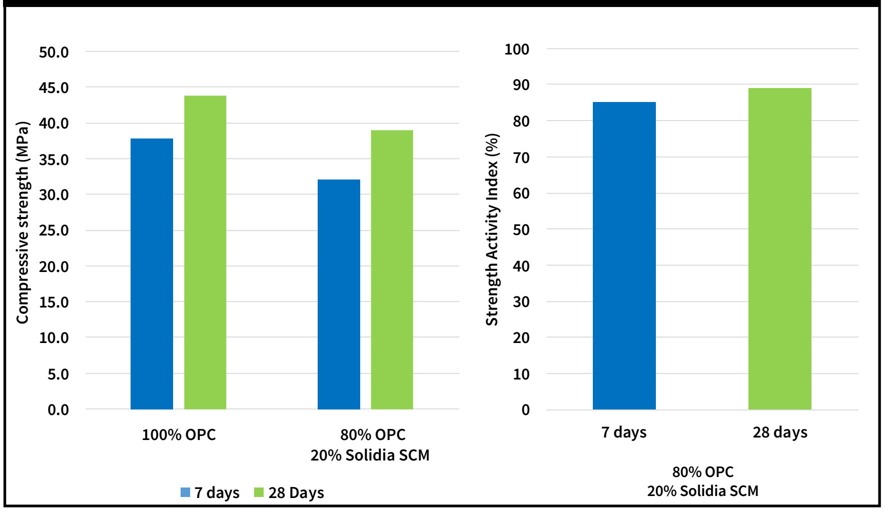

Figure 4: a demonstration pour of concrete with 20% Solidia SCM replacement for OPC

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limestone (shown in the ternary diagram with a dotted line connecting Solidia Cement with silica fume and limestone).

The amorphous silica created during this carbonation process is pozzolanic in nature, ie, it reacts with calcium hydroxide produced during the hydration of OPC, creating additional C-S-H gel in the system. The fine calcium carbonate present in this material reacts with OPC to produce a minor amount of monocarbonate phase (ie, Equations 3 and 4).

$$SiO_2 + Ca(OH)_2 + H_2O \rightarrow CaO\text{-}SiO_2\text{-}H_2O \text{ (C-S-H gel)} \qquad \text{Eq 3}$$

$$3CaO.Al_2O_3 + CaCO_3 + H_2O \rightarrow 3CaO.Al_2O_3.CaCO_3.11H_2O \qquad \text{Eq 4}$$

The formation of additional C-S-H gel reduces the overall amount of calcium hydroxide in the cement paste. This process helps to improve the strength and durability of the concrete over time.

Evaluating the performance of Solidia SCM

To evaluate the performance of Solidia SCM, the Strength Activity Index (SAI) following ASTM C618 at 20 per cent replacement was carried out. The SAI results are provided in Figure 3. The SAI is an indirect measure of pozzolanic activity of SCMs. The minimum compliance requirement of the SAI is 75 per cent at seven-days or 28 days. Solidia SCM meets this SAI requirement at both ages.

Potential reduction in CO_2 emissions

It has been demonstrated that production of Solidia Cement reduces the CO_2 emissions at the kiln by 30 per cent compared to OPC production.[6] The subsequent carbonation of 1t of Solidia Cement is expected to utilise and store up to 240kg of CO_2 gas, thereby creating 1.24t of a solid, carbonated Solidia SCM product.

The creation of Solidia SCM via these two steps represents an opportunity to significantly reduce the amount of OPC used in concrete and, hence, the CO_2 footprint associated with OPC use.

Equally important is the potential to make Solidia SCM in cement plants everywhere around the world. This capability will compensate for both current and future shortages in fly ash and slag supplies.

Current tests are exploring the range of CO_2 savings as well as the performance of Solidia SCMs. The results of these tests will be reported in a future white paper from Solidia. A demonstration pour of concrete with Solidia SCM at 20 per cent replacement of OPC is shown in Figure 4.

Conclusion

Cement and concrete manufacturers are jumping onto the sustainability train, further driving innovation. The introduction of a synthetic SCM can help them remain competitive during the worldwide push towards reducing the environmental footprint of heavy industry and mitigate ongoing SCM supply interruptions and price fluctuations. Solidia SCM is a synthetic material that can be produced in any cement plant with consistent quality. It can be produced through the carbonation process of Solidia Cement, including using flue gas from a cement plant. The production of this SCM and its application in concrete has the potential to reduce the CO_2 footprint significantly compared to OPC concrete. Preliminary results of tests underway show that Solidia SCM substituted OPC mortar meets the strength activity index requirements. ■

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