

# LOW-ENERGY CO<sub>2</sub>-ACTIVATED SELF-PULVERISING CEMENT FOR SUSTAINABLE CONCRETE CONSTRUCTION

Alan Maries<sup>1</sup>, Colin D. Hills<sup>2</sup>, Paula Carey<sup>3</sup>

1 AMSTaR Consultancy, London SW19 8JQ, U.K. [alan.maries@amstar.org.uk](mailto:alan.maries@amstar.org.uk)

2 University of Greenwich, Chatham ME4 4TB, UK. [C.D.Hills@greenwich.ac.uk](mailto:C.D.Hills@greenwich.ac.uk)

3 Carbon8 Systems Ltd., Chatham ME4 4TB, U.K. [paulacarey@c8s.co.uk](mailto:paulacarey@c8s.co.uk)

## ABSTRACT

In order to achieve an efficient and sustainable concrete industry, there is an urgent need to reduce CO<sub>2</sub> emissions from cement manufacture. The innovative scheme described here for the linked production of cement and concrete with low carbon footprint follows a three-stage process. Firstly, a Portland-like cement composition is calcined at reduced temperature and cooled under controlled conditions so that it self-pulverises spontaneously to a powder of normal fineness without grinding. Secondly, CO<sub>2</sub>-rich gas is extracted direct from the cement kiln flue and used to activate this poorly hydraulic cement in the third stage for making precast concrete products. Considerable energy savings are anticipated, and the challenges of process enhancements and scale-up are currently being addressed. In addition to its use in precast concrete items such as blocks, roof tiles, and pipes, other potential on-site applications are foreseen for this cement where low-energy concrete or controlled setting are required.

**Keywords:** Cement, Concrete, Carbon dioxide, Self-pulverising, Carbonation, Low carbon, Activation, Sustainability gains.

## THE SUSTAINABILITY CHALLENGE

### Global Manufacture of Cement and Concrete

With global annual production currently estimated at more than 10,000 million cubic metres (i.e. 10 cubic kilometres!), concrete is by far the most widely used material in the world, more than all other construction materials combined. Thus, although its embodied energy and carbon dioxide (CO<sub>2</sub>) are low compared to other common construction materials (Hammond & Jones 2011), the manufacture of its main active constituent, Portland cement, now exceeds 4,000 million tonnes world-wide (U.S. Geological Survey 2018).

Almost 1 tonne CO<sub>2</sub> is emitted per tonne of cement produced, with just over half the emissions arising from the decomposition of limestone, the remainder from the energy

used in heating and grinding. At such a scale of global production, cement is responsible for approximately 8% of anthropogenic CO<sub>2</sub> emissions (Olivier 2016), third only to transport and energy generation. There is thus an exceptionally urgent need to address CO<sub>2</sub> emissions in the cement and concrete sector.

### **An Energy-Saving Opportunity**

Portland cement is produced by sintering together at around 1450 °C a mixture of limestone (calcium carbonate) and clay (alumino-silicates), quenching the resulting clinker and grinding it to a fine powder consisting of an assemblage of calcium silicate and aluminate phases (Richardson & Taylor 2017).

One of these phases, dicalcium silicate - or '*C<sub>2</sub>S*' in cement shorthand nomenclature - is responsible for long-term strength development in cement. *C<sub>2</sub>S* is normally stabilised in the high temperature (beta) crystal form in cement by fast quenching and by the impurities which exist in the raw materials. The presence of the gamma-form of *C<sub>2</sub>S* (stable at ambient temperature) is revealed by 'dusting' which occurs as the molten mass cools, due to the 10% increase in volume from beta to gamma. This phenomenon is utilised in the Grzymek process for producing alumina (Kapolyi 1980), where the mass of sintered aluminous ore and limestone disintegrates to a fine powder on cooling. Certain related materials such as stainless steel slag are also known to self-pulverise entirely on cooling (Johnson, 2003). Although attractive from an energy-saving perspective, this behaviour is not made use of in cement manufacture because gamma-*C<sub>2</sub>S* does not possess hydraulic properties (Richardson & Taylor 2017) and its formation is therefore normally strongly discouraged.

However, during investigations of rapid strength development in Portland cement by an accelerated carbonation treatment with CO<sub>2</sub> gas at ambient temperature and pressure, gamma-*C<sub>2</sub>S* has been found to carbonate as readily as Portland cement (Bukovsky & Berger 1979, Saito 2010). This finding has been supported by more recent work on self-pulverised stainless steel slag (Johnson 2003). Furthermore, accelerated carbonation has also been proposed as a means of reducing energy consumption and of 'sequestering' CO<sub>2</sub> in the production of precast concrete (Maries & Hills 1986, Maries 2008a & b, Hamilton 2008).

These observations, though unrelated, suggested a combined production procedure whereby a cement composition containing enough *C<sub>2</sub>S* to self-pulverise on cooling could be activated by CO<sub>2</sub> gas captured from the cement kiln and used as binder in a precast concrete production process (Maries 1998).

This proposal was first investigated experimentally in 2009 (Maries et al. 2013). The present paper reports the outcome of that experimental investigation, summarises anticipated sustainability gains, and explores potential uses for this cement, not only in precast concrete items but also in applications where low-energy or controlled setting concrete is required.

## PROOF OF PRINCIPLE

### Synthesis of Self-Pulverising Cement

The synthesis of gamma-C<sub>2</sub>S from pure starting materials requires a higher temperature than if limestone and clay were used (as in commercial cement manufacture) because no fluxing agent is present. Although the literature seems to be a little confused on exactly what conditions are required for sintering and for phase transformation on cooling, the best results were obtained using a thoroughly mixed stoichiometric 2:1 blend of calcium oxide (CaO) and precipitated silica (SiO<sub>2</sub>) as raw materials, with the addition of 0.5% w/w FeO as a 'stabilising' agent. Portions of this mixture were compressed in a 5 g pellet press and calcined in alumina crucibles in a muffle furnace at 1450 °C for 2 hours, then allowed to cool in air at approximately 200 °C/minute to room temperature.

X-ray diffraction traces (Figure 1) confirmed that gamma-C<sub>2</sub>S had actually been synthesised as the major phase, and that some beta-C<sub>2</sub>S remained together with unreacted calcium oxide and silica.

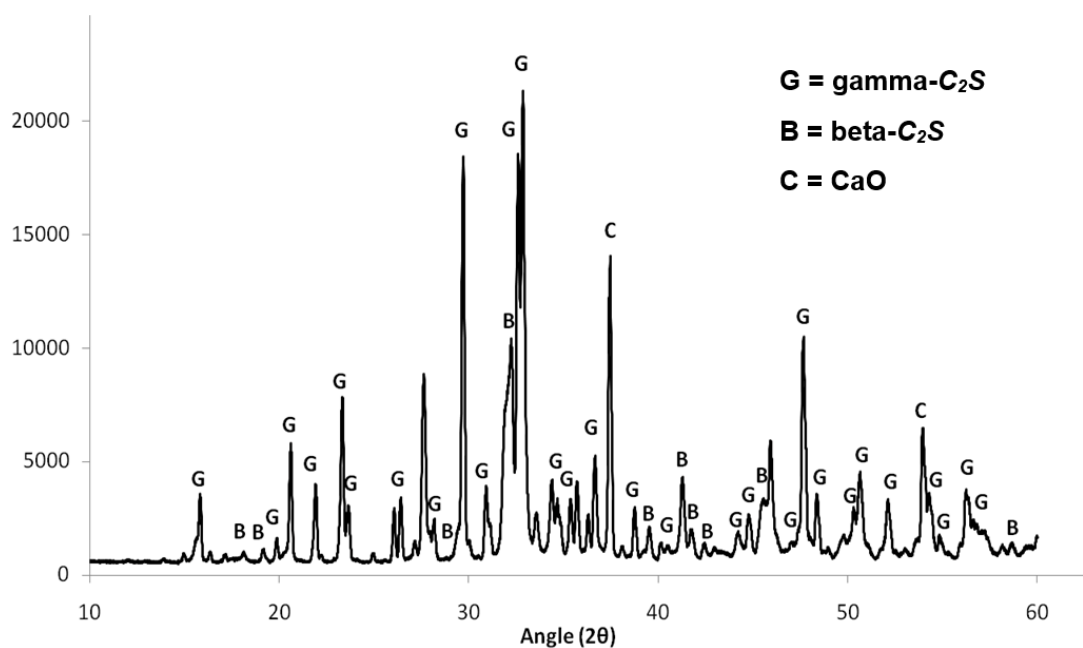


Figure 1. X-ray diffraction traces

Figure 2 shows that the particle size distribution, as measured by a Malvern Laser Sizer, is comparable with that of Portland cement, though with an appreciable fraction of coarser (or possibly agglomerated) particles which it is anticipated could be reduced by optimising the cooling regime.

### Recovery of CO<sub>2</sub> from the Cement Kiln

Viable CO<sub>2</sub> capture technologies are not yet available for the cement industry (Bjerge

& Brevik 2014), but this is not expected to present a problem here. Whereas the concentration of CO<sub>2</sub> by volume is only 14% in coal fired power generation, it is reported to be 14 - 33% by volume in cement kiln exhaust gas, and may be as high as 40% at the end of the pre-calciner (UKMPA 2009). Such levels are high enough for the flue gas to be used 'as found' in the carbonation step that follows.

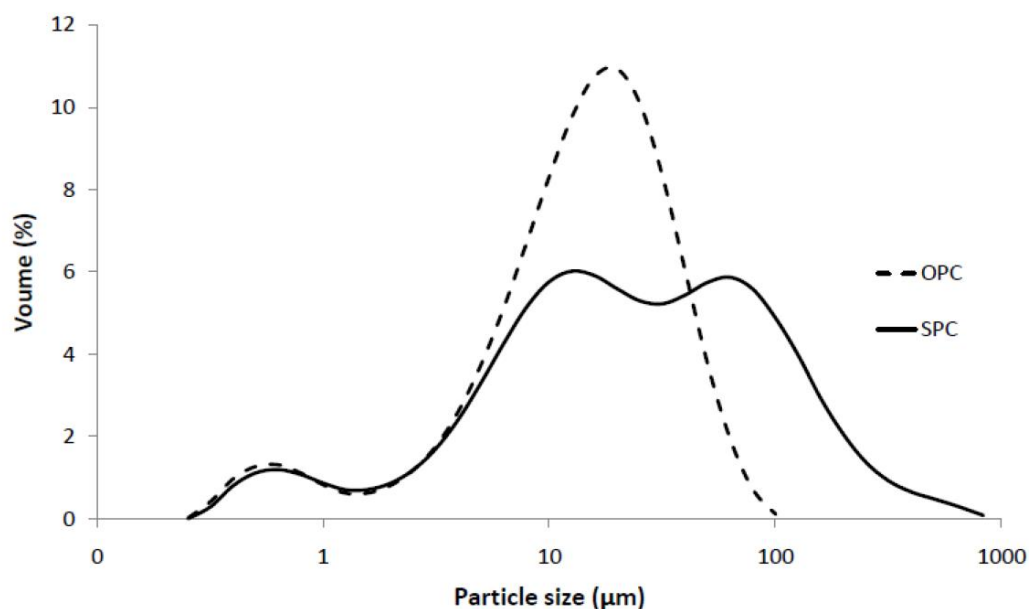


Figure 2. Particle size distributions of self-pulverised (SPC) and Portland (OPC) cements

### Carbonation of Self-Pulverised Cement

Specimens of a 3.0:1:0.3 sand:cement:water mixture were compacted into small cylinders 14 mm in diameter by 8 mm thick. These specimens were exposed to varying concentrations of CO<sub>2</sub> for up to 2 hours, when the progressive uptake of CO<sub>2</sub> gas was observed in a specially designed 'eudiometer' (Maries 2008a), which enables very precise measurements to be taken, as shown in Figure 3. The uptake of 100% CO<sub>2</sub> gas at 1 bar pressure is initially slower for mortar containing gamma-C<sub>2</sub>S ('SPC') than for Portland cement mortar ('OPC'), it reaches a similar level after about 75 minutes and continues to rise thereafter. Experiments with CO<sub>2</sub> gas at concentrations of 100, 50 and 25% by volume in air have demonstrated that 25% appears to be sufficient to carbonate mortars to a reasonable extent. The levels of CO<sub>2</sub> typically found in cement kiln gas noted above (up to 40%) therefore appear sufficient to activate gamma-C<sub>2</sub>S, thus avoiding the need for complex and costly CO<sub>2</sub> recovery systems.

Mortar cylinders made with non-carbonated gamma-C<sub>2</sub>S developed no measurable strength at all when simply cured at 100% RH for several days, thereby demonstrating the poor hydraulic properties of this C<sub>2</sub>S polymorph. However, after only 2 hours carbonation in 100% CO<sub>2</sub>, an indirect tensile strength of about 0.3 MPa was achieved, similar to that of specimens made with Portland cement after 7 days curing.

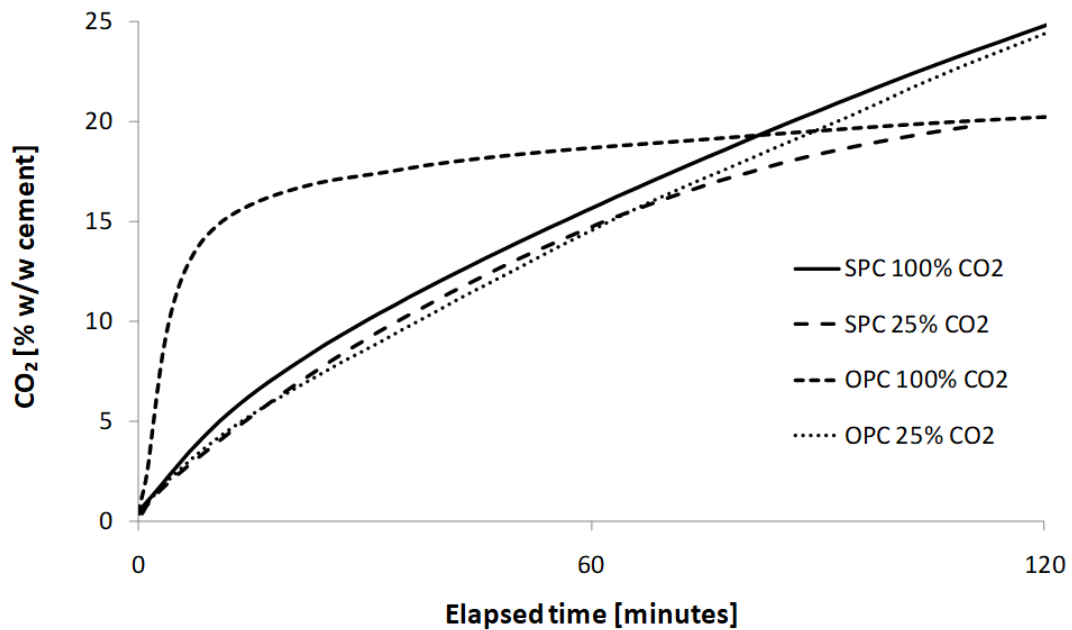


Figure 3. Eudiometer traces showing uptake of CO<sub>2</sub> gas in cement mortar

## SUSTAINABILITY GAINS

These preliminary experimental results provide proof-of-concept that a calcined cement containing substantial amounts of dicalcium silicate will self-pulverise on slow cooling to a powder of cement-like fineness, due to the expansive beta- to gamma-C<sub>2</sub>S phase transformation. This powder, although possessing only weak hydraulic properties, can be activated by accelerated carbonation with CO<sub>2</sub> gas extracted directly from the cement kiln to produce a strong cementitious binder for use in precast and other types of concrete.

If such a process were to be developed on a commercial scale, the following sustainability benefits are envisaged.

### Anticipated Direct Reduction In CO<sub>2</sub> Emissions

- 1) A lower limestone content in the raw mix for the cement would lower ‘chemical’ CO<sub>2</sub> emissions. Calcination at a lower kiln temperature would further reduce CO<sub>2</sub> emissions, and the combined reduction is estimated at 10%.
- 2) Because grinding cement clinker typically consumes 10% of the manufacturing energy of cement (Gartner 2006), its elimination by self-pulverisation would save an estimated 5% of ‘process’ CO<sub>2</sub> emissions.
- 3) Accelerated carbonation of concrete generally consumes around 10% by weight of

- its cement content (Maries 2008a), saving an extra estimated 10% CO<sub>2</sub> emissions.
- 4) By avoiding the need to cure precast concrete at elevated temperature and humidity, energy savings are estimate to be in the order of 5% CO<sub>2</sub>.

These four direct CO<sub>2</sub> emission reductions arising from the new process could therefore amount to 30% of current emissions.

### **Secondary Sustainability Gains**

In addition to reductions in CO<sub>2</sub> emissions, the following secondary sustainability gains are anticipated to arise from a successful application of the new process:

- Lower cement calcination temperatures would permit less costly kiln refractory liners to be used (or possibly even the use of steel-lined kilns).
- Lower calcination temperatures would also reduce fuel consumption.
- The alteration to bulk raw material ratios necessary to form enhanced levels of gamma-C<sub>2</sub>S in the composition will decrease materials costs.
- Cheaper, lower-grade, raw materials could be used, including mineral by-products and hazardous wastes.
- So-called 'belite cements' contain high levels of C<sub>2</sub>S and are attracting renewed interest because they can be produced at reduced temperature from lower-grade materials and can confer enhanced durability on concrete (Gartner 2006). Similar benefits could apply here.
- Production efficiency should be improved through a closed-loop process involving heat and materials transfer, with additional benefits in reduced handling and transport costs.
- Many of the sustainability gains noted above will carry indirect cost benefits, and additional commercial advantages will accrue from the reduction in concrete curing times, such as speedier mould turn-round, smaller plant footprint and greater product versatility.

## **PROCESS DEVELOPMENT**

In order for the concept outlined above to be turned into a commercial proposition, a number of scale-up challenges are being addressed.

### **Calcination Process**

It is believed that this self-pulverising cement could be manufactured in a typical cement plant with only slight modifications. However, one of the potential attractions of making self-pulverising cement is that, because of lower calcium carbonate levels and reduced calcination temperature, it could lend itself to a more efficient calcination process based on a fluidised bed, as has been employed commercially in Poland (Kapolyi 1980) and in Japan (Hashimoto, 1997).

### **Conditions for Self-Pulverisation**

Although doping of the raw materials is considered likely to promote self-pulverising efficacy, the influence of impurities on self-pulverisation is not yet fully understood. Time-temperature-transformation cooling profiles required to ensure self-pulverisation are yet to be defined. There is a risk that the cement may not pulverise adequately under commercial manufacturing conditions, in which case a small amount of crushing or grinding might be necessary.

The issue of heat recovery from the slow cooling process would need to be addressed. Conventional fast air-quenching of semi-liquid cement in the kiln to solid clinker nodules is achieved very efficiently in cement kilns (Gartner 2011), and the new process would require adaptation to an inherently slower cooling regime.

### **Accelerated Carbonation of Concrete**

Because of its high concentration of CO<sub>2</sub>, the gas extracted from the cement kiln could be transferred by pipe for direct use in carbonation in an associated precast concrete plant, without the need for additional costly gas capture technology. Optimal conditions for carbonation of fresh Portland cement mortars and concrete by CO<sub>2</sub> at atmospheric pressure have been extensively studied (Maries 2008a & b), when it was found that in order to allow CO<sub>2</sub> to penetrate the concrete there must be sufficient permeability to the gas. However, the speed of carbonation can be raised by introducing the CO<sub>2</sub> at elevated pressure.

Detailed investigation of the chemistry of the accelerated carbonation of cement has shown that there is considerable potential for further speeding up the carbonation process by catalysing the step where CO<sub>2</sub> becomes hydrated in the aqueous phase (Maries & Hills 2013).

## **POTENTIAL APPLICATION TO PRECAST AND SITE CONCRETE**

Although the research described in this paper is still at an early stage of development, the particular properties of the novel low-energy cement system suggest a range of interesting and novel potential applications.

### **Manufacture of Precast Concrete**

Accelerated carbonation of ordinary Portland cement has already been researched for improving the automated manufacturing of 'standard' precast items such as concrete roof tiles, slabs, and pipes (Maries & Hills 1986). The manufacture of higher value 'difficult' or complex shaped monolithic products such as architectural mouldings and foundry castings could also benefit from the more rapid curing that carbonation introduces.

In addition to the main sustainability gains noted above (low emission, low energy), other characteristics of CO<sub>2</sub>-activated self-pulverising cement might be used to advantage in precast concrete. Because accelerated carbonation lowers the pH of concrete, this cement would be ideal for manufacturing porous concrete for marine

applications such as blocks for coral reef seeding or sponge balls onto which micro-algal colonies would be encouraged to grow for sequestering atmospheric CO<sub>2</sub>.

Despite its delayed setting and hardening, Portland cement has been proposed as a suitable material for making articles by additive manufacturing (3D printing), at scales ranging from millimetres to several metres (Gibbons et al. (2010). The use of a carbonation-activated cement instead would speed up the manufacturing process considerably by ensuring that a layer already deposited could be hardened rapidly to allow the next layer to be laid down immediately.

### **Production of Site Concrete**

Even if the benefits of a combined cement manufacturing operation would be lost, carbonation-activated cement could additionally find use in non-precast concrete applications and site operations where high early strength is not needed, but durability or low embodied carbon are essential. Because of its lower content of tricalcium silicate (C<sub>3</sub>S), less calcium hydroxide would be produced on hydration, thus enhancing the freeze/thaw durability and long-term strength of cement paste (Richardson & Taylor 2017).

Application of carbonation to 'activate' this cement would introduce additional control over the setting process. This would not only result in a low-heat concrete suitable for large-volume pours, but would also suggest its use 'inaccessible' locations such as mines or oil wells, where delayed 'set-on-demand', triggered by injection of CO<sub>2</sub>, might be desirable.

Cements are widely used in waste management applications to immobilise pollutants, and the low pH and controllable setting of this new cement would offer several advantages in the management and handling of wastes containing hazardous substances and/or radioactive elements.

## **CONCLUSIONS**

Although not yet researched beyond lab-scale, the proposal for this novel self-pulverising cement suggests that significant and quantifiable reductions in both CO<sub>2</sub> emissions and process energy can be achieved in manufacture. Its primary use would be as a binder in a linked precast concrete production plant, but there are many other possible uses in site concrete where its 'set-on-demand' behaviour and low pH can increase the range of potential applications.

Two recently developed related technologies, CarbonCure and Solidia Cement, are based on a similar approach. The CarbonCure Masonry System provides controlled doses of gaseous CO<sub>2</sub> into the mixer feeding into a conventional precast masonry production machine, either as a retrofit to existing production equipment or by installing specialized plant infrastructure such as pressure chambers (Monkman 2013).



Because this system uses standard Portland cement, it is reckoned to offset less than 2% of CO<sub>2</sub> emissions from cement production.

Solidia cement is made from the same raw materials that are typically used to make ordinary Portland cement (OPC) clinker, but with kiln feed proportions adjusted so as to produce a clinker rich in low-lime calcium silicate phases such as  $CS$  and  $C_3S_2$  instead of the high-lime phases  $C_3S$  and  $C_2S$  typical of OPC (Sahu et al. 2015). The limestone content is lowered by 30%, allowing sintering at a temperature up to 250 °C below that for OPC. The clinker is then ground to make a cement of similar fineness to OPC which is hardened by carbonation rather than hydration, and total manufacturing CO<sub>2</sub> emissions are estimated to be 30% less than for OPC. In comparison, the novel CO<sub>2</sub>-activated self-pulverising cement described in this paper promises similar reductions in manufacturing energy and CO<sub>2</sub> emissions to those of Solidia cement, but with the added advantage of dispensing with the need for clinker grinding. In addition, its higher clinker calcium content offers greater scope for strength development by carbonation.

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