Graphene's future potential

Reducing carbon emissions in the cement industry is a top priority, but how to achieve that is the subject of considerable research and development. For First Graphene Ltd and Fosroc International, graphene shows great promise for significant CO_2 reductions and performance enhancements.

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Cement additives or cement grinding aids (CGAs) range from pure grinding aids through to functional additives and performance enhancers. The latter is the most common type of product in use today. Performance enhancers can improve the efficiency of the grinding process and improve key mechanical properties, such as compressive strength.

One of the main reasons for using performance enhancers, in addition to the reduction of energy consumption, is the need to reduce the clinker factor of any given cement.

Clinker is not only the most expensive component of cement but also the component responsible for the highest associated CO_2 emissions. If equivalent cement performance can be maintained with a lower clinker factor, this is a win-win situation.

Current performance enhancers typically rely on a combination of glycol and amine chemistries. These give improvements in compressive strength of around 10-20 per cent, while reducing the clinker factor by up to five per cent, although individual cases can vary significantly.

It is not simply a case of adding more product to get a greater increase in strength or a larger reduction in clinker. Because these chemistries interact during the cement hydration process, adding excessive amounts can cause a reduction in performance.

To achieve greater clinker reduction, alternative technologies should be looked at and a collaboration between advanced materials company First Graphene Ltd and Fosroc International, a global manufacturer and supplier of high-performance chemicals for the construction industry, is showing significant promise. The collaboration is looking at utilising graphene, added in very small quantities, to allow higher levels of clinker replacement.

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Graphene background

The significant benefits of graphene have been the subject of extensive R&D since it was first isolated in 2004.

Consisting of carbon atoms arranged in lattice-like structures just a few atoms thick, graphene is the strongest substance ever recorded, having 200-300x the strength of structural steel.

It is extremely lightweight, exhibits exceptional flexibility, has more than five times the electrical conductivity of copper, exhibits superior thermal conductivity characteristics, resists permeation by water and chemicals, and provides a high level of fire retardancy.

However, a long-standing issue is increasing graphene production capacity from laboratory to commercial scale, while simultaneously maintaining consistent quality. Australian Securities Exchange-listed First Graphene has developed the robust, proprietary capability to produce large quantities of consistent quality graphene in a range of formulations. This is being marketed globally under the PureGraph® brand.

The PureGraph range is supplied in the form of graphene nanoplatelets. This means the nanoplatelets are composed of platelets supplied as powders or dispersions. Each platelet is a pristine graphene particle with lateral dimensions in the 1-100µm range but with only nanometre level thickness. This high aspect ratio graphene with large lateral dimensions has been confirmed to improve the physical properties of many materials.

Over the past two years, the company has worked with clients across multiple industries on established products ranging from rubber, plastic composites, cement and concrete to more high-tech applications such as conductive inks and energy storage materials.

First Graphene supplies PureGraph in powdered, pelletised and aqueous paste formats, as well as providing a range of ready-made masterbatches targeted to specific applications.

Graphene and cement

The traditional method of manufacturing high clinker factor cement results in CO_2

emissions of as much as 800-900kg/t of cement. First Graphene's initial R&D work showed that its proprietary PureGraph graphene, when added to cement in the right formulation, provided the same or better strength properties while reducing the amount of clinker required by around 20 per cent.

Even better, only very small additions of PureGraph were required to achieve such results, ensuring manufacturing costs remained competitive.

The work led to First Graphene signing deals with major global cement additive groups including Fosroc International, as well as securing a UK government "Innovate UK" grant for additional research and commercialisation. First Graphene is working with a consortium including Breedon Cement Ltd, construction and regeneration group Morgan Sindall Construction & Infrastructure Ltd, and the University of Manchester's Department of Mechanical, Civil and Aerospace Engineering to develop high performance graphene-enhanced cement.

The company also appointed Australian industry veteran Todd McGurgan as commercial manager for cement and concrete last year to drive its go-to-market strategy. Since his appointment, Mr McGurgan has focussed strongly on the benefits that PureGraph can bring to the cement segment, and helped First Graphene ink cement additive product development and distribution deals with commercial partners across the Asia-Pacific and Africa regions. The company has also appointed distribution partners in the Americas to target multiple industry sectors.

Several research articles have been published that provide some indications about the mechanism of interaction between the hydrating cement phases and graphene.[1,2,3]

Graphene interacts with cementitious binders using a combination of chemical and physical processes. Adhesion between graphene basal planes and cement gels by Van der Waals forces reinforces the hydrated structure. Changes in porosity and hydration at the graphene-cement interface have also been observed.

Therefore, the mechanisms of interaction are different to the ones seen with common amines such as triethanolamine (interaction with the aluminate phase) or triisopropanolamine (interaction with the ferrite phase).

The desired outcome of combining traditional cement additive technologies with PureGraph is an additive effect of the two technologies. An even better outcome is that a synergistic effect has been demonstrated, giving opportunities to reduce the clinker factor even further.

Laboratory trials

First Graphene conducted laboratory trials using a high replacement level Portland limestone cement to demonstrate the effectiveness of the cement additive/graphene combination. The results are summarised in Table 1.

The cement composition was fixed at a limestone replacement level of 30 per cent and the grinding time was adjusted to maintain a Blaine fineness of 5200 ±100cm²/g.

The first point to note is that PureGraph is a very good grinding aid, giving a similar reduction in grinding time to the CGA. However, when the two were combined there was no additional improvement. It is not yet clear whether this is a true observation or an artefact of conducting the work in a laboratory ball mill without an integrated separator.

Mechanical testing on mortar generated some very encouraging results. The mortar tests were conducted according to ASTM C109 using a fixed water-to-cement ratio of 0.485.

The results in Table 2 show that the combination of graphene and CGA produces a much greater improvement across all strengths at a given time than either solution on its own.

Conclusions and next steps

The results from the laboratory trials increase First Graphene and Fosroc International's confidence that the combination of graphene and cement additives is a viable solution for achieving lower clinker factor cements. Work is ongoing to develop potential products that will maximise the cost benefit while also giving the greatest potential for CO_2 reduction.

Full-scale industry trials are planned to take place over the summer as part of the Innovate UK-funded project. ■

Table 1: additive dosage rates and grinding times

Sample	Graphene (%)	CGA (%)	Blaine (cm²/g)	Grinding time (m)
Blank	0	0	5188	118
Blank + PureGraph	0.05	0	5130	100
Blank + CGA	0	0.03	5143	100
Blank + PureGraph & CGA	0.05	0.03	5152	100

Table 2: compressive strength comparison

Sample	Flow (%)	Compressive strength (psi)			
		1 day	3 day	7 day	28 day
Blank	115	782	1802	2432	3328
Blank + PureGraph	120	882	1991	2489	3485
Blank + CGA	116	1067	2347	3172	4082
Blank + PureGraph & CGA	117	1152	2361	3485	4224

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