GRAPHENE ENHANCED CONCRETE:

Studies in the improvement of concrete materials with pristine graphene additives

Authors:

Prof Dusan Losic**,** Director of ARC Graphene Research Hub, School of Chemical Engineering and Advanced Materials, The University of Adelaide.
Dr. Meini Su, Lecturer in Structural Engineering, Department of Mechanical, Aerospace and Civil Engineering, The University of Manchester.
Dr Andy Goodwin, First Graphene Ltd.
Mr. Paul Ladislaus, First Graphene Ltd.

Introduction:

Cement is the most manufactured product on Earth by mass. When combined with water and mineral aggregates it forms concrete which in volume terms, is the most traded material in the world after water. In 2015, the total mass of cement produced was 4.6 billion tonnes. This is equivalent to about 626 kg per capita, a value higher than the amount of human food consumption[1].

With population growth, increased urbanisation and improved living standards of the global population, the demand for concrete products continues to grow at an accelerating rate, see Fig. 1.

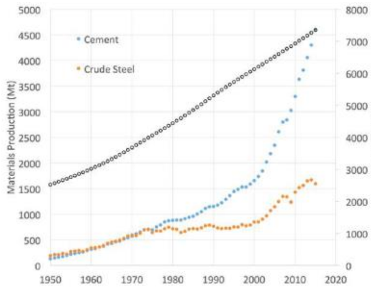

Figure 1 Comparison of cement demand vs. population growth and other key raw materials (reproduced from 1)

The manufacture of cement carries a significant CO_2 burden which is estimated to be 6% of all CO_2 emissions from human activity[1].The industry faces major challenges, notably the pressure to reduce the carbon footprint (CO_2 contribution) of cement-based products.

> **Ordinary Portland Cement (OPC)[1]:**
> *The traditional form of cement is Ordinary Portland Cement (OPC) which is made from locally available materials, typically a mixture of clay and limestone which require grinding and calcining (heating) to make clinker. The clinker is crushed into a fine powder with gypsum to form OPC. The manufacture of 1 tonne of clinker produces 842 kg of CO_2. The heating and processing steps produce ca. 40% of the CO_2 with ca. 60% coming from the CaCO3 to CaO transition during calcination of the clinker*.

The cement industry is investigating a range of alternatives to OPC clinker, known as supplementary cementitious materials or SCMs which includes fly ash, blast furnace slag and natural pozzolans. The UN report on Eco-Efficient Cements concludes that the transition to SCMs will be slow due to local availability, low cost and industry confidence in the current OPC based materials. It is therefore important to focus upon more efficient use of OPC concretes in the short term. In addition, cement-based concrete is the most heavily used material in the construction industry owing to its low-cost manufacture, and excellent compressive strength. Its drawbacks are inherent brittleness, low tensile strength and degradation in aggressive environments all of which contribute to reduced durability and increased maintenance costs.

In the context of the above, the application of new technologies to improve strength and durability of finished concrete products offers a route to improve the efficiency of OPC usage and promote lighter, stronger concrete structures that will help reduce the CO_2 footprint of the industry. In commercial terms, this is an exciting opportunity for materials manufacturers as the precast concrete market size alone is expected to reach USD 145.91 billion by 2027, with CAGR of 6.3% [2] and the concrete admixtures market is forecasted to be worth USD 24.0 billion by 2024, with a CAGR of 9.3%[3].

Graphene Additives in Concrete:

Graphene and graphene oxides are being extensively explored as a new additive to cement and concrete products to improve strength, improve durability and add multi-functionality to cement composites. Multiple research studies and reviews[4,5] have been published which show improvements in compressive strength, tensile strength and resistance to ion transportation; for example in a recent review article Yang *et al*[4], summarise the improvements in compressive strength and flexural strengths observed in 36 independent studies; results are variable due to the different graphene material types evaluated and different experimental methods employed.

In 2018, a paper published by Craciun[6] at the University of Exeter reported an increase of 146% in compressive strength and 79.5% in flexural strength in concrete when graphene materials are added at concentrations of ca. 0.03%w/w in the concrete composite. The researchers used few layer graphene dispersions manufactured by the high shear exfoliation method of Paton *et al*[7], as well as industrial multi-layer graphene and ultrathin graphite. The multi-layer graphene outperforms both the few layer dispersions and the ultra-thin graphite in compressive strength enhancement. The authors describe how the graphene particles aid the formation of calcium silicate hydrate (C-S-H) gels and enhance crystallinity improving strength.

The authors believe that the possible formation of C–S–H crystals along the graphene flakes with high degree of crystallinity combined with the high Young's modulus of graphene leads to a stiffer graphene– C-S-H composite material compared to C–S–H alone. This is consistent with the industrial multi-layer graphene delivering improved performance.

This group also reported a decrease in water permeability of 400% compared to non-graphene doped concrete. This reduced permeability is expected to the prevent the alkali–silica reaction, a swelling reaction that results in serious cracking and critical structural problems extending the durability of the concrete.

In conclusion, the use of graphene admixtures has been shown to increase strength, reduce materials usage (reducing carbon footprint) and potentially increase durability of products. However, further studies are required to fully understand the mechanisms and convince the construction industry that graphene is a viable option for enhancement.

PureGRAPH® Concrete Additives for improved strength

Professor Dusan Losic and co-workers at the University of Adelaide and ARC Graphene Research Hub have completed thorough studies[8,9] of the performance of pristine graphene (PRG) particles on the compressive and flexural strength of cement-based mortars. Working with PureGRAPH® graphene products supplied by First Graphene Ltd., this team was able to investigate the influence of dosages and particle (platelet) size of PureGRAPH® graphene on the physicochemical, microstructural and mechanical performance of OPC cement. The PRG particles were dispersed in water with an industrial plasticiser and blended into the concrete mix as part of the water addition which providing a good distribution of graphene particles in the cement matrix.

Initial studies[8] by the University of Adelaide team showed that compressive strength is increased by 34.3% and tensile strength by 26.9% when PureGRAPH® is added to cement mortar at very low levels of

0.07%w/w in the cement paste (equivalent to ca. 0.01%w/w in concrete). In a new study[9]; the earlier results were further validated with improvements in compressive strength of 34.3% and tensile strength of 38.6% being recorded. In this study, the researchers investigated the impact of platelet dimensions and confirmed that ultra-large PureGRAPH® platelets with average lateral size 56 ± 12µm deliver the largest benefits, Figures 2 and 3. The increases in strength were attributed to improved hydration of calcium silicate hydrate gels and increased frictional adhesion between the platelets and cement gels which explains why the platelet size and aspect ratio are important.

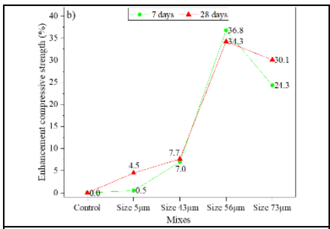

Figure 2 Enhancement in compressive strength at 7 and 28 days of different PRG sizes. Reproduced from 9 with permission.

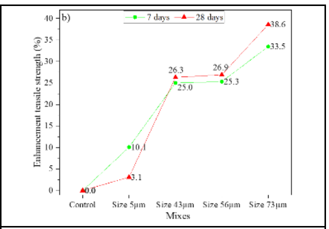

Figure 3 Enhancement in tensile strength at 7 and 28 days of different PRG sizes. Reproduced from 9 with permission.

PureGRAPH® Concrete Additives for reduced water permeability:

Further studies have been completed in the laboratories of Prof. Yong Wang and Dr. Meini Su at the School of Mechanical, Aerospace and Civil Engineering, University of Manchester, UK to investigate the impact of PureGRAPH® graphene additives on the performance of concrete systems.

PureGRAPH® graphene with average lateral size 56 ± 12µm supplied by First Graphene Ltd. was incorporated into cement mixtures by dispersion in plasticiser solution prior to incorporation in the cement paste. The cement paste was prepared and tested in accordance with industry standards (BS 1881-108:1983 *Method for making test cubes from fresh concrete*) and the water permeability tested by a soaking methodology. The results are presented in Fig. 4.

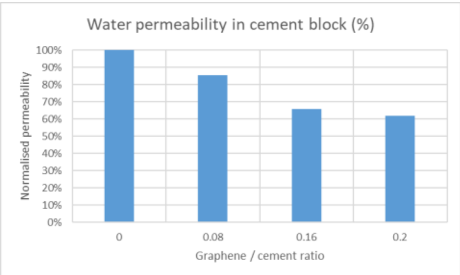

Figure 4 Fig. Water permeability of cement pastes containing PureGRAPH® graphene additive

0.2%w/w loading of PureGRAPH® in cement gives a reduction in water permeability of approximately 40%. The reduction in permeability is derived from the enhanced formation of nucleation sites for the C-S-H hydration crystals and the high surface area of graphene, forming a denser network of interlocked cement crystals. This enhances the mechanical properties and also forms an effective barrier against water penetration[6]. Reducing water penetration is thought to reduce chloride ion diffusion and also prevent the alkali–silica reaction (ASR), a swelling reaction that results in serious cracking and critical structural problems.

PureGRAPH® Concrete Additives for Electrical Conductivity

Dr. Su also examined the impact of PureGRAPH® concrete additives on the electric conductivity of cement paste. PureGRAPH® graphene was incorporated into cement at concentrations of up to 0.2%w/w. The electrical conductivity was subsequently measured by embedding ~~-~~stainless steel wire mesh (electrodes) along the length of the cement mould at the casting stage. Sample blocks of on 60 mm x 25 mm x 18 mm were cured for 28 days prior to measurement. The inner two electrodes act as a voltage measuring unit and the outer two are used for inducing current. This method gives more accurate result compared to a two-point surface contact method because the results are not affected by the contact resistance. The results are presented in Fig.5.

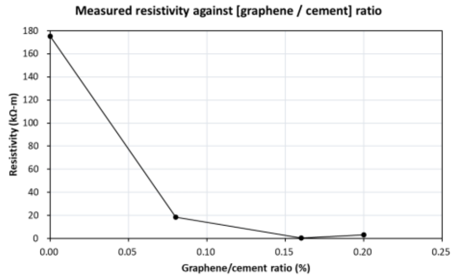

Figure 5 Fig. Electrical Resistivity (kΩm) of cement containing PureGRAPH® graphene additives.

A significant increase in the electrical conductivity of the cement is observed when the graphene dopant level exceeds ca. 0.05 w/w. The researchers propose the significant reduction in electrical resistivity above 0.08%w/w graphene in cement is due to the formation of a continuous conductive path in the cement structure.

PureGRAPH® Concrete Additives for Recycled Aggregate Concrete

In addition to the production and use of cement-based products, the recycling and effective use of demolished concrete aggregate represents an opportunity for further environmental benefits to the construction industry. In the UK alone more than 50 million tonnes of concrete aggregate is re-claimed every year[10]. Effective re-use of this material as an aggregate in new concrete is limited by the reduced performance (compressive strength, tensile strength and Young's modulus).

In a PhD study[11] by Robert Ataria of the School of Mechanical, Aerospace and Civil Engineering, University of Manchester, UK (supervised by Prof. Yong Wang) the impact of graphene additives upon the performance of Recycled Aggregate Concrete (RAC) was investigated. PureGRAPH® graphene concrete additives were dispersed with superplasticiser in water to prepare a cement mortar and then RAC concrete prepared. An enhancement in RAC performance was achieved by washing the recycled aggregate and doping the cement mortar with 0.01%w/w of PureGRAPH® graphene additives. The compressive and tensile strengths of the resulting RAC were enhanced by 43.9% and 24.1% respectively to reach values of 39.14MPa and 3.76MPa which are similar to those of C40 NAC (Natural Aggregate Concrete) a standard concrete manufactured with fresh materials.

Benefits of PureGRAPH® Enhanced Concrete Products:

In summary, published literature demonstrates that graphene concrete additives clearly have the potential to deliver multiple benefits for concrete using industries.

- **The incorporation of small amounts of graphene concrete additives delivers improvements in compressive and tensile strength in concrete, enabling the use of thinner, lighter concrete elements reducing the mass of concrete required for construction projects and simultaneously reducing the CO_2 contribution of the industry.**
- **PureGRAPH® concrete additives also enable the use of recycled concrete aggregate in new concrete structures, as low addition levels can raise the performance of recycled aggregate concretes.**
- **Multiple studies have validated that the large platelet size and high aspect ratio which are accessible with electrochemically exfoliated PureGRAPH® concrete additives are critical for strength enhancement.**
- **PureGRAPH® concrete additives produce a reduction in water and ion permeability which are expected to extend the durability of concrete structures by reducing re-bar corrosion and the alkali–silica reaction, a swelling reaction that can result in serious cracking.**
- **PureGRAPH® concrete additives produce additional properties and benefits including electrical conductivity when used at higher loading levels. These materials will enable development of new smart concrete with built-in sensors to report physical condition, cracks and loading, provide integrated resistive heating and the potential for wireless charging of electric vehicles.**

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