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Graphene for the **construction** sector

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Glossary

3D	Three dimensional
Al_2O_3	Alumina / aluminium oxide
BS	British Standard
C-S-H	Calcium silicate hydrate
CaO	Calcium oxide
CCA	Coarse crushed concrete aggregate
CH	Calcium hydroxide
CO_2	Carbon dioxide
ELCD	European reference Life Cycle Database
EMI	Electromagnetic interference
EN	European Standard
EU	European Union
GGBS	Ground granulated blast-furnace slag
GNP	Graphene nanoplatelet
GO	Graphene oxide
HS2	High Speed 2 railway project
ISO	International Organization for Standardization
ISO/TC	ISO Technical Committee
ISO/TS	ISO Technical Specifications
LCA	Life cycle analysis
NOx	Nitrous oxides
NS	Nanosilica
OPC	Ordinary Portland cement
PCF	Product Carbon Footprint
RA	Recycled aggregate
REACH	European Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals
SCS JV	Skanska Costain STRABAG Joint Venture
SF	Silica fume
SiO_2	Silica / silicon dioxide
vol.%	Percentage by volume
wt.%	Percentage by weight

Introduction

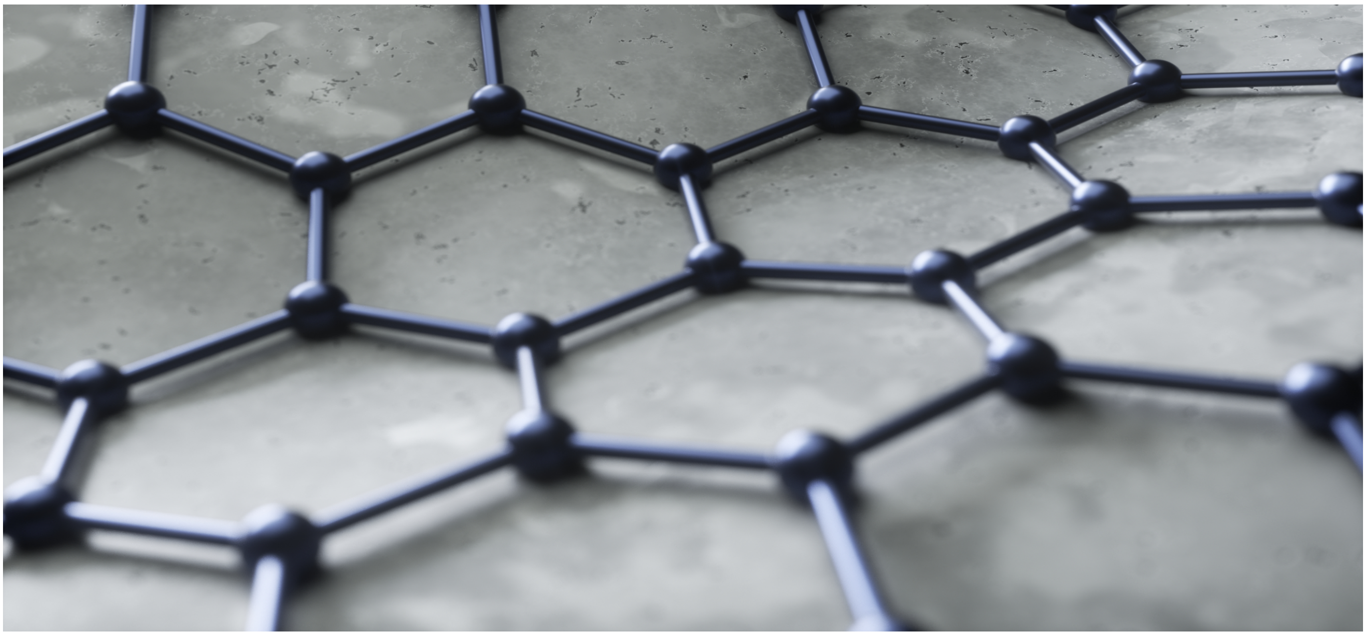
The global buildings and construction sector accounted for 36% of final energy use and 39% of energy and process-related carbon dioxide (CO_2) emissions in 2018. The major component of concrete, cement, is the source of about 8% of the world's CO_2 emissions, according to think tank Chatham House. If the cement industry were a country, it would be the third largest CO_2 emitter in the world - behind China and the US [1].

On the 20th April 2021 the UK government set the world's most ambitious climate change target into law to reduce emissions by 78% by 2035 compared to 1990 levels, and to reach net zero by 2050 [2]. The Carbon Budget will ensure Britain remains on track to end its contribution to climate change while remaining consistent with the Paris Agreement temperature goal to limit global warming to well below 2°C and pursue efforts towards 1.5°C. With huge infrastructure projects underway or on the horizon such as High Speed 2 (HS2) railway, environmentally responsible infrastructure is a key remit to any new development.

UK government analysis finds that costs of action on climate change are outweighed by the significant benefits – reducing polluting emissions, as well as bringing fuel savings, improvements to air quality and enhancing biodiversity [2]. The government expects the costs of meeting net zero to continue to fall as green technology advances, industries decarbonise and private sector investment grows. Reaching net zero will also be essential to sustainable long-term growth and therefore the health of public finances, as well as open up new opportunities for the UK economy, jobs and trade – and the government's ambitious proposals are essential to seizing these opportunities.

A material that promises to significantly enhance the properties of concrete is graphene. Graphene is a relatively young material with enormous potential in a number of applications [3]. Since graphene was first isolated in the UK in 2004, there has been a substantial focus to exploit the material commercially. Graphene is a two dimensional (one atom thick) sheet of carbon atoms that are arranged in a hexagonal crystal lattice, like a honeycomb. **ISO/TS 80004-13:2017** recognizes material up to and including 10 layers as "graphene", from single layer graphene up to graphene nanoplatelet (GNP). Graphene and its derivatives have attracted substantial investment and resources over the last decade for their development into the next generation of composite materials. This is due to the many superlative properties of graphene and its potential to act as reinforcing additives capable of simultaneously imparting significant mechanical property enhancements as well as embedding multi-functional benefits on the host matrix. Graphene has exceptionally good thermal and electrical conductivity, behaves as an impermeable membrane, and is chemically inert and stable. As a result of these properties and many others, graphene became the subject of intense academic and commercial interest. In a recent report, market analysis group IDTechEx, estimated that the graphene market will reach $700m by 2031 [4].

Several companies and infrastructure projects are now investigating the potential of graphene in cementitious composites to enable reduction of carbon footprints or to enable smarter functionality of constructions. In this report we discuss the enhancements that graphene can offer to the construction sector, highlighting key examples and stressing that for the industry to play its part in reducing CO_2 emissions, British and global construction standards need to be reviewed and modified if the industry is to meet the government's targets. The industry also needs to make the case for the whole-life benefits of thermal mass, longevity and ease of maintenance, and to address its suitability to the circular economy. Therefore, new solutions should reduce the volume of the cement used in concrete and mortar and also enhance the durability of as-built structures and infrastructure.



Cement, mortar & concrete

Cement

Cement is a substance used for construction that sets, hardens, and adheres to other materials to bind them together. Cement is seldom used on its own, and it is the binding element in both concrete and mortar [5]. There are two main types of cement: hydraulic and non-hydraulic cement. Hydraulic cement hardens while in contact with water, whereas non-hydraulic cement needs dry conditions. Due to its ease of use and fast drying time, hydraulic cement has become more popular [6].

Common materials used to manufacture cement include limestone, shells, and chalk or marl combined with shale, clay, slate, blast furnace slag, silica sand, and iron ore. Cement manufacturing is a complex process that begins with mining and then grinding raw materials that include limestone and clay, to a fine powder, called raw meal, which is then heated to a sintering temperature >1400 °C in a cement kiln [7]. In this process, the chemical bonds of the raw materials are broken down and are recombined into new compounds. The result is called clinker, which are rounded nodules between 1-25 mm diameter. The clinker is ground to a fine powder in a cement mill and mixed with gypsum (calcium sulphate hydrate) to create cement. Clinker quality depends on raw material composition, which has to be closely monitored to ensure the quality of the cement. Excess free lime, for example, results in undesirable effects such as volume expansion, increased setting time or reduced strength.

Fig. 1 shows a typical lifecycle of cementitious composites. 95% of the CO_2 emissions arise due to the cement production process itself, whereas the remaining 5% is related to the transportation of raw materials and cement-based products. For every metric tonne of cement produced, approximately 900 kg of CO_2 are produced [8]. This equates to approximately 92 kg of CO_2 per metric tonne of concrete. Therefore, the key approaches to reducing CO_2 emissions lie in reducing the cement content or in the reuse or recycling of cementitious composites.

Ordinary Portland cement (OPC) is the most common hydraulic cement that is manufactured and used worldwide. There are five types of Portland cement covered by **ASTM specification C150** with the following features:

- **Type 1** - ordinary Portland cement. A general use cement.
- **Type 2** - used for structures in water or soil containing moderate amounts of sulphate, or when heat build-up is a concern.
- **Type 3** - high early strength cement used when high strength is desired at very early periods.
- **Type 4** - low heat portland cement, used where the amount and rate of heat generation must be kept to a minimum.
- **Type 5** - sulphate resistant portland cement, used where the water or soil is high in alkali.

Beyond these, a number of air-entrained and other blended cements with special performance properties exist.

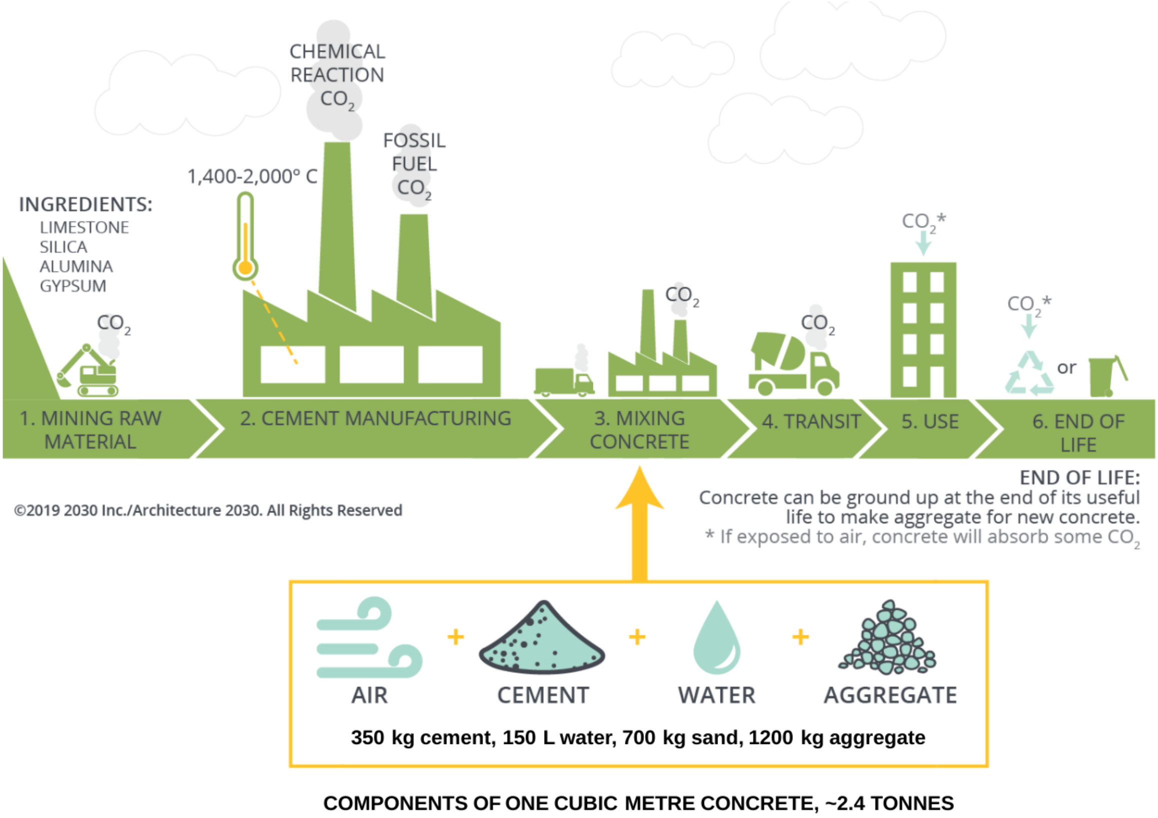


Fig. 1 Typical lifecycle of cementitious composites highlighting the major contributors to CO_2 emissions. Modified from ref. [9].

Cementitious composites

Mortar

Mortar is a material used in masonry construction to fill the gaps and to hold together bricks, concrete blocks, stones, and other masonry materials. It is a mixture of sand, a binder such as cement or lime, and water, applied as a paste which then becomes hard when it cures [10].nMortar serves as the sacrificial element in the masonry, hence should always be softer than the brick it is paired with. When the mortar is harder than the brick it surrounds then the brick will become sacrificial and worn away rather than the mortar [11].

Portland cement mortar (often known simply as cement mortar) is created by mixing Portland cement with sand and water. It was popularised during the late 19th century, and by 1930 it had superseded lime mortar for new construction as it sets hard quickly, allowing a faster pace of construction [11].

Lime mortar is created by mixing sand, lime and water. The type of lime used can be either non-hydraulic limes (those that set when exposed to air) resulting in non-hydraulic lime mortar (known as lime putty) or hydraulic limes (those that set when immersed in water) resulting in hydraulic lime mortar. A pozzolanic additive such as fly ash or brick dust, can be added to a non-hydraulic lime mortar to induce hydraulic setting characteristics [12]. The earliest known use of lime mortar dates to about 4000 BC in Ancient Egypt. Lime mortar is softer than Portland cement mortar and hence, Portland cement mortar should not be used to repair older buildings originally constructed using lime mortar [11].

Most of the mortars used in the UK today come from factory-produced sources as opposed to being mixed on site.

Concrete

Concrete is the most widely used construction material, the second most used material on earth after water [13]. It allows flexibility in structural form as it can be moulded into a multiplicity of shapes, simulating the properties of rock. It is typically composed of a mixture of hydraulic Portland cement, aggregate (crushed stone and/or naturally occurring gravel and sand) and water. The Portland cement chemically reacts with the water, hardens and bonds to the aggregate through a hydration process to form a dense semi-homogenous mass.

Concrete is very strong in resisting compression. Reinforcement (typically steel rebar) is incorporated into the concrete where tensile stresses have to be accommodated. Standard concrete mix designs are based on varying amounts of cement and aggregates of different particle sizes. Design mix concretes are those for which mix proportions finalize based on various lab tests on cylinders or cubes for its compressive strength. A design mix offers the economy on the use of ingredients. The mix is defined by the compressive strength at 28 days and is identified by the strength class. For example, class C25/30 describes a mix which provides a compressive strength of 25 MPa or 30 MPa if a cylinder or a cube is used for testing, respectively. Generally, a C10 is used for patio slabs or non-structural works, C20 is used for domestic floors, C40 for foundations or structural supports, and higher for specialist applications.

Cement hydration

Water causes the hardening of concrete through a process called hydration. Hydration is a chemical reaction in which the major compounds in cement form chemical bonds with water molecules and become hydrates or hydration products [14]. The reactions which occur are mostly exothermic (generate heat). It is possible to get an indication of the rate at which the minerals are reacting by monitoring the rate at which heat is evolved using a technique called conduction calorimetry. The period of maximum heat evolution occurs typically between ~10-20 hours after mixing and then gradually tails off. In a mix containing Portland cement only, most of the strength gain has occurred within a month. Where Portland cement has been partly replaced by other materials, such as fly ash, strength growth may occur more slowly and continue for several months or even a year. Fig. 2 shows this heat evolution as a function of the cement hydration process. The 3 main hydration products shown in Fig. 3 are:

Calcium silicate hydrate (C-S-H): this is the main reaction product and is the main source of concrete strength.

Calcium hydroxide (CH) (or Portlandite): hexagonal platelet crystals formed mainly from tricalcium silicate (alite) hydration and contribute to the concrete's early strength. Alite has a Ca:Si ratio of 3:1 and C-S-H has a Ca:Si ratio of approximately 2:1, so excess lime is available to produce Portlandite.

Ettringite: ettringite is the mineral name for calcium sulphoaluminate, and is the result of the reaction between gypsum and other sulphate compounds with calcium aluminate present in the cement within the first hour.

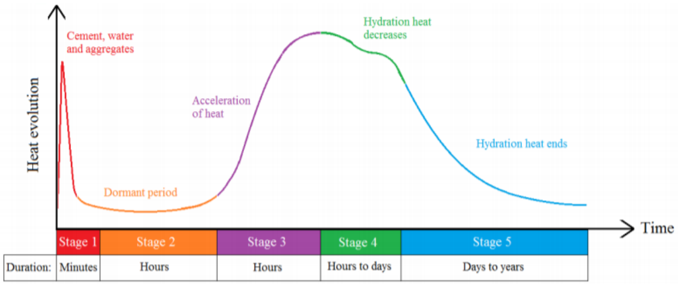


Fig. 2 Schematic illustration of the heat evolution of the cement during the hydration process. Reproduced from ref. [15].

Concrete additives

The volume of cement used is frequently reduced by substituting part of the clinker with supplementary cementitious materials. The most commonly used supplements today are industrial by-products, including ground granulated blast furnace slag, fly ash and silica fume. Finely ground 'fillers' such as finely ground limestone, are also being used with increasing frequency. With the additions of these supplements and inorganic fillers, reductions in Portland cement in the 20-60% range are common, however, further reductions are required to meet new targets to curb climate change.

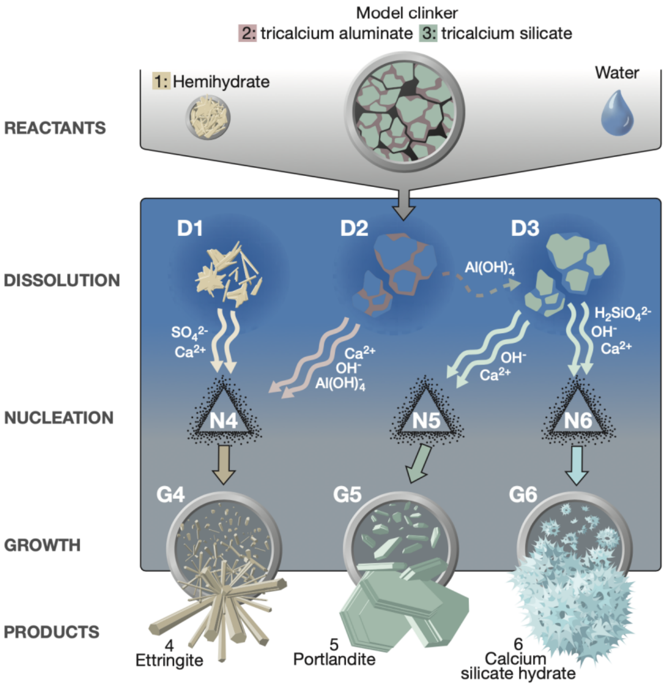


Fig. 3 Schematic representation of the reaction in water of a model cement, composed of hemihydrate and a model clinker that contains tricalcium aluminate and tricalcium silicate. Reaction products are ettringite, portlandite and calcium silicate hydrate (C–S–H). The reactions of dissolution, nucleation and growth are, respectively, marked as D_i, N_i, G_i, with i referring to the phase concerned. The discontinuous line indicates that aluminate ions may influence the dissolution reaction of silicates, which is something that the dispersant can affect indirectly. Reproduced from ref. [16].

Ground granulated blast-furnace slag (GGBS) is a cementitious material and is a by-product from the blast-furnaces used to make iron [17]. The essential difference between OPC and GGBS is that GGBS contains less lime (CaO) but more silica (SiO_2).

Pulverised fly ash (PFA) is a coal combustion product that is composed of the particulates that are driven out of coal-fired boilers together with the flue gases [17]. Fly ash is generally captured by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys. In terms of PFA composition, they include substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline), aluminium oxide (Al_2O_3) and calcium oxide (CaO).

Metakaolin (MK) is obtained by the calcination of kaolinitic clay at a temperature ranging between 500 °C and 800 °C [17]. MK reacts with CH (hydration product) to produce alumina-containing phases.

Silica fume (SF) is the byproduct of the manufacture of silicon for the computer industry [17]. It is many hundreds of times finer than cement. It reacts with lime and water in a similar way to PFA, to produce a binder. It is added to concrete mixes to increase compressive strength and reduce permeability. Typically it is used in a concentration of 5% to 10% of the weight of cement.

Nanosilica (NS) is composed of high purity amorphous silica powder. Because of its small particle size, NS has the advantages of large specific surface area, strong surface adsorption, large surface energy, high chemical purity and good dispersion. Because of these characteristics, its addition can influence three processes: the nucleation effect which, accelerates the hydration of cement; the filling effect, which strengthens the microstructure of the material; and the pozzolanic activity, which produces additional C–S–H gel, improving the mechanical properties of concrete [18].

Admixtures and coatings

Admixtures are those ingredients in concrete other than portland cement, water, and aggregates that can be added to the mixture immediately before or during mixing [17]. Many admixtures could provide a simple route to incorporating graphene or other fillers into a concrete mix, provided there is adequate dispersion and stability. Admixtures can be classified by function as follows:

- Air-entraining admixtures (synthetic detergents, sulphonated lignin, alkylbenzene sulphonates);
- Water-reducing admixtures (alkylbenzene sulphonates, hydroxylated carboxylic acids);
- Plasticizers (Sulphonated melamine formaldehyde condensates, polycarboxylates);
- Accelerating admixtures (calcium chloride, calcium nitrite, calcium nitrate, calcium formate);
- Retarding admixtures (sugars, tartaric acid);
- Hydration-control admixtures (carboxylic acids, phosphorus-containing organic acid salts);
- Corrosion inhibitors (calcium nitrite, sodium nitrite, sodium benzoate);
- Shrinkage reducers (polyoxyalkylene alkyl ether, propylene glycol);
- Alkali-silica reactivity inhibitors (barium salts, lithium nitrate);
- Colouring admixtures (modified carbon black, iron oxide, phthalocyanine);
- Miscellaneous admixtures for workability, bonding, damp-proofing, permeability reducing, grouting, gas-forming, anti washout, foaming, and pumping admixtures.

Coating generally refers to any liquid (polymer or cementitious-based) applied to cured concrete, including cement-based toppings and overlays, paints, and epoxy-aggregate systems. The most commonly used concrete coatings today fall within four basic polymer categories (epoxies, urethanes, acrylics and polyureas) or are hybrids of these polymers.

Graphene-based cementitious composites

Due to the concerns over OPC's inherent brittleness, low tensile strength and poor stability in aggressive environments, continuous attempts have been made to improve the performance of traditional cement composites by adding reinforcing fillers. The interest in incorporating graphene as a filler into cement based materials is driven by the potential multifunctionality it could impart on concretes and mortars. The last few years have witnessed a significant amount of research on graphene reinforced concrete, however, a straightforward assessment of the state of the art is challenging as researchers use different graphene products (with varied thicknesses, lateral sizes, surface areas and surface chemistries) and employ different dispersion techniques to introduce the graphene into the cementitious mix.

The homogeneous dispersion of graphene in water and subsequently in the cement matrix is critical in order for the graphene to manifest its superior properties to cementitious composites. This is particularly challenging when dispersing higher graphene loadings and also if the specific surface area of graphene is very high because of the attractive forces between the graphene sheets and due to the hydrophobic nature of graphene.

In research studies, different types of graphene derivatives such as GNPs and graphene oxide (GO) have been employed as additives in cement-based materials. GNPs comprise multiple stacked graphene sheets typically produced by the relatively low-cost route of exfoliation of graphite (natural or synthetic). Production of GO is significantly more energy intensive using aggressive chemicals, but affords a highly functionalized, higher aspect ratio, higher surface area, water-soluble material that can interact strongly with cementitious materials (Fig. 4).

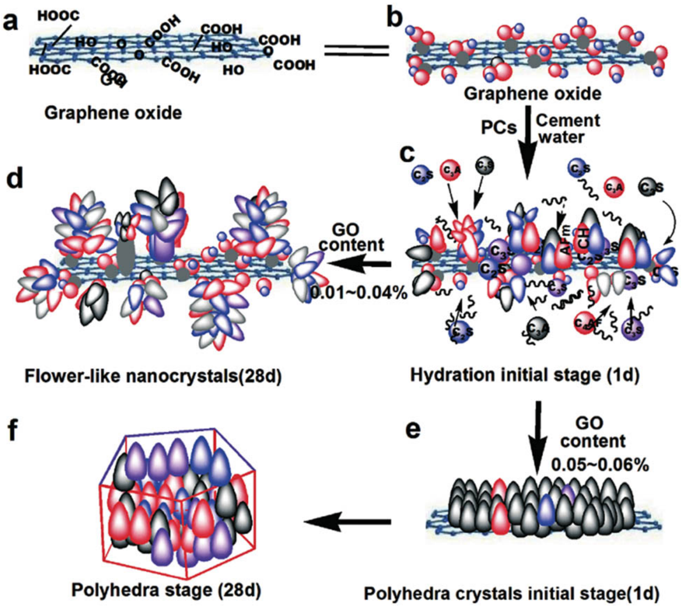


Fig. 4 Schematic diagram of the regulatory mechanism of GO nanosheets on cement hydration crystals. Reproduced from ref. [19]. https://creativecommons.org/licenses/by/4.0/

However, because of the nature of the chemical modification, the mechanical, thermal and electrical properties of GO are significantly diminished compared to GNPs.

The rheology and hence the flowability of concrete is affected by graphene addition; the workability decreases gradually with increased graphene loading and its specific surface area. Graphene with relatively smaller specific surface area consumes less water to wet their surface and results in minor influence on the flowability. Studies have found that increasing the graphene loading above 1 wt.% could reduce the workability of cement paste. Therefore, it is important to find the type of graphene and its loading that gives maximum reinforcement without sacrificing the workability [20]. Many studies conclude that GO reduces the fluidity of cement slurry. Chemical cross-linking of GO nanoflakes with calcium ions form GO aggregates that reduces free water in cement slurry, thereby reducing the fluidity of cement slurry [21].

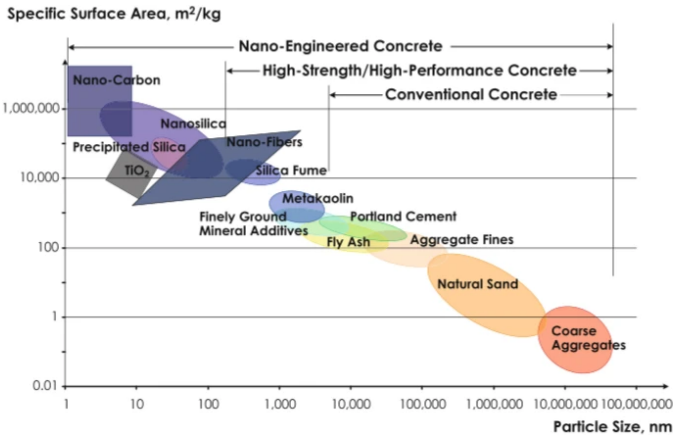


Fig. 5 Comparative analysis of particle size and surface area for various nanofillers, cementitious materials and aggregates. Reproduced from ref. [22]. http://creativecommons.org/licenses/by/4.0/

Graphene-cement hydration

The introduction of graphene-based materials into cementitious composites influences the hydration process and the microstructure of the cement phase which ultimately leads to the overall reinforcement of the composite. Graphene is a two-dimensional nano-filler with high specific surface area (see 'nano-carbon' in Fig. 5) that can act as nucleation seeds and boost the cement hydration reaction at the early stage to generate more cement hydration products, particularly the C-S-H phase; increases the adsorptive properties between the cement particles and enhances the compactability of the cement composite. Also, the nano-filler effect which can fill and divide the coarser pores into finer pores introduces a noticeable reduction in the total porosity and pore diameter of cement composites. These two factors lead to the enhancement of the mechanical performance and water impermeability. The two-dimensional planar structure of graphene enhances the bridging effect among the graphene sheets, cement particles and the cement hydration products, which enhances the load-absorption and load-transfer capacity of the cement composites and reduces the formation and propagation of the microcracks [23].

Different types of graphene, its specific surface area, loading and degree of dispersion lead to different enhancements of mechanical properties. Most studies demonstrate the optimum mechanical properties of cement composites with dosage of graphene within a range of 0.02 wt.%–1 wt.% of the cement component. Graphene dosage over 1 wt.% is considered to be excessive [24]; any agglomerated graphene will reduce the overall nucleation sites for the cement hydration reaction, hinder the movement of fresh cement by locking the water inside, potentially resulting in weak zones in the cementitious composites. This means excessive dosage of graphene could result in a negative influence on the mechanical properties of cement composites [25].

As a material with high thermal conductivity, when uniformly distributed, graphene can boost heat transfer throughout the cementitious composites. Research suggests that this can effectively reduce the early hydration heat of cement, prevent the thermal cracking in mass concrete structures and also enhance the fire resistance of building structures. Studies indicate that the thermal conductivity of graphene reinforced cement mortar can be increased to twice as much as that of the thermal conductivity of plain cement mortar when the dosage of graphene is increased to 5 vol.% [26].

Cementitious composites are also vulnerable to the ingress of water and aggressive elements such as chloride ions, influencing the durability of construction materials, in particular the corrosion of steel rebar. Incorporating graphene in the concrete results in reduction in the critical pore diameter, refinement of the pore structure and increase of the tortuosity path leading to reduction of the water penetration depth, chloride diffusion coefficient and chloride migration coefficient [27].

Smart Structures

Advanced building materials of the future are being envisioned to provide multifunctional smart features such as asset management tracking, self-powering and self-sensing for structural health monitoring applications. Cement composites with electrical conductivity and sensitive piezoresistivity, makes it a reliable and competent structural composite for the use of strain/damage sensing for civil infrastructure providing warning signals if the structural integrity is close to failure, and can also be used as the new generation road pavement material with the potential capability to achieve static/dynamic wireless charging for the electric vehicle to meet the needs of future smart infrastructure development.

Since graphene is electrically conductive, at high enough loadings, uniformly distributed graphene can create a continuous electrical network inside the cementitious composites. Research has shown that the percolation threshold of the graphene reinforced cement mortar is between 2.4-3.6% by volume of cement. As the concentration of graphene exceeds 3.6 vol.%, a continuous electrical path network can be developed and the electrical conductivity of the cement composites becomes insensitive to its moisture content [28]. Although GO can be more easily dispersed in water due to the presence of hydrophilic functional groups, its low electrical conductivity limits the development of the smart-functionality. Developing cementitious material with high electric conductivity while maintaining the fluidity of concrete is challenging as it requires higher graphene loadings added to the composite. In such cases graphene can also be applied as a coating rather than an additive.

Research indicates that homogeneously dispersed graphene in cementitious composites can promote electromagnetic interference (EMI) shielding, which could be used to decrease the electromagnetic emission problems on human health, enhance the privacy of building occupants or provide protection for military applications. The combination of electrical and thermal properties also opens up potential applications in underfloor heating, anti-static flooring, and solid-state heated roads for de-icing applications.

Photocatalysis in a cementitious matrix could have a large effect to decrease air pollution by reducing nitrous oxides (NOx) and enable self-cleaning surfaces, a significant benefit to reducing maintenance costs. Graphene-titania photocatalysts have been reported to degrade up to 70% more atmospheric NOx than standard titania nanoparticles alone.

Researchers from the Department of Architecture and Civil Engineering recently published an article outlining a new concept for rechargeable cement-based batteries. If successful this concept will allow whole sections of multi-storey buildings made of functional concrete for energy storage [29].

These developments open the door to innovation for the smart cities of the future, with a smart home of the future depicted by Italcementi in Fig. 6.

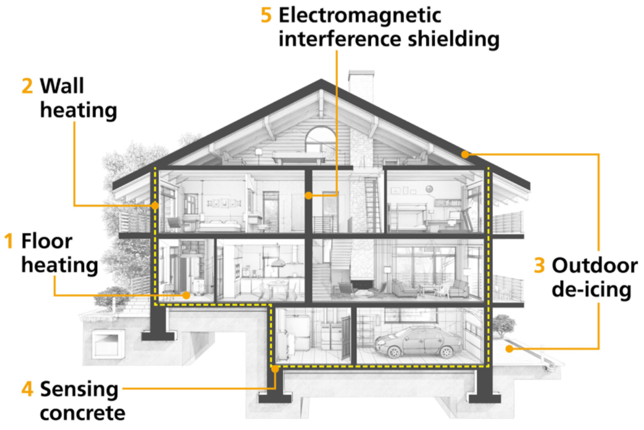


Fig. 6 Heidelberg Cement's Italian subsidiary, Italcementi, a member of the Graphene Flagship project, focuses on several smart concrete applications. Credit: Italcementi.

Graphene enhanced concrete to cut carbon emissions?

Concrete life cycle analysis (LCA)

LCAs seek to measure the environmental impacts associated with all stages of a product (e.g. concrete) or a project (e.g. a building or highway), throughout its life cycle from raw material extraction through to processing, transportation, use and disposal. Because of its enormous production and utilization, environmental assessment of concrete is of great importance with regard to the efforts towards lowering the environmental impact of concrete and creating a sustainable society. The general methodology of LCA is defined in the **ISO 14040** series. There is no single method for conducting LCA studies, but all LCA methods should follow the basic methodological principles defined in these standards [30].

The impact categories relevant for concrete production and utilization are: energy consumption, fossil fuel depletion, climate change, acidification, eutrophication and photo-oxidant creation (smog), human toxicity, solid waste production and mineral resources (sand and stone) depletion. The research performed so far in the area of LCA of concrete shows that the cement production is the largest contributor to all impact categories due to significant CO_2 emission during the calcination process in clinker production and fossil fuel usage. It causes approximately 84% of the total energy use, 93% of the total climate change, 81% of the total eutrophication, 86% of the total acidification and 83% of the total photo-oxidant creation [31]. The contributions of the aggregate and concrete batching plant operations are very small (upto ~5%), while the contribution of the transport phase lies somewhere in between (upto ~20%) [31]. If reinforced by steel or other materials, impact from issues such as corrosion damage should also be considered. However, LCA of concrete and its raw materials is still a limited research area and mainly focuses on energy use and greenhouse gas emissions. Without a complete assessment including other important issues such as toxic emissions, water effluents, and water consumption, especially from admixtures/reinforcing materials and recycled concrete, it is not yet possible to understand the overall environmental and human health implications of concrete and its raw materials, or compare concrete to other building materials.

Data necessary for LCA, such as emission data, are taken from existing databases such as ELCD (European reference Life Cycle Database) and Ecoinvent [32]. LCA software tools also offer access to databases. However, such data are geographically dependent and hence each country/region should have its own database according to its construction industry resources and traditions. Also, development of a comprehensive and robust LCA framework that can be applicable to different variations of concrete mixtures and can quantify the relationship between properties of concrete and how environmental inventories are affected by the variations in these properties is critical.

Offsetting the carbon footprint with graphene

The addition of relatively small amounts of graphene enhances the strength of standard concrete, meaning significantly less cement could be needed to achieve equivalent structural performance, therefore, reducing the carbon footprint. The additional strength might also reduce the need for steel reinforcement to enable further reductions in CO_2 emissions. A University of Cambridge study indicated that if the addition of graphene results in a 5% reduction of the Portland cement, the effect on global warming could reduce by 21% [33]. Another study from the University of Exeter, estimated that 125 g of graphene can decrease the total volume of cement down to 148 kg per cubic metre of concrete (>50 wt% reduction of cement required for the original strength). From an environmental point of view those numbers could account for a total decrease of 446 kg/tonne emissions of CO_2 [34].

Graphene incorporation into construction materials does not come without its own contributions to the carbon footprint. Product Carbon Footprint (PCF) calculations consider the entire life cycle of the product. This means delving into the raw materials that make up graphene, how it is manufactured, transported, used and disposed of. Understanding the PCF of graphene will help manufacturers to understand the impact of their product, and enable process optimisations such that climate neutral products can be offered, and strong carbon reduction targets can be set.

A recent study by Empa, Switzerland [35], shows a broad range of PCFs for graphene based materials utilising different lab scale manufacturing processes. In most cases, electricity use is the largest contributor to CO_2 emissions - switching to decarbonised energy sources will naturally reduce the carbon footprint of the production methods and any resulting products [36]. For high volume construction applications there will ultimately need to be a trade off between cost of graphene production, quality of graphene and contribution to CO_2.

Beyond simple cement reduction calculations, graphene has also been shown to improve the durability of cementitious composites by reducing the water permeability, thermal cracking and abrasion weight loss. Improved durability of construction materials reduces maintenance costs and improves asset life-span. Graphene enabled structural health monitoring of civil infrastructures will also be of great importance to rectify asset integrity and ensure its lifespan [37]. Therefore, taking a more holistic approach is necessary to understand graphene's true benefits.

Construction material standards & what needs to change?

Aside from the standards mentioned in the previous sections, the key standards that govern the construction materials are:

- **BS EN 206:2013** Concrete. Specification, performance, production and conformity
- **BS 8500-1:2015** Concrete. Complementary British Standard to BS EN 206. Method of specifying and guidance for the specifier.
- **BS 8500-2:2015** Concrete. Complementary British Standard to BS EN 206. Specification for constituent materials and concrete

BS EN 206 covers the technical rules that apply to the production of concrete for normal building structures with an intended working life of at least 50 years. **BS 8500** is the complementary British Standard for specifying and producing concrete. Part 1 covers specification and gives guidance to the specifier. Part 2 covers the constituent materials in concrete and contains the information required by the concrete producer, giving more details on requirements for aggregates, additives and admixtures, etc.

Several specific standards exist for cement and different additives for concrete:

- **EN 197** Cement
- **EN 12620** Aggregates for concrete
- **EN 13055** Lightweight Aggregates
- **EN 450** Fly ash for concrete
- **EN 934** Admixtures for concrete, mortar and grout
- **EN 1008** Mixing water for concrete
- **EN 13263** Silica fume for concrete

A report in 2016 on "European standardisation of new and innovative cements" from the Materials Standing Committee of The Concrete Society outlined that "the standardisation of any new product is often a key step to facilitate the wider exploitation, and conformity to a standard gives both specifiers and users added confidence [38]. Without suitable standards in place, there is a risk that fitness for use will need to be demonstrated on a case-by-case basis, with consequent replication of effort and delays in exploitation." Standards that exist solely around additives for concrete will, therefore, need to be developed for graphene-based materials. Also due to the novelty of graphene-based nanomaterials and ongoing assessment of nanoparticle health and safety through UK and EU REACH registration, for example, assessment of the release of such materials would be governed by **BS EN 16637** & **BS EN 16516** Construction products: Assessment of release of dangerous substances.

Overall there are a number of areas where such standards could be improved or modified to enable further sustainable outcomes. The industry often over-prescribes concrete strengths and poses minimum limits to cement content which means addressing carbon footprint concerns is made more challenging if standards are not rethought. The standards seem to fix upon minimum binder amounts (e.g. water/cement ratio, the minimum amount of cement in the range of cement and combination type). In this way, a graphene enhanced concrete can only be considered in terms of improving strength or other performance rather than considering the addition of graphene as a route to further reduce the amount of cement content and, therefore, CO_2 emissions, whilst maintaining performance.

Secondly, although considered, the use of coarse crushed concrete aggregate (CCA) and recycled aggregate (RA) has some limitations. According to **BS 8500-2**, both may be used in designed concrete up to a maximum strength class C40/50. Coarse CCA may be used in any strength class only if not contaminated and the composition is known. In any case the proportion is limited to not more than a mass fraction of 20% of coarse aggregate. A graphene enhanced concrete can overcome the limit of using lower quality CCA and RA because it can improve the mechanical performance. More broadly, there may be the possibility to use a greater content of lower quality CCA and RA materials and still maintain a good level of mechanical performance in cementitious composite materials, which the current standards would not allow.

Versarien Activities

Lab trials and real-life pours

Initial lab scale trials have been performed dispersing both difference Versarien graphene powders (Nanene^{TM} and GNP-HP grades) as well as directly blending water-based Graphinks^{TM} into cementitious mortar and concrete mixes with graphene loadings optimised below 0.3 wt.% in the cement phase. Dispersion of graphene in the cement mix is challenging if performed on the construction site at large scale if it involves complex procedures such as sonication or high-shear mixing. Therefore, pre-fabricated stable graphene dispersions that can be directly added to the cement mix, provide an industrially attractive option. Graphinks^{TM} offers an easy to use product(simply add with the water), with excellent mixing results, offering workability and performance using the construction industry's regular admixture control systems.

Trials with a traditional Type 1 OPC based concrete mix and the addition of Versarien's Graphinks^{TM} showed the following (all tests have been undertaken by an independent test house):

- Improved compression strength (+38%)
- Improved flexural strength (>14% - 45%)
- Increased split tensile strength (>15%)
- Improved water permeability (> 200% - 0-2 mm)
- Faster curing without micro-cracking
- Increased corrosion resistance

These are in line with those results observed by several other universities, namely the University of Exeter [34], and other graphene companies that are investigating mortars and concrete [39], [40].

Through further trials with an international 'readymix' concrete manufacturer, we have developed a graphene enhanced, low carbon, pumpable, commercial mix as typically available at any UK readymix site. This graphene enhanced concrete produced similar performance results as the Type 1 OPC based concrete mix by utilising a fraction of a percent of graphene in the concrete. This was demonstrated on a 3 cubic metre pour in Symonds Yat, Gloucestershire, in collaboration with Kwikhaus UK Ltd, shown in Fig. 7. Future Versarien graphene powders and dispersions for the construction sector will fall within a new family of products called Cementene^{TM}.

In a similar fashion, utilising Versarien's graphene powder products, and in a world-first for the sector, a joint venture between University of Manchester and construction firm Nationwide Engineering laid the floor slab of a new gym in Amesbury, Wiltshire with graphene-enhanced concrete (Fig. 8). Addition of tiny amounts of graphene strengthened the concrete by around 30% compared to standard concrete which allowed removal of 30% of cement and all steel reinforcement. This concrete, referred to as Concretene^{TM}, can be used just like standard concrete, with no new equipment or training is needed in the batching or laying process, and cost-savings can be passed directly to the client.

Fig. 7 Versarien's Cementene^{TM} product being trialled on site in Symonds Yat, Gloucestershire, in collaboration with Kwikhaus UK Ltd.

Fig. 8 Concretente^{TM} slab laid in Amesbury, Wiltshire with 30% cement reduction and no steel reinforcement used. Credit: Nationwide Engineering Ltd.

'Printfrastructure'

In a UK first, on-site 3D reinforced concrete printing is set to deliver environmental, cost and community benefits for Britain's new high speed rail network [41]. The cutting-edge technology, called 'Printfrastructure', will be deployed by HS2 Ltd.'s London tunnels contractor SCS JV (Skanska Costain STRABAG Joint Venture), in a move that represents a major step forward in construction technology.

Printing concrete with computer operated robots will enable SCS JV to make structures on site and with less material, instead of transporting them as pre-cast slabs by road before being assembled and lowered into place by large cranes. As flexible mobile technology, 3D concrete printing enables the technique to be deployed in physically-restricted areas – avoiding the need to develop complicated and potentially expensive logistical plans. Where HS2 construction is happening besides a live railway, it offers an opportunity to deliver works without disrupting the travelling public. Previously, work would have taken place overnight after trains have stopped running, potentially disturbing the local community, or would have required the suspension of services to ensure safe working. Using a computer-controlled robot enables the reinforced concrete structures to be printed with a strengthening unique internal lattice structure, which not only significantly reduces the quantity of concrete required but also cuts waste.

The technology developed by SCS JV's Worcestershire-based partner, ChangeMaker 3D and UK advanced materials specialist, Versarien, takes the high-tech 3D concrete printing process and combines it with graphene, shown in Fig. 9. The aim is to replace traditional steel to help drive improved site safety, greater construction flexibility, shorter build time and a smaller carbon footprint. SCS JV estimates that the concrete used can contribute toward reducing carbon by up to 50%. By removing steel and simplifying the construction process, which will no longer require cranes and significantly fewer delivery trucks, the carbon reduction could be even greater.

Proof of concept trials are due to begin in Spring 2022.

Alongside these developments, ChangeMaker 3D were recently appointed [42] as the UK representatives for **ISO/TC 261**, to define standards and quality requirements for Additive Manufacturing in Building & Construction (Structural and Infrastructure elements) in order to ensure high quality within a 3D Construction Printing facility or off-site printing. This will accelerate the scalable adoption of 3D printing in the Construction industry, enabling greater sustainability for the built environment.

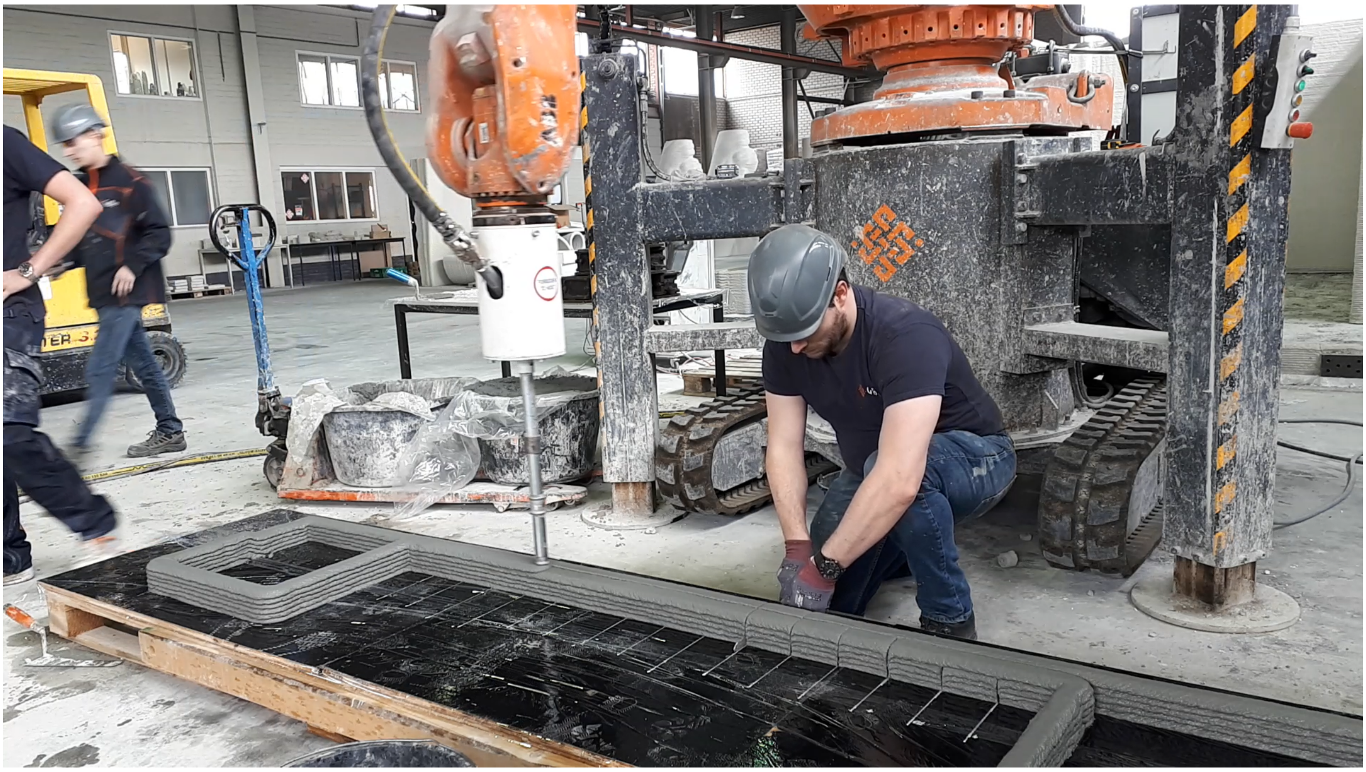


Fig. 9 Versarien's graphene utilised in a 3D printed mortar. Credit: CyBe Construction.

Summary and Future Outlook

Graphene enhanced mortars and concrete are already a reality and the industrial scalability has become clearer and more achievable over the last 12 months. Industrial scalability comes from two aspects - the first is the ability to manufacture graphene to a repeatable required quality in volume and the second, to deliver it and dose and mix using existing (or slightly modified) site equipment.

By optimising the process for volume and quality Versarien has designed and installed processes to deliver both graphene inks by simple addition through existing admixture pump systems as well as increasing production of GNPs in dry powder form for premixed and bagged product development. And through working with global industry partners, evidence is being gathered to show clear performance benefits at a cost sensitive point. This progress in terms of graphene scale-up and large scale demonstration has been well enabled by a £5 million Innovate UK loan under the project title G-SCALE.

Versarien are also taking a proactive approach towards sustainability of graphene and its applications, working closely with the EC Graphene Flagship project to measure the PCFs of our products in order that climate change contributors can be reported with a high level of accuracy & confidence.

The current global climate change crisis represents a crucial opportunity for the construction sector. Currently the industry standards don't always fit with graphene enhanced concrete and traditional standards and metrics will require changing and renewing. The drive towards net zero carbon has created the momentum for industry and sector leaders to collaborate with the new advanced material engineered towards this common goal.

The future opportunities are endless and graphene will no doubt solve many challenges that have yet to be identified. Initially a 'greener' concrete that outperforms existing materials and with a lower carbon footprint will become commonplace. Once the construction sector sees repeatable, real world evidence, the momentum to use this technology will snowball. In anticipation, the graphene engineers and scientists are constantly breaking new boundaries and producing new grades to service the demand. Versarien is at the forefront of this charge and is reaching out to the world to help find the challenges that graphene can resolve.

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