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# Use of Nanomaterials in the Built Environment

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**Abstract:** Climate change is the biggest transformational driver of our built world. This necessitates innovative approaches to combat its effects. Sea levels rising and increase in flooding result in intensified water and chloride penetration in concrete structures. The need for more durable, 'flood-proof' architecture has led to research in graphene oxide. Here concrete with and without an admixture of 0.02% of graphene oxide (by weight of cement) has undergone compressive and flexural strength testing as well as rapid chloride permeability testing. A 6.2% increase in compressive strength and 19.1% increase in flexural strength compared to the reference concrete was determined after 28 days curing time. Additionally, a decrease of 43.3% in chloride permeability was also found. While this study does indicate that graphene oxide enhances concrete durability it holds little statistical significance, as few testing samples were created. Financial limitations meant only 1g of graphene oxide was added to a 50kg concrete mix.

**Keywords:** Nanomaterial, graphene oxide, built environment, concrete.

## 1. Introduction - Concrete

Concrete is the most heavily utilized construction material to date. It is produced from some of the world's most abundant resources and has been for millennia. Archaeological sites from Neolithic times, circa 6500 BC, suggest it was used in modern-day Syria (Akkermans and Schwartz, 2009). Nearly 9000 years later, humanity currently uses twice as much concrete than all other construction materials combined. After water, it is the most consumed material on Earth; each person 'consumes' roughly 3 tons of it per year (Gagg, 2014).

Its extensive use in infrastructure owes to its versatility and that it is inexpensive compared to other building materials. The most common form of concrete consists of Portland Cement (PC), water and aggregates, though the ratios of these components vary according to desired function. The main hydration product of water and PC is calcium silicate hydrate (C-S-H) gel, which is primarily responsible for the strength of cement-based materials (MIT, 2019). The incorporation of admixtures to concrete mixes, to provide different or enhanced properties, has been done throughout time. In the past, creating high performance concrete led to the inclusion of supplementary cementitious materials such as fly ash, blast furnace slag, metakaolin and silica fume (Chuah et al., 2014). In recent years, nanomaterials have been introduced into cement matrices. Their particle sizes, being similar to C-S-H gel, and large surface areas (figure 1) enable reactive and filling properties which effectively reinforce cementitious materials. Nevertheless, non-uniform dispersion of nanomaterials can result in aggregation and agglomeration. This can sometimes provide negative reinforcing effects, making composites weaker and less durable. While desirable, attaining perfectly uniform dispersion of any material in concrete is challenging.

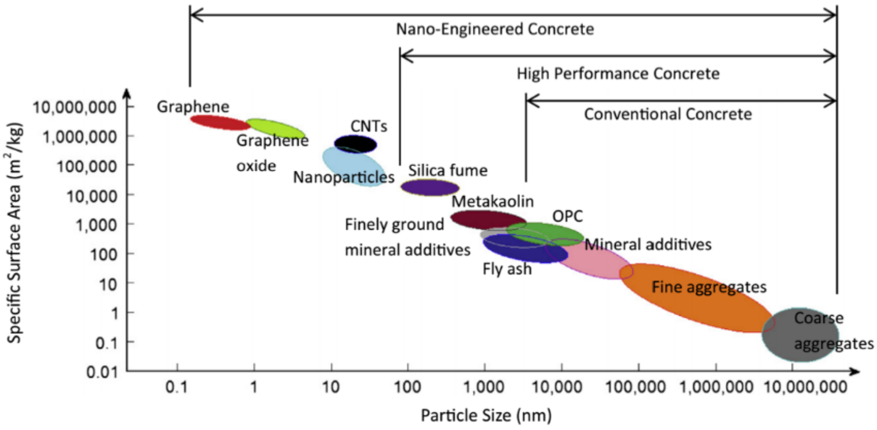
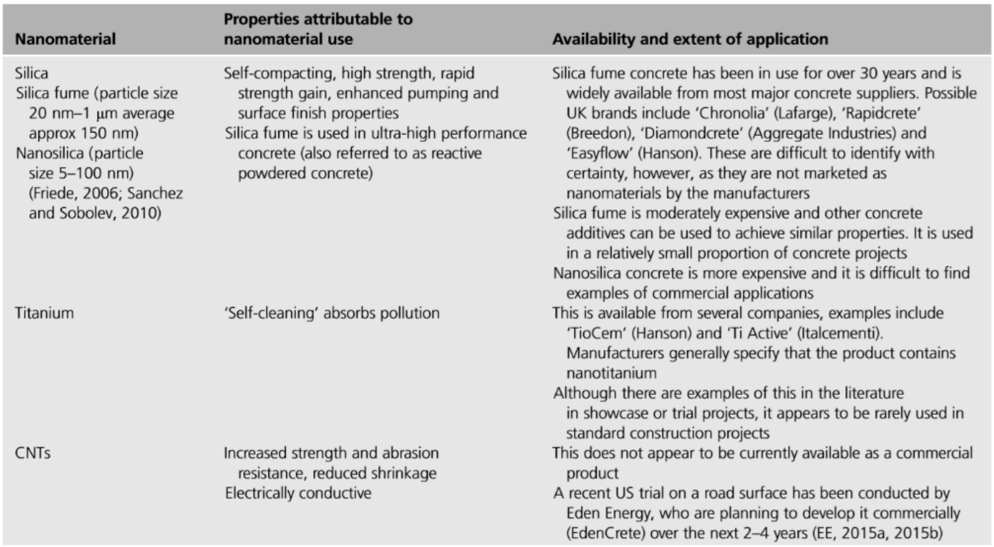


Figure 1: Particle size against specific surface area of concrete constituents (Chuah et al., 2014)

A framework of commercially available nano-enabled construction products, made by Jones et al. (2019), includes nano-engineered concretes, displayed in figure 2. Despite suppliers rarely marketing it as a nanomaterial, silica fume is widely utilized in construction projects. It has a rough particle size of 150nm which falls into the larger bound of nanomaterial size. Nanotoxiologists see little difference, in terms of toxicity, from 100nm (the widely regarded nanomaterial upper bound) to 150 nm (Jones et al., 2019). Silica fume is proven to enhance concrete's compressive and bond strength as well as abrasion and chloride resistance (Ghafoori and Diawara, 1999).



| Nanomaterial | Properties attributable to nanomaterial use | Availability and extent of application |
|---|---|---|
| Silica<br>Silica fume (particle size 20 nm–1 μm average approx 150 nm)<br>Nanosilica (particle size 5–100 nm) (Friede, 2006; Sanchez and Sobolev, 2010) | Self-compacting, high strength, rapid strength gain, enhanced pumping and surface finish properties<br>Silica fume is used in ultra-high performance concrete (also referred to as reactive powdered concrete) | Silica fume concrete has been in use for over 30 years and is widely available from most major concrete suppliers. Possible UK brands include 'Chronolia' (Lafarge), 'Rapidcrete' (Breedon), 'Diamondcrete' (Aggregate Industries) and 'Easyflow' (Hanson). These are difficult to identify with certainty, however, as they are not marketed as nanomaterials by the manufacturers<br>Silica fume is moderately expensive and other concrete additives can be used to achieve similar properties. It is used in a relatively small proportion of concrete projects<br>Nanosilica concrete is more expensive and it is difficult to find examples of commercial applications |
| Titanium | 'Self-cleaning' absorbs pollution | This is available from several companies, examples include 'TioCem' (Hanson) and 'Ti Active' (Italcementi). Manufacturers generally specify that the product contains nanotitanium<br>Although there are examples of this in the literature in showcase or trial projects, it appears to be rarely used in standard construction projects |
| CNTs | Increased strength and abrasion resistance, reduced shrinkage<br>Electrically conductive | This does not appear to be currently available as a commercial product<br>A recent US trial on a road surface has been conducted by Eden Energy, who are planning to develop it commercially (EdenCrete) over the next 2–4 years (EE, 2015a, 2015b) |

Figure 2: Commercially available nanomaterial concretes (Jones et al., 2019)

Graphene is yet to be widely adopted. Nevertheless, it's 2-D surface like quality provides an extra dimension for cement matrices to interact with. Its high specific area and small particle size enhances bonding with host materials. It has an effective ability to diminish concrete porosity, which increases strength and decreases water permeability (Mohammed et al., 2015). This has great significance for built environments that need to adapt to increased water exposure, an issue which CC is making more prominent. Nevertheless, graphene is expensive and difficult to manage on industrial scales (Alkhateb et al., 2013).

Graphene Oxide (GO) can be created by oxidation of graphite which is abundant and inexpensive (Graphene-info.com, 2019). It has hydrophobic graphenic domains and hydrophilic edges (figure 3) emanating from carboxyl groups, which make it highly dispersible in aqueous solutions. It has yet to gain widespread attention and its advances are yet to be fully verified.

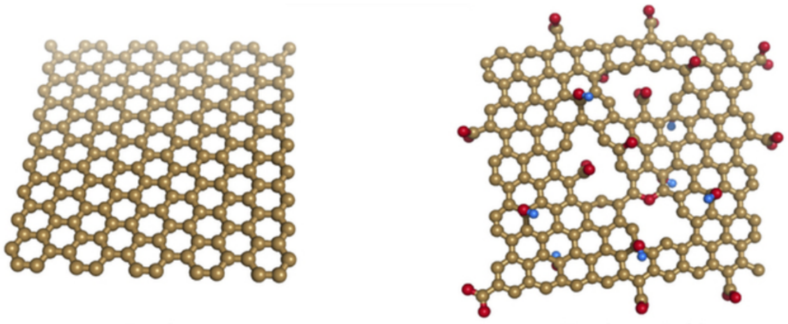


Figure 3: Chemical makeup of graphene and graphene oxide (Ecosia.org, 2019)

## 2. Methodology

The materials used in making the concrete mixes are summarized in table 1.

Table 1: Constituents of concrete mixtures

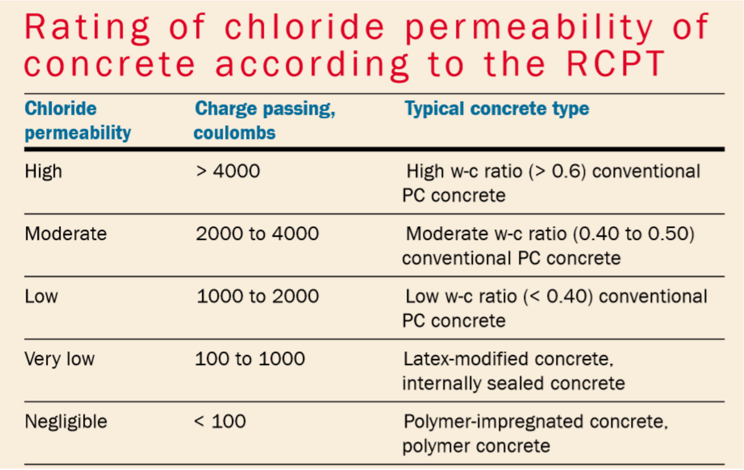
| Material | Product |
|---|---|
| Portland Cement | Blue Circle Procem Cement 52.5N |
| Water | London Tap Water |
| Fine Aggregate | Sand |
| Coarse Aggregate (5mm – 20 mm) | Gravel and crushed stone |
| Superplasticizer | Sika ViscoFlow-2000 |
| GO | GO $H_20$ solution (GrapheneCA GP12101) |

Designing their mixture proportions was constrained by the amount of GO available and that the concrete mixer used required a minimum mix volume of 20L. However, it distributes constituent materials well. 0.02% of GO by weight of cement (5kg of PC) was selected here. The GO was suspended in 1L of water, so the minimum water to cement (w/c) value was 0.45. Smaller w/c values generally give higher strengths. Nevertheless, when including aqueous admixtures to concrete, some water should be introduced to the mix before the admixture to allow the hydration process to begin. A 0.48 w/c was thus chosen. To ensure the mixture had sufficient workability, a superplasticizer was also utilized. The proportion of aggregate was then determined using a volumetric ratio of 1:3.5:7 (cement, sand and coarse aggregate respectively) which is typically exploited for building foundations. Foundations are at most risk of increased water exposure. The final mixture proportions for the GO concrete are presented in table 2. The reference concrete used this design without GO.

Table 2: Mix Design for GO Concrete

| Material | Mixture Proportions (kg/m$^3$) | Batch Weights (kg) |
|---|---|---|
| Coarse Aggregate | 736 | 30 |
| Fine Aggregate | 716 | 15 |
| PC | 250 | 5 |
| Tap Water | 120 | 1.163 |
| Superplasticizer | 5 | 0.1 |
| GO | 0.05 | 0.001 |
| Total | 2555.05 | 51.001 |

The mixture was then placed into moulds and left to set for 24 hours under a polyethylene sheet. Once cast, the specimens were placed in a water curing tank, operated at a temperature of 20°C, for up to 28 days. The preparation of samples followed the BS EN 12390-2:2009 standard. When curing was completed, the samples were then tested. Compressive and flexural strength tests were conducted using the Advantest 9 machine, following the BS EN 12390-1:2012 standard. The Perma was used for the rapid chloride permeability (RCP) measurements. The test indicates how electrically resistant concrete is to the penetration of chloride ions. The widely accepted qualitative relationship, proposed by Whiting et al. (1981), between electrical charge and the long-term chloride penetrability of concrete is displayed in figure 4. The higher the charge the more 'permeable' the material is. While this is a test of electrical resistivity, this is correlated to permeability. This testing follows the ASTM C1202 standard.



Rating of chloride permeability of concrete according to the RCPT

| Chloride permeability | Charge passing, coulombs | Typical concrete type |
|---|---|---|
| High | > 4000 | High w-c ratio (> 0.6) conventional PC concrete |
| Moderate | 2000 to 4000 | Moderate w-c ratio (0.40 to 0.50) conventional PC concrete |
| Low | 1000 to 2000 | Low w-c ratio (< 0.40) conventional PC concrete |
| Very low | 100 to 1000 | Latex-modified concrete, internally sealed concrete |
| Negligible | < 100 | Polymer-impregnated concrete, polymer concrete |

Figure 4: Chloride permeability rating of concrete (Joshi and Chan, 2002)

## 3. Results and Conclusions

The results indicate that the inclusion of GO into concrete enhances its physical properties. The averaged results yielded for the compression tests at 21- and 28-days curing time are presented in figure 5.

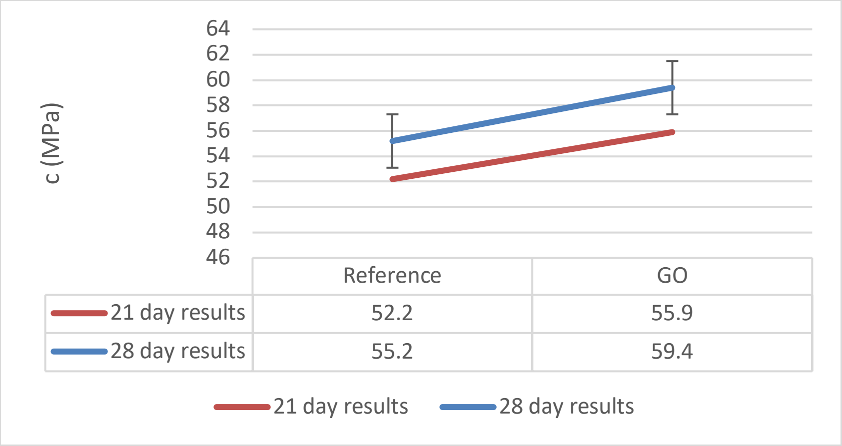


Figure 5: Compressive strength results at 21 (n=1) and 28 days (n=2)

This shows that strength increases with curing time. At 21 days the GO concrete displayed a 5.7% increase in compressive strength and a 6.2% increase at 28 days. Standard error bars could not be included for the 21-day results as only one cube was compressed. As concrete is already compressively strong, what is more valuable is the increase in flexural strength that GO provides. Reinforcing the concrete with GO yielded an increase of 19.1% in flexural strength compared to the reference mix, which is illustrated in figure 6.

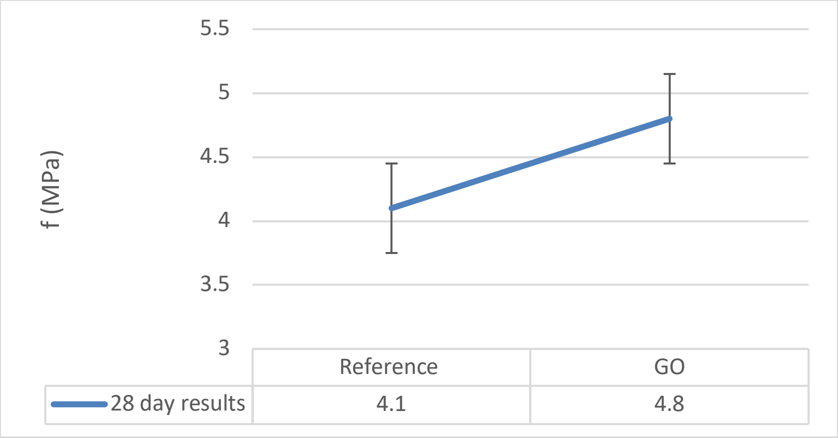


Figure 6: Flexural strength results at 28 days (n=2)

Finally, the results for the RCP test show that the GO concrete is 43.4% less permeable to chloride ions. Figure 7 depicts this decrease.

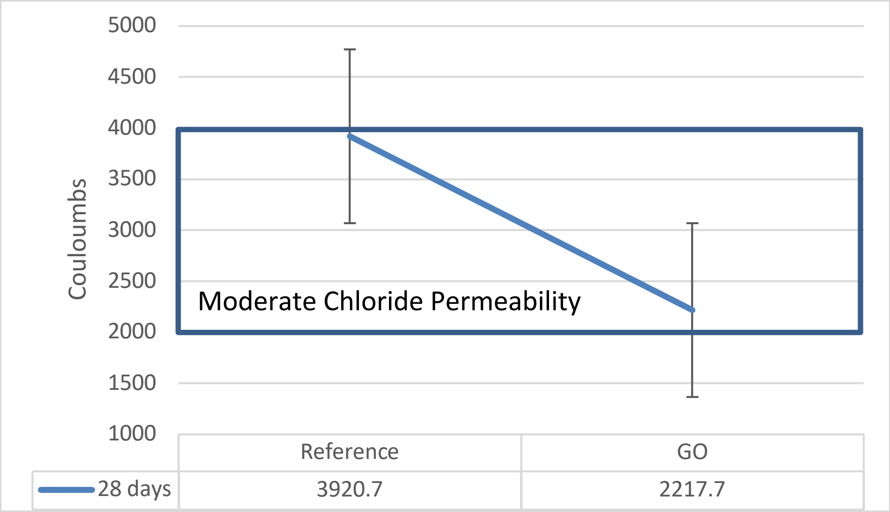


Figure 7: RCP test results at 28 days (n=3)

From the rating of chloride permeability (figure 4) this indicates that both samples have moderate chloride permeability, with both bordering the upper and lower bounds of the moderate range. These results are aligned with the rating scale, as the w/c was 0.48. While this method is widely utilised in the concrete industry, due to its ease of use, there is a great deal of debate regarding its validity. There is no real-life condition where concrete is exposed to these types of voltages. Further the large variation in results indicate the relative inaccuracy of this test method, if the samples are equivalent in quality (GCP, 2016). This depends on distribution of component material, which cannot be commented on as no microscopy/spectroscopy was conducted here. A more accurate method of measuring permeability, which relates more so to the increased water exposure linked to CC, is that set out in BS EN 12390-8:2019. Unfortunately, this apparatus was not available in this investigation. Future studies on GO concrete should use this method to produce more accurate permeability measurements.

The tests conducted on the concrete samples provide indication that GO effectively reinforces concrete. A more comprehensive work should create far more samples for testing.

Little statistical significance was gleaned from measurements here; 100s of samples are necessary for there to be significant proof of enhancement. Evidently, more research is required into GO concrete before it shall be applied to large scale projects. This is aligned to the wider issue nanomaterials in the BE face; more research and proof of benefits is imperative if investors are to risk using them.

## 4. References

Akkermans, P. and Schwartz, G. (2009). *The Archaeology of Syria.* Cambridge: Cambridge University Press, p.63.

Alkhateb, H., Al-Ostaz, A., Cheng, A. and Li, X. (2013). *Materials Genome for Graphene-Cement Nanocomposites.* Journal of Nanomechanics and Micromechanics, 3(3), pp.67-77.

Chuah, S., Pan, Z., Sanjayan, J., Wang, C. and Duan, W. (2014). *Nano reinforced cement and concrete composites and new perspective from graphene oxide*. Construction and Building Materials, 73, pp.113-124.

D. Whiting (1981) *Rapid Determination of the Chloride Permeability of Concrete*, Report No. FHWA/RD81/119, August, Federal Highway Administration, Office of Research & Development, Washington, D.C.

Ecosia.org. (2019). *Ecosia - the search engine that plants trees*. [online] Available at: https://www.ecosia.org/images?q=graphene+oxide+vs+graphene#id=370C6B444E0AF171A3FCC67C88247B87C864462E RED OXIGEN, BLUE HYDROGEN [Accessed 1 Sep. 2019].

Gagg, C. (2014). Cement and concrete as an engineering material: An historic appraisal and case study analysis. Engineering Failure Analysis, 40, pp.114-140.

GCP (2016). *Understanding AASHTO T277 and ASTM C1202 Rapid Chloride Permeability Test*. Tech Bulletin. [online] Ontario: GCP applied technologies.

Ghafoori, N. and Diawara, H. (1999). *Abrasion Resistance of Fine Aggregate-Replaced Silica Fume Concrete*. ACI Materials Journal, 96(5).

Graphene-info.com. (2019*). Graphene Oxide: Introduction and Market News | Graphene-Info.* [online] Available at: https://www.graphene-info.com/graphene-oxide [Accessed 31 Aug. 2019].

Jones, W., Gibb, A., Goodier, C., Bust, P., Song, M. and Jin, J. (2019). Nanomaterials in construction – what is being used, and where?. *Proceedings of the Institution of Civil Engineers - Construction Materials*, 172(2), pp.49-62.

Joshi, P. and Chan, C. (2002). *Rapid Chloride Permeability Testing*.

Mohammed, A., Sanjayan, J., Duan, W. and Nazari, A. (2015). *Incorporating graphene oxide in cement composites: A study of transport properties.* Construction and Building Materials, 84, pp.341-347.