**STUDY OF GRAPHENE NANO PLATELETS IN CONCRETE**

1. **Introduction**

Concrete is the most used construction material which has gone under many evolutions but still due to its huge requirement many modifications are to be made, so it becomes more advanced composite material which helps in increasing the concrete strength[1]. However, the poor tensile strength, high brittleness and easy crazing of cement-based materials restrict high performance concrete’s wide applications. Numbers of methods have been proposed to improve the flexural strength, toughness and decrease micro cracks in cement composites, such as adding usual materials like steel fibers, natural fibers, glass fibers, carbon fibers and synthetic fibers. However, even though fibers can improve the flexural toughness of cement composites significantly by delaying the macro-cracks growth, whereas, they cannot inhibit the micro-cracks formation [4]. In recent years, a growing body of research in nanoengineering has been focused on its potential use in concrete. Incorporating nanomaterials into concrete mixes can significantly improve their microstructure due to their superior chemical and physical properties [1]. It has been reported that nano-particles can fill the voids in cement paste matrix, leading to lower porosity, higher strength, and better durability. However, it should be noted that all the beneficial influences caused by nano-particles may not realize unless being uniformly dispersed in the matrix.[2]Many researchers have paid attention to the usage of nanomaterials, for example, nano-kaolinite clay, nano-silica, nano-TiO2, nano alumina and graphene nanomaterials, in the last decade. Studies have shown that the additive of these nanomaterials could improve the mechanical property and durability of cementitious materials [3]

There are different forms of nanomaterials including CNTs, graphene oxide (GO), reduced graphene oxide (RGO) and graphene nanoplatelets (GNPs) or multi-layer graphene as otherwise known. Among these nanomaterials, CNTs have been widely incorporated into cementitious composites to enhance their material properties. CNTs are molecular-scale tubes of graphene, which is a single-layer sp2- bonded carbon sheet. Pristine graphene as well as CNTs possess outstanding mechanical properties. Graphene has a Young’s modulus of about 1 TPa and a tensile strength of 130 GPa, while CNTs have a tensile strength of 11 to 63 GPa and a Young’s modulus of 0.3 to 0.9 TPa. CNTs can exist as single-walled (SWCNT) or multi-walled carbon nanotubes (MWCNT). Depending on their quality and type, the cost of SWNTs range from $37,500 to $160,000 per kg and the cost of MWCNTs range from $600 to $15,000 per kg [9] but compared to other carbon-based nanomaterials, their two-dimensional structure with a large specific surface area and large surface to volume ratio make GNPs a promising candidate for the development of nano-reinforced cementitious composites. GNPs also can be produced at large-scale for industrial demand and their cost ranges from $65 to $400 per kg [9]. The influence of GNP on the bond stress of HPC was studied. A significant positive effect of the addition of GNP was found on the bond stress which resulted from its bridging action. Further, the loading capacity and failure strain of 0.03% GNP were increased by 30% and 73%. Adding 0.3% GNP improved toughness, flexural strength, tensile strength, and energy absorption capacity by 59%, 276%, 40%, and 187%, respectively [1,5,9,6,10].

1. **Effect of production of graphene nano platelets on environment**

Ioanna Papanikolaou[7] found out that during manufacture of GNP, the graphite is mixed with water and heated. Exfoliation and expansion of the mixture is done using electricity. Water consumption is very less, so it has no effect on nature and toxicity produced while mining and transporting can be reduced through optimization and producing according to requirement. Most harm is done to nature while using electricity in the production of GNPs. By producing electricity through renewable energy production like wind energy, solar energy etc...we can produce graphene without harming nature or eco system. the production of 1 kg of CEM I corresponds to 0.86 kgCO2. Were as GNPs produces 0.17 kg co2 equivalent. So, we can say that the production of GNP is environmentally friendly if used as a supplement [7].

2.1 Selection of GNP product

There are a variety of GNP products available in the market, with different sizes, physical properties, and manufacturing method. All types of GNP are used to enhance the quality of the concrete material but selecting the GNP which provides better concrete strength should be our priority. Below are some of the qualities of GNP which effects the enhancement of cementitious material.

1. The inherent impermeable nature enables graphene-based materials to be barriers to prevent ions diffusion.
2. The nanoscale thickness of GNP could accelerate cement hydration and thus densify the microstructures.
3. The layered morphology of GNP could block the interconnected pores, thus refining the pore systems.

**3) Types of dispersion**

The GNP particles always remains agglomerates in the water. It means that there will not be any homogeneous mixture between concrete and GNP. So, in order to get benefits from the nano materials it needs to be dispersed [8]. There are different ways to disperse GNP in concrete which will affect concrete in different ways. And they are listed below

1. By adding GNP with respect to ratio of cement normally mixed in 10% water with polycarboxylate based superplasticizer and mixed with high shear mixing for 30,60,90 minutes [9].
2. Adding the GNP with 10% water and superplasticizer and sonicating it and mixing it after sonication of 30min in high shear mixing [1,5,9,6,10].
3. The Graphene Suspension can be equally dispersed in ethanol aqueous solution [3].
4. A certain amount of CO890 was dissolved in water using mechanical stirring, then the GNPs powders were added into aqueous CO890 solutions, followed by ultra-sonication for 30 min in a probe sonicator [4].

So, in general GNP are dispersed using superplasticizer and mixed with concrete so that the lumps of GNP should not create the week points in the concrete. It should homogeneously mix with concrete and reduce the pores in concrete which directly increases the physical property of the concrete. Here we must use the polycarboxylate-based superplasticizer because it contains main carbon chain with carboxylate groups and poly ethylene oxide (PEO) side chains. When it is dissolved in water the main carbon chains are absorbed at interface between GNPs, water and PEO side chains. This side chains will help in separating the graphene and surround it with the water particles so that the graphene gets dissolved easily this reaction is called as steric hindrance. An important process to incorporate GNP in concrete.

**4) Physical property**

**4.1 water sorptivity of the above concrete cubes**

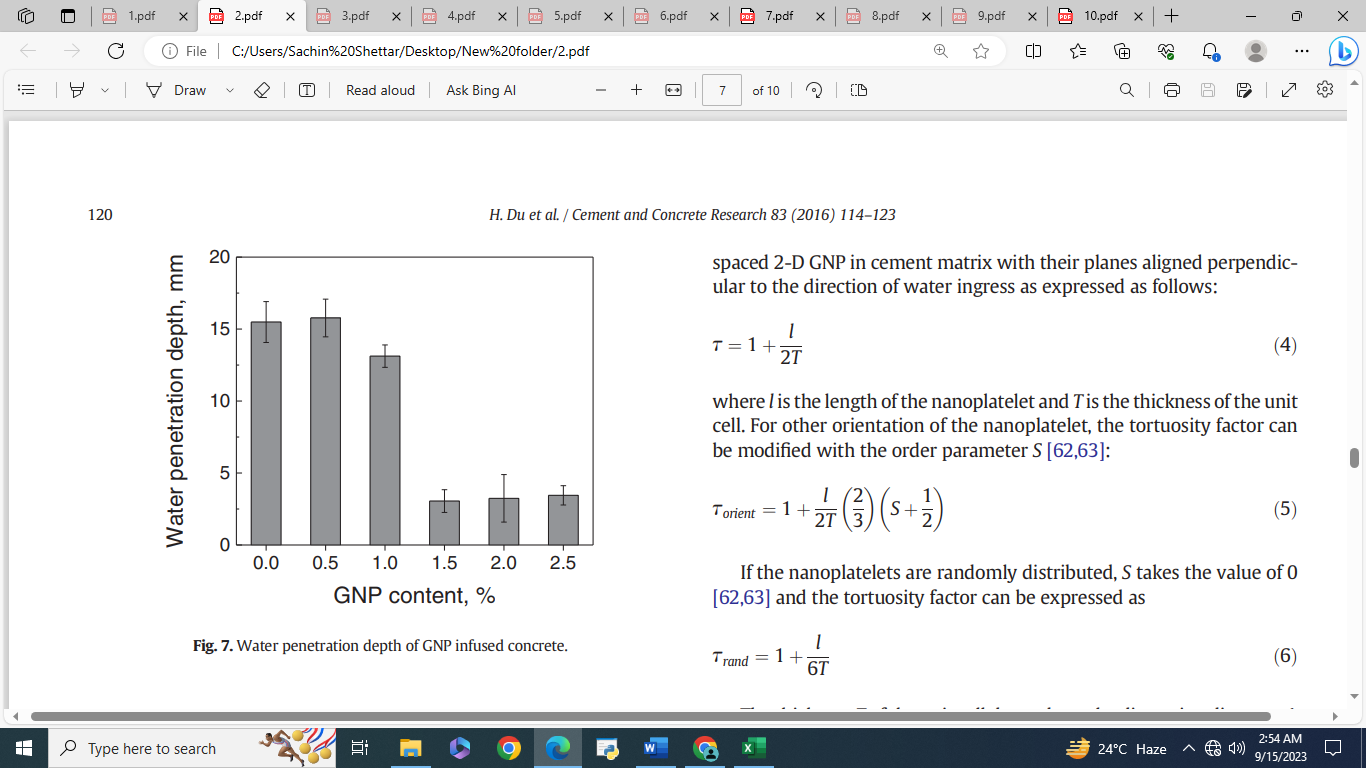
Hongjian Du showed that considering above points a mix proportion of concrete was prepared i.e., in the ratio 1:2.75:0.485 written in the ratio cement: sand: water. And 3 types of GNP were used in this plane cement concrete. Water sorptivity of the above concrete cubes were measured after 28 days using o ASTM C 1585. Results of the experiment showed that GNP having high aspect ratio will enhance the property of the concrete. The three types used in concrete have the property as given in Table 1. [2]

**Table 1 physical property of GNP [2]**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| GNP product | Density, ρ(g/cm3) | Surface area, A (m2 /g) | Diameter, D (μm) | Thickness, t (nm) | Aspect ratio, λ | Purity, % |
| A 3775 | 2.26 | 23.7 | 8.0 | 37 | 215 | 99 |
| M 850 | 2.26 | 13 | 3.6 | 71 | 50 | 99.5 |
| TC 307 | 2.16 | 352 | 2.6 | 3 | 1000 | 99.9 |

In most cases GNP A3775 was selected which enhance the concrete more efficiently. It is selected because it has average aspect ratio and it’s available easily [2].

**4.2 Porosity**  
The pore size distribution for different samples were taken after 28 days curing in the sample without GNP large pores more than 1000 mm and capillary force 1000 mm to 100 mm are detected. But in presence of GNP the pores were negligible but in case of small holes addition of GNP increase the number of pores [4]. But these are not harmful so, the decrease in the large pores and increase in the small pores will ultimately affect the compressive and tensile strength positively the porosity for different GNP is given in below bar graph.[6] The superplasticizer used induced as the dispersed also affect the porosity of the structure for example use of PS,NS,MS decrease the porosity by 12.9%, 15.2%, 16.3%[10].

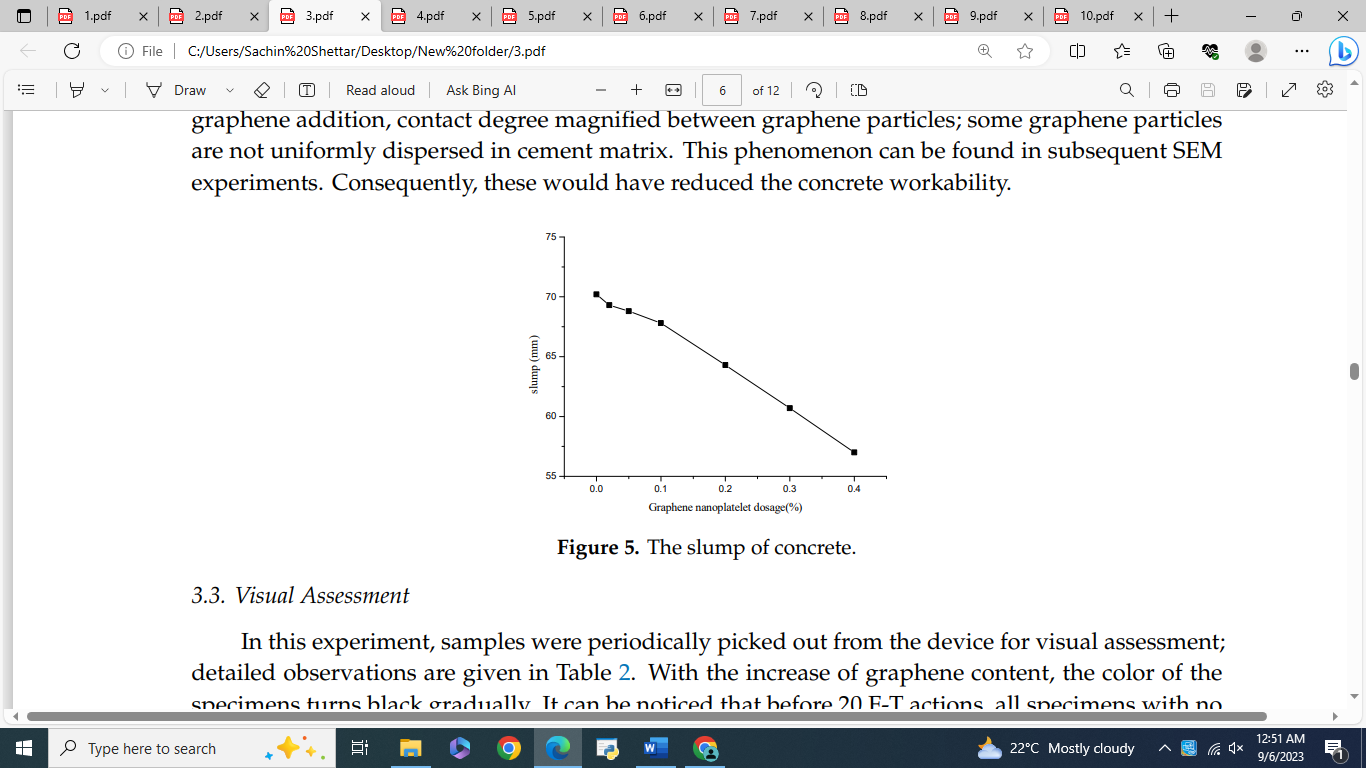


**Figure 1 Water penetration depth of GNP infused concrete [2]**

**4.3 Workability**

There is linear relationship between GNP content and slope. As we already discussed that surface to volume ratio is very large and large area absorbs more water on its surface for the concrete having water cement ratio remains constant. The workability will decrease and also with increase in GNP the particle may not be uniformly distributed. This is found through SEM analysis this will decrease the workability of the concrete [3].

we can use different superplasticizer as the dispersant like poly carboxylate, naphthalene, melamine super plasticizer when its use to display 0.06 weight percent of GNP and used in concrete it decreases its workability. But super pesticides promoted electrostatic repulsion and static repulsion among particles so by adding for practices then not only this first the GNP but also contract the negative effect of GNP so, reduction in workability of concrete for constant super plasticizer [3].

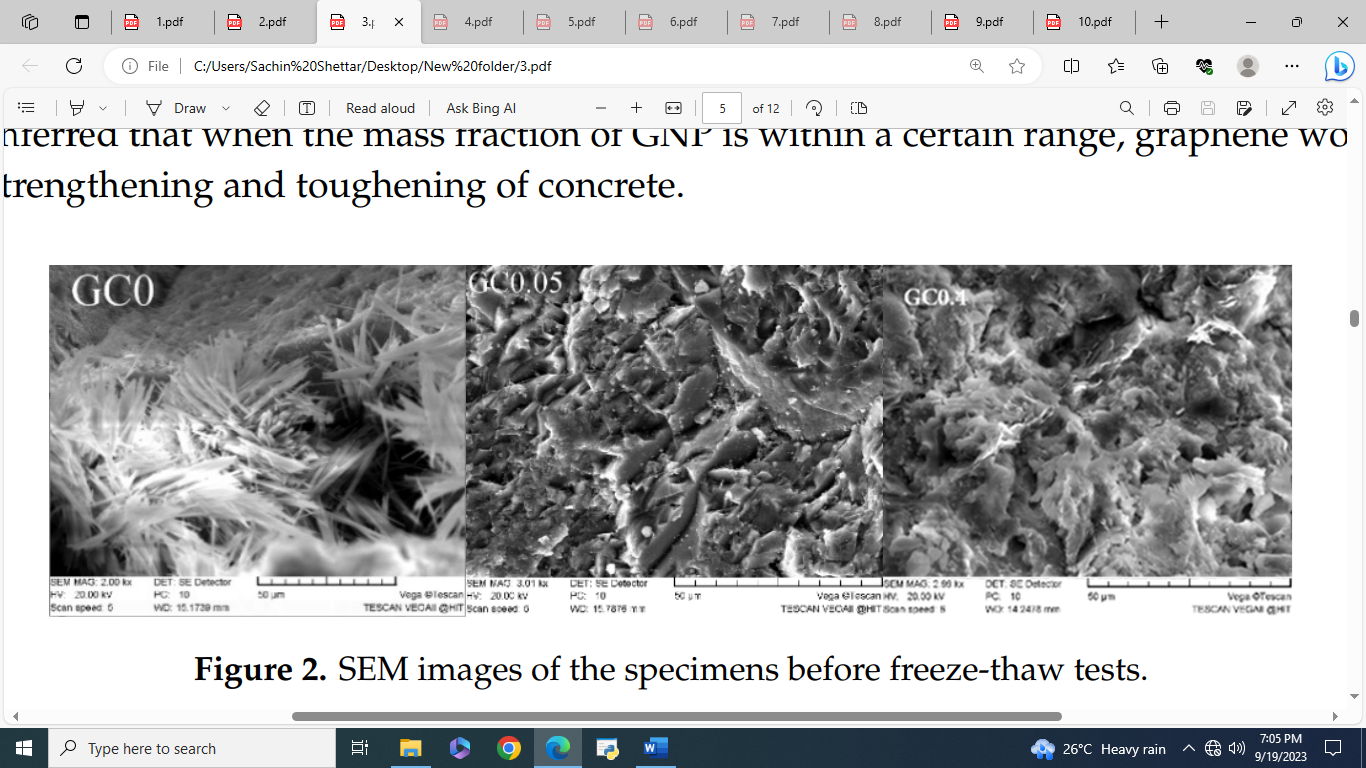
So, in conclusion the workability of the concrete decreases but since we use super plasticizer the effect of GNP on the concrete shows no effect on concretes workability.

**Figure 2 the slump of concrete [8]**

**5) Chemical property**

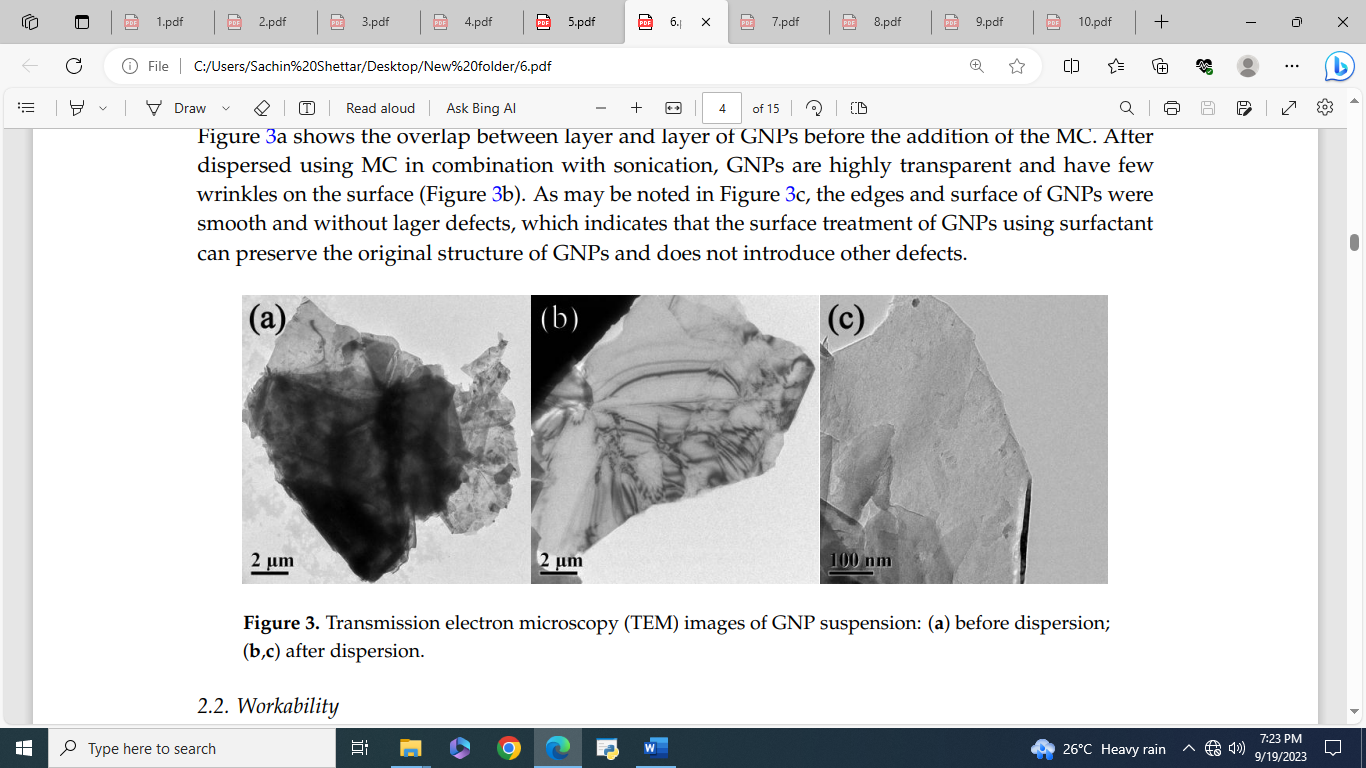
**5.1 SEM and TEM analysis**

Guofang Chen[3], observed that the sample with no GNP has larger volume porosity and contains a lot of acicular and rod cement hydration products, such as AFt, AFm, Ca(OH)2, and C-S-H gel. The graphene nano-particles were reported that it could fill the voids and promote the growth of the hydration products, change the shape and size of hydration crystal, but did not change its type through reacting with cement and graphene. As can be seen from Figure 2, compared with the ordinary concrete specimens, the hydration products of the specimens with GNP are more compact and the microstructure is more uniform, the intersecting microcrystals make the mechanical properties of concrete improved obviously [3,4]. In the below pictures GC represents the presence of GNP and the number represent the percentage of GNP in the concrete.



**Figure 3 SEM images of the concrete specimen with GNP [3]**

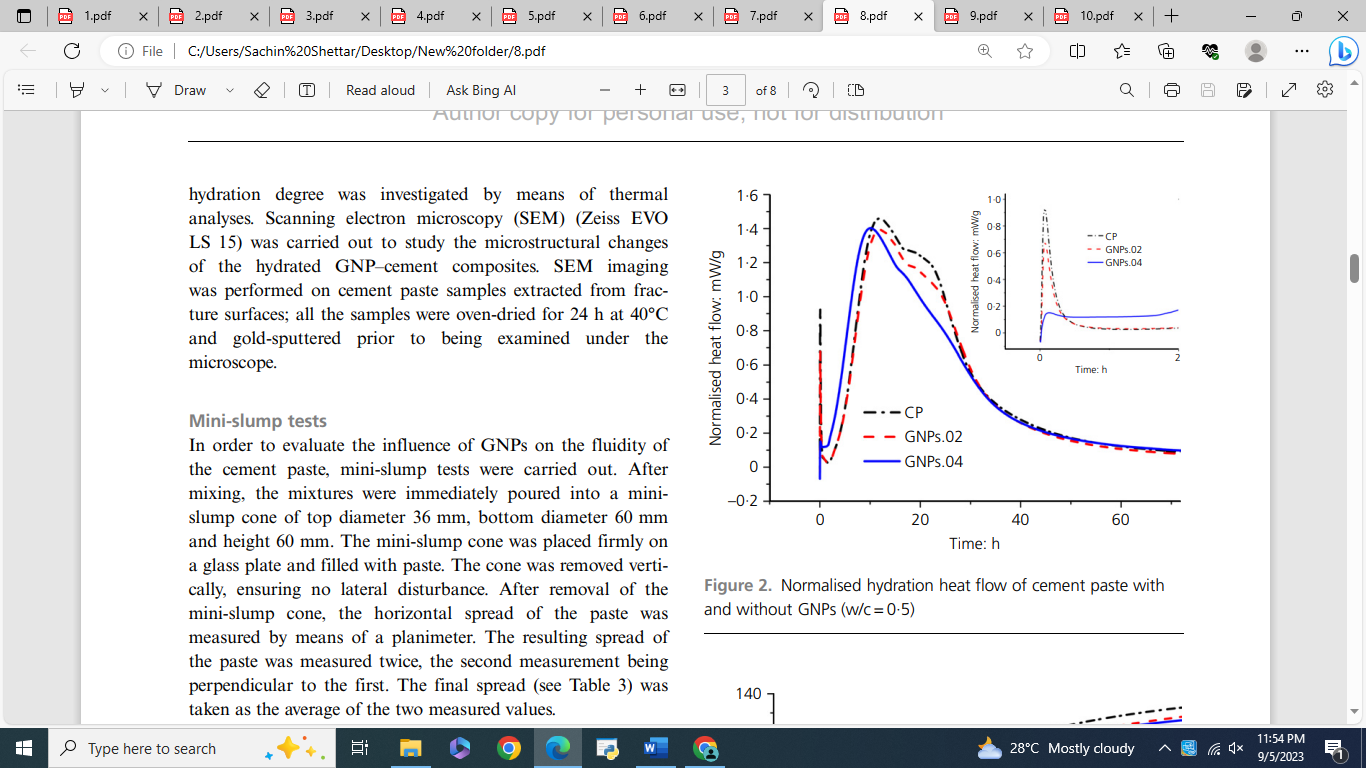
But as we can see the increase in nanoparticles would cause the graphene to concentrate at a point and that concentrated region is weakest point of the concrete. So, the GNP should be within the limits so that it can be homogeneously mixed with the concrete. [3,4]

BaominWang[6], found that optimum dispersing status of GNPs in aqueous MC solution was employed using TEM**.** In the 1st figure below the overlap between layer and layer of GNPs. GNPs are highly transparent so, there will be no change in color of concrete and have few wrinkles on the surface. After its mixed with the superplasticizer and sonicated the edges and surface of GNPs were smooth and without lager defects, which indicates that the surface treatment of GNPs using surfactant can preserve the original structure of GNPs and does not introduce other defects.[6]

**Figure 4 TEM analysis how graphene in presence of poly carboxylate based superplasticizer [6]**

**5.2 Hydration process**

BaominWang[4] showed that GNPs fill micro pores in the cement matrix by being wrapped by hydration products, creating a network-like structure. There is no alteration in the products of hydration process. In cement-based materials GNP in a concrete will increase hydration reaction of cement material in early stage but when it comes to later stages there is little or no reaction on hydration process. These results are obtained through [4]. GuojianJing[8], says that GNP helps in improving hydration process [8]. Other processes like TG analysis and FTIR analysis also indicate the same results.

To study hydration process thermography Matrix analysis system is used. The samples where heated 25-degree Celsius to 1000 degree Celsius at the rate of 10 degree Celsius per minute by continuous supply of Nitrogen flow 70 ml per minute**.** Degree of hydration was analyzed using thermal analysis.

**Figure 5 Particle size distribution of as-received GNPs [8]**

The XRD patterns showed that the diffraction peak shape of samples was approximately the same as plain cement. There were no new phases generated and the structure of ultimate hydration products had no changes in the GNPs cement composites with the addition of GNPs. From Table 2 below it can be seen that the particle size of CH crystal in cement-based mixed with GNPs was smaller than the control sample at different hydration ages. It concludes that GNPs can lessen the particle size of CH crystal. However, the particle size of AFT crystal in cement-based mixed with GNPs was no obvious regular pattern contrast with the control sample. The above results demonstrated that GNPs can accelerate the formation of more crystals in hydration products and decrease the particle size of CH crystal due to the well-distributed of GNPs. In the below table 2, PS, NS, MS indicates poly carboxylate, naphthalene, melamine super plasticizer respectively. And 1, 2, 3, 4 represents 0.03, 0.06, 0.09, 0.12 % of GNP per weight of cement is used respectively.

**Table 2 particle size of CH crystal in cement-based mixed with GNPs [10]**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Samples | GNP(%)  Concentration | Type of  Superplastisizer | 7d particle size(nm) | | 28d particle size(nm) | |
| CH | AFt | CH | AFt |
| PC-1 | 0.00 | PS | 56.8 | 41.2 | 55.6 | 40.6 |
| PS-2 | 0.06 | PS | 55.3 | 42.0 | 54.8 | 38.7 |
| PC-2 | 0.00 | NS | 65.2 | 38.9 | 55.9 | 36.2 |
| NS-2 | 0.06 | NS | 55.1 | 37.8 | 54.2 | 36.9 |
| PC-3 | 0.00 | MS | 57.4 | 39.6 | 56.1 | 37.9 |
| MS-2 | 0.06 | MS | 56.5 | 39.2 | 55.3 | 36.8 |

1. **Mechanical property**

Mechanical properties are enhanced in a concrete by adding GNP. But it should be optimized using different dispersion techniques and different percentage of GNP gives different mechanical property that includes compressive strength and tensile strength. In general, all the paper shows that there is a small increase in the compressor strength and that is noticeable increase in the tensile strength of the concrete. In samples the early-stage strength of the concrete where high compared to the later stage strength. The factors like dispersion techniques, types of superplasticizer used, percentage of GNP also affect the compressive and tensile strength of the concrete.

The compressive strength and the tensile strength of the concrete for different super plasticizer for different percentage of GNP per weight of cement discussed below [1,5,9,6,10].

**6.1 Compressive and Tensile strength**

Fouad Ismail Ismail [1], showed that with addition of 0.02%, 0.05%, 0.1% of GNP and compressive strength increased by 20.82%, 8.41% and 9.48%. the experiment shows that the best GNP content is best suited when added less than 0.1% below are table representing compressive strength and tensile of the given samples.[1]

**Table 3 compressive strength and tensile strength of concrete [1]**

|  |  |  |
| --- | --- | --- |
| Mix ID | Compressive  strength (MPa) | Direct tensile  strength (MPa) |
| GMC-0.00 | 50.6 | 3.66 |
| GMC-0.02 | 61.14 | 4.76 |
| GMC-0.05 | 54.86 | 3.72 |
| GMC-O.10 | 55.4 | 3.89 |
| GMC-0.30 | 48.94 | 3.09 |
| GMC-0.50 | 49.94 | 3.01 |

Researcher use Chinese standards for the measurement of Mechanical properties. They have taken OPC 42.5. size of coarse and fine aggregates were 5 mm and 20 mm respectively. GNP was suspended in the ethanol aqueous solution. Which consists of graphene layers with thickness of 20nm. 4 types of mix were studied with 0.1%, 0.2%, 0.3% and 0.4% GNP and compressive strength of samples are shown in a below table 4.[3]

**Table 4 compressive strength of the concrete [3]**

|  |  |
| --- | --- |
| GNP in % | Compressive  strength (MPa) |
| 0.0 | 31.7 |
| 0.02 | 37.6 |
| 0.05 | 38.8 |
| 0.1 | 37.97 |
| 0.2 | 34.5 |
| 0.3 | 32.15 |
| 0.4 | 28.53 |

Fouad Ismail Ismail[5], use high performance concrete, silica fumes were used as a replacement for 7% of binding material. Fine aggregate of 4.75 mm of specific gravity 2.65 coarse aggregate 5 mm to 10 mm with specific gravity 2.55. Super plasticizer polycarboxylate Ether material was used 0.02%, 0.05%, 0.1%, 0.3%, and 0.5% of cement weight. The compressive strength and tensile strength of these samples were given in table 5 [5].

**Table 5 compressive strength and tensile strength of concrete [5]**

|  |  |
| --- | --- |
| GNP in % | Compressive strength (MPa) |
| 0.00 | 63.25 |
| 0.02 | 76.42 |
| 0.05 | 66.67 |
| 0.10 | 69.25 |
| 0.30 | 61.17 |
| 0.5 | 61.95 |

BaominWang[10], uses polycarboxylate based superplasticizer is used to disperse GNP. In these test paper different disperse techniques were used and compressive strengths were measured. This can a seen below. In first 4 concrete 0.025%, 0.05%, 0.075% and 0.1% of GNP to the weight of concrete where used and next five samples were using different timing of dispersion like shear mixing and ultrasonic. Result of compressive strength are presented in table 6[10].

**Table 6 compressive strength and tensile strength of concrete [10]**

|  |  |  |  |
| --- | --- | --- | --- |
| Dispersion case | High shear  mixing (in min) | Ultra sonication (min) | Compressive  strength (MPa) |
| control | - | - | 39.3 |
| GC1 | 30 | 0 | 43.8 |
| GC2 | 60 | 0 | 44.8 |
| GC3 | 90 | 0 | 43.8 |
| GC4 | 30 | 15 | 43.2 |
| GC5 | 60 | 15 | 45.3 |
| GC6 | 90 | 15 | 36.3 |

The addition of GNP in the concrete mix using superplasticizer as the dispersant increase the compressive strength and tensile strength of the concrete.Only small amount which is less than 0.3% of GNP to the weight of cement can increase the compressive and tensile strength if we increase the dosage it will adversely affect its strength.[1,3,5,9].

**6.2 Pullout test**

Fouad Ismail Ismail[5], Conducts pullout test using UTM with the capacity of 200 kN. The samples had different content of GNPs with the different diameter is 12, 10 and 16 were used.

The result shows that ultimate bond stress was increased for all 0.02, 0.05, 0.1, 0.3, 0.5 weight percentage of GNP given best results but as we have seen the compression strength decreases after 0.3% of the GNP so adoption of 0.02% of GNP is more economical.

The increase in the ultimate bond stress after 0.3% of GNP and decrease in compressive strength can be explained through adhesiveness. When the dosage increased the adhesion between Steel bars and adjacent Concrete also increased. This increases bond behavior between steel and concrete.

The influence of the diameter of bar on bond strength is remarkable on 16 mm bar compared to 10 mm and 12 mm bars. Thus we can say that as the diameter of the bar increases the bond strength due to higher surface area of steel [5].

1. **Reduction in cement with maintaining performance**

The use of GNPs allows for an enhancement in the concrete performance which could in turn lead to a reduction of the cement content required. Below are reported the results of an alternative analysis with a 5% reduction in cement content is assumed.

To produce 1 m3 of this new concrete mix that incorporates 5% less cement, the effect on global warming is 15.29 kgCO2 eq. which is significantly less than the base case that was associated with 19.42 kgCO2 eq. Therefore**,** reducing cement by only 5% can result in a 21% reduction in the global warming potential. This highlights the significance of reducing the cement content whilst maintaining the same service and the positive role that GNP addition can play in the lifecycle impact of concrete [7].

**Conclusion**

The use of GNP in the concrete is a sensitive process but it can be used effectively by engineered methods. Graphene is the wonder material after plastic which can have huge development in many industry including construction industry.

* There are many type of GNP in the market. By using trial and error method by many researchers it is suggested that GNP A3775 is the type of GNP which enhance the concrete more efficiently.
* The use of superplasticizer is very essential while incorporation of the GNP in the concrete but the use of poly carboxylate based super plasticizer is necessary. But here we can see the many types of super plasticizer in the market some of them were tested keeping GNP in constant quantity the results were varying dependent upon the superplasticizer used the porosity of the structure after use of PS,NS,MS superplasticizer decreased the porosity by 12.9%, 15.2%, 16.3%.
* The use of GNP will not change the hydration product but will help in increasing the growth of hydration product and fills the pores and gaps in between which intern increase the strength and durability of the concrete.
* The use of GNP is efficient but only when used in the limited and engineered way if the quantity of the GNP increase then the strength will decrease due to adhesiveness. GNP is not basically a cementitious material so when it is concentrated at a point then the effect will be on concrete property generally 0.3% by weight of cement is the limit.
* The use of GNP can lead to achieve the goal of reduction in the production of the cement though it can’t replace cement but the desired strength can be achieved with less cement. It is seen that 5% reduction in cement content can be achieved, reducing cement by only 5% can result in a 21% reduction in the global warming potential.

**Reference**

[1] Ismail, F. I., Shafiq, N., Abbas, Y. M., Bheel, N., Benjeddou, O., Ahmad, M., & Sabri, M. M. (2022). Behavioral assessment of graphene nanoplatelets reinforced concrete beams by experimental, statistical, and analytical methods. *Case Studies in Construction Materials*, *17*, e01676.

[2] Du, H., Gao, H. J., & Dai Pang, S. (2016). Improvement in concrete resistance against water and chloride ingress by adding graphene nanoplatelet. *Cement and Concrete Research*, *83*, 114-123.

[3] Chen, G., Yang, M., Xu, L., Zhang, Y., & Wang, Y. (2019). Graphene nanoplatelets impact on concrete in improving freeze-thaw resistance. *Applied Sciences*, *9*(17), 3582.

[4] Wang, B., & Shuang, D. (2018). Effect of graphene nanoplatelets on the properties, pore structure and microstructure of cement composites. *Materials Express*, *8*(5), 407-416.

[5] Ismail, F. I., Abbas, Y. M., Shafiq, N., Fares, G., Osman, M., Hussain, L. A., & Khan, M. I. (2021). Investigation of the impact of graphene nanoplatelets (GnP) on the bond stress of high-performance concrete using pullout testing. *Materials*, *14*(22), 7054.

[6] Wang, B., Jiang, R., & Wu, Z. (2016). Investigation of the mechanical properties and microstructure of graphene nanoplatelet-cement composite. *Nanomaterials*, *6*(11), 200.

[7] Papanikolaou, I., Arena, N., & Al-Tabbaa, A. (2019). Graphene nanoplatelet reinforced concrete for self-sensing structures–A lifecycle assessment perspective. *Journal of Cleaner Production*, *240*, 118202.

[8] Jing, G., Ye, Z., Lu, X., & Hou, P. (2017). Effect of graphene nanoplatelets on hydration behaviour of Portland cement by thermal analysis. *Advances in Cement Research*, *29*(2), 63-70.

[9] Jiang, Z., Sevim, O., & Ozbulut, O. E. (2021). Mechanical properties of graphene nanoplatelets-reinforced concrete prepared with different dispersion techniques. *Construction and Building Materials*, *303*, 124472.

[10] Wang, B., & Pang, B. (2019). Mechanical property and toughening mechanism of water reducing agents modified graphene nanoplatelets reinforced cement composites. *Construction and Building Materials*, *226*, 699-711.