

Strength Properties and Micro-structure of Steel Slag Based Hardened Cementitious Composite with Graphene Oxide

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Abstract. For the rapid hardening of concrete, various types of calcium aluminate composite have been used for special purpose as shotcrete or rapid repairing in construction field. However, high cost of calcium aluminates is demerit in the point of expanding usage. In recent years, a new binder for rapid hardening has been introduced as the pulverized ladle furnace slag (RC-LFS) with main components of $C_{12}A_7$ and β - C_2S . Like other traditional cementitious materials, it's use will preserve natural resources and has high environmental advantage with economic efficiency, by transferring the industry byproducts into high value materials. Even though flake state, graphene oxide has high tensile strength and electric conductivity. Then, it can be used to increase strength and thermal properties of concrete and its efficiency depends on the dispersion in the cement matrix. In this paper, we used graphene oxide for increasing the engineering properties in RC-LFS concrete with GGBFS. Test results showed that the 0.05w% of graphene oxide increase the flexural strength to 26% and compressive strength to 16%.

1 INTRODUCTION

Nowadays, many new materials with candidated reinforcing effect for cementitious composite are introduced. Though reinforcing mechanism and reinforcing efficiency are different on case by case, there are special attention to the graphene oxide (GO). GO is mono-layer of 2-hybridized carbon atoms derived from a mixture of carboxyl, hydroxyl, and epoxy functionalities [1,2,3]. It has been reported by Z. Pan and K. Gong et al. that carboxyl acid groups can react with calcium silicate hydrate (C-S-H) to form strong covalent bonds, thereby notably improving mechanical properties of GO-cement composites [4,5].

For high aluminate composite, the properties of graphene oxide reinforced composite haven't been fully documented., This unconventional cementitious material, the binder in this experiment,also been introduced as the pulverized rapid cooling ladle furnace slag (RC-LFS). Ladle furnace slag (LFS) is an industry by-product which generally occupied a large area of the land for store and processing. Thus it has generated a serious environmental

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problem for a long time. Moreover, the slow cooled LFS (by natural air) is hard for recycling, since the slowly cooled process allow the generation of crystal structure which lower the reactivity even after pulverized [6]. On the other hand, slow cooled also lead to high amount of f-CaO which will cause the unsoundness problem [6, 7]. But after rapidly cooled by high-pressure air, the material shows remarkable mechanical properties and high early strength after pulverized. More importantly, many studies have been focusing on finding an alternative which can be used as cement replacement materials. Cement replacement materials are the way to utilized untouchable raw materials and should be a break-solution of a green world. Materials that can be used for replacing cement as a binder can come from several sources namely agriculture, industry, marines etc. [8]. The pulverized RC-LFS as an industry by-product has unique properties on reducing environmental problems and such a solution of sustainable development. Owing to its rapid strength development, pulverized RC-LFS was used in structural applications.

Except RC-LFS, ground granulated blast furnace slag (GGBFS) was also involved. GGBFS remains after the steel making process. Application of GGBFS in construction material development is not only cost effective and resource saving but also reduces the energy and green house gas emissions [9].

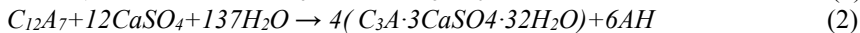
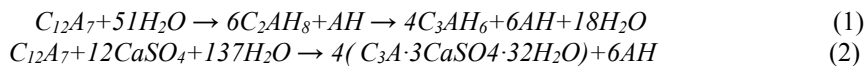
Since the necessity to document the mechanical properties such as flexural and compressive strength of GO reinforced mortar, those properties were evaluated by series experiment and were presented in this paper.

2 EXPERIMENTAL STUDY

2.1 Materials

Within the scope of this paper, four basic materials such as pulverized RC-LFS, α semi-hydrated gypsum, GGBFS, and GO are used. All those material are getting from Korea market.

The hydration of pulverized RC-LFS process very rapidly in the room temperature since the primary hydraulic material is $C_{12}A_7$. Nowadays, gypsum always been involved in the pulverized RC-LFS based composite to hydrate with $C_{12}A_7$ to form ettringite, thus to prevent from transforming from C_2AH_8 to C_3AH_6 as been illustrated in following equations [6].



While the hydration process of $C_{12}A_7$ - $CaSO_4 \cdot nH_2O$ system is very complicated. First of all, the amount of $CaSO_4 \cdot nH_2O$ has to be sufficient to guarantee the stable production of ettringite and can be calculated by using modified Bogue equation [6,7]. Base on the previous studies, chemical retarders are necessary to control the hydration process of $C_{12}A_7$. Since that, citrate acid was involved. GGBFS, as one of the most widely used supplementary cementitious material (SCM) in the construction field, has been documented by many researchers [10, 11,]. The addition of GGBFS to the calcium aluminate cement (CAC) system is reported to change the hydration mechanism of a CAC system. Previous studies have demonstrated that, in CAC-GGBFS blends of suitable ratios, no conversion even at elevated temperatures, even though various types of CAC with different alumina contents were utilized. [12,13,14,15]. The physical and chemical properties of pulverized RC-LFS, gypsum and GGBFS are presented in Table 1.

GO used in this experiment was provided by a Korean Company. To guarantee the good distribution in the cementitious matrix, the aqueous solution was used as presented in Fig.1. The physical properties are shown in Table 2. The package which is provided by the company is 250 ml, and contents 0.75 g solid graphene oxide.

Table 1. The basic physical and chemical properties of LFS powder, gypsum, and GGBFS

Binder	Physical properties		Oxide content(Wt.%)					
	Density (g/cm ³)	Fineness (g/cm ³)	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃
RC-LFS	2.97	6300	10.9	44.5	26.6	4.3	6.6	-
Semi-Gyp	2.72	1100	2.6	40	0.9	0.4	0.3	55.8
GGBFS	2.84	4200	30.3	44.6	13.8	0.5	4.5	4.4

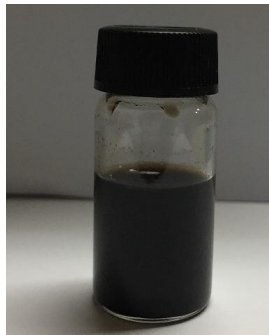


Fig. 1. Graphene oxide aqueous solution.

Table 2. Properties of solid graphene oxide

Carbon (%)	Oxygen (%)	D/G ratio
45-50	40-45	0.99

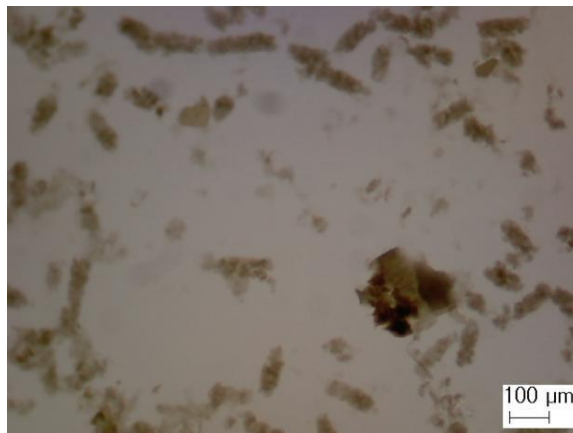


Fig. 2. Graphene oxide aqueous solution under the microscope.

2.2 Experimental plan

The experimental purpose is to illustrate the micro-structure and strength development of RC-LFS base slag cement. Thus the experimental plan is decided and as presented in Table 3. For the fresh composites, the test items include the flow and air content and will follow the ASTM C230 [16] and ASTM C185-08 [17] respectively. For hardened composite, flexural and compressive strength are involved by referencing ASTM C348-14 [18] and ASTM C349 [19].

The fresh concrete was cast in 40*40*160mm prism mold. The curing room for storage

Table 3. Experimental plan

Binder	ID	Dosage of GO	w/b (%)	Test items
Ace*. 100%	A100	0.05 w %	40	-Flow -Air content -Flexural strength -Compressive strength -Microstructure (SEM)
Ace*. 100%+GO	A100GO			
Ace*.75% +GGBFS	A75G25			
Ace*.75% +GGBFS+GO	A75G25GO			
Ace* : pulverized RC-LFS replaced by 25% of α semi-hydrate gypsum				

of the specimens in the mold is maintained at a temperature of $20.0 \pm 1.0^\circ\text{C}$ and relative humidity of $60.0 \pm 5.0\%$. The samples involved in this experiment can be differentiated by different binder material whether containing graphene oxide or not. The control mixtures identified as the mixture without graphene oxide and GGBFS. Other three mixtures contain GGBFS or/and graphene oxide. The different ingredient and ID has been shown in Table 3. The steps of preparing mixtures can be summarized as following:

1. Preparing and measuring binder material.
2. Measuring graphene oxide. The dosage was designed by the solid content of aqueous solution.
3. Modify and recalculate the water amount. Since the graphene oxide solution contains water, adding graphene oxide solution will improve the water-to-binder ratio. So the mixing water will be recalculated.
4. The temperature of all the material will be tested and well keeping in the curing room at 20°C and 60% relative humidity.
5. Mixing method will be based on the ASTM C305-06 [20]. Graphene oxide solution will be added into the mixtures after mixing water, and continued mixing for additional 1 minute at 285 ± 10 r/min.

3 TEST RESULTS AND DISCUSSION

3.1 Flow, air content of fresh mixtures

As a nanomaterial, GO was documented may have an influence on the fresh properties of the mixtures [21]. Since that, the fresh properties of graphene oxide have been tested by ASTM standard. Fresh cement material always illustrated as yield stress fluids [21, 22], and the fresh properties of the mixtures have directly influence on the hardened composite. Thus, in this experiment, the air content and flow properties of GO composites have been evaluated. The experimental outcome is shown in Fig.3. The GO showed different effects on the different matrix. The tendency of air content and flow showed the similarity. First of all, GGBFS can increase the flow by thinning the RC-LFS. Secondly, the GO can decrease the flow when you compare the mixture A75G25 and A75G25GO. It is because of the large

aspect ratio and nucleation effect [1, 23]. While the increasing flow of the mixture A100GO is because the increasing the air content by the GO.

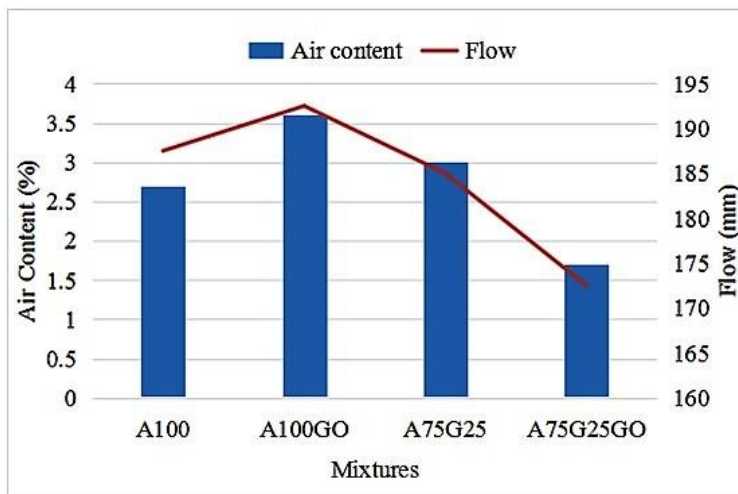


Fig. 3. Air content and flow of GO reinforced composite.

3.2 Flexural, compressive strength and the microstructure

Flexural and compressive strength will be tested after curing for 4 hours, 1 day, 7days and 28 days. The test results as presented in Fig.4. First of all, the binder RC-LFS showed remarkable early strength. The four-hours compressive strength was over 30MPa of mixture A100 and A100GO. Even after replaced by 25 vl.% of GGBFS, the four-hours strength still very closed to 30MPa. After 28 days curing, the compressive of both A100 and A100GO were over 60MPa. The flexural strength also showed high early strength of all four mixtures between 5 to 6 MPa. Secondly, the reinforcing effect of GO showed clearly. From the compare between those four mixtures, the max improvement of compressive strength was over 12.% and the max improvement of flexural strength was over 26%.

The improvement can be summarized as four main reasons. First of all, the function group on the surface of graphene oxide provide high bonding strength between GO and hydrations (such as C-S-H and calcium hydroxide) of cement [1,2,23]. Secondly, as nanomaterial, GO can increase the load-transfer efficiency from cement matrix to the reinforcement [2]. Thirdly, nucleation effect can accelerate the hydration of cement matrix. Moreover, larger regular crystal hydration produce can be generated on the surface of GO and generally cover the GO with curing time. Thus, the concrete with GO shows relatively better engineering performance. Finally, it's also believed that GO nanosheet can provide the crack-bridging effect which has a positive effect on crack resistance [1,2,23]. Base on the previous researches, GO can provide both physical reinforcement and chemical reinforcement at the same time.

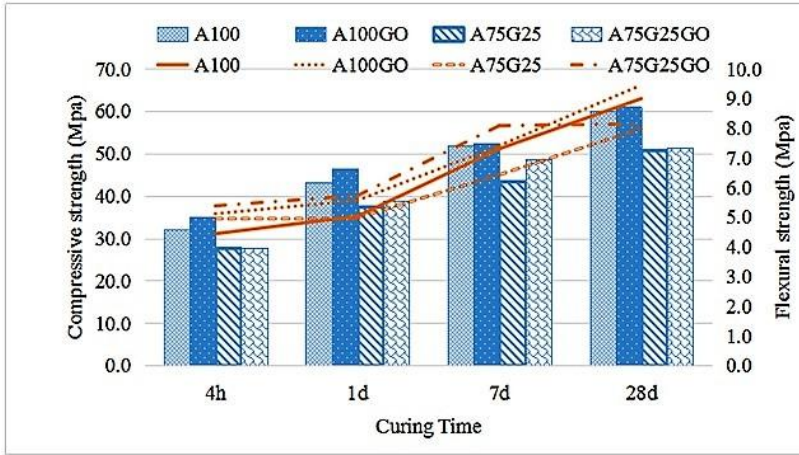


Fig. 4. Flexural and compressive strength.

In order to illustrate the mechanical properties, the microstructure of those mixtures also has been tested by SEM. The test result as shown in Fig.5.

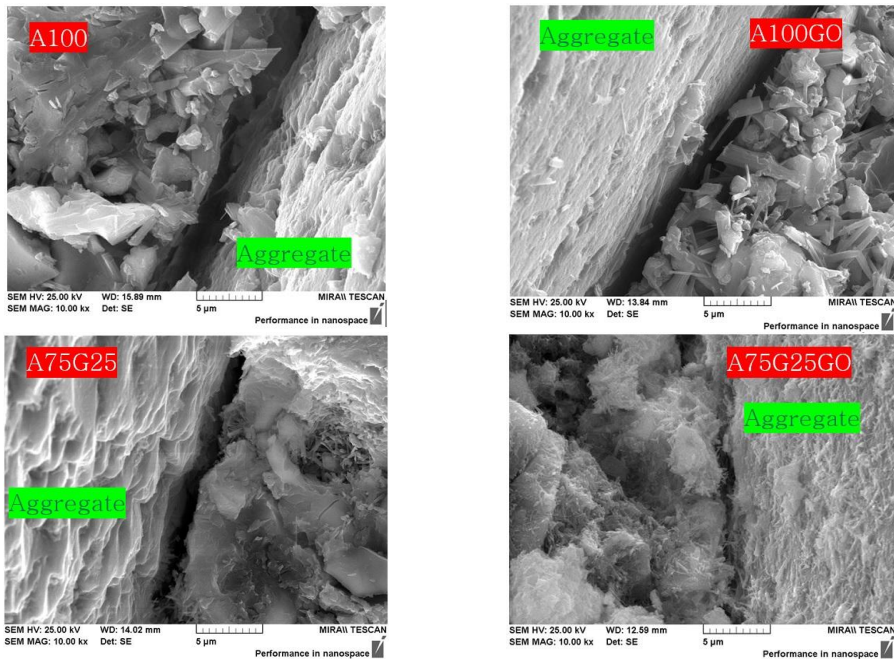


Fig. 5. The microstructure of hardened composite by SEM.

From the test results, the reinforcing effects of GO can also be noticed. The hydration product and the structures showed different. On the other hand, GO is very hard to be located in the matrix due to the nano size and also covered by the hydration productions.

4. CONCLUSIONS

This paper covers the experimental study about the engineering properties of graphene oxide slag based cementitious composites. The experimental outcomes indicate that

graphene oxide can reinforce the hydraulic composite by both physical and chemical bounding. As nano sheet and 2D material with controllable functional groups, graphene oxide shows reinforcing effects. Only 0.05w% by the weight of binder can increase the flexural strength up to 26% and flexural strength up to 12 %.

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