

Preparation and Properties of Alkali-Activated Ground-Granulated Blast Furnace Slag Thermal Storage Concrete

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ABSTRACT

Thermal storage concrete is prepared by using alkali-activated ground-granulated blast furnace slag as cementitious material. To improve thermal conductivity, graphite aggregate is used to replace part of the coarse aggregate, and, furthermore, polypropylene fiber is added to improve the heat resistance performance of the concrete. The compressive strength of concrete specimens before and after heating (up to 450 °C) was tested, and, furthermore, scanning electron microscopy was used to investigate the structure alteration due to heating. Results showed that the partial replacement of coarse aggregate by graphite block could obviously improve the thermal conductivity of the thermal storage concrete. At the same time, the specimen with 30% graphite aggregate replacement still exhibited good mechanical properties. The mechanism of the high residual strength was investigated.

1. INTRODUCTION

With a considerable exhaustion of the traditional fossil energy and increasing environmental pollution due to the use of fossil energy, more and more countries have started to explore alternative energy sources. Solar energy as a kind of green and infinite-reserve energy source has attracted much attention and is being studied widely. There are two main technologies in solar energy utilization, photovoltaic power generation and solar thermal power generation. The latter is now attracting increasing attention as a promising solar energy utilization method for its high energy conversion efficiency. A thermal storage unit is a key component in solar thermal power plants, and it ensures the continuous and steady running of the plants. Because solar energy availability depends on time and weather conditions and electricity demand also varies with time, the energy originally obtained from solar energy needs to be stored (Wu, Reddy, & Rogers, 2001).

Concrete is a low-cost, widely available material, and is an easily processed material for thermal storage in solar thermal power plants. However, for traditional Portland cement concrete, some dehydration reactions take place in the heating cycles, which may cause deformation, cracking, and strength loss. Studies indicate that the compressive strength decreases by about 20% at 400 °C, the specific heat decreases for temperatures between 20 °C and 120 °C, and

the thermal conductivity decreases between 20 °C and 280 °C (Gil et al., 2010). With the development of solar thermal power generation technology, the temperature of the heat transfer medium is getting higher and higher. Thus, it is important to improve the heat resistance ability of concrete.

Alkali-activated slag concrete has many advantages compared to Portland cement concrete. One of these is the relatively high heat resistance ability. Studies show that the thermal stability of alkali-activated binding materials is higher than that of common Portland cement. Some experimental results have shown that the compressive strength of the former even improves after heating due to the sintering reaction or polymerization reaction happening under high temperature (Xu, Li, Shen, Wang, & Zhai, 2010; Zuda, Pavlik, Rovnanikova, Bayer, & Cerny, 2006). In addition, the porosity of alkali-activated slag concrete is commonly low due to the dense matrix and the optimized interfacial transition zone, and so the thermal conductivity is better than that of common concrete, which is good for thermal storage utilization (Kong, Zhang, Ni, Jiang, & Fang, 2009). Zuda et al. (2006) investigated the performances of alkali-activated slag binding material under different thermal loadings, and it was found that the materials had good heat resistance ability, the thermal conductivity can be as high as 1.67 W m⁻¹ K⁻¹, and a suitable aggregate was beneficial for improving the thermal conductivity further. Laing

et al. (2012) utilized slag cement, sand, and gravel to prepare thermal storage concrete that can be used in 500 °C environments. Certain aggregates can be added to control the strength and thermal conductivity of concrete. Graphite is a material with high thermal conductivity, and it can be used as an aggregate in concrete to improve the thermal conductivity. Zhu et al. (2007) added graphite powder into concrete and found that with an increase of graphite content, the thermal conductivity of the concrete increased sharply, but the strength of the concrete decreased.

In this paper, alkali-activated ground-granulated blast furnace slag (GGBFS) was used as a binding material, and graphite particles were used to partly replace the gravel aggregate. Furthermore, some polypropylene fiber was added to improve the heat resistance ability of the concrete. The performances of the concrete were investigated and the mechanisms were analyzed.

2. EXPERIMENTAL METHOD

2.1 Raw materials

The GGBFS used was of S95 grade. Its chemical oxide composition is given in Table 1. Liquid sodium silicate (SiO₂ 27.28%, Na₂O 8.52% and 38–40 Be⁻) was modified by NaOH as the alkali activator with a SiO₂/Na₂O ratio (modulus, Ms) = 1.2, and 35 Be⁻. Chemically pure reagent zinc nitrate was used as retarder to adjust the setting time of the binding material. Naphthalene water reducer was provided by China Construction Third Engineering Bureau Co. Ltd. Graphite aggregates with a size of 2.5–9.5 mm were obtained by crushing graphite product marginally. Polypropylene fibers with a diameter of 20 μm and a length of 12 mm were used.

2.2 Experimental program

2.2.1 Preparation of alkali-activated GGBFS concrete

The concrete proportions used are shown in Table 2. Graphite aggregates were used to replace 0–30 wt% limestone coarse aggregate. Slag, sand, limestone coarse aggregate, graphite aggregates, and polypropylene fiber were mixed, and then alkali activator and water were added and mixed for 2 min. The fresh concrete mixture was cast into a 100 mm × 100 mm × 100 mm cubic mold and compacted, and then covered by a plastic film to prevent water from evaporating. After curing for 1 day in room environment, the specimens were demolded and cured at a temperature of 20 ± 2 °C and relative humidity of 95%.

Table 2. Concrete proportion (kg m⁻³).

Raw materials	G0F	G10F	G20F	G30F	G10F0	G0F0
GGBFS	450.0	450.0	450.0	450.0	450.0	450.0
Alkali activator	167.9	167.9	167.9	167.9	167.9	167.9
Water	39.8	39.8	39.8	39.8	39.8	39.8
Sand	750.0	750.0	750.0	750.0	750.0	750.0
Limestone coarse aggregate	1170.0	1053.0	956.0	819.0	1053.0	1170.0
Graphite aggregate	0.0	117.0	234.0	351.0	117.0	0.0
Polypropylene fiber	0.9	0.9	0.9	0.9	0.0	0.0
Water reducer	7.5	7.5	7.5	7.5	7.5	7.5
Zinc nitrate	4.5	4.5	4.5	4.5	4.5	4.5

2.2.2 Properties test

The compressive strength of concrete specimens after 3, 7, and 28 days was measured. To evaluate the heat-resistance properties, specimens at the age of 28 days were heat-treated, and the compressive strength of heat-treated specimens was measured. Heat treatment of specimens was carried out in several steps. Firstly, specimens were placed in an oven at 60 °C for 12 h and then heated to 105 °C and kept at 105 °C for 12 h. Following this, the specimens were heated to 450 °C and kept at 450 °C for 2 h, and finally cooled to room temperature.

The hot wire method was used to measure the thermal conductivity of specimens at the age of 28 days. The experiments were performed using a QTM-500 thermal conductivity meter.

3. RESULTS AND DISCUSSION

3.1 Compressive strength of alkali-activated GGBFS concrete

Figure 1 shows the compressive strength of alkali-activated GGBFS concrete specimens G0F, G10F, G20F, and G30F with graphite aggregate content of 0, 10%, 20%, and 30%, respectively, at 3, 7, and 28 days. Early strength of alkali-activated GGBFS concrete developed quickly. Compressive strength of specimens at 3 days and 7 days is about 80% and 90% or more of that at 28 days, respectively. Compressive strength of concrete with graphite aggregates is lower than that without graphite aggregates at the same age. The decrease in strength is related to the dosage of graphite aggregate and the age. For concrete G10F

Table 1. Chemical composition of GGBFS (wt%).

CaO	SiO ₂	Na ₂ O	MgO	Al ₂ O ₃	P ₂ O ₅	SO ₃	K ₂ O	TiO ₂	Fe ₂ O ₃	SrO	ZrO ₂	BaO	Loss
39.86	32.26	0.30	8.31	13.89	0.01	2.92	0.53	0.88	0.34	0.11	0.04	0.25	-0.6

with 10% graphite aggregate at the age of 3 days, the decrease is only about 5%. However, the compressive strength of concrete at 7 and 28 days decreased more obviously as the dosage of graphite aggregate increased. Compared with G0F without graphite aggregate, the compressive strength of G30F with 30% graphite aggregate decreased by about one-third. The decrease of compressive strength of concrete with the addition of graphite aggregate is mainly caused by the low strength of graphite compared to normal limestone aggregate. However, compressive strength of all specimens even the concrete with 30% graphite aggregate is still higher than 45 MPa.

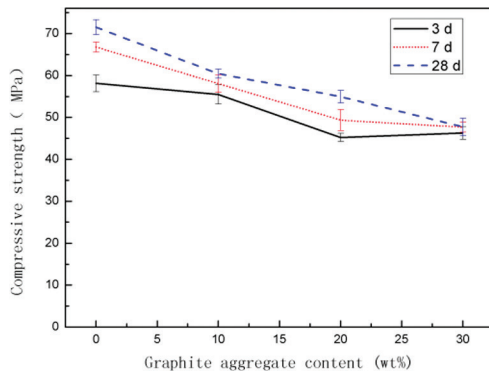


Figure 1. Compressive strength of concrete specimens.

3.2 Heat-resistance properties of concrete

Figure 2 shows the compressive strength and residual strength rate of concrete specimens at 28 days before and after heating at 450 °C. Compressive strength of all heated concrete specimens was lower than that of unheated specimens. However, the residual strength rates of alkali-activated GGBFS concrete specimens are obviously higher than that of ordinary concrete. The residual strength rates of all specimens were higher than 90%. DTG-TG-DSC curves of alkali-activated GGBFS paste shown in Figure 3 indicated that the thermostability of hydration products in alkali-activated GGBFS paste is higher than that in ordinary cement paste.

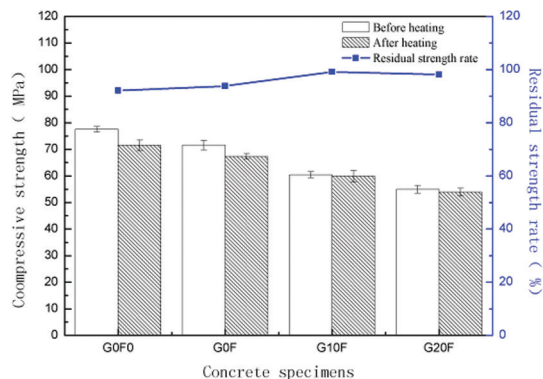


Figure 2. Compressive strength and residual strength rate of concrete specimens at 28 days before and after heating.

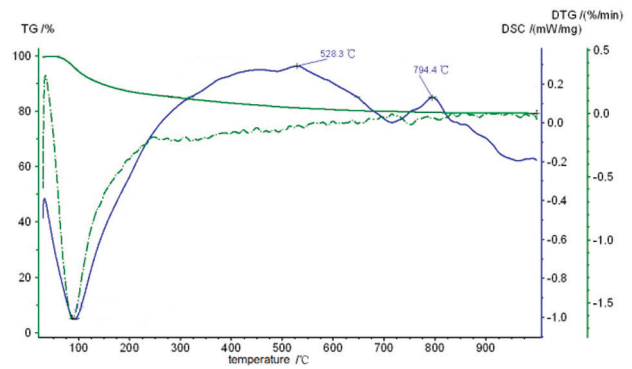
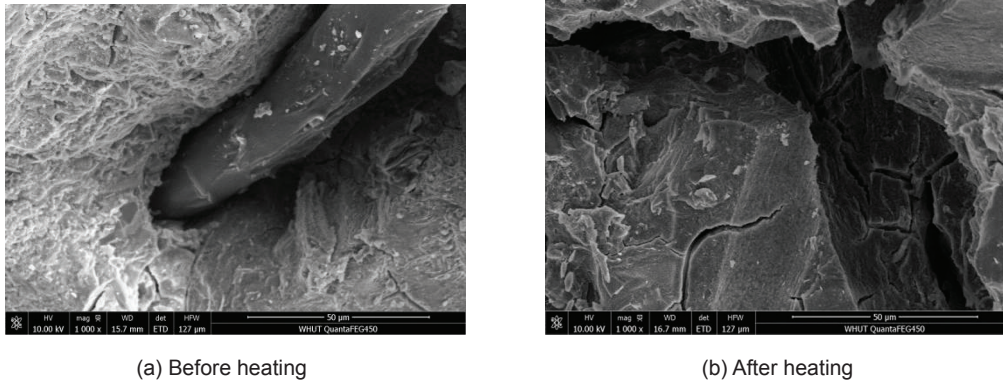


Figure 3. DTG-TG-DSC curves of alkali-activated GGBFS paste.

The residual strength rate of G0F with polypropylene fiber shown in Figure 2 is slightly higher than that of G0F0 without polypropylene fiber, although the compressive strength of unheated G0F is slightly lower than that of unheated G0F0. When concrete is added with graphite aggregates, the heat-resistance properties of the concrete improved further. The residual strength rate of G10F or G20F with polypropylene fiber and 10% or 20% graphite aggregate is much higher than that of G0F0 without polypropylene fiber or graphite aggregate. Low elastic modulus of polypropylene fiber and the increase of air content caused by the addition of polypropylene fiber lead to a negative effect on compressive strength of concrete (Yao, Ma, Tan, & Wu, 2000); however, the effect is limited because of the low dosage of polypropylene fiber. When the concrete is heated, polypropylene fiber in G0F melted at approximately 160–170 °C. The melted fiber leaves a free path for water vapor to escape. This can be seen from the scanning electron microscopy image of heated G0F in Figure 4(b). And the melted polypropylene is helpful for pressure relief. Thus, the addition of polypropylene fiber is beneficial to improve the heat resistance of concrete and prevent explosive spalling of concrete (Bošnjak, Ožbolt, & Hahn, 2013; Kalifa, Chene, & Galle, 2001). Good thermal conductivity of graphite aggregate reduced thermal stress, which is also one of the reasons that G10F and G20F exhibited good heat-resistance properties.

3.3 Thermal conductivity of concrete

Figure 5 shows thermal conductivity of alkali-activated GGBFS concrete specimens versus graphite aggregate content. Concrete specimens in Figure 5 are G0F, G10F, G20F, and G30F with 0%, 10%, 20%, and 30% graphite content, respectively. Addition of graphite aggregate improved obviously the thermal conductivity of concrete, and the thermal conductivity of concrete increased as the graphite content increased. Thermal conductivity of G0F without graphite aggregate is about $1.4 \text{ W m}^{-1} \text{ K}^{-1}$, whereas it is $1.8 \text{ W m}^{-1} \text{ K}^{-1}$ at a graphite aggregate content of

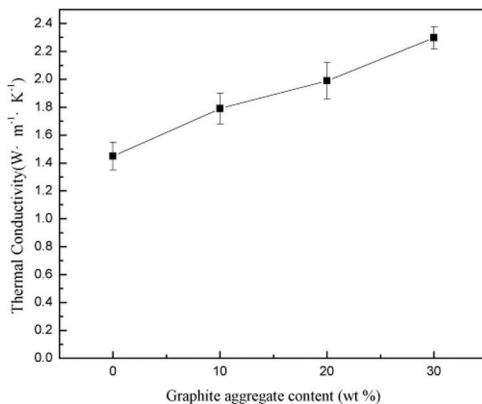


(a) Before heating

(b) After heating

Figure 4. Scanning electron microscopy images of G0F.

10%. The thermal conductivity of concrete is $2.3 \text{ W m}^{-1} \text{ K}^{-1}$ at a graphite aggregate content of 30%, which is about 1.6 times that of the value for G0F. Graphite is a material with good thermal conductivity. Thermal conductivity of ordinary graphite is $5\text{--}20 \text{ W m}^{-1} \text{ K}^{-1}$. Data shown in Figure 5 indicate that a good way to improve thermal conductivity is by partially replacing ordinary aggregates by graphite aggregates.


Figure 5. Thermal conductivity of concrete specimens.

4. CONCLUSIONS

Thermal storage concrete prepared using alkali-activated GGBFS, graphite aggregate, limestone aggregate, polypropylene fiber, chemical admixture, and water exhibited good compressive strength, heat resistance, and thermal conductivity. The residual strength rates of all concrete specimens after heating at $450 \text{ }^\circ\text{C}$ are higher than 90%. The residual strength rate of alkali-activated GGBFS concrete with polypropylene fiber and 10% or 20% graphite aggregate is nearly 100%. Addition of graphite aggregate improved the thermal conductivity of concrete. Thermal conductivity increased by 60% at a graphite aggregate content of 30%.

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REFERENCES

- Bošnjak, J., Ožbolt, J., & Hahn, R. (2013). Permeability measurement on high strength concrete without and with polypropylene fibers at elevated temperatures using a new test setup. *Cement and Concrete Research*, 53(11), 104–111.
- Gil, A., Medrano, M., Martorell, I., Lázaro, A., Dolado, P., Zalba, B., & Cabeza, L. F. (2010). State of the art on high temperature thermal energy storage for power generation, Part 1—Concepts, materials and modellization. *Renewable and Sustainable Energy Reviews*, 14, 31–55.
- Kalifa, P., Chene, G., & Galle, C. (2001). High-temperature behaviour of HPC with polypropylene fibers: From spalling to microstructure. *Cement and Concrete Research*, 31(10), 1487–1499.
- Kong, D. Y., Zhang, J. Z., Ni, T. Y., Jiang, J., & Fang, C. (2009). Research progress on alkali-activated binders and concrete. *Journal of the Chinese Ceramic Society*, 37(1), 45–47. (in Chinese).
- Laing, D., Bahl, C., Bauer, T., & Fiss, M. (2012). High-temperature solid-media thermal energy storage for solar thermal power plants. *Proceedings of the IEEE*, 100(2), 516–524.
- Wu, B. Q., Reddy, R. G., & Rogers, R. D. (2001). *Novel ionic liquid thermal storage for solar thermal electric power systems*. Proceedings of Solar Forum 2001, Solar Energy: The Power to Choose, Washington, DC, USA; April 21–25.

- Xu, H., Li, Q., Shen, L. F., Wang, W., & Zhai, J. P. (2010). Synthesis of thermostable geopolymer from circulating fluidized bed combustion (CFBC) bottom ashes. *Journal of Hazardous Materials*, 175, 198–204.
- Yao, W., Ma, Y. P., Tan, M. H., & Wu, K. R. (2000). Effects of polypropylene fibers on the physical and mechanical properties of cement based composites (I)—mechanical properties. *Journal of Building Materials*, 3(3), 235–239. (in Chinese).
- Zhu, J. Q., Zhang, B., & Zhou, W. B. (2007). Preparation and performances investigation of sensible heat storage material. *Energy Saving*, 4, 32–36. (in Chinese).
- Zuda, L., Pavlik, Z., Rovnanikova, P., Bayer, P., & Cerny, R. (2006, July). Properties of alkali activated aluminosilicate material after thermal load. *International Journal of Thermophysics*, 27(4), 1250–1263.