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## RESEARCH ON RESISTANCE TO SULFATES OF FLY ASH BASED GEOPOLYMERIC RECYCLED CONCRETE

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### ABSTRACT

Fly ash based geopolymer concrete (FGC) and ordinary Portland cement concrete (PCC) were designed and studied on the resistance to sulphate attack, which were tested in 5% solutions of sodium sulphate with dry-wet cycles according to preset national standard GB/T 50082-50082. The experimental results are assessed by the variations of structural morphology, compressive strength, dynamic elastic modulus, weight and volume. The microstructure of the specimens attacked by sulphates was also investigated using scanning electron microscope (SEM) technique. In this paper, the damage mechanism and interaction influence factors of FGC and PCC in the same erosion condition are analyzed and discussed. Furthermore, suggestions on experimental methods suitable for ash based geopolymer concrete resistance to sulphates are proposed.

### KEYWORDS

Geopolymer concrete, sulphate attack, dynamic elastic modulus, microstructure, test method.

### INTRODUCTION

Cement is one of the most popular construction materials in the world. It is absolutely necessary to the structures but has serious energy consuming and environmental pollution problems during the manufacturing process. However, in recent years, with rapid development of modernization, the nationwide output of cement keeps increasing and always ranks first in the world. The government and public have realized this pressing issue and more and more concern about the development and transition of cement industry. Meanwhile, increasingly studies on cement alternatives and construction waste recycling are conducted. Geopolymer is considered as a kind of green concrete (Duxson et al. 2007a). It is typically formed by reaction between solid aluminosilicate and sodium silicate solution



under highly alkaline conditions. The previous research shows that geopolymer concrete has superior mechanical and chemical properties to ordinary concrete (e.g. Duxson et al.2007b; Sofi et al.2007; Bakharev 2005; Sata et al. 2012; Shi et al.2012a, 2012b). Therefore, fly ash based geopolymer concrete not only substitute cement, but also reuse industry waste, which exhibits great application prospect.

As an innovative material, the durability research on FGC is vitally important for its application. The resistance to sulphate attack is one of the most important durability indices. In general, the reaction products of geopolymer concrete are aluminosilicate gel but not C-S-H gel created in PCC. However, the experimental method and analysis theory are both accordingly to PCC. Therefore, in order to investigate the damage mechanism and influencing factors for geopolymer concrete, this study tested the sulphates effect to the properties of FGC as well as discussed the feasibility of the test method.

The experiments conducted according to “Standard for test methods of long-term performance and durability of ordinary concrete (GB/T 50082-2009)”. The performances of FGC and PCC are studied by evaluating the effect on structural morphology, compressive strength, dynamic elastic modulus and changes in weight and volume. The damage mechanism is further analyzed by SEM, EDS and ICP-OES methods.

## EXPERIMENTAL PROGRAM

### Materials

The materials needed in the experiment include coarse aggregate, fine aggregate, cement, fly ash, alkali solution, sodium sulphate and dilute sulphuric acid. Due to the fine aggregate exposure to open air, the moisture varies from time to time. They were put into the oven to dry before the mixing. Cement is 32.5 ordinary Portland cement. Fly ash (Class F) was used as the main aluminum and silicate source for synthesizing of geopolymeric binder. The average diameter is 1.586 $\mu$ m, and the chemical composition is presented in Table 1.

Table 1. Chemical composition of fly ash

Component	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	Na <sub>2</sub> O	Loss on ignition
Property(%)	74.18	9.44	5.53	4.22	2.48	1.46	1.41	0.96	0.32	0.82

The alkali solution mixed with sodium silicate solution (Na<sub>2</sub>SiO<sub>3</sub>) and sodium hydroxide solution (NaOH). Na<sub>2</sub>SiO<sub>3</sub> solution is the liquid in pale yellow colour with 3.2-3.4 modulus. The chemical composition of Na<sub>2</sub>SiO<sub>3</sub> solution is Na<sub>2</sub>O-28.2%, SiO<sub>2</sub>-26.2% and H<sub>2</sub>O-45.6% by mass. NaOH solution was made by distilled water dissolving pure NaOH flakes into 10mol/L. The alkali solution should be prepared one day ahead of the test. 5% sodium sulphate solution was made by sodium sulphate of 99% purity dissolving in distilled water. The solution used to adjust pH value of soaking solution was made by diluting concentrated sulphuric acid into 1mol/L.

### Specimen Preparation

The mixture design of FGC and PCC is summarized in Table 2. The specimens of 100 mm × 100 mm × 100mm cube were prepared for testing compressive strength. The prism specimens of 100mm × 100mm × 400mm are for dynamic elastic modulus test. The mixing of the concrete was conducted in a mechanical mixer according to the procedure in GB/T 50081-2002. After mixing, the mixture was poured into mould and covered under polyethylene sheets to avoid water from evaporating.

The specimens of PCC were cured for 24 h in the laboratory environment. And then, demould and transferred to standard curing case at 20 °C ± 2 °C with moisture of 95%. The FGC specimens were kept

in the oven at 80 °C for 24h, followed by removal of specimens from the moulds and storage in the standard curing case. After curing for 26 days, the specimens for sulphate attack test were moved out of the curing case into oven at 80 °C for 24h. The surfaces of the specimens were polished by machine. Other specimens were kept curing in the case until test day. After taking out of the oven, the specimens cooled down in the laboratory environment. And then, they were moved into automatic dry-wet cycle machine tank for the test. The test machine is controlled automatically according to GB/T 50082-2009. One complete cycle lasts for about 24 hours.

Table 2. Summary of concrete mixture proportions (Kg/m<sup>3</sup>)

Concrete	Coarse aggregate	Fine aggregate	cement	Fly ash	Na <sub>2</sub> SiO <sub>3</sub> solution	NaOH solution	Water
PCC	1208	592	400	-	-	-	200
FGC	1318	647	-	437	156	62	-

The specimens for SEM test were selected from the broken sections of the compressive experiments and carried out on Hitachi S-4800. All the specimens were soaked in the absolute alcohol for one day, following by drying at 60 °C for 15 min. The specimens were coated with Au prior to the analysis.

## RESULTS AND DISCUSSIONS

### Soaking Solution pH Change

As is known to all, whatever PCC or FGC, the concretes present alkalinity. The researches show that the pH value of the soaking solution takes great influence on the damage mechanism resistance to sulphate attack (Kumaravel and Girija 2013; Santhanamet al.2001). According to GB/T50082-2009 requirements, pH value of the soaking solution should be controlled within 6-8 by adjusting with dilute sulphuric acid. The pH value is confirmed by PHS-3C equipment. The pH value of soaking solution before the test was measured with 7.1-7.5 which is alkaline. During the cycling process, the pH value was found increasing gradually and finally tending towards stability. This is because for PCC, alkalinity derives from the hydration product calcium hydroxide (Ca(OH)<sub>2</sub>). The hydroxyl ions separated out accompanying by the whole damage process. The source of alkalinity of FGC comes from the unreacted alkali solution NaOH. It dissolved faster than that of Ca(OH)<sub>2</sub> which results in the greater alkalinity of the soaking solution in the preliminary period.

### Compressive Strength

The loss of the compressive strength is the most important evaluation index for resistance to sulphate attack test. The compressive strength tests were performed on 200kN electro-hydraulic mechanical testing machine. The test results are shown in Figure 1 and Figure 2. Control group refers to the cubic samples cured in the standard curing case for compressive test. The results illustrate the compressive strength of PCC increases by days. The compressive strength of PCC control group at 58-days corresponding to 30-cycles increases 34% compared with the strength at 28-days. The compressive strengths of PCC cycle group concrete dropped firstly and then grew up gradually. For FGC control group concrete, the compressive strength is basically increasing. The compressive strength at 58-days is greater than 11% of that at 28-days. Although the increment is smaller than PCC, the overall compressive strength of FGC is stronger. Therefore, FGC has greater initial strength. Compared with PCC and FGC concretes, the variation of compressive strength is similar. The compressive strength of the specimens exposed to sulphate attack went through the procedure of descending and increasing. This is because there are some complex dynamic chemical reactions happening during the sulphates erosion process. On one hand, the sulphates destroy the original structure of the concrete. On the other hand, some second hydration reactions or polymerizations occurred when PCC and FGC were soaked in the same solution, which could make up the strength missing from the front part. So, the overall strength depends on the stronger aspect. Meanwhile, due to this is a dynamic process, the final strength fluctuated during the testing.

According to GB/T50082-2009, the corrosion resistance coefficient is defined to assess the resistance to sulphates attack, as follows:

$$K_f = \frac{f_{cn}}{f_{c0}} \times 100\% \quad (1)$$

where,  $K_f$  is the corrosion resistance coefficient;  $f_{cn}$  is the compressive strength after  $n$  cycles testing;  $f_{c0}$  is the compressive strength of control group concrete corresponding to cycle group.

The corrosion resistance coefficients of PCC and FGC at different cycles are listed in Table 3. The results show the variations of the compressive strength during the test. But the rationality to define the corrosion resistance class totally depends on this single coefficient is to be discussed, as well as judge to stop the test by the coefficient descend to 75%. On one hand, the greater initial strength of FGC would limit the later strength growth, so the coefficient  $K_f$  would increase. On the other hand, during the erosion process, FGC concrete influenced by the further polymerization reaction, which result in greater strength growth and also increase the value of  $K_f$ .

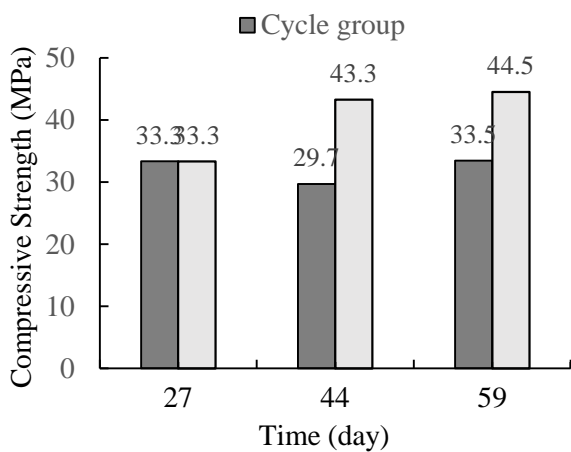


Figure 1. Compressive Strength of PCC

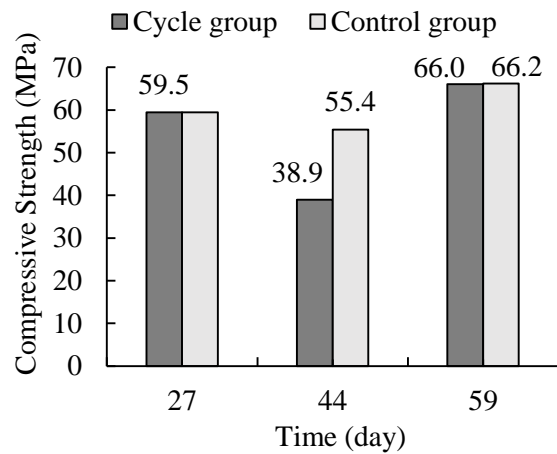


Figure 2. Compressive Strength of FGC

Table 3. Corrosion resistance coefficient of PCC and FGC

Cycle number	0	15	30
PCC	100%	69%	75%
FGC	100%	59%	100%

### Weight and Volume Change

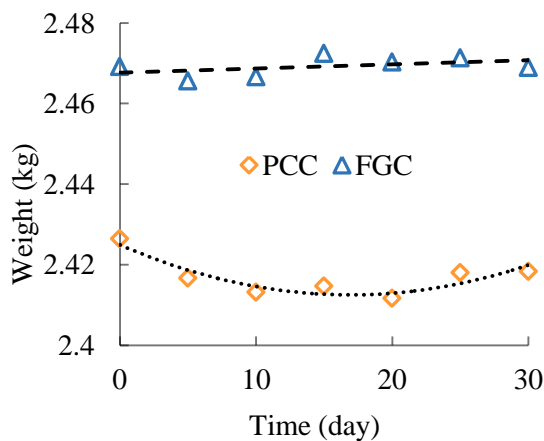


Figure 3. Average weight changes of 100mm cubes in cycles

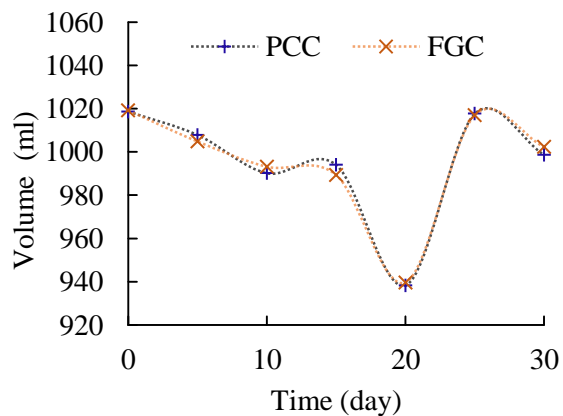


Figure 4. Average volume changes of 100mm cubes in cycles

The weight and volume of the specimens changed during the testing which illustrates the changes of the inner material's quantity. The weight of the samples was tested by electron balance with 1g accuracy. The volume of the cube samples was measured by water displacement method. The test results are shown in Figure 3 and Figure 4. It can be found that the changes of weight are very few. The variation is about 0.3% for FGC and no more than 0.6% for PCC. There is slight variation of weight between FGC and PCC. Overall, the weight of FGC specimens keeps increasing slightly during the test. However, the weight of PCC decreased a little bit and then went up gradually. This is related to the chemical reactions during the erosion process. In the preliminary stage,  $\text{Ca(OH)}_2$  was dissolved into the soaking solution. But some chemical reactions kept producing new matters, such as ettringite. So, this might due to the mass decreased more than increased at the early stage, while it reversed at the later period. On the other hand, the volume changes of FGC and PCC are similar. The curves descend until 20 cycles and then rise again. This is because the drying shrinkage of the concrete before 20-cycles period is significant. While, after that due to some new reaction products with dilatibility were produced, the volume became greater again. But the spalling and dissolving of the concrete result in the final volume being smaller than the initial one.

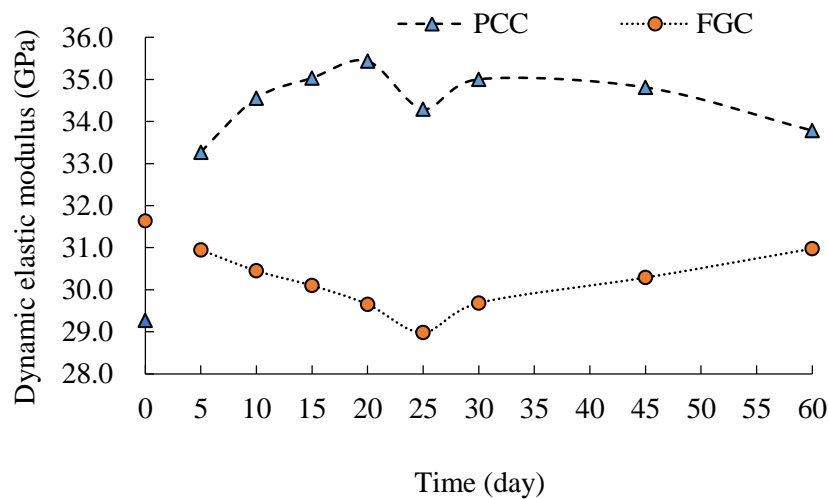


Figure 5. Changes in dynamic elastic modulus

### Dynamic elastic modulus

The dynamic elastic modulus is measured according to sympathetic vibration theory. The resonated frequency of the specimens is measured by equipment and then calculated to dynamic elastic modulus  $E_d$  by the formula as:

$$E_d = 13.244 \times 10^{-7} \times \frac{WL^3 f^2}{a^4} \quad (2)$$

where,  $E_d$  is dynamic elastic modulus (GPa);  $a$  is the side of the cubic section (mm);  $L$  is the length of the specimen (mm);  $W$  is the weight of sample, accurate to 0.01kg;  $f$  is the transverse frequency (Hz).

The dynamic elastic moduli of the specimens by cycles are depicted in Figure 5. The values of dynamic elastic modulus of FGC and PCC are both dropped at around 25-cycles. After that, dynamic elastic modulus of FGC kept increasing, while that of PCC went up a little bit until 30-cycles and then decreased gradually. It can be seen that dynamic elastic modulus of FGC is always smaller than that of PCC. Meanwhile, the corresponding compressive strength of FGC is greater than that of PCC. Therefore, the deformation of FGC is greater than PCC at the same stress. The tested dynamic elastic modulus variation of PCC is similar to the results of Qiao (2008, 2009). The study explained that the changes of  $E_d$  effected by two aspects. On one hand, when the samples are soaked in the solution subject to sulphuric acid, free water permeates into the concrete's capillary. During drying process, due to the increase in temperature, unreacted cement particles will have second hydration reaction with free water to produce hydrated calcium silicates and hydrated calcium aluminates. These products will

fill the capillary pores and increase the density of the concrete, which improve the dynamic elastic modulus. On the other hand, because the moisture condition varies greatly, only a little free water participates in second hydration reaction. Then, the left free water evaporate and results in more micro cracks and pores. Especially when the hydration reaction finished, the latter one takes over the primary reason, which lead to the decrease of the dynamic elastic modulus. These two reasons exist simultaneously. At the preliminary stage, the first reason plays a major part. The second cause dominates in the later period. For FGC specimens, some unreacted fly ash particles and NaOH solution should also be considered besides the reasons mentioned above. The knee point at 25-cycles demonstrates that some beneficial reactions may be finished before this point. The more complicated reaction process should be studied further.

## SEM

Scanning electron microscope (SEM) test is an effective way to observe and investigate the erosion damage mechanism. Figure 6 shows the microstructure of FGC and PCC at different cycles. 0, 15 and 30 indicate the dry-wet cycle numbers. In Figure 6(a), there are many unreacted fly ash particles embedded in the dense paste. Compared with very few pores in FGC-0, the image of FGC-15 shows many pores and broken fly ash particles. The fly ash particles reduced obviously in FGC-30, instead many laminated zeolite like structures appeared. The structure seems still compact at 30-cycles. Compared with FGC, the images of PCC show obvious different microstructure at three cycle stages. Before the concrete attacked by sulphates, the microstructure of PCC-0 is tight and uniform. At 15 cycles, many needle-like and coralloid crystal, voids and cracks can be seen. In PCC-30, the morphology of the gel exhibits in flake, floc and fiber-shaped. Taken the aforementioned analysis into account, at the preliminary stage of the dry-wet cycles, the structure of the samples is heavily damaged. However, some new products make up the framework to a certain degree in later period. The changes of microstructure morphology are in accordance with the macro performances.

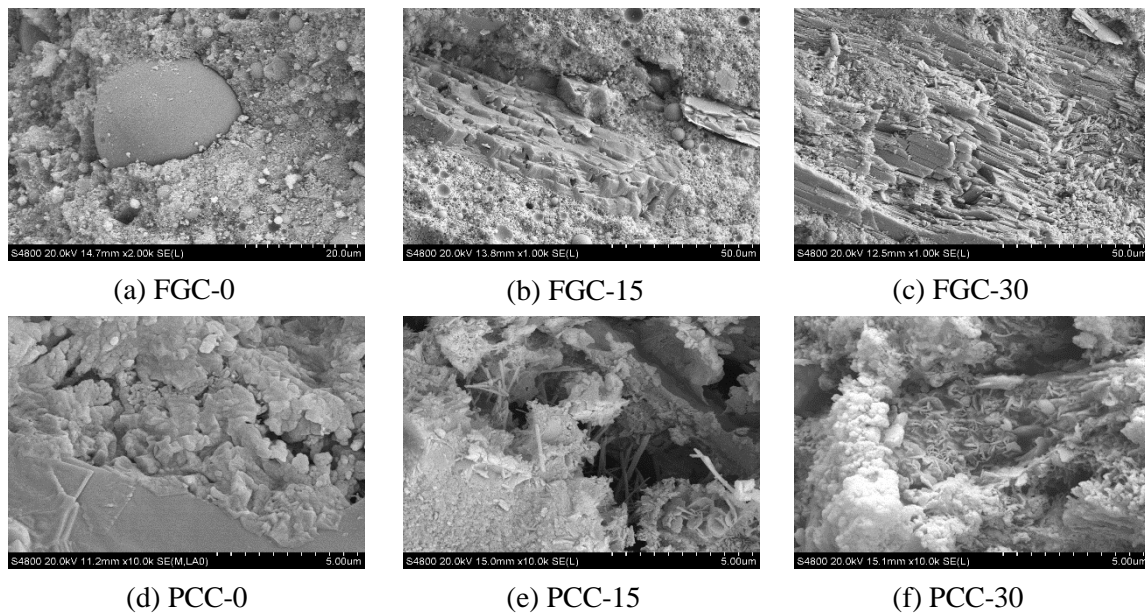


Figure 6. Microstructure morphology of different specimens

## Erosion Damage Mechanism

According to the above series of experiments and analysis, the process of the concrete subjected to sulphate attack can be summarized. Overall, when FGC and PCC specimens are immersed in  $\text{Na}_2\text{SO}_4$  solution, various soluble chemical elements of the concrete and the solution in the capillary begin transferring and exchanging. These performances cover the whole process. Firstly, some excess  $\text{OH}^-$  in

FGC release into soaking solution very fast and result in the pH value of the soaking solution increased. At the same time, large quantity of  $\text{Ca}(\text{OH})_2$  came from PCC also dissolve into soaking solution, which led to the concentration of Ca increased. As more and more  $\text{Na}_2\text{SO}_4$  solution with  $\text{Ca}^{2+}$  penetrate into FGC pores, many unreacted fly ash and  $\text{Na}_2\text{SiO}_4$  solution start to dissolve and response. This could make the structure with many voids and pores which is harmful to the concrete. On the other hand, the active ingredient in fly ash, such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  can react with  $\text{Ca}(\text{OH})_2$  to produce hydration aluminium silicate gel. With the help of heating period of the test, it provides good condition for the further polymerization in FGC. The voids can be filled and the tight structure can prevent from the sulphates attack. Therefore, geopolymer concrete performs different properties and various microstructure morphologies at different erosion stages.

## CONCLUSIONS AND DISCUSSIONS

The resistance to sulphates of fly ash based geopolymer concrete is investigated and discussed by a series of experiments. Some conclusions can be drawn as:

1. Under the same sulphates erosion condition, the changes of compressive strength of geopolymer concrete and ordinary concrete are similar. According to the judgment criterion of present standard GB/T 50082-2009, geopolymer concrete performs no better than ordinary concrete. However, considering the later development of compressive strength, dynamic elastic modulus and microstructure morphology, geopolymer concrete behaves more stable subjected to sulphate attack.
2. Dynamic elastic modulus can rationally explain the damage mechanism during the erosion process. It is suggested that dynamic elastic modulus can be used as one of the criterions to assess the concrete resistance to sulphate attack.
3. The better resistance to sulphate attack of geopolymer concrete result from two aspects. On one hand, the much denser microstructure can slow down the corrosion of the sulphates. On the other hand, the more stable polymerization products are less affected by sulphates.
4. In order to further understand the reaction mechanism of geopolymer concrete subjected to sulphates attack, as well as the influence of experimental conditions to the properties, it is suggested the geopolymer concrete should be tested separated from other concrete to avoid interference.

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