Research Article

Study on Mechanical and Microscopic Properties of Fly Ash Cement-Based Materials in High Geothermal Environment

Yehong Hu, Wen Xie, Feng Zou, Jialei Yang, Tian Xi, Ruijun Li, Xin Wang, and Xuefeng Xu

1 China Nuclear Industry Huachen Construction Engineering Co., Ltd., Xi'an, Shaanxi 712000, China
2 School of Civil Engineering, Southwest Jiaotong University, Chengdu 610031, China

Correspondence should be addressed to Xuefeng Xu; raymond_xu@my.swjtu.edu.cn

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Through simulating a hot and humid environment of high-ground-temperature tunnel and taking advantage of mechanics performance testing, differential thermal analysis (DTA) technology, and scanning electron microscope (SEM) observation technology, the macroscopic and microscopic properties of cement-based materials and their performance improvement measures can be investigated. Also, the mechanism of improvement can be revealed from the perspective of the hydration degree and microstructure. The experimental results indicate that under the hot and humid environment of high ground temperature, adding fly ash could efficiently weaken the early high-temperature curing effect of cement-based materials, improving their physical properties. But the mechanical strengths of cement-based materials go through a transformation from increase to decline with the rise of fly ash, appearing a maximum value in the process. Meanwhile, the differential thermal analysis and the microstructure analysis show that a hot and humid environment enhances the pozzolanic activity of fly ash and an appropriate ratio of fly ash could improve the microstructure of cement slurry, but when fly ash covers more than 30% of the mix of cement-based materials, the quantity of the alkaline exciting agent, calcium hydroxide, is not enough to meet the needs of the active effect of fly ash and the hydration degree of fly ash becomes extremely low. Last, under a hot and humid environment of high ground temperature, fly ash saturation in cementing material should range from 20% to 30% in mass of total binder, which makes for long-term performance of cement-based materials.

1. Introduction

With the progress of design theory and construction technology, more deep-buried long tunnels will be built in railways, highways, hydropower, interbasin water transfer, and mineral resources, and the problem of high ground temperature is becoming more and more prominent [1–6]. Through the temperature and humidity environment monitoring and drilling monitoring of high ground temperature tunnel, high ground temperature of tunnel mainly appears in two forms: one is hot-dry (as shown in Figure 1(a)), that is, in places with good geological structure, the heat in the geological layer is transmitted to the tunnel surface through rocks, and the other is hot-humid (as shown in Figure 1(b)), that is, in the sections of fault fracture, fault turning composite, and rock fracture, the degree of fracture development is high, and the geothermal water is enriched to form hot springs. Among them, the heat loss is blocked in the humid and hot environment, and the internal temperature of concrete may rise to a higher range, forming a negative effect of early curing under high temperature, resulting in the reduction of hydration degree and strength in the later stage. At present, the high-temperature, humid and hot tunnel mainly focuses on its external measures, ventilation, and cooling, while the mechanism research on the properties of materials is less. These studies mainly investigate the influence of the external environment on the performance of cement-based slurry, including steam environment and high-temperature environment caused by fire. Through simulating the high-temperature environment...
and designing a similar maintenance system, the temperature variation range is controlled to reflect the performance of cement-based slurry in a hot and humid environment of high ground temperature tunnel.

The research in literature [7–10] has shown that the adverse effect of high-temperature early curing effect on the mechanical properties of shotcrete at the age of 7 days in a 70°C humid and hot environment has been fully reflected. At present, there have been some studies on the properties of cement-based materials in high-temperature environment. For example, literature [11] studied the microstructure degradation process and degradation law of cement-based materials at high temperatures up to 400°C. References [12, 13] studied the hydration properties of composite cementitious materials under steam curing conditions. The curing system is to put them into 20°C water for curing to the specified age after steam curing for 8 hours. Literature [14] studied the effect of high-temperature curing on the hydration degree and micromorphology of composite cementitious materials. The curing system is to take them out after curing in an oven at 65°C for 7 days and then put them in standard curing. Although these related studies have certain reference significance, there are great differences in maintenance system, maintenance conditions, design mix proportion, and research focus compared with the engineering background of high-temperature tunnel humid and hot environment. The measured temperature at 3 m in the advance exploratory hole of Sangzhuling tunnel 1#, cross tunnel of Lalin railway, under construction is as high as 82.3°C, which may face a higher hot spring effect in the later stage. Duan and Zhang [15] claim that temperature and humidity are shown to be the most relevant factors affecting adhesion strength, whose loss is related to the microdamage in the shotcrete layers closest to the rock. For reducing thermal damage, Zhao and Yan [16] adopted ventilation and artificial cooling to reduce the heat damage caused by high ground temperature in the tunnel. However, there is little research on high-temperature tunnel materials.

The performance of concrete in high-temperature humid and hot environments needs to be further improved, and the mechanical performance of Shotcrete in a humid and hot environment is largely reflected in the hydration performance of cement-based materials with cement as the main cementitious material. Fly ash is a kind of industrial waste, which has volcanic ash effect, microaggregate effect, and particle shape effect. Proper addition can not only weaken the negative effect of high-temperature maintenance but also reduce the amount of cement and meet the low-carbon requirements. However, if the content is unreasonable, it may lead to problems such as low strength. It is of great theoretical significance and application value to analyze the mechanical properties and micromechanism of fly ash cement-based materials with different content in high-temperature, humid and hot environments.

Taking this as the research background, this paper simulates an 85°C humid and hot environment; studies the appropriate content and improvement effect of fly ash in a humid and hot environment through mechanical property test of cement-based materials, differential thermal analysis technology, and scanning electron microscope technology; and reveals the improvement mechanism from the perspective of hydration degree and micromorphology.

2. Test Design

2.1. Working Condition Design and Mix Proportion Design. In order to explore the improvement measures for the performance of cement-based materials in the humid and hot environment of high-temperature tunnel, select the representative water binder ratio and design six groups of mix proportion conditions for research, in which the content of fly ash is 0%, 10%, 20%, 30%, 40%, and 50% of the total mass of cementitious materials. The cement used in the test is Dujiangyan Lafarge P.O42.5 ordinary Portland cement. The fly ash is grade I fly ash produced by Suining thermal power plant (density: 2.1 g/cm³, fineness: 4.4%, water demand ratio: 90%, and loss on ignition: 3.8%; Chinese ISO standard sand). The mix proportion design of each working condition is shown in Table 2.
2.2. Test Method. The cement-based paste should be cast rapidly into moulds with sizes of 40 mm × 40 mm × 160 mm. Three specimens were formed for each condition. In this case, the casted specimens were manufactured by means of vibration technology with a vibrating table. Following the final setting, all specimens were placed into a water tank with a constant temperature of 85°C, which was used to simulate the hot-humid environment of high-temperature geothermal tunnels, as illustrated in Figure 2. After 7 days of curing, the samples were prepared for mechanical property test, DTA (differential thermal analysis) test, and SEM (scanning electron microscopy) test.

The mechanical properties of cement-based mortar specimens were measured by automatic constant stress compressive and flexural testing machines. DTA curve was obtained by differential thermal analysis, and the hydration products and hydration degree were analyzed. The micro-morphology of hydration products of cement-based materials under different working conditions was measured by scanning electron microscope, and the degradation law and degradation mechanism of micromorphology of cement-based materials were analyzed. At the same time, energy-dispersive X-ray spectroscopy (EDS) was performed on a JSM 7800F microscope.

3. Test Results and Analysis

3.1. Mechanical Property Analysis. The mechanical properties of the specimens tested under constant heat curing to 7 d at 85°C humidity and heat curing conditions are shown in Table 3.

In order to more intuitively observe the change trend of mechanical properties of cement-based mortar specimens with different fly ash content, the flexural and compressive data under various working conditions are drawn into column diagrams, as shown in Figures 3 and 4.

It can be seen from Table 3 and Figures 3 and 4 that the flexural and compressive strength of cement-based mortar specimens gradually increases with the increase of fly ash content under the condition of hot-humid curing and low fly coal content. When the content of fly ash increases to about 30%, the flexural and compressive strength reaches the maximum. Then, with the further increase of fly ash content, the flexural and compressive strength gradually decreases.

Compared with the working condition with the appropriate amount of fly ash, the negative effect of high-temperature curing under 0% FA working condition has been reflected at the age of 7 days, and the flexural and compressive strength are relatively low. This is mainly because the hot-humid temperature is too high and the heat loss is blocked. The internal temperature of cement-based materials may rise to a higher range, forming a high-
temperature early curing effect. The hydration product shell rapidly formed on the surface of cement particles prevents water from entering the cement core, so as to reduce the hydration degree in the later stage and make the hydration products not dense. The fly ash cement-based material is sensitive to temperature and suitable for steam curing. After mixing with water, although the fly ash itself does not undergo hydration and condensation hardening, a significant hydration reaction occurs in Ca(OH)\(_2\) solution, as is shown in the following equations:

\[ x\text{Ca(OH)}_2 \cdot \text{SiO}_2 + m\text{H}_2\text{O} \rightarrow x\text{CaO}\cdot\text{SiO}_2\cdot(x + m)\text{H}_2\text{O} \]  
\[ y\text{Ca(OH)}_2 \cdot \text{Al}_2\text{O}_3 + n\text{H}_2\text{O} \rightarrow y\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot(y + n)\text{H}_2\text{O} \]  

Adding fly ash in a humid and hot environment not only can weaken the early maintenance effect of high temperature but also can effectively promote the secondary hydration of fly ash. However, when the content of fly ash is too large, the mineral composition of cement decreases relatively. At this time, the alkalinity of cement paste cannot meet the requirements of the activity effect of fly ash. Therefore, two times hydration can only form less C-S-H gel, and the degree of hydration of fly ash is very low, showing a decrease in strength.

Therefore, from the macromechanical property test results, the performance of cement-based materials can be improved by adding fly ash in a humid and hot environment, and the appropriate content should be 20%–30% of the total amount of cementitious materials. Differential thermal analysis and SEM test will explore the mechanism from the perspective of hydration degree and micromorphology.

3.2. Differential Thermal Analysis. The DTA curve of the tested substance is obtained through differential thermal analysis. When there is a thermal effect, the DTA curve will have an upward or downward peak. The greater the thermal effect, the higher the peak and the larger the area. The corresponding hydration products are determined according to the temperature peaks of the curve, and the hydration degree and hydration mechanism are qualitatively analyzed based on the principle of differential thermal analysis.

Ca(OH)\(_2\) in cement-based materials, as an alkaline activator for hydration of fly ash, undergoes the following thermal decomposition reaction at a certain temperature:

\[ \text{Ca(OH)}_2 \rightarrow 400^\circ\text{C} \rightarrow 500^\circ\text{C}\text{CaO} + \text{H}_2\text{O} \]  

Therefore, the content of Ca(OH)\(_2\) in cement-based materials can be determined qualitatively by the DTA curve.

Grind the samples under various working conditions into powder, sieve them with a 300-mesh sieve, and weigh 15 mg for the differential thermal analysis test, and the test results are shown in Figures 5 and 6 and Table 4.

From the above chart, it can be seen that the decalescence peaks of the downward concave curve appear in DTA curves of all working conditions in the range of 400–500°C and 700–800°C, which correspond to the decomposition of Ca(OH)\(_2\) and CaCO\(_3\), respectively. CaCO\(_3\) is mainly derived from the carbonation of Ca(OH)\(_2\), but for each condition, the environmental conditions of DTA analysis are the same, so the carbonation of Ca(OH)\(_2\) in the sample does not affect the analysis of the relative content of Ca(OH)\(_2\) between samples. Under the condition of the total amount of cementitious materials, with the increase of fly ash content, the content of cement mineral composition decreases, and the content of Ca(OH)\(_2\) produced by C\(_3\)S and C\(_2\)S hydration in the system decreases, while the demand for secondary hydration increases. Therefore, the area of a decalescence peak on the DTA curve decreases monotonously with the increase of fly ash content in the range of 400–500°C, so it can be qualitatively obtained by the DTA curve. The content of Ca(OH)\(_2\) in the sample decreases with the increase of the amount of fly ash.

In the hydration process of the whole system, cement hydration generates Ca(OH)\(_2\), and the secondary hydration of fly ash consumes Ca(OH)\(_2\). With the increase of fly ash content, the secondary hydration and dispersion filling of fly ash are strengthened; the consumption of Ca(OH)\(_2\) is increased; and the pore structure of cement stone is continuously dense. At the same time, the pozzolanic effect of fly ash should be brought into full play to improve the microstructure of slurry, gradually increase the strength of slurry, and achieve the improvement effect. When the content of fly ash is too high, the content of Ca(OH)\(_2\) in the system is very low, but the content of fly ash is very large. The alkalinity of the slurry cannot meet the requirement of activating fly ash and can only generate less C-S-H gel, and the macroscopic performance is reduced by strength. Therefore, excessive fly ash content will reduce the strength and cannot achieve the effect of improvement.

3.3. Micromorphology Analysis. The microstructure of a material plays a decisive role in its macroproperties, and the macromechanical properties are the comprehensive
The micromorphology of 0% FA under the curing condition of 85°C humid and hot environment at the age of 7 days is analyzed. The typical microstructure and EDS image are shown in Figures 7 and 8. Figure 7(a) shows that due to the early curing effect of high temperature, the hydration products under 0% FA condition are relatively loose, which are mainly composed of fibrous C-S-H colloid (type I), granular C-S-H colloid (type III), Ca(OH)$_2$ crystals deposited therein, and many pores. Due to the high temperature of moisture and heat, the hydration product shell caused by the excessive hydration rate prevented the water from entering the cement core. In Figure 7(b), a large amount of fibrous C-S-H gel could be observed at 7d age.

3.3.2. Appropriate Amount of Fly Ash. The content of 10%∼30% fly ash is the growth section of cement-based mortar strength. Figures 9–11 show the micromorphology and EDS image under 20% FA and 30% FA conditions, respectively. It can be seen from the analysis of Figures 9 and 10 that the slurry structure is dense under the condition of adding an appropriate amount of fly ash. The slurry structure is mainly composed of dense type III C-S-H colloid and Ca(OH)$_2$ deposited between them. At the same time, there are network C-S-H colloid (type II) and fly ash balls covered by hydration products. Type II or type III C-S-H gel is deposited around the fly ash particles. A few fly ash particles are surrounded by fibrous C-S-H gel, and the particles of the fly ash are strongly bonded with the surrounding hydration products. Therefore, there are almost no hemispherical holes left in the section after the extraction of the photospheric and fly ash balls. The analysis indicates that hydrothermal curing is helpful to stimulate the volcanic ash effect of fly ash. It also forms more C-S-H gel with hydration of CH. The fly ash has a microaggregate effect, which is beneficial to the late strength growth of cement-based materials and reduces the negative effect of early maintenance of high temperature caused by moisture and heat curing. For the 20% FA condition, particularly, the hydration products mainly consist of reticular C-S-H gels (type II), C-S-H gels (type III), and deposited Ca(OH)$_2$ crystals, with a few bare smooth nonhydrated fly ash balls. With the increase of age, there is almost no smooth fly ash ball. Moreover, as the high-temperature geothermal environment greatly accelerates the volcanic ash effect of the fly ash, the structure of the slurry is more compact. Therefore, the late strength of 20% fly ash is higher than the BP condition.

3.3.3. Excess Fly Ash. With the continuous increase of fly ash content, 40%∼50% FA is the decreasing section of cement-based mortar strength. Figure 12 shows the micromorphology under 40% FA condition. Since the micromorphology under the 50% FA condition is basically consistent with the phenomenon and law of 40% FA, it will not be shown here due to space limitation and will be analyzed together.

Compared with the above conditions, Figure 12 shows that there are a large number of exposed smooth and unhydrated fly ash balls under 40% FA and 50% FA.
Figure 7: Microstructures of 0% FA: (a) hydration products and (b) C-S-H gelation.

Figure 8: EDS image (scale bar 30 μm).

Figure 9: Microstructures of 20% FA: (a) 500× and (b) 2,000×.

Figure 10: Microstructures of 30% FA: (a) 500× and (b) 2,000×.
conditions, and there are very fine and short fibers (0.1 μm∼0.2 μm long) around many fly ash particles; the slurry hydration product is mainly composed of fibrous C-S-H colloid, approximately smooth fly ash balls, and a large number of pores. Grudemo believes that [17] the possible crack path units of cement paste include: (1) sheet cracks between Ca(OH)₂ crystals, (2) radial cracks through the inner and outer rubber shells, (3) spherical cracks around the residual anhydrous core, and (4) adjacent to the junction area between the outer rubber shells. For fly ash cement paste, in addition to the above four crack path units, the fifth one, the spherical crack around the fly ash ball, should be added [18]. It can be clearly seen from the scanning electron microscope in Figure 12(b): there are a large number of bare smooth fly ash balls, and hemispherical holes left after the fly ash balls are pulled out on the fracture surface. Due to the excessive amount of fly ash, the Ca (OH)₂ produced by cement hydration is relatively small, the hydration of fly ash particles is seriously insufficient, and the bond between fly ash particles and surrounding hydrates is very weak. When there is external tensile stress, the pores around fly ash balls become weak links and crack.

4. Conclusions

The following conclusions are obtained from the macro- and micromechanical properties of cement-based materials by scanning electron microscopy:

(1) In a high-temperature, humid and hot environment, adding an appropriate amount of fly ash can effectively weaken the negative effect of early maintenance at high temperature of cement-based materials and improve the mechanical properties of cement-based materials.

(2) With the increase of fly ash content, the strength of cement-based materials first increases and then decreases, and there is a maximum when the content is 30%. The macro- and micromechanism test show that the appropriate content of fly ash in a high-temperature, humid and hot environment should be 20%∼30% of cementitious material, and the maximum should not exceed 30%.

(3) DTA shows that due to the decrease of cement mineral composition and the secondary hydration effect of fly ash, the content of hydration product Ca(OH)₂ decreases with the increase of fly ash content. When the content of fly ash exceeds 30%, the amount of alkaline activator Ca(OH)₂ is not enough to meet the demand for fly ash activity effect.

(4) Micromorphology analysis shows that hydrothermal curing is helpful to stimulate the volcanic ash effect. It forms more C-S-H gel with hydration of cement hydration product CH, and the appropriate amount of fly ash is conducive to the later strength growth of cement-based materials. However, if the content of fly ash is too large, the Ca(OH)₂ generated by cement hydration is relatively small; the hydration of fly ash particles is seriously insufficient; and there are a large number of light spheres and caves on the fracture.
surface, resulting in the reduction of the strength of cement-based materials.

**Data Availability**

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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