Early mechanical properties of high calcium fly ash cement soil

DONG Yu-ping\textsuperscript{1}, ZHANG Yu-pei\textsuperscript{2}, LIU Yu-xiang\textsuperscript{1}

\textsuperscript{1}Xi’an FanYi University, Shaanxi Xi’an 710105;
\textsuperscript{2}China Reilway First Survey And Design Institute Group Co., Ltd., Shaanxi Xi’an 710043

E-mail: 529460217@qq.com

Abstract: In order to improve the comprehensive utilization rate of industrial waste fly ash materials, this paper attempts to add high calcium fly ash to cement soil to study the effect of high calcium fly ash on the performance of cement soil materials and its strength formation mechanism. By designing the cement soil strength test and the excitation test, the early stage strength of the cement soil material can be improved by adding a certain amount of high-calcium fly ash and activator, which provides the application of high-calcium fly ash in engineering. It is also a supplement and improvement of the theoretical application system of fly ash materials.

1. Introduction

Due to the relatively abundant coal resources in China, the energy structure dominated by thermal power generation will continue for a long period of time in the future \cite{1}. As more and more large-scale units are put into operation, more lignite and sub-bituminous coal with high volatiles are used as power fuels, and correspondingly, more high-calcium fly ash is discharged. In some areas of Shanxi Province, high calcium fly ash emissions have far exceeded low calcium fly ash. These high-calcium fly ashes are piled up in large quantities, which not only wastes land resources, but also seriously pollutes the environment, posing obstacles to the sustainable development of the power industry. To this end, how to turn solid waste slag fly ashes into useful materials, many scholars have proposed a series of comprehensive utilization methods. According to the research data, many researchers have added fly ash to cement soil, which can significantly improve the strength and other properties of cement soil, and has obtained valuable research results. For example, Pang Wentai, Shen Xiangdong\textsuperscript{2}and others scholars use the principle of cement solidified soil technology, by adding fly ash in cement soil, and then using strong alkali to stimulate fly ash cement soil to prepare new materials with high strength and durability; Cui Yongcheng\textsuperscript{3}designed the orthogonal experimental scheme L9(3\textsuperscript{4}) to study the fly ash cement soil with water content, cement content, fly ash content and age; He Wenxiu and Shen Xiangdong\textsuperscript{4}applied industrially produced waste fly ash and relatively inexpensive glass fiber to cement soil; An PengPeng, Liu Wenxiao\textsuperscript{5}and other people conducted experimental research on the strength characteristics of cemented fly ash stirred saturated loess. Through a large number of experimental studies and practice tests, fly ash cement soil has been widely used in practical engineering. At present, most researchers are working hard to study the application of
low-calcium fly ash in cement-soil engineering, but there is still a lack of research on the application of high-calcium fly ash. In this paper, the high-calcium fly ash is added to the cement soil to study the variation of the influence of different high-calcium fly ash on the strength of cement soil under different ages. The effects of five chemical reagents on the early strength of high calcium fly ash cement soil were studied to further improve the theoretical application system of fly ash materials.

2. Test

2.1 Test materials and methods
The cement is the ordinary Portland cement PO42.5 produced by Xi'an Lantian Yubai Cement Co., Ltd. The main performance index parameters are shown in Table 1; the soil is taken from the 2m underground of Taiyigong Town, Chang'an District, Xi'an. The main performance index parameters are shown in Table 2. The chemical composition of high calcium fly ashes is shown in Table 3.

Table 1 Performance indicators of P.O.42.5 portland cement

| Check items | Fineness (%) | Initial time (min) | Final time (min) | Loss on ignition (%) | Compressive strength (MPa) | Flexural strength (MPa) |
|-------------|--------------|--------------------|------------------|----------------------|----------------------------|------------------------|
| measured value | 1.2          | 133                | 286              | 1.02                 | 25.3                       | 50.6                   |

Table 2 Physical properties of soil

| Natural Moisture content (%) | liquid limit (%) | Plastic Limit (%) | optimum water content (%) | Compaction maximum Dry density (g/cm³) | Engineering classification of soil |
|------------------------------|------------------|-------------------|---------------------------|----------------------------------------|----------------------------------|
| 29.93                        | 33               | 27.75             | 23.18                     | 1.64                                   | silt                             |

Table 3 Chemical composition of high calcium fly ash

| composition | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | Na₂O |
|-------------|------|-------|-------|-----|-----|------|
| scope       | 54%  | 20%   | 4.3%  | 16.5% | 2.8% | 3.4% |

The prepared soil, cement, fly ash and chemical reagents are uniformly mixed according to a certain ratio, and are put into a test mold with a diameter of 39.1 mm and a height of 80 mm, and compacted in three layers, and placed in a standard culture box for culturing. After reaching the set age, the unconfined compressive strength of each set of test pieces was measured.

2.2 The design of test plan
In this test, the cement content is 15%, the high calcium fly ash content is 0, 5%, 10%, 15%, 20%, respectively. The unconfined compressive strength of the 3d, 7d, and 28d tests was tested, and the unconfined compressive strength value was the average compressive strength value of each of the three test pieces. (The amount of cement and high calcium fly ash is the percentage of soil sample.)

Fig 1. High calcium fly ash soil compressive strength
3. Analysis of test results

From Figure 1, the trend of strength change of high calcium fly ash cement soil under different ages can be seen: (1) The strength of high-calcium fly ash cement soil increases with age. This is mainly due to the small amount of cement clinker in the cement soil, and the primary hydration product of the early clinker minerals is also reduced, and the secondary hydration must be carried out after one hydration \(^6\). (2) The strength of high-calcium fly ash cement soil first increases and then decreases, and there is an optimal range of high-calcium fly ash: high calcium fly ash content is 15%-20%. When the content of high calcium fly ash is below 15%, the strength of cement soil shows a downward trend, but the decrease is not obvious. This is mainly due to the fact that the physical filling effect and morphological effect of high calcium fly ash are not obvious; When the content of high calcium fly ash is between 15% and 20%, the strength of cement soil increases rapidly because of the physical filling effect and morphological effect of high calcium fly ash. When the dosage is 20%, the high-calcium fly ash can better fill the pores inside the cement soil, so that the compactness of the cement soil is improved, and the strength of the cement soil is also improved \(^7\). Finally, when the content of high-calcium fly ash exceeds 20%, the strength of cement soil shows a significant decline. This is mainly because the strength of the cement soil is generated by the cement-soil aggregate structure. When the amount of high-calcium fly ash increases, the amount of cement and soil also decreases correspondingly, resulting in reduced strength.

4. Excitation test design and analysis of test results

4.1 Excitation test design

In order to effectively improve the early strength of cement soil and enable high-calcium fly ash to dissociate Ca\(^+\) with colloidal particles in the early stage, the strength excitation test of high-calcium fly ash cement soil was designed. Five chemical reagents of NaOH, Na\(_2\)SO\(_4\), NaHCO\(_3\), CaCl\(_2\), and Ca(OH)\(_2\) were added to the high-calcium fly ash cement soil. According to the results of the strength test, the optimal dosage of high calcium fly ash is 20%, and the unconfined compressive strength test is carried out for 7 days. The effects of these five chemical activators on the early strength formation of high calcium fly ash cement soil were studied. The five chemical activators dosages were 0.5%, 1.0%, 1.5%, and 2.0%, and the chemical agent dosage was the percentage of the sum of soil, cement, and high-calcium fly ash.

![Fig 2. early strength activators of high calcium fly ash cement soil](image)

Figure 2 is the variation of the effects of five chemical activators on the early strength of high calcium fly ash cement soil. It can be seen from the figure that five chemical activators can effectively improve the early strength of high-calcium fly ash cement soil, mainly due to the volcanic ash effect of cement soil in advance under five activators. The fly ash volcanic ash effect is produced by using alkali as an activator and sulfate as an activator to stimulate the activity of active SiO\(_2\) and Al\(_2\)O\(_3\) in high calcium fly ash to produce hydrated calcium silicate gel, hydrated calcium aluminate gel and hydrated calcium sulfoaluminate \(^6\). This reaction increases the strength of the high-calcium fly ash cement soil, but the degree of action of the five activators is different, which is related to the strength
When the dosage is 1.5%, the order of the strength of the 7d high-calcium fly ash cement soil by five chemical reagents is: NaOH ≈ Na₂SO₄ > NaHCO₃ > CaCl₂ > Ca(OH)₂. The curve is first increased and then decreased. There is an optimal range for the amount of activator: the amount is around 1% to 1.5%. The main reason for this phenomenon is that when the amount of the activator is small, the reaction cannot be fully carried out, and the potential activity of the high calcium fly ash cannot be fully excited; When the amount of the activator is too large, the concentration of OH⁻ is too high, and the reaction occurs rapidly, forming a protective film on the surface of the cement soil particles to prevent the reaction from proceeding, resulting in slow development of strength \[9\].

In addition, Ca(OH)₂ has a gentle tendency to stimulate the strength of 7d high calcium fly ash cement soil. This indicates that Ca(OH)₂ can hardly stimulate the strength of high-calcium fly ash cement soil, while in literature\[10\], Ca(OH)₂ can stimulate the early stage strength of low-calcium fly ash cement soil.

5. Early strength mechanism of high calcium fly ash cement soil

After adding a certain amount of high-calcium fly ash and activator to the cement soil, the early strength of the cement-soil material can be obviously improved. The early strength improvement of this cement soil material is mainly reflected in the following aspects:

(1)Aggregate structure and ion exchange of cement soil. The hydration of cement clinker produces C-S-H gel, C-A-H gel and Ca(OH)₂ crystals, which are filled in the soil and coagulated with the colloidal particles in the soil to form the agglomerate structure of the soil. At the same time, the surface of the colloidal particles in the soil with Na⁺ and K⁺ can dissociate Ca⁺ from Ca(OH)₂ in the cement soil to carry out the equivalent adsorption exchange, which is the main reason for the certain structural strength of the cement soil.

(2)Physical filling effect and morphological effect of high calcium fly ash. The physical filling effect and morphological effect of high calcium fly ash is a property of itself and a source of early stage strength of cemented soil. When high-calcium fly ash is added to the cement soil, the cement-soil particles are fully wetted by water and have a water film. The water film is a good lubricant, which is beneficial to the sliding of the cement soil agglomerate particles, which makes the cement soil agglomerate particles uniformly and stably dispersed, thereby improving the early stage strength of the cement soil. Schematic 3 is as follows.

![Fig. 3 A schematic diagram of high calcium fly ash acting on cement and soil pellets](image)

(3)High calcium fly ash volcanic ash effect. The volcanic ash effect is that, the cement clinker hydration product Ca(OH)₂ is an alkali activator. The gypsum is a sulfate activator and chemically reacts with the active SiO₂ and Al₂O₃ contained in the high calcium fly ash to form a hydrated calcium silicate gel and a hydrated calcium aluminate gel. The high-calcium fly ash is calcined at a high temperature for a long period of time, so that the surface of the high-calcium fly ash is covered with a thick outer shell, which requires the long-term action of the cement clinker hydration product Ca(OH)₂ and the outer shell. The thicker shell covering the high calcium fly ash is broken to promote the volcanic ash effect with the active SiO₂ and Al₂O₃. Therefore, the early strength development of fly ash cement soil is slow. In order to improve the early strength of cement soil, alkali activator and sulfate activator are added to the cement soil to cause the volcanic ash effect to occur in advance.
6. Conclusion

(1) The proper amount of high-calcium fly ash can be added to the cement soil to improve its early stage strength. The optimum dosage of high-calcium fly ash is 20%.

(2) The early release of Ca(OH)$_2$ from high-calcium fly ash requires a certain alkaline environment.

(3) Through the excitation test, when the amount of the five chemical activators is 1.5%, the order of the strength of the 7d high calcium fly ash cement soil is: NaOH≈Na$_2$SO$_4$>NaHCO$_3$>CaCl$_2$>Ca(OH)$_2$. There is an optimal range for the amount of activator: the dosage is 1% to 1.5%.

Acknowledgments

Fund project: natural special project in shaanxi province department of education (18JK1006)

Author introduction:
Dong Yuping (1985 -), female, kailu people in Inner Mongolia, a master's degree, lecturer, mainly engaged in the teaching of civil engineering and building new materials studied.

References:
[1] LEI Rui, FU Dong-sheng, LI Guofa etc. Research progress of fly ash comprehensive utilization[J]. clean coal technology, 2013,3 (19): 106-108.
[2] PANG Wen-tai, SHEN Xiang-dong. Effect of freeze-thaw cycle on mechanical properties of cement and soil[J]. Highway, 2012, 9 (9): 30-32.
[3] CUI Yong-cheng. research on compressive strength of fly ash cement soilin yinchuan based on orthogonal test[J]. journal of hubei university(natural science),2016.37 (1) :54-57.
[4] HE Wen-xiu,SHEN Xiang-dong. Mechanical Behavior of Glass Fiber and Fly Ash Soil-cement[J]. Journal of Highway and Transportation Research and Development.2012, 29 (3): 12-16.
[5] AN Peng-peng. LIU Wen-xiao, YANG You-hai, Experimental Research on the Factors Affecting the Strength of Saturated Loess Mixed with Cement and Fly Ash[J]. RAILWAY STANDARD DESIGN, 2014, 58(12):59-62.
[6] HUANG Li-juan. Orthogonal experimental studies on the influence of fly ash to The compressive strength of cement-soil [J] . JOURNAL OF HE NAN POLYTECHNIC UNIVERSITY (NATURALSCIENCE) , 2009, 28( 3) : 352 – 356 .
[7] DU Jin-sheng, SHEN Xiang-dong. Experimental study on the affect of different amount of fly ash on the strength of lightweight aggregate concrete[J]. Concrete, 2011,1: 95-97.
[8] PENG Xiao-qin. Civil engineering materials[M].ChongQing:Chongqing University Press, 2013.1.
[9] ZHEG Wen-zhong, ZOU Meng-nan,WANG Ying. Literature review of alkali-activated cementitious materials[J]. Journal of Building Structures2019,40 (1) : 28-39.
[10] TANG Qing-qing , ZHANG Li-juan, SUN Guo-wen, WANG Cai-hui. Early Activity of Triethanolamine-Calcium Hydroxide Activates toHigh Volume Fly Ash in Cement-Gel System[J]. BULLETIN OF THE CHINESE CER AMIC SOCIETY, 2018,37 (9) : 2737-2742.