

The Influence of Diatomite on the Strength and Microstructure of Portland Cement

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Abstract. To study the influence of the types and mixing amount of diatomite on the Portland cement, we prepared the cement specimen doped with the calcined first-grade, first-grade and second-grade diatomite, tested the 3d, 7d, 14d compressive strength, and studied and discussed phase, structure and morphology of diatomite in the binary system by the method of XRD, SEM. Experimental results show that with the addition of diatomite, the strength of cement paste increase; the optimal contents of calcined first-grade, first-grade and second-grade diatomite in Portland cement are 5%. Compared to the blank group, the strength of specimen can be increased by 54.6%, 15.4% and 10.2%, respectively; At the same time, the 7d microscopic hydration of different diatomite particles were analyzed through the experiment, and the shell of calcined diatomite particles were better hydrated than that of first-grade and second-grade diatomite particles. The results indicate that the diatomite can improve the strength of cement paste, the hydration of different diatomite particles can influence the growth of cement paste strength.

Keywords: Diatomite, Portland cement, Strength and microstructure

1 Introduction

Currently for the concrete, there are more researches on fly ash and Silicon ash, but less on diatomite. The volcanic ash activity of fly ash is low, the reaction rate of it is fairly slow, if replacing cement with fly ash, the development of the early strength of concrete will be rather slow. And the volcanic ash activity of silicon ash is high, which can improve the early strength of concrete, but the influence of Silicon ash on the growth of the post-strength of concrete is not obvious. Given the good properties of diatomite^[1], such as the unique structure in order arrangement, stable performance, acid resistance, solid particles, large pore volume, large specific surface area especially the large internal specific surface area and good volcanic ash activity^[2], diatomite is applied to the light wall materials, thermal insulation wall materials^[3], insulating bricks and other building materials abroad, and in recent years there are some researches of relative projects on diatomite in building materials at home, for example, Sun Qinghe^[4] et al developed the C60 high performance recycled concrete by using compound low content of highly active calcined diatomite and high content of fly ash admixtures technique, studied and discussed

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the modification effect and mechanism of calcined diatomite for the recycled concrete mechanics and the resistance of permeability and freezing ;Zhou zhongyi^[5] used calcined diatomite as the admixture for high performance concrete, verifying various performance indexes of the calcined diatomite as the admixture for high performance concrete was better than those of silica ash through the contrast experiment between them ;Zhang Guohui^[6] et al studied the pavement performance of diatomite modified asphalt concrete and so on. However, few scholars study on the microstructure of different diatomite particles in the diatomite - Portland cement binary system with different types of diatomite , thus this paper studies the influence of the types and content of diatomite on the strength and the microtopography of different diatomite particles in the Portland cement.

2 Experimental Raw Material, Test Methods and Mixture Ratio Designed

Raw Materials Cement: The ordinary Portland cement PO.42.5 made by Xiao Ye Tian cement plant in Dalian. Diatomite: Tianyuan catalyst co., LTD in Linjiang city, Jilin province. (The compositions for different types of the diatomite are shown in table 1). Water reducer: Naphthalene water reducer; Water: The ordinary tap water in Shenyang city.

TABLE 1 THE COMPOSITION OF DIFFERENT TYPES OF DIATOMITE

The types of diatomite	SiO ₂ %	Al ₂ O ₃ %	TFe %	CaO %	MgO%	Na %	Loss%
Calcined first-grade diatomite	93.04	2.83	0.92	0.35	0.18	0.17	0.26
First-grade diatomite	82.97	3.74	1.48	0.33	0.4	0.35	8.13
Second-grade diatomite	72.29	7	1.54	0.61	0.7	0.48	13.16

Test Methods and Mixture Ratio Designed

As shown in Table 2 , this test adjust the content of different types of diatomite in the ordinary Portland cement system with a water cement ratio of 0.42 and the fixed water reducing agent(naphthalene water reducing agent accounting for 0.2% of the cementing material) . First, putting 84 g of water and 0.4 g of water reducer in a pot according to the mixture ratio, adding the mixer of cement and diatomite to the mixing pot, start the net paste blender to stir slowly and quickly for 2 minutes respectively, put the mixed paste into a 20*20*20 mold, cured in standard curing box under the condition of constant temperature (20 °C), measure the compressive strength of cement paste specimen at the curing age of 3d、 7d、 14d, respectively. Second, take out a block in the center area of the specimen after the strength test, terminate its cement hydration after soaking in an absolute ethyl alcohol for 7 days, take out the test block at the curing age of 7 d to dry in a 60 °C drying oven, make the samples conduct XRD and SEM tests respectively, analyze the hydration of diatomite -Portland cement system and the hydration microstructure of diatomite particles.

TABLE 2 CEMENT PASTE COMPOSITION DESIGN

No.	The replacement rate of diatomite (%)	Diatomite (g)	Cement (g)	Water (g)	Water reducer (g)
O	0	0	200	84	0.4
G1	5	10	190	84	0.4
G2	10	20	180	84	0.4
G3	15	30	170	84	0.4

3 Test Results and Analysis

The Influence of the Diatomite Types on the Strength of Portland Cement.

Figure 1 shows the compressive strength of the paste specimen in diatomite - Portland cement system mixed with different types and contents of diatomite at the curing temperature of 20 °C.

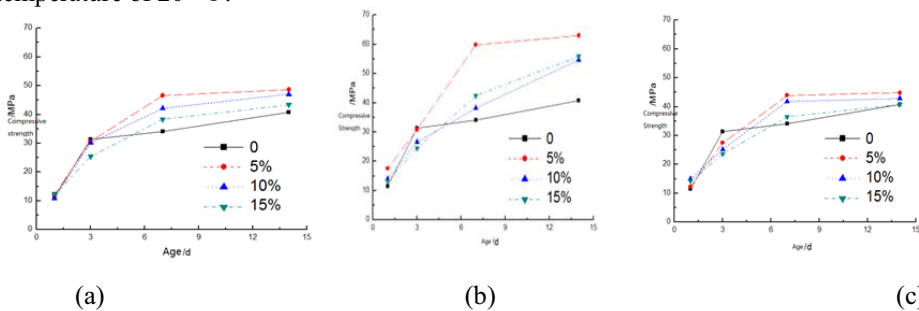


Fig 1 The compressive strength of the paste mixed with different types of diatomite

(a)The sample mixed with calcined the first-grade diatomite (b) The sample mixed with the first-grade diatomite (c) The sample mixed with the second-grade diatomite

From the (a) (b) (c) of Figure 1, at the age of 1~3d , the strength growth rates of cement paste blocks mixed with diatomite are virtually identical, the strength of the blank specimen (0%) and its growth rate are higher than that of the specimen with different mixing amounts, this is mainly because diatomite absorbed some water ,which affected the hydration of some cement particles, resulting in that the strength of cement paste specimen with different contents of diatomite were slightly below that of the blank specimen ;at the age of 3~14d, the strengths of cement paste specimen mixed with mixing amount of diatomite all were higher than that of the blank group, and the strengths of the specimen with the mixing amount of 5% all were higher than those of the specimen with the mixing amount of 10% and 15% , which shows the diatomite which was mixed to replace some cements can improve the strength of the cement paste specimen ,the $Ca(OH)_2$ was produced by the hydration of the SiO_2 and cement particles in the diatomite particles and SiO_2 generated C-S-H gel in the secondary hydration reaction to increase the compressive strength of the cement, the large mixing amount of diatomite will lead more diatomite particles that were not involved in the secondary hydration , which is unfavorable for the development of cement paste strength . at the age of 14d,the corresponding cement block strengths for

calcined first-grade ,the first-grade and second-grade of diatomite are 62.99MPa、47.02MPa、44.91MPa ,respectively, and compared with the blank sample strength (40.75MPa),the specimen strengths can increase 54.6%、15.4%、10.2%, respectively.

Comparing (a) with (b) in Figure 1 shows that, at the age of 3~14 d , with different mixing amounts the strength growth rates of the specimen mixed with calcined first-grade diatomite are higher than that of the specimen mixed with first-grade diatomite, the reason is that the calcined first-grade diatomite is more active than the first-grade diatomite, the calcined first-grade diatomite particles in the Portland cements is better hydrated than the first-grade diatomite particles, and can generate more C-S-H gel, which makes the diatomite particles and cement hydration products be lapped closely. Comparing (b) to (c) in Figure 1 shows that, there is a consistent tendency of the growth rate of cement specimen strength, with different mixing amounts the strength of the specimen mixed with first-grade diatomite is slightly higher than that of the specimen mixed with first-grade diatomite ,the Table 1 shows us that the compositions of diatomite and second-grade diatomite are nearly the same, except that the content of SiO₂ in the first-grade diatomite is higher than second-grade diatomite, in the first-grade diatomite particles there is more SiO₂ which react with Ca(OH)₂ in the process of hydration to generate C-S-H gel dense cement paste, which increases the strength of specimen.

The Effect of Different Types of Diatomite on the Hydration of Portland Cement

Figure 2 shows the 7d XRD analysis of the hydration of different types of diatomite with a content of 5% in Portland cement , A, B, C, D are the XRD curves for blank specimen, 5% calcined first-grade diatomite specimen,5% first-grade diatomite specimen,5% second-grade diatomite specimen ,respectively. The characteristic peak of C3S in the diagrams is at 2θ= 32.21 °, and the characteristic peak of CH at 2θ=18.08 ° and 34.14 °.

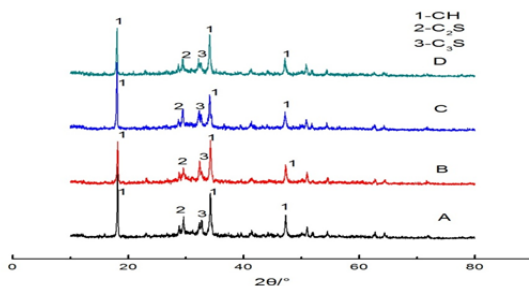


Fig 2 The 7 d XRD diagrams of diatomite - Portland cement hydration

(1: Calcium hydroxide - CH, 2: Dicalcium silicate - C₂S, 3: Tricalcium silicate - C₃S)

Figure 2 shows that, the crystalline substances in the cement paste mixed with diatomite mainly include the reactants (C₃S and C₂S) and the products(Ca(OH)₂), compared with the blank specimen , there is no change in phase component . The main specific diffractive peaks of C₃S in the specimen B is better than in the blank A, which shows the C₃S that take part in the hydration reaction in the specimen B is less than in the blank specimen A , this is because the diatomite particles absorb the water, then the water participating in the hydration reaction is decreased, and the hydration of C₃S in Portland cement early become slow . The main specific diffractive peaks of Ca(OH)₂ in the specimen C is weaker than in the specimen D, that is because the content of SiO₂ in the first-grade diatomite is higher than in the second-grade diatomite, and the secondary hydration reaction consumes more Ca(OH)₂.

The hydration morphology of different types of diatomite particles in the Portland cement

The SEM can analyze the hydration morphology of the diatomite particles in cement, observe the crystalline degree of diatomite particles, $\text{Ca}(\text{OH})_2$, hydrated calcium silicate (C-S-H) gel and other hydration products and the overlapping ratio of hydration microstructure.

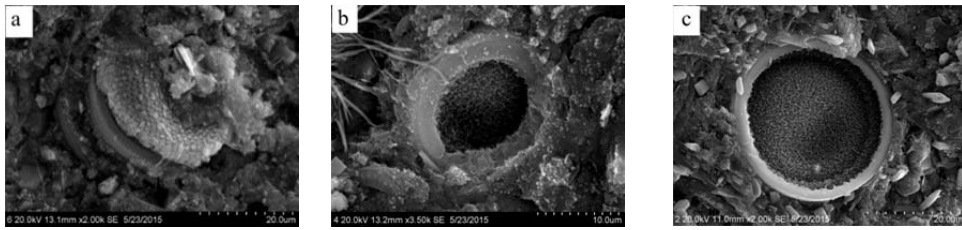


Fig 3. The 7d hydration morphology of different types of diatomite particles in Portland cement

(a): Calcined first-grade diatomite particles (b):First-grade diatomite particles (c):
Second-grade diatomite particles

Figure 3 shows that, different types of diatomite of 7 d in Portland cement all had the traces of hydration, but the degree of their hydrations is different: (a) the shell of calcined first-grade diatomite particles has completely disappeared, cement hydration products and diatomite particles are lapped closely, the first-grade and second-grade diatomite particles in (b) and (c) does not completely disappear. The degree of the disappearance of the diatomite particles shell to a certain extent reflects the hydration degree of the particles, the higher the degree of hydration, the better the diatomite particles and cement hydration products is lapped, the higher the strength of Portland cement. The calcined first-grade diatomite particles in (a) were hydrated better than the first-grade and second-grade diatomite particles in (b) and (c), because the SiO_2 in calcined diatomite is more active, has more broken Si-O keys, can better to produce secondary hydration reaction with the $\text{Ca}(\text{OH})_2$ generated by cement hydration reactants to generate C-S-H gel, which make the diatomite particles and cement be lapped closely, and increase the cement paste strength, so the strength of cement specimen mixed with the calcined first-grade diatomite is higher than that of the cement paste mixed with first-grade and second-grade diatomite.

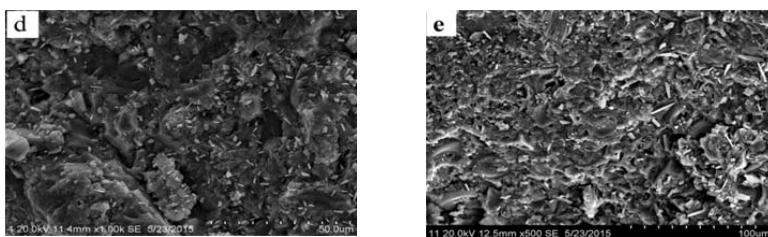


Fig 4 Blank specimen contrast with the 7d hydration morphology of the Portland cement mixed with 5% calcined first-grade diatomite particles

(d) Blank specimen (e) The specimen mixed with 5% calcined first-grade diatomite

Figure 4 shows that, the hydration products of Portland cement in (d) blank specimen are not lapped closely so as to cause many gaps, and hydration products of (e) Portland cement mixed with calcined first-grade diatomite were lapped closely, for which there are three reasons: First, the diatomite particles with filling effects can fill the gap between the cement particles and cement hydration products; Second, the mixed diatomite absorbing water resulted in less free water in cement paste, and the cement paste become more dense; Third, the SiO_2 in diatomite particles reacted with the $\text{Ca}(\text{OH})_2$ produced by the hydration

of cement to generate the hydrated calcium silicate gel, the particles and the cement hydration products were lapped closely.

4 Conclusions

(1) Adding diatomite improved the strength of cement paste, the strength of the cement paste mixed with the first-grade diatomite is higher than that of the cement paste mixed with first-grade or second-grade diatomite; the optimal dosage of Calcined first-grade diatomite, first-grade diatomite and second-grade diatomite all are 5%; compared with the blank specimen, the compressive strength of cement paste specimen has increased by 54.6%, 15.4% and 15.4% respectively.

(2) The crystalline substance in the cement paste mixed with diatomite, like that in the blank specimen, includes the reactant C_3S and C_2S and the product $Ca(OH)_2$; the water absorption of diatomite reduces the early hydration rate of C_3S in the cement, the diatomite particles produce secondary hydration reaction, the content of 7d $Ca(OH)_2$ in the cement paste is reduced.

(3) Calcined first-grade diatomite particles were better hydrated than first-grade and second-grade diatomite particles, with the diatomite mixing, the microstructure of cement paste become more compact, the hydration products are increased, and the gaps within the system are reduced.

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