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Preparation and Performance of Geopolymers

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Abstract: The influence of each factor on the reaction of geopolymers material was investigated by using the orthogonal experimental design method, which got the optimal condition of reaction. Based on this results the performances of geopolymers were investigated. The results are as follows: (1) The effect of each factor on the compressive strength of geopolymers was different; (2) For paste the optimal condition of reaction is that the modulus and the concentration of sodium silicate solution are 1.2 and 40%, the calcined temperature and calcined time of kaolin are 800 ℃ and 2 h, and the liquid-solid ratio is 1.25; (3) When the pH value of solution is higher than 1, the compressive strength of Geopolymers will not decrease as that in the water; (4) As the calcined temperature of samples were lower than 700 ℃ the heat-resistant of geopolymers was good;(5) Geopolymers is unlikely to react with the active aggregate.

Key words: geopolymers; cross experimental design method; optimal condition; performance

1 Introduction

Portland cement is an indispensable building material, but the production of Portland cement consumed a lot of regenerative resource. And the widely usage of cement inevitably have resulted in environmental pollution and overage consumption of energy and resource. Therefore, preparation of cementitious materials with less energy consumption and less waste generation has aroused worldwide concerns and interests[1]. Geopolymers is a kind of material that can be synthesized through the reaction between sodium silicate solution and metakaolin at room temperature in which metakaolin shoule be calcined at 500-900 ℃ in advance. French professor Davidovits found there existed three-dimensional silicate-aluminum product in the ancient buildings which has the same structure as zeolite, and then he designated this product as "geopolymers"[2-4].

There are a lot of reports throughout the world which mainly concern the influence of a single factor on the performance of geopolymers[5-8]. Using the orthogonal experimental design method, aiming at five factors and four levels, the influence of several factors, including the liquid-solid ratio of the paste, the modulus and concentration of sodium silicate solution, the calcined parameters for metakaolin such as temperature and the calcined duration, on the compressive strength of geopolymers material is investigated in this paper. On the basis of this experiment, a variety of performances of the samples prepared with the optimal parameters were determined.

2 Experimental

2.1 Raw materials

(1) Kaolin: The chemical composition of kaolin is shown in Table 1. Kaolin was calcined at 4 different temperatures (600,700,800,900 ℃) for 1,2,3,6 h.

(2) Sodium Silicate solution: the modulus and concentration of the solution is 1.8 and 42.5% respectively, where the modulus denotes the mole ratio of SiO_2 to Na_2O, and the concentration denotes the mass percentage of total Na_2O and SiO_2 in the solution. The original sodium silicate solution was modified to specific parameters to be used in experiment by mixing appropriate NaOH (Analytic reagent) and water.

Table 1 Chemical composition of kaolin /mass%

SiO_2	Al_2O_3	Fe_2O_3	MaO	K_2O	Na_2O	CaO	LOI
47.90	36.17	0.51	0.64	0.15	0.13	0.05	13.73

2.2 Methods

(1) Compressive strength

Metakaolin and sodium silicate solution were mixed in a beater according to the specific prescription and then the pastes were poured into the 20×20×20(mm) moulds.

The paste and standard sand were mixed

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according to Chinese Standard GB175-1999. But the volume ratio of paste to ISO standard sand was fixed at 0.43.

All samples were demoulded after 1 d and then cured at 20 ℃, relative humidity 90% for 3 d, 7 d, 28 d, and tested the compressive strengths.

(2) Acid-resistant performance

Mixed the paste and sand in accordance with Chinese Standard GB2420-81. The samples were cured at 20 ℃, relative humidity 90% for 1 d and demoulded. And then the samples were cured in 50 ℃ for 7 days. After that the samples were soaked in different acid solution for 28 d.

(3) Heat-resistant performance

Mixed materials in proportional and the mortars were cured at 20 ℃, relative humidity 90% for 28 days. Then the samples were calcined at different temperatures (300-1 000 ℃) for 2 hours.

(4) Alkali-aggregate reaction

The samples were prepared according to GB/T14685-2001. Then the mortars were cured at 20 ℃, relative humidity 90% for 1 day and demouleded to test the initial lengths of the mortars. Then soaked the samples in 1 mol/L NaOH at 80 ℃ for 14 days and tested expansion ratio. If the expandable ratio of mortar prepared by Portland cement is higher than 0.20%, the aggregate is active.

3 Results and Discussion

3.1 Orthogonal experiment

3.1.1 Choice of factors and levels

Geopolymer is the reaction production of sodium silicate solution and metakaolin, so the parameters of these two raw materials will influence the reaction. From Fig.1 it can know that the kaolinite used in this experiment turn to metakaolinite between 492.4 ℃ and 974.6 ℃, so the calcined temperature of kaolin are 600 ℃, 700 ℃, 800 ℃, and 900 ℃. The calcined time of kaolin longer than 6 h has no more contribution to the compressive strength of geopolymer (shown in Table 2), so the calcined time of kaolin are 1 h, 2 h, 3 h, and 6h. The results in Table 3 show that the optimal modulus of sodium silicate solution is 1.2-1.4, then the modulus of sodium silicate solution are chosen as 1.0-1.6. When the concentration of sodium silicate solution is 45%, the paste prepared with it is too ropy to mould, so the concentration of sodium silicate solution are 30%-45%. The liquid-solid ratio is also an important factor which markedly influences the fluidity of the paste, and it needs to satisfy the fluidity to mould. When the concentration of solution is 45% and the liquid-solid ratio is lower than 1.25, the paste is hard to mould. When the concentration of solution is 30% and the ratio is higher than 2.00, the solid powder separates the solution. So the liquid-solid ratio is 1.25-2.00.

3.1.2 Design and results of orthogonal experiment

$L_{32}(4^9)$ orthogonal experimental design table was used. The five factors were the modulus (*m*) and the concentration (*c*) of sodium silicate solution, the calcined temperature (*t*) and the calcined time of kaolin (*d*), and the liquid-solid ratio (*r*).The factors were

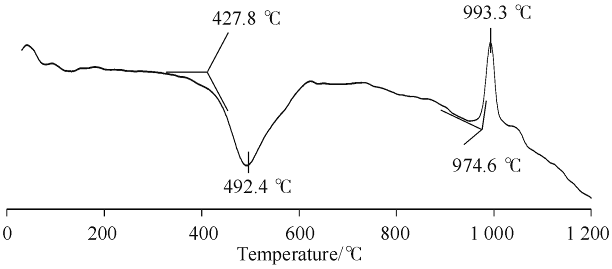

Fig.1 Curve of thermal analysis of kaolinite

Table 2 Compressive strength of geopolymer paste* prepared by metakaolin calcined at 600 ℃

Calcined time of kaolin /h	1	2	3	6	9	12
3 d compressive strength/MPa	10.65	28.71	38.36	39.87	37.10	37.10

*the proportions of paste are as follows: the modulus and concentration of sodium silicate solution is 1.2 and 40% respectively, and the liquid-solid ratio is 1.50.

Table 3 Compressive strength(3d) of geopolymers paste * prepared by different modulus of sodium silicate solution

Modulus of sodium silicate solution	1.0	1.2	1.3	1.4	1.5	1.6	1.8
3 d compressive strength/MPa	14.4	26.71	24.72	23.03	19.45	14.53	5.09

*the proportions of paste are as followings: the concentration of sodium silicate solution is 42.5%, the liquid-solid ratio is 1.50, and the metakaolin was calcined at 600 ℃ for 2 h.

Table 4 The relationship between modulus, concentration and viscosity of sodium silicate solution at 20 ℃

Modulus	1.0				1.2				1.4				1.6			
Concentration /%	30	35	40	45	30	35	40	45	30	35	40	45	30	35	40	45
Viscosity /$\times 10^{-3}$Pa•s	21.5	74.0	120	1 250	17.5	49.5	130	1 950	13.0	32.0	90.0	590	9.0	33.0	60.0	62.0

arranged in the row one to row five of the table as *m, c, t, d*, and *r*.

The analyses of the experimental results were as follows:

(1)The smaller the modulus of sodium silicate solution, the higher the compressive strength of geopolymers. This is because the alkalinity of sodium silicate solution is increased when the modulus of it is decreased, and then the activation of metakaolinite is improved.

(2)The influence of the concentration of sodium silicate solution on the 3 d, 7 d compressive strength is very significant. The higher the concentration, the higher the compressive strength of geopolymers. When the concentration achieves 45%, the viscosity of sodium silicate (shown in Table 4) is too large to interfere with the process of reaction. The optimal concentration of the sodium silicate solution is 40%.

(3)The influence of the calcined temperature of kaolin on the compressive strength is significant. From Fig.1 the kaolin used in this experiment is decomposed at 492.4 ℃ and begins to transit to γ-Al_2O_3 crystal at 974.6 ℃. It can be extrapolated that the appropriate calcined temperature of kaolin for the highest reactivity should be between the two characteristic temperatures. The optimal calcined temperature of kaolin is 800 ℃ from the analysis of the cross experiment results.

(4)The influence of the calcined time of kaolin on the compressive strength is also significant. If the calcined time is too short the hydroxide would have no time to escape. When the calcined time is too long, the kaolin would transit to spinel with small crystal degree. At these two situations, the reactivity of metakaolinite would be decreased, and the compressive strength of geopolymers would be decreased as well.

(5)The smaller the liquid-solid ratio, the higher the compressive strength of geopolymers. This can be explained that with the smaller liquid-solid ratio, the less space of the pores is formed in the system. The reaction production can be filled in the pores and then densify the sample.

Based on the cross experiment results, the optimal parameters to prepare the geopolymers are as followings: the modulus and the concentration of sodium silicate solution are 1.2 and 40%, respectively, the calcined temperature and calcined time of kaolin are 800 ℃ and 2 h, and the liquid-solid ratio is 1.25.

3.2 Compressive strength of geopolymers mortar

The orthogonal experiment only checked the influence of each single factor on the compressive strength of geopolymers, but the alternant influence of each factor didn't be examined. For the calcined temperature and calcined time of kaolin mainly influence the activity of metakaolin, the influence of calcined temperature and calcined time of kaolin would be trifle under the condition that the metakaolin has high activity. We designed the follow mortar experiment for the sake of validating the results of the cross experiment and examining the alternant influence of the modulus and the concentration of sodium silicate solution.

Based on the experimental results, the mortar specimen of geopolymers were prepared with the metakaolin calcined at 800 ℃ for 2 h. But the liquid-solid ratio was 1.50 for the needs of fluidity. The compressive strength results were shown in Table 5. The influence of sodium silicate solution on the compressive strength of geopolymers mortars is consistent with that of the experimental results. But the alternant influence of the modulus and the concentration of sodium silicate solution on the compressive strength is more than that of each single factor. In fact the alternant influence affects the alkalinity of the solution under the same conditions. That is to say the higher the alkalinity of sodium silicate solution, the higher the compressive strength of geopolymers.

3.3 Acid-resistant performanc of geopolymers

The results of acid resistant performance of geopolymers were shown in Table 6.

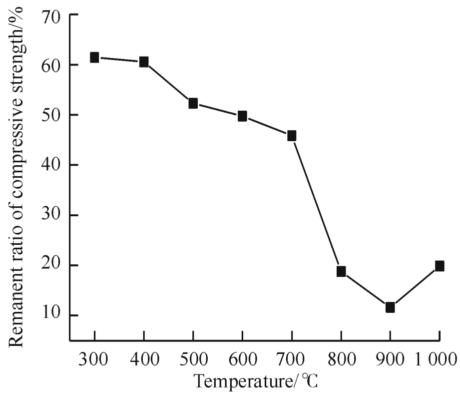

Fig.2 Influence of temperature on the compressive strength

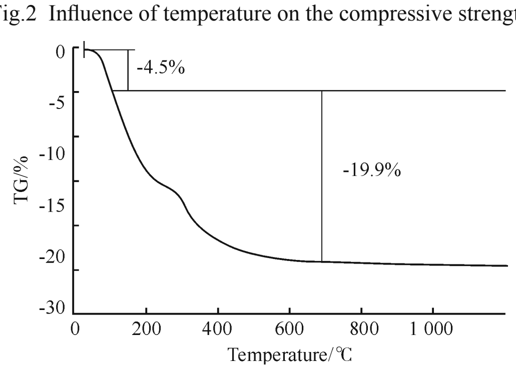

Fig.3 The TG curve of geopolymers

Table 5 Compressive strengths of geopolymers mortars

The parameter of geopolymers	Compressive strength /MPa		
	3 d	7 d	28 d
Sodium silicate solution: 1.2, 40%	44.83	61.02	65.68
Sodium silicate solution: 1.2, 30%	28.48	34.42	39.73
Sodium silicate solution: 1.6, 40%	33.88	55.36	57.30
Sodium silicate solution: 1.6, 30%	5.73	12.66	23.80

Table 6 Acid-resistant property of geopolymers in different kinds of acid

Varieties of the acid	HCl	HNO_3	H_2SO_4	pH=1
Concentration of the solution(mol • L^{-1})	Compressive strength remanent ratio of geopolymers /%			
0.5	83.5	70.7	53.9	
2	43.0	37.9	32.1	101.3
6	41.8	27.8	-	

Note: "-"means the sample was eroded.

Table 7 Remanent ratio of the compressive strength of geopolymers after calcined at different temperatures

Temperature /℃	300	400	500	600	700	800	900	1 000
Remanent ratio of compressive strength/%	61.42	60.55	52.28	49.75	45.84	18.80	11.64	19.87

Table 8 The expandable ratio of different materials

Kind of materials	Geopolymers	Alkali-slag	Cement 1*	Cement 2*
Expansive ratio / %	0.0399	0.0848	0.2440	0.2592

*cement 1 and cement 2 are Portland cement.

Table 9 The Na^+ leaching of geopolymers and alkali-slag at different age

Kind of materials	Na^+ leaching amount/mol				Na^+ leaching ratio /%			
	3 d	7 d	28 d	90 d	3 d	7 d	28 d	90 d
Geopolymers	0.0134	0.0110	0.0091	0.0095	16.46	13.47	11.19	11.60
Alkali-Slag	0.0359	0.0316	0.0303	0.0259	42.92	37.78	36.18	30.90

When the geopolymers mortars were soaked in the pH=1 acid solution for 28 d, the compressive strength of geopolymers kept the same as that in the water. When the samples were soaked in the acid solutions whose concentrations were higher than 0.5 mol/L, the compressive strengths of geopolymers were decreased. The sample was suffered with different erosion degrees in different acid solutions.

The reaction production of geopolymers is a kind of three-dimensional structure in which the tetrahedral SiO_4 and AlO_4 units are polycondensed with the alkaline ions balancing the charge[9]. It is mainly the amorphous analogue of zeolite and feldspar. Although most of alkalis are fixed into the three-dimensional structure, some alkali can remain in soluble form. This free alkali is easily dissolved, which generates an increase in the porosity of the specimen and consequently a decrease of its strength[10]. When the pH value of acid solution is 1, the free alkali can balance the H^-, the compressive strength will not decrease. But when the concentration of H^- is higher, many free alkalis react with the H^- and cause the decrease of strength. And because the concentration of H^+ in H_2SO_4 solution is twice as much as that of the other acid solutions at the same molar concentration, the compressive strengths is much more decreased in the H_2SO_4 solution than that in other acid solutions.

3.4 Heat-resistant performance of geopolymers

From Table 7, it can be observed that when the calcined temperature of mortars is lower than 700 ℃ the remanent ratios of compressive strengths of geopolymers are higher than 45%; when the temperature is raised to 800 ℃ and above, the remanent ratio of the compressive strength is sharply decreased to 18.8% and less; this remanent ratio is increased a little at 1 000 ℃.

Fig.3 shows the TG curve of the geopolymers sample. The sample weight is continuously decreased until about 700 ℃ which is attributed to the lost water in the geopolymers. When the samples were calcined at 300-700 ℃, the structure of geopolymers became looser along with the lost water, so the compressive strength of geopolymers was decreased step by step. When the temperature is raised to 700 ℃ and above, the structure of the reaction production would be destroyed and resulted in the sharply decrease of compressive strength. When the samples were calcined at 1 000 ℃, the samples may be sintered to induce the little increase of compressive strength.

3.5 Alkali-aggregate reaction

From the results (Table 8), it shows that the expansive ratios of the both cements are larger than 0.2%, indicating that the aggregate is active. The expansive ratios of geopolymers and alkali activated slag are lower than 0.1%, especially the expansive ratio of geopolymers is only half of that of alkali activated slag. It may be said that the probability of alkali-aggregate reaction occurred in geopolymers is much lower than that in alkali activated slag.

The three necessary conditions of alkali-aggregate reaction are a certain concentration of available alkali, the active aggregate, and a certain humidity. If the concentration of available alkali is much lower than the certain concentration (0.76%), no deleterious expansion occurs.

From Table 9 it can know that the Na^+ leaching of geopolymers is lower than that of alkali-slag. Different kinds of dissociative ions in the hole and the ions can hydrolyze OH^-. The OH^- will react with the active aggregate. The more Na^+ leaching amount the more hydrolyzed OH^- to react with active aggregate. So the alkali-slag has more expandable ratio than geopolymers.

4 Conclusions

a) The effect of each factor on the compressive strength of geopolymers was different.

b) The optimal parameters to prepare the geopolymers paste are as followings: the modulus and the concentration of sodium silicate solution are 1.2 and 40% respectively, the calcined temperature and calcined time of kaolin are 800 ℃ and 2 h, and the liquid-solid ratio is 1.25.

c) When the pH value of solution is higher than 1, the compressive strength of Geopolymers will not decrease as that in the water.

d) As the calcined temperature of samples was lower than 700 ℃ the heat-resistant of geopolymers was good.

e) Geopolymers was unlikely to react with the active aggregate.

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