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EFFECT OF RETARDER ON REACTION PROCESS OF METAKAOLIN-SLAG-BASED GEOPOLYMER

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ABSTRACT

Metakaolin-slag-based geopolymer is a type of green cementitious material. In order to solve the engineering problem that the geopolymeric paste sets fast at high temperature, a kind of retarder-BCH has been developed. The setting time of the pastes incorporated with different contents of BCH are measured. The effects of BCH on geopolymerization process is researched by analyzing the heat evolution of alkali-activation reaction, the chemically combined water content and the microstructure of the pastes. Results indicate that the optimum retarding dosage of BCH is 5.0%. The hydration rate and the exothermicity rate of geopolymeric paste (20 ℃) are reduced. The initial setting time of the paste at 80 ℃ extends for 17.3 times than the pastes without BCH. Alkali-activation reaction at 20 ℃ has later and lower exothermic peak than reaction without BCH. The reaction at 80 ℃ undergoes a period of 4~6 h and is longer than that without BCH (0.25~1.0 h). The content of chemically combined water of reaction product and reaction rate reduce apparently before geopolymer solidifies totally. The main reason that BCH has an effective retarding influence on geopolymerization, as revealed by SEM and EDS is that BCH participated in the reaction and produced precipitation adsorption on the surface of reacted particles.

Key words: *Geopolymer, Reaction Process, Geopolymeration, Retarder, Metakaolin, Slag*

1. INTRODUCTION

Geopolymer, a type of green cementitious material, is formed by the alkaline activation of aluminosilicate raw materials (metakaolin, slag etc.). Geopolymerization consists of dissolution, polymerization, reorganization and hardening [1]-[4]. After hardening the materials have excellent compressive strength, compactness, durability and anticorrosion [5]-[9]. The less CO_2 emission is another important advantage for geopolymer compared with ordinary portland cement (OPC). In recent years geopolymer has been studied extensively [10]-[14].

Metakaolin-slag-based geopolymer derived from metakaolin and slag which are both highly active and hardens fast when they are alkali-activated with alkaline activator, especially at high temperature [15]-[19]. Many researchers have studied the reaction and retarding methods of alkali activation about metakaolin and slag [20]-[21]. Research on setting control at high temperature of metakaolin-slag-based geopolymer remains a new topic.

Geopolymerization is totally different from the hydration process of OPC, and the retarders for OPC are usually useless. This research has developed a retarder, named of BCH. The experiments are aimed to study the retarding efficiency and mechanism by testing the heat evolution process of alkali activation, chemically combined process of reaction product, and structure/morphology.

2. EXPERIMENTAL

Metakaolin was obtained from Suzhou, China, and the granule surface area is 750 m^2/kg. Slag was obtained from Nanjing, China, and the granule surface area is 410 m^2/kg. The main chemical compositions of the two raw materials are presented in Table 1. The alkaline activators used in this study were produced from the mixture of sodium hydroxide in flake form (NaOH with 98% purity) and sodium silicate solution ($w(Na_2O)=8.10\%$, $w(SiO_2)=26.85\%$, $w(H_2O)=65.05\%$). Sodium hydroxide and water were mixed into sodium silicate solution to adjust the molar ratio of SiO_2 to Na_2O of 2.0 and water content of 70%. The activator was prepared at least 24 h prior to use. BCH retarder, is self-made compound by reaction of organic dibasic acid and some alkali metal salt.

The paste of geopolymer contains 60% metakaolin and 40% slag (mass ratio), and the liquid-solid ratio of the system is 0.89 ml/g. The setting time of the paste was measured at 80℃.

In order to test the heat release of the pastes, they were put in STA449C preheating system at 20 ℃, and then the heat release of the system was recorded. The hardened products were dried and coated with gold to analyze the microstructure and the composition by using JSM-5900 and EDS. The samples were immerged into ethanol and were kept after filtering and drying. Then the samples were weighed for 1-2g through crucible with constant weight and calcinated for 30 minutes at air condition at 950 ℃. The difference in weights was used to calculate the chemically combined water content.

Table 1 Main Composition (Mass Fraction, %) Of Metakaolin And Slag

Oxide	Metakaolin	Slag
Al_2O_3	44.03	19.84
SiO_2	52.20	36.86
CaO	0.31	31.75
K_2O	0.69	0.53
Na_2O	0.15	0.37
Fe_2O_3	0.65	0.80
MgO	0.27	8.53

3. RESULTS AND DISCUSSION

3.1 Effects Of BCH Dosage On Setting Time Of Geopolymer Pastes

Effects of BCH dosage on setting time of geopolymeric pastes cured at 80 ℃ are shown in Table 2. For the paste without BCH, the initial setting time and final setting time are 18 minutes and 26 minutes, respectively. The setting time increases as the content of BCH is increased. When the content of BCH is 5.0%, the retarding effect is the best. The initial setting time and finial setting time are 329 min and 342 min respectively, and they are prolonged to 17.3 times and 12.2 times separately than the neat paste. Therefore, 5.0% is an optimum dosage for the paste in this research. More than 5.0% BCH will shorten the setting time than 5.0% BCH does.

Table 2 Effects Of BCH Dosage On Setting Time Of Geopolymer Pastes (80 ℃)

Addition / %	Setting time / min		Addition / %	Setting time / min	
	initial time	final time		initial time	final time
0	18	26	5.0	329	342
1.0	72	106	6.0	318	335
2.0	106	147	7.0	263	298
3.0	162	211	8.0	253	296
4.0	276	329	9.0	247	292

3.2 Retarding Mechanism Of BCH

3.2.1 Heat evolution of geopolymerization

Calorimetry is an effective method of analyzing the reaction process of cementitious materials. Geopolymerization is a complex physical/chemical process, and a great deal of chemical reaction heat is released during the reaction process for metakaolin or slag systems. Then according to the analysis of heat evolution the reaction process and reaction rate could be characterized [22]. This experiment tests the reaction heat through STA449C, and collects data with changes of different alkali activation systems. Putting samples in instrument can disrupt testing environment, and affect stability of data at initial stage. Considering that if the reaction rate is too fast at high temperature, the date are not precise, since this experiment was performed at 20 ℃.

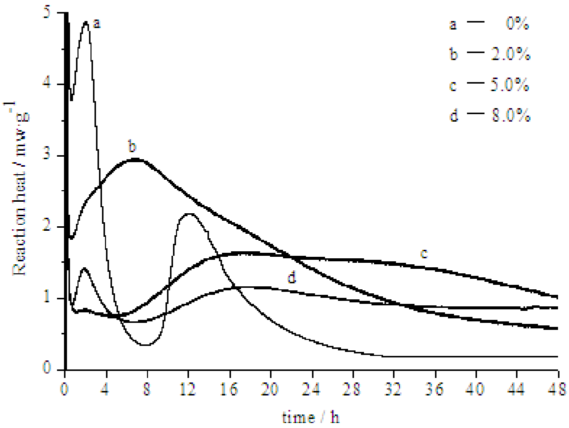


Fig.1 Effects Of Retarder Dosage On Heat Evolution Of Different Alkali Activation Systems

Effects of retarder dosage on heat evolution of different alkali activation system are presented in Fig.1. The first exothermic peak of the neat paste at 1.97 h. The second exothermic peak appears at 11.96 h (V=2.18 mW/g). Due to that heat release rate decreases sharply until to 25.0 h, BCH dosage could reduce heat release rate. When the dosage is 2.0%, there is a larger exothermic peak and this heat release rate gets to maximum at 6.7 h (V=2.94 mW/g). It should be due to the overlap of exothermic peaks from dissolution and alkaline activation. When the dosage of BCH is 5%, the exothermic peak intensity of the system decreases obviously. But the retarding effect is obvious. There is still heat release in the system at 48 h, and the intensity of the peak is higher than the neat paste. When the BCH dosage is 8.0%, an exothermic peak appears at 1.8 h, and the peak is smaller. The reason for this phenomenon may be that BCH reacts with other iron in this system, and the condensation and hardening are accelerated.

Effects of retarder dosage on metakaolin- and slag-based geopolymer are presented in Fig.2. When the dosage is 5.0%, reaction rate decreases obviously. Time of congealment is prolonged, and the alkali-activation is restrained.

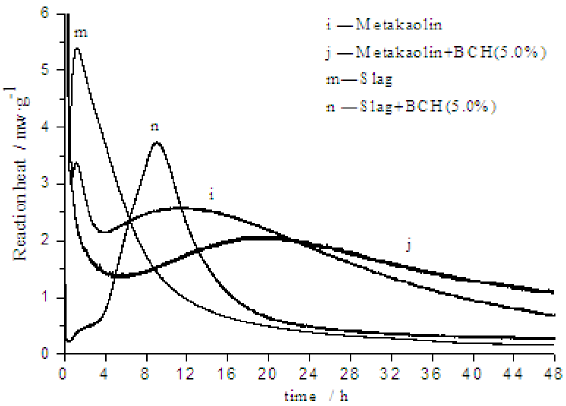


Fig.2 Effects Of Retarder Dosage On Metakaolin- And Slag-Based Geopolymers

When BCH is added into the system contained metakaolin and slag, the exothermic peaks appear later than the neat paste. When the dosage is 5.0%, the strongest exothermic peak of alkali-activation of slag appears at 9.02 h. And the strongest peak of alkali-activation of metakaolin appears at 20.74 h. Obviously, BCH has the function of delaying the reaction rate of alkali-activation of metakaolin and slag.

3.2.2 Chemically combined water of geopolymer

Water exists in ways of chemically combined water and non-chemically combined water in cementitious materials [23]. The chemically combined water means that the water connects with other elements by chemical bonds and hydrogen bonds. The bonding strength is high and the water can exist stably in hydration product of cementitious materials. Testing chemically combined water is a main method of analyzing hydration process, hydration degree and hydration rate of cementitious materials. And the content of chemically combined water increases with hydration degree increasing.

Geopolymer belongs to alkali-activated cementitious materials, and geopolymerization accompanies with a great deal of hydration reactions. Therefore, this study analyzes the effect of BCH on geopolymerization by testing chemically combined water content of reaction product and this will reveal some information about reaction extent. The effects of retarder BCH on the content of chemically combined water during alkali-activation at 80 ℃ is presented in Fig.3.

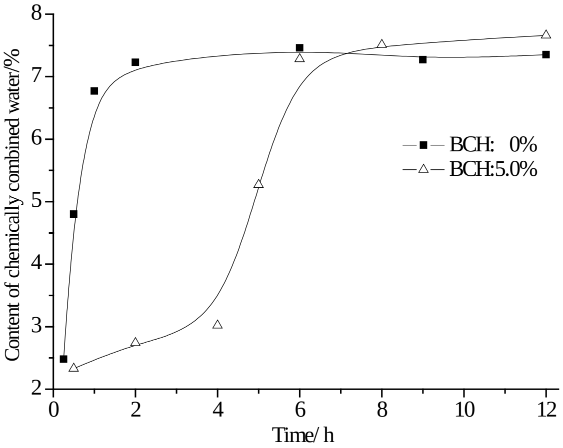


Fig.3 Effects Of Retard BCH On The Content Of Chemically Bonded Water During Alkali Activation

It is observed the dosage of BCH (5.0%) has little effect on content of chemically combined water of reaction products in later stage（>12 h). However, there is a big difference in the contents of chemically combined water at early stage. The content of chemically combined water of the neat paste decreases sharply at 0.25~1 h, and after 2 h the content of chemically combined water does not changes too much. So geopolymerization mainly occurs during 0.25~1 h, and basically finished within 2 h. When dosage is 5.0%, the change of content of chemically combined water is smaller in 0.5~4 h, but content increases fast in 4~6.

3.2.3 Morphology of geopolymer pastes

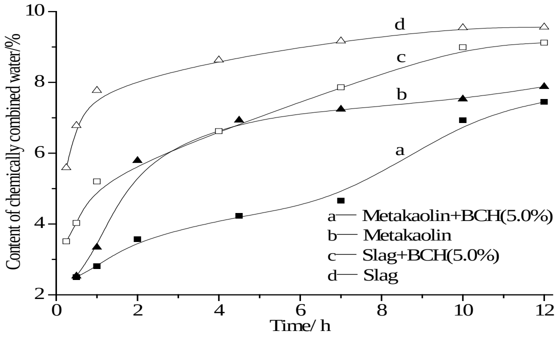
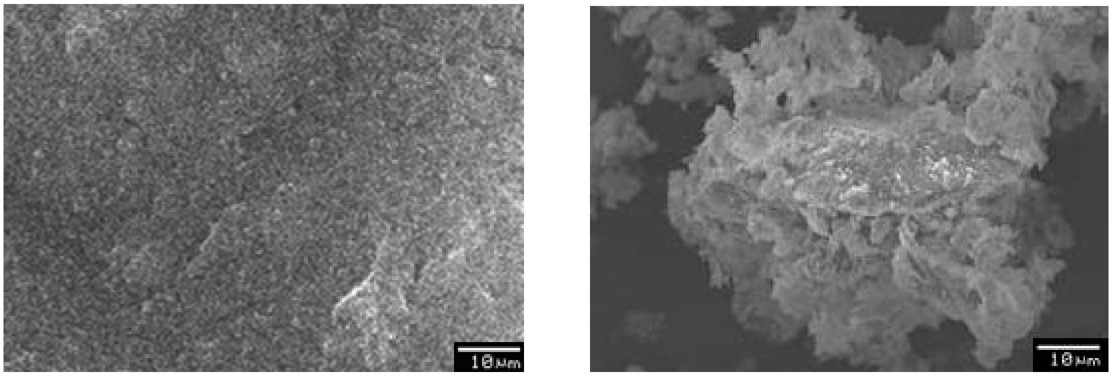


Fig.4 Effects Of Retard BCH On The Content Of Chemically Bonded Water During Alkali Activation Of Metakaolin And Slag

Effects of retarder BCH (5.0%) on the content of chemically combined water during alkali-activation of metakaolin and slag is presented in Fig.4. After alkali-activation reaction content of chemically combined water of paste with pure metakaolin is lower. When 5.0% of BCH is mixed with pure metakaolin, in the same reaction time, the content of chemically combined water is lower than geopolymer derived from metakaolin without BCH. When slag reacts with sodium silicate solution, content of chemically combined water at the initial stage (0~0.25 h) is higher, and the content increases significantly during 0.25~1 h. The reaction rate of alkali-activation with slag is faster than alkali-activated metakaolin. Adding BCH into the system, content of chemically combined water in initial stage decreases sharply (content is 3.51% at 2.5 h), and content of chemically combined water is lower than the system of slag without BCH during the same reaction time (content is 5.20% at 1 h). Therefore, the addition of BCH could decreases reaction rate of slag.



(A) Without BCH *(B) With 5.0% BCH*

Fig.5 SEM Micromorphology Of The Pastes (80 ℃×1 H)

The SEM micromorphology of the pastes reacted for 1 h at 80 ℃ is presented in Fig.5. The neat paste of geopolymer reacts fast at 80℃, and solidifies to continuous compact hardened specimen. When 5.0% BCH is added into the system, reaction rate of the raw material is reduced obviously. Reaction product at 1 h exists in the granular form, and there is coherent substance on its surface.

SEM micrograph and EDS spectra of the initially formed neat geopolymer (without BCH) and geopolymer with 5.0% BCH are presented in Fig.6 and Fig.7. In Fig.6, the image shows that the sample is formed with irregular particles of raw materials. By analyzing region A and B with EDS, this experiment can show that main elements in region A are Si, Al and Ca. Main elements in region B are Si and Al. Content of Ca in region A is higher than region B. Therefore particles in region A are particles of slag, and particles in region B are particles of metakaolin. Fig.7 shows the geopolymeric paste with 5.0% BCH, and SEM picture shows that there is a paste-like substances adhering on surface of the sample. By analyzing region C with EDS, except for Si, Al and Ca, some Me (4.88%) is found, indicating that Me^{n+} from BCH adheres on the surface of particles.

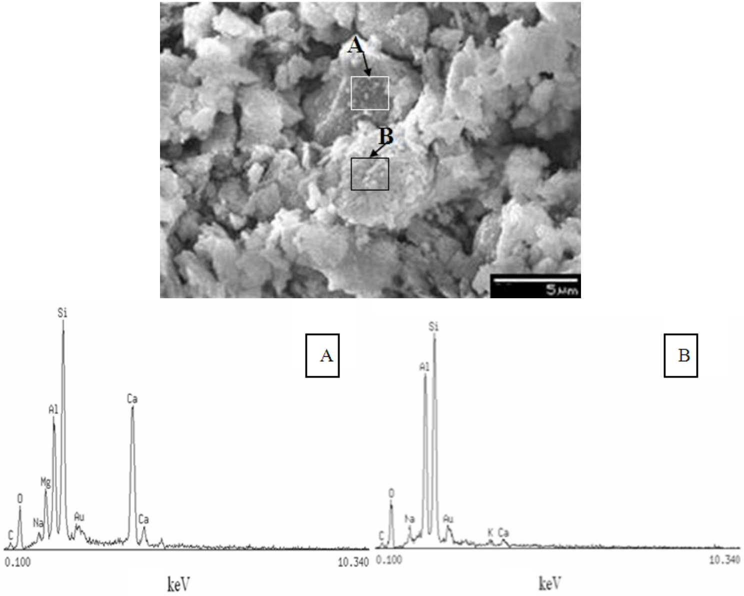


Fig.6 SEM Micrograph And EDS Spectra Of Area A And B Of The Initially Formed Geopolymer (Without Retard)

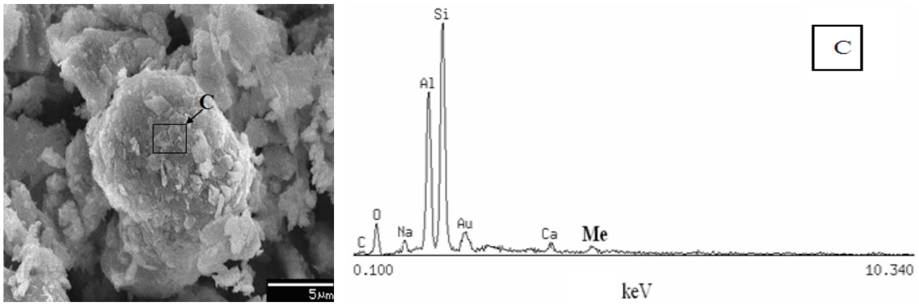


Fig.7 SEM Micrograph And EDS Spectra Of Area-C Of The Initially Formed Geopolymer (With 5.0% BCH)

By analyzing the heat evolution process of geopolymerization, the content of chemically combined water, and the results by SEM and EDS, it can be seen that BCH can retard process of geopolymerization. Metal ions Me^{n+} ionized from BCH solution react with OH^- and SiO_4^{4-}, and the retarding effects could be caused by Me^{n+} reacts with OH^- and SiO_4^{4-}, and the insoluble precipitations adhering on the surface of metakaolin and slag particles intercept geopolymerization.

4. CONCLUSIONS

a) Retarder BCH can retard reaction rate of geopolymerization. When the dosage of BCH is 5.0%, the initial setting time and finial setting time of geopolymerization at 80 ℃ are prolonged up to 17.3 times and 12.2 times, rsepectively.

b) When the dosage of BCH is 5.0%, the heat evolution rate of geopolymerization at 20 ℃ reduces compared to neat paste, and heat evolution time is prolonged. BCH has obvious retarding effects on both alkali-activation of metakaolin and slag.

c) When dosage of BCH is 5.0%, chemically combined water of geopolymer is obviously lower than content of neat paste at 80 ℃. Indicating the reaction degree of alkali activation is reduced. Chemically combined water is 3.02% at 4 h (growth rate during 0.5~4 h is 29.61%), and content of the neat paste is 6.77% at 1 h (growth rate during 0.25~1 h is 172.98%).

d) The neat paste reacted for 1 h at 80 ℃ is continuous compacted hardened specimen. But when the dosage of BCH is 5.0%, the reaction products exist in the granular form and coherent substance contained Me^{n+} adhered on surface of particles intercept process of alkali-activation.

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