Control of Setting Time of Fly Ash Geopolymer

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Abstract. Nowadays, Portland cement is widely used in industrial and civil construction, road traffic, water conservancy, and other construction fields. In order to promote the wide application of geopolymers in engineering, this study is to solve the problem of the fast setting and hardening of geopolymers. The performance and compressive strength are affected, and the optimal ratio is obtained.This study identified an effective retarder for fly ash geopolymer by examining the influence of various retarders on its setting time, flow properties, and compressive strength. A novel method for determining the critical pouring time of fly ash geopolymer is proposed. The retarders investigated include zinc nitrate powder, barium chloride, sodium pyrophosphate, glycerol, boric acid, borax, citric acid, and sodium gluconate. Both simple and complex retarding agents were prepared. The effects of different retarders on fly ash geopolymers were analyzed using SEM tests. When the barium chloride content is less than 2%, $BaSiO_3$ precipitates form in the fly ash geopolymer system.

Keywords: Fly ash, Module, Setting time, Retarding agent, geopolymer

1 Introduction

In recent years, the price of cement has increased annually, leading to a significant rise in construction costs[1]. Davidovits used metakaolin as the raw material to create a new type of inorganic green cementing material for building plates, naming it geopolymer[2]. Geopolymers possess superior properties compared to Portland cement materials and show promising development prospects in many fields[3]. In recent years, the rising price of metakaolin has led to the use of silico-aluminate materials like fly ash and slag as substitutes in geopolymer production, becoming a major research focus[4]. Geopolymer has superior mechanical properties and durability compared to Portland cement[5][6][7]. Yi Longsheng et al[8]indicate, When the water-binder ratio is between 0.35 and 0.43, the setting time of geopolymer is essentially unaffected by changes in the water-binder ratio. Qiao Fei et al[9] The results show that most retarding agents suitable for traditional cement-based materials do not affect geopolymers.

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1.1 Materials

The experiment used ordinary 42. 5 grade Yingshan cement produced by Fuxin Daying Cement Factory. Table 1 lists its main chemical composition. Table 2 indicates that the cement's stability and setting time comply with standard cement criteria.

Table 1. Chemical composition of cement%

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	LOSS
60.47	23.22	4.51	2.33	1.16	0.87	1.23	4.22	1.99

Table 2. Physical properties index of cement

Specific surface area m^2/kg	Density g/cm^3	Setting time /min		Stability
		Initial set	Final set	
343	3.41	181	240	Up to standard

This experimnt utilized grade I low-calcium fly ash produced and processed by Fuxin Thermal Power Plant. Tables 3 and 4 present its chemical composition and physical properties.

Table 3. Chemical composition of fly ash

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	LOSS
52.31	28.59	4.01	6.22	2.05	2.05	1.62	1.79	3.41

Table 4. Physical properties index of fly ash

Density g/cm^3	Specific surface area m^2/kg	Water content %	Water requirement %	Strength activity index %
2.34	528.5	1.2	94	76

1.2 Sample Preparation

This paper utilizes a cementing material ratio of 85:15 for fly ash and cement. NaOH is used to adjust the modulus of sodium silicate as a compound activator. Under these conditions, a clean slurry system of fly ash geopolymer was prepared, and

40mm×40mm×40mm test blocks were fabricated using a commonly used method for fly ash geopolymer preparation.

2 Testing

Setting time test: Due to the lack of a universal standard for determining the setting time of geopolymers, this study utilizes the GB/T1346-2011 method[10], which is designed for water consumption, setting time, and stability testing of cement standard consistency. Flow test: Please refer to GB/T8077-2012[11], entitled Test method for uniformity of concrete admixtures. Unconfined compressive strength: This study used 40mm×40mm×40mm cube specimens for compressive strength testing, following the guidelines in GB/T50081-2019[12]"Test Method Standard for Physical and Mechanical Properties of Concrete".

3 Results

The number indicates the amount of polymers in the retarder, while the letter denotes the type of retarder. The number represents the percentage of the retarder in the mass of the cementing material. For instance, Z stands for 4% zinc nitrate buffer solution, and B, N, H, S, P, C, and T represent barium chloride, sodium pyrophosphate, glycerol, boric acid, borax, citric acid, and sodium gluconate, respectively.

3.1 Effect of Retarder on Setting Time

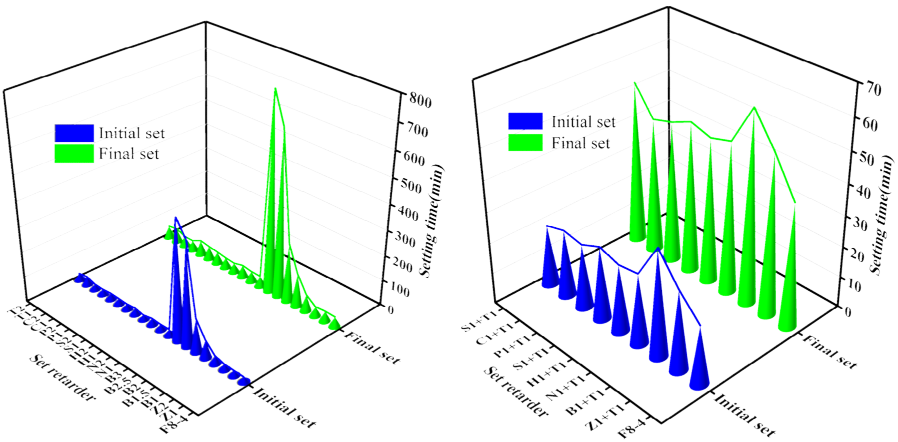

Fig. 1. Effect of different retarders on setting time of fly ash geopolymer

Figure 1(a) illustrates the variation trend in setting time among single retarders. Most of these retarders show minimal deviation in setting time compared to F8-4, except under conditions where sodium gluconate content is 1% and with the inclusion of barium chloride. At 1% sodium gluconate content, the initial and final coagulation times were 34 minutes and 55 minutes, respectively, marking a 15-minute increase compared to F8-4.

Barium chloride, when used as a retarder, significantly extends the setting time of fly ash geopolymer. Moreover, the setting time increases markedly with higher barium chloride content. Thus, barium chloride serves as a potent retarder capable of significantly prolonging the setting time of fly ash geopolymer.

3.2 Analysis of Action Mechanism of $BaCl_2$

As shown in Figure 2, the geopolymer products of F8-4 exhibit relatively dense characteristics, whereas those of B1. 5 and B2 are relatively porous. The binding between fly ash particles and geopolymer products is compromised due to the loose coating of geopolymer on the fly ash particles, resulting in significantly lower compressive strength for B1. 5 and B2 compared to F8-4 during the early stages. The reaction between barium chloride and water glass deposits a relatively dense coating on the slag particle. This occurs primarily because the SiO_3^{2-} in the activator reacts with Ba^{2+} from barium chloride, leading to the formation of $BaSiO_3$ precipitation.

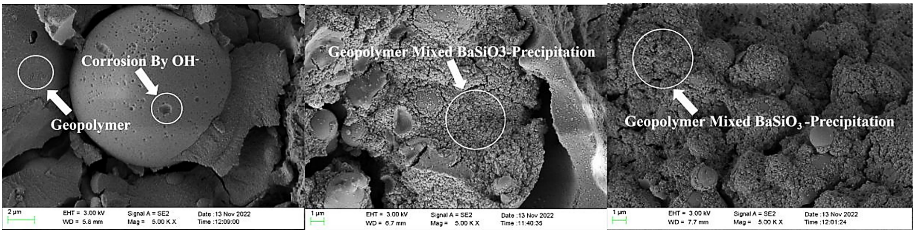

Fig. 2. Micro-morphology of F8-4, B1. 5 and B2 at 3d age

Figure 3 illustrates that the geopolymer products of B1. 5 and B2 remain loosely structured at 7 days, indicating poorer geopolymerization compared to F8-4. This suggests that the amount of $BaSiO_3$ precipitation in the system has not significantly changed. In contrast to F8-4, the density of geopolymer products in B1. 5 and B2 differs significantly, with slight improvements in internal voids compared to day 3, yet with more unreacted fly ash particles present. This indicates insufficient hydrolysis of $BaSiO_3$ by water molecules at 7 days, leading to limited geopolymerization. Consequently, the compressive strength increase of B1. 5 and B2 is less pronounced between 3 and 7 days.

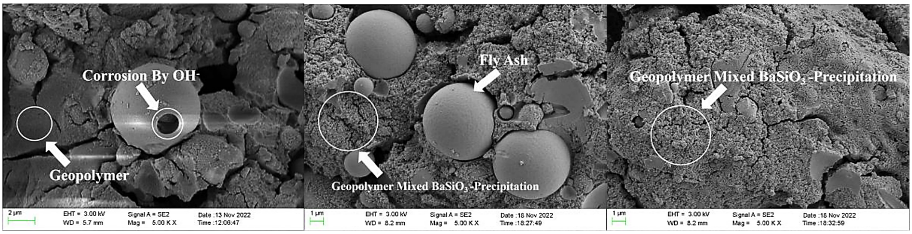

Fig. 3. The micro-morphology of F8-4, B1. 5 and B2 at 7d age

Figure 4 Dense geological polymerization products are clearly observed in the system, indicating a change in $BaSiO_3$ precipitation. During this period, most $BaSiO_3$ precipitates in the B1.5 and B2 systems underwent hydrolysis, resulting in a significant decrease in geopolymer mixed with $BaSiO_3$ precipitates and a notable increase in product density. With B1.5 and B2 exposed to a warm, humid environment for an extended period at 28 days, water molecule penetration depth increases over time, leading to $BaSiO_3$ precipitation hydrolysis and subsequent release of more OH^-. The released OH^- continues to participate in geological polymerization reactions, significantly enhancing the degree of geological polymerization within the structure.

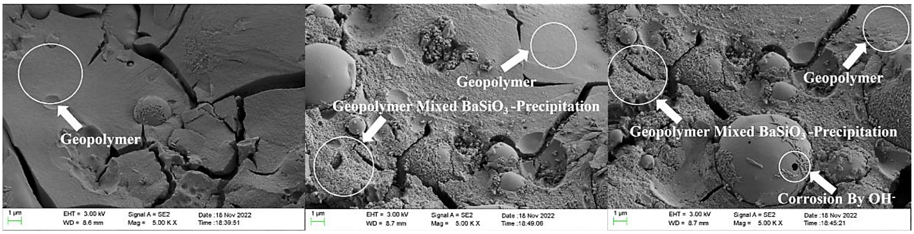

Fig. 4. Micro- morphology of F8-4, B1. 5 and B2 at 28 d age

4 Conclusions

1. Test results indicate that barium chloride significantly prolongs the setting time of fly ash geopolymer, unlike other retardants which are less effective. When barium chloride content is ≤ 2%, early strength is affected, yet 28-day compressive strength remains largely unchanged.

2. The addition of barium chloride leads to $BaSiO_3$ precipitation in the activator solution, reducing the content of SiO_3^{2-} and OH^- involved in geopolymerization.

3. To find out how to effectively extend the setting time of geopolymers and not the retarder which can cause any adverse effect on compressive strength is an urgent problem to be solved in current research.

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