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Study on the Performance of Alkali-Based Geopolymer under Vacuum and Freeze-Thaw Cycles

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At present, researches on alkali-based geopolymer were mainly conducted under normal temperature or high temperature conditions, while few studies on alkali-based geopolymer under low temperature (<25 ℃) or vacuum conditions have been reported. Since the slag-based geopolymer reacts quite rapidly at normal temperature, the depolymerization and polycondensation processes can be properly separated by low temperature conditions, which is beneficial for the study of the reaction process and mechanism of the alkali-based geopolymer. At the same time, the performance of the alkali-based geopolymer under vacuum and freeze-thaw cycles is explored in this paper, and the recycling and reuse of water is realized.

1. Introduction

The alkali-based geopolymer is a mixture. The main components include: ground slag powder and potassium hydroxide solution. After mixing of the two substances, alkali can be obtained, which has good gelling property and therefore can be used as a component of cementing material. However, due to external environmental factors, the performance of the alkali-based geopolymer changes under different environmental conditions, especially under vacuum and freeze-thaw cycles, so this paper simulates vacuum and freeze-thaw cycle conditions to study the performance of alkali-based geopolymer.

2. Literature review

Studies have shown that calcination of mud at 800 °C results in the formation of active Si, Al and Ca due to the dehydroxylation of clay minerals and the decarbonation of calcite (Rakhimova et al., 2018). Marl is suitable for use as a geopolymer precursor. Therefore, the study of marl with high calcite/aluminosilicate ratio as a geopolymer precursor and limestone as a mineral additive for this geopolymer have a very important impact on the further development of inorganic binders.

Two geopolymers of Si: Al of 2.0 and 5.0 were prepared using fly ash and different alkali activators (sodium aluminate, sodium silicate and sodium hydroxide) as starting materials. Through the toxic leaching test, the aluminate-excited geopolymer is more suitable for fixing lead ions. Si: Al of geopolymer blocks is a key factor in the immobilization of lead ions. It has also been shown that lead ions act as a balancing charge in the structure of geopolymers (Lee et al., 2016). After mixing the nitric acid solution and the sodium hydroxide solution, the synthesized sample was immersed in distilled water and various concentrations of NaCl, HCl and NaOH solutions. It was found through testing that heavy metal ions were successfully immobilized in kaolin/molecular sieve geopolymer samples. The greater the concentration of heavy metal ions, the higher the amount of immobilization (El-Eswed et al., 2015). Geopolymer cement was prepared from fly ash, sodium hydroxide and sodium silicate solution to improve its fire resistance. The synthesized base geological compound has a higher thermal conductivity after being calcined at a high temperature. At the same time, the degree of cracking and spalling is also at a minimum. The remaining carrying capacity is 61%-71%, which is more than 50% better than traditional cement performance (Sarker and Mcbeath, 2015). An insulating, sound insulating and refractory material was synthesized from fly ash and polypropylene fibers. Insulation, sound insulation, fire resistance and other mechanical properties were tested. The sound absorption coefficients of the 2 cm and 4 cm thick sheets were 0.3 and 0.8, respectively. This material has a very low thermal

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conductivity (Leiva et al., 2015). By changing the relative ratio of Na: Al and water, the chemical composition of the fly ash base polymer was changed, and its performance was adjusted. Na: The ratio of Al to water enables the fly ash base polymer to have extremely high bond strength and thermal stability with a short set time. Therefore, fly ash base polymer can prepare coating materials with excellent high temperature stability and durability by regulating Na:Al and water-solid ratio (Khan et al., 2015). The effect of the incorporation of heavy metal chromium, zinc and iron on the structure of alkali-treated geopolymers was investigated. The detrimental effect of heavy metals on strength may be due to their presence as hydroxides rather than their incorporation as charge balancing cations in the geopolymer structure. Leaching tests in simulated acid rain showed that geopolymers with a molar ratio of SiO2 / Al2O3 = 1.78 were able to immobilize all three metals in a safe leachate level. Geopolymers are strong enough to withstand treatment and transportation, and can hold waste containing these heavy metals for storage or disposal (Waijarean et al., 2017). The fly ash base polymer coating and alkali solution are used to improve the durability of the volcanic ash concrete. The test found that a dry-wet cycle treatment in a 10% sulfuric acid solution accelerated the damage process. The chloride solution was used to evaluate its penetration depth. It was found that sodium hydroxide solution and sodium silicate solution treatment significantly improved the durability of volcanic ash concrete (Wiyono and Hardjito, 2015). The geopolymer mortar is prepared by using high calcium fly ash and different concentrations of NaOH. The geopolymer mortar repair material has excellent shear strength and bending stress characteristics under the condition of high concentration of NaOH (Phoongernkham et al., 2015). The geopolymer gelling material is prepared using chromite ore and an alkali activator. Then, it is mixed with river sand and gravel aggregate to prepare the geopolymer concrete sample. The material was immersed in a magnesium sulphate solution to study its resistance to sulfate corrosion. Tests have found that higher concentrations of magnesium sulfate solution can significantly increase the compressive strength of base geologic compounds (Bodor et al., 2016).

In summary, the above research work mainly involves adding and changing different alkali activators including sodium hydroxide, sodium aluminate and sodium silicate. Furthermore, the heavy metal ion content of geopolymers and the properties such as heat resistance and corrosion resistance were investigated. Therefore, three alkali activators of powdered water glass, liquid water glass and sodium hydroxide are used to prepare geopolymers. The reuse of moisture was studied to prepare a material with good mechanical properties.

3. Method

3.1 Experimental raw materials and equipment

There are many factors affecting the activity of slag and fly ash. The internal factors include the chemical composition of the substance, the vitreous substance content and fineness; while external factors include curing temperature and other additives. Figure 1 shows the active component content of the general blast furnace slag and fly ash and the active components of the slag and fly ash used in this experiment, as well as the active components of the tektite and volcanic ash used in this experiment.

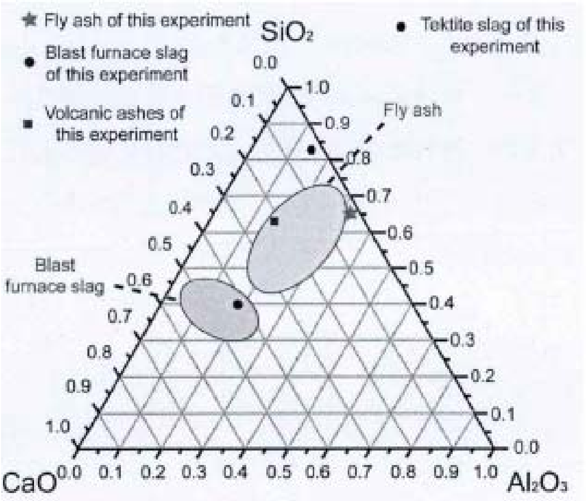

Figure 1: Contents of active components of blast furnace slag and fly ash and active components of slag and fly ash used in this experiment

The main raw material slag used in this experiment is the local slag, and the appearance is grayish white. The main chemical composition and content of the slag can be measured by XRF. The density is 2.96g/cm3 and the specific surface area is 1.44 m3/g. The slag was placed in an oven at 105°C for 3h before use, and then cooled to room temperature and sealed for storage.

Table 1: Main chemical composition and content of slag

Chemical composition	Content
CaO	36.91
SiO2	33.98
Al2O3	15.22
MgO	9.27

Particle size analysis and XRD analysis are shown in Figures 2 and 3. As can be seen from Figure 2, the particle size (D50) of the slag is mainly concentrated at 10.49 pm. The XRD data in Figure 3 shows that a large dispersion peak is formed near 31°, which indicates that the slag is mainly amorphous, almost no crystal structure exists, only a small amount of Ca4Si2O6(CO3)(OH)2. It's because the slag is quenched with a large amount of water at the time of generation, it has no time to form the crystal structure, instead it forms slag with vitreous substances. Therefore, the content of the vitreous substance determines the activity of the slag, and it is understood that most of the oxides in the slag are free.

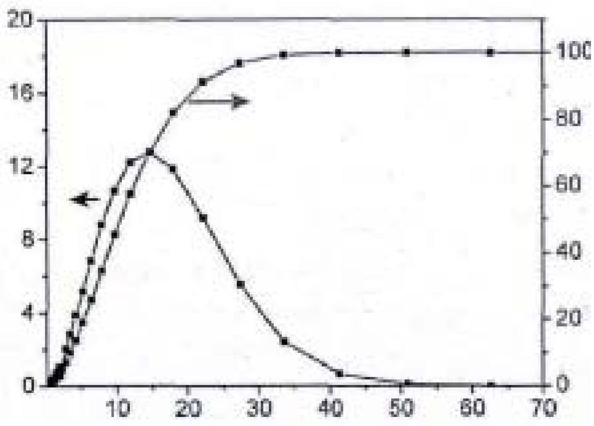

Figure 2: Particle size distribution of slag and XRD diagram (a)

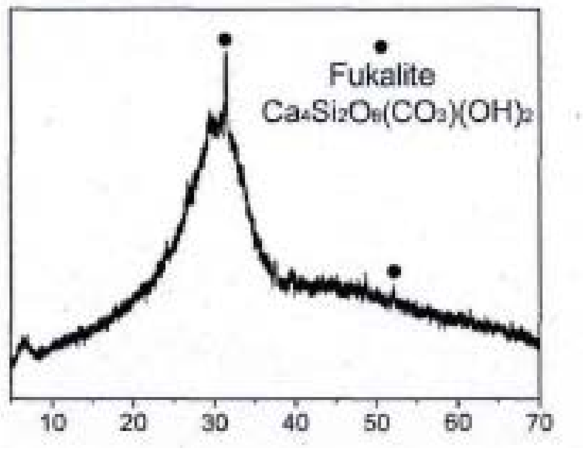

Figure 3: Particle size distribution of slag and XRD diagram (b)

3.2 Test steps

The test steps mainly include X-ray Powder Diffraction (XRPD) test, Scanning Electron Microscope (SEM)/Energy Disperse Spectroscopy (EDS), compressive strength test, and Inductive Coupling Plasma Spectrometer (ICPS). The details are as follows.

2.2.1 XRPD test. All XRD data of this paper were tested by Rigaku Mini Flex600 instrument. The test conditions were: continuous scanning, CuK-beta target, working voltage 40Kv, working current (tube current) 15mA, scanning angle 2θ = 5° ~ 70°, step size 0.02°.

2.2.2 SEM/EDS. The sample was first sonicated in absolute ethanol for 5 min, then metal was sprayed on the surface, and photographed by a S-3400 scanning electron microscope to obtain the required electron micrographs and element distribution pictures.

2.2.3 Compressive strength test. The compressive strength of all samples in this experiment was tested by the electronic universal testing machine DNS100. The displacement rate was 0.5mm.min. Six parallel samples were made for each sample, and ensure at least three samples' standard deviation were within 10%. The average value is taken as the compressive strength of the sample, and the error is calculated.

2.2.4 ICPS. In this paper, the concentration of different ions in the slurry was characterized by optima5300DV ICPS. The test conditions were: plasma flow rate 15L/min and atomized gas flow rate 0.6L/min. The pump speed was 100rpm, sample delivery speed was 1.2 ml/min, when testing different ions, use deionized water to wash for 15s.

4. Results

4.1 Initial setting and final setting time

When the mineral is under alkali-activated conditions, the generated hydration products will form a three-dimensional network structure. When the reaction reaches a certain level, the geopolymer slurry will lose its original fluidity and form a shape, this reaction process is called condensation. In actual use, the geopolymer slurry needs a certain amount of time for mixing and construction. Therefore, the setting time of the geopolymer slurry is quite necessary for its application, and many factors will affect the setting time of the geopolymer slurry. For example, the properties of the slag, the type of activator, environmental factors, and various admixtures, and the like. Figure 4 shows the effect of the mass ratio of slag to dry powder water glass (sodium silicate) on initial setting and final setting time.

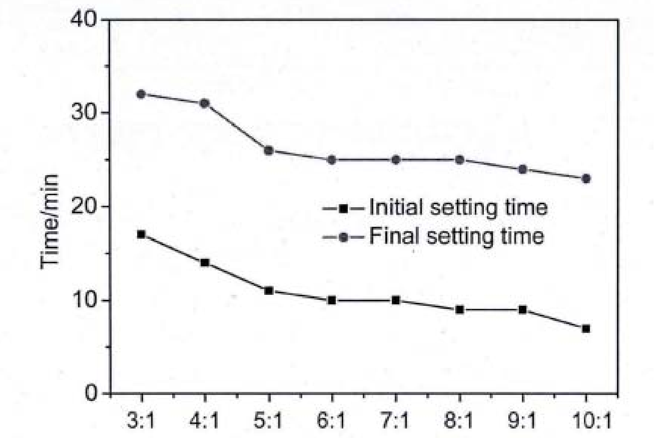

Figure 4: Influence of mass ratio of slag to dry powder sodium silicate on initial setting time and final setting time

Figure 4 shows the slag-based geopolymer activated by the solid water glass. When the modulus of the solid water glass is fixed, the initial setting and final setting time decrease as the amount of solid water glass increases. The reaction of the alkali-activated slag-based polymer is a process of depolymerization – rearrangement – polycondensation. When the alkali activator content is reduced, the depolymerization process is shortened, resulting in a shorter solidification process. At the same time, the solid water glass generates a large amount of heat during the dissolution process, and the solidification process of the slag is very sensitive to temperature. Therefore, when solid water glass is used as the activator, a retarder is required to control the solidification time.

4.2 Initial setting and final setting time of liquid water glass based geopolymer

It can be seen from Figure 5 that in the slag-based geopolymer activated by liquid water glass, when the modulus of the liquid water glass is fixed, the initial setting time decreases as the water glass addition amount decreases, and the final setting time increases as the amount of water glass addition decreases. Although the ratio of the slag-based geopolymer activated by liquid water glass is the same as that of the solid water glass, the soluble molecular species and content thereof are different. Because the glass sodium silicate molecules in the solution can be depolymerized into soluble molecules, this is quite different from the situation that the large amount of heat released by dry powder water glass dissolving in water would accelerate the solidification speed of the slag-based geopolymer, so it results in the change of the final setting time is different from that of the solid water glass activator, and the final setting time is prolonged.

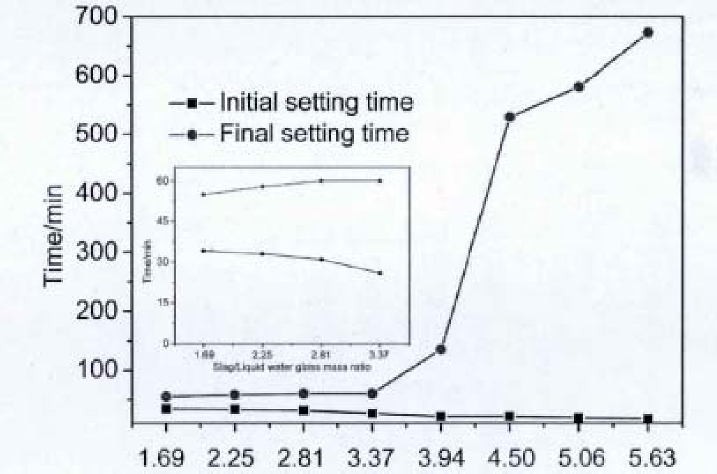

Figure 5: Influence of mass ratio of slag and liquid water glass on initial setting time and final setting time

4.3 Initial setting and final setting time of the sodium hydroxide based geopolymers

It can be seen from Figure 6 that the slag-based geopolymer activated by sodium hydroxide has a reduced initial setting and final setting time as the amount of sodium hydroxide addition increases. This is similar to the solid water glass activation process, as the amount of activator increases, the process of depolymerization and polycondensation is prolonged, thereby increasing the overall setting time.

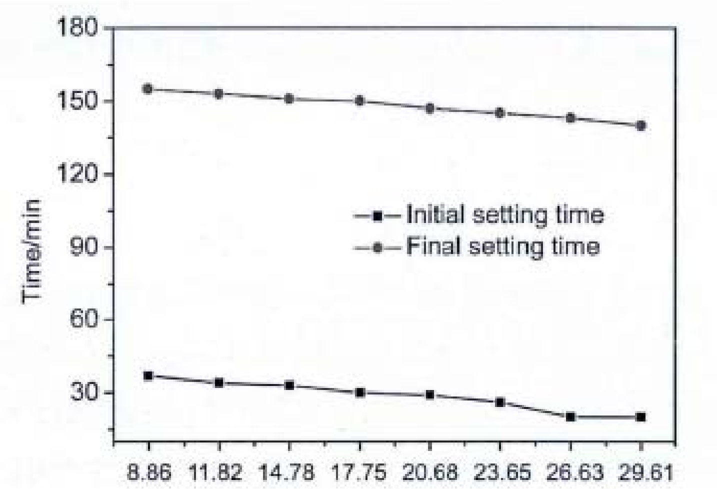

Figure 6: Influence of mass ratio of slag and sodium hydroxide on initial setting time and final setting time

4.4 Compressive strength

The compressive strength is an important measuring indicator for the slag-based geopolymer in practical applications. In this paper, the compressive strength is used to optimize the ratio of the slag-based geopolymer.

5. Conclusion

By studying the effects of three kinds of alkali activators, dry powder water glass, liquid water glass and sodium hydroxide on the reaction process and sample properties of geopolymers, this paper concluded that the initial setting time of the three has a same trend. The change trend of the final setting time of the liquid water glass is different from that of the other two; the variation of compressive strength of the three curing time is consistent, but the compressive strength performance of dry powder water glass is more excellent, the best slag/dry powder water glass mass ratio is 5:1; the change of the shrinkage rate of the three alkali activator samples is consistent. The largest shrinkage is liquid water glass, followed by dry powder water glass, the smallest is sodium hydroxide, and the hydration heat of the three alkali activators is characterized by DSC. It is concluded that the reaction process of dry powder water glass and liquid water glass is very close, and the reaction process of sodium hydroxide is different from the other two. Looking forward, the environment studied in this paper does not fully represent the environment faced by alkali-based geopolymer, so it needs to be improved in later research.

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