

Research on preparation and performance of fly ash-based geopolymer cementing material

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Abstract. In this paper, the compressive strength of geopolymer cementing material prepared by the fly ash instead of metakaolin is researched and the micro-topography is observed by SEM. According to the result, for the geopolymers prepared by the fly ash with mass fraction of 20%, 40% and 60% instead of metakaolin, the phase component of the load failure plane is rather disorder with many spherical fly ash particles and fractures; compared with the geopolymers prepared by metakaolin, the compressive strengths of samples at all ages are not high. C-S-H phase discovered in the crystalline phase analysis of samples indicates that there is hydration reaction at the same time of geological polymerization. It can be seen through the SEM micro-topography diagram that samples with the 30% metal impurity content are of compact structure and low porosity; however, when the metal impurity content is excessive, there are still some unreacted metal impurity particles due to the lower metal impurity activity and the declined alkali-activated effect of metal impurity.

Key words. Fly ash, Polymer, Cementing material, Preparation.

1. Introduction

As one of the actively researched non-metallic materials in the international community recently, geopolymer cementing material is a kind of new inorganic polymer material obtained by metakaolin or other silicon-aluminum materials activated by alkali in lower temperature. Compared with Portland cement, this kind of material is widely applied in fields such as automobile and aviation industry, civil engineering, non-iron foundry industry, traffic engineering, toxic and radioactive wastes treatment. Scholars at home and abroad have made extensive research on the geopolymer cementing material. For instance, Panias D et.al have prepared the fly ash-based geopolymer material and researched the influence of alkali activators i.e. sodium

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hydrate and sodium silicate on the compressive strength; Zhu Xiaomin, Hou Yunfen et.al have made research on the preparation and performance of fly ash-based geopolymer material.

Both fly ash and metakaolin are the main raw materials to produce geopolymer cementing material; they are of similar properties. The development of metakaolin has been constrained to a certain degree due to its constantly rising price. Fly ash is the byproduct of thermal power generation, it is a kind of extremely thin spherical particle with higher pozzolanic activity. Statistically, the annual discharge of fly ash in China is more than 200 million tons. Currently, except for the part used to produce the cement admixtures and aerated concrete bricks, there are still a large number of fly ash being discharged as waste, which has caused serious environmental pollution. Therefore, it is of great significance to prepare the geopolymer cementing material by the fly ash that is rich in production and less expensive instead of the metakaolin.

In this paper, the metakaolin is partly replaced by the fly ash in Liupanshui District as the raw material to prepare the geopolymer cementing material with sodium silicate and sodium hydrate being the activators; the compressive strength is tested and the micro-topography is observed as well.

2. Experiment

2.1. *Experiment materials*

Metakaolin: obtained from the Liupanshui kaolinite screened by the 80- μm square hole screen after being calcined under 800 $^{\circ}\text{C}$, roasted for 6h and naturally cooled to room temperature. Alkali activator: prepared by water glass (in solid state) commercially available and sodium hydrate (chemically pure). Water: running water. Fly ash: Low-calcium fly ash from a power plant, the components of which are as shown in Table 1; the X-ray diffraction pattern is as shown in Fig.1.

Table 1. Chemical components of fly ash (1%)

$\omega(\text{Al}_2\text{O}_3)$	$\omega(\text{SiO}_2)$	$\omega(\text{CaO})$	$\omega(\text{SO}_3)$	$\omega(\text{Fe}_2\text{O}_3)$	$\omega(\text{other})$
8.31	53.48	6.32	0.62	6.52	4.75

2.2. *Preparation of fly ash geopolymer*

The weighted water glass and water are placed into the beaker to stir, NaOH is added during the stirring, afterwards the beaker shall be sealed up with preservative film to avoid the evaporation of water; stop stirring after NaOH is completely dissolved and stirred evenly, it can be cooled to room temperature and placed for 24h before being used. The modulus of water glass of activators prepared in this experiment is 1.79, the water cement ratio of stirred slurry is 0.45, the specific ratios are seen in Table 2.

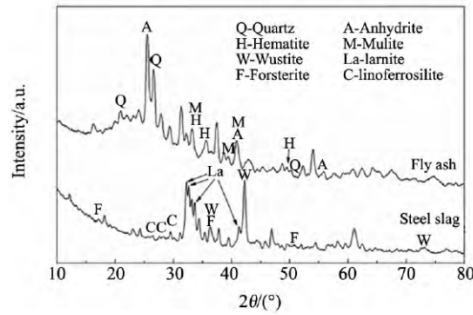


Fig. 1. X-ray diffraction pattern

Table 2. Ratios of geopolymer slurry

No.	Fly ash+ metal impurity/%	Fly ash/g	Metal impurity /%	AA/g	SiO ₂ /Al ₂ O ₃	SiO ₂ /CaO	SiO ₂ /SO ₃	SiO ₂ /Fe ₂ O ₃
1	0	100	0	66.09	3.59	7.54	0.07	20.48
2	10	90	10	66.09	3.75	7.02	0.15	20.48
3	20	80	20	66.09	3.92	6.48	0.25	20.48
4	30	70	30	66.09	4.18	5.95	0.37	20.48
5	40	60	40	66.09	4.48	5.44	0.51	20.48
6	50	50	50	66.09	4.88	4.91	0.68	20.48

2.3. Sample preparation

A certain amount of fly ash and metal impurity shall be weighted respectively, the total mass of the powder shall be 100g, in which the content of metal impurity shall be respectively 0, 10%, 20%, 30%, 40% and 50%. Mix them up evenly in the slurry mixer, add the prepared activator and mix them up completely; pull the slurry into the 20mmx20mmx20mm hexagonal steel die and seal it up with plastic film before being put into the curing box. The geopolymer samples can be obtained after the curing under 60° and ordinary pressure for 24 h and room temperature in the air for 28 d after the module unloading; the performance shall be tested. The ratios of geopolymer slurry can be seen in Table 2.

2.4. Characterizations of geopolymer

In this experiment, the TYE 300D pressure tester is adopted to test the compressive strength of samples with different contents of metal impurity by taking the mean value of the three samples in each group. The Japanese Smartlab9000 X wave line diffractometer is adopted to make the phase analysis; the Nicolet and chemical bond are adopted for analysis; the KBr presser transmission method is adopted to make the micro-topography analysis on the samples with the scanning electron microscope within the scanning scope of 4000~500cm⁻¹.

3. Result and discussion

3.1. Setting time and compressive strength

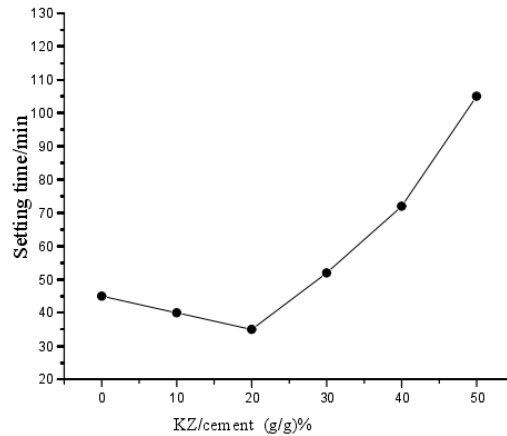


Fig. 2. Influences of content of slag on the setting time of geopolymer cementing material

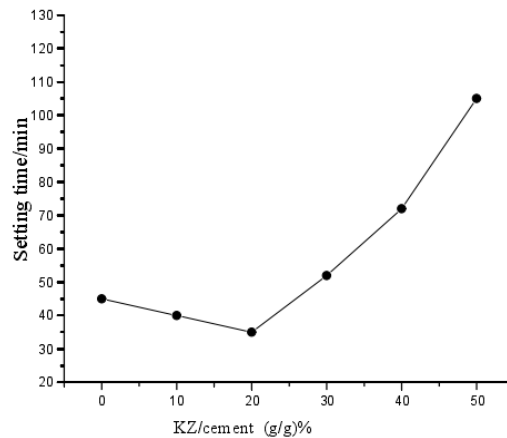


Fig. 3. Influences of content of slag on the compressive strength of geopolymer cementing material

It can be seen from the above two figures that at the early stage as the slag adds and its content increases, the compressive strength of geopolymer cementing material also increases, in the meantime, the setting time is shortened; when the content is higher than 30%, the compressive strength of geopolymer cementing material declines and when the content of slag is higher than 20%, the setting time is accordingly extended.

As the Ca rich in the Ca-laden phase in calcareous materials dissolves out faster

than Si and Al contained in silicon-aluminum raw materials, the generation of hydrated calcium silicate and hydrated calcium aluminate can be promoted by adding a certain amount of Ca^{2+} ions; also it will provide $2+$ positive ions to the molecular chains of geopolymer at the same time of playing an active role in promoting the geo-polymerization as well as the formation reaction of hydrated calcium silicate and hydrated calcium aluminate. To a certain degree, the setting time of cementing system can be regulated, the Ca gel phase has made up the microcracks in the system caused by the geo-polymeric polycondensation; in the meantime, due to the irregularity and obvious angularity, the added slag particles will be effective in aggregate filling and improving the early compressive strength of samples.

In this experiment, as the ratio of KZ/fixed ash increases, the compressive strength of geopolymer samples present a trend of increasing first and then decreasing. This is because that when the ratio of KZ/fixed ash is excessive, a large amount of Ca^{2+} will react with OH^- to produce $\text{Ca}(\text{OH})_2$ to reduce the alkalinity of the geo-polymerization system and exert a negative influence on the dissolving of Si and Al in the silicon-aluminum materials as well as the subsequent hardening process. As a result of the excessive ratio of KZ/fixed ash, there will be a large amount of CSH gels produced in the system, the excessive flocculating hydrated calcium silicate gels might influence the spatial continuity of geopolymers and play a role of impurity, so that the spatial continuity of network-shaped aluminosilicate gels and exert a negative influence on the chemical properties of samples.

3.2. SEM and EDS analysis

The microstructure of geopolymer cementing material GM-3-5 and the Ca-laden polymer cementing material mixed with 30%KZ are observed through the scanning electron microscope; the results of regional element analysis on the two of them are as shown in Figure 4-5.

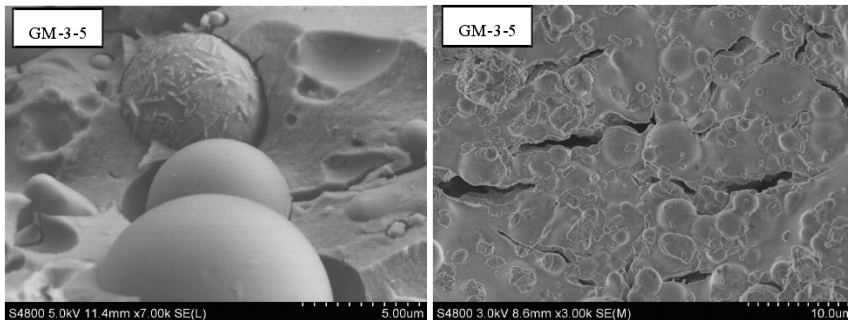


Fig. 4. Geopolymer cementing material SEM without KZ

Figure 4 and 5 are the compressive fracture plane SEM pictures of geopolymer material GM-3-5 and the 30% and 50% Ca-laden geopolymer cementing materials; Figure 6 is the regional element analysis of the GM-3-5 and the 30% Ca-laden geopolymer cementing material EDS. It can be seen from the three figures that the main components of ordinary GM-3-5 not being Ca-laden are the aluminosilicate

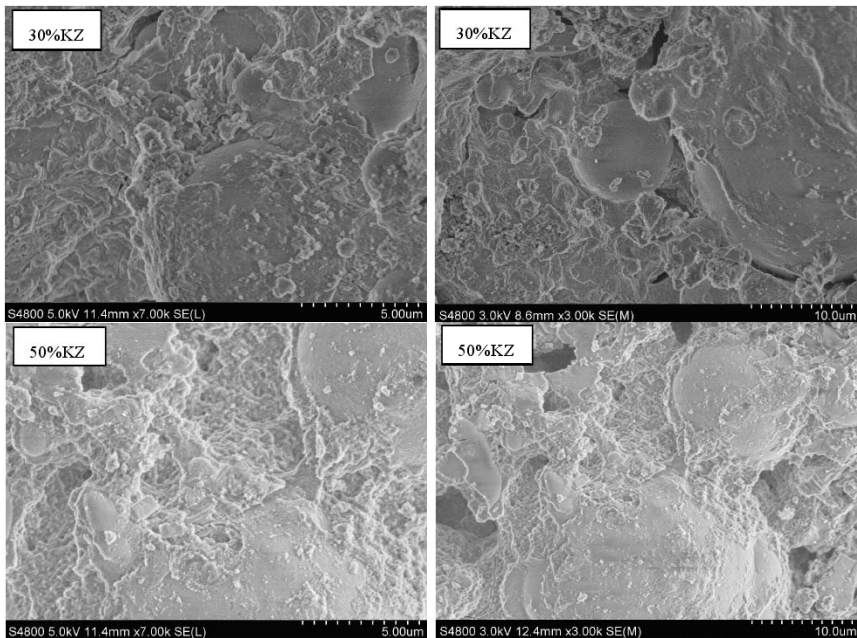


Fig. 5. Geopolymer material SEM mixed with 30%KZ and 50%KZ

cementing material and the fly ash glass phase undissolved to participate in the polymer reaction; the main elements are Si, Al, O, Na with less Ca element. It indicates that most of the active spherical glass phases have the alkali-activated geopolymerization, the produced inorganic polymer 3D network structured cementing material is of the $-O-Si-O-Al-O-$ structure while only a few CSH and $Ca(OH)_2$ are produced. There will be microcracks caused by polycondensation dehydration on the surface of geopolymer cementing material GM-3-5, other parts are rather smooth and compact; the unreacted fly ash glass phases being filled in the cementing materials have played a role in aggregate support.

Due to the production of hydrated Ca cementing material, the main element components of Ca-laden geopolymer cementing material mixed with 30% slag are Ca, Si, Al, O and Na; some flocculating hydrated cementing products i.e. CSH are added on the surface of geopolymer, which has made up the microcracks caused by the polycondensation of silicon-aluminum material geopolymer. In the meantime, the fly ash and hydrated product $Ca(OH)_2$ have the pozzolanic reaction, the production of low CA-SI-ratio CSH gels and ettringite crystals has increased the compactness of geopolymer and improved the mechanical properties of the geopolymer cementing material.

The microstructure of Ca-laden geopolymer cementing material mixed with 50% slag is looser than the former two; excessive slag will result in the production of massive CSH gels and $Ca(OH)_2$, which has blocked up the continuity of geopolymer aluminosilicate gel and will greatly lower the alkalinity of the system. To a cer-

tain degree, it has influenced the process of alkali-activated geo-polymerization and exerted a negative influence on the overall strength of the system.

3.3. Phase XRD analysis

It can be seen from Figure 6 that the phase composition of geopolymer cementing material is basically unchanged and remains based on the amorphous phase after being added with the 30% slag; the CHS peak is slightly strengthened than before, which means the CSH generation in the geo-polymerization system mixed with 30% slag is increased.

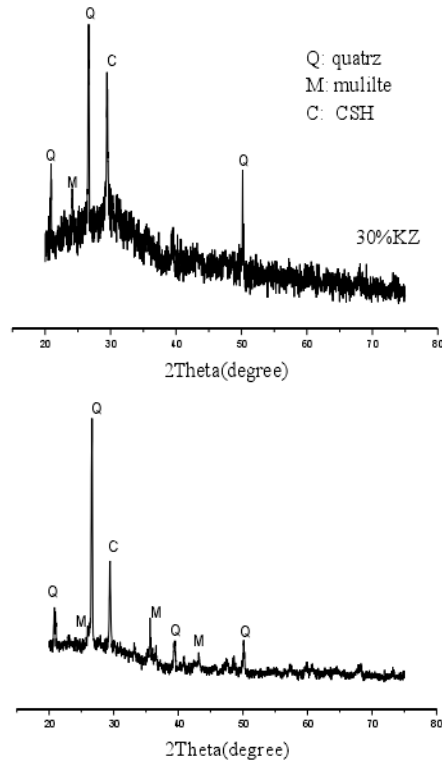


Fig. 6. Geopolymer 28d XRD mixed with 30% slag and without slag

The XRD pattern of fly ash-based geopolymer containing metal impurity is as shown in Figure 7. The pattern phase of fly ash-based geopolymer containing metal impurity is slightly changed in comparison with the singly-activated fly ash while the patterns of samples with different contents of metal impurity are basically the same. The disappearance of anhydrite diffraction peak in the fly ash-based geopolymer indicates that the anhydrite has participated in the geo-polymerization under the alkali-activated conditions. There remain the diffraction peaks of quartz, mullite and hematite; their peak strengths will decline gradually as the content of fly ash increases. In the fly ash-based geopolymer containing metal impurity, the disap-

pearance of diffraction peak of β - C_2S indicates that it has the hydration reaction in alkaline environment and produces C-S-H; the disappearance of diffraction peak of boltonite might produce brucite. The diffraction peaks of iozite and clinoferrosilite still exist, the peak strengths are gradually strengthened as the content of metal impurity increases, which means they are of stable properties and don't participate in reactions. In addition, the diffraction peak of C-S-H gel appears in all test blocks and its peak strength is gradually strengthened as the content of metal impurity increases.

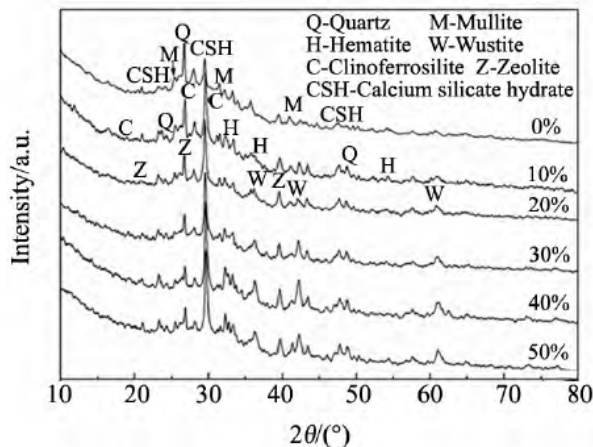


Fig. 7. X-ray diffraction pattern of fly ash-based geopolymer containing metal impurity

4. Conclusion

The influence mechanism of basic mixture ratios of geopolymer cementing material and all factors on the compressive strength of cementing material is discussed through the orthogonal experiment, the phase composition before and after the geo-polymerization is characterized and analyzed through XRD and IR to optimize the technologies of preparing the geopolymer cementing material. The influences of Ca-laden material (slag) on the performance and microstructure of geopolymer cementing material are analyzed and discussed through the setting time, compressive strength test at all ages as well as the microcosmic SEM and element EDS. According to the result:

The sample is of the optimal properties when it is prepared at the Si/Al mole ratio of 2.5, the NaOH ($M_{NaOH}/M_{Solid\ gray}\%$) content of 7.5 and the soluble SiO_2 ($M_{SiO_2}/M_{Solid\ gray}\%$) content of 7.5%. The proper silica-alumina ratio of the raw material can make the amount of SiO_4 and AlO_4 groups inside the system within the proper proportional band, the reaction process can be maximized; the excessive or inadequate NaOH will influence the process of geo-polymerization; with certain alkalinity, the setting time and compressive strength of the system can be regulated

by the soluble SiO_2 .

The phase after geo-polymerization is basically unchanged, there is no other obvious crystalline phase produced except for a few C_3S and C_2S . The main component of raw material amorphous glass phase will produce the amorphous aluminosilicate gel after the alkali-activated reaction.

When the ball milling time is 2h; the average fineness of the fly ash reaches the minimum value; when the ball milling time is 3h, the fly ash activity is the highest and the compressive strength of sample reaches the maximum value. The overlong stirring time will disorganize the generation of spatial network structure of aluminosilicate gel, the optimal stirring time is 5min; it will promote the geo-polymerization rate to increase the curing temperature but the influence on the system strength is insignificant. A certain amount of water is helpful to the process of geo-polymerization while excessive water will exert a negative influence on the setting time and strength of the system.

A certain amount of Ca-laden material (slag) being added into the Ca silicate gel produced in the reaction can make the microstructure of the system more compact and be helpful to the rapid setting and strength growth of the sample; in case of excessive content, the continuity of system will be disturbed, the setting time of sample will be prolonged and the strength of system will be lowered.

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