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Study on Structure and Properties of Kaolin Composites-based Geopolymers

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In order to study the pore structure and corrosion resistance of kaolin composite-based geopolymers, in this paper, kaolin composite-based geopolymers were prepared by replacing fly ash with 15%, 25%, 35%, 50%, and 60% kaolin. Three different low-temperature curing methods were used to study the effect of kaolin ratio on the pore structure and corrosion resistance of geopolymers. The results show that with the increase of kaolin amount added, the corrosion resistance of the composites-based geopolymers increases first and then decreases, and the composite-based geopolymers with 35%kaolin content has the smallest total porosity and the pores are mostly harmless pores; the different low-temperature curing methods had little effect on the total porosity of kaolin composite-based geopolymers, and the corrosion resistance performance was not much different. The anti-corrosion performance of the 1d low-temperature standard-curing and 60°C curing method was better.

1. Introduction

Geopolymer is an inorganic compound material with pozzolanic activity, and it is widely used as construction materials, sealing materials, heat-resisting materials and high-strength materials (Majidi, 2013) for its excellent compressive strength, freeze-thaw resistance, and corrosion resistance; its preparation process is relatively simple, and it also can make use of industrial waste so as to reduce the burden on the environment. Therefore, the study of geopolymers has important significance for reducing environmental pollution, improving the performance of building materials and expanding its application range.
Metakaolin, obtained by firing kaolin (Morgenstern, 1967; Kakali, 2001) at a specific temperature, is an active silica-alumina mineral that can be used to improve the mechanical properties of composite-based geopolymers (Wild, 1996). Incorporation of kaolin into concrete (Sabir, 2001) or silicate materials can improve its durability. There are a large number of domestic and foreign researches on kaolin composite geopolymer reaction mechanism (Poon, 2001) and related studies on its anti-permeability and corrosion resistance (Kong, 2007; Duxson, 2007). In this paper, kaolin and fly ash are used as raw materials for composite geopolymers to study the influence of the content and the preparation process of kaolin on the structure and corrosion resistance of composite geopolymers.

2. Geopolymers

2.1 Chemical structures of geopolymers

The excellent properties of geopolymers are related to its stable structure on the one hand, it is a three-dimensional network zeolite structure composed of alumina-oxygen tetrahedron and silica–oxygen tetrahedron; on the other hand, it may be because it can avoid the expansion caused by the alkali-aggregate reaction.

2.2 Chemical reaction mechanism of geopolymers

The reaction of geopolymers is a complex process (Rahier, 2007). For the studies of its reaction mechanism, what's currently widely accepted is the theory of disaggregation and polycondensation proposed by the French scholar J. Davidovits. He believes that the process of setting and hardening of composite geopolymers is a

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process in which the aluminum-oxygen bonds and silicon-oxygen bonds in raw materials containing aluminum and silicon broke and reassembled under the action of alkaline catalysts.

2.3 Preparation of kaolin composites-based geopolymers

2.3.1 Chemical composition of kaolin and fly ash

The main chemical composition of kaolin powder and fly ash are shown in Table (1) and Table (2).

Table 1: Main chemical composition (by mass) of metakaolin (wt %)

Compositions	SiO2	Al2O3	GaO	SO3	Fe2O3	Na2O
Content	54.68	41.38	0.05	0.30	0.39	0.38

Table 2: Main chemical composition (by mass) of fly ash

Compositions	SiO2	Al2O3	GaO	SO3	Fe2O3	Na2O
Content/%	58.50	29.88	3.58	0.36	2.97	0.69

2.3.2 Chemical preparation process

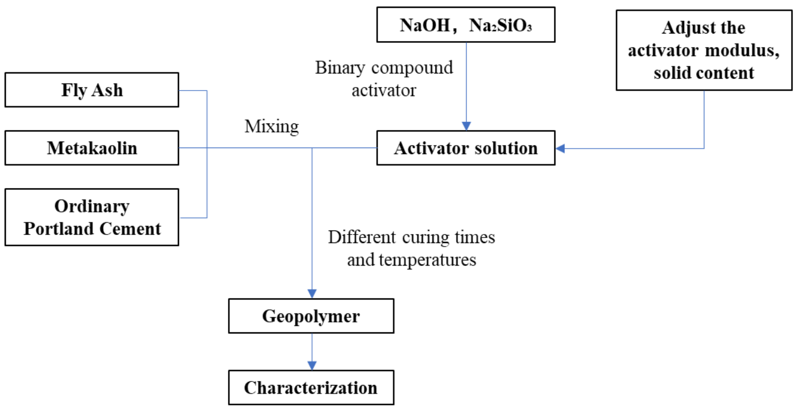

Figure 1: Preparation process of geopolymers

Figure (1) shows the preparation process of kaolin composite-based geopolymers, the raw materials are prepared according to a certain ratio.

3. Effect of kaolin ratio on the structure and chemical properties of geopolymers

3.1 Experiment design

The composite-based geopolymers were prepared by mixing kaolin, fly ash and ordinary Portland cement. This study examined the effect of kaolin ratio on the structure and chemical properties of geopolymers. The design scheme is shown in the following table (3). The addition amount of kaolin is 15wt%, 25wt%, 35wt%, 50wt% and 60wt%, respectively. To ensure that the sample has good fluidity, with the increase in the amount of kaolin added, the corresponding water-cement ratio should also increase.

Table 3: Mix ratio of geopolymers

No.	Metakaolin Percentage (%)	Water-cement Ratio (wt%)
C15	15%	0.45
C25	25%	0.48
C35	35%	0.53
C50	50%	0.57
C60	60%	0.62

3.2 Effect of kaolin ratio on the pore structure of geopolymers

The pore size distribution of geopolymers with different kaolin ratio after 28 days of curing. As can be seen from the figure that, the pores in sample C15 are about 20 nm at the most, the pores of C35 are mainly distributed at less than 10 nm, and the pores of C60 are about 100 nm. The experimental results show that with the increase of the content of kaolin, the pore size decreases first and then increases. When the content of kaolin is 35wt%, the pore size at this time is the smallest and all pores are gel pores.

Table 4: Porosity of the geopolymer

No.	Total Porosity (%)	Porosity of Pores at all levels (%)			
		r>200nm	50nm<r<200nm	20nm<r<50nm	r<20nm
C15	39.14	2.88	0.50	26.08	9.68
C35	18.38	2.31	0.58	0.45	15.04
C60	45.95	2.06	37.20	4.08	2.61

Some studies have shown that the size of pores in geopolymers has a direct relationship with the strength of the material. The porosity of this experiment is shown in Table (4). It can be seen from the table that the sample with the smallest total porosity is C35, which is a composite geopolymer containing 35wt% kaolin, the porosity for pores less than 20 nm is about 15%, indicating that a large amount of aluminosilicate gel is formed inside the geopolymer, and it has excellent chemical properties; in sample C15, more than 35% of the pores are harmless and less harmful, so there is little effect on the chemical properties; for sample C60, about 40% of the pores are harmful pores, which may be due to a higher water-cement ratio.

3.3 Effect of kaolin ratio on microscopic morphology of geopolymers

According to the experimental results of the pores, the SEM scan results of the samples C15 and C35 are shown in the following figure (2). Comparing the cross-section structure diagrams C and A of samples C15 and C35, we can see that the cross-section of sample C15 is significantly looser than that of sample C35, and there are significant cracks; this result may be due to the cracks caused by moisture evaporation and shrinkage during the curing drying process. Comparing figures B and D of the fly ash particles of two samples shows that the particles of sample C15 are more complete and the surface is covered by gel; the particles of sample C35 have partially broken and deformed, and there are tiny gel particles, more complete dissolution polymerization has occurred.

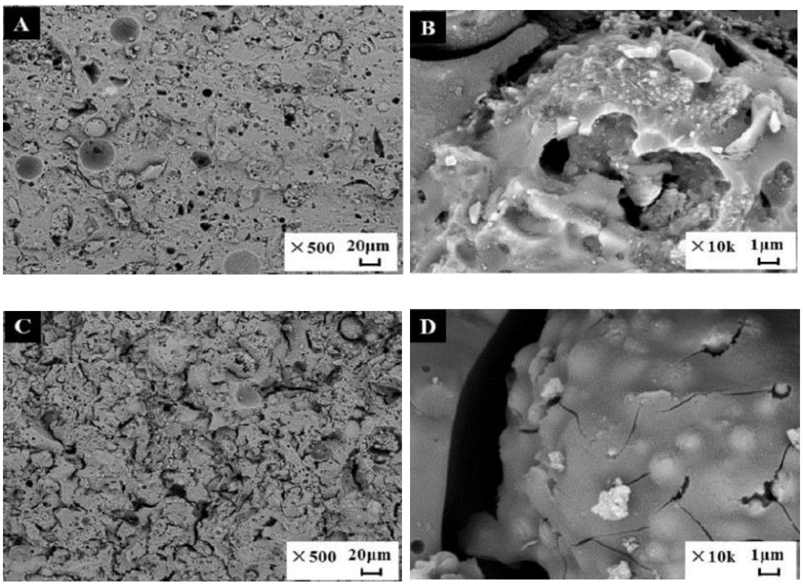

Figure 2: SEM diagrams of geopolymers (A: Sample C35X500, B: Sample C35X10K, C: Sample C15X500, D: Sample C15X10K)

3.4 Effect of kaolin ratio on corrosion resistance of geopolymers

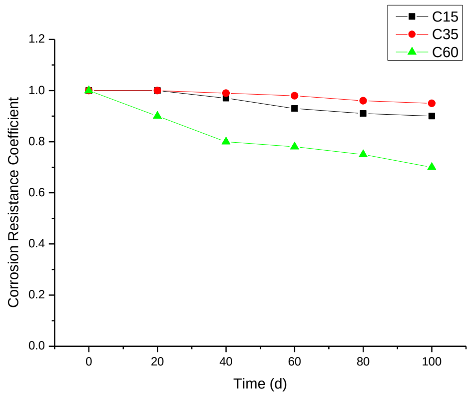

Figure 3: Relationship of corrosion resistance coefficient of samples with metakaolin dosage

The durability of geopolymers is related to the size and distribution of the pores inside the geopolymers, some corrosive media will enter the inside of the geopolymers through the pores and react with the geopolymers so as to cause damage. Through studying the corrosion resistance of kaolin with different ratios, we can research the relationship between corrosion resistance and the pore structure of geopolymers. Geopolymers with different ratios are subjected to standard curing for 28 days and then are immersed in a corrosive medium for corrosion resistance testing. The test results are shown in the following figure (3).
The experimental results find that the corrosion resistance and porosity of kaolin composite-based geopolymers are basically the same, and the pores in C15 and C35 are essentially harmless. After 100 days of soaking, the corrosion resistance coefficients can maintain above 0.90; however, due to the large pores of C60, corrosive substances enter the matrix, therefore, the corrosion resistance coefficient continues to decline, reaching about 0.75 after about 100 days.

4. Effect of curing conditions on the structure and chemical properties of composite-based geopolymers

The preparation process has a great influence on the structure and function of geopolymers. In this experiment, the following three curing methods in Table (5) are used to study the influence of processing conditions on the pore structure, microstructure, and corrosion resistance of geopolymers.

Table 5: Different curing condition

No.	Method
1#	Standard
2#	Standard 1Day + 60℃ Curing Condition
3#	60℃ Curing Condition

4.1 Effect of curing conditions on the pore structure of geopolymers

The pore size distribution of kaolin composite-based geopolymers after 28 days of curing under different curing conditions is shown in the following figure (4) and the pore size characteristics are shown in Table (6). The experimental results show that the pore diameters obtained under the three curing conditions are mainly harmless pores with diameter less than 20 nm, and the pores obtained by the curing method 2# are even smaller, this is because low temperature conditions are favorable for maintaining the structural order of geopolymers, in the process of 60°C curing at later period, there are more reaction products filled into the pores, and finally the porosity is greatly reduced. For the curing method 3# which adopted higher temperature in the initial stage, the structure of geopolymers is destroyed in the early stage, forming larger pores, which is also the direct cause of the increase of pores with diameters from 20 nm to 50 nm in the table. Overall, the effect of the change of three curing temperatures on the total porosity is not significant, all remain at about 36%.

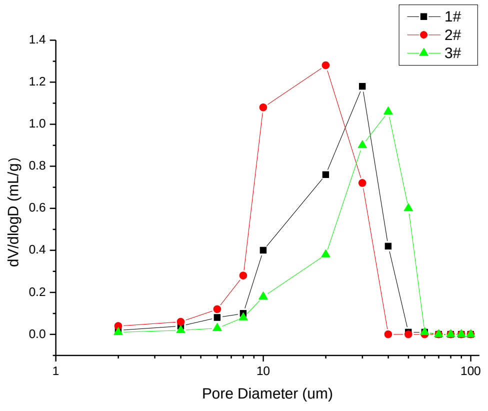

Figure 4: Pore size distribution of samples at different synthesis temperature

Table 6: Porosity of geopolymers cured 28d at different synthesis temperatures

No.	Total Porosity (%)	Porosity of Pores at all levels (%)			
		r>200nm	50nm<r<200nm	20nm<r<50nm	r<20nm
1#	35.39	1.27	0.18	0.32	33.62
2#	35.46	1.55	0.23	0.26	33.42
3#	36.86	1.67	0.14	6.40	28.65

4.2 Effect of curing conditions on microscopic morphology of geopolymers

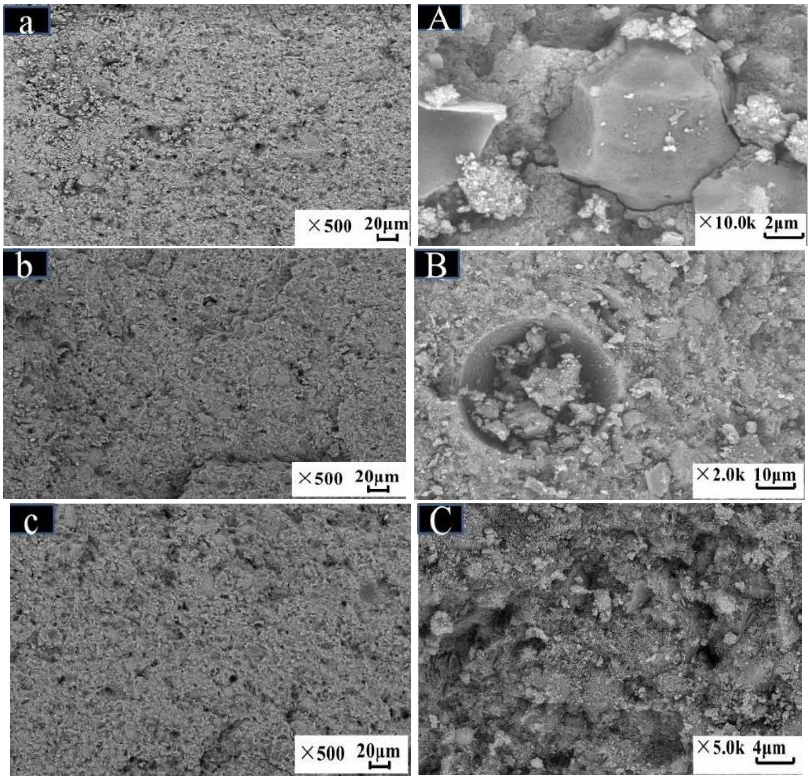

Figure 5: SEM diagrams of geopolymers prepared at different curing condition (a: 1#-28d, b: 2#-28d, c: 3#-28d, A: 1#-7d, B:2#-7d, C:3#-7d)

The cross-section topography of the three curing methods is shown in Figure (5) below, in which figures (A), (B), (C) and (a), (b), (c) are photos of the samples that are cured for 28d and 7d respectively. By observing the photos, we can see that, the air pores obtained under the three curing methods are relatively small and distributed uniformly, which is in agreement with the experimental results of porosity.
From Figure (A), it can be seen that there are still particles that didn't occur reaction in the sample under standard curing conditions, but there are no large pores, the polymerization reaction proceeds at a lower rate, undissolved particles can easily crack under the action of external forces, the force between the particles and the gel is relatively weak. In figure (B), under the second curing condition, it can be observed that the particles have fully dissolved and combined with the gel to form dense tissues, and the binding force between the tissues is also strong. Figure (C) shows unevenly distributed punching holes, and the structure of the gel phase is also loose, it might because the temperature is too high at early stage, the dissolution reaction occurs too fast and the silicon and aluminum in the particles are difficult to precipitate.

4.3 Effect of curing conditions on corrosion resistance of geopolymers

The experimental results show that the corrosion resistance of the three curing methods is similar, which is consistent with the results of the distribution of the internal pore size and structure of the three curing methods. Among them, the performance of the second curing method is better. It's because when adopting low-temperature curing in the early stage, the water content is sufficient, the alkali activator can fully contact and react with the powder material to produce precursor, and then the curing temperature is turned up to help accelerate the diffusion of particles within the geopolymers, so that the dissolution reaction continues and the particles inside the structure can form a new structural integrity, therefore it can improve the overall corrosion resistance of geopolymers.

5. Conclusion

This paper uses kaolin and fly ash as the main raw materials to prepare kaolin composite-based geopolymers, the structure and chemical properties of geopolymers were studied by the ratio of kaolin and the preparation process, the following conclusions are obtained:
(1) With the increase of kaolin amount added, the corrosion resistance of composite-based geopolymers increases first and then decreases, which is related to the large porosity within the geopolymers, the composite-based geopolymers with 35% kaolin content have the smallest total porosity, and most of the pores are harmless pores.
(2) Different low-temperature curing methods have little effect on the total porosity of the kaolin composite-based geopolymers, and the effect of corrosion resistance performance is similar. The anti-corrosion effect of 1d low-temperature standard curing and 60°C curing methods is better.

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