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Study on the Activity of Metakaolin Produced by Traditional Rotary Kiln in China

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Abstract: This paper analyzed the activity of coal-based metakaolin and non-coal-based metakaolin (ordinary metakaolin) commonly used in the Chinese market. The content of kaolin was detected by XPF. The phases of kaolin, metakaolin and corresponding alkali-excited reactants were detected by XRD. The contents of Al (IV), Al (V) and Al (VI) in kaolin and metakaolin were analyzed by ^{27}Al NMR. The micromorphology of kaolin and metakaolin were observed by SEM. The water-resistance of alkali-activated metakaolin was tested by immersion experiment. The results showed that a lot of corundum and quartz were present in the coal-based metakaolin, which was caused by over calcination. Furthermore, large amounts of sillimanite, quartz and cristobalite existed in ordinary metakaolin with a low content of amorphous aluminum silicate, which was caused by excessive impurities in the raw materials and over calcination. These crystalline substances could not react in an alkali solution, and their existence reduced the activity of the two metakaolins. Both of the two metakaolin production methods need to be improved to increase the activity.

Keywords: activity; metakaolin; kaolin; crystals; over calcination

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1. Introduction

Kaolin contains mainly mineral kaolinite and several impurities, such as quartz and dolomite. Kaolinite is a 1:1 layered silicate crystal; it is mainly composed of silicon-oxygen tetrahedron and aluminum hydroxide octahedron. Kaolinite hardly dissolves in acid solutions at low temperatures (<80 °C). In alkali solutions, silicon (Si) and aluminum (Al) will be released and then slowly dissolved [1]. Kaolinite shows a high activity only under high pressures and high temperatures [2]. In order to improve the activity of kaolin at room temperature, kaolin needs to be treated, and calcination is a common treatment. Calcined kaolin is generally called metakaolin. It is generally believed that 500–800 °C is the appropriate temperature for dehydroxylation of kaolinite [3,4]. In this process, the Al (VI) in kaolinite is transformed into Al (IV) and Al (V) to form amorphous aluminum silicate. When the high temperature is maintained continuously during the calcination process, spinel, mullite and other crystals will be generated. In this process, Al (IV) and Al (V) will be transformed into Al (VI) [4]. Metakaolin will rapidly dissolve and release Al and Si in strong alkali solutions and then produce geopolymer, zeolite, illite and other products according to the reaction environment (temperature, pressure, pH, etc.) [5,6]. Under the same environment, the activity of metakaolin is much higher than that of kaolin, which makes the application range of metakaolin more extensive [7,8]. The activity of metakaolin in this paper is not a concept with the pozzolanic activity of Portland cement [9]. Geopolymer is often considered as a new type of cement, so some characteristics of ordinary cement are often used to evaluate geopolymer, which includes pozzolanic activity. Pozzolanic activity of ordinary cement refers to the rate at which the oxides of silicon and aluminum in raw materials react with calcium oxide in water to form

hydrated calcium silicate and hydrated calcium aluminate. The activity of metakaolin refers to the rate at which the oxides of silicon and aluminum in raw materials dissolve (release Si and Al) under the action of alkali solution, and then dehydrate and polycondensate to form geopolymer, zeolite, etc. Although metakaolin has certain pozzolanic activity, and there seems to be some relationship between metakaolin activity and pozzolanic activity, pozzolanic activity is more proposed for Portland cement, while metakaolin activity in this paper is more targeted at geopolymers, zeolites, etc.

Kaolin in China is divided into coal-based kaolin and non-coal-based kaolin (ordinary kaolin), according to the source site. The coal-based kaolin, also known as coal gangue, is a solid waste discharged in the process of coal mining and coal washing, or an ore with lower carbon content and harder than coal near coal seams in the process of coal formation. The coal-based kaolin has been studied by some scholars in China [10,11]. There are many types of non-coal-based kaolin (ordinary kaolin), such as Chinese clay and ceramic clay. The ordinary kaolin is further classified into soft kaolin and sandy kaolin according to the content of sand (quartz, mica, feldspar, etc., with particle size >50 μm) in the material. The difference between them is that the sand content of the former is less than 50%, while that of the latter is more than 50%. Sandy kaolin needs to remove sand before it can be used to produce metakaolin. The sandy kaolin can be used to produce metakaolin only after removing the sand.

The main method of preparing metakaolin from kaolin is calcination by rotary kiln in China. The rotary kiln is a piece of traditional equipment to produce ordinary cement clinker. However, the composition, chemical and physical properties of ordinary cement clinker and metakaolin are different, and the reaction mechanism and performance characteristics of their corresponding products—cement and geopolymer—are also different. Some scholars have analyzed the activity of metakaolin from the aspects of exothermic peak temperature and exothermic time [9]. This article studied the activity of metakaolin obtained by traditional rotary kiln calcination in China from the perspective of the microstructure.

2. Materials and Methods

2.1. Materials

Kaolin and metakaolin: The 1250 mesh (10 μm) water-washed coal-based kaolin (Figure 1a) and the corresponding metakaolin obtained by rotary kiln calcination (650 °C~850 °C, 4 h) (Figure 1b) come from Gongyi, Henan Province, China. The 1250 mesh non-coal-based kaolin (ordinary kaolin) (Figure 2a) and the corresponding metakaolin obtained by rotary kiln calcination (650 °C~850 °C, 4 h) (Figure 2b) come from Datong, Shanxi Province, China. This kaolin and metakaolin from these two origins are very common in the Chinese market.



(**a**) (**b**)

Figure 1. Coal-based kaolin (**a**) and coal-based metakaolin (**b**).



(**a**) (**b**)

Figure 2. Ordinary kaolin (**a**) and ordinary metakaolin (**b**).

Alkali activator: the corresponding alkali solution was prepared by mixing sodium silicate solution with the module (Si/alkali metal) of 2.25 and density of 1.3 g/mL (20 °C), sodium hydroxide particles (purity ≥ 98%) and deionized water. The dosage of various materials (sodium silicate solution, sodium hydroxide particles and deionized water) was based on the compositions of the two metakaolin to balance the ratio of geopolymer gel. After configuration, the alkali activator was cooled for 6 h at 20 °C and 50% relative humidity (RH) by membrane (common plastic) covering [12,13].

2.2. Geopolymer Gel Preparation (20 °C, 50% Relative Humidity)

The geopolymer gel kept the Si/Al mole ratio (MR) at 2, Al/Na MR at 1 and H_2O/Na_2O MR at 15, because under this formula, high activity metakaolin is easy to form geopolymer with better performance after being excited by alkali [12,13]. The geopolymer gel was prepared by mixing metakaolin and the corresponding alkali solutions. These alkali solutions were used to balance the MR of Si/Al, Al/Na and H_2O/Na_2O due to the different composition of the two metakaolin. In the formulation, silicon (Si) came from metakaolin and sodium silicate solution, sodium (Na) came from sodium silicate solution and sodium hydroxide particles, aluminum (Al) came from metakaolin and hydrogen (H) came from sodium silicate solution, sodium hydroxide particles and deionized water.

2.3. Samples Preparation

The geopolymer gel was added to the 5 × 5 × 5 cm cube mold, and then the mold with film covering was put in the oven at 60 °C [14]. The sample was obtained from the mold after being cured for 7 days.

2.4. Chemical Detection

Methods: All materials used for X-ray fluorescence spectrometer (XRF, Axios, Panalytical, Almelo, The Netherlands), X-ray diffraction (XRD, D8 Advance, Bruker, Karlsruhe, Germany), nuclear magnetic resonance (NMR, AVANCE III HD 400, Bruker, Zurich, Switzerland) and scanning electron microscopy (SEM, Zeiss SIGMA, Carl ZEISS, Cambridge, UK) were in powder state. The powders of kaolin and metakaolin were obtained from raw materials, and the alkali-activated metakaolin powder was obtained from the cubic sample by grinding. XRF with a maximum voltage of 30 kV and a maximum current of 1mA was used to detect the element and oxide content of coal-based kaolin and ordinary kaolin powder. XRD (Cu Kα radiation under a voltage of 40 kV and a current of 30 mA) was used to detect the phase of kaolin, metakaolin and alkali-activated metakaolin, and the software

TOPUS (version 4.2) was used for the analysis of XRD patterns based on Rietveld analysis. The NMR of ^{27}Al with a spinning speed of 12 kHz was used to analyze the content of Al (IV), Al (V) and Al (VI) in kaolin, metakaolin and alkali-activated metakaolin. The SEM was used to observe the micromorphology of kaolin and metakaolin.

2.5. Immersion Test

The immersion test was used to detect the water-resistance of alkali-activated metakaolin. The cubic sample made of alkali-activated metakaolin was immersed in water for 10 days, and the morphological changes of the sample and the color changes of water were observed at this stage.

3. Results

The content of iron oxides in coal-based kaolin were much higher than that in ordinary kaolin, as shown in Table 1. After calcination in 650–850 °C, the organic matter mainly composed of carbon and hydrogen in kaolin disappeared, but the total amount of metal elements would not change. The content of iron in coal-based kaolin accounted for about 6.5%, which was an important reason for the red color of coal-based kaolin and metakaolin (Figure 1a,b). The lower iron oxide content caused the color of ordinary kaolin and metakaolin to be white rather than red (Figure 2a,b). Therefore, without any treatment, there was no essential difference in the color of the same type of kaolin and metakaolin.

Table 1. Composition of coal-based kaolin and ordinary kaolin (by XRF).

Coal-Based Kaolin				Ordinary Kaolin			
Element	**Conc**	**Compound**	**Conc**	**Element**	**Conc**	**Compound**	**Conc**
Si	49.268%	SiO_2	49.088%	Si	57.432%	SiO_2	52.815%
Al	37.751%	Al_2O_3	44.144%	Al	38.724%	Al_2O_3	45.355%
Fe	6.500%	Fe_2O_3	3.136%	Ti	1.308%	TiO_2	0.704%
Ti	3.581%	TiO_2	2.181%	Fe	1.060%	Fe_2O_3	0.473%
Ca	0.990%	CaO	0.523%	K	0.665%	K_2O	0.265%
K	0.931%	K_2O	0.424%	Ca	0.444%	CaO	0.201%
Cl	0.243%	Cl	0.094%	Zr	0.106%	ZrO_2	0.044%
Zr	0.212%	SO_3	0.089%	Cl	0.039%	SO_3	0.034%
V	0.114%	ZrO_2	0.084%	S	0.035%	V_2O_5	0.026%
S	0.093%	V_2O_5	0.077%	V	0.030%	Cl	0.014%
Sr	0.077%	P_2O_5	0.053%	Cr	0.029%	CuO	0.014%
Cr	0.069%	Cr_2O_3	0.031%	Zn	0.023%	ZnO	0.009%
P	0.067%	SrO	0.028%	Sr	0.021%	Cr_2O_3	0.008%
Ga	0.024%	Ga_2O_3	0.010%	Pb	0.019%	Ga_2O_3	0.008%
Nb	0.019%	MnO	0.008%	Ga	0.018%	MnO	0.007%
Th	0.018%	NbO	0.007%	Mn	0.017%	SrO	0.007%
Mn	0.017%	Y_2O_3	0.006%	Cu	0.013%	PbO	0.007%
Y	0.014%	ThO_2	0.006%	Nb	0.010%	NbO	0.006%
Ni	0.008%	NiO	0.006%	Y	0.007%	Y_2O_3	0.003%
Cu	0.004%	CuO	0.005%				

3.1. Coal-Based Metakaolin Activity

In coal-based water-washed kaolin, the main crystals were quartz (3.6%), kaolinite (82.9%) and dolomite (2.8%) (Figure 3a). The main components of kaolin after calcination are quartz (25.1%), sillimanite (2.7%), corundum (30.9%) and amorphous materials (41.3%) (Figure 3b). The amorphous materials in Figure 3b contained amorphous aluminum silicate obtained by the calcination of kaolinite and the amorphous substances in raw material (kaolin). The quartz crystal detected in Figure 3b contained quartz impurities before kaolin calcination and new quartz generated during calcination. When kaolin was calcined at the temperature of 650–850 °C in the rotary kiln for about 4 h, the sillimanite does not further form mullite and other crystals; the temperature for the formation of mullite crystals usually needs to be more than 1000 °C [15]. Corundum crystals in coal-based metakaolin

mainly exist in the form of γ-Al_2O_3, and when the temperature is further increased, it would be converted into α-Al_2O_3 on the structure of γ-Al_2O_3.

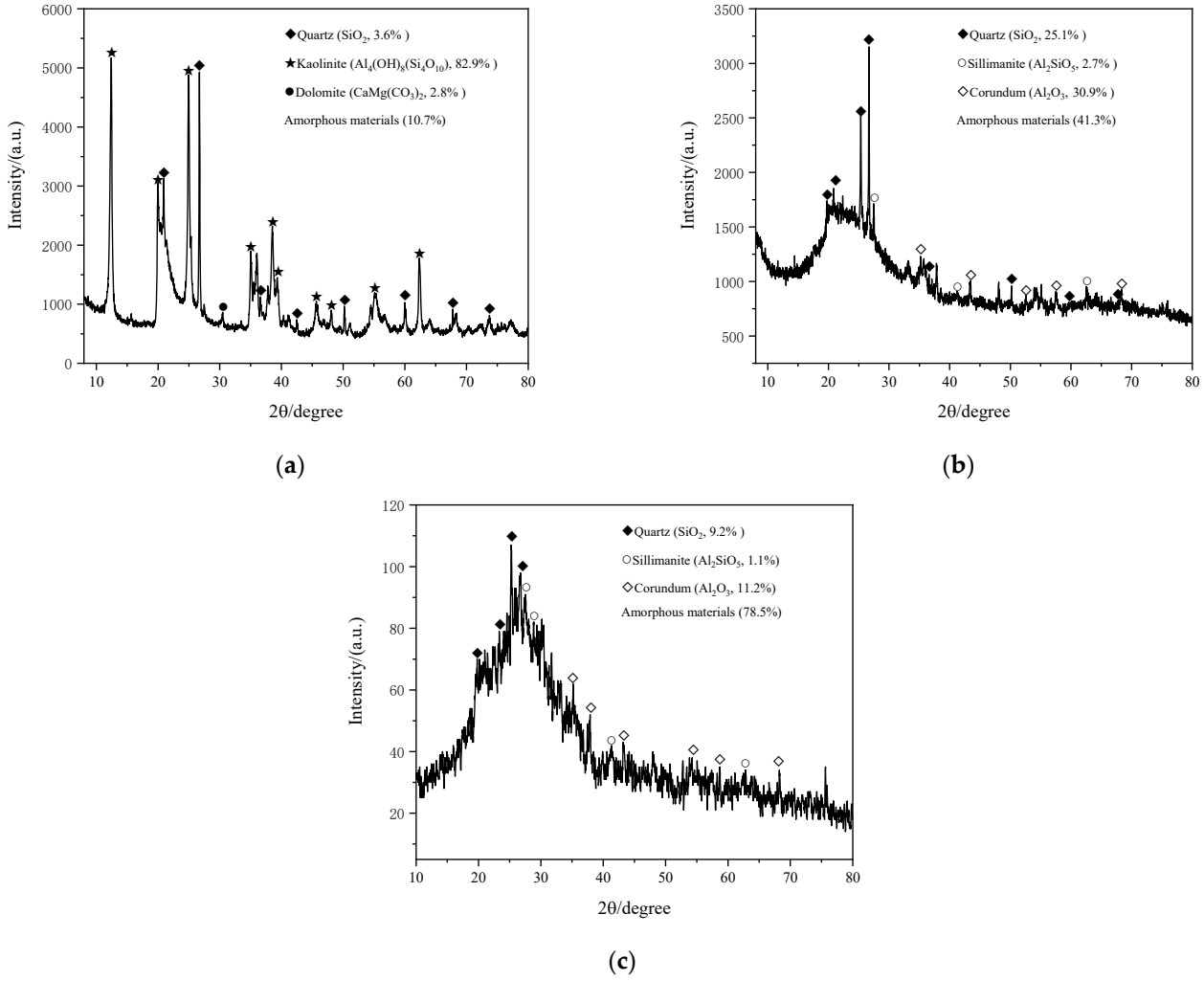


Figure 3. XRD of coal-based kaolin (**a**), metakaolin (**b**) and alkali-activated metakaolin (**c**).

According to previous studies, the chemical shift of four-coordinated aluminum (Al (IV)) in silicon aluminum compounds is at 50 ± 20 ppm [16,17]. With respect to Al $(H_2O)_6^{3+}$, the chemical shift of five-coordinated aluminum (Al (V)) is at 30 ± 10 ppm, and the six-coordinated aluminum (Al (VI)) is at 0 ± 15 ppm [18,19]. Before calcination of coal-based kaolin, aluminum (Al) mainly existed in kaolinite crystals in the form of Al (VI) with a chemical shift of 2.55 ppm (Figure 4a) because kaolinite ($Al_4(OH)_8(Si_4O_{10})$ accounted for the most (82.9%) while no aluminum existed in quartz (SiO_2) and dolomite ($CaMg(CO_3)_2$) (Figure 3a). Figure 5a shows a typical layered structure of kaolinite. In the NMR of coal-based metakaolin, there was the main peak at 13.1 ppm, and a small peak at 5.44 ppm (Figure 4b), which proved that after calcination, most of the aluminum still existed in the form of Al (VI) (Figure 4b), and the mineral composed of Al (VI) here was no longer kaolinite, but sillimanite and corundum crystals and amorphous aluminum silicate. The content of corundum crystal was much higher than that of sillimanite because Al in sillimanite usually exists in the form of Al (VI) and Al (IV) at the same time, while the Al detected in Figure 4b was still dominated by Al (VI); this was also verified by the quantitative analysis of XRD in Figure 3b (2.7% sillimanite and 30.9% corundum). Figure 5b shows that after calcination, the obvious layered structure of kaolin had been destroyed and replaced by the disordered scale-like arrangement structure.

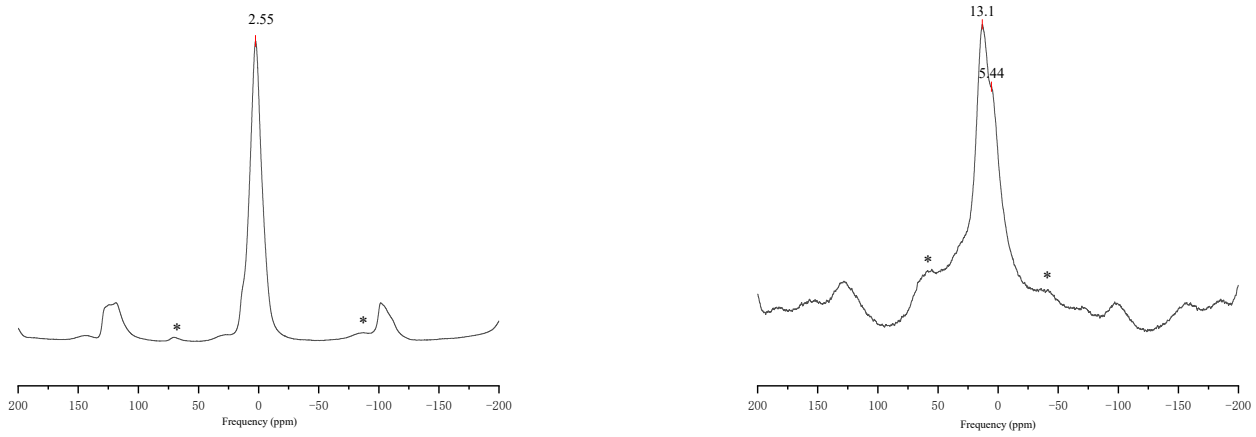


Figure 4. ^{27}Al NMR of coal-based kaolin (**a**) and metakaolin (**b**). * indicates rotational bands.

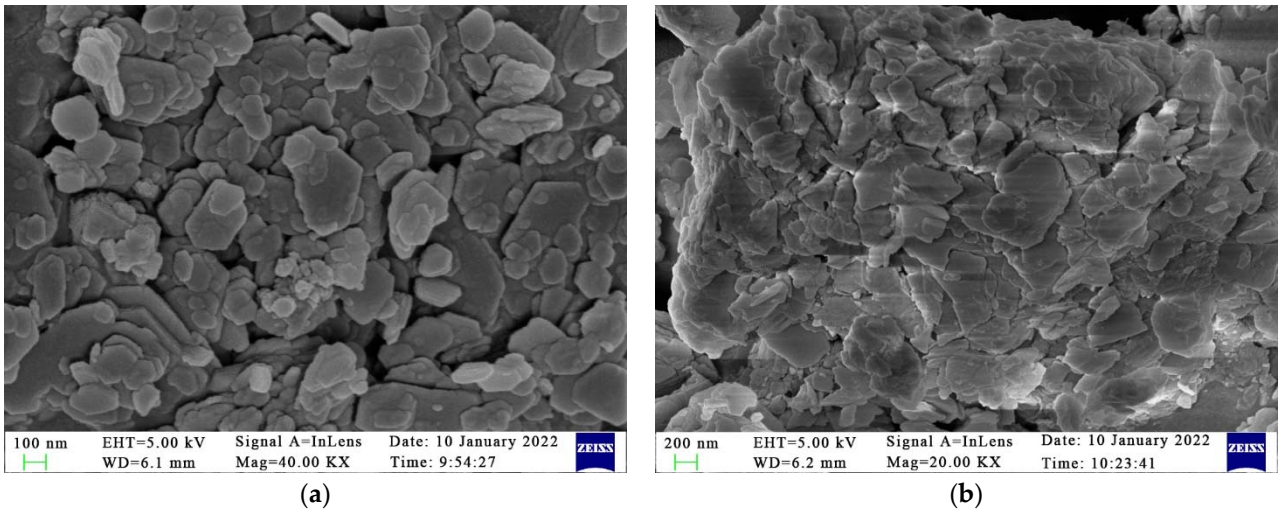


Figure 5. SEM of coal-based kaolin (**a**) and metakaolin (**b**).

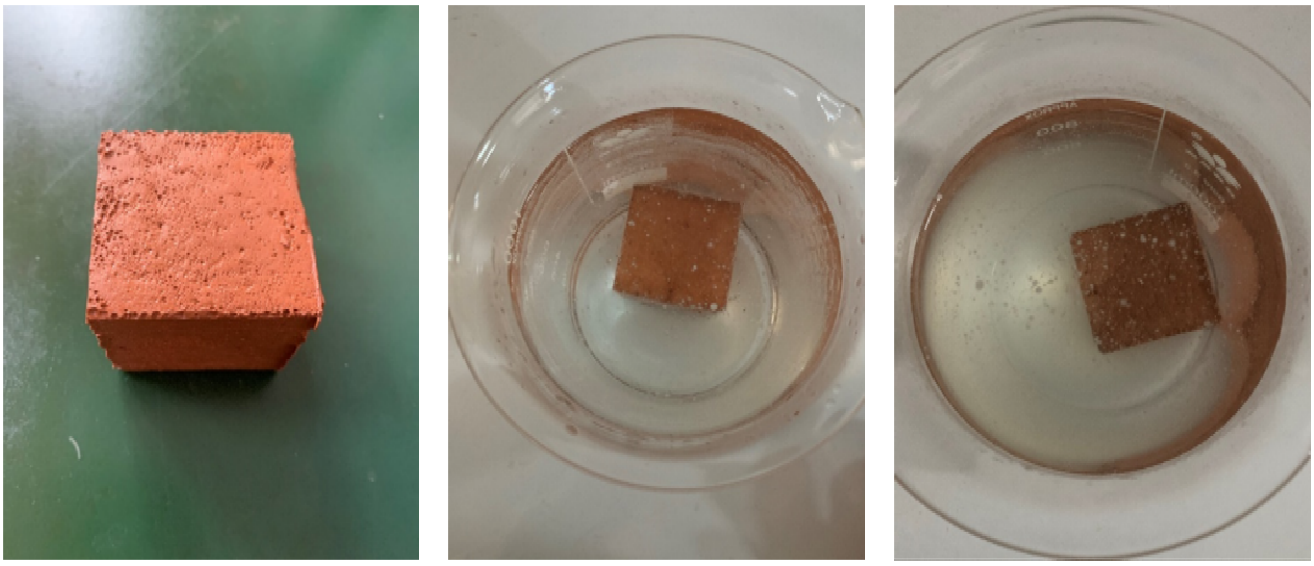
In this experiment, the main reaction process of calcining coal-based kaolin to metakaolin was inferred as "coal-based kaolin reaction (CKR) (1), (2) and (3)", and the form of aluminum was indicated in parentheses after the substance (if aluminum was included). First, kaolinite in kaolin was decomposed at 650–850 °C to form amorphous aluminum silicate (AAS) containing Al (IV), Al (V) and Al (VI) (CKR 1). With the prolongation of heating time, Al (IV) and Al (V) in AAS disappeared, while quartz and the new AAS, mainly containing Al (VI), formed (CKR 2), and the morphological changes of aluminum (from Al (IV), Al (V), and Al (VI) to Al (VI)) in AAS were inferred according to previous studies that Al (IV) and Al (V) decreased while the Al (VI) increased in an over-calcination environment (high temperature or continuous heating) [4,19]. Another result of over calcination was that a part of the new AAS was decomposed to form corundum and quartz under continuous high temperature (CKR3).

$$\underset{Kaolinite\ (\mathrm{Al\ (VI)})}{Al_2O_3.2SiO_2.4H_2O} \xrightarrow{650\ ℃\sim850\ ℃} \underset{AAS\ (\mathrm{Al\ (IV), Al\ (V), Al(VI)})}{Al_2O_3.2SiO_2.nH_2O} + 4H_2O \qquad \text{CKR (1)}$$

$$\underset{AAS\ (\mathrm{Al\ (IV), Al\ (V), Al(VI)})}{Al_2O_3.2SiO_2} \xrightarrow{650\ ℃\sim850\ ℃\ (over\ calcination)} \underset{Quartz}{xSiO_2} + \underset{AAS\ (\mathrm{Al(VI)})}{Al_2O_3(2-x)SiO_2} \qquad \text{CKR (2)}$$

$$\underset{AAS\ (Al(VI))}{Al_2O_3.(2-x)SiO_2} \xrightarrow{650\ ℃ \sim 850\ ℃\ (over\ calcination)} \underset{Corundum\ (Al\ (VI))}{Al_2O_3} + \underset{Quartz}{(2-x)SiO_2} \quad \text{CKR (3)}$$

The activity of metakaolin depended on the content of amorphous materials produced by kaolin during calcination. If many crystals appear in the calcination process, the activity of metakaolin will be greatly negatively affected; because these crystals are difficult to dissolve and release Si and Al under the action of alkali activator at room temperature and normal pressure [1,19,20]. In most cases, these crystals do not participate in the reaction between metakaolin and the alkali activator. When the amorphous material is dissolved, depolymerized and polycondensated under the action of the alkali activator to form the geopolymer, these crystals are fused with geopolymer in a very independent form. The qualitative analysis of substances in alkali-activated metakaolin (Figure 3c) was based on the presence of crystals containing quartz, sillimanite and corundum. These crystals existed in metakaolin before the reaction, and they did not participate in the reaction in the alkali solution but were mixed with the reactant. As the reactant solidified, these crystals interacted with the reactant in the form of van der Waals force and hydrogen bond. When the solidified product encountered water again, the geopolymer composed of silicon-oxygen and aluminum oxygen tetrahedron obtained by polymerization would not dissolve in water due to its strong chemical bonds, but the geopolymer would separate from the crystals because the geopolymer and the crystals were connected by intermolecular forces. The destruction of intermolecular forces in water would negatively affect the water stability of the overall structure of the solidified product. Figure 6a shows the specimen before the immersion test. Figure 6b shows the specimen after immersion for 3 days, and Figure 6c shows the specimen after immersion for 10 days. The color of the liquid used for soaking has changed significantly, and some substances were separated from the test block.



(**a**) (**b**) (**c**)

Figure 6. Alkali-activated coal-based metakaolin specimen before immersion (**a**), after immersion for 3 days (**b**) and 10 days (**c**).

The aluminum in coal-based metakaolin mainly exists in the form of Al (VI), which was different from that in highly active metakaolin studied by some scholars [21]. Generally, in highly active metakaolin, Al exists in the form of Al (IV), Al (V) and Al (VI), and the content of Al (V) is higher than that of Al (IV) and Al (VI). The content of Al (V) can reflect the activity of metakaolin to a certain extent [4]. Obviously, the activity of coal-based kaolin in this experiment is low. However, the XRD pattern of the reactants (Figure 3c) shows

that there was a wide broad peak (diffuse peak) between 20 and 40 degrees (2θ), which is larger than the broad peak (Figure 3b) between 20 and 30 degrees (2θ) before reaction, indicating that the crystallinity of the material turned worse, meaning the coal-based metakaolin still generated geopolymer under the action of the alkali activator, and the increased content of amorphous materials (78.5%) in Figure 3c proved this. Moreover, in addition to the amorphous geopolymer, the content of amorphous materials in Figure 3c also contained unreacted amorphous substances in the mixed solution of metakaolin and the alkali activator. Therefore, the content of geopolymer could be reflected by amorphous materials to some extent but it was not the entire amorphous materials.

In this experiment, the low activity of coal-based metakaolin was caused by over calcination, which was different from the formation reason of low-activity metakaolin analyzed by some scholars before [19,22]. In previous studies, the formation reason of low-activity metakaolin was that kaolin was calcined in a high-vapor-pressure environment in a rotary kiln, and the hydroxylation of kaolin was not complete so that the layered structure of most kaolin itself was not damaged. At low temperature and normal pressure (<80 °C), the solubility of kaolin in strong alkali is much lower than that of metakaolin in the same environment [1]. Kaolin reacts layer by layer by releasing Si and Al in strong alkali. The reaction speed is slow, and the products are illite, zeolite and aluminosilicate (metastable mesophase of potassium feldspar), not the geopolymer composed of silica tetrahedron and alumina tetrahedron. In this case, the activity of metakaolin was reduced. The low activity of metakaolin in previous studies and this study were both due to the existence of many crystals and the low content of amorphous aluminum silicate in metakaolin. However, the reason for the formation of low-activity metakaolin in previous studies was incomplete calcination, and in this study, the formation reason for low-activity metakaolin was excessive calcination.

3.2. Ordinary Metakaolin Activity

In ordinary kaolin, there were mainly crystals such as quartz (23.8%), kaolinite (17.3%), illite (21.2%) and pyrophyllite (31.5%) (Figure 7a). During the calcination process, the content of kaolinite was greatly reduced, and at the same time, illite and pyrophyllite were decomposed, resulting in the formation of some new crystals, such as sillimanite (54.3%), and a small number of amorphous materials (8.9%) (Figure 7b). Compared with coal-based metakaolin, amorphous aluminum materials in ordinary metakaolin were lower. The XRD of ordinary metakaolin had almost no broad peaks (Figure 7b), while the coal-based metakaolin had an obvious broad peak between 20 and 30 degrees (2θ) (Figure 3b). Different from coal-based kaolin, ordinary kaolin had a higher quartz content (23.8%). The mass proportion of quartz decreased after calcination, probably because part of the quartz was converted to cristobalite. The composition of ordinary metakaolin was also very different from that of coal-based metakaolin. The ordinary metakaolin formed more sillimanite (54.3%), and the content of sillimanite in ordinary metakaolin was the most abundant of all crystals (Figure 7b).

On the NMR of metakaolin, peaks were found at 61.4, 46.6, 10.6 and 2.5 ppm (Figure 8b). The first two corresponded to Al (IV) and the last two corresponded to Al (VI). The simultaneous presence of Al (IV) and Al (VI) was an important feature of sillimanite, while the aluminum in kaolin before calcining was mainly in the form of Al (VI) (Figure 8a) existing in minerals containing kaolinite, illite and pyrophyllite (Figure 7a). In this experiment, in addition to kaolinite (17.3%), the crystals in ordinary kaolin also included quartz (23.8%), illite (21.2%) and pyrophyllite (31.5%). Figure 9a shows the flaky illite with needle-like tips in kaolin, which was quite different from the kaolinite in microstructures (Figure 5a); the morphology of calcined ordinary kaolin had changed greatly (Figure 9b). In addition, at the calcination temperature of 650–850 °C, coal-based kaolin was more inclined to form crystals composed of Al or Si alone, such as corundum and low-temperature quartz. While in the crystals of calcined ordinary kaolin, aluminum and silicon often existed in a composite

form, such as sillimanite. This was related to the types of chemical substances and element contents in raw materials, which needs to be further explored.

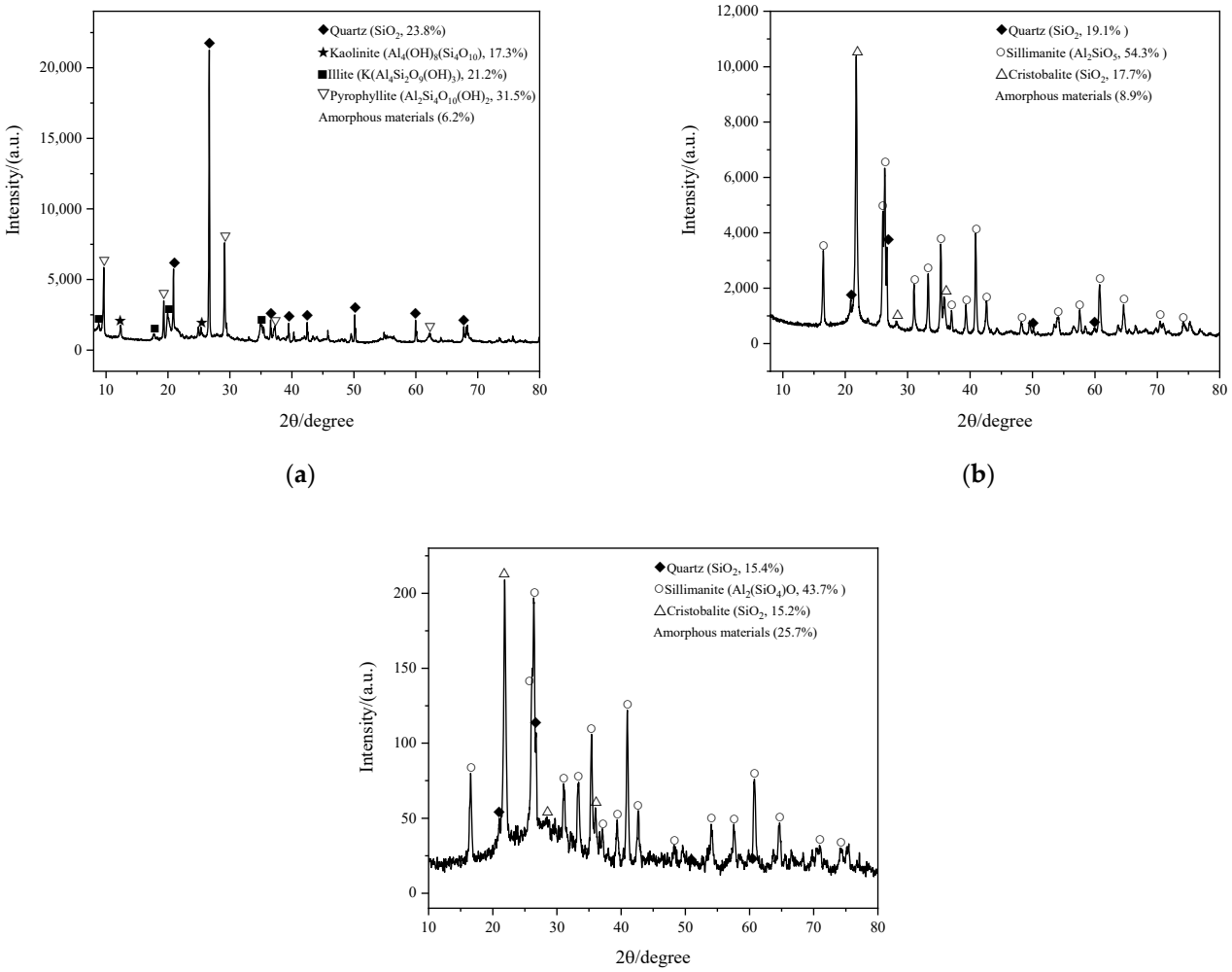


Figure 7. XRD of ordinary kaolin (**a**), metakaolin (**b**) and alkali-activated metakaolin (**c**).

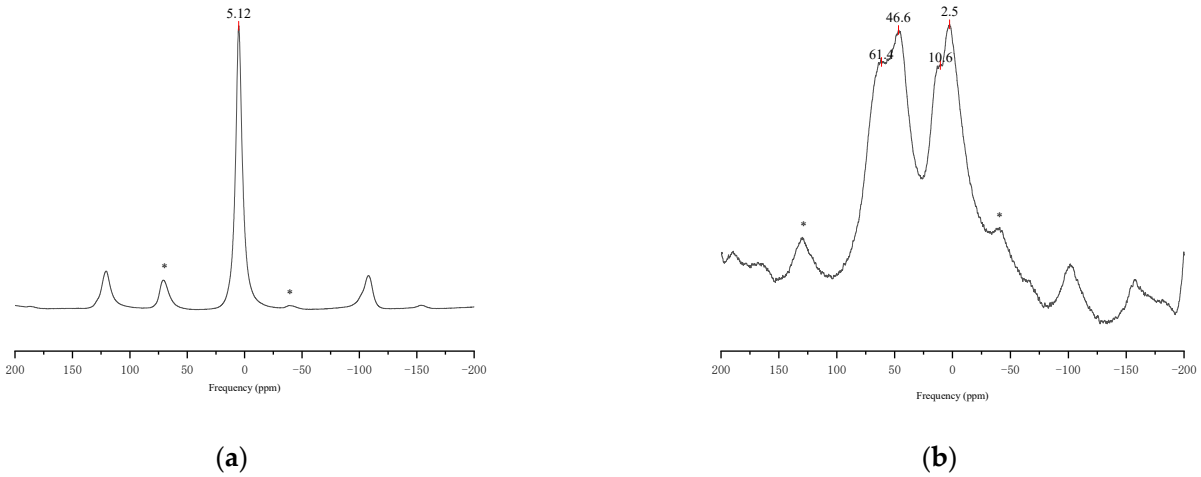
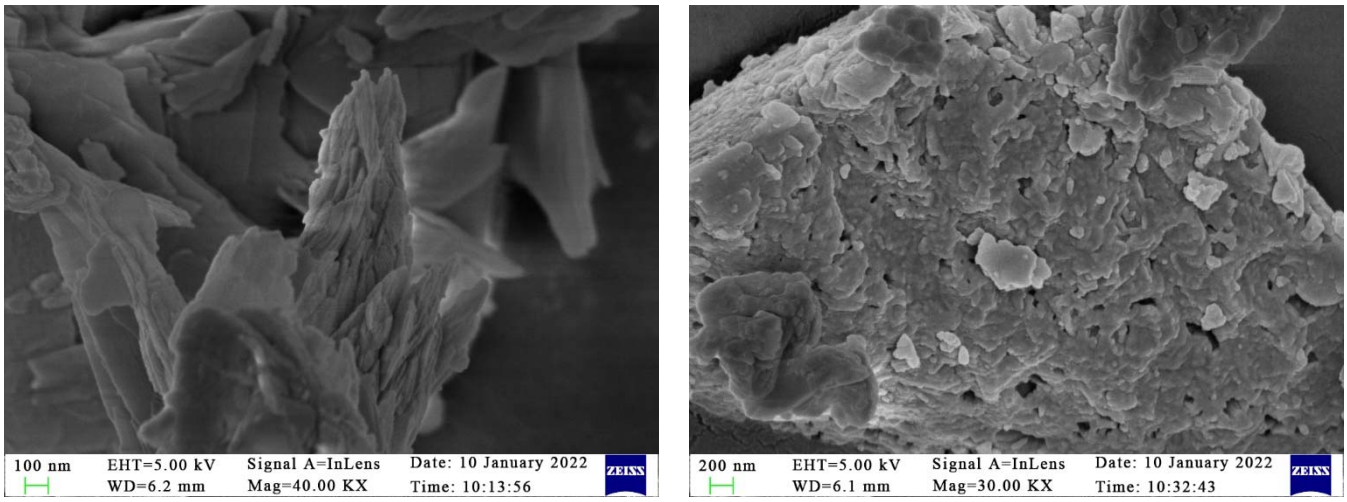


Figure 8. ^{27}Al NMR of ordinary kaolin (**a**) and metakaolin (**b**). * indicates rotational bands.



(**a**) (**b**)

Figure 9. SEM of ordinary kaolin (**a**) and metakaolin (**b**).

The main reaction process of calcining ordinary kaolin to metakaolin in this experiment was inferred as "ordinary kaolin reaction (OKR) (4), (5), (6), (7), and (8)" (the form of aluminum was indicated in parentheses after the substance (if aluminum was included)). The pyrophyllite was the most abundant in ordinary kaolin, which was decomposed into sillimanite and quartz at 650–850 °C (OKR 4). In the initial stage of calcination, illite and kaolinite were also decomposed, and the former mainly formed sillimanite (OKR 5) and the latter formed amorphous aluminum silicate (AAS) (OKR 6). With the extension of heating time, ordinary kaolin might also have similar consequences produced by over calcination, such as coal-based kaolin, because although the kaolinite content (17.3%) was relatively low, if no over calcination existed, Al (V) might be detected on the NMR spectrum and the content of amorphous materials might increase obviously rather than the small change from 6.2% (Figure 7a) to 8.9% (Figure 7b), and in addition, the appearance of cristobalite from the conversion of quartz at 650–850 °C proved the existence of over calcination. In OKR 7, Al (IV) and Al (V) in AAS converted to Al (VI), accompanied by the formation of quartz. In the process of over calcination, a part of the quartz (mainly from raw materials before calcination, calcined pyrophyllite and kaolinite) transformed to cristobalite (OKR 8).

$$\underset{Pyrophyllite\ (Al\ (VI))}{Al_2O_3.4SiO_2.H_2O} \xrightarrow{650\ ℃ \sim 850\ ℃} \underset{Sillimanite\ (Al\ (IV), Al(VI))}{Al_2O_3.SiO_2} + \underset{Quartz}{3SiO_2} + H_2O \quad \text{OKR (4)}$$

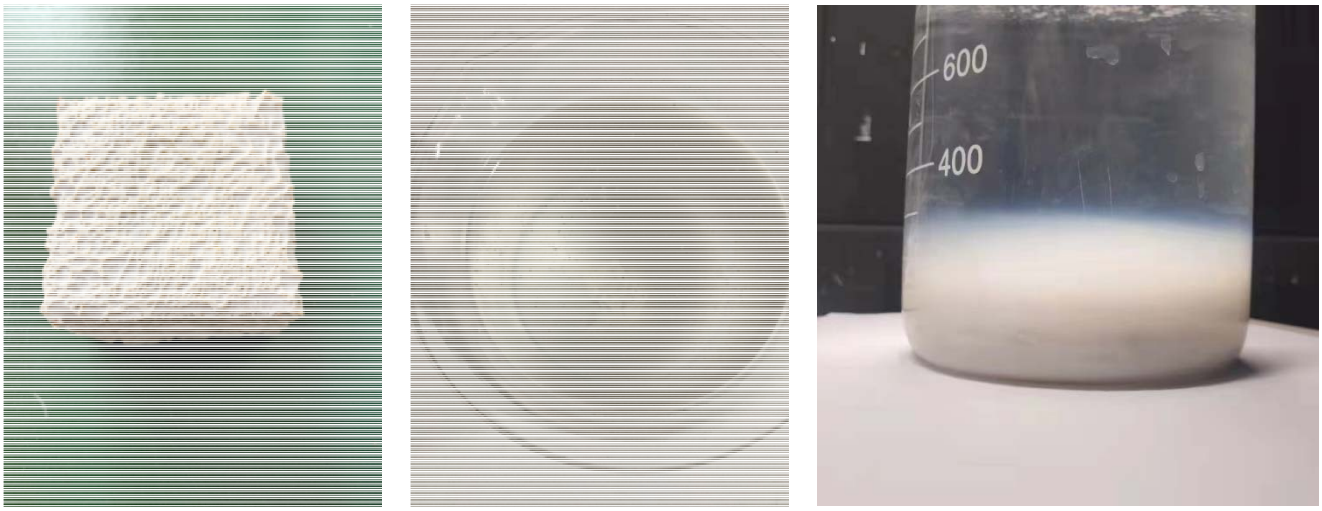
$$\underset{Illite\ (Al\ (VI))}{2K(Al_4OSi_2O_9(OH)_3)} \xrightarrow{650\ ℃ \sim 850\ ℃} K_2O + \underset{Sillimanite\ (Al\ (IV), Al(VI))}{4Al_2O_3.SiO_2} + 3H_2O \quad \text{OKR (5)}$$

$$\underset{Kaolinite\ (Al\ (VI))}{Al_2O_3.2SiO_2.4H_2O} \xrightarrow{650\ ℃ \sim 850\ ℃} \underset{AAS\ (Al\ (IV), Al\ (V), Al(VI))}{Al_2O_3.2SiO_2.nH_2O} + 4H_2O \quad \text{OKR (6)}$$

$$\underset{AAS\ (Al\ (IV), Al\ (V), Al(VI))}{Al_2O_3.2SiO_2} \xrightarrow{650\ ℃ \sim 850\ ℃\ (over\ calcination)} \underset{Quartz}{xSiO_2} + \underset{AAS\ (Al(VI))}{Al_2O_3(2-x)SiO_2} \quad \text{OKR (7)}$$

$$\underset{Quartz}{SiO_2} \xrightarrow{650\ ℃ \sim 850\ ℃\ (over\ calcination)} \underset{Cristobalite}{SiO_2} \quad \text{OKR (8)}$$

The activity of ordinary metakaolin was significantly lower than that of coal-based metakaolin in this experiment. Figure 7b shows that there was an unobvious broad peak from 20 to 35 degrees (2θ), indicating that the ordinary metakaolin had polymerized in alkali solution, but the amount of geopolymer generated was not much. The amplitude of the broad peak can reflect the content of amorphous materials (containing AAS obtained by calcination of kaolinite and amorphous substances in raw materials) to a certain extent. Compared with the coal-based metakaolin having more amorphous materials (41.4%) (Figure 3b), the amorphous materials content (8.9%) of ordinary metakaolin was much lower (Figure 7b). At room temperature, the amount of geopolymer formed by metakaolin after alkali excitation mainly depended on the content of amorphous materials in metakaolin before reaction. The formation of the geopolymer could be understood as the dissolution, depolymerization, dehydration and polycondensation of amorphous materials. The existence of too many crystals will directly reduce the activity of metakaolin because, at room temperature, the solubility of crystals composed of aluminum and silicate (such as kaolinite and sillimanite) in the alkali solution was very low, which would negatively affect the subsequent depolymerization and polycondensation reactions. After immersion in water for 3 days, the specimen (Figure 10a) made of ordinary metakaolin after alkali excitation had obvious structural damage (Figure 10b). After 10 days of immersion in water, the specimen was almost destroyed. Viewed from the side, the white pastes insoluble in water were dispersed at the bottom of the beaker (Figure 10c).



(**a**) (**b**) (**c**)

Figure 10. Alkali-activated ordinary metakaolin specimen before immersion (**a**), after immersion for 3 days (**b**) and 10 days (**c**).

The nuclear magnetic resonance spectrum of aluminum in typical high activity metakaolin shows a trident shape, and each peak corresponds to aluminum with different coordination bonds [20]. The Al in ordinary metakaolin in this experiment mainly existed in the form of Al (IV) and Al (VI) (Figure 8b). Although the broad peak of ordinary metakaolin after alkali excitation (Figure 7c) was slightly enlarged relative to that before alkali excitation (Figure 7b), the extent of polymerization was still very limited, and in addition, the broad peak might also be partly caused by unreacted amorphous substances in the mixed solution of metakaolin and alkali activator. Compared with coal-based metakaolin in this experiment, the activity of ordinary metakaolin was lower. Like the problems existing in the production of coal-based metakaolin, excessive calcination was also an important reason for the low activity of ordinary metakaolin (OKR 4). The crystals (such as sillimanite and cristobalite) generated in the calcination process were not only difficult to dissolve, depolymerize and polycondensate in the alkali solution but also hindered the ion exchange of amorphous aluminum silicate in the alkali solution and further reduced the activity of metakaolin. However, another reason

for the low activity of ordinary metakaolin was the low content of kaolinite in raw materials. Compared with the XRD of coal-based kaolin (Figure 3a), the signal of kaolinite in ordinary kaolin was not obvious (Figure 7a), while the proportion of quartz, illite and pyrophyllite in ordinary kaolin was also larger than that of kaolinite. Pyrophyllite, illite and quartz are more difficult to form amorphous substances than kaolinite when calcined in a rotary kiln (650–850 °C), and usually, they need to be treated by special mechanical or physical methods before being used as geopolymer raw materials [19]. Due to the higher content of kaolinite in coal-based kaolin, more AAS was generated after calcination, and this is an important reason why ordinary metakaolin had lower activity than coal-based metakaolin.

4. Conclusions

In this paper, the activity analysis of two types of metakaolin commonly used in the Chinese market was carried out by XRF, XRD, ^{27}Al NMR and immersion test. The conclusions are as follows:

(1) The kaolinite accounted for a large proportion of coal-based kaolin, and the product of coal-based kaolin calcined in a rotary kiln was mainly amorphous aluminum silicate. Due to the over calcination of kaolin, aluminum in amorphous aluminum silicate mainly existed in the form of Al (VI). Some quartz and corundum were also formed in this calcination process, and they did not participate in the reaction of metakaolin and alkali activators to form geopolymer. When the mixture of coal-based metakaolin and alkali activator hardens after reacting, these crystals and geopolymer are connected by intermolecular forces, and upon encountering water, the crystals and geopolymer separated as intermolecular forces broke.

(2) Low kaolinite purity and over calcination were two negative effects on the activity of ordinary metakaolin. The pyrophyllite and illite in ordinary metakaolin were difficult to produce amorphous substances that could be used as geopolymer raw materials in a traditional rotary kiln. Their calcination led to excessive sillimanite and cristobalite, which were difficult to react in an alkali solution at room temperature; over calcination further reduced the content of amorphous substances in the reaction products. The geopolymer content in the hardened mixture after the reaction of ordinary metakaolin and alkali activator was very small. When encountering water, the whole mixture was quickly destroyed with the break of intermolecular force.

Both coal-based and ordinary metakaolin need to avoid over calcination to reduce the production of crystals. For ordinary kaolin, raw materials need to be further purified or pretreated for pyrophyllite and illite in order to generate more amorphous substances in the calcination process and improve the activity as geopolymer raw materials.

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