Reaction mechanism of metakaolin materials prepared by calcining coal gangue

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Abstract

Metakaolin-based auxiliary cementitious materials fabricated by coal gangue were achieved. The temperature and time required for the preparation of metakaolin materials from the calcination of coal gangue were optimized based on the analysis of the reaction characteristics and kinetics during the calcination of coal gangue. The phase, microstructures, and activity analysis of the products were performed, and the effect of calcination conditions on the activity of the product was ascertained. The results of thermal analysis-infrared spectra combined experiments indicated that the dehydroxylation of kaolinite was a one-step reaction during the calcination of coal gangue within a temperature range of 379.8°C–737.3°C. According to the General Integration, Flynn-Wall-Ozawa and Kissinger methods, the activation energy $E$ of dehydroxylation of kaolinite is 181.62 kJ·mol$^{-1}$ and pre-index factor $A$ is $10^{9.27}$ s$^{-1}$ for calculating the calcination time of metakaolin. The experimental results show that high-activity metakaolin products, that with a dissolution rate of 64.79–71.57 wt% of activated alumina and with an effective dissolution rate of 68.82–94.35 wt% of activated silica, are prepared under the condition of calcination for 15 min and the temperature of 700°C–825°C. The kinetic model simulation results for the calcination time at different temperatures correspond to the experimental results.

1. Introduction

Coal resources play a vital role in the current energy supply worldwide, especially in China [1]. As a solid waste generated during coal mining and coal washing, coal gangue production is enormous, accounting for about 10%–15% of coal production [2]. In China alone, the output of raw coal was 3.97 billion tons, and the emission of coal gangue was 380 million tons in 2019 [3]. The total amount of coal gangue was stockpiled as high as up to 7 billion tons [4]. However, the utilization rate of coal gangue in China is about 20%. At present, the comprehensive utilization of coal gangue has become a vital issue in the view of optimization of resources and the concerns about the environment [5]. Coal gangue containing kaolinite can be used to prepare metakaolin by calcination. Metakaolin is a typical supplementary cementitious material with very high pozzolanic reactivity [6]. Some studies have shown that the properties of the cementitious materials can be considerably improved the mechanical strength and durability by adding a certain proportion of metakaolin [7–13]. Hence, the preparation of highly active metakaolin-based supplementary cementitious materials using coal gangue as the precursor, is a current research hotspot.

Kaolinite, which is the main component of coal gangue, has a typical layered stable structure because the layers are combined with hydrogen bonds [14]. Thus, the stable structure must be destroyed to amorphous nature to improve chemical reaction activity [7]. Calcining and grinding are the main methods to improve kaolinite chemical activity, and calcination is a critical step in converting kaolinite to metakaolin [15, 16]. Kaolinite is typically calcined for more than 2 h, which consumes a lot of energy, and reduces the activity of
metakaolin products due to excessive calcination [17–20]. According to a large number of thermal analysis experiments, kaolinite can typically complete the dehydroxylation reaction within 30 min to form metakaolin, indicating that it is theoretically feasible to shorten the calcination time [21–24]. But, metakaolin activity is closely related to calcination conditions, and the effect of shortened calcination time on product activity needs to be studied [18, 25]. Unlike the calcination of natural kaolin, there is still a certain amount of carbon in coal gangue, which is another essential component that affects kaolinite activation during calcination [26]. In the calcination process of coal gangue, the characteristics of decarburization are also worthy of attention. Besides, thermal analysis is usually performed under linear heating conditions. Still, the calcination conditions in the actual process are similar to isothermal ones, and the calcination time parameters based on thermal analysis need to be optimized. Therefore, it is necessary to explore the reaction mechanism, calcination time and product properties of metakaolin prepared from coal gangue.

In this paper, based on the thermal analysis-infrared spectra combined experiments (STA-FTIR), the kinetics of dehydroxylation and decarburization reactions of coal gangue was characterized. The reaction time at different temperatures was predicted according to the obtained kinetic equation. The metakaolin products prepared under different conditions were characterized by phase analysis, scanning electron microscopy, energy spectrum, analysis of active silicon and active aluminum dissolution. The relationship between calcination temperature and time on product activity was obtained.

2. Experiments

Coal gangue, which is a gray-black lump, was obtained from Luliang, Shanxi Province in China. The samples were crushed to below 5 mm with a jaw crusher and fully dried at 105 °C ± 0.5 °C in the oven. The dried granular materials were ground into a fine powder with a particle size of fewer than 30 μm. The x-ray Diffractometer (XRD, D/MAX-2200, Japan Rigaku Corporation) was used to analyze the mineral composition of the materials. The working control conditions of the instrument were Cu target Kα ray, tube voltage 45 kV, tube current 40 mA. The composition of the raw materials is shown in figure 1. X-ray fluorescence spectrometer (XRF, S4PIONEER, German Bruker Company) was employed for elemental analysis of coal gangue samples. The x-ray tube parameters were 4.2 kW, 60 kV (Max), 140 mA (Max). The elemental analysis of the raw materials is shown in table 1. The flammability analysis of raw materials uses the SDTGA5000 industrial analyzer (Hunan Sande Company). The flammability analysis results are shown in table 2.

Table 1. Elemental analysis of coal gangue/wt%.

| SiO₂ | Al₂O₃ | Fe₂O₃ | K₂O | TiO₂ | MgO | Na₂O | SO₃ | CaO | Cl | P₂O₅ | ZnO₂ | Total |
|------|-------|-------|-----|------|-----|------|-----|-----|----|------|------|-------|
| 56.38| 24.37 | 1.87  | 1.23| 1.29 | 0.78| 0.14 | 0.165| 0.06| 0.12| 0.125| 86.60 |

Figure 1. XRD pattern of coal gangue.

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The test parameters of the thermal analyzer (NETZSCH 409PC STA, German) and infrared spectrometer (Bruker FTIR-7600, German) were 90% N₂ + 10%O₂ atmosphere, flow rate of 75 ml min⁻¹, heating rate of
5 °C min⁻¹, 10 °C min⁻¹, 15 °C min⁻¹, and 20 °C min⁻¹, sample mass of 5.0 ± 0.5 mg. The primary reactions occurring in coal gangue calcination and the respective temperature regions were determined by analyzing the TG, DTG, and FTIR data.

General Integration, Flynn Wall Ozawa, and Kissinger methods were used to calculate the calcination reaction kinetics of coal gangue, and the reliability of the results was verified [27]. The kinetic equation was used to predict the calcination time of coal gangue under different temperature conditions.

The detectable mineral phases in the raw materials are kaolinite and quartz. Combining the XRD and XRF results, the contents of kaolinite, quartz, and carbon in coal gangue were 61.28 wt%, 27.47 wt%, and 5.47 wt%, respectively.

![Figure 2. TG and DTG curves of coal gangue under different heating rates.](image1)

![Figure 3. Infrared absorption spectrum of escaped gases from the coal gangue under a heating rate of 15 °C min⁻¹.](image2)

**Table 2.** Combustibility analysis results of coal gangue.

| content (wt%) | Q_ad/(MJ/kg) | H_ad (wt%) |
|--------------|---------------|------------|
| Mad | V_ad | A_ad | FC_ad |
| 0.973 | 8.147 | 89.403 | 5.47 | 4.328 | 1.27 |

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respectively. The maximum working temperature of the muffle furnace (Carbolite CWF12/13, England) was 1200 °C, and the temperature control accuracy was ±5 °C. The setting temperature of the calcination experiment was kept in the range of 700 °C–825 °C. In the experiment, 15 g coal gangue was weighed and spread evenly in a square crucible (the thickness of the material layer was less than 2 mm) to ensure good heat and mass transfer.

XRD and SEM with energy spectrum were used to identify the mineral phases and microstructures of the product, respectively. The content of active SiO2 in the product was determined by the potassium fluosilicate volumetric method, while the content of active Al2O3 was determined by EDTA complexometric titration method [28, 29]. The calcination effect was characterized by the mass content of the dissolvable active substance.

3. Results and discussion

The TG and DTG spectra of coal gangue samples is shown in figure 2. Main weight loss occurred during the calcination of coal gangue, in the temperature range of 397 °C to 710 °C, representing a continuous process with an average weight loss rate of 8.62 wt%. These features are similar to those reported in the literature [30]. According to the mineral composition of the raw materials, the theoretical weight loss of kaolinite dehydration was 9.71 wt%. A slight weight loss of about 0.25 wt% was observed even after 710 °C. Under the four kinds of heating rates of 5 °C min−1, 10 °C min−1, 15 °C min−1, and 20 °C min−1, the maximum temperature for weight loss rate was 516.4 °C, 536.8 °C, 543.7 °C and 558.1 °C, respectively.

The 3D infrared absorption spectrum (15 °C min−1) of the gas released from the coal gangue sample during calcination is shown in figure 3. The gas products released during the calcination of coal gangue produced infrared absorption mainly in the range of 1200 cm−1–2000 cm−1, 2260 cm−1–2400 cm−1 and 3400 cm−1–4000 cm−1. The absorption intensity changes in peak 1 and peak 3 were consistent, and the time corresponding to the maximum infrared absorption intensity was 2236 s (at a temperature of 559 °C). The time corresponding to the maximum infrared absorption intensity on peak 2 was 3607 s (at a temperature of 902 °C). The infrared absorption spectra of the gas released at different times (temperatures) is analyzed from figure 3, and the results are shown in figure 4.

Infrared absorption spectra of escaped gases at different temperatures are shown in figure 4. The infrared absorption of the released gases at 1200 cm−1–2000 cm−1 and 3400 cm−1–4000 cm−1 conforms to the infrared absorption characteristics of H2O (g). The infrared absorption at 2260 cm−1–2400 cm−1 is consistent with the infrared absorption characteristics of CO2 gas. So the gaseous products released during the calcination of coal gangue are mainly H2O (g) and CO2.

According to the mineral analysis of the raw material and flammability analysis shown in figure 1 and table 2, H2O (g) is largely generated by the dehydrogenation of kaolinite into metakaolinite. At the same time, CO2 is formed primarily by the combustion of carbon (actually coal) in coal gangue. The corresponding reaction is as follows [8, 31]:

$$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}(g)$$  (1)

$$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$$  (2)
As the change of infrared absorption intensity reflects the change in gas-release flow rate, the reaction characteristics of the coal gangue calcination can be resolved by analyzing the infrared absorption spectrum of H₂O (g) and CO₂. The infrared absorption intensity of H₂O (g) and CO₂ with time is plotted, as shown in figure 5.

The apparent release process starts at 379.8 °C and ends at 737.3 °C. According to the changing trend of the differential curve 2 in figure 5(a), release of H₂O (g) during the calcination of coal gangue was a continuous process. The temperature for maximum release intensity was determined to be 538.7 °C.

The combustion reaction characteristics of carbon in coal gangue calcination can be analyzed from figure 5(b). The process of releasing CO₂ during the calcination of coal gangue can be divided into three stages. The temperature range of the first stage was 135.4 °C–291.1 °C, and the infrared absorption intensity of CO₂ in this stage changed slightly. The temperature range of the second stage was 291.1 °C–557.5 °C. The emission intensity of CO₂ in this stage was enhanced. In the third stage, the main stage of CO₂ emission, the temperature range was 557.5 °C–998.6 °C, and the maximum emission occurred at 811.7 °C. Metakaolin can be formed entirely below 737.3 °C, but it is difficult to remove carbon in this temperature range completely.

The calculation results of coal gangue calcination reaction kinetics are shown in table 3. The apparent activation energy calculated by the three methods is fairly close, as shown in table 3. The linear correlation coefficients (r) are all above 0.98, indicating that the calculation results are reliable. Since the fitting process of the general integral method includes the screening of mechanism function, so the average value is taken as the final result. The function expression and the physical meaning of mechanism function as determined by the general integration method are listed in table 4.

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The kinetic analysis results based on TG data show that the apparent activation energy of the fine coal gangue powder’s calcination is 178.92 kJ·mol⁻¹, which is similar to the literature [32]. The reaction kinetic equation is as follows:

![Figure 5. Infrared absorption intensity of H₂O (g) and CO₂ with time. (a) The infrared absorption intensity of H₂O (g) (b) The infrared absorption intensity of CO₂.](image-url)
In practical applications, the calcination of coal gangue is typically carried out under approximately isothermal conditions. The reaction time of metakaolin prepared by calcining coal gangue at constant temperature can be calculated using the kinetic equation (3). Consequently, the range from 700 °C to 825 °C is selected, and the calculation is performed in steps of 25 °C. The results showing the variation of the reaction conversion rate with the calcination time calculated under isothermal conditions are presented in figure 6.

Two distinct characteristics of the reaction from coal gangue to metakaolin are presented in figure 6. Firstly, the response is significantly affected by temperature. The reaction rate increase dramatically with the increase in calcination temperature. Secondly, the reaction rate is high in the early stage and then low in the later stage. The calcination time of coal gangue reported in literature was 2–4 h, or even longer, which indicates a very slow reaction rate \([26, 27]\). However, the prediction obtained through kinetic equation (3) shows that the conversion rate of metakaolin in the temperature range of 700 °C–825 °C was more than 99.9% in 791.42 s.

To verify the rationality of the kinetic prediction, the coal gangue was calcined in a muffle furnace with a thin material layer. Since the thickness of the material layer in a muffle furnace is thicker than that in a thermal analysis crucible, and so the time taken to complete the calcination reaction is longer. Therefore, 15 min was chosen as the calcination time. The XRD pattern of the calcined product is shown in figure 7.

\[
(1 - \alpha)^{-1} - 1 = 10^{9.27} \exp\left(-178.92/RT\right)t
\]

Figure 6. Prediction of reaction conversion rate with calcination times under isothermal conditions.

Figure 7. XRD spectrum of the calcined product \((t = 15 \text{ min})\).
peaks (positions 1 and 2) of kaolinite can be found to weaken, even disappear, and display typical amorphous characteristics after calcination for 15 min. Since the raw materials contain structurally stable quartz, prominent characteristic peaks of quartz could still be found in the product (position 3). The diffraction intensity of kaolinite decreased gradually (position 1) with the increase of the calcination temperature at the same calcination time, indicating that the conversion degree of kaolinite continues to increase. However, the x-ray diffraction of the kaolinite at position 2 does not disappear entirely in the calcination time of 15 min, indicating that there is still a small amount of kaolinite. There is a prominent x-ray diffraction peak at position 4 under the calcination condition of 825 °C, which indicates that crystallization begins to appear in metakaolin.

The dissolution experiments on active alumina and active silica were carried out on the calcined coal gangue. The dissolution rate was taken as the index to evaluate the calcination effect. The calculation formula of the dissolution rate is as follows:

\[ Y = \frac{m_L}{m_0} \times 100\% \]  

In the formula, \( Y \) is the dissolution rate (%), \( m_L \) is the mass of the dissolved active substance, and \( m_0 \) is the mass of alumina or silica before dissolution.

The results of the dissolution rate analysis of the calcined coal gangue are shown in figure 8. The dissolution rate of alumina in the calcined product is 64.79 wt%–71.57 wt%, and that of silica is 35.06 wt%–48.07 wt% after calcination at 700 °C–825 °C for 15 min. The data for alumina dissolution is close to that of the fully calcined activated alumina [33], which indicates that the calcination time of 15 min is enough under the condition of thin material layer accumulation (the thickness was less than 2 mm). In fact, activated silica oxide largely comes from the decomposition of kaolinite. Assuming that all the silicon in kaolinite gets converted into active silicon oxide for conversion, the effective dissolution rate of active silicon oxide is 68.82 wt%–94.35 wt%. The maximum rate of activated alumina dissolution is at 775 °C, and the maximum dissolution rate of activated silica appears at 750 °C. Temperature has a significant effect on the dissolution rate of activated silica and activated alumina. Insufficient or excessive calcination reduces the dissolution rate.

The microstructures of coal gangue samples before and after calcination are shown in figure 9. The coal gangue samples shown in figure 9(a) are consistent with the typical layered structure of kaolin [34]. The layered structure of kaolinite is destroyed gradually with the extension of calcination time, as shown in figures 9(b)–(f). After calcination for 20 min, the sintering characteristic appears and the layered structure is not obvious. Energy spectrum analysis shows that the main elements present in the raw material are Al, Si, O, and a small amount of Ti and C. Compared with that before calcination, the content of Al and Si increased, while the content of O decreased, which is due to the loss of O during the dehydroxylation of kaolinite. The relative contents of Al, Si and O do not change significantly after calcination for 7 min.

4. Conclusions

(1) The kinetic equation of coal gangue calcination reaction is established by Flynn-wall-Ozawa, Kissinger and general integration methods. It is predicted that kaolinite can be completely calcined in 700 °C–825 °C for 15 min. The experimental results are consistent with the modeled predictions.
When calcined at 750 °C for 15 min, the kaolinite in coal gangue is transformed into metakaolin and the comprehensive dissolution rates for active silicon and active aluminum are at their highest. The product is sintered and the activity is reduced as the calcination time is prolonged.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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