Research Status Quo and Exploration for Calcination and Activation Mechanism of Mullite Prepared from Gangue

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Abstract. The preparation of mullite refractory materials is one of the main applications of the current comprehensive utilization of gangue. In practice, it is found that it is not ideal to prepare mullite through direct calcination of gangue at high temperature. With reference to the preparation process of gangue cement clinker, it is necessary to perform the calcination and activation of gangue to increase its activity. The research on the gangue calcination and activation mechanism focuses on the change in the chemical compositions and microstructure. The author summarized and sorted a large amount of reference information and concluded that the gangue calcination and activation mechanism is that the chemical activity is changed due to the transformation of kaolinite dehydration to metakaolinite and caused by the change in the interlayer structure of kaolinite.

Keywords: Mullite, Gangue, Calcination and Activation, and Interlayer Structure.

1. Background
Mullite is a kind of aluminum-based aluminosilicate mineral. The content range of pure mullite is 100%. It contains a high percentage of aluminum and is resistant to high temperature and corrosion. Microstructurally, mullite is arranged in a chain shape and takes the basic [AlO₆] octahedron as a stable framework. With thermal processes, it can form long-column and needle shapes with crystals extending along the axis, thus forming a solid framework network. As a result, it features refractoriness up to 1850°C, refractoriness under load, good thermal-shock stability, and resistance to chemical erosion. It is an ideal composition of high-grade refractory and is widely used in metallurgy, glass, ceramics, chemical, electric power, national defense, gas and special cement and as a preference of the refractory industry.

Gangue is one of the largest amount of dumps of industrial wastes. With the development of the coal mining industry, its dump is still rising. There are many hazards. The comprehensive utilization of gangue has been researched extensively at home and abroad. However, a small number of research results have been applied only in industrial production for technical and economic reasons. Therefore, a large amount of gangue has not been utilization reasonably.

For the preparation of mullite mainly by using gangue, the current research focuses on sintering methods, sintering temperature, temperature holding time, influence of impurities, additives, etc. And, many research achievements have been made.
At present, mullite is researched very extensively, for example, the synthesis, modification, application, etc. of mullite, and great progress has been made. How to synthesize mullite using gangue has become a research hotspot in mullite research due to the urgent pressure of gangue dump and resource utilization.

Zhang Zhimin [1] has carried out research on gangue synthesizing mullite since earlier days. The approaches and methods of gangue synthesizing mullite are found out by analyzing the characterization, properties, and phase diagrams of gangue. And, the theoretical basis is given.

Ni Wen et al. [2] performed a feasibility Research on how to synthesize mullite clinker by using gangue, alumina, and aluminum hydroxide. The experimental results show that mullite can be synthesized from gangue and alumina at 1550°C, of which density is approaching the theoretical density at 1600°C, and from gangue and aluminum hydroxide at 1500°C, of which density is approaching the theoretical density at 1550°C. The samples that are synthesized from gangue and alumina feature the best performance and the highest purity of compositions.

Yang Zhongzheng et al. [3] prepared mullite by using high bauxite, gangue and a small amount of $\text{Al}_2\text{O}_3$ as raw materials with grinding, filtering, drying, forming, calcination and other processes. The performance of the product reaches the world’s advanced level.

Li et al. [4] synthesized mullite-based ceramics by using gangue and $\text{Al(OH)}_3$ and researched the influence of the raw material mixing ratio and temperature on product performance.

Ji et al. [5] synthesized mullite by using gangue and $\gamma-\text{Al}_2\text{O}_3$ as raw materials and researched the influence of $\text{La}_2\text{O}_3$ additive on the product performance.

However, in the process of gangue sintered into mullite, it was found that the gangue needs to be treated for activation to obtain high-quality mullite.

Many researchers are committed to researching to improve the activity of gangue in order to make effective use of gangue. The activity exciting methods include thermal activation, mechanical activation, alkali excitation, and microwave-irradiation excitation, etc. As a cement addition, gangue is usually pretreated with chemical activation and thermal activation processes. However, no relevant research on the mechanism of mullite prepared from gangue calcination activation- thermal activation treatment process is found. In this article, the research results of similar mechanisms and methods are sorted to explore the activation mechanism of gangue preparing mullite to provide a theoretical basis for practical production.

2. Gangue Activity and Its Influencing Factors

The level of gangue activity depends not only on its chemical compositions and grinding fineness, but also mainly on its phase compositions and structure. Because undisturbed gangue is formed naturally over time, the minerals it contains are structurally stable crystals with low activity, of which chemical reaction ability is low. Natural gangue has a certain volcanic ash activity due to the presence of amorphous $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$. It is an active mixing material. There are many factors influencing the activity of gangue, mainly including the chemical compositions and microstructure of gangue.

2.1. Influence of Chemical Compositions

The chemical compositions of gangue have different influences on its activity. The $\text{SiO}_2$ in gangue has a great influence on the formation of glass in gangue. However, if its content is biased high, $\text{MgO}$ and $\text{CaO}$ cannot be combined with it, causing more significant influence on the activity of gangue, especially when it is present in crystalline minerals; the activity of gangue is better if the content of $\text{Al}_2\text{O}_3$ is relatively low; the higher the content of $\text{CaO}$ is, the higher the reaction activity of gangue is; $\text{MgO}$ can accelerate the glass formation of the gangue, good to forming microstructural unevenness. However, if its content is biased high and it is of presence in a periclase state, the volume will be expanded due to hydration, resulting in poor stability. Therefore, the $\text{MgO}$ content in gangue should not be too high.
2.2. Influence of Microstructure
Microstructurally, materials with many structural defects, crystal lattice distortion or amorphous shape have higher reaction activity. The analysis of the influence of gangue structure on the activity can be found from many references. Fresh and weathered gangues feature a stable crystalline structure, of which atoms, ions, molecules and other particles are arranged regularly and in an orderly manner, causing that they have very low activity or are basically inactive.

3. Research Status Quo for Calcination and Activation Mechanism

3.1. Change in Chemical Compositions
Qing Song et al. [6] researched the thermal activation mechanism of gangue from the perspective of change in chemical compositions. Generally, the higher the contents of SiO$_2$ and Al$_2$O$_3$ in gangue are, the higher its activity after calcination is.

The calcination of gangue is for the two purposes of as follows. On the one hand, the gangue is sandwiched in the coal seam and contains carbon to differing degrees; because carbon has an influence on the strength, water demand, and durability of cement, the gangue not combusted spontaneously must be calcined to remove carbon before utilization; on the other hand, after calcined, the kaolin composition in gangue will be dehydrated and decomposed at a certain temperature to generate metakaolin and amorphous silica and alumina. The reaction equations are expressed as follows:

$$
550-700°C \quad Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O
$$

$$
700-900°C \quad Al_2O_3 \cdot 2SiO_2 \rightarrow Al_2O_3 + 2SiO_2
$$

Song Xiwen et al. [7] believe that, during the decomposition phase of bauxite (at 400 to 1200 °C), its empholite and kaolinite begin to dehydrate at 400 °C, and, the reaction takes place sharply at 450 to 600 °C and is completed at 700 to 800 °C. The corundum pseudomorph formed after the dehydration of empholite still retains the original profile of empholite with blurred edges and is gradually changed into corundum at high temperature. After dehydrated, kaolinite will form metakaolinite which is changed to mullite and amorphous SiO$_2$ at a temperature higher than 950°C. The latter is changed into cristobalite at high temperature, of which chemical reaction equations are expressed as follows:

$$
400-600°C \quad \alpha-Al_2O_3 \cdot H_2O \rightarrow \alpha-Al_2O_3 (\text{corundum pseudomorph}) + H_2O
$$

$$
400-600°C \quad Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O
$$

$$
950°C \quad 3(Al_2O_3 \cdot 2SiO_2) \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2
$$

3.2. Microstructural Change
Ye Danian et al. [8] think that the additions used in cement must be active. From the perspective of crystal chemistry, it is required that the addition should have a cracked or crackable silicon-oxygen tetrahedron framework. The process of exciting the activity of gangue is to promote the increase in cracked or crackable silicon-oxygen tetrahedron framework in gangue. When gangue is heated to a certain temperature, generally being 600 to 950 °C (i.e. in the medium-temperature active area), the original clay mineral crystallized phase will be decomposed, destroyed and then changed into amorphous crystalline, making gangue active. Researches show that the stratified structure of kaolinite in calcined gangue at 900°C is disintegrated, the aluminum-oxygen octahedron is destroyed, and, the aluminum changes partially from 6-coordination to 4-coordination, making that it has activated alumina.

Song Xuyan et al. [9] consider that the structure of gangue is highly different before and after calcination. The structure of gangue is denser before calcination and basically loose after calcination. This is mainly caused by the structural expansion, compositions’ volatilization, etc. of gangue under calcination at high temperature, resulting in multiple micropores, multiple broken bonds, multiple solvents, and amorphous substances with higher internal energy.

Johnson [10], Zheng Yonglin, et al. [10] determined that calcined gangue featured a certain activity, but its activity was not increased with the increased calcination temperature.
Gong Chenchen et al. [12] consider that the calcination is an effective means to excite the activity of gangue, which aims to use high temperature to make the particles in the microstructure of gangue generate a fierce thermal movement and remove the bound water in the mineral. And, the Ca, Mg, Fe and other cations reselect the interstitial positions, causing that the silicon-oxygen tetrahedron and the aluminum-oxygen trihedron are impossible to fully polymerize the growth chain, forming a large number of breaking points at the free end. The particles can no longer be arranged regularly, forming a thermodynamically unstable glass-phase structure, resulting in that the gangue after calcination contains a large amount of active silica and alumina for the purpose of activation.

Yang Zhiqiang et al. [13-14] experimentally and theoretically researched and analyzed the causes of the activity. The research shows that the calcination of gangue at a certain temperature can destroy its complete crystals, causing that the chemical bonds are opened, and the crystal form changes, the crystal is distorted, and a large number of crystal defects appear. And, due to rapid cooling, some of the generated molten masses cannot crystallize slowly but exist in the form of glass. These feature an irregular network structure mainly composed of silicon-oxygen tetrahedron and aluminum-oxygen trihedron [15]. And, during the melting phase of gangue, the microparticles inside the gangue are in a state of sharp thermal movement at high temperature. In such a case, the silicon-oxygen tetrahedron and aluminum-oxygen trihedron cannot be fully polymerized to form long chains but can form just short chains, resulting in more breaking points of short silicon-oxygen chain and aluminum-oxygen chain in the molten mass. This is equivalent to having more free ends, causing the increased activity of the calcined gangue.

Greek scholars G. Kakali, S. Tsivilis, E. Badogiannis et al. [16] researched the influence of minerals on the activity of calcined kaolin. Their researches show that, for the purpose of effective utilization of gangue, it must first be reasonably heat-treated and that the best heat treatment system is that the calcination is carried out at 650°C and the temperature is held for 3h.

Yang Nanru, Guo Wei et al. [17] researched the phase compositions and structural change in gangue during thermal activation. The research shows that, after gangue is calcined at 900°C, the structure of kaolinite is completely destroyed and the obtained metakaolinite features the best activity.

Alumina is a commonly used raw material for synthesizing mullite, of which activity is changed greatly with its varied structural state. For being used for synthesizing mullite, γ-\(\text{Al}_2\text{O}_3\) has a better effect than \(\alpha-\text{Al}_2\text{O}_3\). Within the temperature interval that \(\gamma-\text{Al}_2\text{O}_3\) is transformed into \(\alpha-\text{Al}_2\text{O}_3\), the reaction rate is increased greatly. Mullite can be synthesized with \(\alpha-\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\). However, the reaction is not easy to take place. Although amorphous \(\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\) have a high activity, they do not easily generate mullite. The residual corundum phase can be found in the clinker after calcination.

Among the raw materials containing \(\text{SiO}_2\), quartz and crystal present a crystal form transformation at the synthesis temperature. The increase in the defect concentration causes the increased diffusion rate of ions, which is conducive to the solid-phase reaction and sintering.

3.3. Conclusions of Research

Based on the summary of the above references, the author believes that the fundamental of calcination and activation of gangue is the change in structure leading to the varied chemical activity and the dehydration process of kaolinite changing into metakaolinite.

Kaolinite is a typical bi-layer silicate expressed by a chemical formula of \(\text{Al}_4[\text{SiO}_{10}](\text{OH})_8\). The cross-sectional structure of its layer unit is shown in the following figure. The layer unit is a bi-layer structure composed of a silicon-oxygen layer and an empholite layer. The entire crystal consists of these layer units that are stacked in parallel and is a triclinic system. The coordination number of \(\text{Al}^3+\) is 6. 2 of them are \(\text{O}^2-\) and 4 of them are \(\text{OH}^-\), forming \([\text{Al(OH)}_2]_6\) octahedron. It is these two \(\text{O}^2-\) that connect the empholite layer and the silicon-oxygen layer. Because inside the layers is electronically neutral, the layers are theoretically of a physically bonding junction, causing that kaolinite is easy to dissociate to form small plate-like crystals. In addition, due to the contact between \(\text{OH}^-\) and \(\text{O}^2-\), the layers are of hydrogen bonding. During the calcination process, the hydrogen bonding was destroyed so that the silicon-oxygen layer and the empholite layer are connected only by physical bonds and the bonding force is significantly
reduced. At the same time, a large number of pores are formed, creating good conditions for subsequent mullite generation. The testing results of SEM, XRD, and DTA-TG in the above references can well demonstrate this conclusion. Differential thermal analysis of gangue calcination is shown in the following Figure 1:

![Differential Thermal Analysis of Gangue](image)

**Figure 1.** Differential Thermal Analysis of Gangue

4. Conclusion

By summarizing a large number of literature reports and theoretical research results, the author believes that the calcination and activation mechanism of gangue is caused by the dehydration process of kaolinite, with microstructural change leading to the varied chemical activity, creating good conditions for subsequent mullite generation. The future researches should focus on how to accelerate and increase the degree of destruction of the kaolinite interlayer structure and further increase the gangue degree of activity.

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