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Investigation on the Activity Activation and Cementitious Property of Coal Gangue with High Iron and Silica Contents

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Abstract. The activity of coal gangue by thermal activation and composite activation technologies was investigated. The crystal composition, framework structure and morphology change were analyzed by XRD, FT-IR and SEM, respectively. The cementitious property of coal gangue was measured by strength test. The results showed that thermal activation decomposed kaolinite in coal gangue, and formed the metastable structure with a porous state, multiple internal broken bonds and large specific surface areas. Based on thermal activation, the added lime provided the alkaline environment, then this reduced the bond energy of reactant particles and the degree of crystallinity of quartz in coal gangue. The two activation methods could effectively improve the cementitious property of coal gangue based unburned bricks, and that the composite activation technology was superior performance.

1. Introduction

Coal gangue is a complex industrial solid waste excavated in the mining production and washed in the preparation process [1]. The stockpile of coal gangue can cause serious pollution which included local environment and the health of residents in the mining area. However, coal gangue contains clay minerals, quartz, carbonate minerals and pyrite, which can be utilized as resources [2, 3]. The application of coal gangue in building materials has attracted widespread attentions because of its high consumption. But its ratio of use as a cement additive is less than 15%, this is because the stable crystal structure of coal gangue has low pozzolanic activity and weak cementitious property [4]. How to effectively improve the activity, changing the structural state and phase composition, and enhancing the cementitious property of coal gangue are the key of the efficient utilization of coal gangue in building materials.

Generally, coal gangue was mainly activated by mechanical activation, thermal activation, chemical activation and a combination of two and more than two kinds of activation method, namely, composite activation. Li et al. [5] studied the conversion mechanism of thermal activation process, the results showed that calcined component Al_2O_3•$2SiO_2$•$2H_2O$ was converted into Al_2O_3•$2SiO_2$, and amorphous SiO_2 and Al_2O_3, which were the main sources of the activity of coal gangue. Gu and Wang et al. [6] implemented the comparative study on the activation of coal gangue and coal gangue cement by chemical activators. The results showed that the strength of coal gangue cement increased significantly by the activators with 2 %Na_2SO_4 and 4 %$Ca(OH)_2$.

Liu et al. [7] studied the mechanical activation of calcined coal gangue and found that mechanical activation gradually made the kaolin crystal into amorphous state, and crystalline degree of α-quartz was decreased. Coal gangue after the different activation process, and the cementitious property was markedly enhanced.

These activation methods of mechanical activation, thermal activation, chemical activation and composite activation can effectively enhance the activity of coal gangue. Whether these methods can

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effectively enhance the activity of coal gangue with high iron and silica contents remains unknown, which is activation method better to prepare cementitious materials. In this paper, the coal gangue of Liupanshui areas was used as the raw material. We adopted the thermal activation and composite activation to determinate the coal gangue influence of mineral composition, crystal structure, morphology change. The cementitious property of coal gangue based unburned bricks were further measured. This way provided scientific and technical references for the preparation of cementitious materials by coal gangue with high iron and silica contents.

2. Experimental procedures

2.1 Raw materials

Coal gangue used in this experiment was obtained from Liupanshui city. Slag was collected from Shuicheng Iron and Steel Group Co., Ltd. Lime was industrial grade, and the effective calcium oxide content was 80%. Cement (P.O.32.5) was supplied from Liupanshui cement plant. Sodium sulfate as analytical reagent was produced by Xiya Reagent Factory.

2.2 Coal gangue activation procedure and preparation of coal gangue based unburned bricks

Coal gangue was grinded by GJ- III pulverizer and screened by 120 mesh sieve. The coal gangue was named as R-gangue. Coal gangue powder grinded to 120 meshes was placed in XL-III muffle furnace, heated to 800°C, preserved for four hours, and cooled to room temperature. The activated coal gangue was named as T-gangue. Lime and coal gangue powder grinded to 120 meshes (mass ratio 1:9) was heated from room temperature to 800°C, preserved for four hours, and cooled to room temperature. The mixture was grinded to 180 meshes by XMB-70 rod mill. The active coal gangue was named as CTM-gangue.

The activated coal gangue, slag, cement, sodium sulfate and lime were mixed at the mass ratio of 37:6:5:1:1. The moisture content of mixture was 22%. The 40 mm × 40 mm × 160 mm test bricks were prepared in the ZT-96 cement mortar swing table, and conducted with steam curing for 12 hours at 90°C, then taken out after natural cooling.

2.3 Testing conditions

The crystal phase composition of samples was analysed using X'Pert PRO X-ray diffractometer (PANalytical, Netherlands). The framework of samples was analyzed by the Nicolet FTIR-IS50 spectrometer (Nicolet, USA). Morphology of samples was analyzed using Zeiss Sigma X-Max 20 field-emission electron microscope (ZEISS, Germany). The strength tests were analyzed using YAW-2000 compression- testing machine (HST/ST, China).

3. Results and discussion

3.1 XRD analysis

XRD patterns of coal gangue by different activation methods were presented in figure 1. We could find that the mineral compositions in coal gangue mainly included quartz, kaolinite, mica, siderite and anorthite, etc. The characteristic peaks of kaolinite disappeared in thermal activation coal gangue, and the peak intensity of quartz and anorthite was weakened obviously. Kaolinite belonged to a layered structure, and the dehydration and decomposition reaction occurred at 700-1000°C. Quartz belonged to the trigonal system, and anorthite belonged to triclinic system. They had stable chemical nature, and were not likely to be activated. In addition to the above characteristics of thermal activation, composite activation coal gangue also showed the characteristic peaks of lime. Compared with raw coal gangue, the activated coal gangue had sharp peaks at 20.6°, 29.2°, and 32.9°, which was caused by crystal transformation of the mineral components.

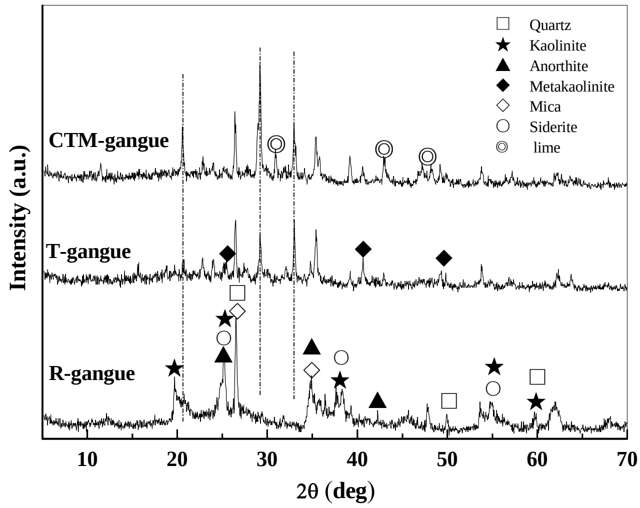


Figure 1. XRD patterns of coal gangue with different activation methods.

3.2 FT-IR analysis

Figure 2 displayed the FT-IR of coal gangue by different activation methods. The absorption peak at 1122cm^{-1} of R-gangue corresponded to the Si-O-Si stretching vibration absorption peak. The absorption peak at 1627cm^{-1} corresponded to Si-O-Si asymmetric stretching vibration and O-Si-O stretching vibration absorption peak. 876cm^{-1} was attributed to Si-O-Si bending vibration absorption peak, 3439cm^{-1} was related to O-H stretching vibration absorption peak. These absorption peaks indicated that coal gangue contained kaolinite mineral [8]. 1431cm^{-1} corresponded to CO_3^{2-} stretching vibration absorption peak, indicating that the coal gangue contained carbonate. 469cm^{-1} was the characteristic bands of quartz. The sharp degree of the stretching vibration absorption peak at 469cm^{-1} of the activated coal gangue was decreased. That suggested that the degree of crystallinity of quartz in the activated coal gangue was reduced. An absorption peak appeared at 558cm^{-1} after the activated coal gangue, and this was a characteristic spectra of metakaolinite [8, 9]. It resulted from that kaolinite was decomposed in the process of activation, and metakaolinite was formed. This was consistent with XRD analysis results. In addition, O-H stretching vibration absorption peak of $Ca(OH)_2$ occurred at 3623cm^{-1} and 3698cm^{-1}, this showed that the added CaO was carbonized and slaked in the composite activation process.

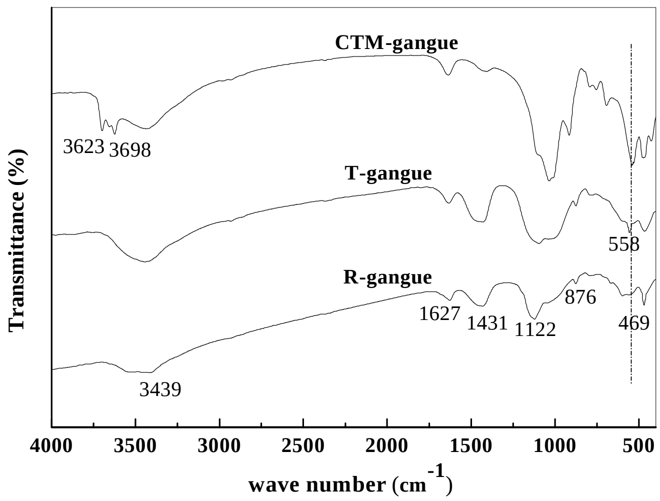
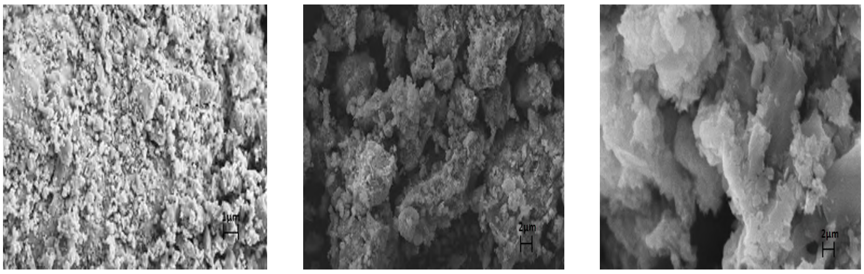


Figure 2. FT-IR patterns of coal gangue with different activation methods.

3.3 SEM analysis
SEM patterns of coal gangue by different activation methods were showed in figure 3. Coal gangue in figure 3(a) had compact structure. Combined with XRD, it could be seen that it was composed of massive quartz and granular kaolinite. In figure 3(b), the structure of coal gangue presented a loose state, and a large number of microspores occurred. This was due to the decomposition of kaolinite and organic carbon during the thermal activation process. The structures were connected with the porous state, multiple broken bonds, soluble matters, high internal energy [10]. Composite activation coal gangue in figure 3(c) also showed some molten states. The added lime as the mineralizer reduced the reaction bonding between particles, increased the chemical activity, and promoted the solid phase reaction. Meanwhile, the liquid phase property was changed, which was conductive to enhance the cementitious property of building materials prepared by coal gangue.



(a) R-gangue (b) T-gangue (C) CTM-gangue

Figure 3. SEM patterns of coal gangue with different activation methods.

Based on the above analysis, decomposition of kaolinite was the main source of the activity of coal gangue. After heat activation, the kaolinite removed the hydroxyl and the original layer structure was kept. However, the atoms had undergone large dislocation, forming metakaolinite with poor crystallinity. Metakaolinite could be further transformed into amorphous SiO_2 and Al_2O_3. The mineral structure was in metastable state with porous state, multiple internal broken bonds and large specific areas. On the one hand, coal gangue decreased the particle size by mechanical activation and increased the specific areas, the particle surface free energy increased. On the other hand, the lime which was added to coal gangue provided an alkaline environment promoting the decomposition of mineral and reducing the bond energy between the reactant particles, then the reaction activity was improved [11].

3.4 Cementitious property
In order to compare the activity of the activated coal gangue, the coal gangue based unburned bricks were prepared according to the method in 1.2. The compressive and flexural strengths were tested at 3d, 7d, and 28d as shown in figure 4 and 5. The strength standard of test bricks was accordance with JC/T422-2007 MU15 standard.

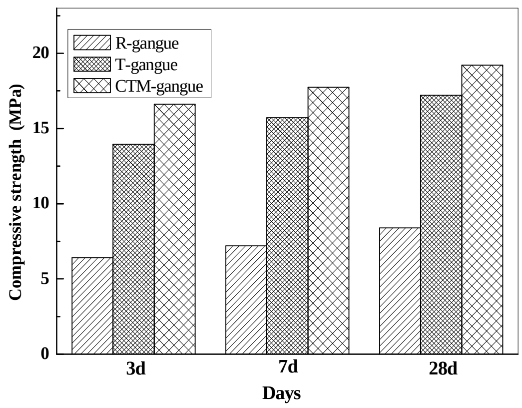


Figure 4. Compressive strength of coal gangue based unburned bricks.

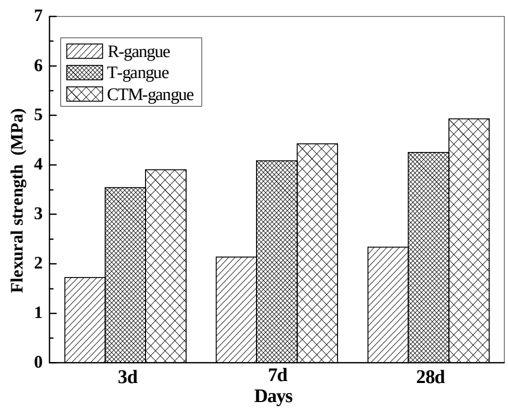


Figure 5. Flexural strength of coal gangue based unburned bricks.

As shown in figure 4 and 5, the compression and flexural strengths of the unburned bricks prepared by the activated coal gangue were higher than those of the unburned bricks prepared by raw coal gangue. In the experiment process, we found that the unburned bricks prepared by raw coal gangue had black powder on the surface, which seriously affected the appearance quality of the test bricks. Moreover, the strength of the test bricks were not up to the requirements. The two kinds of activation methods could effectively improve the cementitious property of coal gangue based unburned bricks. The cementitious property of composite activation was better than that of the single thermal activation. The compressive strength at 3d was 16.62MPa, and the flexural strength was 3.90MPa. At the 28d, the compressive strength was improved by 15.64%, and the flexural strength was improved by 26.41%. The cementitious property could fully satisfy the standard of JC/T422-2007 MU15.

4. Conclusions

i: The activity of coal gangue with high iron and silica contents in Liupanshui was activated. The thermal activation decomposed kaolinite in coal gangue to form the metastable structure with porous state, multiple internal broken bonds and large specific areas. Based on thermal activation, lime added in the composite activation provided the alkaline environment, which reduced the bond energy between the particles in reactant and the degree of crystallinity of quartz in coal gangue.

ii: The thermal activation and composite activation could effectively improve the cementitious property of unburned bricks. The effect of composite activation on the coal gangue was better than single activation. The cementitious property of the unburned bricks prepared by composite activation coal gangue could fully meet the standard of JC/T422-2007 MU15.

5. References

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