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Investigation on the activation of coal gangue by a new compound method

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ABSTRACT

In order to comprehensively utilize coal gangue as the main raw material in cementitious materials, improving its cementitious activity is a question of fundamental importance. In this paper, we present a new compound mechanical-hydro-thermal activation (CMHTA) technology to investigate the activation effect of coal gangue, and the traditional mechanical–thermal activation (TMTA) technology was used as reference. The purpose of this study is to give a detailed comparison between these two methods with regard to the mineral composition, crystal structure and microstructure, by XRD, IR, MAS NMR, XPS and mechanical property analysis. The prepared coal gangue based blended cement, containing 52% of activated coal gangue C (by CMHTA technology), has a better mechanical property than activated coal gangue T (by TMTA technology) and raw coal gangue. The results show that both of the TMTA and CMHTA technologies can improve the cementitious activity of raw gangue greatly. Moreover, compared with TMTA, the mineral phases such as feldspar and muscovite in raw coal gangue were partially decomposed, and the crystallinity of quartz decreased, due to the effect of adding CaO and hydro-thermal process of CMHTA technology.

1. Introduction

Coal gangue is a complex industrial solid waste discharged when coal is excavated and washed in the production course. Its major chemical composition is SiO_2 and Al_2O_3, and its major mineralogical composition is quartz and feldspar [1]. The amount of coal gangue accumulated in China has already reached 3.8 billion tons; moreover, the stockpile of gangue is increasing at a rate of 0.2 billion tons per year [2]. The disposal of such a large quantity of this solid waste requires a lot of land and has caused many serious environmental problems.

Many studies have been carried out to investigate the use of coal gangue in building materials [3–6]. However, the utilization rate of coal gangue in cement as admixture is always lower than 15% [7] due to its weak cementitious capability. In order to abundantly utilize coal gangue in cementitious materials, how to improve its cementitious activity is a question of fundamental importance.

Generally, coal gangue can be activated in three ways: physical activation (mechanical activation), thermal activation, and chemical activation. Mechanical activation is a physical process, taking place in mechanical activators (especially ball mill), aimed at improving the material's activity by only decreasing the particle size without the need for the application of chemical reagents. Guo et al. [8] conducted a study on structure and pozzolanic activity of calcined coal gangue during the process of mechanical activation, and they found that with the decreasing grain size, the pozzolanic activity increases and is attributed to the disorganization of 6-coordinated aluminum and Q^3 silica. Thermal activation is a universal method, which has been widely studied by many researchers in China. The activity of coal gangue can be improved in terms of the disorganization of contained clay during thermal activation. Song et al. [6] reported that calcined coal gangue at 700 °C has better activity. They also mentioned that calcination with calcium was a good method to improve its activity, which has positive effect on the decomposition of silicon-oxide polyhedron. Meanwhile, Brindley and Nakahira [9,10] investigated the phase transformation of kaolinite in the process of temperature rising, and indicated that metakaolin formed at 500 °C, and then turned to Si spinel at 925 °C and mullite at 1400 °C, respectively. Chemical activation is a method using chemical agents, especially alkali solution, to react with amorphous aluminosilicates, such as metakaolin or calcined clays, which can produce inorganic binders with excellent physical and chemical properties, named "Geopolymer" [11]. But before chemical activation, the coal gangue should be calcined to increase its amorphous aluminosilicates before being used with chemical activation.

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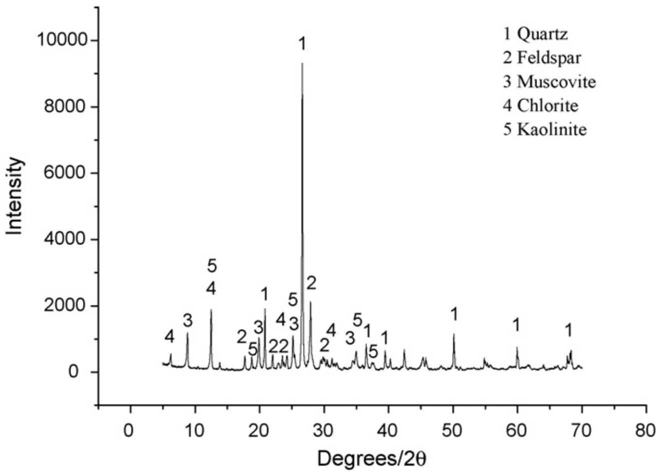

Fig. 1. XRD pattern of raw coal gangue.

It is very common that we combine some of these methods together to treat the coal gangue, especially mechanical and thermal activation. In this paper, we present a new compound mechanical-hydro-thermal activation (CMHTA) technology (described in detail in Section 2.2) to investigate the activation of coal gangue, and traditional mechanical–thermal activation (TMTA) technology was used as reference. The purpose of this study is a detailed comparison between these two methods regarding to the mineral composition, crystal structure and microstructure. For the first time, differences and similarities between these were highlighted by means of XRD analysis, IR spectroscopy, ^{27}Al and ^{29}Si MAS NMR spectroscopy, and XPS analysis.

2. Experimental procedures

2.1. Raw materials

Coal gangue used in this experiment was from Beijing Fangshan. The mineralogical phase was determined by XRD as shown in Fig. 1. Granulated blast-furnace slag was supplied by Tangshan steel refining plant, with Blaine's specific surface area of 452 m^2/kg. A sample of clinker from Jingdong cement plant was employed for this investigation. The chemical composition and physical properties of the raw materials are presented in Table 1.

2.2. Activation methods

The schematic diagrams of traditional mechanical–thermal activation and compound mechanical-hydro-thermal activation technologies are shown in Fig. 2. In the technology of TMTA, the raw coal gangue was dry milled for 30 min to the Blaine's specific surface area of 520 m^2/kg. After being calcined at 800 °C for 2 h, the activated coal gangue (T) was cooled in air, and then used for the preparation of cementitious materials to conduct its activity evaluation test. The CMHTA technology is a little different to TMTA, and the differences in CMHTA mainly reflected on three aspects: firstly, 8% CaO was added to the raw material, wet milled for 20 min to the Blaine's specific surface area of 518 m^2/kg; secondly, the mixed milled materials were treated by hydro-thermal processing at 80 °C for 6 h; thirdly, the materials were granulated with diameter of 10 mm. Then, the materials were calcined at 800 °C for 2 h, generating activated coal gangue (C).

Table 1
Chemical composition and physical properties of raw materials by XRF.

Oxides (%)	Coal gangue	Slag	Clinker
SiO_2	56.11	34.97	21.98
Al_2O_3	16.78	13.98	5.54
CaO	3.11	40.40	60.38
Fe_2O_3	7.02	1.92	5.13
Na_2O	1.84	0.18	0.25
K_2O	6.98	0.38	2.17
MgO	1.68	8.17	3.03
LOI	6.38	0.03	1.52
Specific surface, Blaine (m^2/kg)	–	452	465

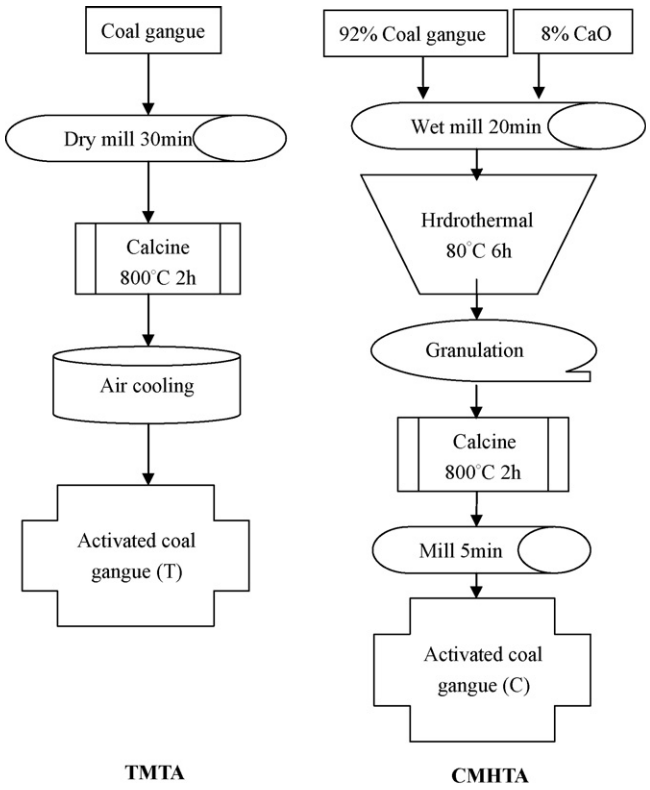

Fig. 2. Schematic diagrams of traditional mechanical–thermal activation (TMTA) and compound mechanical-hydro-thermal activation (CMHTA) technologies.

2.3. Testing conditions

The elemental compositions of raw materials were performed with the X-ray fluorescence (XRF-1700) analyzer.

X-ray powder diffraction data were collected using a Rigaku D/max-RB powder diffractometer, with Cu Kα radiation (40 kV; 100 mA).

Fourier transform infrared (FTIR) spectra were acquired using a Spectrum GX, PE FTIR spectrometer in absorbance mode using the KBr pellet technique (1–2 mg sample with 200 mg KBr).

^{29}Si and ^{27}Al solid-state MAS NMR spectroscopy was carried out at a Bruker AM 300 spectrometer operating at 59.62 and 78.20 MHz for the ^{29}Si and ^{27}Al resonance frequencies, respectively.

X-ray photoelectron spectroscopy (XPS) was collected with a PHI-5300 ESCA spectrometer, with Mg/Al Kα radiation. The experimental conditions were a source power of 400 W and pass energy of 37.25 eV with an analysis chamber pressure lower than 6×10^{-8} Pa.

Test on strength development was carried out according to Chinese Standard GB/T17671-1999 [12], with a water to cement ratio of 0.50 and cement to sand ratio of 1:3. Mortar specimens in size of 40.0 mm × 40.0 mm × 160.0 mm were cured in a moist cabinet at 95% humidity, at 20 °C for 24 h after demoulding and then placing in the isothermal curing cabinet at the previously mentioned humidity and temperature until the desired testing ages.

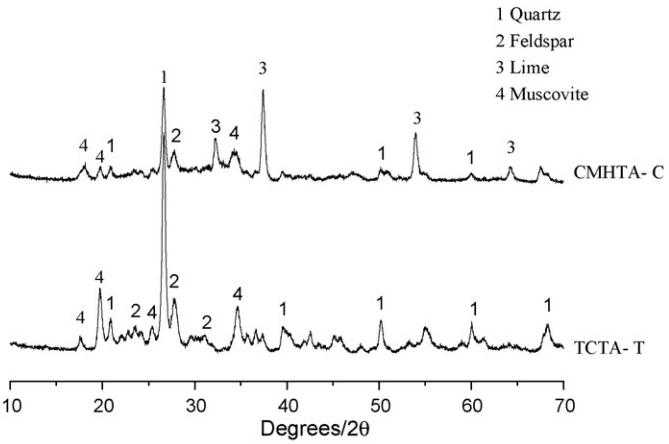

Fig. 3. XRD patterns of activated coal gangue C and T by CMHTA and TMTA technologies.

3. Results

3.1. XRD analysis

XRD patterns of activated coal gangue C and T by CMHTA and TMTA technologies are presented in Fig. 3. Compared with Fig. 1, we can find that the there was no trace of chlorite ($Mg_5AlSi_3AlO_{10}(OH)_8$) and kaolinite ($Al_2Si_2O_5(OH)_4$) both in activated coal gangue C and T, which had been decomposed to active SiO_2 and Al_2O_3 [13]. The obvious differences between these are as follows: in activated coal gangue T, the crystal structures of feldspar ($KAlSi_3O_8$) and muscovite ($KAl_3Si_3O_{10}(OH)_2$) still existed in TMTA technology, but the peaks decreased apparently in gangue C. On the other hand, the crystallinity of quartz in gangue C was also decreased. It can be concluded that gangue C has a better activity than gangue T because of the changes of crystallinity of feldspar, muscovite and quartz in the process of CMHTA.

3.2. IR analysis

Fig. 4 displays infrared spectra of activated coal gangue C and T by CMHTA and TMTA technologies. The absorption at 1088 cm^{-1} is related to anti-symmetric stretching mode of Si–O, and the bands at 799, 774, 697 cm^{-1} are attributed to symmetric stretching vibration of Si–O–Si, while the absorption at 469 cm^{-1} is due to bending mode of Si–O [14], in which the bands at 1088, 799 and 469 cm^{-1} are indicative of quartz. We can find that these principal bands are broader in CMHTA-C gangue, moreover, the wavenumber of bending mode of Si–O shifts from 469 to 485 cm^{-1}, which confirms that the degree of crystallinity of quartz in CMHTA-C gangue decreases [15]. In CMHTA-C gangue, an absorption band at 1479 cm^{-1} is related to anti-symmetric stretching mode of $CO_3{}^{2-}$ ions [16] and a sharp band at 3644 cm^{-1} is associated to O–H stretching vibrations of $Ca(OH)_2$. It is presumed the added CaO was carbonized and slaked in the process of CMHTA, respectively. In addition, the band at 558 cm^{-1} in TMTA-T gangue is indicative of the presence of metakaolin [17]. Because of its high water absorbent, the absorption bands at 3439 and 1632 cm^{-1} related to O–H stretching and bending modes of molecular water, respectively, are existing. Nevertheless, the band of metakaolin was not found in CMHTA-C gangue. This observation suggests that active SiO_2 and Al_2O_3 were formed from metakaolin, so the activated coal gangue C has a better activity.

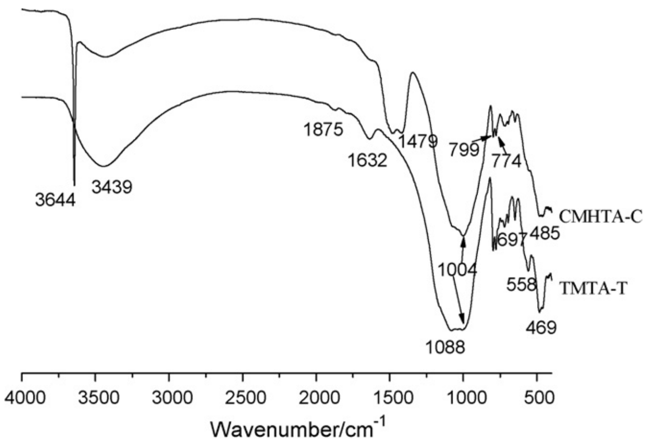

Fig. 4. IR spectra of activated coal gangue C and T by CMHTA and TMTA technologies.

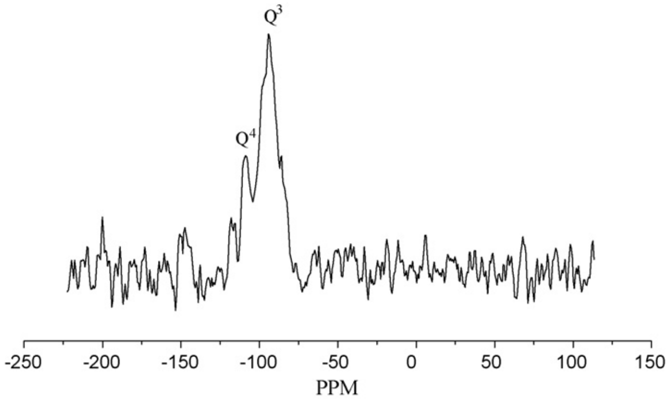

Fig. 5. NMR patterns of ^{29}Si of activated coal gangue T by TMTA technology.

3.3. ^{29}Si and ^{27}Al MAS NMR analysis

Figs. 5 and 6 show the MAS NMR patterns of ^{29}Si of activated coal gangue T and C by TMTA and CMHTA technologies, respectively. The different chemical shifts in spectra are normally interpreted in terms of the different silicon Q^n environments, where n denotes the number of bridging oxygen linked to other Si atoms for each Q (SiO_4) units [18]. Thus, Q^4 are Si in frame shaped structure and highest polymers, Q^3 are Si in layered groups, and Q^0 are Si in orthosilicate groups (discrete tetrahedral SiO_4). Compared with Figs. 5 and 6, it is easy to find that the Q^4 groups have decreased,

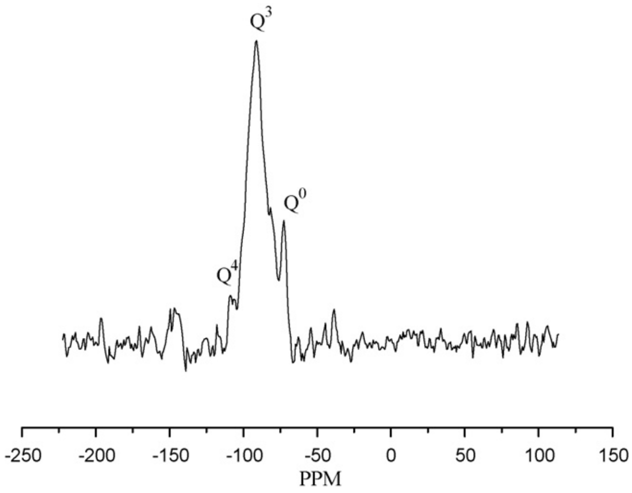

Fig. 6. NMR patterns of ^{29}Si of activated coal gangue C by CMHTA technology.

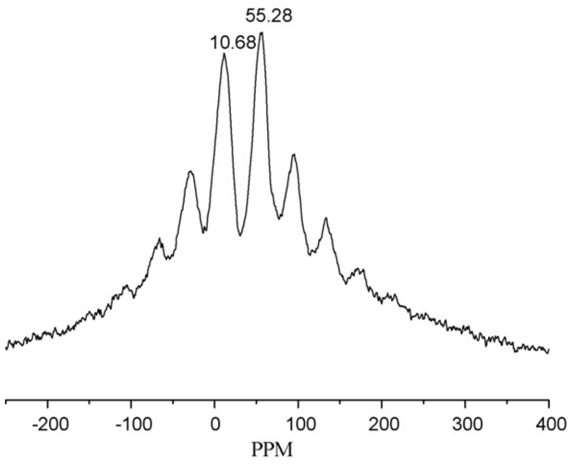

Fig. 7. NMR patterns of ^{27}Al of activated coal gangue T by TMTA technology.

while Q^3 and Q^0 have increased in gangue C, which can draw the conclusion that the polymerization degree of gangue C is lower than that of gangue T.

The MAS NMR patterns of ^{27}Al of activated coal gangue T and C by TMTA and CMHTA technologies are present in Figs. 7 and 8. The bands centred approximately at 55 ppm are assigned to 4-coordinated (tetrahedral) Al, and the spectral range for 6-coordinated (octahedral) Al displays two sharp bands at 10 and 14 ppm. The comparison between these highlights a general evolution from gangue T to C: an increase of the 4-coordinated Al content and a corresponding decrease for Al in 6-fold coordination.

These findings are in complete agreement with the conclusions obtained from XRD and IR spectra; a decrease in the degree of polymerization from activated coal gangue T to C, which means activated coal gangue C has a better activity.

3.4. Mechanical properties

In order to compare the activity of gangue C and T with raw gangue, we prepared a new kind of cementitious material, using coal gangue, slag, clinker and gypsum as raw material. The designed proportion of this cementitious material is listed in Table 2. The flexural and compressive strength of coal gangue based cementitious materials are shown in Figs. 9 and 10. As might be expected, both the flexural and the compressive strength of activated gangue T and C based blended cements are higher than that of raw gangue based blended cement, which demonstrate that these two activation methods can improve the cementitious activity of raw gangue greatly. Moreover, the strength of activated gangue C based blended cement is the highest among these three blended cements, and the mechanical properties are well comparable with those of 42.5 ordinary Portland cement.

It can be inferred from the data that it is feasible to use activated coal gangue to replace up to 52% of the raw materials to produce cementitious materials, which is eminently suitable for road construction. In addition, the consumption of clinker is only 20%, so it has important environment and economic significances.

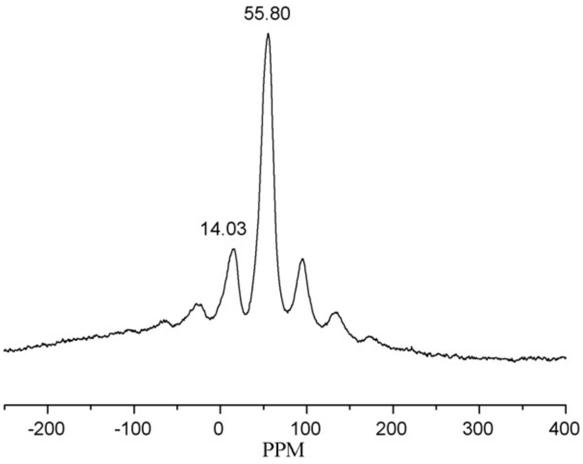

Fig. 8. NMR patterns of ^{27}Al of activated coal gangue C by CMHTA technology.

Table 2
Composition of coal gangue based cementitious material (%).

Coal gangue	Clinker	Slag	Gypsum
52	20	22	6

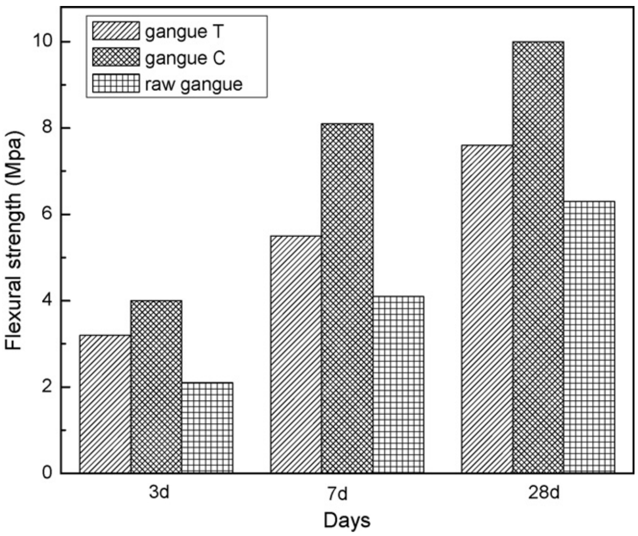

Fig. 9. Flexural strength of raw gangue, gangue T and gangue C based cementitious material.

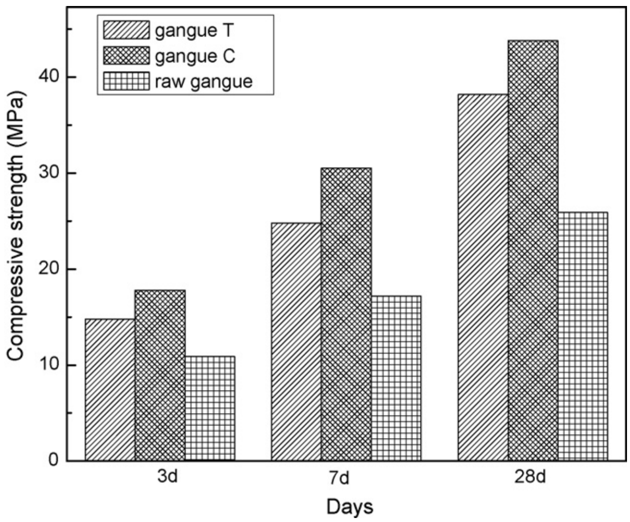

Fig. 10. Compressive strength of raw gangue, gangue T and gangue C based cementitious material.

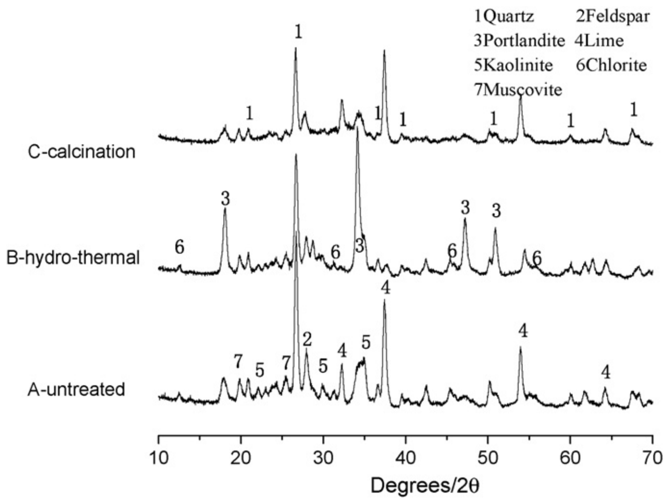

Fig. 11. XRD patterns of activation of coal gangue with added CaO for each step.

4. Discussion

The major differences between CMHTA and TMTA technologies include: the adding of CaO and hydro-thermal process. It is known that the activation of coal gangue using calcination with calcium has good effect, and some studies were carried out by Song and co-workers [19,20]. Because of the low content of CaO in raw coal gangue, we add some CaO in activation process. The main reaction is SiO_2 and CaO to generate C_2S at 1150 °C, which improves the activity of coal gangue. However, the role of CaO in this system is different.

Generally speaking, the CMHTA technology includes three steps: mechanical activation, hydro-thermal activation and calcination. In the process of wet mill, the added CaO was slaked with an amount of water, which formed $Ca(OH)_2$ and released heat, which are beneficial to hydro-thermal activation. In order to investigate the role of CaO for each step, XRD and XPS analysis were used. In the XRD patterns (Fig. 11), sample A is for mixed coal gangue and CaO, B is for hydro-thermal activated gangue, and C is for calcined gangue. Due to the presence of $Ca(OH)_2$, the pH value of hydro-thermal activation solution was raised to 12, and this chemical environment helps to erode quartz and feldspar. From Fig. 11, it can be seen that the peak intensity of quartz and feldspar declines in sample B, suggesting crystal lattice deformation of quartz and decomposition of feldspar in the alkali environment. Casey et al. [21] studied the decomposition mechanism of feldspar with CaO in hydro-thermal solution, and they explained that OH^- reacted with K^+ and Na^+ contained on the surface of feldspar, resulting in the breaking of Al–O band and formation of silicon-rich ($SiO_2{\cdot}nH_2O$) precursor. After calcination, chlorite and kaolinite decomposed, at the same time, the crystallinity of quartz, muscovite and feldspar decreased gradually in sample C.

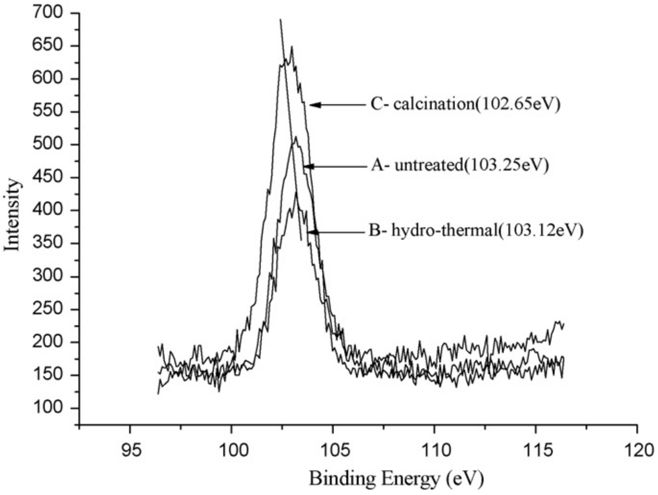

Fig. 12. Si 2p binding energy of activation of coal gangue.

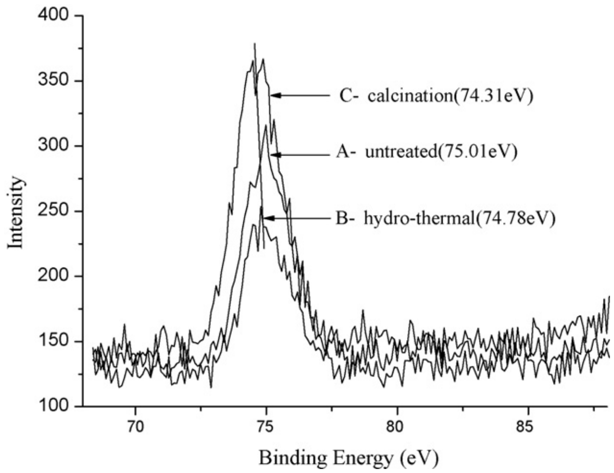

Fig. 13. Al 2p binding energy of activation of coal gangue.

The binding energies of Si 2p and Al 2p of activated coal gangue are present in Figs. 12 and 13. As described above, we obtained the same result. The Si 2p binding energy decreased from sample A to C, which means the degree of Si–O polymerization reduced [22,23]. Barr et al. [24] reported that aluminum binding energies are dependent upon coordination number. Tetrahedrally coordinated aluminum generally has a lower binding energy than octahedrally coordinated aluminum, i.e. 73.4–74.55 and 74.1–75.0 eV, respectively. These findings are consistent with the data from MAS NMR analysis.

It can be inferred from these analyses, the added CaO provides a suitable chemical environment to promote the decomposition of feldspar and muscovite in hydro-thermal process. Moreover, in the calcination process, the active CaO is helpful to decrease the crystallinity of quartz. As a result, the activated coal gangue C has a better cementitious activity by CMHTA technology.

5. Conclusions

From the analyses above, we can draw the conclusions as follows:

(1) According to the comparison of mechanical properties coal gangue based blended cement, both of the TMTA and CMHTA technologies can improve the cementitious activity of raw gangue greatly.
(2) The activation effect by CMHTA technology is better than TMTA. We use these activated coal gangue to prepare a new kind of blended cement with slag and small amount of clinker, in which the consumption of activated coal gangue is up to 52%. This kind of blended cement not only consumes large quantities of coal gangue, has a good mechanical property, but also saves a lot of natural resources for the cement clinker.
(3) Compared with TMTA, the mineral phases such as feldspar and muscovite were partially decomposed, and the crystallinity of quartz decreased by CMHTA technology. That is why activated coal gangue C has a better cementitious activity.

(4) In the process of CMHTA technology, the added CaO provides a suitable chemical environment to promote the decomposition of feldspar and muscovite in hydro-thermal process. Moreover, in the calcination process, the active CaO is helpful to decrease the crystallinity of quartz.

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