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Research on cementitious behavior and mechanism of pozzolanic cement with coal gangue

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Abstract

In this paper, the mechanical property of coal gangue in the activatory process is studied by using the method of orthogonal experiment, and then the micromechanism of various coal gangues is determined by modern test methods such as scanning electron microscope (SEM) and nuclear magnetic resonance (NMR). The experiment can approve those results: when proper amount of gypsum and fluorite were taken as for mineralizer in the course of calcinations of added-calcium coal gangue, much micropore can appear in microstructure and it can be in more molten state; spectrum peak of ^{29}Si in this kind of coal gangue is not only in splitting decomposition, but also in broadening; the mechanical property of coal gangue calcined with calcium is in accordance with microstructure.

Keywords: Coal gangue; Orthogonal design; Scanning electron microscope; Nuclear magnetic resonance; Si–O polyhedron

1. Introduction

Coal gangue is industrial residues that are discharged when coal is excavated and washed in the production course of coal mine, and is one of industrial solid wastes with biggest discharging. Its major chemical compositions are SiO_2 and Al_2O_3 etc., and its major mineral compositions are quartz and feldspar and so on [1]. According to statistic [2], the integrative discharging of coal gangue is equal to 15–20% of raw coal, and the accumulative total of stockpile may reach more than 7 thousand million ton. Coal gangue discharged every year in the Xuzhou area can add up to more than 2 million tons, and over the years can have been stored up 50–60 million tons. Existing coal gangue in large quantities has become a serious problem for environment pollution. In recent years, coal gangue more and more extensively has been synthetically used at home and abroad, among which it was excessively applied to research on the production of cement [3], but utilization rate is lower than 15% [2]. However, it may be a kind of effective method that the quantity of utilization can increase through raising of activity of coal gangue [4,5].

Many researches show that [5–7] cementitious capability of the fresh coal gangue is very weak. But by using the method of calcination the activity of coal gangue can be improved. Research [8] shows that calcined coal gangue at 700 °C has better activity. Another method of increasing activity is that CaO is added when calcining coal gangue. So it can be easily encroached by alkaline solution such as $Ca(OH)_2$ etc., and the skeleton of aluminosilicate can be broken, and SiO_4^{4-} and AlO_4^{5-} can be dissolved. And they can react with $Ca(OH)_2$ to produce CSH and CAH, then cementitious behavior of system can be improved. So the addition of CaO can be beneficial to improvement of activity of coal gangue.

In this paper, original coal gangue and added-calcium coal gangue that is made up of limestone, fluorite and gypsum were calcined under high temperature, and then tests were carried out through strength test, SEM and NMR.

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2. Raw materials and analysis

2.1. Chemical composition of raw materials

The primary raw materials in this experiment included coal gangue from Xuzhou, Beijing and Shandong and clinker from Jiangnan Onoda cement plant. Limestone and gypsum were taken from Nanjing Qinglongshan cement plant, among which the content of SO_3 in gypsum was 29.20%. Fluorite and sodium sulfate were chemical reagents. The chemical composition of raw materials was listed in Table 1.

2.2. Ore composition analysis [9]

2.2.1. Xuzhou coal gangue

It is gray, compact lump and white carbonate in lamina through the naked eyes observation. It shows sandy structure, cementation by base type. Chipping is associated with mostly subrounded, few subangular and perfectly rounded forms, and particle size consists in 0.1–0.3 mm under microscope. Microstructure of the major composition of Xuzhou coal gangue is shown as Fig. 1.

Fig. 1A(a)–A(b) show the microstructure of feldspar in Xuzhou coal gangue. But feldspar in Fig. 1A(a) has been in sericitization and in Fig. 1A(b) has been in chloritization. At the same time, it can be seen that albite twins and crossed twins consist in feldspar. Fig. 1B shows the microstructure of quartz. It shows that microstructure of certain particle is magnified and the latter shows entire microstructure of large quantity of quartz. Fig. 1C shows microstructure of dark mineral that mostly consists in chloritization and carbonatation. Dark mineral and detritus of sillcalite distribute in disorder in the granule of other minerals.

In addition, it can still be seen that there is much recrystallization in detritus of sillcalite and little of mica, carbonate and detritus of ruffite occur dispersedly. The agglutinate in ore parts which have been in recrystallization is argillaceous.

2.2.2. Beijing coal gangue

It is black with brown, partly metal luster and compact lump through naked eyes observation. And it shows crystalloblast of nemaline under microscope. Microstructure of the major composition of Beijing coal gangue is shown as Fig. 2.

Fig. 2A shows the microstructure of sillimanite in Beijing coal gangue. Furthermore, it can still be seen that sillimanite is in spindly basaltiform, and partly bent, partly get together to bunchiness, blanketlike, radiated, and is in parallel–axial extinction and a little has been in alteration. Fig. 2B shows the microstructure of mica, which is in tiny lepidosome and distributed comparatively evenly. Fig. 2C shows the microstructure of quartz, and it is obvious that the granule of quartz is tiny and part of outline is vague. Some particulate such as carbonaceous, argillaceous particle and mica etc. can blend to anomalous superfine stripe.

The crack of rock is filled up partly by mica and sillimanite of argillaceous alteration and little sillcalite, partly by carbonaceous particle and mixture.

2.2.3. Shandong coal gangue

It is gray and compact lump. Partly it is in drastic reaction with HCl through naked eyes observation. It shows sandy structure, cementation by base type. Chipping is associated with mostly subangular and subrounded forms, and particle size consists in 0.05–0.2 mm and little is a bit big under microscope. Microstructure of the major composition of Beijing coal gangue is shown as Fig. 3.

Fig. 3A shows the microstructure of feldspar in Shandong coal gangue. It can be seen that albite twins consist in part of feldspar most of which has been in sericitization, argillation and carbonatation. Fig. 3B shows the microstructure of quartz. It is still observed that undulating extinction and increasing of secondary quartz lie in parts of quartz. Fig. 3C shows that there is a little dark mineral in this kind of ore. Moreover, detritus of sillcalite distributes in disorder between quartz and feldspar, and dark mineral some of which is replaced by ferric oxide is in chloritization and carbonatation, and mica is not often seen in ore, and the agglutinate in ore is carbonate and little is argillaceous.

3. Research on pozzolanic cement with coal gangue by orthogonal design

3.1. Experimental methods

In this experiment, fineness of raw materials, strength of mortar and setting time were tested, respectively, in accordance with China standard GB8074, GB17671 and GB1346.

3.2. Experimental contents

In order to improve the strength of pozzolanic cement with coal gangue, and to reach final intent to use coal

Table 1
Chemical composition of raw materials w/%

Raw material	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	R_2O	Total
Beijing coal gangue	11.76	49.9	24.41	6.42	0.82	1.59	0.12	2.06	1.46	0.88	–	99.42
Xuzhou coal gangue	13.32	55.50	18.15	5.42	3.38	1.23	0.64	1.67	0.64	–	–	99.95
Shandong coal gangue	16.78	48.82	19.03	4.47	2.03	2.29	–	0.19	1.43	–	–	95.04
Clinker	–	21.74	5.06	3.56	66.6	0.88	0.81	0.55	0.05	–	0.41	99.25
Limestone	–	5.50	1.37	0.47	50.72	1.35	–	–	–	–	–	–

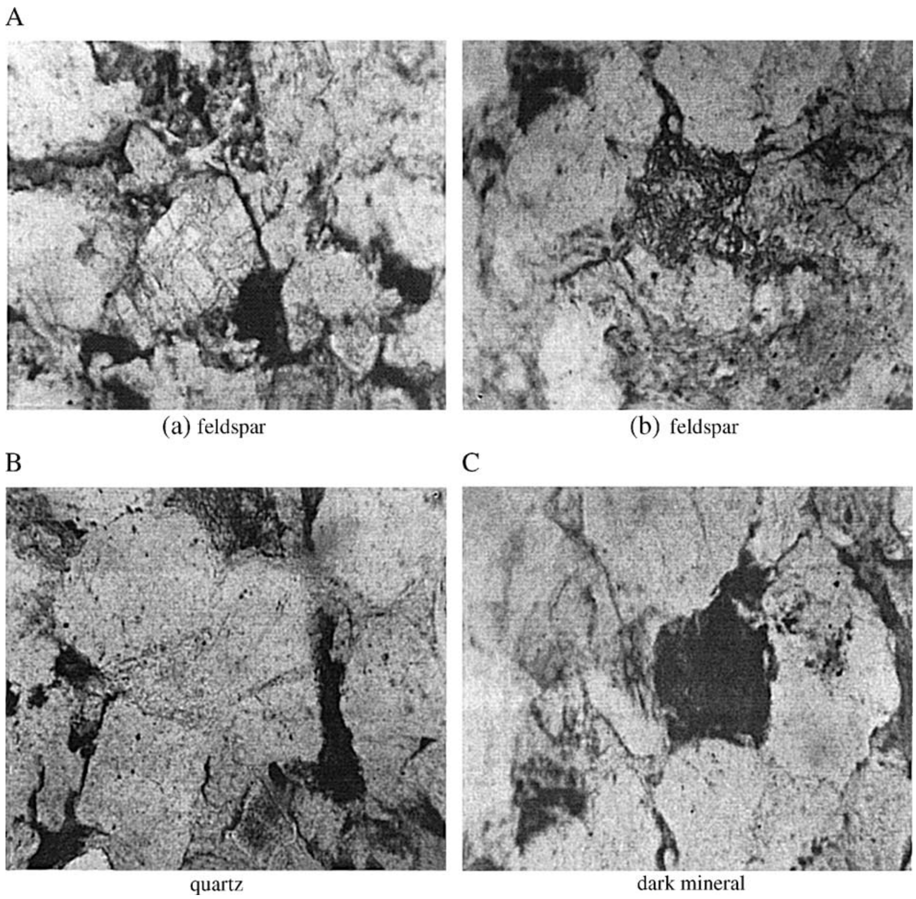


Fig. 1. Microstructure of Xuzhou coal gangue.

gangue, besides ingredient and fineness of coal gangue were changed in cement, thermo-activation was still adopted [10,11]. Orthogonal design was introduced so as to make these factors in optimized combination. $L_{27}(3^5)$ orthogonal table was designed among which five factors are species of coal gangue, fineness of coal gangue, means of thermo-activation, species of additives and amount of coal gangue, and three experiments can be made for each factor. The proportion of raw materials was listed in Table 2 and the results in experiment can be shown as Table 3. The results of analysis of compressive strength were listed in Table 4.

From the strength results (see Table 3), it can easily be seen that No. 6 and No. 9 have ideal strength results. Their coal gangue amount is 30% and 20%, respectively. Through simple calculation for the result of this orthogonal experiment (see Table 4), it can be analyzed which level of every factor is better, from which sometimes better condition can be found and it can also be estimated which factor is important.

From the result of orthogonal experiment, it can be found that there is an optimized combination of every factor such as species of coal gangue and means of thermo-activation. And it can be seen that, besides the influence of amount of coal gangue is very apparent, means of thermo-activation also has a more important influence on the strength of compound cement. Furthermore, different coal gangue can bring different impact on the strength. But the influence of fineness is very indistinctive and in other words it can be ignored in error limit.

4. Structural property and discussion

From the basic viewpoint of material science, there is close relation between structure and property of material. The relation between property and its microstructure can be made in virtue of SEM and NMR.

Xuzhou coal gangue was only chosen to discuss for the sample of orthogonal experiment. It was calcined under 1000 °C and 700° C and with CaO, among which coal gangue calcined under 1000 °C is used as comparison with other samples.

4.1. Testing conditions

SEM test was carried out on JSM-5900 scanning electron microscope for morphology observation of various coal gangues.

MAS testing of ^{29}Si was carried out on MAS 4 mm/15 kHz solid probe. In the NMR experiment, intensity of magnetic field is 11.74 T, and resonance frequency of ^{29}Si is 99.35 MHz. Sampling of MAS testing of ^{29}Si is made by sequence of

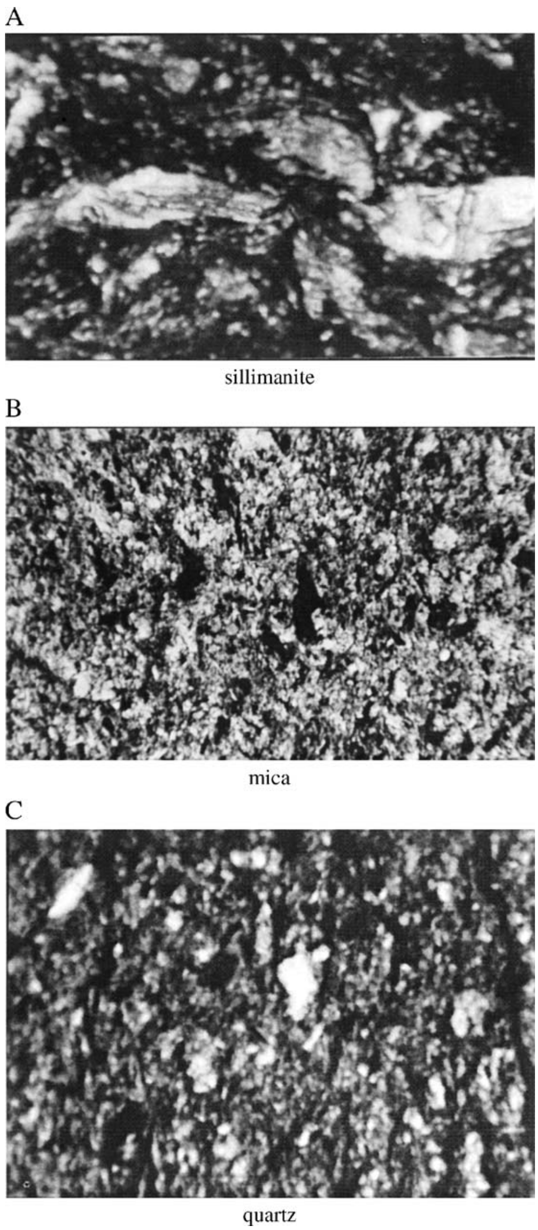


Fig. 2. Microstructure of Beijing coal gangue.

single impulse, and corresponding breadth of impulse of 90° is 4.0 μs, energy of impulse is 13.00 dB, delay time between pulses is 0.25 s and spinning rates effectively used are 15 kHz.

4.2. Results and discussion

4.2.1. Results of SEM

Through SEM [12,13], microstructure of coal gangue in its activatory course such as morphological characteristic of the granule may be studied and analyzed. SEM spectra of various coal gangues were listed in Fig. 4.

In Fig. 4, SEM spectra of various coal gangues can be shown. From Fig. 4a, it can be found that the microstructure of uncalcined coal gangue is comparatively compact. However, from Fig. 4b to d, there is a great change in microstructure of coal gangue after calcination and calcination with calcium.

By comparing coal gangue calcined under 700 °C with under 1000 °C in microstructure, it may be discovered that much micropore can appear in the spectrum of the former, but under 1000 °C part can be in the molten state and these melts can fill in the interspace which is left behind volatilization of some composition in the process of calcinations. This kind of phenomenon can explain why in the active range of low temperature the activity of coal gangue calcined under 700 °C was optimum. So in orthogonal experiment coal gangue calcined under 700 °C was chosen to be studied.

By comparison of calcined coal gangue and coal gangue calcined with calcium, there are some slight differences in

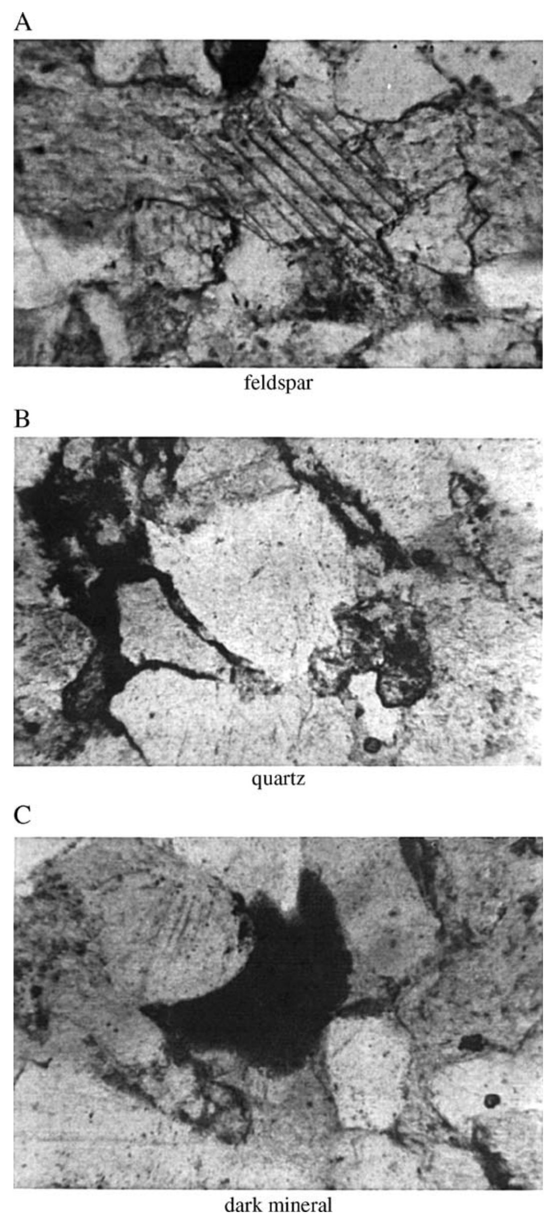


Fig. 3. Microstructure of Shandong coal gangue.

Table 2
Proportion of raw materials in orthogonal experiment

Serial number	Species of coal gangue	Fineness of coal gangue/(±10 m^2/kg)	Means of thermo-activation	Species of additives	Amount of coal gangue/%
1	Xuzhou	300	Uncalcination	Gypsum	20
2	Xuzhou	300	Under 700 °C	Calcined gypsum	30
3	Xuzhou	300	With calcium	Sodium sulfate and gypsum	40
4	Xuzhou	350	Uncalcination	Calcined gypsum	40
5	Xuzhou	350	Under 700 °C	Sodium sulfate and gypsum	20
6	Xuzhou	350	With calcium	Gypsum	30
7	Xuzhou	400	Uncalcination	Sodium sulfate and gypsum	30
8	Xuzhou	400	Under 700 °C	Gypsum	40
9	Xuzhou	400	With calcium	Calcined gypsum	20
10	Beijing	300	Uncalcination	Gypsum	40
11	Beijing	300	Under 700 °C	Calcined gypsum	20
12	Beijing	300	With calcium	Sodium sulfate and gypsum	30
13	Beijing	350	Uncalcination	Calcined gypsum	30
14	Beijing	350	Under 700 °C	Sodium sulfate and gypsum	40
15	Beijing	350	With calcium	Gypsum	20
16	Beijing	400	Uncalcination	Sodium sulfate and gypsum	20
17	Beijing	400	Under 700 °C	Gypsum	30
18	Beijing	400	With calcium	Calcined gypsum	40
19	Shandong	300	Uncalcination	Gypsum	30
20	Shandong	300	Under 700 °C	Calcined gypsum	40
21	Shandong	300	With calcium	Sodium sulfate and gypsum	20
22	Shandong	350	Uncalcination	Calcined gypsum	20
23	Shandong	350	Under 700 °C	Sodium sulfate and gypsum	30
24	Shandong	350	With calcium	Gypsum	40
25	Shandong	400	Uncalcination	Sodium sulfate	40
26	Shandong	400	Under 700 °C	Gypsum	20
27	Shandong	400	With calcium	Calcined gypsum	30

both structure of the shape. The latter, besides being with much micropore, can be in more molten state and this difference is in virtue of introduction of fluorite and gypsum that can play the role of directional mineralizer in the course of calcinations [14]. The mineralizer can reduce bond energy between the particle of reactant, raise its chemical activity, promote the reaction of solid phase, speed up decomposition of $CaCO_3$, and strengthen the reactive ability of SiO_2 and CaO and, at the same time, can still change the property of liquid and take from viscosity and surface tension of liquid.

4.2.2. Results of NMR

Solid high-resolution nuclear magnetic resonance is one of the important methods of study on structure. The adaptability of it for every sample is very strong, and it can not only be used to structural analysis of solid materials with higher crystallinity, but also of solid materials with lower crystallinity and non-crystalline substances [15–17].

Si and Al are principal parts of the chemical composition of coal gangue, and what change on their structural levels in the activatory process is the key of the influence on the strength of compound cement with coal gangue. Through NMR, the research of structural level can be made from the environment of Si and Al atom and the relation between each other in the activatory process of coal gangue [18,19]. Being confined to the length of this paper, only ^{29}Si-NMR spectra are used for the study. ^{29}Si-NMR spectra of various coal gangues are listed in Fig. 5.

Table 3
Physical properties of the compound cement

Serial number	Flexural strength/MPa		Compressive strength/MPa		Setting time/h:min	
	3 days	28 days	3 days	28 days	Initial	Final
1	6.1	8.0	28.0	42.7	2:03	2:38
2	5.0	7.7	22.6	38.2	2:26	2:46
3	4.6	8.5	18.2	30.1	2:22	2:42
4	3.4	5.4	13.7	22.4	2:35	3:19
5	6.4	8.7	26.5	41.4	1:42	2:24
6	5.7	8.3	26.4	49.0	2:37	3:04
7	5.3	6.9	20.9	27.9	2:42	3:04
8	4.7	8.4	18.0	37.9	2:00	2:50
9	6.6	9.1	31.8	49.9	1:45	2:25
10	3.7	5.4	13.3	20.5	2:31	3:10
11	5.6	7.1	26.6	34.6	2:10	2:44
12	5.6	8.1	22.3	32.6	1:50	2:29
13	4.1	6.5	19.3	30.3	2:16	2:53
14	3.5	5.2	14.1	18.4	1:55	2:30
15	6.3	8.4	29.6	47.8	1:33	2:12
16	5.9	7.4	21.9	29.6	2:02	2:50
17	4.5	7.2	19.6	31.7	1:56	2:36
18	4.8	8.1	19.9	36.6	1:14	2:14
19	5.0	6.7	20.5	31.9	2:37	3:40
20	4.7	7.3	18.3	33.2	2:02	2:40
21	5.4	7.2	22.6	30.9	1:53	2:34
22	5.9	7.0	24.4	39.4	2:12	2:50
23	5.6	8.6	24.6	35.1	1:25	2:19
24	4.6	7.2	20.2	35.9	2:01	2:52
25	4.1	5.4	16.8	20.9	1:54	2:42
26	6.5	9.1	29.6	48.9	1:46	2:31
27	5.8	7.9	25.2	41.2	1:53	2:43

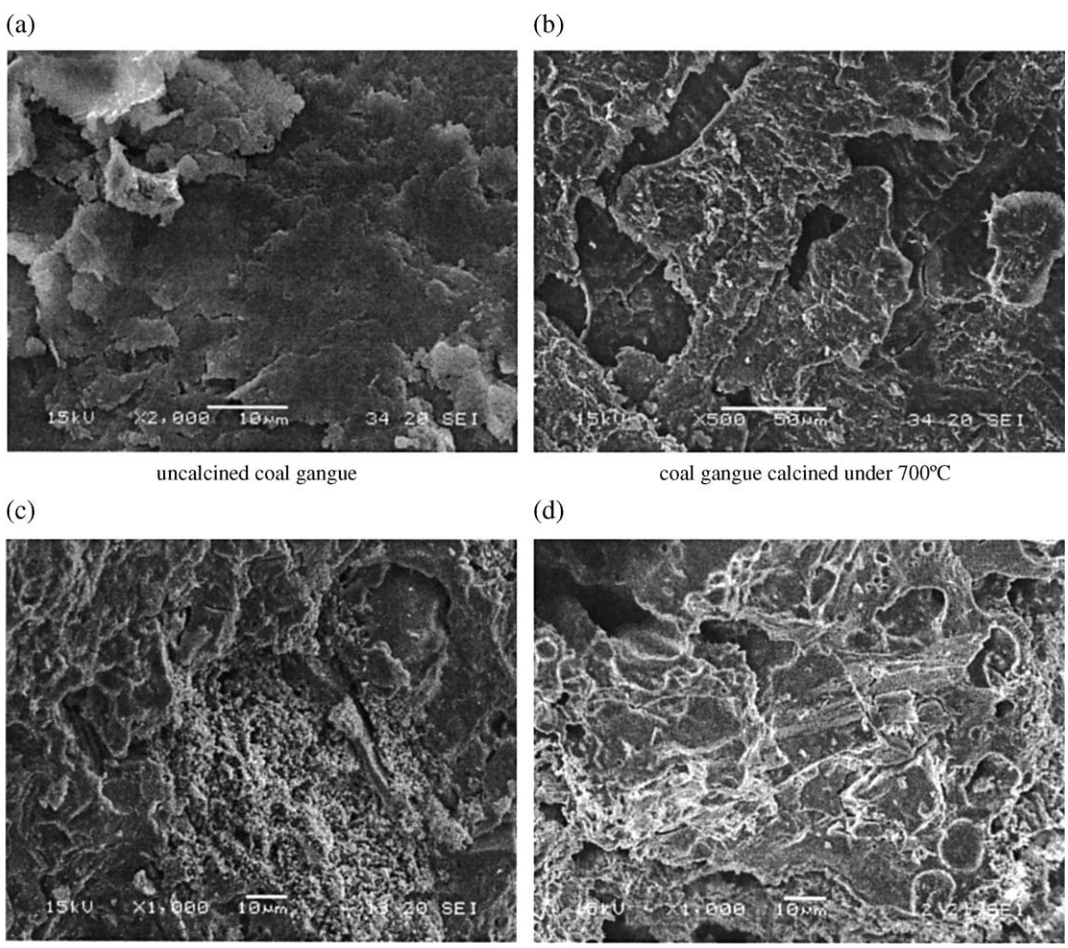
Table 4
Analysis of the results of compressive strength

	Species of coal gangue		Fineness of coal gangue/(±10 m^2/kg)		Means of thermo-activation		Species of additives		W (coal gangue)/%	
	3 days	28 days	3 days	28 days	3 days	28 days	3 days	28 days	3 days	28 days
t1	22.9	37.7	21.7	32.7	19.9	29.5	22.8	38.4	26.8	40.6
t2	20.7	31.3	22.1	35.5	22.2	35.5	22.4	36.2	22.4	35.3
t3	22.5	35.3	22.6	36.0	21.2	39.3	20.9	29.6	16.9	28.4
R	2.2	6.4	0.9	3.3	2.3	9.8	1.9	8.8	9.9	12.2

It can be found from Fig. 5 that after calcination and Ca-calcination, the structure of Si–O polyhedron of coal gangue has made a notable variation.

In Fig. 5a Si–O polyhedron of uncalcined coal gangue is in dissymmetrical polymeric state, and this can be manifested as spectrum peak of broadening of dissymmetrical structure, which is dominated by Q^2 dissymmetrical structure with chemical shift in −84.7 ppm [20]. But mineral composition of coal gangue is comparatively complex and each mineral cannot exist in single state, which may make chemical shift of ^{29}Si in uncalcined coal gangue in excursion to high magnetic field. So it can be estimated that Si–O polyhedron of uncalcined coal gangue may be in Q^3 dissymmetrical structure. In addition, in Fig. 5a it can be also discovered that a little spectrum peak can occur in −103.8 ppm where Si–O polyhedron belongs to Q^4 dissymmetrical structure [20].

After coal gangue have been calcined, chemical shift of Si–O tetrahedron is not fixed, but in excursion to higher field strength. Under 700 °C spectrum peak of ^{29}Si has been split, which can be attributed to calcinations, at the same time it can be displaced to low polymeric state. Under 1000 °C, peak shape of ^{29}Si can become more sharp and spectrum peak oppositely is displaced to high polymeric state, and chemical shift of Si–O tetrahedron can be in larger excursion which mainly shows Q^4 dissymmetrical structure with chemical shift in −110.2 ppm. In the experiment of mechanical property, the performance of coal gangue



(a) uncalcined coal gangue
(b) coal gangue calcined under 700ºC
(c) coal gangue calcined under 1000ºC
(d) coal gangue calcined with calcium

Fig. 4. SEM spectra of various coal gangues.

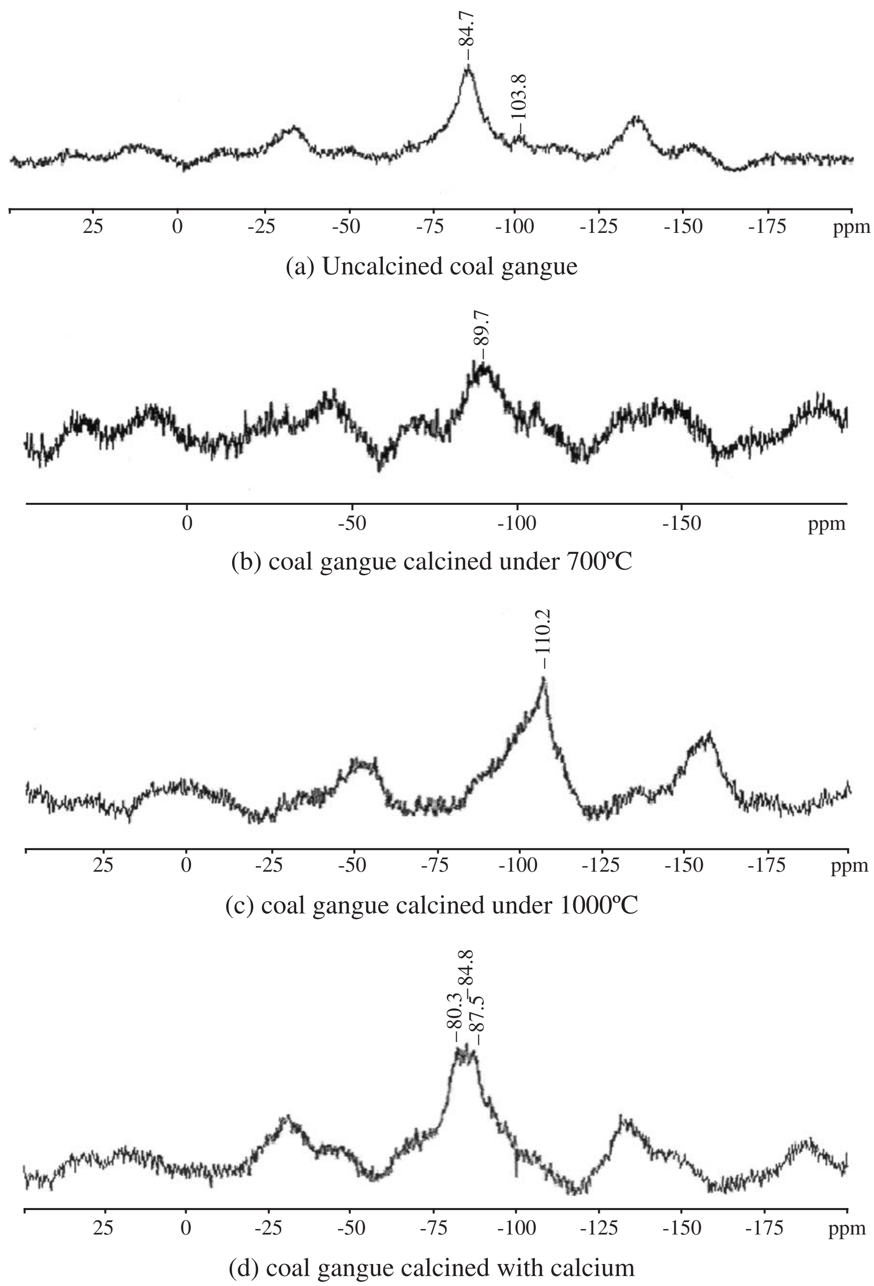


Fig. 5. ^{29}Si-NMR spectra of various coal gangues.

calcined under 700 °C was most perfect, which was better than the result under 1000 °C. Such was the case with the analysis of the result under other temperatures.

In coal gangue calcined with calcium Ca^{2+}, SO_4^{2-} and F^- are introduced. Si–O polyhedron is dominated by Si–O tetrahedron. But as a result that each Si–O tetrahedron is in different surrounding environments and some can be replaced by other ions, spectrum peak of ^{29}Si is not only in splitting decomposition, but also in broadening. Furthermore, vitreous body and amorphous material may occur. These characteristics can make Si–O polyhedron split to that of the separation with Q^0, Q^1 and Q^2 structure [15]. This phenomenon in the experiment of mechanical property may show that the result of strength can be obviously improved, which can be attributed to the introduction of fluorite and gypsum. Compared to the microstructure of SEM, it can be discovered that the conclusion of two was consistent.

5. Conclusions

(1) There have been greater influences on activity of coal gangue by means of thermo-activation, but different methods can play the different parts of excitation of activity of coal gangue.

(2) By orthogonal experiment, it can be found that the activity of coal gangue can be improved perfectly. Calcination with calcium can greatly improve the activity of coal gangue in virtue of mineralizers such as fluorite and gypsum.
(3) By analysis of various coal gangues through modern testing methods such as SEM and XMR etc., it can be known that the microstructure of coal gangue can be in great changes by calcinations and calcinations with calcium, which in mechanical property can show the variety of strength, and the conclusion of two is consistent.

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