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Correlation between ^{29}Si polymerization and cementitious activity of coal gangue[*]

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Abstract: A new method for estimating the degree of $[SiO_4]^{4-}$polymerization of coal gangue is presented. The method uses the relative bridging oxygen number (RBO) based on nuclear magnetic resonance (NMR) techniques. X-ray diffraction (XRD) and ^{29}Si NMR techniques have been used to study phase transitions and silicate polymerization of coal gangue calcined at different temperatures or co-calcined. It has been found that phase transition of clay minerals causes silicate polymerization to change with temperature. In this study, cementing activity and RBO were determined to be inversely related. Generally, activated coal gangue with lower RBO had better cementitious activity.

Key words: Degree of polymerization, Relative bridging oxygen number (RBO), Nuclear magnetic resonance (NMR), Coal gangue, Cementitious activity
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INTRODUCTION

Coal gangue is a complex industrial solid waste that is discharged when coal is excavated and washed in the production process. It contains clay minerals whose crystalline phase decomposes and yields active silica or alumina when calcined or spontaneously combusted (Thompson, 1947; Mc Conville *et al.*, 1998). If these active substances and lime are combined in water, cementitious activity occurs in the mixture. Therefore, gangue has good prospects for use as a general building material (Sun *et al.*, 2004; Li *et al.*, 2006; Zhang and Sun, 2009). Related studies (Armesto and Merino, 1999) have shown that properties such as mineral composition, degree of $[SiO_4]^{4-}$ polymerization, glass crystal ratio and crystallinity all influence the activity of aluminum silicon materials. The effect of silicate polymerization on cementitious activity has been recognized, but there are still no standardized methods for quantifying the effect. Currently, common techniques for estimating $[SiO_4]^{4-}$ polymerization include light scattering (Strauss *et al.*, 1953) and a trimethylsilylation method (TMS) (Tamas *et al.*, 1976; Chen *et al.*, 1987). These methods are used to evaluate silicate polymerization in silicate solution, but are not fit for studying silicate polymerization in solid materials. Moreover, these methods have complicated procedures with poor reproducibility in experimental results. Based on the silicate melt polymerization theory, Masson *et al.*(1970) and Dou and Liu (1981) proposed using the average length of polymer to evaluate the degree of silicate melt polymerization. The mathematical relationship between average chain length $\bar{x}_n$ and composition was established. This method obviously cannot be applied to silicon aluminum materials with highly complex structural components. Richardson and Groves (1997) studied the nuclear magnetic resonance (NMR) spectra of slag hydration products in water and potassium hydroxide solution. He proposed using the mean average chain length (MCL) as a way to evaluate the degree of polymerization of

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silicon and oxygen polyhedron:

$$MCL = \frac{2\left[Q^1+Q^2(0\text{Al})+3(1\text{Al})/2\right]}{Q^1}, \qquad (1)$$

where Q^1, Q^2, Q^2(1Al) are corresponding areas of resonance peaks.

This method is simple and easy to conduct. However, since the indicator, MCL, was proposed for use only for particular hydration products it has a limited scope of application.

As the number of bridging oxygen atoms changes with the degree of $[SiO_4]^{4-}$ polymerization, we propose the concept of relative number of bridging oxygen (RBO) and study the correlation between RBO and cementitious activity in coal gangue.

RBO METHOD

The NMR technique is an effective way to study atomic coordination structure (Engelhardt *et al.*, 1989; Liu, 2001; Murgier *et al.*, 2004). Indeed, for ^{29}Si NMR, various coordination structures can be deduced from the observed chemical shifts. Some relationships between coordination structure parameters and ^{29}Si chemical shift are presented in Fig.1.

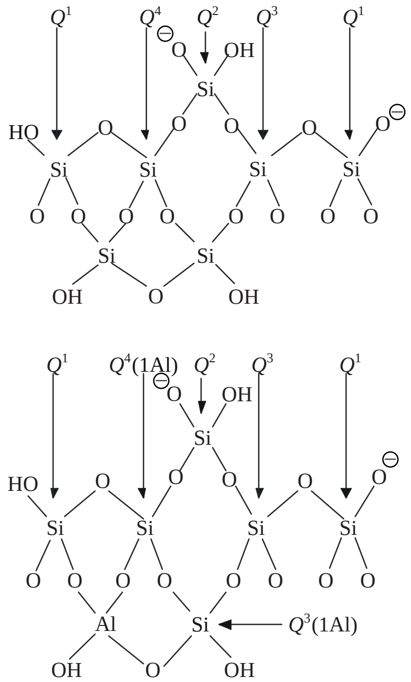


Fig.1 Coordination structure diagram of ^{29}Si in silicate

Coordination structures can be divided into Q^0, Q^1, Q^2, Q^3, and Q^4 units based on the coordination number (n of Q^n) of bridging oxygen around the ^{29}Si. A change in the degree of $[SiO_4]^{4-}$ polymerization leads to NMR peak shifts (Wang, 2003). The number of bridging oxygen would change from Q^n to Q^{n-1} if a Si—O—Si chemical bond breaks (Fig.1). However, if two Si—O⊕ combine to form a Si—O—Si bond, the Si coordination structure would change from Q^n to Q^{n+1}. Therefore, the change in bridging oxygen number can be used as an indicator of polymerization or depolymerization reactions in the system. To formalize this idea, the concept of RBO is proposed. The RBO can be calculated from the relative peak area:

$$RBO=\frac{1}{4}\cdot\frac{\sum n\cdot Q^n}{\sum Q^n}, \qquad (2)$$

where Q^n corresponds to the peak area of Si with coordination number n.

In Eq.(2), we start with the assumption that all Si coordination structures are Q^4 while the RBO value is 1. The other structural units, Q^0, Q^1, Q^2, and Q^3, are the result of depolymerization of Q^4 units. So the bridging oxygen number ratio of Q^n units and assumed Q^4 can be used to evaluate the degree of deploymerizaton of assumed Q^4. Furthermore, the ratio value (RBO) can also be applied to silicate polymerization. Conversely, if the Q^4 unit is deploymerized sufficiently to Q^0, all Si coordination structures are Q^0 and silicate polymerization is minimized. At the same time, the RBO value is 0.

To improve the accuracy of calculation, the preconditions, such as chemical shifts determination, structure classification, peak overlap separation and peak area calculation, must be conducted as meticulously as possible. The ranges of ^{29}Si chemical shifts for different structural units of silicate samples are shown in Table 1 (Lippmaa *et al.*, 1980). Research has shown that the chemical shifts deviate when Si atoms are substituted with Al atoms. In fact, the deviation range increases with substitution number (Engelhardt, 1987). In a general model, the coordination structure can be written as Q^n(mAl), where m is the number of substituted Al atoms such that $m<n$ and $n<4$. As chemical shifts resulting from substitution may lead to incorrect structure classification, the substitution effect would be ignored in the standard

Q^n chemical shift range in this study. However, for the chemical shifts between Q^n~Q^{n+1}, which arise mainly because of substitution effects of neighboring coordination atoms, the coordination structure should be classified as Q^{n+1}.

Table 1 Ranges of ^{29}Si chemical shifts for different structural units of silicate species

Connectivity	Type	Chemical shift ($\times10^{-6}$)
Q^0	Orthosilicate (monomer)	−66~−74
Q^1	Pyrosilicate (dimmer)	−77~−82
Q^2	Linear chains or ring	−85~−89
Q^3	Cross-linked chains	−92~−100
Q^4	3D network	−103~−115

EXPERIMENT

Materials

The coal gangue used in this experiment was from Fangshan, Beijing, China, while clinker was from the Xingang, Beijing Cement Plant, China. The specific surface area of ground coal gangue was 545 m^2/kg. The chemical composition of raw materials tested using X-ray fluorescence (XRF) (XRF-1700, Japan) is shown in Table 2.

Table 2 Chemical composition of raw materials (%, w/w)

Raw material	Chemical composition					
	SiO_2	Al_2O_3	CaO	K_2O	MgO	Fe_2O_3
Gangue	45.57	16.35	1.93	2.85	1.56	6.02
Clinker	21.94	5.27	64.1	1.77	1.88	2.96

Testing conditions

Ground coal gangue was calcined at 600, 900, or 1200 °C for 3 h. Coal gangue and calcium oxide were mixed together at a ratio of 10 to 1 before being co-calcined at 800 °C for 3 h.

The strength of coal gangue mortar was tested according to the China Standard GB/T17671-1999 (1999). Coal gangue and clinker were mixed together at a ratio of 1 to 1. The water to solid ratio was 0.30.

X-ray diffractometer (XRD) analysis was conducted using a Rigaku D/max-RB XRD (Japan) with Cu K_α radiation, 40 kV voltage, 100 mA current and 2θ scanning, at a scanning speed of 4 °/min.

NMR analysis was conducted using a BRUKER-AM300 (Germany). A zirconia rotor with a diameter of 7 mm and a length of 20 mm was used. The ^{29}Si NMR testing resonant frequency was 59.62 MHz and the rotor working frequency was 4000 r/s; the repeat time delay was 2 s and the sampling time was 0.246 s; the pulse width was 45° and the spectral width was 30 kHz; the test temperature was room temperature. The NMR data were analyzed using NUTS software.

RESULTS AND DISCUSSION

Phase transition of calcined coal gangue

XRD patterns of coal gangue calcined at 600, 900, or 1200 °C and precondition gangue are shown in Fig.2. The diffraction peaks of different phases in gangue are clear and sharp. This indicates a high degree of crystal in crystalline phases and a small amount of amorphous phase in gangue. The principal mineral phases in gangue are quartz, muscovite, leuchtenbergite and a small amount of feldspar. For all calcination temperatures, no obvious change was observed in the diffraction peaks of quartz and feldspar.

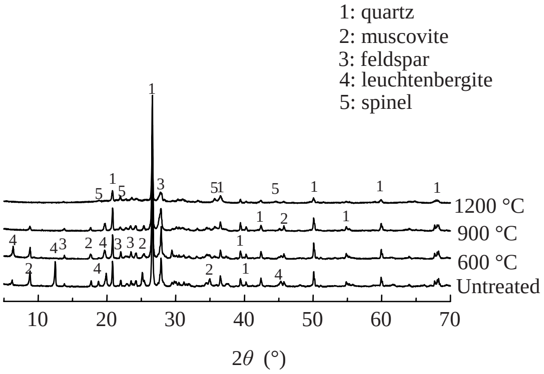


Fig.2 XRD pattern of coal gangue at precondition gangue and 600, 900, 1200 °C

In XRD patterns, a diffraction peak $(\bar{1}17)$ of muscovite becomes lower at 600 °C. Other diffraction peaks of muscovite appear to weaken at 900 °C and disappear at 1200 °C.

The diffraction peak (002) of leuchtenbergite weakened significantly at 600 °C, but diffraction peak (001) strengthened slightly. As leuchtenbergite is a clay mineral with a three-octahedron structure, the hydroxyl between lamellar would break away at a certain temperature. At the same time, the hydroxyl of

2:1 lamellar is unchanged, so diffraction peak (001) intensifies (Yang, 1992), while the other diffraction peaks weaken or even disappear.

As the calcination temperature reaches 1200 °C, the hydroxyl of the talc layer breaks away from the structure. The diffraction peaks disappear with destruction of leuchtenbergite structure. New diffraction peaks (at 2θ=35.56°, 18.80°, 30.99°, that is, d=0.246, 0.470, 0.288 nm) appeared at 1200 °C. These peaks are diffraction peaks (311), (111) and (220) of spinel which is a product of leuchtenbergite decomposition at high temperatures.

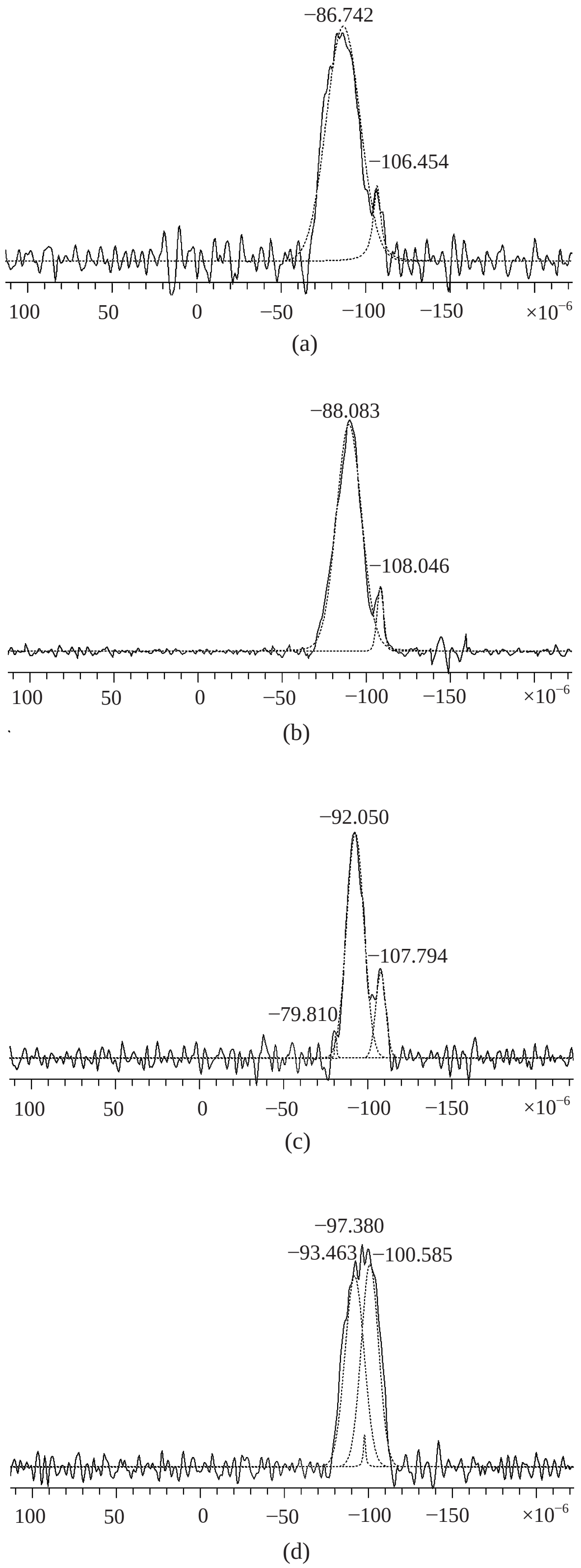
Correlation between degree of polymerization and cementitious activity of calcined gangue

NUTS is a "toolbox" of professional software for processing and displaying NMR data, which calculates peak separations, line fitting curves and relative peak areas.

^{29}Si magic angle spinning (MAS)-NMR spectra of precondition gangue and gangue calcined at 600, 900, and 1200 °C respectively are shown in Figs.3a~3d. Fig.3a shows ^{29}Si MAS-NMR spectra of precondition gangue. There are two clear resonance peaks partly overlying each other whose chemical shifts are -86.742×10^{-6} and -106.454×10^{-6}. The chemical shifts of these two peaks are in the range of Q^2/Q^4 units. The ^{29}Si MAS-NMR spectra were analysed using NUTS software and the other two independent imaginal line peaks were obtained. The relative area ratio of these two peaks was 100 to 7.3.

^{29}Si MAS-NMR spectra of calcined gangue at 600 °C are shown in Fig.3b. There are two clear resonance peaks, with chemical shifts of -88.083×10^{-6} and -108.046×10^{-6} for Q^2/Q^4 groups in silica polymorphs. The shape of the peaks is more acuate than those in Fig.3a and they are separated from each other significantly. Fig.3a analysis methods were used, peaks were separated and calculated. The relative area ratio of these two peaks was 100 to 3.58.

From the spectra of gangue calcined at 900 °C (Fig.3c), the peak of Q^2 is divided into two resonance peaks, with chemical shifts of -79.810×10^{-6} and -92.050×10^{-6} respectively. The intensity of the Q^4 peak at -107.794×10^{-6} was strengthened. These three peaks correspond to $Q^1/Q^2/Q^4$ structure units. Overlapping peaks were separated by software. The calculated ratio of areas was: 2.63 to 100 to 7.70.



(a)

(b)

(c)

(d)

Fig.3 ^{29}Si MAS-NMR spectra of (a) precondition gangue, (b) gangue calcined at 600 °C, (c) 900 °C and (d) 1200 °C

The shapes of MAS-NMR spectra from coal gangue melted at 1200 °C (Fig.3d) were different from those above. The divided resonance peaks restack together. The Q^4 resonance peak in Fig.3b disappears. There are three visible peaks. Their chemical shifts, at -93.463×10^{-6}, -97.380×10^{-6}, and -100.585×10^{-6} respectively, are in the range of $Q^{2\sim3}/Q^3/Q^{3\sim4}$ units. After peak separation and relative area calculation, the resulting area ratio was 92.49 to 1.2 to 100.

^{29}Si MAS-NMR spectra of co-calcination gangue are shown in Fig.4. A new clear sharp resonance peak at -69.865×10^{-6} for Q^0 units was obtained. The chemical shifts of the other two resonance peaks were -88.802×10^{-6} and -105.143×10^{-6}, corresponding to Q^2 and Q^4. The same method was used to determine the relative area ratio: 41.69 to 100 to 9.01.

^{29}Si structure units of clay minerals in coal gangue such as leuchtenbergite and muscovite correspond to $Q^{2\sim3}$ (Chen, 1996), but the ^{29}Si structure units of quartz and feldspar correspond to Q^4. Quartz and feldspar are more stable than clay minerals. There is little change in the calcination process. But clay minerals decompose which induces ^{29}Si structure units to change from $Q^{2\sim3}$ to $Q^{1\sim2}$. As there are only small amounts of Q^1 and Q^3, the resonance peaks in the spectra belong to the Q^2 range. When the calcination temperature rises to 900 °C, almost all clay minerals decompose, so there is a weak resonance peak corresponding to Q^1. As the calcination temperature reaches 1200 °C, other peaks except quartz and spinel in the XRD pattern disappear, so the Q^4 resonance peaks in NMR pattern strengthen.

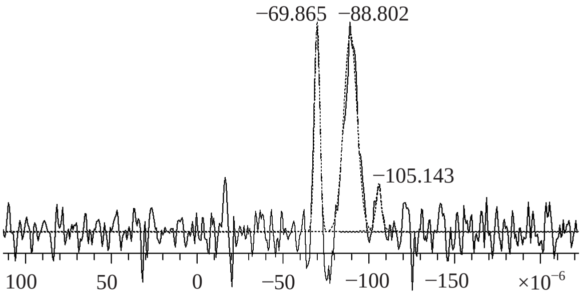


Fig.4 ^{29}Si MAS-NMR spectra of co-calcined gangue

The relative number of bridging oxygen resulting from different calcined gangue and co-calcined gangue estimated from the RBO formula are presented in Table 3.

Table 3 RBO of activitied coal gangue

	Precondition	600 °C	900 °C	1200 °C	Co-calcined
Q^0	–	–	–	–	41.69
Q^1	–	–	2.63	–	–
Q^2	100	100	100	–	100
Q^3	–	–	–	93.69	–
Q^4	7.37	3.58	7.70	100	9.01
RBO	0.535	0.518	0.527	0.879	0.392

The RBO of gangue calcined at 600 and 900 °C were slightly lower than those of the precondition coal gangue. The RBO value increased markedly at 1200 °C. The abrupt increase in RBO value results from the mixture becoming molten causing $[SiO_4]^{4-}$ to polymerize. The degree of polymerization reaction at this temperature is much greater than depolymerization, so the RBO value of gangue calcined at 1200 °C increases significantly. These results show that the degree of polymerization of coal gangue first decreases and then increases with higher calcination temperatures. Song (2004) reached a similar conclusion about the degree of polymerization of calcined coal gangue. This indicates that the RBO of aluminum silicon material could be used to estimate the change in the degree of polymerization.

The results from standard tests of the mechanical properties of mortar with precondition, co-calcined coal gangue and gangue calcined at 600 or 900 °C are shown in Fig.5. The mortar was cured for 3, 7, or 28 d. From the experimental data, the mechanical strength of calcined gangue at 600 °C was significantly higher than that of precondition gangue. But the mechanical strength of coal gangue calcined at 900 °C was slightly lower than that at 600 °C. The mechanical strength decreased dramatically when the calcination temperature rose to 1200 °C. The pozzolanity of the calcined coal gangue arises from the decomposition products of clay minerals—active silica or alumina. From the results of XRD, the peaks of spinel and quartz were intensified in gangue at 1200 °C. These two phases are too stable to react with lime. NMR results also showed that the structure units Q^4, which correspond to frame structure, increase significantly at 1200 °C. Frame structure is the most stable structure for silicate minerals and was unlikely to react with other materials in this system. So the mechanical properties decreased when the calcination temperature was 1200 °C.

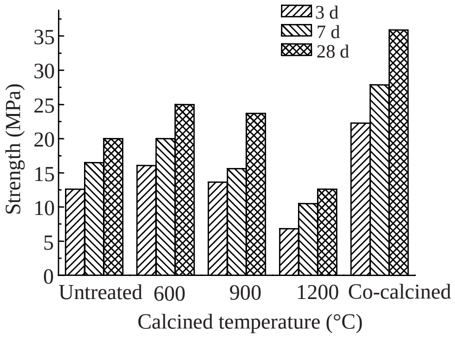


Fig.5 Mechanical properties of mortar with coal gangue cured for 3, 7, or 28 d

A negative correlation was found between the RBO and mechanical strength (Fig.6). But the negative correlation was nonlinear. There was little difference in RBO between coal gangue with precondition and 900 °C calcination, but the mechanical strength of precondition gangue was significantly lower than that of gangue calcined at 900 °C. This results from the full crystal structure of clay minerals strengthened by chemical stability, although the degree of Si-O polymerization of clay minerals with chip structure is not high. So the cementitious activity of raw coal gangue is significantly lower than that of gangue calcined at 900 °C (Feng, 2000; Gu and Wang, 2008). Many factors influence cementitious activity. Among these factors, the degree of polymerization is important (Qian and Cai, 2004). Generally, cementitious activity benefits from a reduction in the degree of polymerization. Thus, reducing the degree of polymerization is an important way to optimize cementitious activity. The RBO provides an effective way to evaluate the degree of Si-O polymerization, which has a negative correlation with cementitious activity.

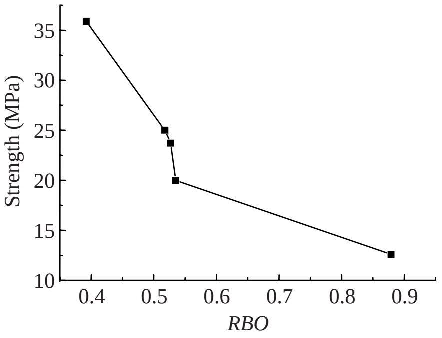


Fig.6 Correlation between RBO and cementitious quality

CONCLUSION

(1) The RBO provides an effective way to evaluate the degree of Si-O polymerization in coal gangue.

(2) An increase in calcination temperature first decreases the calcined gangue's RBO. Higher calcination temperatures ranging from 900~1200 °C improve the RBO values. The RBO values increase significantly at 1200 °C.

(3) Co-calcination of gangue produces a large number of Q^0 structures, which leads to a decrease in RBO value and a significant increase in the cementitious activity of the gangue sample.

(4) The correlation between RBO and cementitious activity is inverse and nonlinear.

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