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Pozzolanic behaviour of compound-activated red mud-coal gangue mixture

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ABSTRACT

The pozzolanic behaviour of compound-activated red mud-coal gangue has been investigated through TG, DTA, XRD, FTIR and ^{27}Al MAS NMR. From viewpoint of reaction kinetics, it is found that the pozzolanic reaction mechanism of the compound-activated red mud-coal gangue — lime system is clearly consistent with diffusion control up to 14 days, and the reaction rate constant calculated from Jander equation decreases with the increase of CaO addition in the system. The hydration products formed in the red mud-coal gangue — lime systems at ambient temperature are essentially aluminous C–S–H and $Ca_3Al_2O_6.xH_2O$. From TG analysis results, it is thought that the high amount of $Ca(OH)_2$ in the pastes of studied system is not conducive to the continual increase of non-evaporable water content of the hydration products. Of particular interest, ^{27}Al MAS NMR proved to be an effective technique to obtain valuable information of $Al^{[4]}$ in C–S–H and $Al^{[6]}$ in $Ca_3Al_2O_6.xH_2O$.

1. Introduction

It is known that China has a large capacity of alumina production. However, 0.8–1.5 tons of red mud is generated by per ton of alumina production. It was estimated that over 7 million tons of red mud is impounded annually in China [1]. The large emission of red mud from alumina production has caused severe environmental problems. Meanwhile, there is also a huge capacity of coal production in China. While coal gangue generated from the coal production is a non-ignorable issue. The vast majority of coal gangue is stockpiled, not only causing local ecological and environmental problems, but also threatening the safety of local residents. To ensure the safety of red mud and coal gangue, recycling these two solid wastes has been a challenging task urgently considered by the government authorities in China. Utilizing red mud and coal gangue as cement additions or part cement replacement materials could be a promising direction to effectively consume the huge amounts of these two solid wastes, leading to the prime interest of savings on energy resources and reduction of environmental pollution.

It has been reported that calcined red muds are pozzolanic [2]. For red mud derived from bauxite-calcination method, a calcination temperature of 600 °C has generally given the best cementitious properties [3,4]. Due to bauxite-calcination-method red mud contains some quantities of amorphous aluminosilicate materials and gibbsite, they can be transformed into reactive silica and alumina during the calcination process, resulting in some pozzolanic properties. The cementitious property of raw coal gangue is very weak. Calcination under 600–700 °C can significantly improve the activity of coal gangue due to the decomposition of clay minerals to form active silica and alumina [5,6]. Besides, addition of CaO or other calcium source during calcination can further improve the activity of coal gangue [7,8]. Considering that bauxite-calcination-method red mud contains large amount of calcium oxide in its chemical composition, we used the bauxite-calcination-method red mud as calcium source to enhance the activity of coal gangue through compound activation method [9]. In our previous literature [9], it was found that compound activation method can significantly improve the cementitious behaviour of red mud-coal gangue mixtures, and appropriate amount of red mud can promote the decomposition of chlorite and lower the crystallinity of quartz occurring in the coal gangue. We have also conducted an experiment on using the subsequent red mud-coal gangue mixture as pozzolanic materials blending with blast furnace slag, clinker and gypsum to produce cementitious material, and it has been demonstrated that the developed red mud-coal gangue based cementitious material had good physical and mechanical properties [10]. However, a confusing question present in most readers' minds might be: what is the pozzolanic behaviour of the compound-activated red mud-coal gangue mixture?

Pozzolanic behaviour is usually defined as the capability of a pozzolanic material reacting with lime in the presence of water at ordinary temperatures to form cementitious compounds. Pozzolanic materials generally used in the cement industry include natural volcanic ash, metakaolin, calcined clays or industrial by-products such as slag, fly ash, calcined red mud and calcined coal gangue. Among all

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of them, metakaolin has been proved to be an excellent pozzolan, and the hydration behaviour of metakaolin-Ca$(OH)_2$ system has been widely investigated [11–15]. Hydration products of metakaolin-Ca$(OH)_2$ system with water at 20 °C are essentially C_2ASH_8, C–S–H and C_4AH_{13} [11]. As a typical example of pozzolanic reaction, the investigations on the hydration of metakaolin-Ca$(OH)_2$ system can provide some valuable references for the study of pozzolanic reaction of industrial by-products. However, owning to the complicated mineralogical phases present in the industrial by-products, it is necessary to investigate the pozzolanic reaction behaviour of industrial by-products so as to find effective solutions for their applications in the cement industry.

The purpose of this paper is to investigate the pozzolanic behaviour of the compound-activated red mud-coal gangue mixture. This research focuses on two parts: one of the parts aims to describe the mechanism of pozzolanic reaction in the red mud-coal gangue – lime system from viewpoint of reaction kinetics; and the other part aims to use instrumental techniques such as thermogravimetry (TG), differential thermal analysis (DTA), X-ray diffraction (XRD), Fourier transform infrared (FTIR) and ^{27}Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) to obtain valuable information on the hydration products of red mud-coal gangue – lime system.

2. Experimental

2.1. Materials

Red mud used in this work was from Shandong alumina refining plant, the process of which is bauxite-calcination method. Coal gangue was obtained from Fangshan, Beijing. The mineralogical phases of raw red mud and coal gangue determined by XRD are presented in Fig. 1. The red mud-coal gangue mixture investigated in this paper was prepared through compound activation method, the schematic diagram of which is shown in Fig. 2. In the compound activation process, the red mud and coal gangue were firstly mixed together at a ratio of 3:2. With water/solid ratio of 0.3, the red mud-coal gangue mixtures were granulated and then dried at 100 °C for 6 h. Subsequently, the mixtures were calcined at 600 °C for 2 h in a programmable electrical furnace, and then removed from the furnace and allowed to cool spontaneously to room temperature in air. Finally, they were ground in a laboratory ball mill for 6 min to Blaine's specific surface area of 425 m^2/kg, and the resultant material was referred to as compound-activated red mud-coal gangue. The mineralogical phases and SEM image of the compound-activated red mud-coal gangue are presented in Figs. 3 and 4, respectively.

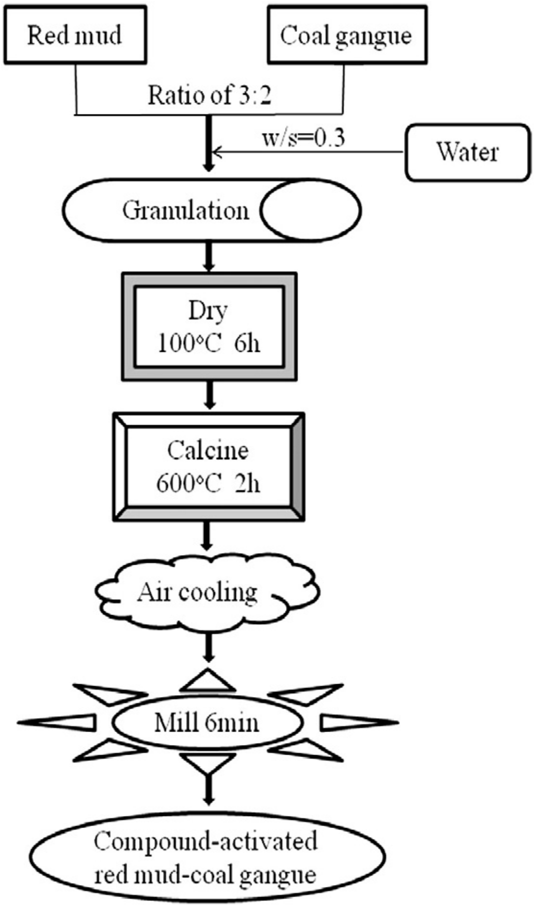

Fig. 2. Schematic diagram of compound activation for red mud-coal gangue.

The chemical composition (analyzed using X-ray fluorescence technique) and physical properties of raw red mud, coal gangue and the compound-activated red mud-coal gangue are shown in Table 1.

2.2. Experimental procedure

The compound-activated red mud-coal gangue and CaO were mixed at different ratios by weight. Three different compositions were selected as shown in Table 2. With water/solid ratio of 0.5, pastes of the above compositions were prepared using distilled–deionized

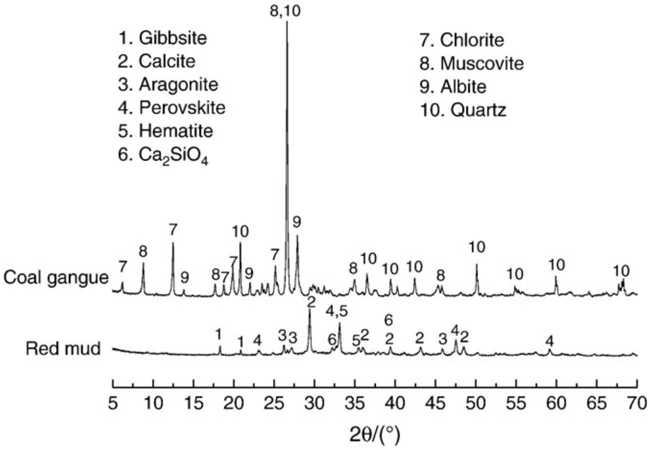

Fig. 1. Mineralogical phases of raw red mud and coal gangue.

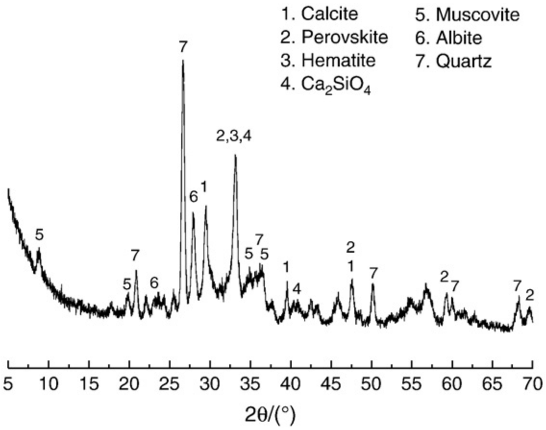

Fig. 3. XRD pattern of compound-activated red mud-coal gangue.

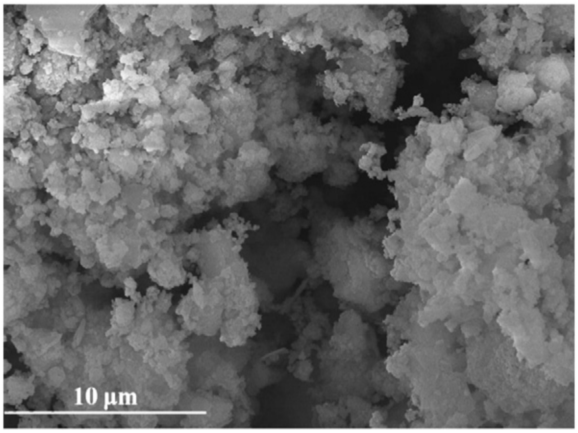

Fig. 4. SEM image of compound-activated red mud-coal gangue.

water to constitute the compound-activated red mud-coal gangue — lime system. The pastes were sealed in small plastic bags to prevent the hydrates from atmospheric CO_2 uptake, and then cured in a humidity chamber at 20 °C and constant 95% relative humidity. The specimens were taken out at selected curing time, up to a maximum of 90 days. The hydration of the specimens were quenched by alcohol drenching and dried at 60 °C in a vacuum oven for further characterization.

The hydration products present in the red mud-coal gangue — lime system were identified and analyzed by XRD, TG-DTA, FTIR and ^{27}Al MAS-NMR. XRD analysis was conducted on Rigaku D/max-RB X-ray diffractometer with CuKα radiation (40 kV, 200 mA). TG-DTA analysis was performed on Netzsch STA 449 C Thermal analyzer, and the hydrated samples were heated from room temperature to 1000 °C (stripping gas: dry N_2, heating rate: 10 °C/min). FTIR spectra of the hydrated samples were recorded on a Spectrum GX Perkin-Elmer Fourier transform infrared spectrometer using the KBr pellet technique (1~2 mg sample with 200 mg KBr). ^{27}Al solid-state MAS NMR spectroscopy was carried out using a BRUKER-AM300 spectrometer (Germany) operating at 78.20 MHz for the ^{27}Al resonance frequency. ^{27}Al MAS NMR spectra were processed using NMR Utility Transform software (NUTS). NUTS is a toolbox of professional software for processing NMR data. Deconvolution of the ^{27}Al MAS NMR spectra was done by line fitting procedure as implemented in NUTS. The line fitting procedure was initiated by manually picking a set of peaks as a starting point. After the fit procedure, peak separations, line fitting curves and relative peak area values can be obtained.

Table 1
Chemical composition and physical properties of red mud, coal gangue and compound-activated red mud-coal gangue.

Oxides (%)	Red mud	Coal gangue	Compound-activated red mud-coal gangue
SiO_2	17.78	49.41	38.92
Al_2O_3	6.27	21.32	12.63
CaO	37.52	2.52	26.31
Fe_2O_3	12.32	6.02	11.90
Na_2O	2.75	1.44	2.59
K_2O	0.46	2.85	1.90
MgO	1.15	1.56	1.60
TiO_2	3.27	0.94	2.72
SO_3	0.49	0.65	0.64
L.O.I	17.76	12.75	3.53
Specific gravity	2.75	2.59	2.73
Specific surface, Blaine (m^2/kg)	415	385	425

Table 2
Mix proportions of the compound-activated red mud-coal gangue and CaO (wt.%).

Symbol	Red mud-coal gangue	CaO
SC1	90	10
SC2	85	15
SC3	80	20

3. Results and discussion

3.1. Mechanism of pozzolanic reaction in the red mud-coal gangue — lime system

To study the pozzolanic reaction mechanism of the compound-activated red mud-coal gangue, TG analysis was used to measure the amount of CaO consumed by the red mud-coal gangue at different hydration times. Fig. 5 shows the results for samples of SC1, SC2 and SC3. The reacted CaO presented in Fig. 5 means that the CaO was consumed by the compound-activated red mud-coal gangue to perform pozzolanic reaction. It can be seen that the amount of reacted CaO increases with the hydration time. For SC1 specimen, close to 47% and 55% of the CaO has reacted at 1 day and 14 days, respectively, and the rate of CaO consumption decreases from 14 days onwards. For SC2 specimen, about 48% of the CaO has reacted at 7 days, and from 7 days onwards the rate of CaO consumption decreases. For SC3 specimen, close to 46% of the CaO has reacted at 14 days, and the CaO consumption rate decreases from 14 days onwards. Except the data at 3 days, the reaction degree of CaO along high to low order is: SC1 > SC2 > SC3.

The Jander equation, which is based on Fick's parabolic law of diffusion, has been used satisfactorily to describe the mechanism of pozzolanic reaction. Ramezanianpour and Cabrera [16] used a modification of Jander equation to describe the mechanism of pozzolanic reaction in microsilica – lime and trass – lime systems. Cabrera and Rojas [15] used the Jander equation to describe the mechanism of hydration of metakaolin – lime – water system, and it was reported that the kinetics of the metakaolin – lime system is consistent with diffusion control for the first 120 h.

In the present study, the Jander equation was also used with an attempt to reveal the mechanism of reaction in the compound-activated red mud-coal gangue – lime system. The famous Jander equation is presented as below:

$$F(x)=\left(1-\sqrt[3]{1-x}\right)^2={}^{2}kt\Big/_{r^2}=Kt \qquad (1)$$

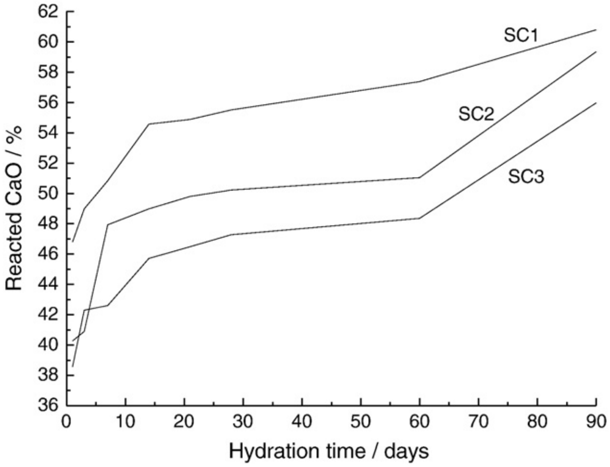

Fig. 5. Amount of reacted CaO versus hydration time as determined from TG.

This kinetic model assumes that the reaction interface is a contracting sphere, and thus in Eq. (1), x refers to the fraction of the sphere that has reacted; r is the initial radius of the beginning sphere; k is the constant of parabolic rate; K corresponds to the constant of reaction rate, which is a constant proportional to k; and t refers to reaction time.

Eq. (1) implies that a plot of $F(x)$ versus t would be a straight line, and K is equal to the slope of straight line. If the amount used of the reacted CaO shown in Fig. 2 as x to calculate $F(x)$, the linearity of a plot of the calculated $F(x)$ against hydration time could provide a good criterion to determine whether the pozzolanic reaction is consistent with diffusion control. Plots of $F(x)$ versus hydration time for specimens of SC1, SC2 and SC3 are shown in Fig. 6, and the regression equations obtained are:

$$\mathrm{SC1}: F(x) = 0.00129t + 0.03549 \quad R = 0.99505 \tag{2}$$

$$\mathrm{SC2}: F(x) = 0.00128t + 0.02431 \quad R = 0.90969 \tag{3}$$

$$\mathrm{SC3}: F(x) = 0.00076t + 0.02347 \quad R = 0.93385 \tag{4}$$

During the process of plotting $F(x)$ against hydration time, it was found that the data from 14 days onwards no longer fitted the linear relation, therefore the data points after 14 days were not used in calculating the regression lines. The reaction rate constant K obtained from Eqs. (2), (3) and (4) represents the reaction rate up to 14 days in SC1, SC2 and SC3, respectively. They are:

$$K_{\mathrm{SC1}} = 12.9 \times 10^{-4},$$

$$K_{\mathrm{SC2}} = 12.8 \times 10^{-4},$$

$$K_{\mathrm{SC3}} = 7.6 \times 10^{-4}.$$

The present results indicate that the mechanism of pozzolanic reaction in the compound-activated red mud-coal gangue – lime system is consistent with diffusion control up to 14 days, and the calculated rate of reaction constant from the Jander equation decreases with the increase of CaO addition in the system.

3.2. Hydration products of red mud-coal gangue – lime – water system

3.2.1. XRD analysis

Fig. 7 shows XRD patterns of the red mud-coal gangue — lime system hydrated for 1 day. It can be seen that calcium silicate hydrate (C–S–H) is occuring in the hydrated systems of SC1, SC2 and SC3, and small amount of okenite ($CaSi_2O_5.2H_2O$) occurs in the hydrated SC3 specimen. Besides, all the XRD patterns show some diffraction peaks corresponding to portlandite ($Ca(OH)_2$), quartz (SiO_2), albite ($Na(Si_3Al)O_8$), calcite ($CaCO_3$), perovskite ($CaTiO_3$), and hematite (Fe_2O_3). However, the intensities of diffraction peaks corresponding to a same phase are varied, mainly due to the different hydration degree and different mixing proportions for raw materials. $Ca(OH)_2$ is a crystalline product from the reaction between CaO and water. It is consumed by the reactive SiO_2 occurring in the compound-activated red mud-coal gangue to form C–S–H gel and small quantities of okenite. The left phases of quartz, albite, calcite, perovskite, and hematite are unreacted phases which are obtained from the raw materials of coal gangue and red mud.

Fig. 8 shows XRD patterns of the red mud-coal gangue — lime system hydrated for 28 days. Comparing with the XRD patterns in Fig. 7, it is found that the diffraction peaks of $Ca_3Al_2O_6$. xH_2O (C_3AH_x) appear in the XRD patterns of SC1, SC2 and SC3 hydrated for 28 days.

Fig. 9 shows XRD patterns of the red mud-coal gangue — lime system hydrated for 90 days, which are similar to the XRD patterns presented in Fig. 8. Hydrates formed in the specimens SC1, SC2 and SC3 cured for 90 days are essentially C–S–H gel and hydrated calcium aluminate (C_3AH_x). Traces of okenite are occurring in the specimen SC3 hydrated for 28 days. As hydration progresses, okenite tends to disappear until after 90 days curing.

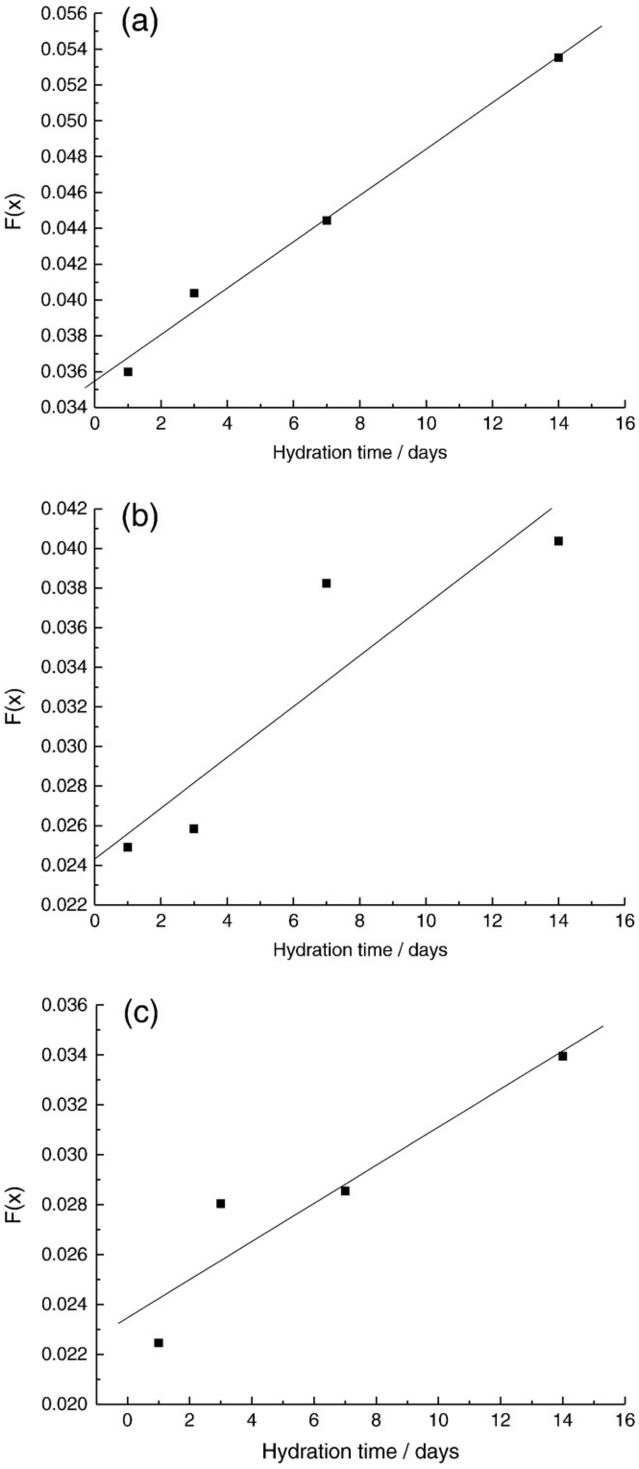

Fig. 6. Regression lines from the results of $F(x)$ versus hydration time: (a) SC1, (b) SC2, (c) SC3.

De Silva and Glasser [14] have reported that in the metakaolin — calcium hydroxide mixtures cured at 20 °C, the principal hydrates found amongst the reaction products after 10 days of hydration were tetra calcium aluminium hydrate (C_4AH_{13}), gehlenite hydrate (C_2ASH_8) and amorphous C–S–H; as hydration progressed, C_4AH_{13} tended to disappear and the hydration products were C_2ASH_8 and C–

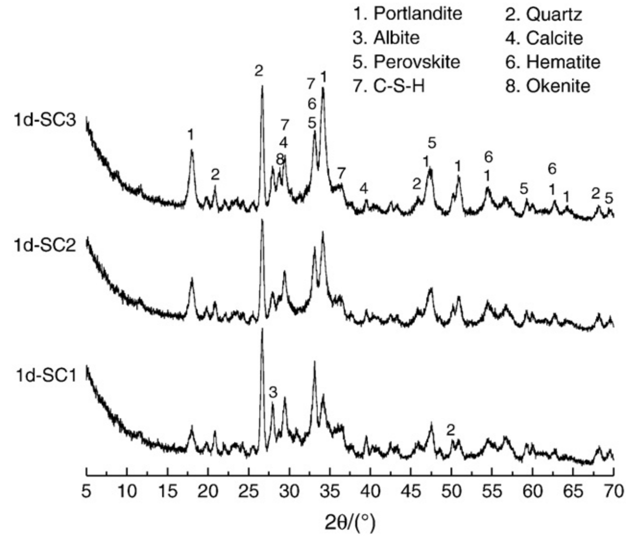

Fig. 7. XRD patterns of red mud-coal gangue — lime system hydrated for 1 day.

S–H after 180 days of hydration. They believed that the appearance of C_4AH_{13} at initial stages of hydration is a metastable phenomenon resulted from supersaturation of the aqueous phase related to calcium hydroxide; high concentrations of the Ca^{2+} and OH^- in the pore solution can maintain a pore fluid composition that enables C_4AH_{13} to precipitate. From this point of view, it is thought that high concentrations of Ca^{2+} and OH^- in the pore solution of hydrated red mud-coal gangue — lime system could provide a pore fluid composition which allows C_3AH_x to precipitate.

Based on the above analysis, it is known that the hydration products in the compound-activated red mud-coal gangue — lime system are essentially C–S–H and C_3AH_x. No C_4AH_{13} or C_2ASH_8 normally appeared during the hydration of metakaolin – lime system was detected in the present investigated system. So it is possible to propose a hydration reaction with respect to the compound-activated red mud-coal gangue – lime system as follows:

$$SiO_2\cdot Al_2O_3 + Ca(OH)_2 + H_2O \rightarrow C_3AH_x + C{-}S{-}H \tag{5}$$

where $SiO_2\cdot Al_2O_3$ represents reactive siliceous and aluminous substances occurring in the compound-activated red mud-coal gangue.

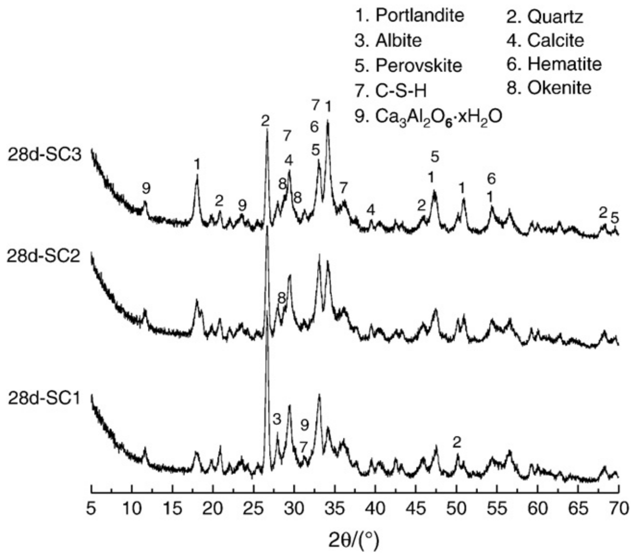

Fig. 8. XRD patterns of red mud-coal gangue — lime system hydrated for 28 days.

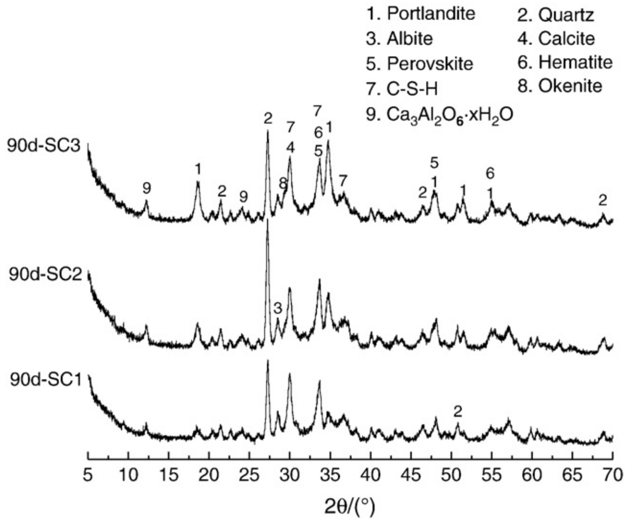

Fig. 9. XRD patterns of red mud-coal gangue — lime system hydrated for 90 days.

3.2.2. FTIR analysis

The infrared spectra of the red mud-coal gangue — lime system hydrated for 28 days, as well as the spectrum for the original compound-activated red mud-coal gangue, are displayed in Fig. 10. Specimens SC1, SC2 and SC3 hydrated for 28 days show analogous IR spectra. Except the spectra of compound-activated red mud-coal gangue, all show adsorption band at 3643 cm^{-1}, related to Ca—OH stretching vibration in $Ca(OH)_2$. This band increased from SC1 to SC3, indicating that the amount of $Ca(OH)_2$ in the hydrated system increased with the increase of CaO addition. The bands at 3533 and 3431 cm^{-1} are associated with Si—OH vibration in SiO_4 tetrahedra of C–S–H gel and Al—OH stretching mode in the $Al(OH)_6$ octahedra of $Ca_3Al_2O_6.xH_2O$, respectively. The band around 1637 cm^{-1} corresponds to the H—O—H vibration of water. As the samples during the whole preparation course were sealed in plastic bags to avoid carbonation, the band around 1418 cm^{-1} is associated with anti-symmetric stretching mode of CO_3^{2-} ions in calcite, which is derived from the original red mud.

In the IR spectra of initial compound-activated red mud-coal gangue, the bands at 995, 797 and 463 cm^{-1} are associated with anti-symmetric Si—O stretching vibration, symmetric Si—O stretching vibration and in-plane Si—O bending vibration within SiO_4 tetrahedra, respectively. They are key bands corresponding to quartz. However, it is observed that the band centered at 995 cm^{-1} moves to lower frequencies around 970 cm^{-1}, as a result of the formation of new reaction products with respect to ongoing hydration, suggesting the presence of C–S–H gel. In addition, it is noted that the band at 797 cm^{-1} in the initial material

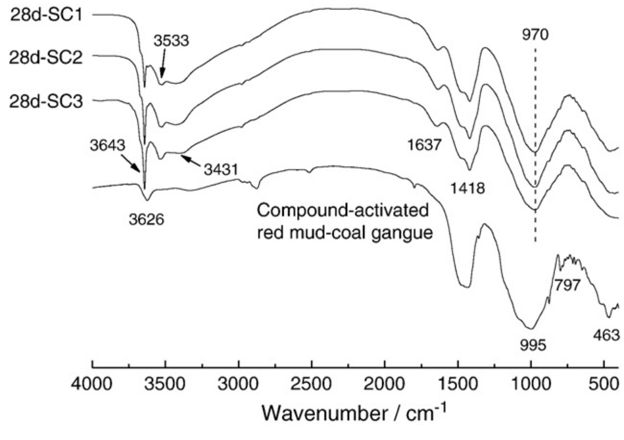

Fig. 10. FTIR spectra of red mud-coal gangue — lime system hydrated for 28 days.

disappeared, and the other band at 463 cm^{-1} tended to weaken in the hydrated specimens of SC1, SC2 and SC3.

3.2.3. TG-DTA analysis

Fig. 11 shows DTA curves of the red mud-coal gangue — lime system hydrated for different times. It is observed that in all cases there are three well-defined endothermic processes. The first region located within 100–400 °C involves a broad band attributed to the loss of absorbed and structural water from the main hydrates of pozzolanic reaction. The peak around 140–150 °C is mainly corresponding to the dehydration of C–S–H gel. However, it is difficult for the detection of $Ca_3Al_2O_6.xH_2O$ from DTA curves owing to the overlapping of some lines. The second region located within 400—475 °C corresponds to the dehydroxylation of $Ca(OH)_2$, and the third region at 650–750 °C is associated with the decarbonation of calcite.

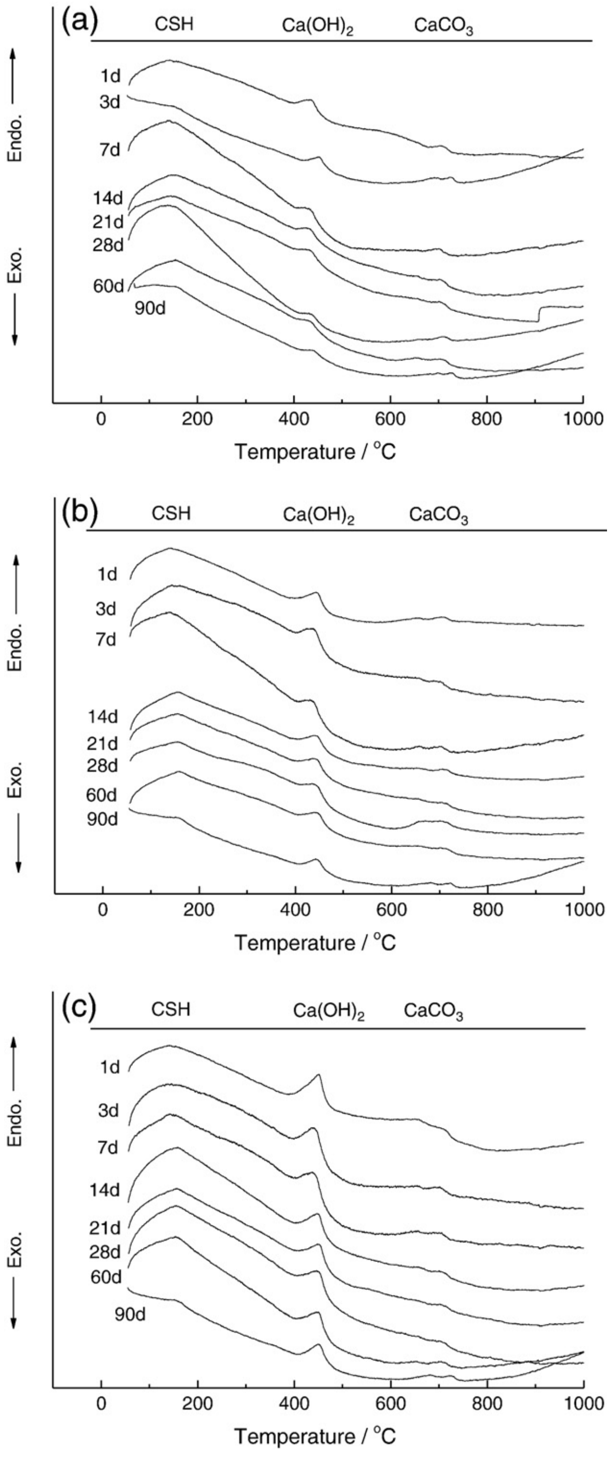

Fig. 11. DTA curves of red mud-coal gangue — lime system hydrated for different times: (a) SC1, (b) SC2, (c) SC3.

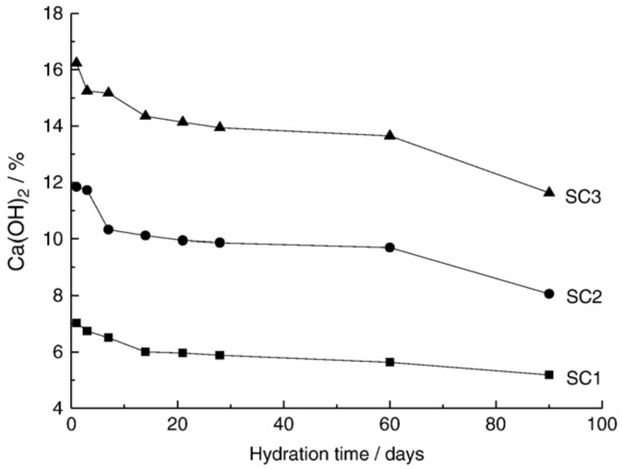

Fig. 12. $Ca(OH)_2$ content within pastes of the red mud-coal gangue — lime system hydrated for different times.

According to the second region (400–475 °C), TG analysis was used to determine the content of $Ca(OH)_2$ within pastes of the red mud-coal gangue — lime system hydrated for different times. The results of specimens SC1, SC2 and SC3 are shown in Fig. 12. It is noted that with the increase of hydration time, $Ca(OH)_2$ content in all the three specimens is lowered by the pozzolanic reaction, but at a same hydration time, the $Ca(OH)_2$ content increases as the CaO addition is increased in the raw mix proportion.

The content of non-evaporable water within pastes of the red mud-coal gangue — lime system hydrated for different times, determined by TGA, is presented in Fig. 13. To reflect the amount of hydrates from pozzolanic reaction, the non-evaporable water studied here does not involve the chemically bound water of $Ca(OH)_2$. As it was expected, the non-evaporable water content in the hydrated specimens of SC1, SC2 and SC3 increases with the hydration age. As shown in Fig. 13, the developing curves of non-evaporable water obtained for SC1, SC2 and SC3 exhibit three stages, which are described as rapidly increasing stage, continually increasing stage, and gently increasing stage. The non-evaporable water content for all the three specimens increases very rapidly before 7 days. However, different developing stages appear from 7 days onwards. For specimen SC1, the non-evaporable water

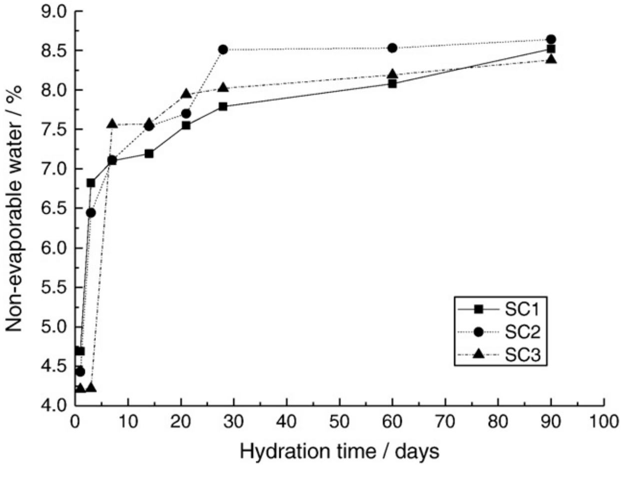

Fig. 13. Non-evaporable water content within pastes of the red mud-coal gangue — lime system hydrated for different times.

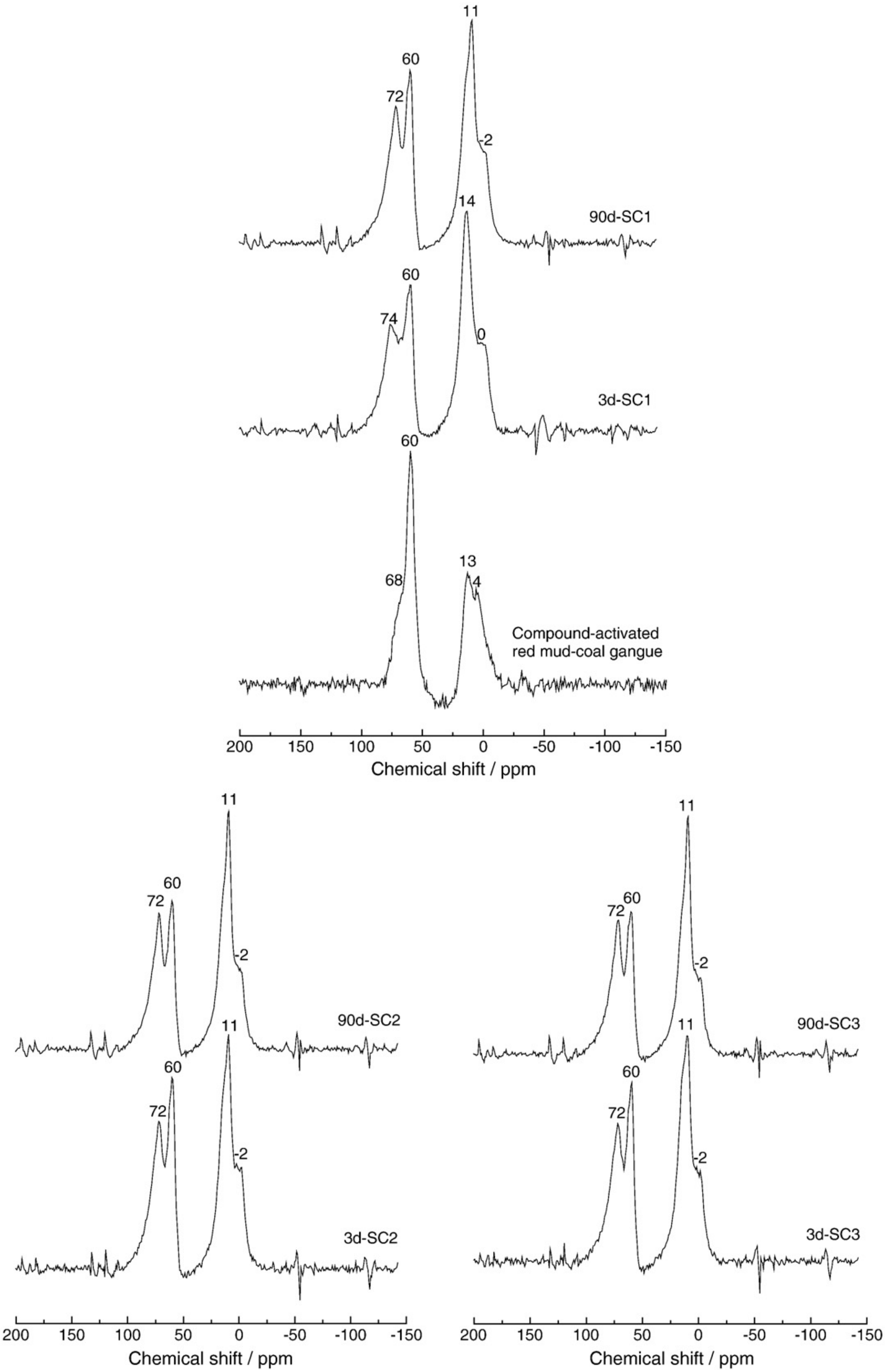

Fig. 14. ^{27}Al MAS NMR spectra for the pastes of SC1, SC2 and SC3 hydrated for 3 and 90 days.

content increases continually from 7 to 90 days; for specimen SC2, it increases continually from 7 to 28 days, but gently develops from 28 days onwards; for specimen SC3, it continually increases from 7 to 21 days, but gently develops after 21 days. It seems that the gently increasing stage appears earlier with the increase of $Ca(OH)_2$ content from SC1 to SC3. Thus, it is possible to say that the high amount of $Ca(OH)_2$ in the pastes of red mud-coal gangue — lime system is not conducive to the continual increase of non-evaporable water content.

The three stages mentioned above can reflect some details about the reaction process. At early stage, the pozzolanic reaction is dominated by diffusion control. In the alkaline environment supplied by $Ca(OH)_2$, reactive SiO_4^{4-} and AlO_2^- ions dissolved from the surface of compound-activated red mud-coal gangue particles can quickly react with $Ca(OH)_2$ to produce cementitious hydrates such as C–S–H gel and C_3AH_x, resulting in a rapidly increasing stage observed in Fig. 13. As the hydration is going on, the amount of cementitious hydrates generated from the pozzolanic reaction increases, and the thickness of reaction products' layer also increases. Due to the dissolved SiO_4^{4-} and AlO_2^- need to pass through the products' layer to react with $Ca(OH)_2$, the diffusion rate of SiO_4^{4-} and AlO_2^- is decreased gradually with the increase of layer thickness, leading to a gradual decline of pozzolanic reaction rate. Therefore, the production rate of cementitious hydrates decreases to display a continually increasing stage as presented in Fig. 13. At later stage, when the reaction is hard to be progressed through diffusion control, the pozzolanic reaction could be mainly dominated by topochemical reaction, and the reaction rate would be much slower than before. However, additional deep research is required to investigate the topochemical reaction of compound-activated red mud-coal gangue — lime system at later stage.

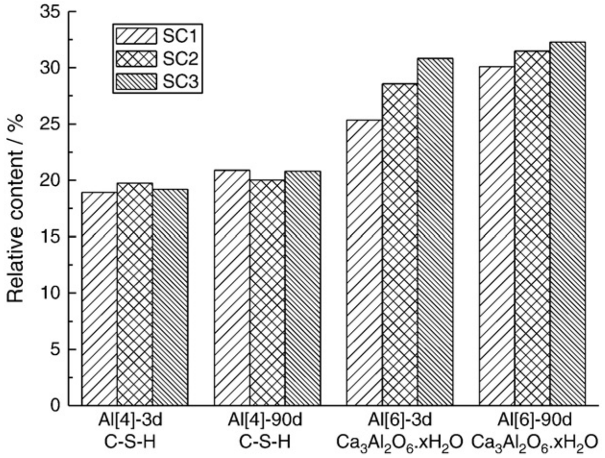

Fig. 15. Relative content of $Al^{[4]}$ in C–S–H and $Al^{[6]}$ in $Ca_3Al_2O_6.xH_2O$ for the pastes hydrated for 3 and 90 days.

3.2.4. *^{27}Al MAS NMR analysis*

^{27}Al MAS NMR can be utilized to analyze the coordination state of Al in crystalline and poorly-crystalline phases. Fig. 14 shows ^{27}Al MAS NMR spectra for the pastes of SC1, SC2 and SC3 hydrated for 3 and 90 days. Including spectrum of the initial compound-activated red mud-coal gangue, each spectrum exhibits four main peaks at 68 ~ 74, 60, 11 ~ 14, and − 2 ~ 4 ppm. The resonances within 60 ~ 74 ppm are assigned to tetrahedrally coordinated Al ($Al^{[4]}$), while the resonances within − 2 ~ 14 ppm are related to octahedrally coordinated Al ($Al^{[6]}$). Comparing with the spectrum of compound-activated red mud-coal gangue, the spectra for the hydrated pastes of SC1, SC2 and SC3 obviously show the peaks around 72 ~ 74 ppm, and the peaks at 11 ~ 14 ppm increase relatively. Following Love et al. [17], the broad peak with a maximum at approximately 70 ppm is assigned to $Al^{[4]}$ in C–S–H phase. Therefore, combining the above XRD and IR analysis of the hydration products, the peaks at 72 ~ 74 ppm are associated with $Al^{[4]}$ in C–S–H gel, and the intensified peaks around 11 ~ 14 ppm are due to $Al^{[6]}$ in $Ca_3Al_2O_6.xH_2O$. The spectra for the hydrated pastes also includes peaks at 60 ppm for residual $Al^{[4]}$ and peaks around − 2 ~ 0 ppm for residual $Al^{[6]}$ in unreacted red mud-coal gangue.

The spectra shown in Fig. 14 were further analyzed by means of NUTS, and the results obtained from deconvolution of the ^{27}Al MAS NMR spectra are summarized in Table 3. The relative amount of $Al^{[4]}$ and $Al^{[6]}$ in the compound-activated red mud-coal gangue is 53.9% and 46.1%, respectively. To describe clearly, the peaks near 68 ~ 74, 60, 10 ~ 14, and − 2 ~ 4 ppm are symbolized as $Al^{[4]}{}_1$, $Al^{[4]}{}_2$, $Al^{[6]}{}_1$,and $Al^{[6]}{}_2$, respectively. Before hydration, the relative amount of $Al^{[4]}{}_1$ and $Al^{[6]}{}_1$ is 14.73% and 14.96%, respectively; while after hydration, the relative amount of $Al^{[4]}{}_1$ and $Al^{[6]}{}_1$ increases significantly to about 34% and over 40%, respectively. The increment can be thought as the relative content of $Al^{[4]}$ in C–S–H gel, and $Al^{[6]}$ in $Ca_3Al_2O_6.xH_2O$. The calculated data for the pastes of SC1, SC2 and SC3 hydrated for 3 and 90 days are plotted in Fig. 15.

An intriguing observation is that the relative content of $Al^{[4]}$ in C–S–H gel varies not too much as hydration progresses, while the relative content of $Al^{[6]}$ in $Ca_3Al_2O_6.xH_2O$ increases with the hydration time. At a same hydration time, the relative content of $Al^{[6]}$ in $Ca_3Al_2O_6.xH_2O$ along high to low order is: SC3 > SC2 > SC1. According to the above TG analysis, it is known that the $Ca(OH)_2$ content within the hydrated pastes along high to low order is: SC3 > SC2 > SC1. Large amount of $Ca(OH)_2$ in the hydrated SC3 paste is indicative of higher

Table 3
Results obtained from deconvolution of the ^{27}Al MAS NMR spectra.

Sample		$Al^{[4]}$		$Al^{[6]}$	
		$Al^{[4]}{}_1$	$Al^{[4]}{}_2$	$Al^{[6]}{}_1$	$Al^{[6]}{}_2$
Compound-activated red mud-coal gangue	Peak position (ppm)	68.0	59.6	13.3	4.4
	Peak area	37.62	100	38.21	79.57
	Integral (%)	14.73	39.15	14.96	31.16
3d-SC1	Peak position (ppm)	73.9	60.5	14.0	0
	Peak area	83.47	32.72	100	31.92
	Integral (%)	33.64	13.19	40.30	12.87
90d-SC1	Peak position (ppm)	72.3	60.3	11.2	− 1.8
	Peak area	79.06	28.56	100	14.41
	Integral (%)	35.61	12.86	45.04	6.49
3d-SC2	Peak position (ppm)	72.3	60.2	11.2	− 2.1
	Peak area	79.19	32.92	100	17.55
	Integral (%)	34.48	14.33	43.54	7.64
90d-SC2	Peak position (ppm)	72.4	60.3	11.0	− 1.7
	Peak area	74.82	27.7	100	12.76
	Integral (%)	34.75	12.87	46.45	5.93
3d-SC3	Peak position (ppm)	72.3	60.2	11.6	− 1.8
	Peak area	74.08	29.62	100	14.64
	Integral (%)	33.93	13.57	45.8	6.7
90d-SC3	Peak position (ppm)	72.5	60.4	10.7	− 1.7
	Peak area	75.24	27.74	100	8.7
	Integral (%)	35.54	13.11	47.24	4.11

concentrations of Ca^{2+} and OH^{-} existing in the aqueous phase of SC3, so that supersaturation of aqueous phase related to $Ca(OH)_2$ could occur easily in the system which has higher content of $Ca(OH)_2$. Combining both results of the relative content of $Al^{[6]}$ in $Ca_3Al_2O_6.xH_2O$ and the content of $Ca(OH)_2$ within the hydrated pastes of SC1, SC2 and SC3, it is further approved that the higher concentrations of Ca^{2+} and OH^{-} provide sufficient pore fluid compositions which are required for the precipitation of $Ca_3Al_2O_6.xH_2O$. According to this viewpoint, the conclusion drawn from Fig. 13 that "high amount of $Ca(OH)_2$ in the pastes of red mud-coal gangue — lime system is not conducive to the continual increase of non-evaporable water content" can be further explained. As higher amount of $Ca(OH)_2$ in the hydrated paste enables C_3AH_x to precipitate quickly on the surface of red mud-coal gangue particles, the diffusion rate of SiO_4^{4-} and AlO_2^{-} dissolved from the compound-activated red mud-coal gangue will be decreased gradually, resulting in a decline for the production rate of cementitious hydrates correspondingly.

4. Conclusions

The mechanism of pozzolanic reaction in the compound-activated red mud-coal gangue — lime system is clearly consistent with diffusion control up to 14 days, and the calculated rate of reaction constant from the Jander equation decreases with the increase of CaO addition in the system.

An in-depth characterization of the main reaction products formed in the compound-activated red mud-coal gangue — lime system was conducted by using several techniques. In all cases, the hydration products formed at ambient temperature for the studied system are essentially aluminous C–S–H and $Ca_3Al_2O_6.xH_2O$. From TG analysis results, it is thought that the high amount of $Ca(OH)_2$ in the pastes of red mud-coal gangue — lime system is not conducive to the continual increase of non-evaporable water content of the hydration products.

Of particular interest, ^{27}Al MAS NMR proved to be an effective technique to obtain valuable information of $Al^{[4]}$ in C–S–H gel and $Al^{[6]}$ in $Ca_3Al_2O_6.xH_2O$. The data from the deconvolution of the ^{27}Al MAS NMR spectra indicates that the relative content of $Al^{[4]}$ in C–S–H gel varies not too much as hydration progresses, while the relative content of $Al^{[6]}$ in $Ca_3Al_2O_6.xH_2O$ increases significantly with the hydration time.

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