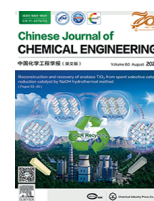




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Full Length Article

Mechanical strength and the degradation mechanism of metakaolin based geopolymer mixed with ordinary Portland cement and cured at high temperature and high relative humidity

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ABSTRACT

Geopolymer is a new type of eco-friendly cementitious material, and its superior drying and high temperature resistance has been widely recognized. The service performance of geopolymer under 150 °C high-temperature hydrothermal conditions is still less discussed. In this paper, the mechanical strength of pure metakaolin system with low calcium content and metakaolin-cement system with high calcium content under hydrothermal and non-hydrothermal conditions were studied. The results show that under 150 °C hydrothermal conditions, the strength of pure metakaolin geopolymer sharply decreases by reduction rate of 81.8% compared to the sample under 150 °C drying conditions, while the strength of metakaolin-cement geopolymers is well retained with only a slight decrease of 14.4%. This is mainly because the predominantly hydration product sodium aluminosilicate (N-A-S-H) gel of pure metakaolin system undergoes the process of “dissociation–repolymerization–crystallization” under 150 °C hydrothermal conditions, resulting in the loss of cementation ability and obvious deterioration of mechanical strength. In the metakaolin-cement system, the high-calcium calcium silicate gel (C-A-S-H) gel maintains a stable structure, thereby maintaining the macroscopic strength of the material under the hydrothermal conditions.

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1. Introduction

Geopolymer is a new type of cementitious material formed by the reaction between aluminosilicate raw materials and alkali activator. The product is a three-dimensional network-structured aluminosilicate gel composed of silica tetrahedron and aluminum oxide tetrahedron [1,2]. Geopolymers have the advantages of exceptional mechanical strength, corrosion resistance, high temperature resistance and excellent durability [3–6]. More importantly, the geopolymer manufacturing process avoids the high energy consumption and huge CO₂ emission with respect to clinker production, compared with ordinary Portland cement (OPC) [7,8]. Because of their performance advantages and low CO₂ emission, geopolymer materials have been considered substitutes for OPC.

With the continuous development of the petroleum industry, deep oil and gas exploration frequently confronts formations such as high temperature, high pressure, high permeability, and high corrosion environment, resulting in worse cementing environment and more complex cementing process. Although various types of oil and gas well cements have been specifically developed, they did not provide satisfactory performance in deep-reaching wells, confronting problems such as strength degradation, and chemical corrosion [9,10]. Geopolymer could be an ideal option as the cementing materials for such deep-reaching wells thanks to the superior high temperature and corrosion resistance as reported [10–13]. Currently, the properties of geopolymer systems under high temperature application have been explored. It is reported that the compressive strength of geopolymer is mainly influenced by the curing temperature as compared to the other parameters including alkaline concentration and curing period [14]. High-temperature curing generally accelerates the early strength of geopolymers [15–17], due to the increase of both the dissolution and polycondensation rates and the rapid formation of the geopolymeric structure [18,19]. Liew *et al.* [20] reported that the

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strength development of metakaolin geopolymer pastes was extremely slow and compressive strength increased with the increasing curing temperature. Yuan *et al.* [21] reported that with the increase of curing temperature, microstructures of metakaolin geopolymers become denser and thus resulting in improvement of the mechanical properties. Peng *et al.* [22] found that the geopolymers cured at 20 °C had very low compressive strengths (<5 MPa) even after being cured for 28 d. Nevertheless, when the curing temperature was heightened to 80 °C, the corresponding samples had relatively high compressive strengths up to 38.3 MPa. Suppiah *et al.* [23] also found the same phenomenon in fly ash geopolymers. They observed that the samples cured at 90 °C had superior strength after 24 h compared with 60 °C. But they also pointed out that there is a possibility of strength reduction at very high curing temperatures (>100 °C). In addition, the strength changes of geopolymers and hardened OPC pastes exposed to elevated temperatures have also been studied. It was found that geopolymers after exposure to elevated temperature 200–600 °C show almost no change in compressive strength while the OPC mortar significantly loses the strength with the development of larger crack width [24], indicating that geopolymer did perform better than OPC when subjected to a dry and thermal environment [25,26].

The advantages of geopolymers in high temperatures and dry environments are apparent. However, in oil well cementing engineering, cementitious materials are often encountered in the high temperature up to 200 °C, high humidity (RH > 30%–50%) or even water saturated environment. At present, the strength of geopolymers in such harsh service environment is still unclear. Indeed, the product of geopolymerization is amorphous hydrated sodium aluminosilicate (N-A-S-H) gel that can be considered as metastable amorphous zeolites that were unable to crystallize due to inadequate water/solid ratio [27]. Accordingly, some researchers have utilized geopolymers to the *in-situ* synthesis of artificial zeolite under hydrothermal conditions. Kolousek *et al.* [28] used metakaolin-based geopolymers under hydrothermal conditions (100 or 140 °C, 1–7 d age) to prepare products containing rhombic and cross-zeolite structures. Liu *et al.* [29] prepared faujasite zeolite using fly ash geopolymer under hydrothermal conditions of 80–110 °C with curing time of 6–48 h. These research results demonstrate that the gel structure of the geopolymers will be changed under hydrothermal conditions [30,31] which is likely to cause performance variation of the geopolymers. Therefore, it is essential to disclose the mechanical strength and the microstructural changes of the geopolymers in hydrothermal service conditions.

In this paper, the mechanical strength and the degradation mechanism of the metakaolin base geopolymer have been studied under high temperature and hydrothermal conditions. In addition to the pure metakaolin geopolymer system, metakaolin and ordinary Portland cement were mixed to prepare metakaolin-cement geopolymers. The properties of the obtained geopolymers under hydrothermal and non-hydrothermal conditions were compared, and the underlying mechanism was preliminarily discussed.

2. Experimental

2.1. Materials

Metakaolin (MK) and ordinary Portland cement (OPC) were used to prepare test specimens. Metakaolin was produced by calcining kaolin clay at 600 °C and ordinary Portland cement 42.5 R complying GB8076-2008 was provided by China United Cement Corporation. The chemical composition of metakaolin and cement is shown in Table 1. It is seen that calcium content in MK is very low and aluminum content is significantly high in comparison with OPC.

AR grade sodium hydroxide ($\geq 98\%$) and an industrial product of sodium silicate solution with a mass concentration of 38% were used to prepare the sodium hydroxide-sodium silicate composite activator. The chemical composition of the sodium silicate is $\text{Na}_2\text{O} \cdot 3.26\text{SiO}_2$, with modulus (molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$) $M_s = 3.26$.

2.2. Methods

2.2.1. Specimen systems

Three groups of geopolymers were prepared in this study. When the pure metakaolin was used as the powder material in the paste, the sample was abbreviated as MK100. When the mixtures of metakaolin and OPC with mass ratio of 75:25 and 50:50 were used to prepare the geopolymers, the obtained samples were respectively denoted as MK75C and MK50C.

The preparation of geopolymer paste usually involves three key parameters, the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$. $\text{SiO}_2/\text{Al}_2\text{O}_3$ mainly affects the dissolution and polycondensation reaction of geopolymers, which plays a key role in the polymerization stage of silicon-aluminum skeleton in the aluminosilicate inorganic polymer gel [32,33]. $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ reflects the charge balance status in the aluminosilicate gel system [34], while $\text{H}_2\text{O}/\text{Na}_2\text{O}$ regulates the concentration of the alkaline solution in the reaction system, and thus the dissolution rate of aluminosilicate minerals. Both too low and too high ratios of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ will negatively affect the formation of the products [35,36]. The studies of Silva *et al.* [37] and Duxson *et al.* [38] showed that good mechanical properties of metakaolin-based geopolymers could be achieved when $\text{SiO}_2/\text{Al}_2\text{O}_3$ is about 3.0–4.0, and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ is about 1.0. For the selection of $\text{H}_2\text{O}/\text{Na}_2\text{O}$, according to the research of Cui *et al.* [39], the geopolymer has better mechanical properties when it is about 13–17. Based on the results of previous literatures, the MK powders in the three geopolymer systems in this study are all activated by sodium hydroxide-sodium silicate solution, and the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ was selected as 3.5, 1.0 and 13.6. For the cement in MK75C and MK50C systems, additional water besides the activator solution was added and the ratio of the additional to cement (W/C) was fixed at 0.4 according to the oil well cement specification. The mix proportions for preparation of the geopolymer pastes are given in Table 2.

2.2.2. Mixing and curing test

Metakaolin and cement were mixed by hand for 5 min first. Activator solution which had been prepared according to Table 2 in advance and kept at 20 °C, was then poured gradually into the dry components. The mixing was synthesized in planetary mixer for 15 min until a homogenous paste was obtained. The paste was then cast in cubic molds of 40 mm × 40 mm and vibrated on a vibrating table to liberate trapped air bubbles.

Five different curing conditions were adopted for the test pastes, including pre-curing and post-curing. As described in Table 3, CUC-1, CUC-2 and CUC-3 were directly cured in the conditions of 25 °C RH90% for 24 h, 80 °C RH90% for 24 h, and 80 °C RH90% for 4 h respectively, without pre-curing, while the preparation of CUC-4 and CUC-5 involved pre-curing at 80 °C RH100% for 4 h and afterwards post-curing at 150 °C for 20 h respectively under drying condition (RH < 10%) and hydrothermal condition (in waterlog condition).

2.2.3. Compressive strength test

The compressive strength test is performed in accordance with the standard GB/T17617-2021 “Test method of cement mortar strength (ISO method) [40]”. Before the test, all test samples were cooled to room temperature.

Table 1

Chemical composition (%) of MK and OPC

	Al ₂ O ₃	SiO ₂	CaO	Na ₂ O	K ₂ O	SO ₃	Fe ₂ O ₃
MK	46.32	49.90	0.18	0.21	0.12	0.04	0.61
OPC	5.07	21.28	64.58	0.55	–	0.93	3.86

Table 2

Mixture proportions of three pastes

Paste system	MK/g	OPC/g	Activator solution/g			Additional water/g
			Sodium silicate solution	NaOH	Water	
MK100	500	–	787.0	89.0	62.0	–
MK75C	375	125	590.0	67.0	46.5	50
MK50C	250	250	393.5	44.5	31.0	100

Table 3

Different curing conditions of three pastes

Curing condition	Pre-curing			Post-curing		
	Temperature/°C	Time/h	RH/%	Temperature/°C	Time/h	RH/%
CUC-1	–	–	–	25	24	90
CUC-2	–	–	–	80	24	90
CUC-3	–	–	–	80	4	90
CUC-4	80	4	90	150	20	<10
CUC-5	80	4	90	150	20	Waterlog

2.2.4. Characterization of geopolymer systems

After the samples were crushed, the solvent exchange method using anhydrous isopropanol was adopted to terminate the reaction as selected curing ages [41]. Then the samples were completely ground into fine powder and dried in a desiccator under N₂ flow at atmospheric pressure and 25 °C to avoid carbonation and any possible changes of the hydration products [41]. The products of the solid samples were determined by means of X-ray diffraction (XRD, Bruker, Germany) D8 Advance with monochromatic Cu K α radiation ($\lambda = 0.154059$ nm) was used to record the diffraction patterns under the 2θ range of 5° to 70° with a scanning speed of 2 (°)·min^{−1}. Thermogravimetric (TG) analyses were conducted with a NETZSCH (Germany) STA 2500 device using approximately 20 mg of sample. The mass loss of the samples was recorded from 30 °C up to 980 °C with a heating rate of 10 °C·min^{−1} under N₂ atmosphere. The porosity analysis data were obtained by nitrogen adsorption method at 77.35 K using Micromeritics (USA) ASAP2020. The ²⁹Si nuclear magnetic resonance (NMR) measurement was performed at room temperature using Agilent (USA) 600 MHz NMR spectrometer with a 4 mm cross polarization/magic angle spin (CP/MAS) probe. The ²⁹Si MAS NMR single-pulse experiments were recorded at 79.49 MHz with the spinning speed of 8000 Hz. The chemical shifts of the ²⁹Si MAS NMR spectra were referenced to an external sample of tetramethylsilane (TMS). Scanning electron microscope (SEM) observations for geopolymer samples were carried out at the curing age of 1 d using a Quanta (USA) 200 FEG microscope. An equipped energy dispersive X-ray spectroscopy (EDS) in the TEM enabled a direct analysis on the elemental composition of the selected phases observed by transmission electron microscope (TEM, JEM-101, JEOL, Japan), and the crystal type of these phases could be further analyzed by the selected area electron diffraction (SAED) technique in the meantime.

3. Results and Discussion

3.1. Compressive strength test

As shown in Fig. 1, under the curing condition of CUC-2, the compressive strength of MK100 group is significantly higher than

that of CUC-1, but is basically similar to CUC-3. This indicates that the thermal curing can substantially promote strength development of the pure metakaolin system at the same curing age of 24 h, and the reaction degree at the age of 4 h is almost close to that of 24 h under thermal curing condition. Kirschner *et al.* [42] also discovered that the reaction of metakaolin-based polymer was mostly completed after curing at 75 °C for 4 h. The MK100 group formed after curing at 80 °C for 4 h was then cured at 150 °C in dry (CUC-4 and saturated CUC-5) conditions to the age of 24 h. The strength of sample under CUC-4 condition is moderately lower than that under CUC-3 conditions, indicating that the 150 °C drying condition has unobvious negative effect on strength. However, the compressive strength of the sample cured under CUC-5 condition sharply decreased by reduction rate of 81.8% compared to the sample under CUC-4 condition. As shown in Fig. 2, the sample of MK100 group at this time appears to be in a loose powdery particle state and practically loses its cementitious ability.

Similar to metakaolin system, 80 °C thermal curing can also improve the strength of the metakaolin-cement system. The com-

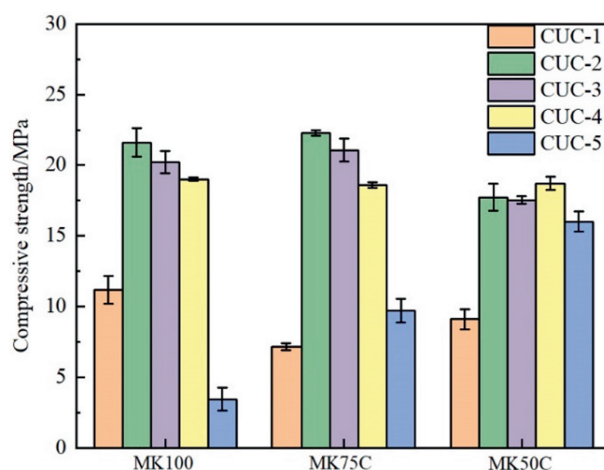


Fig. 1. Compressive strength of three pastes obtained from different curing conditions.

pressive strength at 4 h is also approximately the same as that at 24 h. When the temperature rises to 150 °C, the compressive strength of MK100 and MK75C group decreases slightly, while the strength of MK50C group increases. However, under the 150 °C waterlog condition (CUC-5), the MK100 group virtually lost its compressive strength, with loose powdery particles shown on the sample surface (Fig. 2). Interestingly, the strength of MK75C and MK50C groups is well retained under CUC-5 curing conditions. In addition, the strength of MK50C group with higher calcium content decreases less than that of MK75C group, and still retains a compressive strength of about 16 MPa with only a slight decrease of 14.4%. Moreover, the appearance of the samples here is intact without obvious damage, as shown in Fig. 2.

The elevation of curing temperature promotes the development of geopolymer strength, due to the increase of dissolution of metakaolin particles and polymerization reaction [19] which has been widely reported [15–17]. This study also verified that both metakaolin system and metakaolin-cement system have high strength under high temperature and dry conditions. Interestingly, under high temperature hydrothermal conditions, the low calcium metakaolin system almost loses its compressive strength, while the high calcium metakaolin-cement system maintains a high strength. The mechanism of this phenomenon is explained below.

3.2. XRD analysis

Fig. 3 shows the XRD patterns of the geopolymers obtained under different curing conditions. It can be seen from Fig. 3(a) that the XRD of MK100 samples cured under the conditions of CUC-1–CUC-4 are all dispersive diffraction peaks in the range of $2\theta = 25^\circ$ – 30° , indicating that the reaction products are amorphous silica aluminate gels. Since there is no calcium in the system, the resulting gel should be sodium aluminosilicate gel (N-A-S-H gel) [43,44]. However, after the MK100 sample was cured under CUC-5 condition, the XRD of the sample changes to sharp diffraction peaks, indicating that the reaction product has changed from amorphous gel to crystalline structure. Based on Jade analysis software and the related literature [31,45–48], it is supposed that the crystals Na-P zeolite structure ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$) are mainly generated after crystallization, which diffraction peaks are observed at 12.5° , 17.7° , 21.7° , 28.2° and 33.4° of 2θ .

Fig. 3(b),(c) indicates that under the conditions of CUC-1–CUC-4, the XRD patterns of MK75C and MK50C groups also show the

presence of amorphous aluminosilicate gel structure in the range of $2\theta = 25^\circ$ – 30° , and diffraction peaks of tobermorite structure similar to C-S-H gel appear near $2\theta = 30^\circ$ and $2\theta = 32.5^\circ$ [49,50], indicating that in addition to the sodium-containing N-A-S-H gel, calcium silicate gel (C-A-S-H gel) with a layered structure appears in the reaction product [51–53]. However, under CUC-5 curing condition, although the diffraction peak of C-A-S-H gel structure at $2\theta = 30^\circ$ in MK75C group is retained, the retention is already very insignificant, indicating that the N-A-S-H gel with a large proportion in the products still has obvious crystallinity. But, in the MK50C group with higher calcium content, although the diffraction peak of zeolite structure appears in the XRD pattern under CUC-5 curing condition, the dispersive diffraction peaks in the range of $2\theta = 25^\circ$ – 30° and the diffraction peaks of C-A-S-H gel structure near $2\theta = 30^\circ$ and $2\theta = 32.5^\circ$ are basically intact. The MK50C group has lower crystallization products compared to MK100 and MK75C groups. This may be due to that the main products of MK50C are C-A-S-H gels, which are more stable than N-A-S-H under hydrothermal conditions.

From the strength results and the changes of crystalline structure of the products, it can be seen that high temperature environment of 150 °C does not directly promote the crystallization of the silicate product gel under dry condition. Only when the product gels are subjected to hydrothermal conditions of 150 °C, crystallization of the products occurs to form zeolite, resulting in the deterioration of strength. This is consistent with the literatures [45,54,55], which also found the transition of amorphous gels into crystalline zeolites leading to a certain loss of compressive strength. However, the C-A-S-H gel containing calcium can maintain the gel stability under hydrothermal conditions at 150 °C compared with N-A-S-H gel and thus the high strength is retained.

3.3. TG-DTG analysis

The thermal analysis method was used to characterize the composition changes of the geopolymers in MK100, MK75C, and MK50C systems under different curing conditions. It can be seen from Fig. 4(a) that under the CUC-2 and CUC-3 curing conditions, the MK100 groups lost weight in the temperature range of 100–250 °C. According to literatures [51–53,56], only bound water in the gel is removed within this temperature range. The mass losses of the sample are basically identical under the two conditions, which further proves that the reaction degree of geological poly-

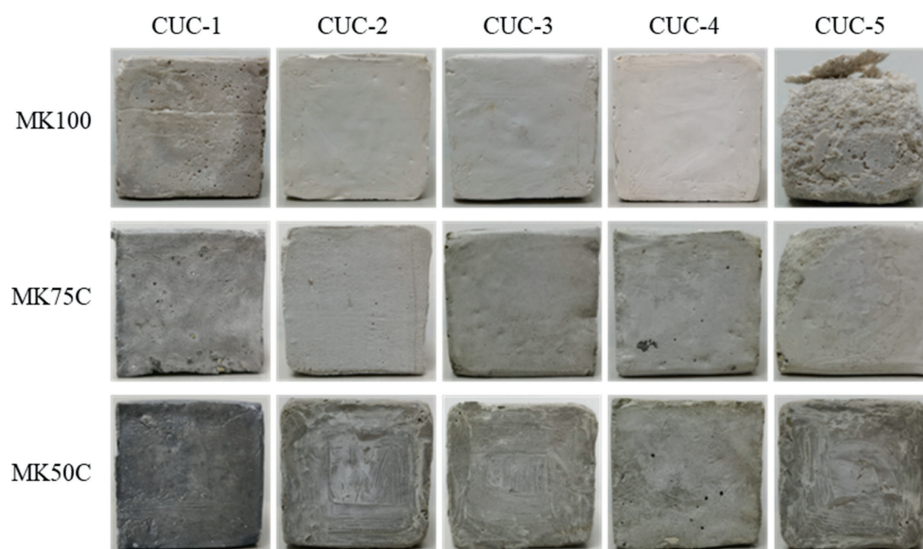
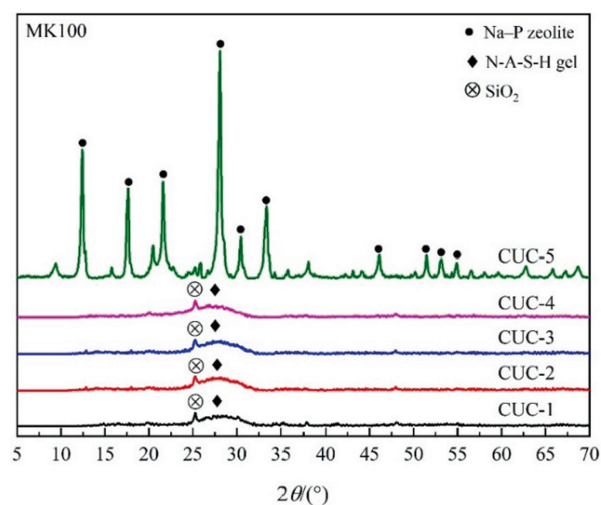
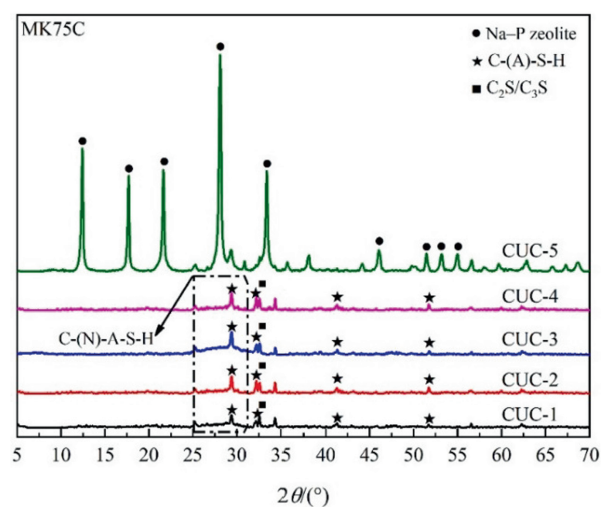


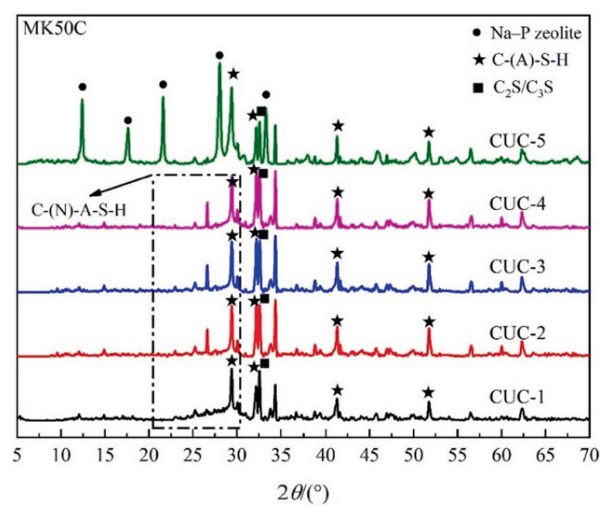
Fig. 2. Images of the three pastes obtained from different curing conditions.



(a)



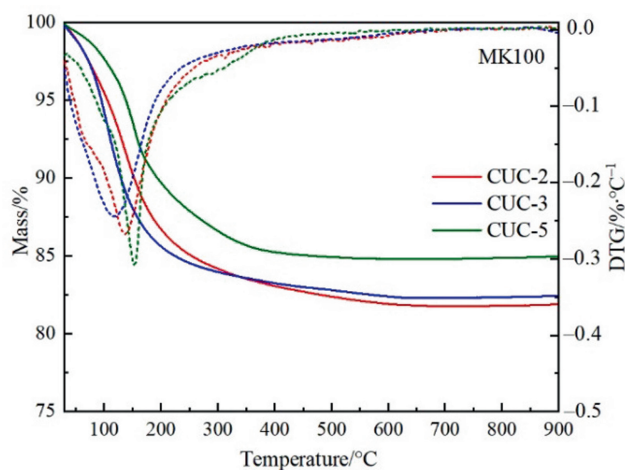
(b)



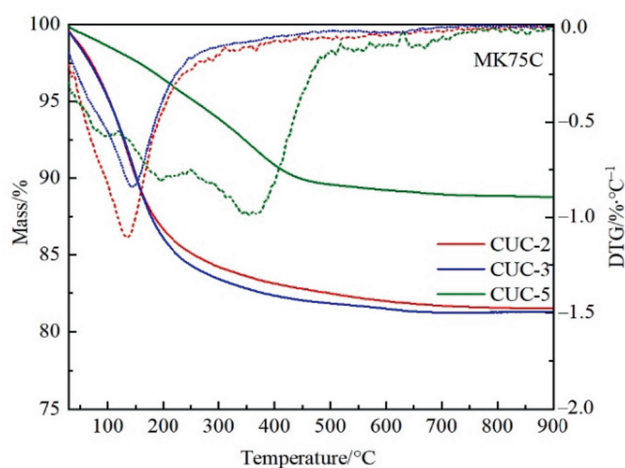
(c)

Fig. 3. XRD patterns of the three pastes obtained from different curing conditions: (a) MK, (b) MK75C, (c) MK50C.

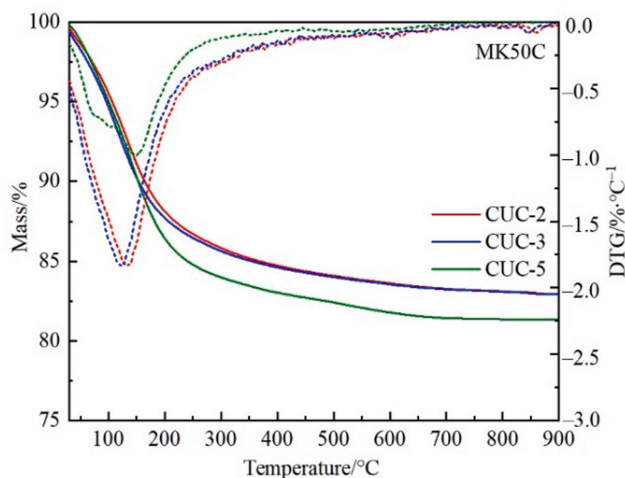
merization in MK100 is basically the same after curing at 80 °C for 4 and 24 h. However, under the condition of CUC-5, the mass loss of MK100 group is significantly reduced, and the temperature



(a)



(b)



(c)

Fig. 4. TG-DTG curves of the three pastes obtained from different curing conditions: (a) MK100, (b) MK75C, (c) MK50C.

range of thermal mass loss is expanded to 100–400 °C. The thermal mass loss of MK100 group under CUC-5 curing condition is about 15.1%, while the figure is about 18.2% under CUC-2 curing condition. This change may be caused by the phenomenon that the pores

in the zeolite structure formed by the crystallization of N-A-S-H gel at 150 °C hydrothermal condition are too small [44,57] to bind more water molecules.

Fig. 4(b),(c) shows thermogravimetric curve of metakaolin-cement system. It can be seen from Fig. 4(b) that the mass loss of MK75C is basically consistent under the CUC-2 and CUC-3 conditions, while it is also significantly reduced under CUC-5 curing conditions. At 100–250 °C and 250–450 °C in the DTG curve of the sample under CUC-5 curing condition, two obvious thermogravimetric rate peaks appear, indicating that the sample has two stages of mass loss. The first stage is mainly due to the loss of bound water in the non crystallized gels, including the cement hydration product calcium-silicate-hydrate (C-S-H) gel and a small part of N-A-S-H gels [51–53,56]. As for the second stage of mass loss, this may be due to the delayed heat conduction caused by the entanglement between the uncrystallized gel and the crystals in the sample. The outer gels first remove bound water, and then the bound water in the crystal loses at higher temperature. However, different from MK100 and MK75C groups, it can be seen from Fig. 4(c) that the TG curves of MK50C samples under three curing conditions are basically similar and the thermal mass loss occurs in the temperature range of 100–250 °C. This indicates that the bound water contents in the gel structure are essentially the same and the gel compositions are comparable. In fact, it can be seen from Fig. 4(c) that the MK50C samples even present a higher mass loss under CUC-5 condition. This may be because the hydration degree of metakaolin-cement system is improved and more C-A-S-H gels are produced with the increase of temperature [19–21].

3.4. Porosity

Fig. 5 shows the pore structure of MK100 and MK50C groups tested by the nitrogen adsorption method. It can be seen that the MK100 group under CUC-2 curing condition has the highest total porosity, while the total porosity is considerably lower under CUC-5 curing condition compared to the other two curing conditions. On the other hand, the most probable pore size of MK100 group under CUC-1 and CUC-2 curing conditions is about 20–25 nm, while the figure is only about 5 nm under CUC-5 curing conditions.

As shown in Fig. 5(b), the total porosity of MK50C group under CUC-1 and CUC-2 curing conditions is basically the same. However, the total porosity of MK50C group under CUC-5 curing conditions is moderately smaller than the other two curing conditions. Although the total porosity of MK50C group decreases under CUC-5 condition, the most integrable pore size of the sample under CUC-5 curing condition is about 30 nm, slightly larger than that under CUC-1 and CUC-2 curing conditions, which is in the range of 15–20 nm. This may be due to the precipitation of some crystals in the original gel matrix under hydrothermal conditions [30,58]. In the high-calcium geopolymers, some completely precipitated crystals fill the original pore space, resulting in the decrease of porosity, and the other part of the crystals which are not completely precipitated from the gel can form interfaces with the gel, causing the most probable pore size to increase.

It is worth noting that under CUC-5 curing conditions, the total porosity and the most probable pore size of MK100 group are much smaller than MK50C group. Theoretically, the compressive strength of MK100 group should be higher than MK50C group, but the experimental results are just the opposite. This is because under CUC-5 curing conditions, a large number of gels in the low-calcium pure kaolin geopolymer crystallizes to generate zeolite crystals [44], resulting in the loss of cementation capacity.

3.5. NMR analysis

^{29}Si NMR has been used to further study the changes in reaction products under CUC-2 and CUC-5 curing conditions. It can be seen from Fig. 6(a),(b) that the peak of the MK100 group products under CUC-5 curing condition is visibly shifted compared with that of the products under CUC-2 curing condition, and a new peak appears at $\delta = -91.30$. This demonstrates that the chemical structure of N-A-S-H gel in MK100 group is changed considerably under the hydrothermal condition of 150 °C.

As shown in Fig. 6(c) and (d), the ^{29}Si NMR patterns of MK50C obtained from the two curing conditions, are virtually identical under indicating that the hydrothermal condition of 150 °C does not lead to structural change the C-A-S-H gel generated in MK50C group, which is consistent with the results of XRD in Section 3.2. It is further clarified that N-A-S-H gel will undergo obvious structural changes under saturated water condition of 150 °C, while C-A-S-H gel with high calcium content is stable enough against the hydrothermal treatment of 150 °C.

The original ^{29}Si NMR spectra were then deconvoluted into individual Gaussian peaks to further analyze the Si coordination environment in the samples [59–61]. In this paper, Q^0 , Q^1 , Q^2 , $Q^2(1\text{Al})$, $Q^3(1\text{Al})$, $Q^3(2\text{Al})$, $Q^4(0\text{Al})$, $Q^4(1\text{Al})$, $Q^4(2\text{Al})$, $Q^4(3\text{Al})$ and $Q^4(4\text{Al})$ are derived after deconvolution, whose chemical shifts are located at -68 ± 5 , -76 ± 4 , -78 ± 5 , -84 ± 4 , -90 ± 4 , -94 ± 4 , -110 ± 5 , -101 ± 4 , -95 ± 4 , -91 ± 4 and -85 ± 4 respectively [44,61–66]. The proportion of each $Q^n(m\text{Al})$ structure are shown in Table 4, and the calculated and fitted patterns are shown in Fig. 7.

Fig. 7(a),(b) and Table 4 give the fitting results of NMR deconvolution curves of MK100 group under CUC-2 and CUC-5 curing conditions, as well as the proportion of each $Q^n(m\text{Al})$ structure. It can be seen from the results that the chemical structures of Si in MK100 group under 80 °C curing conditions are mainly $Q^2(1\text{Al})$ and $Q^4(4\text{Al})$ structures, accounting for 19.3% and 19.7%, respectively. The proportions of $Q^3(2\text{Al})$, $Q^4(1\text{Al})$, $Q^4(2\text{Al})$ and $Q^4(4\text{Al})$ structures are significantly increased under saturated water condition of 150 °C, while the other structures decrease obviously, and the structures of $Q^4(0\text{Al})$ and $Q^4(3\text{Al})$ basically disappear. The Si/Al ratios in MK100 group under CUC-2 and CUC-5 curing conditions are calculated to be 1.30 and 1.23, respectively [51,62,67], according to the Eq. (1) [62] and the contents of chemical structure $Q^4(m\text{Al})$ ($m = 0, 1, 2, 3, 4$) shown in Table 4.

$$\text{Si/Al}_{\text{N-A-S-H gel}} = \frac{\sum_{m=0}^4 Q^4(m\text{Al})}{\sum_{m=0}^4 \frac{m}{4} Q^4(m\text{Al})} \quad (1)$$

In the N-A-S-H gel generated under CUC-2 curing conditions, Q^0 , Q^1 , Q^2 , $Q^2(1\text{Al})$, $Q^3(1\text{Al})$ and $Q^3(2\text{Al})$ structures are grafted onto the aluminosilicate main chain to form a network gel structure, in addition to the main chain structure dominant by $Q^4(m\text{Al})$ ($m = 0, 1, 2, 3, 4$). However, the proportion of aluminum in the main chain structure has increased significantly under the CUC-5 curing condition, indicating that the gel structure of the original product has undergone reorganization, and the process is shown in Fig. 8. In the 150 °C saturated water condition of CUC-5, the free alkali ions inside the sample dissolve into the water to form an alkaline environment. Since the amorphous N-A-S-H gel is in a thermodynamic metastable state [27,45], it can be re-dissolved in the alkaline solution [58]. The silicon-aluminum structure dissociates into $[\text{Al}(\text{OH})_4]^-$ and $[\text{Si}(\text{OH})_4]$ and then undergoes condensation polymerization to integrate part of the original branched chain structure into the main chain, thus forming a crystalline structure dominated by $Q^4(4\text{Al})$ backbone and $Q^3(2\text{Al})$ branched chains. In this way, the original amorphous gel structure is ordered, and

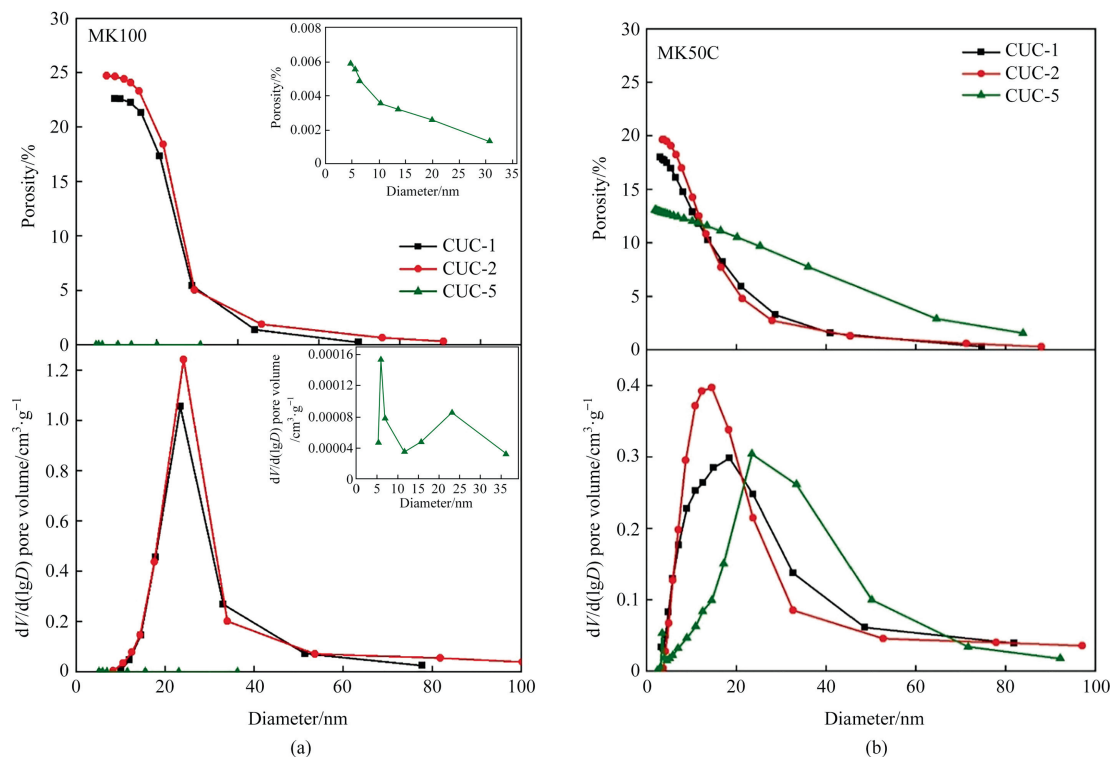


Fig. 5. Pore structure of the pastes treated under different conditions: (a) MK100, (b) MK50C.

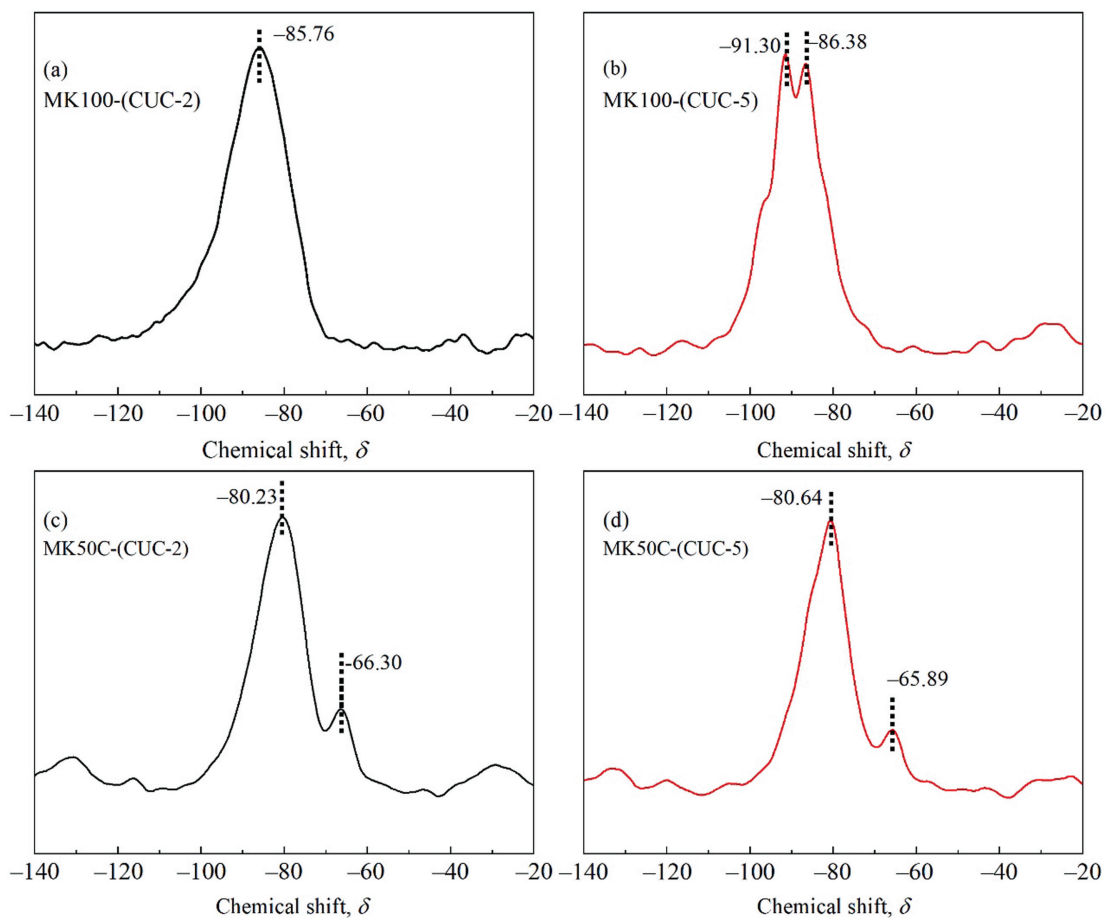


Fig. 6. NMR curves of the pastes obtained from different curing conditions: (a) MK100-(CUC-2), (b) MK100-(CUC-5), (c) MK50C-(CUC-2), (d) MK50C-(CUC-5).

Table 4
Proportion of $Q^n(mAl)$ structure in MK100 and MK50C pastes

Site type	Proportion/%			
	MK100		MK50C	
	CUC-2	CUC-5	CUC-2	CUC-5
Q^0	4.48	1.47	9.01	8.96
Q^1	11.03	4.90	5.62	5.64
Q^2	0.00	0.00	17.08	16.97
$Q^2(1Al)$	19.30	12.43	26.21	25.71
$Q^3(1Al)$	12.41	3.20	3.02	3.03
$Q^3(2Al)$	9.06	31.15	6.02	6.05
$Q^4(0Al)$	2.15	0.52	0.00	0.00
$Q^4(1Al)$	1.18	2.02	0.00	0.00
$Q^4(2Al)$	6.70	13.89	2.22	2.23
$Q^4(3Al)$	13.99	0.00	11.61	13.30
$Q^4(4Al)$	19.70	30.42	19.21	18.11

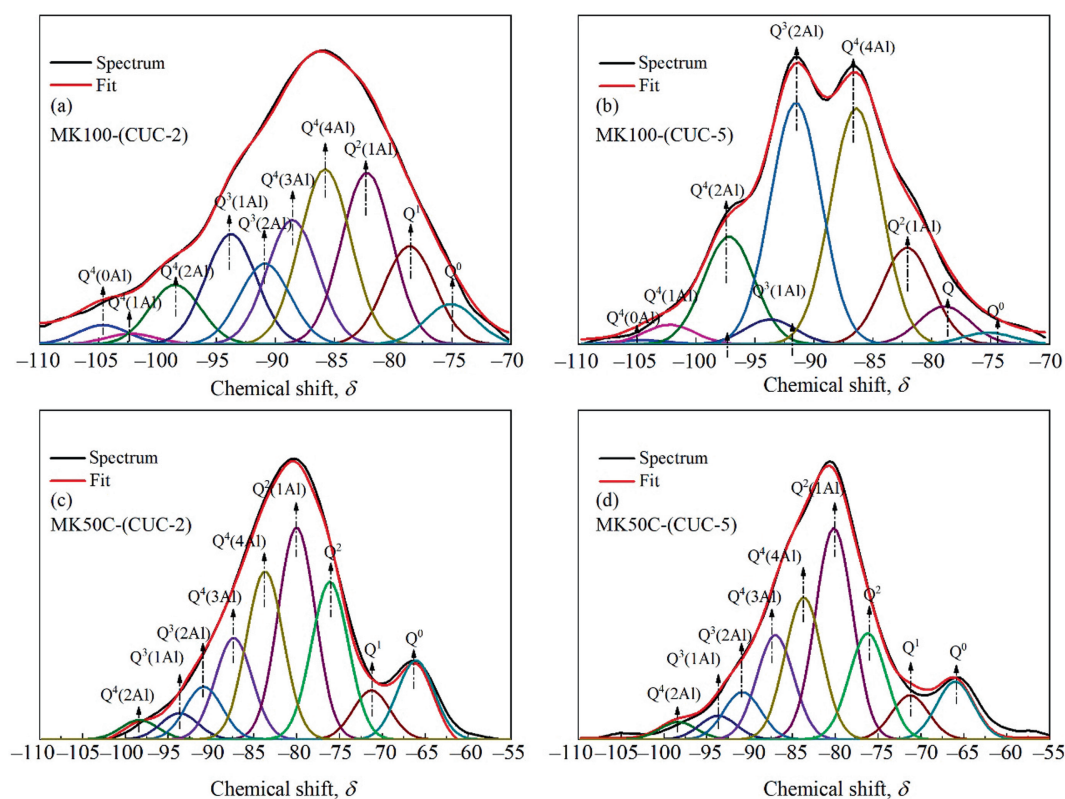


Fig. 7. Deconvolution results for ^{29}Si NMR spectra of the pastes obtained from different curing conditions: (a) MK100-(CUC-2), (b) MK100-(CUC-5), (c) MK50C-(CUC-2), (d) MK50C-(CUC-5).

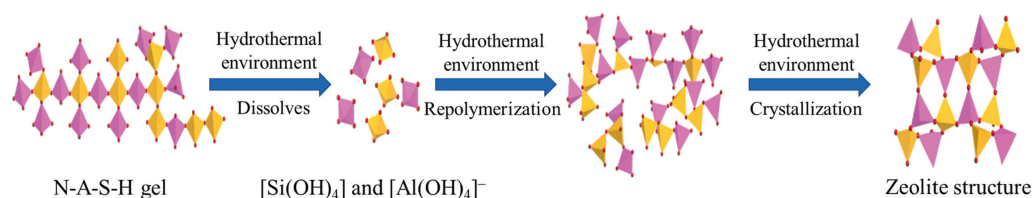


Fig. 8. The sequential changes of N-A-S-H gel under hydrothermal conditions.

the content of aluminum element in the main chain structure is increased. This process can be summarized as “dissociation–repolymization–crystallization”.

As can be seen from Fig. 7(c) and (d) and Table 4, there is no significant difference in the type and content of each $Q^n(mAl)$ in

MK50C group under the two curing conditions. The chemical structure of Si in MK50C group under CUC-2 curing condition is principally Q^2 , $Q^2(1Al)$ and $Q^4(4Al)$, which is still the same under CUC-5 curing condition but the relative content has a slight decline. It can be seen that the main gel generated in the kaolin–cement system

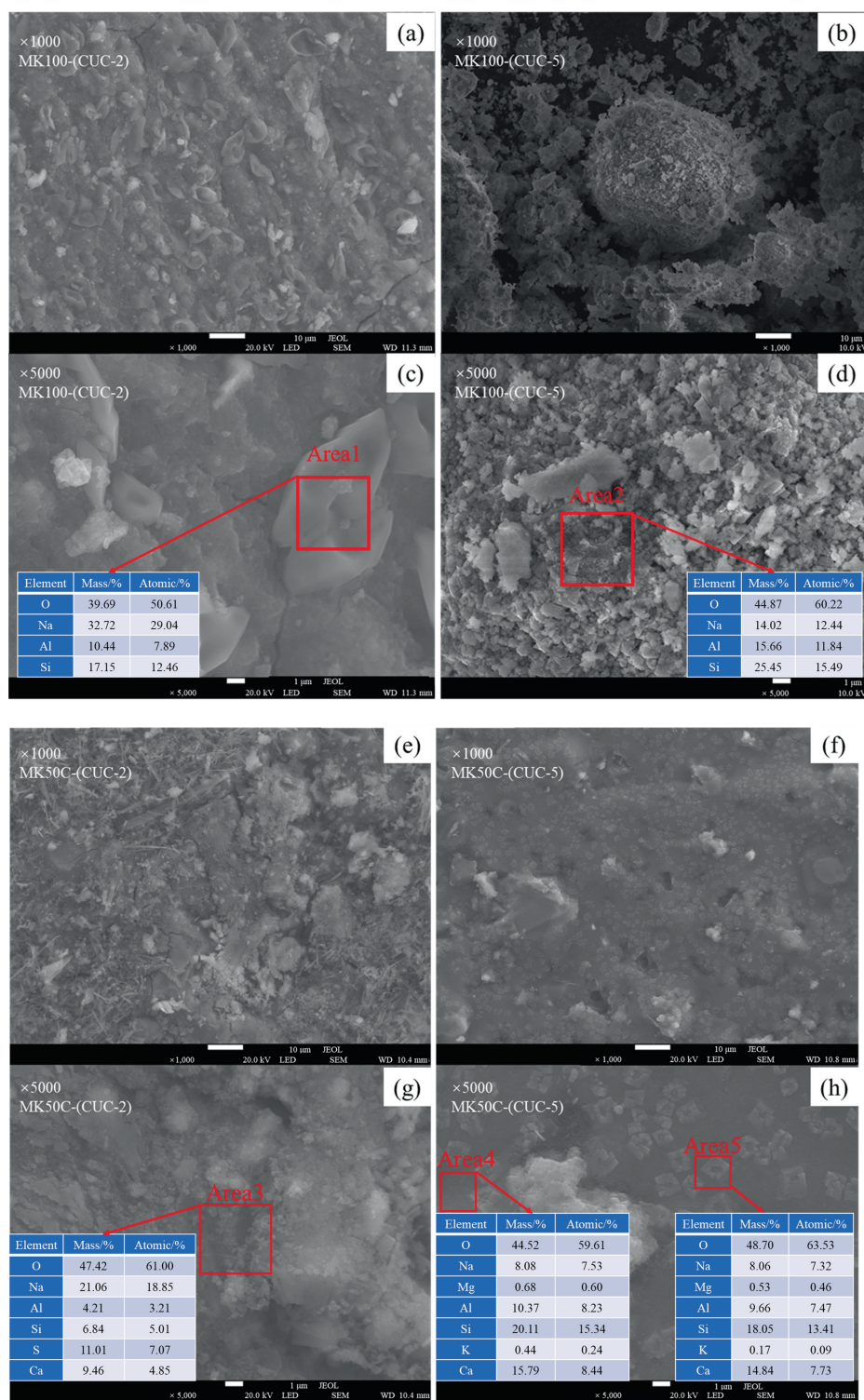


Fig. 9. SEM images of the pastes obtained from different curing conditions.

has not undergone significant internal structural reorganization in the saturated water condition of 150 °C. The main product of group MK50C is C-A-S-H gel, which is similar to Tobey mullite structure. The order of C-A-S-H structure is higher than that of N-A-S-H gel, and its thermodynamic properties are more stable under hydrothermal conditions. On the other hand, although the backbone of C-A-S-H gel is mainly composed of three main structures, Q^1 , Q^2 and $Q^2(1Al)$, the results demonstrate the presence of $Q^4(4Al)$

structure. This indicates that a certain amount of N-A-S-H gel is also doped in the C-A-S-H gel.

3.6. SEM and TEM analysis

The gel transformation of MK100 group at different curing conditions is verified by SEM and TEM analysis as shown in Figs. 9 and 10. It is seen that the reaction products of MK100 group are cemen-

ted together into a whole structure under CUC-2 curing conditions, forming a dense cementitious matrix. However, under the condition of CUC-5 curing, as shown in Fig. 9(b), the SEM image exhibits a loose matrix, which are evidently different from the gel obtained under CUC-2 curing conditions. It can also be seen from the TEM image (Fig. 10(b)) that the interconnection between particles is too loose to hold the whole structure. The EDS results of Area1 and Area2 (as shown in Fig. 9(c),(d)) show that although the reaction products are all composed of Na, Al, Si and O, the element composition ratio of the products has changed substantially under CUC-2 and CUC-5 curing conditions, with Si/Al molar ratios of 1.58 and 1.31, respectively. From the electron diffraction pattern, it can

be seen that the samples of group MK100 under CUC-2 curing condition display a dispersive diffraction pattern, indicating that the product is amorphous gel, while the samples under CUC-5 curing condition show a concentric ring diffraction pattern, indicating that the product is a polycrystalline crystal composed of multiple crystal grains. Based on the results in Sections 3.2 and 3.5, it can be deduced that the gel products under CUC-2 curing conditions are N-A-S-H gels, which are tightly cemented forming a dense microstructure. However, the spherical particles under CUC-5 curing condition are Na-P zeolite crystals with residual gel on the surface. The spherical particles are very loose and basically lose the cementation ability. This further indicates that the crystallization

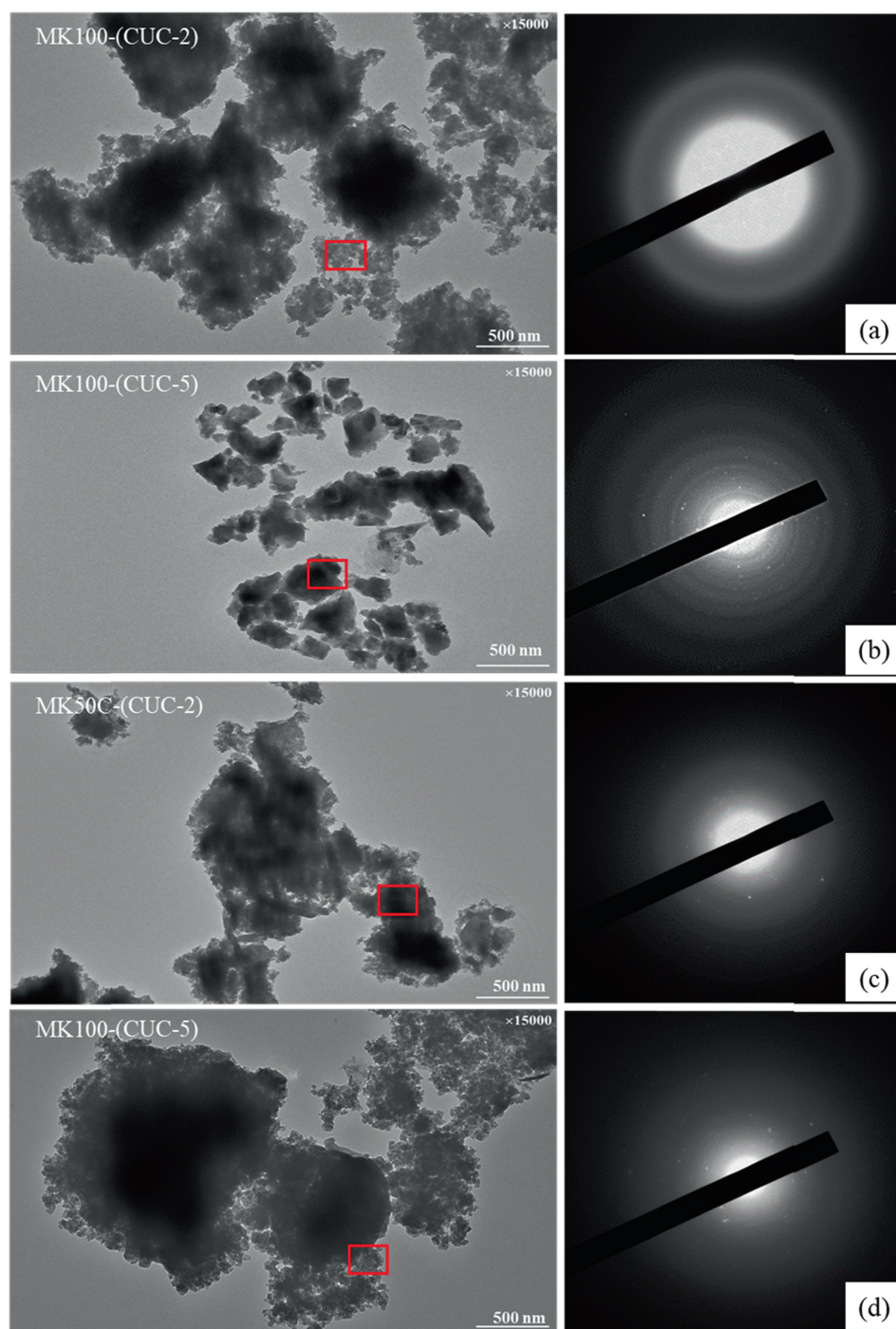


Fig. 10. TEM images and electron diffraction patterns of the pastes obtained from different curing conditions.

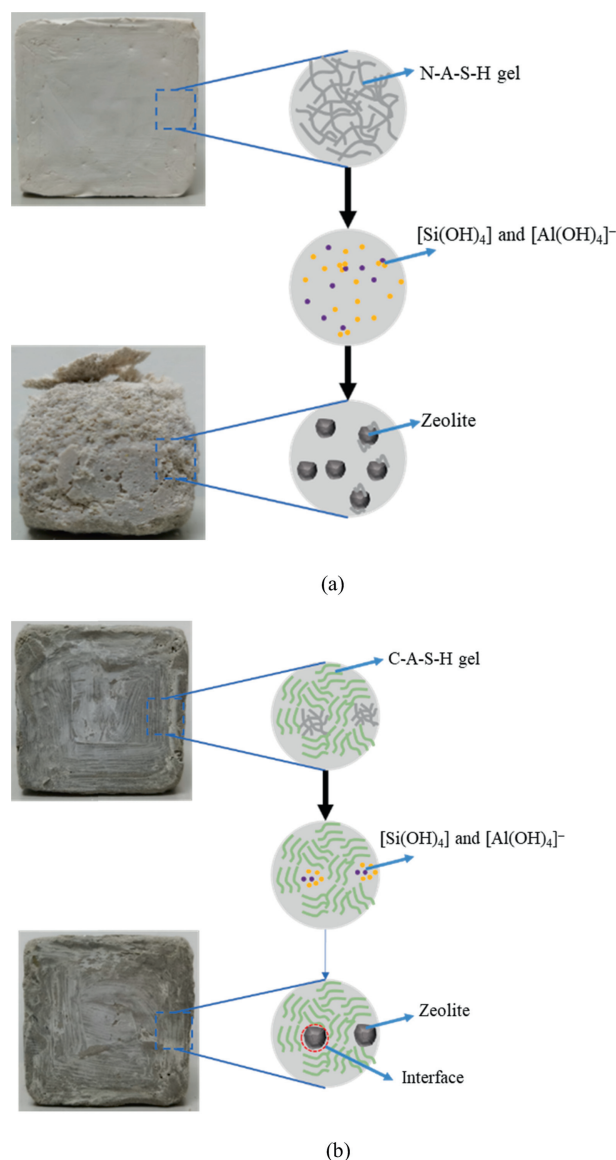


Fig. 11. Schematic diagrams of microstructure changes of the pastes under different curing conditions: (a) MK100, (b) MK50C.

of N-A-S-H gel under 150 °C saturated water condition is the main reason for its strength degradation [45,54].

The micromorphology of MK50C group is different from that of MK100 groups as shown in Figs. 9 and 10. Different from MK100 group, the products of MK50C groups both have dense matrix structures under both CUC-2 and CUC-5 curing conditions. Furthermore, the diffraction patterns of MK50C group (Fig. 10(c) and (d)) are all diffuse patterns under the two curing conditions, demonstrating that the products under the two conditions are predominantly amorphous gel. However, as shown in Fig. 9(h), some cubic structures appear in the matrix gel under CUC-5 curing condition. In addition, the EDS tests of Area3–Area5 (Fig. 9(g) and (h)) show that the products are mostly composed of Na, Al, CA, Si, O, and S elements. The element composition in Area3 shows that under CUC-2 curing condition the products are mainly composed of C-S-H gel and C-A-S-H gel, due to the incorporation of Portland cement. The EDS test results of Area4 and Area5 show that the product of MK50C group samples is still predominantly calcium-containing aluminosilicates

under CUC-5 curing condition. Area4 is dominated by gel matrix, while the product structure in Area5 has undergone certain changes relative to gel. The Si/Al molar ratios of Area4 and Area5 are 1.86 and 1.80, respectively, while Ca/Si values are 0.55 and 0.57, respectively. The products of two areas have essentially consistent elemental composition, indicating that the cubic product in Area5 is precipitated from matrix gel and cemented with the gel, so that the overall microstructure remains intact without losing the cementing property.

Based on the abovementioned results, the relevant mechanism of the different strength changing behaviors between MK100 and MK50C under 150 °C saturated water condition is proposed. As shown in Fig. 11(a), for the low-calcium MK100 group composed of pure metakaolin, the main product is N-A-S-H gels. In the 150 °C saturated water environment, N-A-S-H gel re-dissociates into the silicon aluminum monomer in water and further reorganizes to form Na–P zeolite crystals [58]. The resulting zeolite crystalline particles leads to loss of the cementation capability of the matrix and thus deterioration of mechanical strength. For the high-calcium containing system of MK50C group composed of metakaolin and cement, however, the main products are N-A-S-H and C-A-S-H gels. As shown in Fig. 11(b), the two gels are interwoven to form the matrix. When the samples are placed in a high-temperature hydrothermal environment, the N-A-S-H gel will also undergo the process of “dissociation–repolymerization–crystallization”. But in this environment, the C-A-S-H gel is more stable than N-A-S-H and does not re-dissociate, thus retaining the cementitious property of the matrix. Due to the crystallization of N-A-S-H in the hydration products, defects increased in the cemented matrix structure, resulting in a slight decrease in strength.

4. Conclusions

In this paper, the mechanical strength and the degradation mechanism of pure metakaolin system and metakaolin-cement system under hydrothermal and non-hydrothermal conditions were studied. Based on the results reported above, the following conclusions can be drawn:

- (1) Under high-temperature hydrothermal conditions of 150 °C, the strength of pure metakaolin geopolymer decreases markedly, while the metakaolin-cement geopolymers have lower degree of strength decrease;
- (2) The product of pure metakaolin geopolymer is predominantly N-A-S-H gel, while the metakaolin-cement geopolymer system is mainly C-A-S-H gel. Compared with the high-calcium C-A-S-H gel, N-A-S-H gel exhibits a more obvious crystallization tendency under high-temperature hydrothermal conditions;
- (3) The N-A-S-H gel undergoes the process of “dissociation–repolymerization–crystallization” under high-temperature hydrothermal conditions, resulting in the change of internal chemical structure. The crystallized zeolite grains basically lose the cementation ability, leading to an obvious decrease in the mechanical strength;
- (4) The high-calcium C-A-S-H gel, which has a higher degree of ordered structure and better thermodynamic stability, does not undergo the same “dissociation–repolymerization–crystallization” process as N-A-S-H gel under hydrothermal conditions. As a result, material gelation is not damaged, thereby ensuring macroscopic strength. However, due to the crystallization of the N-A-S-H gel doped in the matrix, microscopic defects increase, resulting in a slight decrease in the macroscopic strength.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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