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Effects of halloysite in kaolin on the formation and properties of geopolymers

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ABSTRACT

A kaolin containing 31 wt.% halloysite and a relatively pure kaolin were selected to study the effects of halloysite on the dissolution behavior of precursors and the formation of geopolymers. The Al and Si concentrations in the leached solutions were studied by inductively coupled plasma-optical emission spectrometry (ICP-OES). The reaction process of metakaolin–activator mixtures was monitored by isothermal conduction calorimetry (ICC) while the reaction products were examined by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and mercury intrusion porosity (MIP). Results showed that the halloysite containing kaolin and its metakaolin possessed higher Si and Al dissolution rate than the purer kaolin and its metakaolin. When mixed with sodium silicate activator at 20 °C, the presence of halloysite in kaolin led to a higher geopolymerization rate of metakaolin as reflected by the heat evolution rate. The presence of halloysite improved the reactivity of metakaolin but did not change the geopolymerization pathway under 20 °C air curing and 80 °C steam curing conditions. The products from the two metakaolins had a similar XRD characteristic (i.e. a typically amorphous diffraction). Only a minor difference in the pore distribution and the porosity was found between those products from the two sources of metakaolins.

1. Introduction

The challenges of high energy and resource consumption have driven the cement and concrete industry to pursue alternatives to Portland cement. Alkali-activated aluminosilicates, usually termed ‘geopolymers’, are a new family of cementitious materials [1]. They have shown high potential for manufacturing sustainable concrete with a reduced environmental footprint [2]. In general, geopolymers are synthesized from the reaction of solid aluminosilicate precursors with alkaline solution at ambient or elevated temperature. Precursors can be a single source or a mixture of clays (usually kaolin, either raw or via thermal treatment to metakaolin) [3,4], pozzolanics [5,6] and various industrial wastes and by-products, such as fly ash and slag [7,8].

Among these precursors, metakaolin has a high reactivity and relatively purer composition compared to the others and has been extensively studied to understand the geopolymer formation mechanisms [9,10]. In addition, metakaolin-based geopolymers possess many interesting properties, such as low permeability [11], good thermal stability [12] and high bonding strength [13]. However, current understanding and controlling of geopolymer paste and hardened products is still far from meeting the requirements of wide application as alternatives to traditional cement binders. Fundamental research into the influences of nature and mineral components in kaolin or metakaolin on the behaviors of paste and hardened products has received very limited attention.

Kaolin usually composes of kaolinite as the major mineral component together with many other secondary minerals, including quartz, halloysite, dickite, nacrite and anatase. The reactivity of quartz is lower than kaolin (much lower than metakaolin) due to their different dissolution behavior under strong alkaline conditions [14]. Although the chemical composition of dehydrated halloysite, dickite, and nacrite is the same to kaolinite, their structural characteristics are quite different. Halloysite has a tubular structure while kaolinite has a sheet structure [15]; in dickite all the inner-surface hydroxyl groups participate in the bonding between layers, whereas in kaolinite only two out of the three hydroxyl groups contribute to the bond [16]. It has been demonstrated that different hydroxyl groups result in different dehydroxylation behavior [17], which may consequently affect the reactivity of kaolin [18]. Therefore, it is believed that these secondary minerals present in kaolin will certainly influence the reaction process and final properties of geopolymer. The influence of secondary minerals illite and quartz has been examined by Zibouche et al. [19] and it was found that 20 wt.% of illite and 10 wt.% of quartz did not prevent the geopolymerization reaction but changed the micro-morphology and leaching behavior of the hardened products. As

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the variety and quantity of secondary minerals vary from source to source, fundamental research into the impact of secondary minerals in kaolin is necessary, particularly from the perspective of future wide application of geopolymers, which will likely need a large volume of kaolin from different clay deposits.

The purpose of this work is to elucidate the effect of halloysite present in kaolin on the preparation of metakaolin-based geopolymer. Pure halloysite has been used in geopolymer synthesis and proved to be a good starting material after thermal treatment [20–22]. However, little information has been reported on the effects of halloysite as a secondary mineral in kaolin in geopolymer synthesis. Kaolin associated with halloysite is abundant in many deposits around the world, for example in southern China [23], thus the research on this kind of kaolin has a particular value in the selection of source materials for geopolymer application. This work provides a comparative study of two different kaolins for a better understanding of the dissolution behavior and the geopolymerization products: one contains 31 wt.% of halloysite while the other is a relatively pure kaolin.

2. Materials and methods

2.1. Materials

The halloysite-containing kaolin (denoted K1) was from Longyan Donggong (Fujian province, China) and the relatively pure kaolin (denoted K2) was from Suzhou deposit (Jiangsu province, China). Both K1 and K2 were heated at 700 °C for 1 h in an air atmosphere to obtain their corresponding metakaolins, denoted MK1 and MK2. The specific surface areas of K1 and K2 determined by BET method were 12.8 m^2/g and 10.7 m^2/g respectively. Table 1 gives the composition of MK1 and MK2 as detected by X-ray Fluorescence (XRF). K1 contains 52.3 wt.% of kaolinite, 31 wt.% of halloysite and 9.1 wt.% of quartz [24] while K2 contains 91 wt.% of kaolinite and 6.4 wt.% of quartz as calculated by supposing the Al_2O_3 is only from kaolinite while the LOI is due to dehydroxylation of kaolinite. Fig. 1 shows the XRD analysis of kaolins and metakaolins. It is difficult to distinguish halloysite from kaolinite in Fig. 1 due to their high similar basal structure parameters of unit cell: c_0 of halloysite is 0.72 nm while it is 0.715 nm for kaolinite; and that is why a dimethylsulfoxide saturation method combined with quantitative XRD method was applied in the quantitative analysis of K1 [24]. In the current study, a quantitative analysis of mineral components has not been repeated. The diffraction at 29.45° (2θ) is probably attributed to some calcium and/or magnetite minerals. It is clear that an amorphous phase is formed after thermal treatment, as reflected by the broad diffraction over 15–35° (2θ).

Table 1
Chemical composition of MK1 and MK2 in mass%, as determined by XRF (LOI: loss on ignition at 1000 °C).

	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	LOI
MK1	51.98	40.29	0.34	1.02	0.39	5.26
MK2	49.66	41.88	0.29	0.60	0.66	6.49

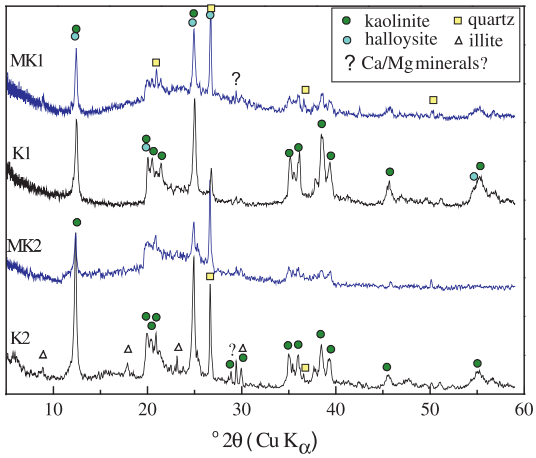

Fig. 1. XRD patterns of source kaolins K1 and K2 and 700 °C × 1 h thermally treated metakaolins MK1 and MK2.

The alkaline activator used was prepared by mixing chemical grade NaOH with commercial sodium water glass (original modulus of 3.33, Na_2O 9.28 wt.% and SiO_2 29.91 wt.%), then adding distilled water to adjust the concentration, combined to give a mole ratio SiO_2:Na_2O of 1.2 and total solids concentration of 35 wt.%.

2.2. Methods

2.2.1. Specimen preparation and strength test

The metakaolin was mechanically mixed with the activator at a constant liquid/solid ratio of 0.64 mL g^{-1}. The slurry was cast in plastic molds (Ø25 × 37.5 mm) and set at 20 ± 2 °C for 24 h, then demolded, followed by further curing under two conditions: air condition (20 ± 2 °C, relative humidity 90 ± 5%) and steam condition (80 ± 3 °C, relative humidity 100%). Compression test of these cylinder specimens were performed on a WHY-200 Auto Compressive Resistant Tester (Hualong, Shanghai) at the curing ages of 1 d, 15 d and 30 d.

2.2.2. Leaching test

A 'semi-static' leaching test was conducted for both kaolins and metakaolins. 1 g of kaolin or metakaolin was mixed with NaOH solution at a constant solid/liquid ratio of 1:30 for 5 min in a polypropylene tube at 25 ± 2 °C. In the total 24 h of continuous leaching, the tube was vibrated for 2 min at each interval of 3 h to prevent the possible condenzation caused by sedimentation of particles. After centrifugation, 2.5 ml of clear solution was acidified with HCl solution (2 mol/L) to pH <1 and diluted to 25 ml. Concentrations of Si and Al in the diluted solution were then determined by using a Optima 2000DV ICP-OES instrument (Perkin-Elmer, USA).

2.2.3. Isothermal conduction calorimetry

Previous work has shown that isothermal calorimetry is a useful method to observe the geopolymerization process in real-time [4,25]. Reaction heat flow can be recorded by using a 3114/3236 TAM Air isothermal calorimeter (Thermometric AB, Sweden). In this study metakaolins were mixed with activator at a liquid/solid ratio of 0.8 g mL^{-1}. The higher liquid/solid ratio than that in preparation of compression specimen enables the paste more easily to be mixed. Mixing and data processing specification was described elsewhere [25].

2.2.4. X-ray diffraction (XRD)

Powder XRD was obtained by using an ARL X'TRA X-ray diffractometer (Thermo Scientific, Switzerland) with Cu Kα radiation (45 kV, 30 mA) at a scan rate of 10° min^{-1} from 5° to 80°(2θ). The powder of kaolins and metakaolins were characterized directly. Geopolymer samples were firstly broken into 2–3 mm, ground in acetone and then dried at 65 °C for 4 h before testing.

2.2.5. Scanning electron microscopy (SEM)

Morphology of kaolins, metakaolins and geopolymers were observed on a JSM-5900 SEM (JEOL, Tokyo, Japan) at an accelerating voltage of 15 kV.

2.2.6. Mercury intrusion porosity (MIP)

MIP is an appropriate method to compare the pore size distribution of geopolymers for comparative purposes. It was performed by using a Poremaster GT–60 (Quantachrome, USA). Before testing, a drying procedure for geopolymers was carefully carried out: specimens at a given age were firstly crushed into 3 mm pieces, stored in absolute ethanol at least for 24 h and finally dried at 65 °C for 4 h.

3. Results and discussion

3.1. Leaching property of kaolins and metakaolins

The leaching result of kaolins and metakaolins in 4, 6, 8, 10 and 12 mol L^{-1} NaOH solutions is summarized in Table 2. The concentration of Al and Si in the leached solutions increases with the NaOH concentration increasing. This is in agreement with the experimental observations from Xu and van Deventer [26]. It is clear that the dissolution rate of K1 is much higher than that of K2. There are two factors that may contribute to the higher solubility of M1: the higher specific surface area and the presence of halloysite. The specific surface area of K1 is 1.2 times over K2. If it is assumed the dissolution rate of kaolin is proportional to its specific surface area at the beginning of leaching, then K1 should dissolve around 1.2 times of Al and Si over K2. However, the absolute amount of Al dissolved out from K1 in the leaching period is 4 times of that dissolved out from K2, while Si from K1 is 3 times higher than that from K2. It implies that the presence of halloysite in K1 greatly improves the dissolution rate.

After thermal treatment, metakaolins show quite different dissolution behavior. The Al concentration in the leached solution of MK1 is similar to that of MK2, however, the Si concentration in the leached solution of MK1 is much higher. This is most likely because of the selective dissolution of Al from MK2 [27], which also found for K2. Comparing the concentration of Al and Si in leached solutions before and after thermal treatment of kaolin, the thermal treatment is an effective method to improve the dissolution of clay precursor, particularly for K2. Comparing the absolute amount of Si and Al leached out from metakaolins to that leached out from kaolins, it can be seen that K1 is already of high dissolution rate before thermal treatment.

The dissolution of aluminosilicate precursors at strong alkaline condition is the first step of geopolymerization. Therefore, the dissolution rate is a reflection of reactivity of the precursors, and is one of the most important factors affecting the followed formation of geopolymer gels [26]. Various thermal treatment procedures have been applied so as to obtain 'metakaolin' with improved reactivity. Previous work found that the treatment at 900 °C is an optimum temperature for the relatively pure kaolin [17], while a most recent study reports that treatment at 700 °C is optimum [28]. Thermodynamically, kaolinite can be transferred into metakaolinite from 527 °C [29]. An 'optimum' procedure should depend on the physical and mineralogical properties of the kaolins from different sources, including their particle size and mineral components. From the perspective of industrial application of geopolymers, the kaolin that is already of high reactivity or can be easily treated, either at a relatively lower temperature or with a shorter duration, is obviously a preferred raw material. With this point of view, K1 is more suitable for geopolymer synthesis, which will be further elucidated by the following results.

3.2. Heat evolution of geopolymerization

Fig. 2 plots the heat evolution of the two geopolymerization systems of MK1 and MK2 at 20 °C in the first 50 h. Heat evolution rate data are plotted separately from the beginning of mixing to 1 h (Fig. 2a left part) and up to 50 h (Fig. 2a right part) with two different scales, so that the two exothermic peaks are more distinguishable. The earlier exothermic peak shows the maximum rate for MK1 and MK2 is 22.5 mW g^{-1} and 19.5 mW g^{-1} respectively,

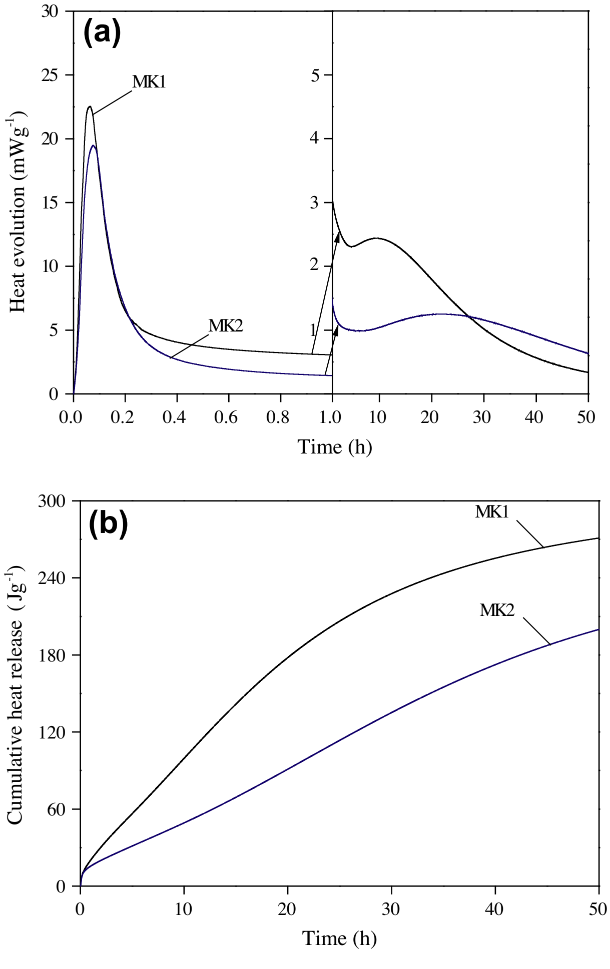

Fig. 2. Heat evolution rate (a) and cumulative heat release (b) of geopolymerization systems of MK1 and MK2 reacted with sodium silicate activator at 20 °C.

Table 2
Leaching of kaolins and metakaolins in NaOH solutions for 24 h, as determined by ICP-OES (mg L^{-1}).

NaOH (mol L^{-1})	K1		K2		MK1		MK2	
	Al	Si	Al	Si	Al	Si	Al	Si
4	178.3	126.6	45.4	37.2	270.6	280.4	253.3	117.5
6	283.6	193.7	60.9	41.5	359.3	334.2	308.5	204.1
8	342.5	239.0	73.0	48.2	400.7	384.6	338.0	233.2
10	364.2	272.0	84.8	53.9	401.1	391.9	390.8	263.7
12	404.6	295.4	96.8	61.2	467.6	463.0	395.1	287.0

which are consistent with the calorimetry results found by Granizo and Blanco [30] and Rahier et al. [31]. With reaction continuing, the heat evolution rate declines, until the later exothermic peak appears. The later exothermic peak shows the maximum rate of MK1 system is 2.5 mW g^{-1}, which is 1.3 mW g^{-1} higher than that of MK2 system. The later maximum rate appears after 10 h and 20 h of reaction respectively for MK1 and MK2, after which both of the two reaction systems go into a rate declining stage. From the declining trend shown in Fig. 2a, MK2 will take a longer time to complete its early geopolymerization. In the first 50 h, the heat release of geopolymerization system MK1 and MK2 is 270 J g^{-1} and 200 J g^{-1} respectively (Fig. 2b).

The early exothermic peak is due to the dissolution of metakaolin while the latter exothermic peak is due to the polymerization of dissolved Al and Si oligomers [25,32]. It is often difficult to attribute those overlapping peaks to each reaction, i.e. dissolution, polymerizations and probably together with rearrangement, because these reaction processes can take place in parallel; however the heat evolution rate can be reasonably used to compare the reactivity of precursors under a given activation condition. From Fig. 2 MK1 processes a faster dissolution and polymerization compared to MK2. This is consistent with the dissolution result, although the alkaline solution used is different. It strongly suggests that the presence of halloysite in K1 makes a great contribution to the higher reactivity of MK1.

3.3. Compressive strength development of geopolymers

Fig. 3 shows the compressive strength development of geopolymers under different curing conditions. After 1 day of 80 °C steam curing, the compressive strength of geopolymer from MK1 reached 73 MPa while it was 57 MPa for geopolymer from MK2. At room temperature, geopolymers from MK1 and MK2 achieved 56 MPa and 29 MPa after 1 day of curing. The faster strength development of geopolymer from MK1 is consistent with the higher dissolution rate and the faster heat release rate. With curing at 80 °C continuing to 15 d, the compressive strength declined, which is also found in previous work [4,33].

Curing temperature is an important factor determining both the reaction process and final properties of geopolymer [34,35]. At a low temperature curing condition the strength develops slowly, particularly for fly ash-based geopolymerization systems, which are therefore usually cured at high temperature around 60–90 °C [36–40]. As the division lines between 'high' and 'low' temperature are suggested to be 40–80 °C [35], in this study, 20 °C and 80 °C are selected as low and high temperature to examine the effect of the presence of halloysite in kaolin on the strength development of geopolymer at different curing conditions. Despite a higher initial compressive strength, geopolymer from MK1 exhibits a similar strength development trend to that of geopolymers from MK2. It means that the presence of halloysite in kaolin can improve the strength of geopolymers at an early age but it will not change the mechanism of strength gain or loss when geopolymers are under low or high temperature curing condition.

3.4. Microstructure of geopolymers

Geopolymers synthesized from MK1 and MK2 are both XRD amorphous (Fig. 4). The broad diffraction hump starting from 25° (2θ) and ending around 35° (2θ) in each pattern indicates the formation of geopolymeric gels that are also found in many other studies [19,20,22,32,35]. Under 80 °C steam curing conditions, diffractions between 15° (2θ) and 19° (2θ) are broader when compared with those cured at 20 °C. This may result from the formation of zeolite-like phases under the hydrothermal condition [35]. There is no conspicuous diffraction difference between geopolymers from MK1 and MK2 except for the higher characteristic diffraction of residual kaolinite in geopolymer from MK1. Comparing the XRD patens of geopolymers with those of metakaolins (Fig. 1), the higher kaolinite diffraction is most probably due to more kaolinite residual in MK1 when K1 was thermally treated. However, it is difficult to specify the reaction extent of metakaolin in geopolymers by XRD because of the difficulty in identifying the amorphous precursors from the highly amorphous geopolymerization product.

The SEM images of kaolins and metakaolins are shown in Fig. 5. Halloysite tubes with a diameter of ~150–350 nm and various length are present in K1 (Fig. 5a), while kaolinite K2 (Fig. 5b) is in a typical sheet shape [41]. After being thermally treated, MK1 and MK2 keep their original shape (Fig. 5c and d). The thermal treatment is in fact a dehydroxylation process, which can decrease the amount of hydrogen groups bonding between Al–O octahedron sheet and Si–O tetrahedron sheet and consequently makes OH$^-$ and Na$^+$ freer to move in the sheet interspace in early stage of geopolymerization [17]. It is notable in Table 2 that before thermal treatment, K1 is already able to dissolve a comparable amount of Al and Si to MK2. This interesting result is supposed related to the structural nature of halloysite, rather than the effect of minor difference in the average specific surface area of particles. Halloysite has a tubular structure given by the randomly displaced sequence

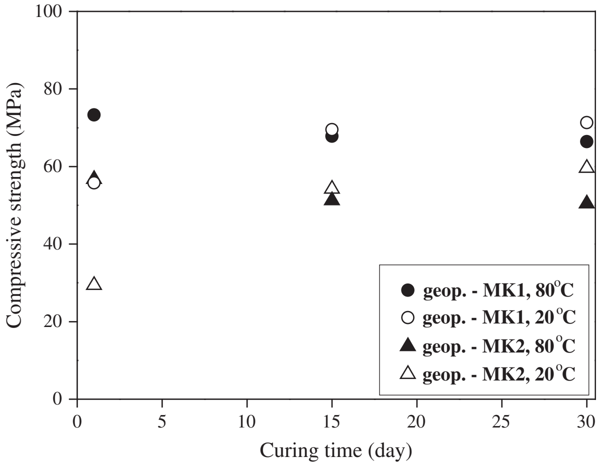

Fig. 3. Compressive strength of geopolymer samples (geop.) from MK1 and MK2 under 20 °C air curing and 80 °C steam curing conditions.

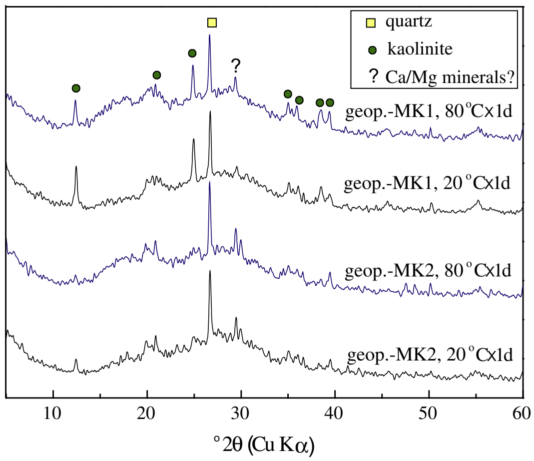

Fig. 4. XRD patterns of geopolymers from MK1 and MK2 by air curing at 20 °C and steam curing at 80 °C for 1 day.

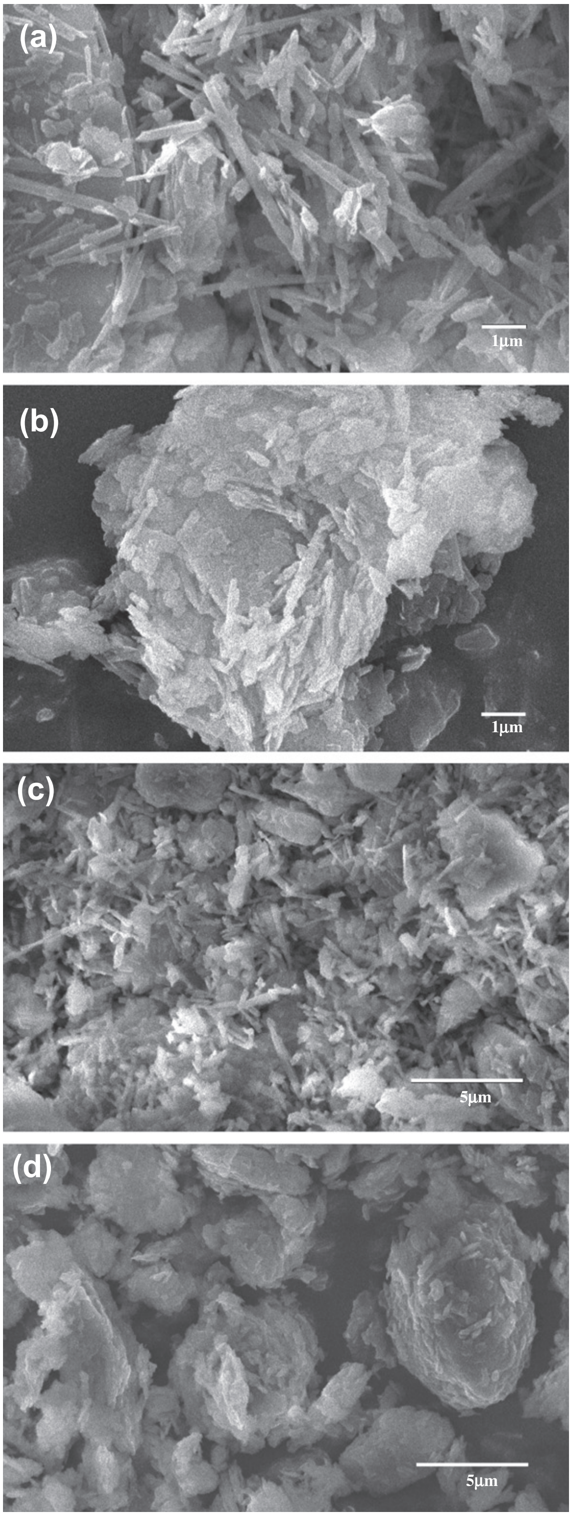

Fig. 5. SEM micrographs of source kaolin K1 (a) and K2 (b), and their 700 °C × 1 h thermally treated metakaolins MK1 (c) and MK2 (d).

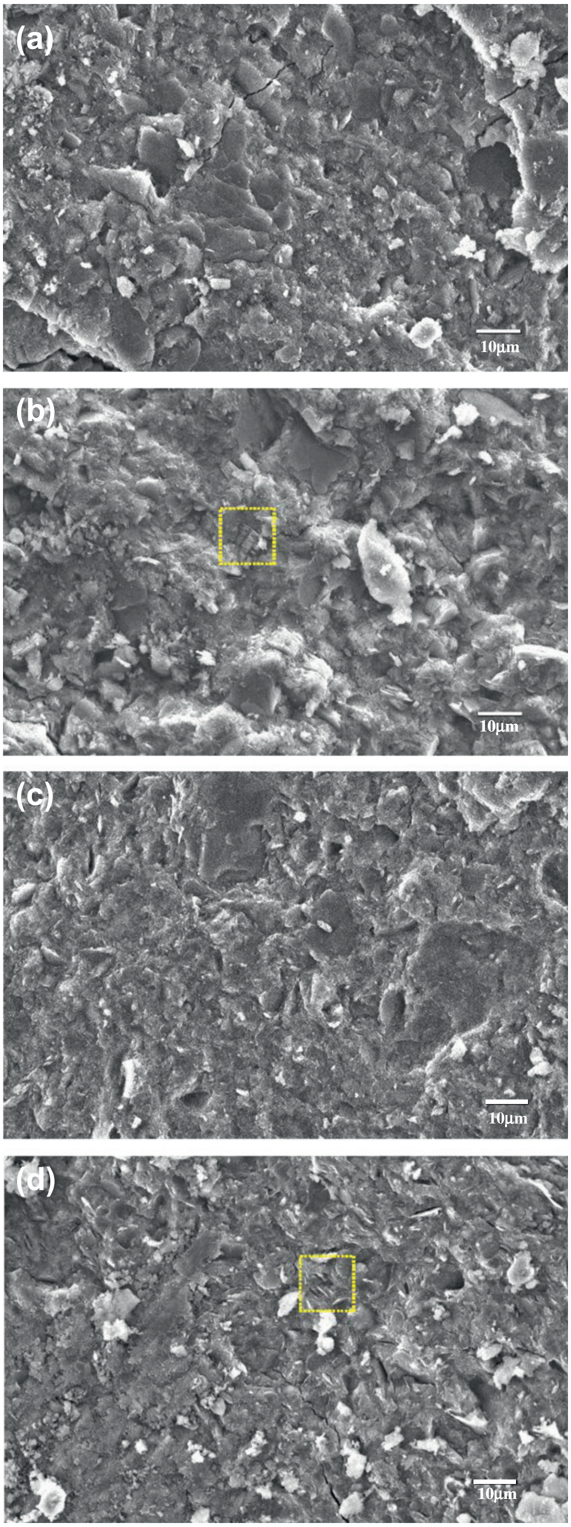

Fig. 6. SEM micrographs of geopolymers from MK1 by 20 °C air curing (a) and 80 °C steam curing (b), and from MK2 by 20 °C air curing (c) and 80 °C steam curing (d). The squares regions in (b) and (d) contain residual metakaolin particles.

of the individual two-sheet layers (Si–O tetrahedron and Al–O octahedron) along the b axis [42]. Such a disordered structure makes the deconstruction of the Si–O–Si and Al–O–Si fast, since the alkaline solution can easily attack the tube from both the inside and outside surface.

After being activated, geopolymers derived from MK1 and MK2 do not show a significant difference in micro-morphology (Fig. 6). Overall, the geopolymers either from MK1 or MK2 are composed of geopolymeric gels and residual metakaolin particles, and some pores as well. Visible residual precursor particles embedded in the matrix are more conspicuous in geopolymers obtained by high temperature curing, regardless whether from MK1 (Fig. 6b) or from MK2 (Fig. 6d). The fracture surface of geopolymers obtained at the low temperature curing condition appears slightly more flat.

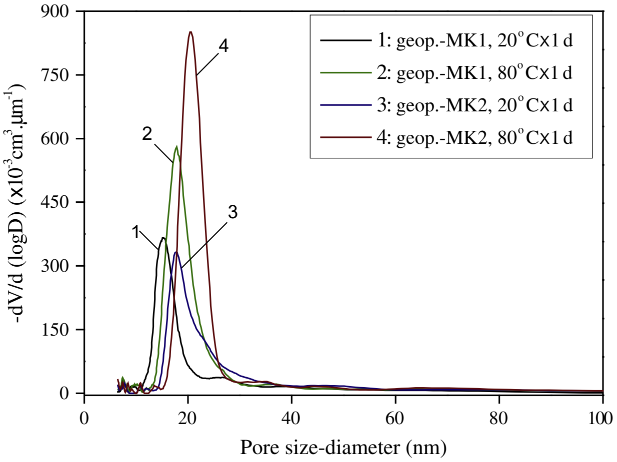

Fig. 7. Pore size distribution of geopolymers from MK1 and MK2 by air curing at 20 °C and steam curing at 80 °C for 1 day.

Fig. 7 presents the pore size distributions of geopolymers. Most pores are at the range of 10–30 nm. The geopolymers from MK1 at 20 °C and 80 °C have the most probable pores size of 15.2 nm and 17.8 nm respectively, and their corresponding intraparticle porosities are 10.6% and 15.7%. On the contrast, the geopolymers from MK2 at 20 °C and 80 °C have the most probable pores size of 17.7 nm and 20.5 nm while their corresponding porosities are 10.8% and 17.9%. It is clear that the presence of halloysite in K1 shifts the pore size distribution toward the low value, which means using MK1 can synthesize a geopolymer matrix with smaller microspores at both low and high temperature.

4. Summary

The halloysite present in kaolin as a second mineral component was found to have a positive effect on the metakaolin-based geopolymer synthesis. The dissolution rate of kaolin K1, which contains 31 wt.% halloysite, and its corresponding metakaolin MK1 was higher compared to that of a pure kaolin K2 and its metakaolin MK2. The absolute leached amount of Al and Si from K1 was comparable to that from MK2. In the case of using sodium silicate solution as activator, MK1 showed a faster geopolymerization rate compared to MK2. In addition, its consequent geopolymers also exhibited a faster compressive strength development at both low and high temperature curing conditions.

The mechanism of strength gain or loss under a low or high temperature curing condition has not been altered by the presence of halloysite in source kaolin. The microstructure property of geopolymer from MK1 was nearly the same as that of geopolymer from MK2. This investigation indicates that the halloysite-containing kaolin possesses very high geopolymerization reactivity. Using this kind of kaolin to synthesize geopolymer may reduce the environmental footprint, since less energy is required to thermally treat kaolin so as to obtain a reactive precursor.

Acknowledgements

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References

[1] Davidovits J. Geopolymers: inorganic polymeric new materials. J Therm Anal 1991;37(8):1633–56.
[2] Duxson P, Provis JL, Lukey GC, van Deventer JSJ. The role of inorganic polymer technology in the development of 'green concrete'. Miner Eng 2007;20:1261–77.
[3] Davidovits J, Sawyer JL. Early high strength mineral polymer. US Patent 4509958; 1985.
[4] Zhang Z, Yao X, Zhu H, Chen Y. Role of water in the synthesis of calcined kaolin based-geopolymer. Appl Clay Sci 2009;43:218–23.
[5] Verdolotti L, Iannace S, Lavorgna M, Lamanna R. Geopolymerization reaction to consolidate incoherent pozzolantic soil. J Mater Sci 2008;43:865–73.
[6] Bondar D, Lynsdale CJ, Milestone NB, Hassani N, Ramezanianpour AA. Effect of type, form, and dosage of activators on strength of alkali-activated natural pozzolans. Cem Concr Compos 2011;33(2):251–60.
[7] Chindaprasirt P, Rattanasak U, Jaturapitakkul C. Utilization of fly ash blends from pulverized coal and fluidized bed combustions in geopolymeric materials. Cem Concr Compos 2011;33(1):55–60.
[8] Zuda L, Drchalová J, Rovnaník P, Bayer P, Keršner Z, Černý R. Alkali-activated aluminosilicate composite with heat-resistant lightweight aggregates exposed to high temperatures: mechanical and water transport properties. Cem Concr Compos 2010;32:157–63.
[9] Duxson P, Lukey GC, Separovic F, van Deventer JSJ. Effect of alkali cations on aluminum incorporation in geopolymeric gels. Ind Eng Chem Res 2005;44:832–9.
[10] Duxson P, Provis JL, Lukey GC, Mallicoat SW, Kriven WM, van Deventer JSJ. Understanding the relationship between geopolymer composition, microstructure and mechanical properties. Colloids Surf A 2005;269:47–58.
[11] Zhang Z, Yao X, Zhu H. Potential application of geopolymers as protection coatings for marine concrete I. Basic properties. Appl Clay Sci 2010;49:1–6.
[12] Subaer, van Riessen A. Thermo-mechanical and microstructural characterization of sodium-poly(sialate-siloxo) (Na-PSS) geopolymers. J Mater Sci 2007;42:3117–23.
[13] Hu S, Wang H, Zhang G, Ding Q. Bonding and abrasion resistance of geopolymeric repair material made with steel slag. Cem Concr Compos 2008;30:239–44.
[14] Brantley SL. In: Brantley SL, Kubicki JD, White AF, editors. Kinetics of mineral dissolution, in kinetics of water-rock interaction. New York: Springer [chapter 5]. p. 151–210; 2008.
[15] Konta J. Clay and man: clay raw materials in the service of man. Appl Clay Sci 1995;10:275–335.
[16] Giese RF. Interlayer bonding in kaolinite, dickite and nacrite. Clay Clay Miner 1973;21:145–9.
[17] Zhang Z, Yao X, Zhu H. Activating process of geopolymer source material: kaolinite. J Wuhan Univ Technol-Mater Sci 2009;24(1):132–6.
[18] Shvarzman A, Kovler K, Grader GS, Shter GE. The effect of dehydroxylation/amorphization degree on pozzolanic activity of kaolinite. Cem Concr Res 2003;33:405–16.
[19] Zibouche F, Kerdjoudj H, de Lacaillerie J-B d'Espinose, van Damme H. Geopolymers from Algerian metakaolin. Influence of secondary minerals. Appl Clay Sci 2009;43:453–8.
[20] MacKenzie KJD, Brew DRM, Fletcher RA, Vagana R. Formation of aluminosilicate geopolymers from 1:1 layer-lattice minerals pre-treated by various methods: a comparative study. J Mater Sci 2007;42:4667–74.
[21] MacKenzie KJD, O'Leary B. Inorganic polymers (geopolymers) containing acid-base indicators as possible colour-change humidity indicators. Mater Lett 2009;63:230–2.
[22] Tailby J, MacKenzie KJD. Structure and mechanical properties of aluminosilicate geopolymer composites with Portland cement and its constituent minerals. Cem Concr Res 2010;40:787–94.
[23] Wilson IR. Kaolin and halloysite deposits of China. Clay Miner 2004;39:1–15.
[24] Lin Z. Determination of the mineral compositions of kaolin deposit of Longyan Donggong of Fujian Province. Report of the mineral composition and process properties of kaolin deposit of Longyan Donggong of Fujian Provinc, Geoscience research institute of Fujian Province; 1987. p. 9–13 [in Chinese].
[25] Yao X, Zhang Z, Zhu H, Chen Y. Geopolymerization process of alkali–metakaolinite characterized by isothermal calorimetry. Thermochimica Acta 2009;493:49–54.
[26] Xu H, van Deventer JSJ. The geopolymerisation of alumino-silicate minerals. Int J Miner Process 2000;59(3):247–66.
[27] Torres Sánchez RM, Pérez De Vargas SL, Soto E, Basaldella EI. Influence of kaolinite crystalline structure in the production of Al_2O_3 by alkaline lixiviation. Mater Lett 2003;57:1167–70.
[28] Elimbi A, Tchakoute HK, Njopwouo D. Effects of calcination temperature of kaolinite clays on the properties of geopolymer cements. Constr Build Mater 2011;25:2805–12.
[29] Матвеев ГМ, Мчедлов–Петросян. Thermodynamics of silicates (1972). Transformed in Chinese by Pu X and Chen J, China Construction Industry Book Con; 1983. p. 322–3.
[30] Granizo ML, Blanco MT. Alkaline activation of metakaolin – An isothermal conduction calorimetry study. J Therm Anal 1998;52:957–65.
[31] Rahier H, van Mele B, Wastiels J. Low-temperature synthesized aluminosilicate glasses. 2. Rheological transformations during low-temperature cure and high-temperature properties of a model compound. J Mater Sci 1996;31(1):80–5.
[32] Provis JL, Duxson P, van Deventer JSJ, Lukey GC. The role of mathematical modelling and gel chemistry in advancing geopolymer technology. Chem Eng Res Des 2005;83(A7):853–60.
[33] van Jaarsveld JGS, van Deventer JSJ, Lukey GC. The effect of composition and temperature on the properties of fly ash- and kaolinite-based geopolymers. Chem Eng J 2002;89:63–73.
[34] Muñiz-Villarreal MS, Manzano-Ramírez A, Sampieri-Bulbarela S, Gasca-Tirado JR, Reyes-Araiza JL, Rubio-Ávalos JC, et al. The effect of temperature on the

geopolymerization process of a metakaolin-based geopolymer. Mater Lett 2011;65:995–8.

[35] Provis JL, Lukey GC, van Deventer JSJ. Do geopolymers actually contain nanocrystalline zeolites? A reexamination of existing results. Chem Mater 2005;17(12):3075–85.

[36] Puertas F, Martínez-Ramírez S, Alonso A, Vasquez T. Alkali-activated fly ash/slag cements: strength behaviour and hydration products. Cem Concr Res 2000;30(10):1625–32.

[37] Palomo A, Grutzek MW, Blanco MT. Alkali-activated fly ashes: a cement for the future. Cem Concr Res 1999;29(8):1323–9.

[38] Brough AR, Katz A, Sun G-K, Struble LJ, Kirkpatrick RJ, Young JF. Adiabatically cured, alkali-activated cement-based waste forms containing high levels of fly ash: formation of zeolites and Al-substituted C–S–H. Cem Concr Res 2001;31(10):1437–47.

[39] Steveson M, Sagoe-Crentsil K. Relationships between composition, structure and strength of inorganic polymers. Part 2. Fly ash-derived inorganic polymers. J Mater Sci 2005;40(16):4247–59.

[40] Škvára F, Jílek T, Kopecký L. Geopolymer materials based on fly ash. Ceram Silikaty 2005;49(3):195–204.

[41] Aparicio P, Galán E, Valdrè G, Moro D. Effect of pressure on kaolinite nanomorphology under wet and dry conditions. Correlation with other kaolinite properties. Appl Clay Sci 2009;46:202–8.

[42] Brindley George W. Structural mineralogy of clays. Clays Clay Miner 1952;1:33–43. doi:10.1346/CCMN.1952.0010105.