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Synthesis, characterization and relevant mechanisms of one-part geopolymeric cement by calcining low-quality illite clay with alkali

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ABSTRACT

Precursors synthesized through thermal activation of low-quality illite clay with alkali (NaOH or Na_2CO_3) were hydrated by only adding water to synthesize one-part geopolymer pastes, and the strength and the microstructures of relevant specimens were characterized. An acceptable compressive strength was obtained when the hydrated specimens were cured at 80 °C for 3 d. Thermal decomposition of the clay is distinctly altered by adding alkali, and the octahedral-coordinated Al turns into tetrahedral Al after calcination according to IR analysis. Besides illite, most of the quartz in the clay is converted to X-ray amorphous geopolymer precursors. The nepheline formed during calcination disappears at elevated temperature 950 °C. It is found that the compressive strength of one-part geopolymers is positively related to the content of nepheline in the clinkers. Partial dissolution of clinker particles in water facilitates cementing property. No crystal hydrate is found during hydration so the cementing mechanism is proposed to be X-ray amorphous zeolite-like gel as what in two-part geopolymers.

KEYWORDS

Low-quality illite clay;
One-part geopolymer;
Cement;
Calcination.

INTRODUCTION

Portland cement (PC) contributes substantial carbon dioxide emissions as well as causes other environmental problems[1,2]. Geopolymer is framework structures generally synthesized from a two-part mixture consisting of solid aluminosilicate raw materials. This synthesis occurs by using a thermally activated dehydroxylation and alkali silicate solution[3-5]. Geopolymeric cement (GC) is considered more environmentally friendly[6] because of its low energy consumption, good mechanical properties and low pollution emissions. However, the two-part GC which contains alkaline solutions and aluminosilicate sources has several limitations. Caustic and sticky alkali could complicate the preparation and the application of geopolymer[7] and make it relatively costly. Kaolin is almost the only practical, natural raw material used for geopolymerisation. Therefore, raw material choices are still limited. A new processing method of synthesizing one-part (simple water addition) GC similar to PC is introduced. In 2008, Duxson and Provis recommended the preparation of an ideal geopolymer glass precursor to synthesize one-part GC though the detailed method was not given[8]. Geothermal silica and sodium aluminate were combined with water to form a solid binder[9]. Kolousek et al. proposed a new method for synthesizing geopolymer and the method involved a reactive precursor and calcining low-quality kaolin with sodium and potassium hydroxide at 550 °C. However, the compressive strength was considerably low[10]. Solid-state synthesis through thermal reaction of halloysite with LiOH followed by hydration of the product resulted in fragile and crumbly products[11]. Kaolin was calcined with K_2CO_3 to form $KSiAlO_4$ products as the starting materials for the synthesis of zeolites[12]. Feng et al. synthesized one-part geopolymers through thermal activation of albite with alkali at 1000 °C, and the compressive strength of the geopolymeric sample reached 30 MPa after curing for 7 d[13]. However, the alkali content was much higher than that of typical GC.

High-quality kaolin with more than 35% alumina is a limited resource. Nevertheless, it is used as a raw material of GC. On the other hand, the common aluminosilicate clays are abundant and low cost with high Si/Al mole ratio compatible with GC in terms of its chemical composition with a Si/Al mole ratio of 2 to 6[14]. They usually contain a lot of quartz besides clay minerals. Thermal activation of quartz with alkali will result in sodium silicate which is beneficial to geopolymerisation. Through the controlled alkali-thermal process of aluminosilicates, the practical product will contain amorphous alkaline aluminosilicate, which is active for geopolymerisation. Thus, the common low-quality clay with high Si/Al ratio can be a potential raw material for one-part geopolymerization[15].

Low-quality illite clay is low cost, available worldwide. The current study focuses on the suitability of low-quality illite clay to form one-part GC through thermal activation with alkali (NaOH or Na_2CO_3). X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectral (FTIR) analysis, thermogravimetry (TG) and differential scanning calorimetry (DSC) are applied to characterize the clay, the clinkers, and the one-part geopolymers and discuss the mechanisms involved in calcination and hydration.

EXPERIMENTAL SECTION

Materials

Low-quality illite clay acquired from the redbed in Xiangtan China was ground to obtain 90% of particles that measure <75 μm. According to full silicate analysis, the chemical composition of the clay was 82.48% SiO_2, 9.72% Al_2O_3, 1.03% K_2O, 4.01% Fe_2O_3, 0.87% Na_2O, and 0.54% CaO (on a mass basis). Sodium carbonate Na_2CO_3 and sodium hydroxide NaOH were of analytical reagent grade and supplied by Guangfu Company in Shanghai.

Thermal treatment

The illite clay powder, which was ground to obtain 95% of particles that measure <75 μm, was mixed with NaOH or Na_2CO_3 with respect to the mass of the clay. The mixtures were heated in a laboratory muffle furnace to the predetermined temperature (650 °C to 950 °C) which increased at an increment of 10 °C/min, then kept at a fixed temperature for 3 h before being cooled to room temperature. The ground clinkers were sealed against atmospheric carbonation and hydration prior to analysis and synthesis.

Geopolymerization and curing

The alkali-thermal clinker powders were directly mixed with water at a water/solid ratio of 0.3 and stirred for 3 min in a cement paste mixer. The pastes were placed in 40×40×40 mm^3 molds, sealed with a plastic bag, and cured at 80 °C for 3 d and at 20 °C for 25 d in air with >90% humidity. The specimens were subjected to compressive strength for 3, 4, 7, and 28 d. The 4 d compressive strength was obtained from the pastes soaked in water at 20 °C for 1 d after curing at 80 °C for 3 d to determine the softening coefficient.

Softening coefficient=4 d compressive strength/3 d compressive strength **(1)**

Sample characterization

The illite clay, calcined clinkers (precursors), and cured geopolymer samples were analyzed by using FTIR. The spectra were recorded from 4000 cm^{-1} to 500 cm^{-1} by using a PE2000 FTIR Spectrum Spectrometer, and the specimens were prepared by using the KBr pellet technique. Powder XRD was conducted on a Bruker D8-Advance diffractometer from Germany with CuKα radiation at 35 kV and at 40 mA. Each sample was scanned with 2θ between 3° to 70°, a step increment of 0.01°, and a scanning rate of 8 °/min. SEM was conducted by using JSM-6380LV from JEOL Japan to characterize the microstructures of the clay, the clinkers, and the hydrates. Energy disperse spectroscopy (EDS) was adopted to analyze the chemical composition of the microdomain by using EDX-Genesis 60s from EDAX in USA. TG/DSC was conducted at 10 °C/min from 30 °C to 1300 °C in air by using a Mettler Toledo TGA/DSC1/1600HT. Compressive strength values were determined by using a NYL-600 pressure testing machine from WuXi.

RESULTS AND DISCUSSION

Compressive strength and softening coefficient

TABLE 1 lists the compressive strength of the hydrated pastes from the thermally activated illite clay with alkali at different temperatures and cured at 80 °C for 3 d following standard curing before tests. Though no paste curing at room temperature gains strength, all the pastes curing at 80 °C successfully harden except those hydrated from the clinkers with 25% NaOH at 950 °C (19% Na_2O). The 3/28 d compressive strength of 32.1/26 MPa indicates that the low-quality illite clay is fit for synthesizing one-part geopolymers.

The one-part geopolymer pastes from the illite clay with 20% NaOH (16% Na_2O) calcined at 750 °C exhibits the highest 3 d to 28 d compressive strength among the pastes from the precursors calcined with 15% to 25% NaOH at 650 °C to 950 °C. Among NaOH content of 15%, 20%, and 25%, 20% NaOH was most suitable for obtaining the highest compressive strength of the hydrates, and the optimal calcination temperature is 750 °C among 650, 750, 850, and 950 °C when NaOH is added as alkali activator.

Generally speaking, Na_2CO_3 as an alkali activator has the same effect on the illite clay as NaOH with an equal amount of Na_2O content. However, Na_2CO_3 can better activate the clay with a wider calcination temperature range and higher alkali content (19% Na_2O) than NaOH, as is shown by the compressive strength. NaOH can thermally activate the clay effectively only at 750 °C, and the lower and higher calcination temperatures cannot effectively lead to sufficient compressive strength. Moreover, Na_2CO_3 can effectively activate the clay with calcination temperature from 650 °C to 950 °C and results in the one-part geopolymers with sufficient strength (to see TABLE 1). The optimal calcination temperature of 850 °C among 650, 750, 850 and 950 °C results in the largest compressive strength at varied curing times.

The softening coefficients of the pastes ranged from 0.56 to 2.19. The compressive strength <10 MPa is too low to be precisely tested by using a pressure test machine, so the softening coefficients calculated under this condition produce excessive errors. The acceptable softening coefficients are between 0.80 and 1.04, with an average value of 0.94 when the questionable data are rejected. Thus, the one-part geopolymer pastes are quite water-resistant.

TABLE 1 : Compressive strength values and softening coefficients for one-part geopolymers

Calcination Temperature (°C)	Activating alkali	Mole ratio of Na_2O/Al_2O_3	Compressive strength (MPa)				Softening coefficient
			3d	4d	7d	28d	
950	25% NaOH	3.25	0	0	0	-	-
850	20% NaOH	2.60	0.7	0.7	0	-	1
750	15% NaOH	1.95	8.4	5.7	5	7.5	0.68
750	20% NaOH	2.60	32.1	25.7	24.1	26	0.8
750	25% NaOH	3.25	2.6	5.7	7.6	-	2.19
650	20% NaOH	2.60	3.7	1.8	3.3	-	0.56
950	33% Na_2CO_3	3.25	4.1	3.5	2.7	-	0.85
850	33% Na_2CO_3	3.25	15.3	15.9	27.5	-	1.04
750	25% Na_2CO_3	2.60	14.2	13.7	10.9	-	0.96
650	25% Na_2CO_3	2.60	10.8	10.2	9.2	-	0.94

Thermal analysis

Figure 1 shows the TG curves for the low-quality illite clay and the finely ground clay mixed with 20%

sodium hydroxide or 33% sodium carbonate. The first evident weight loss of approximately 1.74% for the illite clay below 100 °C is related to the adsorbed water, whereas the second evident weight loss of approximately 1.91% is observed after 420 °C and is most intense at approximately 475 °C for the hydroxy water loss in illite[16]. The DSC found an endothermic valley in the same temperature region (Figure 2). The DSC valley at 573 °C, which appears in all three samples, is due to the reversible α-β quartz transition and indicates high quartz content in the illite clay in line with 82.48% mass of SiO_2.

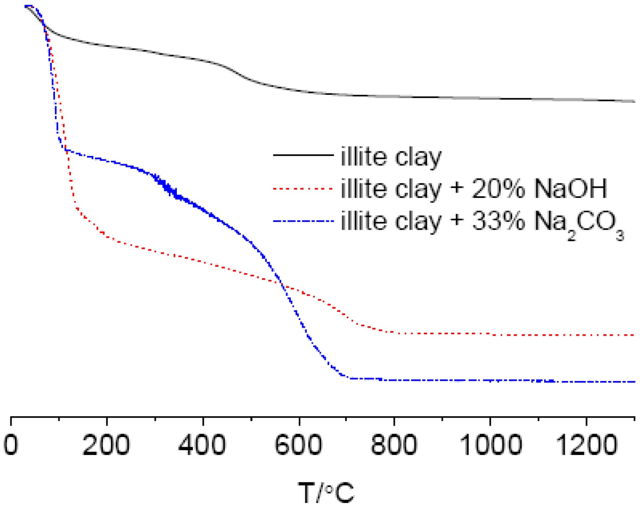

Figure 1 : TG curves of illite clay, illite clay + 20 wt% NaOH, and illite clay + 33 wt% Na_2CO_3.

The illite clay with 20% NaOH exhibits two defined weight losses before 800 °C (Figure 1). The largest weight loss (9.35%) was obtained at 92 °C with a sharp endotherm in the heat flow (Figure 2) caused by the evaporation of the strongest adsorbed water associated with NaOH among the three samples. Approximately 4.68% weight loss occurred in the range of 200 °C and 800 °C that attributes to the deprivation of structural water of NaOH and the illite clay. This condition does not exhibit an obvious endothermic valley probably, for it occurs within a wide temperature range (Figure 2). A broad endothermic valley between 800 °C and 1120 °C, with the most violent point at 1085 °C, is ascribed to the gradual formation of sodium aluminosilicate glassy phases. Unlike raw illite clay, the clay with 20% NaOH does not exhibit violent dehydration at around 475 °C. Therefore, alkali considerably alters the thermal decomposition of the illite clay and reduces the vitrifying temperature of the clay. The distinct endotherm at around 1185 °C probably attributes to abrupt melting of the clay.

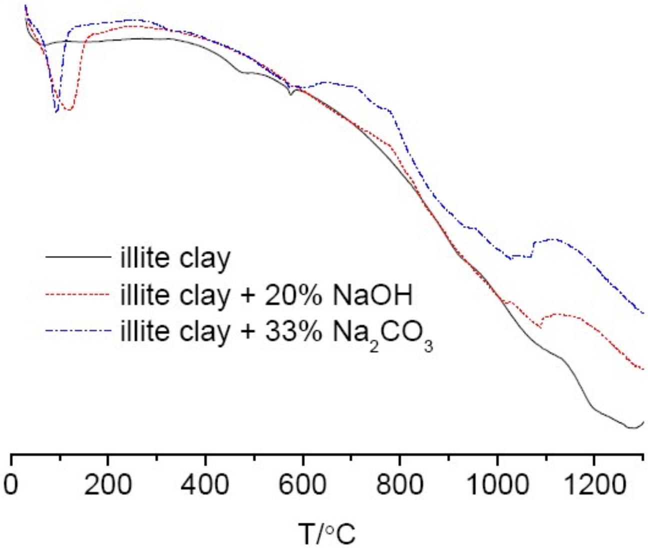

Figure 2 : DSC curves of illite clay, illite clay + 20 wt% NaOH, and illite clay +33 wt% Na_2CO_3.

The TG and DSC features of the illite clay with 33% Na_2CO_3 are similar to that with 20% NaOH. Approximately 6.63% weight loss of absorbed water was found at around 116 °C for the clay with 33% Na_2CO_3, which is much less than that of the sample with 20% NaOH at around 92 °C (Figure 1). Approximately 9.38% mass loss between 200 °C and 800 °C is resulted from the loss of structural water of illite mineral and the release of CO_2 accompanied by the decomposition of sodium carbonate. Two low endothermic valleys at 600 °C and 745 °C were observed (Figure 2). The valley at 600 °C might be related to the loss of structural water for the system with alkali, and Na_2CO_3 might decompose at 745 °C. Above 800 °C, no further notable weight loss occurred (Figure 1), and the DSC found a more evident endothermic valley at around 1027 °C than when 20% NaOH was added. This phenomenon may be attributed to the melting of the clay. Thus, Na_2CO_3 as alkali is apparently somewhat more effective than NaOH in activating illite clay.

FTIR analysis

The FTIR spectra in Figure 3 depict the characteristic peaks of the illite clay at 3701 cm^{-1} and 3624 cm^{-1} which correspond to the OH^- stretching vibration. The valley at 1033 cm^{-1} is attributed to the Si-O bonds in the SiO_4 molecules and the valley at 913 cm^{-1} corresponds to the exterior OH vibrations. The bands at 793 cm^{-1} and 688 cm^{-1} are due to Si-O symmetric stretching. Absorption at 535 cm^{-1} is related to Si-O-Al^{VI}, where the Al is in octahedral coordination[17]. A weak valley found near 1640 cm^{-1} in all formulae is caused by the bending vibrations of water. Except for the raw clay, both formulae of the calcined clay and the corresponding hydrate did not exhibit a Si-O-Al^{VI} valley at 535 cm^{-1}, which indicates that the octahedral-coordinated Al in illite turns into tetrahedral-coordinated Al[17] after being thermally disposed at 750 °C with 20% NaOH. All valleys related to structural water, such as 910, 3624, and 3701 cm^{-1}, were not found in the curves of both the thermally disposed clay and the relevant hydrate. The valley related to adsorbed water, which is weakly bound with aluminosilicates near 1640 cm^{-1}, appeared very weak for the thermally disposed alkali sample (Figure 3[b]) but stronger for its hydrate (Figure 3[c]). The one-part geopolymer (the hydrate) (Figure 3[c]) exhibited a sharp valley at around 1458 cm^{-1} which is attributed to the influence of the CO$_3^{2-}$ ions by the subsequent curing[18].

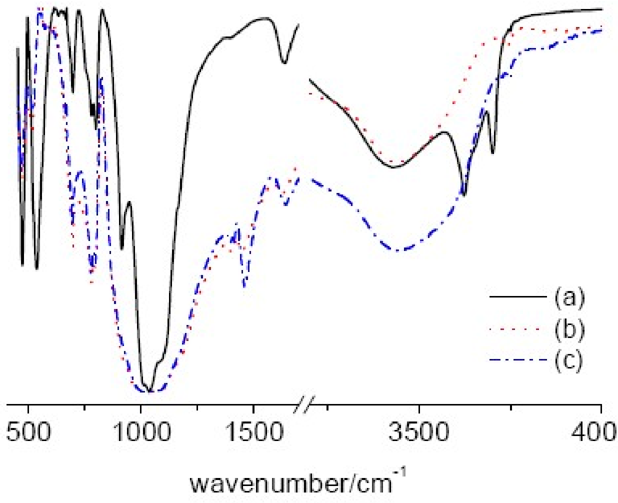

Figure 3 : FTIR spectra for illite clay (a), illite clay calcined at 750 °C with 20% NaOH (b), and the corresponding hydrate (c).

XRD analysis

Figure 4 presents the XRD patterns of the low-quality illite clay, the clay with 20% NaOH calcined at 750 °C, and its hydrate. The minerals in the low-quality illite clay include quartz, illite and hematite. Compared with the raw clay, the clay calcined at 750°C with NaOH shows no illite and hematite but has a new mineral, nepheline (NaAlSiO$_4$). The hydrates of the clinkers exhibit XRD characteristics similar to those of the clinkers although the hydrates are different from the clinkers and have solidified. This phenomenon indicates that the hydration reaction produces XRD-amorphous phases, which strengthen the one-part geopolymers similar to those two-part geopolymers with XRD-amorphous zeolite-like sodium aluminosilicates.

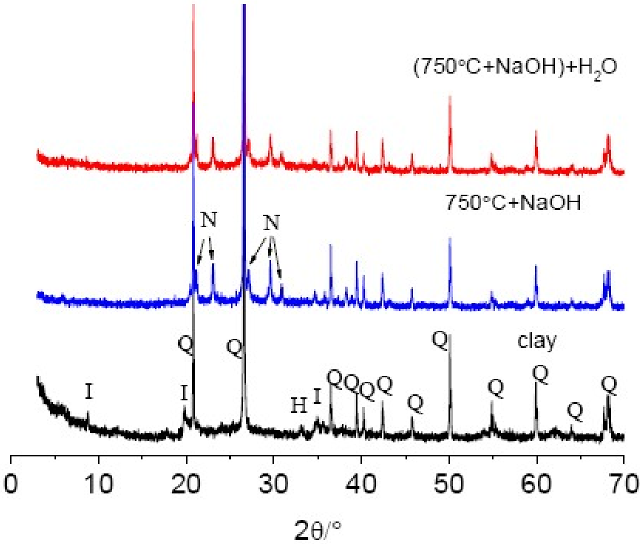

Figure 4 : XRD patterns for illite clay at different conditions including raw clay, calcined clay with NaOH at 750 °C, and the corresponding hydrate. Peaks marked with letters are Q-quartz (PDF#89-1961), I-illite (PDF#26-0911), H-hematite (PDF#33-0664), and N-nepheline(PDF#35-0424).

The phase characteristics of the thermally activated illite clay with alkali vary with the calcining temperature. The XRD patterns of the calcined clinkers, which are thermally activated with NaOH at different temperatures, are shown in Figure 5. Illite and hematite disappear, but nepheline appears in the calcined clay at 650 °C. Nepheline content increases when calcined at 750 °C. However, all the other minerals almost disappear, and the clinkers attain a glassy phase when the calcination temperature increases to 950 °C. A small amount of quartz remains, as is indicated by the strongest XRD peak of quartz (Figure 5).

SEM and EDS analysis

Figure 6 presents the morphologies of the raw illite clay, the calcined clay thermally treated with alkali (precursors of geopolymers), and the hydrates under SEM.

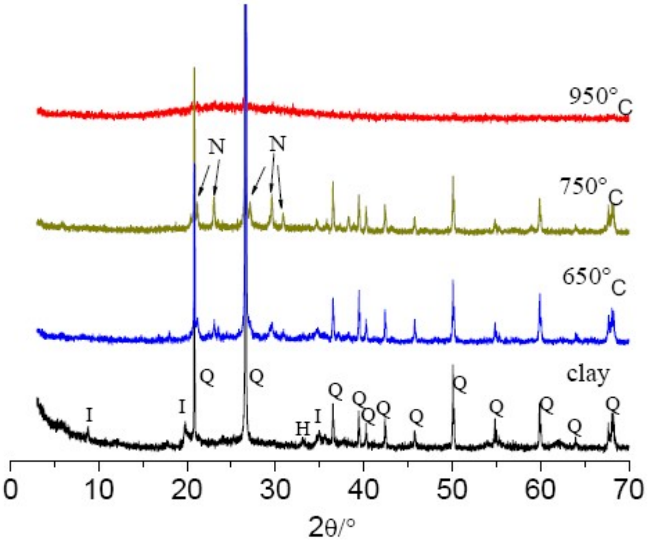

Figure 5 : XRD patterns for the illite clay calcined with NaOH at different temperatures compared with the clay.

The positions of the microdomain for EDS analysis are also marked in Figure 6, and the chemical compositions of the microdomain are shown in TABLE 2. The raw illite clay is mainly composed of dozens of micron-sized grainy quartz (Figure 6[1]) and several micron-sized flaky illite (Figure 6[2]). The clay with 20% NaOH calcined at 750 °C shows a type of glass with numerous air holes (Figure 6[3]). The geopolymers hydrated from the clinker powders exhibit cementing characteristics, and the particles agglomerate with each other in smooth edge-dissolved morphologies that attribute to partial dissolution of the precursor powders at the edges in water (Figure 6[4]). This type of geopolymer pastes is characterized by high compressive strength. By contrast, the clay calcined at 950 °C with NaOH appears as a kind of compact glass without air holes (Figure 6[5]). In its hydrates, the multiangular particles aggregate loosely and hardly react with water (Figure 6[6]), and the pastes are weak in compressive strength (to see TABLE 1). Thus, the morphologies of the clinkers and the hydrates are consistent with the strength of the one-part geopolymers. SEM depicts no new mineral crystal morphology, including nepheline, in the clinkers. Therefore, nepheline is inferred to be poorly crystallized, very small, difficult to be visualized, and present at low amounts.

The chemical analysis of the microdomains (by using EDS in TABLE 2) shows that all the illite clay calcined with NaOH and the corresponding hydrates possess a chemical composition similar to those of geopolymers with superfluous alkali (Na or K). However, compared with the raw clay, the contents of SiO_2 for the microdomains are evidently low except for the hydrates in Figure 6[6]. This phenomenon agrees with the fact that quite a lot of quartz in the clay remains so the actual contents of SiO_2 for the microdomains in the clinkers and the hydrates were low than the average composition. The microdomain with high content of SiO_2 might consist of quartz.

Calcination and geopolymerization mechanism for one-part geopolymers

The calcination temperature considerably influences the strength of the one-part geopolymers, and the largest compressive strength is obtained when the clay is thermally activated with NaOH at 750 °C. At the same time the clinkers show the highest contents of nepheline and air holes with quite high content of quartz, whereas the clinkers calcined at either 650 °C or 950 °C have less or no nepheline and result in hydrates with less or no compressive strength, respectively. Hence, the mineral phases of the clinkers considerably influence geopolymerization, and the content of nepheline appears to be positively related to the compressive strength of the hydrates, although nepheline is not only inert in

TABLE : 2 Element atom content of the microdomains determined by using EDS

Graph number in Figure 6 for the microdomain	Average chemical composition of the clinker	Na	K	Al	Si	Approximate ratio of (Na+K):Al:Si
3	(Na2O)2.6(K2O)0.1Al2O3 (SiO2)13.7	11.68	0.50	6.57	16.11	2:1:3
4	(Na2O)2.6(K2O)0.1Al2O3 (SiO2)13.7	13.06	0	3.28	14.12	4:1:4
5	(Na2O)3.3(K2O)0.1Al2O3(SiO2)13.7	10.87	0.77	3.48	17.36	3:1:4
6	(Na2O)3.3(K2O)0.1Al2O3(SiO2)13.7	8.28	0.61	1.58	22.81	6:1:15

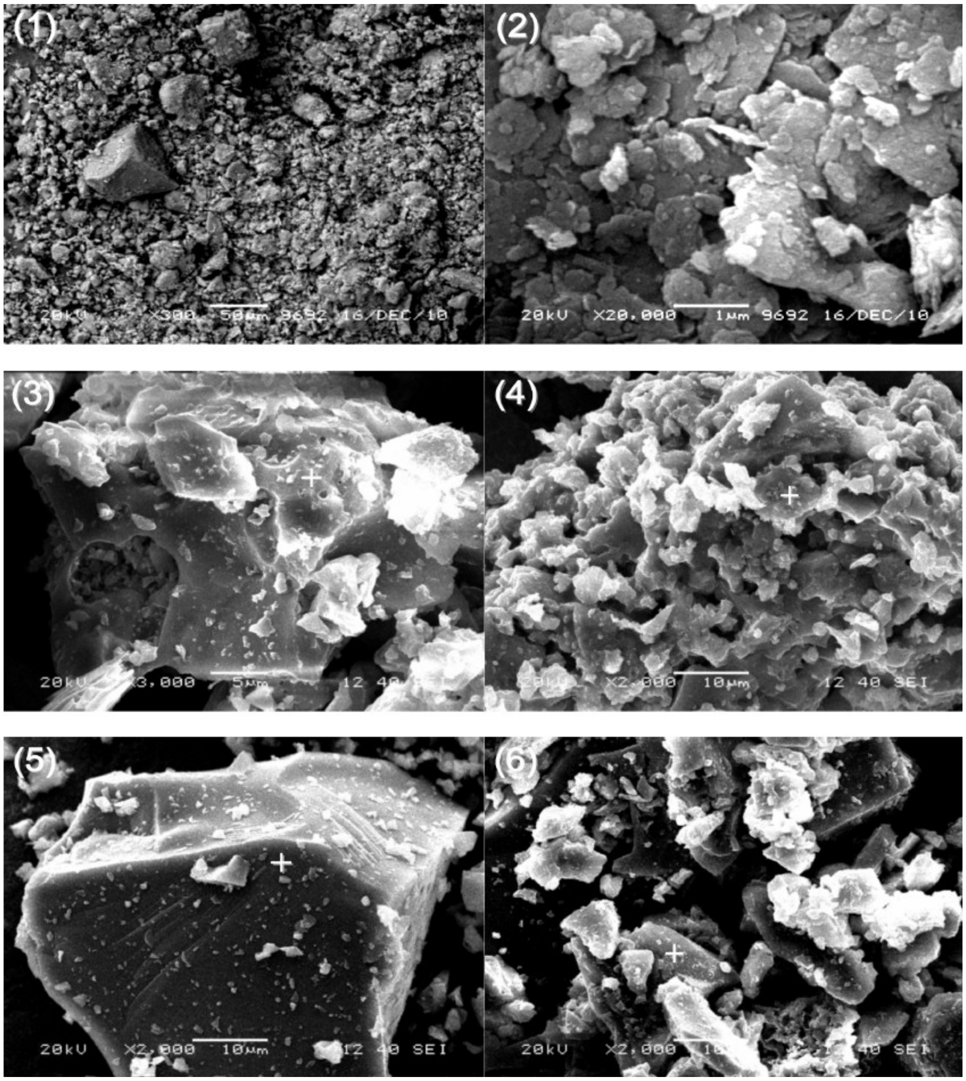

Figure 6 : SEM images of the illite clay, its clinkers thermally treated with alkali, and the corresponding one-part geopolymers. (1) the illite clay; (2) illite in the clay; (3) the clay calcined at 750 °C with 20% NaOH and (4) the corresponding hydrate; (5) the clay calcined at 950 °C with 25% NaOH and (6) the corresponding hydrate. The white cross indicates the position of EDS.

geopolymerization but also consumes active Al for geopolymerization.

The presence of appropriate crystal phases indicates the binding activities of the clinkers. The calcined clay with NaOH results in weaker hydrates than those with Na_2CO_3. The former clinkers are almost in a glassy state, and the latter contain a certain amount of quartz, as shown by the XRD patterns in Figure 7. So too high calcination temperature results in glassy clinkers and does harm to cementing activity of the clinkers.

When the illite in the present clay is presented as $K_2O{\cdot}mAl_2O_3{\cdot}nSiO_2{\cdot}pH_2O$, the calcination reactions with NaOH are given as reactions (2) and (3).

$$K_2O\cdot mAl_2O_3\cdot nSiO_2\cdot pH_2O+SiO_2+NaOH\rightarrow$$

$$(Na,K)_2O\cdot mAl_2O_3\cdot qSiO_2(glass)+H_2O \qquad \textbf{(2)}$$

$$K_2O\cdot mAl_2O_3\cdot nSiO_2\cdot pH_2O+SiO_2+NaOH\rightarrow$$

$$(Na,K)_2O\cdot Al_2O_3\cdot 2SiO_2(nepheline)+H_2O \qquad \textbf{(3)}$$

Only the active alumina and silica can lead to produce nepheline and also make the calcined clay geopolymerically active, so the reaction (3) can indicate the geopolymeric activity of the clinkers.

The hydration and geopolymerization reactions for the calcined precursors in water might be in accordance with reaction (4)

$$(Na,K)_2O\cdot mAl_2O_3\cdot qSiO_2+H_2O\rightarrow$$

$$Na_2O\cdot Al_2O_3\cdot nSiO_2\cdot pH_2O(zeolite) \qquad \textbf{(4)}$$

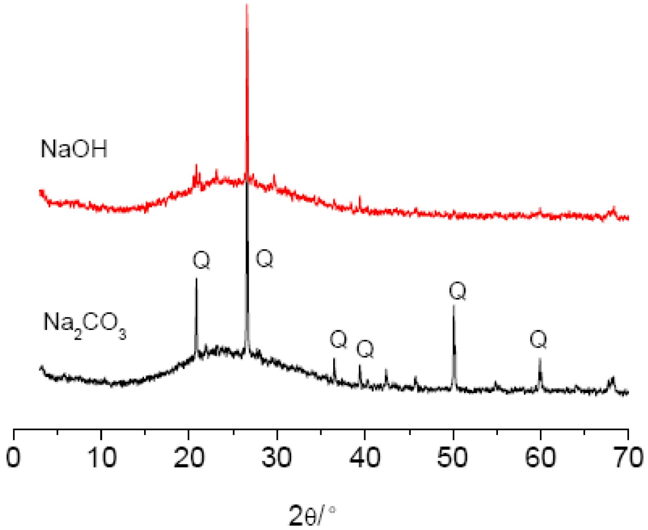

Figure 7 : XRD patterns for thermally activated illite clay with alkali at 950 °C using NaOH or Na_2CO_3 with the same Na_2O content.

However, zeolite is not observed in our hydrates. Therefore, only zeolite-like phases which cannot be detected by XRD, like those in conventional geopolymers, are suggested to form during hydration and offer binding properties.

The clinkers calcined with alkali at too high temperature are melted and turn into glass without geopolymeric activity. Kong Lingjiang et al[19] found that the active alumina and silica contents of the calcined kaolin are both affected by the calcination temperature when kaolin is calcined. The content of active silica always increases with calcination temperature, but the content of active alumina, which is tetrahedral-coordinated, increases with calcination temperature first, but decreases rapidly with calcination temperature at high temperature. It might be also the case with the calcined low-quality illite clay adding alkali. The maximum total contents of active alumina and active silica for geopolymerization are produced by calcining at moderately high temperature 750 °C. Almost all the silica had turned into active silica when the calcination temperature elevated to 950°C since quartz hardly remains, but then the content of active alumina become too lower to synthesize nepheline and do harm to geopolymerization when mixed with water.

CONCLUSIONS

1) Thermal stimulation of illite clay with alkali for geopolymeric precursors was used as a step in the evolution of one-part GC. Through water addition, the ground precursor of low-quality illite clay, which was calcined with 20% NaOH at 750 °C or 33% Na_2CO_3 at 850 °C, obtained water resistance with a rather high compressive strength.
2) The TG/DSC predicts that the addition of alkali distinctly alters the thermal decomposition of the clay, and the octahedral-coordinated Al in the clay turns into tetrahedral-coordinated Al according to IR analysis. During thermal activation with alkali at 650 °C to 950 °C, the minerals in the raw clay, including illite, hematite, and most of quartz, decreased and disappeared. In addition, nepheline initially increased, and then decreased and disappeared when increasing calcination temperature. At the same time, the compressive strength of the corresponding one-part geopolymers initially enhanced and then decreased. No new mineral produced in the formation of one-part geopolymers.
3) It is proposed that the activity of Al changes with calcination temperature different from that of Si, and the maximum total contents of active Al and active Si for geopolymerization are produced by calcining the clay with alkali at moderately high temperature 750 °C, which is indicated by the content of nepheline in the precursors. The hydrolysis of the XRD-amorphous sodium aluminosilicates is inferred to induce the formation of zoelite-like aluminosilicates, which contain chemical bonding water and render the hydrated pastes cementing and water resistant.

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