Effect of phosphoric acid content on the microstructure and compressive strength of phosphoric acid-based metakaolin geopolymers

Li Gao, Youxiong Zheng, Yan Tang, Jianwei Yu, Xingchang Yu, Bingxin Liu*

Qinghai Provincial Key Laboratory of New Light Alloys, Qinghai Provincial Engineering Research Center of High Performance Light Metal Alloys and Forming, Qinghai University, Xining, 810016, PR China

ARTICLE INFO

Keywords:
- Materials science
- Materials chemistry
- Metakaolin
- Phosphoric acid
- Geopolymers
- Amorphous phase

ABSTRACT

The phosphoric acid-based metakaolin geopolymers were prepared by regulating H₃PO₄/Al₂O₃ ratios. X-ray diffraction (XRD), thermogravimetry and differential scanning calorimeter (TG-DSC), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to determine the reaction process and phase formation. The results showed that the metakaolin calcined from Kaolinite mainly consisted of quartz crystalline phase and amorphous phase. The diffraction peak for quartz obviously became lower with the increasing of H₃PO₄/Al₂O₃ ratios. The excessive quartz from metakaolin did not totally take part in the chemical reaction. The polymeric structure of -P-O-Si-O-Al-O constitutes the main building block of phosphoric acid-based metakaolin geopolymeric structure. The optimized compressive strength was 29/C₆² MPa with H₃PO₄/Al₂O₃ molar ratio = 1.3:1. The simulation of the total deformation under 29 MPa load and the total heat flux at 1400 °C of the phosphoric acid-based metakaolin geopolymers with H₃PO₄/Al₂O₃ molar ratio of 1.3:1 on finite element method verified the failure mechanism and the excellent thermal stability at high temperature.

1. Introduction

Geopolymer first recongnized in 1908 is a developing research field for utilizing mineral clays and industrial wastes (Hamdi et al., 2019; Palomo et al., 2014; Provis, 2014). It was utilized to manufacture precast structures, concrete and fixation of toxic metal waste (Ji and Pei, 2019; Davidovits, 2011). The raw materials for producing geopolymers include kaolinite and blast furnace slag (Orçelik and White, 2016). Through hydrolysis and dissolution, Si and Al are released and can be polymerized to form geopolymers. The main advantages of kaolinite was its good dispersibility and availability of the bond sequence Si–O–Al (Davidovits, 2011).

The geopolymer is prone to generating viscous mortar during processing, so workability in geopolymers is poor and difficult to adjust. This means that the traditional construction industry practices cannot be used for geopolymeric cements. Lloyd et al. (2010) showed that the alkaline geopolymer surfaces are easy to alkali, therefore geopolymer structures will be not able to resist corrosion. Lloyd (2009) found that for instance geopolymers have a strength loss during use. Furthermore, the thermal stability of the alkali-activated geopolymers was poor due to the phase transformation (Barbosa and MacKenzie, 2003; Provis et al., 2009). In comparison to the alkali-based geopolymers, the acid-based geopolymers exhibit excellent thermal stability (Le-ping et al., 2010; Liu et al., 2012). Currently, research on phosphoric acid-based polymers has attracted growing interest (Morcy et al., 2019). For examples, Sellami et al. (2019) prepared phosphoric acid-based metakaolin geopolymer with conductivity of 10⁻⁷ S/cm at temperatures above 625 °C, which can be used as a good thermal insulator. Mathivet et al. (2019) performed a thorough study on structural evolutions of acid-based geopolymers. However, there have been few studies about compressive strength of acid-based geopolymers.

In this work, we have successfully synthesized phosphoric acid-based geopolymers by kaolinite and phosphoric acid. The effect of H₃PO₄/Al₂O₃ molar ratio on compressive strength of the synthesized geopolymers was investigated. The reaction mechanisms and characteristics of the acid-based geopolymers were studied by means of XRD, FTIR, TG-DSC and SEM.

* Corresponding author.
E-mail address: liubx408@nenu.edu.cn (B. Liu).

https://doi.org/10.1016/j.heliyon.2020.e03853
Received 21 February 2020; Received in revised form 31 March 2020; Accepted 21 April 2020
2405-8440/© 2020 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
2. Experimental
2.1. Materials
Kaolin (Al$_2$O$_3$·2SiO$_2$·2H$_2$O) was purchased from kaolin company, China. Distilled water and phosphoric acid (85 wt%, AR) was used in the experiment.

2.2. Sample preparation
Metakaolin was prepared by calcining Kaolin at 800 °C for 120 min to dehydrate. The phosphoric acid solution was mixed by stirring in a mixer for 30 min to obtain a homogeneous slurry with molar ratios of H$_3$PO$_4$/Al$_2$O$_3$ from 1.0:1 to 1.4:1. The mass ratio of solid to liquid was 1:1 in the slurry. The slurry was poured into cubic molds (60 mm × 60 mm × 60 mm), and the molds were sealed to suppress water loss. All specimens were cured at ambient temperature for 7 days. After demolded, the samples were cut into cubic shape with dimension of 20 mm × 20 mm × 20 mm.

2.3. Characterization
X-ray fluorescence (XRF, EDX 1800B) was used to analyze chemical compositions of samples. The average particle size of metakaolin was tested by laser particle size analyzer (Mastersize 2000). Compressive strength was measured on cubic specimens with dimension of 20 mm × 20 mm × 20 mm and loaded with a crosshead speed of 0.5 mm/min by a mechanical testing machine (SHIMADZU AG-2000G). X-ray diffraction (D8 advance A25, Cu Kα) was employed to monitor the phase formation in the 2θ range from 10 to 80° with a step size of 0.02°. Differential scanning calorimetry (DSC Q200) and thermogravimetry (TG STA449F3) were used to investigate the thermal stability. TG-DSC experiment was carried out with a heating rate of 10 °C/min. FT-IR (VERTEX 70V) was used to analyze chemical bonding state in the structure. Scanning electron microscopy (SEM, JSM 6700F, JEOL) was used to analyze the microstructures of geopolymers after sputtering gold coating on the surfaces.

3. Results and discussion
The average particle size of metakaolin by calcining Kaolin was 15.1 μm. The chemical compositions of kaolin and metakaolin determined by XRF were shown in Table 1.

3.1. XRD analysis
Figure 1 shows the XRD patterns of metakaolin and geopolymers with different H$_3$PO$_4$/Al$_2$O$_3$ molar ratios. Pattern (a) of metakaolin reveals that there

| Raw materials | Chemical composition (wt/%) |
|---------------|---------------------------|
|               | SiO$_2$ | Al$_2$O$_3$ | SO$_2$ | K$_2$O | Fe$_2$O$_3$ | TiO$_2$ | ZnO | P$_2$O$_5$ | MgO |
| Kaolin        | 56.63   | 34.74      | 4.61   | 1.46   | 0.82      | 0.59    | 0.32 | 0.27      | 0.17 |
| Metakaolin    | 57.06   | 37.80      | 0.61   | 1.72   | 0.94      | 0.60    | 0.34 | 0.27      | 0.12 |

Figure 1. XRD patterns of metakaolin and geopolymers with different H$_3$PO$_4$/Al$_2$O$_3$ ratios. Q, Quartz (PDF # 79-1906). (a) Metakaolin; (b) H$_3$PO$_4$/Al$_2$O$_3$ = 1.0:1; (c) H$_3$PO$_4$/Al$_2$O$_3$ = 1.1:1; (d) H$_3$PO$_4$/Al$_2$O$_3$ = 1.2:1; (e) H$_3$PO$_4$/Al$_2$O$_3$ = 1.3:1; (f) H$_3$PO$_4$/Al$_2$O$_3$ = 1.4:1.

Figure 2. Compressive strength of the geopolymers with different H$_3$PO$_4$/Al$_2$O$_3$ molar ratios.
were quartz crystalline phase and amorphous phase in metakaolin. As for the XRD patterns of geopolymers with different H₃PO₄/Al₂O₃ ratios (Pattern (b) ~ Pattern (f)), even though there still were quartz crystalline phase and amorphous phase in each sample, the diffraction peak for quartz obviously became lower with the increasing of H₃PO₄/Al₂O₃ ratios. The remaining quartz peak indicated that excessive quartz from metakaolin did not take part in the chemical reaction. Other impurities were not found.

3.2. Compressive strength

Figure 2 illustrates the compressive strength of the geopolymers with different H₃PO₄/Al₂O₃ molar ratios. The compressive strength of phosphoric acid-based geopolymers were 14.4 MPa, 14.9 MPa, 26.2 MPa, 29 MPa and 23.16 MPa, respectively, when the molar ratio of H₃PO₄/Al₂O₃ was 1:1 to 1.4:1. As shown in Figure 2, the optimized compressive strength was 29 ± 2 MPa with H₃PO₄/Al₂O₃ molar ratio = 1.3. The compressive strength with 1.2–1.4 H₃PO₄/Al₂O₃ molar ratio of geopolymers was about twice of those of the geopolymers with 1.0–1.1 H₃PO₄/Al₂O₃ molar ratio. The amount of elicitor acid was not enough to excite the metakaolin when the H₃PO₄/Al₂O₃ molar ratio was less than 1.2, while excessive phosphoric acid made the samples difficult to cure when the H₃PO₄/Al₂O₃ molar ratio was larger than 1.4.

Figure 3 is the finite element analysis about total deformation of the geopolymers with different loads. The simulation process was performed on the ANSYS Workbench simulation platform. As shown in Figure 3 (a) and (b), the total deformation of the geopolymer gradually was increased with the increasing of the load. The deformation of the surface (the surface under direct stress) was the largest compared with other parts (Figure 3 (b)). This indicated that when the load reached the limit that the polymer can bear, the surface of the sample first cracked and gradually spreaded to other parts of the sample, eventually leading to the destruction of the whole sample.

3.3. SEM analysis

Figure 4 indicates the microstructure of the phosphoric acid-based geopolymers with H₃PO₄/Al₂O₃ molar ratio of 1.3. The geopolymer was mainly composed of lamellar, as observed in Figure 4 (a), and the dense amorphous glassy geopolymer matrices and some particle can be clearly seen in Figure 4 (b). The particles were probably the quartz
and the Al tetrahedral units of phosphoric acid solution, the Si 3.5. Thermal analysis
phosphoric acid-based metakaolin geopolymer structure. formed during geopolymerization constitutes the main structural unit of
and metakaolin was believed to be a mental results and previous studies (Liu et al., 2012; Cao et al., 2005), the
kaolinite at 800 cm	p3.4. FT-IR analysis
spectra of the geopolymer, so the broad absorption band around
The band around 1600 cm
to dehydroxylation. The exothermic peak between 995 and 1050 °C
and the exothermic peak between 1300 and 1400 °C were attributed to
formation of mullite and transformation of cristobalite from quartz.
Despite the one exothermic peak, the mass kepted almost unchanged
between 600 and 1450 ºC. Therefore, the phosphoric acid-based meta-
kaolin geopolymers exhibited an excellent thermal stability and were
stable at temperature up to 1400 ºC.

Figure 6 is the finite element analysis about the total heat flux at
different temperature of geopolymers with H3PO4/Al2O3 molar ratio
of 1.3. The heat flux at the edge portion of the geopolymers was larger
relative to other parts, which may be due to uneven stress inside the cube.
The overall heat flux of the geopolymers was much larger than the heat
flux at room temperature (Figure 7 (a)) when the temperature reached
1400 °C (Figure 7 (b)), but its highest heat flux was still low. It was
consistent with the analysis results of TG-DSC, indicating that the
phosphoric acid-based metakaolin geopolymers were provided with su-
perior thermal stability at high temperature. 4. Conclusion
Phosphoric acid-based metakaolin geopolymers were synthesized by
metakaolin, phosphoric acid and distilled water, and the -P-O-Si-O-Al-O
structure formed after geopolymer formation. The acid-based metakaolin
geopolymers were composed of glassy amorphous phase and small
amounts of quartz. The phase composition of these geopolymers con-
sisted of amorphous phase and minor amounts of quartz. Excessive quartz
from metakaolin did not totally take part in the chemical reaction. The
intensities of quartz peak decreased when H3PO4/Al2O3 ratios increased,
therefore the excitation effect of acid activator is observed. The opti-
mized compressive strength was 29 ± 2 MPa with H3PO4/Al2O3 molar
ratio = 1.3. The results of the finite element analysis of total deformation
indicated that the geopolymer first cracked from the surface under load
and gradually spread to other parts until the sample was completely
destroyed. The excellent thermal stability at 1400 °C of the geopolymers
was proved by the finite element analysis of total heat flux of the
geopolymers.

3.5. Thermal analysis

TG-DSC curves in the temperature range from 50 to 1450 °C relative to other parts, which may be due to uneven stress inside the cube.

Figure 7 illustrates FT-IR spectra of metakaolin and phosphoric acid-
based geopolymer with H3PO4/Al2O3 molar ratio = 1.3. The presence of
two key vibrational modes in FT-IR spectra of metakaolin, 1089 cm
to dehydroxylation. The exothermic peak between 995 and 1050 °C
due to dehydroxylation. The exothermic peak between 995 and 1050 °C
and the exothermic peak between 1300 and 1400 °C were attributed to
formation of mullite and transformation of cristobalite from quartz.

Figure 7 is the finite element analysis about the total heat flux at
different temperature of geopolymers with H3PO4/Al2O3 molar ratio
of 1.3. The heat flux at the edge portion of the geopolymers was larger
relative to other parts, which may be due to uneven stress inside the cube.
The overall heat flux of the geopolymers was much larger than the heat
flux at room temperature (Figure 7 (a)) when the temperature reached
1400 °C (Figure 7 (b)), but its highest heat flux was still low. It was
consistent with the analysis results of TG-DSC, indicating that the
phosphoric acid-based metakaolin geopolymers were provided with su-
perior thermal stability at high temperature. 4. Conclusion
Phosphoric acid-based metakaolin geopolymers were synthesized by
metakaolin, phosphoric acid and distilled water, and the -P-O-Si-O-Al-O
structure formed after geopolymer formation. The acid-based metakaolin
geopolymers were composed of glassy amorphous phase and small
amounts of quartz. The phase composition of these geopolymers con-
sisted of amorphous phase and minor amounts of quartz. Excessive quartz
from metakaolin did not totally take part in the chemical reaction. The
intensities of quartz peak decreased when H3PO4/Al2O3 ratios increased,
therefore the excitation effect of acid activator is observed. The opti-
mized compressive strength was 29 ± 2 MPa with H3PO4/Al2O3 molar
ratio = 1.3. The results of the finite element analysis of total deformation
indicated that the geopolymer first cracked from the surface under load
and gradually spread to other parts until the sample was completely
destroyed. The excellent thermal stability at 1400 °C of the geopolymers
was proved by the finite element analysis of total heat flux of the
geopolymers.

Declarations

Author contribution statement

Li Gao: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or
data; Wrote the paper.
Youxiong Zheng: Performed the experiments; Contributed reagents,
materials, analysis tools or data.
Yan Tang: Analyzed and interpreted the data.
Jianwei Yu, Xingchang Yu: Performed the experiments.
Bingxin Liu: Conceived and designed the experiments.

**Funding statement**

This work was supported by the Natural Science Foundation of Qinghai Province, China (2020-ZJ-764); National Natural Science Foundation of China, China (21804078); Thousand Talents Program of Qinghai Province.

**Competing interest statement**

The authors declare no conflict of interest.

**Additional information**

No additional information is available for this paper.

**References**

Barbosa, V.F.F., MacKenzie, K.J.D., 2003. Synthesis and thermal behaviour of potassium sialate geopolymers. Mater. Lett. 57, 1447–1482.

Cao, D., Su, D., Lu, B., Yang, Y., 2005. Synthesis and structure characterization of geopolymeric material based on metakaolinite and phosphoric acid. J. Chin. Ceram. Soc. 33, 1385–1389.

Davidovits, J., 2011. In: Geopolymer Chemistry and Applications, third ed. Institute Geopolymer, Saint-Quentin, France, p. 612.

Davidovits, J., 1994. Geopolymers: man-made rock geosynthesis and the resulting development of very early high strength cement. J. Mater. Educ. 16, 91–137.

Douri, H., Louati, S., Baklouti, S., Arous, M., Fakhfakh, Z., 2014. Structural, thermal and dielectric properties of phosphoric acid-based geopolymers with different amounts of H3PO4. Mater. Lett. 116, 9–12.

Hamdi, N., Ben Messoud, I., Srarha, E., 2019. Production of geopolymer binders using clay minerals and industrial wastes. Compt. Rendus Chem. 22, 220–226.

Ji, Z., Pei, Y., 2019. Bibliographic and visualized analysis of geopolymer research and its application in heavy metal immobilization: a review. J. Environ. Manag. 231, 256–267.

Le-ping, L., Xue-min, C., Shu-heng, Q., Jun-li, Y., Lin, Z., 2010. Applied Clay Science Preparation of phosphoric acid-based porous geopolymers. Appl. Clay Sci. 50, 600–603.

Lloyd, R., 2009. Accelerated ageing of geopolymers. In: Provis, Van Deventer (Eds.), Geopolymers: Structure, Processing, Properties and Industrial Applications. CRC Press, pp. 139–166.

Lloyd, R., Provis, J., Van Deventer, S.J.S., 2010. Pore solution composition and alkali diffusion in inorganic polymer cement. Cement Concrr. Res. 40 (9), 1386–1392.

Liu, L.P., Cui, X.M., He, Y., Liu, S.D., Gong, S.Y., 2012. The phase evolution of phosphoric acid-based geopolymers at elevated temperatures. Mater. Lett. 66, 10–12.

Mahivet, V., Josin, J., Ghazouni, A., Sobradi, I., Celierier, H., Rossignol, S., Parlier, M., 2019. Acid-based geopolymers: understanding of the structural evolutions during consolidation and after thermal treatments. J. Non-Cryst. Solids 512, 90–97.

Morsy, M.S., Rashad, A.M., Shoukry, H., Mokhtar, M.M., 2019. Potential use of limestone in metakaolinite-based geopolymer activated with H3PO4 for thermal insulation. Construct. Build. Mater. 22, 117088.

Ozçelik, V.O., White, C.E., 2016. Nanoscale charge-balancing mechanism in alkali-substituted calcium-silicate-hydrate gels. J. Phys. Chem. Lett. 7 (24), 5266–5272.

Palomo, A., Krivenko, P., Garcia-Lodeiro, I., Kavalerova, E., Malteva, O., Fernandez-Jimenez, A., 2014. A review on alkaline activation: new analytical perspectives. Mater. Construcción 64 (315), 22.

Provis, J.L., Yong, C.Z., Duxson, P., van Deventer, J.S.J., 2009. Correlating mechanical and thermal properties of sodium silicate-fly ash geopolymers. Colloids Surfaces A Physicochem. Eng. Asp. 336, 57–63.

Provis, J.L., 2014. Geopolymers and other alkali activated materials: why, how, and what? Mater. Struct. 47, 11–25.

Sellami, M., Barre, M., Toumi, M., 2019. Synthesis, thermal properties and electrical conductivity of phosphoric acid-based geopolymer with metakaolin. Appl. Clay Sci. 180, 105192.

Smith, B., 1999. Infrared Spectral Interpretation: A Systematic Approach. CRC Press, New York.

Wang, H., Li, H., Yan, F., 2005. Synthesis and mechanical properties of metakaolinite-based geopolymer. Colloids Surfaces A Physicochem. Eng. Asp. 268, 1–6.