Material Strength and Applied Mechanics
A. Khotsianovsky and Y. Chen (Eds.)

doi:10.3233/ATDE240529

Mechanical Properties of Acid Activated Metakaolin

Martin KEPPERT[a,1], Vojtěch POMMER[a], Jitka KREJSOVÁ[a], Lukáš GILL[a], Michala BRENÍKOVÁ[a], Martina URBANOVÁ[b], Eva VEJMELKOVÁ[a] and Dana KOŇÁKOVÁ[a]
[a] *Czech Technical University in Prague, Faculty of Civil Engineering, Department of Materials Engineering and Chemistry, Thákurova 7, 166 29 Praha 6, Czech Republic*
[b] *Institute of Macromolecular Chemistry CAS, Department of Structural Analysis, Heyrovského nám. 1888/2, 162 00 Praha 6, Czech Republic*
ORCiD ID: Martin Keppert https://orcid.org/0000-0002-6878-1291
Vojtěch Pommer https://orcid.org/0000-0003-4066-1930
Jitka Krejsová https://orcid.org/0000-0001-5734-7804
Martina Urbanová https://orcid.org/0000-0003-1316-6395
Eva Vejmelková https://orcid.org/0000-0002-1553-5054
Dana Koňáková https://orcid.org/0000-0003-1345-4813

Abstract. Acid (usually by phosphoric acid) activation of aluminosilicate precursors provides a new group of inorganic materials with promising chemical and thermal stability. The three mixtures in system metakaolin – phosphoric acid were prepared; they differed in Al/P molar ratio (1, 1.5, 2). Compressive and bending strength were determined in the age of 1 week; the 1 day 60 °C curing was applied. The highest compressive strength reached sample with Al/P ratio 1.5, what falls within the range found in literature. The porosity of the samples increased with the increasing Al/P ratio, thus there was not any simple relationship between strength and porosity. It implies that Al/P ratio influenced not only porosity and pore size distribution, but also the nature of activated cementing product.

Keywords. Metakaolin, phosphoric acid, acid activation, posorimetry

1. Introduction

Acid activation of aluminosilicates constitutes a less popular and studied way of materials synthesis compared to the well-known alkaline activation. The available aluminosilicate precursors are the same (metakaolin, fly ash, blast furnace slag, volcanic ash etc.) while the activators are acids – phosphoric or boric, or their salts [1, 2]. The present study delas with H_3PO_4-activated metakaolin as kind of benchmark system within this field [1, 3]. There is not a fully accepted view on the molecular structure of phosphate geopolymers; either the material can be composed from Si-O-P-O-Al three dimensional network or there are two networks: $AlPO_4$ and Si-O-P-O-Si [4].

---

[1] Corresponding Author: Martin Keppert, E-mail: martin.keppert@fsv.cvut.cz

The application fields of phosphate geopolymers are not intended to be found in common civil engineering as concrete alternative due to relative scarcity and high price of phosphoric acid (even though there are some activities to find a waste source of a H_3PO_4 alternative [5]). However the high thermal and chemical stability of phosphate geopolymers can be of interest in the field of nuclear technology both in construction and waste solidification fields [1, 6], for production of thermally stable foams [7] or coating for sub-ambient radiative cooling [8].

The mechanical properties are of crucial importance for each material; the results published in literature on mechanical properties of acid activated metakaolin are summarized in Table 1. In all of the so far published works scholars have used compressive strength as the indicator of successful (geo)polymerization of the studied systems. Since the setting of phosphate geopolymers at ambient temperature may be extremely slow (in a range of several weeks [9]), most of authors applied a curing regime. The most common applied regime is 60 °C for 24 hours. However the two-step curing may also be very successful as it is documented in [10, 11]. The data summarized in Table 1 are first of all illustrating that the compressive strength results (even those measured in the same age and after the same curing applied) are highly scattered even most of the authors used concentrated phosphoric acid and metakaolin. Obviously individual metakaolins may differ in their composition and particle size distribution; the individual laboratory practice may likely contribute to the different results as well. The goal of the present paper has been to evaluate the possibility of phosphoric acid activation of metakaolin Mefisto L05 produced industrially in Czech Republic by company ČLUZ.

Table 1. Selected results published in literature on mechanical properties of phosphate-metakaolin geopolymers.

Reference	Al/P	Curing	Testing time days	Compressive strength MPa
[5]	N/A	60 °C, 168 h	7	63
[10]	2	80 °C, 24 h; 60 °C, 72 h	N/A	60
[11]	1.2	40 °C, 24 h; 60 °C, 24 h	3	123
[12]	1	60 °C, 24 h	14	146
[13]	1	60 °C, 24 h	28	6.6
[14]	1	60 °C, 24 h	22	34
[15]	?	60 °C, 24 h	28	94
[16]	?	60 °C, 24 h	28	54.4
[17]	N/A	60 °C, 24 h	28	87.7
[18]	1.5	ambient	7	29
[19]	1	60 °C, 24 h	28	58
[20]	N/A	ambient	15	21

2. Experimental

Industrially produced metakaolin Mefisto L05 (ČLUZ Nové Strašecí, Czech Republic) (composition in Table 2) was activated by 85% H_3PO_4. The ratio of reactants was adjusted to molar ration Al/P to be 1, 1.5 and 2; the resulting composition of prepared mixtures are presented in Table 3. The mixtures were casted to 100 x 20 x 20 mm moulds. The curing applied was consistent with the most common in this system (60 °C, 24 hours), testing time 7 days. The bending and compressive strength were determined. The pore size distribution was measured by Mercury Intrusion Porosimetry by devices Pascal 140 and 440 (Thermo Electron). The morphology of samples was examined by SEM in back scattered electrons by Phenom XL device (Phenom-World). The samples were coated by Au/Pd before the experiment.

Table 2. Chemical composition of metakaolin (% by mass, examined by XRF).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	TiO_2
51.8	41.9	1.1	0.1	0.9	0.9	1.7

Table 3. Composition of prepared mixtures (in g).

	PG 1	PG 1.5	PG 2
metakaolin	300	300	300
H_3PO_4	277	184	139
water	90	100	110

3. Results and discussion

The compressive and bending strength of phosphate geopolymers in age of 7 days are depicted in Fig. 1. The highest compressive strength reached sample with Al/P molar ratio 1.5, what is in agreement with [18] but more correct would be the statement that the obtained results fall within the broad range of similar results summarized in Table 1. Bending strength of phosphate geopolymers has not been presented in the reviewed papers; here the relatively best performance reached sample PG 1. This material was apparently less brittle than the others what was caused by higher content of phosphoric acid which is bringing higher toughness to this kind of material.

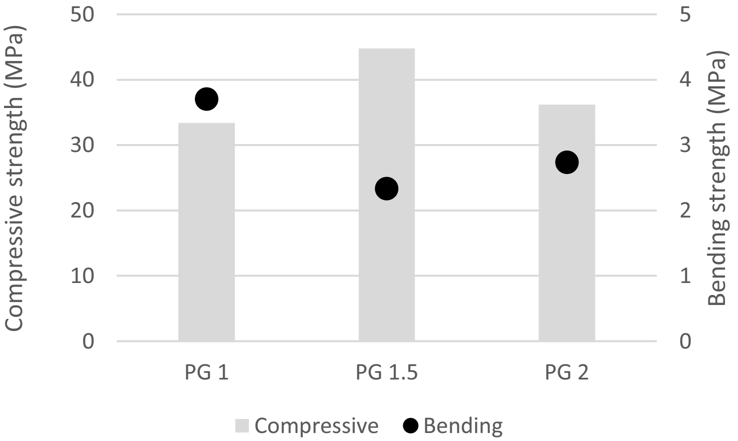

Figure 1. Compressive and bending strength of phosphate geopolymers.

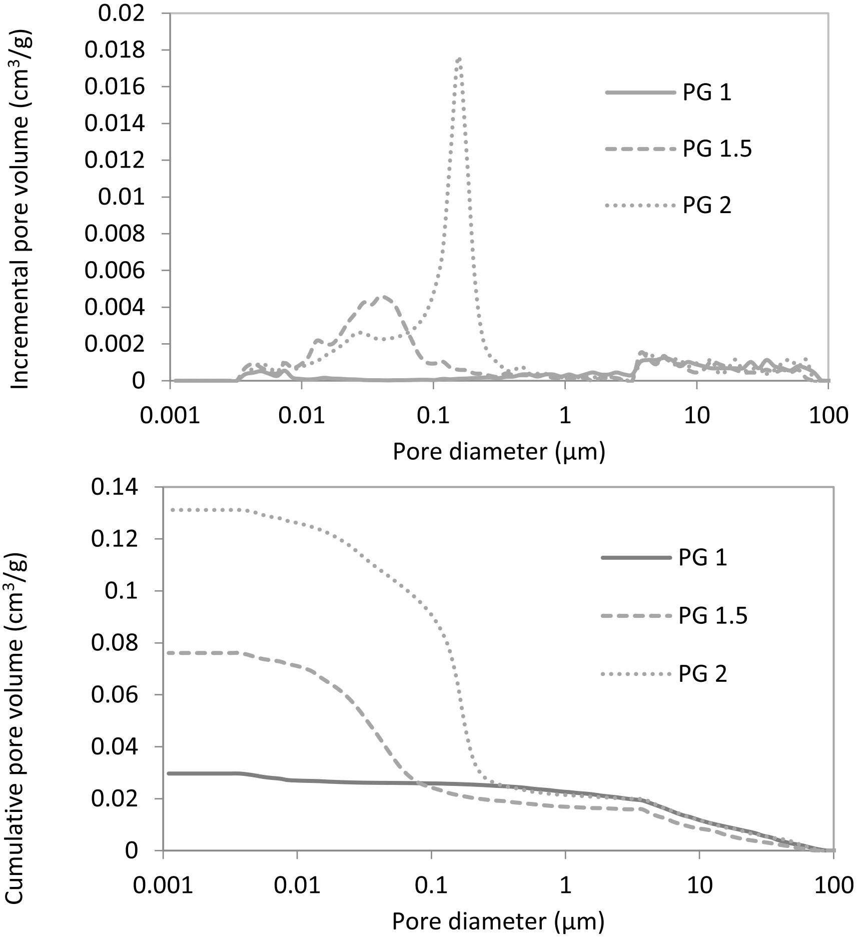

Figure 2. Incremental and cumulative pore size distribution curves of phosphate geopolymers.

The mechanical properties of porous materials are usually derived from their pore system. Typically in concrete, higher porosity means lower strength. The pore system of phosphate geopolymers was characterized by Mercury Intrusion Porosimetry (Fig. 2). Apparently the pore system of three prepared materials has been very different. First of all, it has to be mentioned that the used devices Pascal 140 and 440 are performing the MIP experiment in two steps – at low pressure station (100 to 3 micrometers) and at high pressure station (from 3 μm to 1 nm). It explains certain discontinuity in porosimetry curves. However, it may be concluded that all three samples contain low – and equal – amount of large pores/voids of diameter between 3-100 μm. The dissimilarity of individual samples lies in area of smaller pores. While PG 1, containing the highest amount of phosphoric acid, contain almost any smaller pores, the PG 1.5 and PG 2 feature significantly higher porosity. Both samples may be classified as unimodal pore system but with different average pore size (0.04 and 0.14 μm respectively) very different cumulative pore volume. Briefly, higher Al/P ratio means higher porosity and larger pores. The only porosimetry data published so far on the (non-foamed) phosphate geopolymers were found in [14]; there authors found also unimodal pore system. Unfortunately, authors of [14] used varying concentration of activator thus their data are not directly comparable with those in Fig. 2. However the higher H_3PO_4 concentration caused more compact product what is certain equivalent of the lower Al/P ratio applied in this paper.

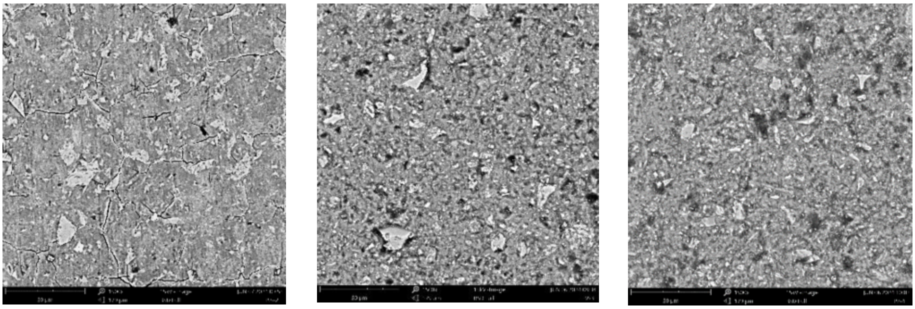

Figure 3. SEM images of PG 1 (left), PG 1.5 and PG 2 samples.

The SEM microphotographies (Fig. 3) are in qualitative accordance with the porosimetry results. The material PG 1 features the most compact structure while the higher metakaolin content is increasing the porosity. Unfortunately the PG 1 sample contains also some apparent cracks.

When one compares the results of mechanical properties and porosimetry it is apparent there is not a simple linear relationship between porosity and strength in phosphate geopolymers (as it is common in concrete). The highest compressive strength reached sample with medium porosity; or – the most compact material PG 1 has not the highest strength. It implies that there are differences between individual mixtures not only in porosity but also in chemical structure, in the nature of activated cementing product. These aspects will by studied deeply in the ongoing research.

Conclusions

Phosphoric acid was used for activation of metakaolin Mefisto L05 with Al/P molar ratios 1, 1.5 and 2. The best compressive strength (44.8 MPa after 7 days) was obtained in mixture Al/P 1.5. However this sample had much higher porosity than Al/P = 1. It implies that the composition of activated product plays important role in the strength control, apart from porosity.

Acknowledgements

This research has been supported by the Czech Science Foundation, under project No 24-11171S.

References

[1] Katsiki A. Aluminosilicate phosphate cements– a critical review. Adv App Ceram. 2019; 188(5):1572239, doi: 10.1080/17436753.2019.1572339

[2] Rozek P, Florek P, Król M, Mozgawa W. Immobilization of Heavy Metals in Boroaluminosilicate Geopolymers. Materials 2021; 14(214):14010214, doi: 10.3390/ma14010214

[3] Aguiar Park J, Pimenta MM, da Silva Bezerra AC. Acid Activation in Low-Carbon Binders: A Systematic Literature Review. Buildings 2024; 14(83):14010083, doi: 10.3390/ buildings14010083

[4] Mathivet V, Jouin J, Gharzouni A, Sobrados I, Celerier H, Rossignol S, Parlier M. Acid-based geopolymers: Understanding of the structural evolutions during consolidation and after thermal treatments. J Non-Crys Sol. 2019; 512:90-97, doi 10.1016/j.jnoncrysol.2019.02.025

[5] Guo C, Wang K, Liu M, Li X, Cui X. Preparation and characterization of acid-based geopolymer using metakaolin and disused polishing liquid. Ceram Int. 2016; 42:9287-9291, doi: 10.1016/j.ceramint.2016.02.073

[6] Kim B, Kang J, Shin Y, Yeo T, Um W. Immobilization mechanism of radioactive borate waste in phosphate-based geopolymer waste forms. Cem Conc Res. 2022; 161:106959, doi: 10.1016/j.cemconres.2022.106959

[7] Gualtieri ML, Romagnoli M, Gualtieri AF. Preparation of phosphoric acid-based geopolymer foams using limestone as pore forming agent – Thermal properties by in situ XRPD and Rietveld refinements. J Europ Ceram Soc. 2015; 32:3167-3178, doi: 10.1016/j.jeurceramsoc.2015.04.030

[8] Yang N, Xuan Q, Fu Y, Ma X, Lei D, Niu J, Dai J-G. Phosphate activated geopolymer-based coating with high temperature resistance for sub-ambient radiative cooling. Sust Cities Soc. 2024; 100:104992, doi: 10.1016/j.scs.2023.104992

[9] Celerier H, Jouin J, Tessier-Doyen N, Rossignol S. Influence of various metakaolin raw materials on the water and fire resistance of geopolymers prepared in phosphoric acid. J Non Cry Sol. 2018; 500:493-501, doi: 10.1016/j.jnoncrysol.2018.09.005

[10] Perera DS, Hanna JV, Dabis J, Blackford MG, Latella BA, Sasaki Y, Vance ER. Relative strengths of phosphoric acid-reacted and alkali-reacted metakaolin materials. J Mater Sci. 2002; 43:6562-6566, doi: 10.1007/s10853-008-2913-6

[11] Lin H, Liu H, Li Y, Kong X. Properties and reaction mechanism of phosphoric acid activated metakaolin geopolymer at varied curing temperatures. Cem Conc Res. 2021; 144:106425, doi: 10.1016/j.cemconres.2021.106425

[12] He Y, Liu L, He L, Cui X. Characterization of chemosynthetic H_3PO_4–Al_2O_3–$2SiO_2$ geopolymers. Ceram Int. 2016; 42:10908-10912, doi: 10.1016/j.ceramint.2016.03.224

[13] Louati S, Hajjaji W, Baklouti S, Samet B. Structure and properties of new eco-material obtained by phosphoric acid attack of natural Tunisian clay. App Clay Sci. 2014; 101:60-67, doi: 10.1016/j.clay.2014.07.015

[14] Louati S, Baklouti S, Samet B. Geopolymers Based on Phosphoric Acid and Illito-Kaolinitic Clay. Adv Mat Sci Eng. 2016; 2016:2359759, doi: 10.1155/2016/2359759

[15] Tchakouté HK, Rüscher CH, Kamseau E, Andreola F, Leonelli C. Influence of the molar concentration of phosphoric acid solution on the properties of metakaolin-phosphate-based geopolymer cements. App Clay Sci. 2017; 147:184-194, doi: 10.1016/j.clay.2017.07.036

[16] Tchakouté HK, Rüscher CH, Kamseau E, Djobo JNY, Leonelli C. The influence of gibbsite in kaolin and the formation of berlinite on the properties of metakaolin-phosphate-based geopolymer cements. Mat Chem Phys. 2017; 199:280-288, doi: 10.1016/j.matchemphys.2017.07.020

[17] Bewa CN, Tchakouté HK, Fotio D, Rüscher CH, Kamseu E, Leonelli C. Water resistance and thermal behavior of metakaolin-phosphate-based geopolymer cements. J Asian Ceram Soc. 2018; 6(3): 271-283, doi: 10.1080/21870764.2018.1507660

[18] Gao L, Zheng Y, Tang Y, Yu J, Yu X, Liu B. Effect of phosphoric acid content on the microstructure and compressive strength of phosphoric acid-based metakaolin geopolymers. Heliyon 2020; 6(4):e03853, doi: 10.1016/j.heliyon.2020.e03853

[19] Tian Q, Yu X, Sui Y, Xu L, Lv Z. The effect of water on metakoalin phosphate-based geopolymer properties. Ceram Silik. 2022; 66(2):236-244, doi: 10.13168/cs.2022.0018

[20] Zribi M, Samet B, Baklouti S. Effect of curing temperature on the synthesis, structure and mechanical properties of phosphate-based geopolymers. J Non Cry Sol. 2019; 511:62-67, doi: 10.1016/j.jnoncrysol.2019.01.032