

Synthesis of geopolymer binder from the partially de-aluminated metakaolinite by-product resulted from alum industry

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Érkezett: 2022. 05. 02. ▪ Received: 02. 05. 2022. ▪ <https://doi.org/10.14382/epitoanyag-jsbcm.2022.25>

Abstract

In this study an experimental work has been done to test the feasibility of using partially de-aluminated metakaolin (PDK) with metakaolin (MK) in the production of geopolymer binder. The chemical composition and physical properties of de-aluminated metakaolin was tested. For this purpose, metakaolin (MK) was partially substituted with partially de-aluminated metakaolin (PDK) at ratios of 0-60% by weight. The alkaline activator was NaOH. Geopolymer pastes were cured at room temperature. The compressive strength was measured by testing standard cubes at 7 and 28 days. Satisfactory results have been achieved by using 15, 20, 30, 35 wt.% of PDK. Hence it was suggested to use the local metakaolin with added proportions of PDK up to 35% of metakaolin to produce economic geopolymer binder. It is technically feasible, resulting in a sustainable and environmentally friendly source of vitreous material. The effect of PDK on porosity and compressive strength were tested. The internal microstructure, and hydration were investigated by using modern methods such as, Thermo-gravimetric (TGA) and differential thermal analysis (TGA, DTGA), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The findings assure the potentiality for the application of PDK as a siliceous material can be used in manufacturing of geopolymer cement.

Keywords: partially de-aluminated metakaolin (PDK), geopolymer, metakaolin, compressive strength, microstructure

Kulcsszavak: részben alumíniummentesített metakaolin (PDK), geopolimer, metakaolin, nyomószilárdság, mikroszerkezet

1. Introduction

Geopolymer is a good binding material which can be used in several construction fabrications, since it can be casted in situ at the ambient temperature like ordinary mortar/concrete but of higher surface quality. Stained geopolymer paste can be fabricated by using metakaolin and various pigments. Geopolymer product has better resistance against acid and heat compared to Ordinary Portland Cement (OPC) concrete or mortar [1-4].

The natural siliceous rocks and OPC can be replaced by geopolymer binder with better physical and chemical properties such as acid and saline water resistance, early development of mechanical strength [5-7].

Geopolymer was patented by using of the highest rank of clay minerals (kaolin), as a source of alumina and silica for preparation of geopolymer through the reaction of the kaolin with alkaline silicate solution [8-10]. It's commonly carried out by the interaction of a fine ground aluminum silicate materials with an alkali metal silicate solution at room temperature forming polymer chain (-Si-O-Al-O-) [11, 12]. Geopolymer is a type of amorphous aluminous-siliceous cementitious material which can be produced by polymerization reaction

of aluminum silicates materials with alkali metals solutions. Geopolymeric mortar/concrete can be produced by using of pozzolana, which is a waste material obtained from various activities. The numerous characteristics of inorganic polymer can be determined from civil works in term of the mechanical characteristics such as compressive strength for geopolymeric mortar and concrete, resistance to chemicals attack [13-16] excellent repairing substances for ancient constructions, to the modern applications in aircraft which utilizes the property of anti-fire characteristics of the geopolymer blends [17, 18]. Various geopolymer blends does not ignite, or evolve gases even after extended exposure of heat. Therefore, they are excellent inert materials for aircraft lining cabins, floor panels, sidewalls, and insulators for wires [19, 20].

The inorganic and physical chemistry, with other geological science such as mineralogy, geochemistry and engineering, utilized the unique characteristics of geopolymer. The potential applications of geopolymer includes: refractory, low energy ceramic tiles, tech composites for aircraft interior and automobile decoration artifacts, thermal insulation, thermal shock refractories, concretes, certain blends for construction repairing and supporting, radioactive and toxic waste containment immobilization, archaeological restoration [21-24].

Metakaolinite is a greatly utilized as one of the precursors starting materials for manufacturing of geopolymeric binder, and is produced by calcination of kaolinite clay. The thermal treatment of clay minerals in the range from 550 up to 800 °C causes dehydroxylation of from the internal structure of the clay mineral. The coordinated hydroxyl groups of the octahedral aluminate sheet are lost and the structure becomes disordered meta-phase in which the internal crystalline structure of clay minerals is collapsed. The stable phase of the distorted kaolinite is reactive and is called pozzolanic material [25, 26]. Calcination of kaolinite at higher temperatures causes reorganization of the internal structure and crystallization forming spinel and mullite minerals [27, 28]. Several studies have reported the using of byproduct or waste materials in the manufacturing of geopolymer, such as fly ash and granulated slag as an aluminum silicate materials [29, 30]. This reaction yields water, while in OPC hardening, water is required for startup of hydration reactions. Upon heating of OPC concrete at 300 °C, dehydration takes place yielding dehydrated products causing shrinkage and formation of calcium oxide and carbonation of calcium at 500 °C, further heating up to 800 °C calcium carbonate decomposes forming caustic lime, while, geopolymer become stable up to 1000 °C. Ordinary Portland Cement (OPC) is the primary ingredient in concrete of structure of the buildings, and the roads and bridges. Production of cement releases the major greenhouse gas CO₂. Heating of limestone and fossil fuels result in CO₂. Hence to reduce CO₂ emissions it is required to find an alternative for the traditional cement [31, 32].

PDK is a by-product of aluminum sulphate industry and it derives from acid leaching of MK (e.g. calcined kaolin, Al₂O₃·2SiO₂). As result of the de-alumination process, the SiO₂/Al₂O₃ ratio and BET values are increased. The increasing of specific surface observed as consequence of acid attack was found due to the increasing of the pore volume [33].

It was found that mixing of PDK and lime and using isothermal calorimetric tests, PDK shows an appreciable pozzolanic activity [34, 35]. The pozzolanic activity of PDK in blended cements was also demonstrated by the same method. They also reported that PDK exhibits higher BET values than silica fume. Other researchers have also shown that the porous structure of calcined kaolin particles does not collapse owing to the acid attack [36].

Zhang et al. [37] investigated the effect of the three key ratios “SiO₂/Al₂O₃, M₂O/Al₂O₃, H₂O/M₂O” on the production of metakaolinite-based geopolymers, where M is alkali metal ions (Na⁺ or K⁺). Several blends of different mole ratios SiO₂/Al₂O₃, Na₂O/Al₂O₃, H₂O/Na₂O were adopted to examine their impacts on the mechanical strength. The results of all tests that were obtained exhibit that the ratios Na₂O/Al₂O₃ and H₂O/Na₂O had direct impact on the compressive strength. It was found that highest compressive strength (34.9 MPa) was recorded at a ratio SiO₂/Al₂O₃= 5.5, Na₂O/Al₂O₃= 1.0 and H₂O/Na₂O = 7.0. These ratios achieved complete geopolymerisation reaction. Referring to the results of the current paper, it was found that the compressive strength increases with increase in quantity of PDK to reach maximum at SiO₂/Al₂O₃=2.8, Na₂O/Al₂O₃ = 0.9 and H₂O/Na₂O = 13.7. These ratios may differ from the above,

this attributed to the raw materials and the preparation of alkaline silicates from DK, and so, the compressive strength of the concrete relies upon the quantity of activated aluminum silicates materials in the precursors, the activating solution type and the curing temperature as reported by [38, 39].

From the above results obtained, it was noted that there is no need for higher temperature curing, whereas activation was preceded properly. Geopolymer concrete produced show higher compressive strength without need to add sodium silicate, as sodium silicate was formed during activation process as a result of the chemical reaction between activated silicate in PDK and the stoichiometry amount of sodium hydroxide. Workability of geopolymer concrete is very low at the nominal blends. So, superplasticizer of any type or little excess water has to be added to facilitate workability.

In this study an experimental work has been done to test the feasibility of using industrial wastes of PDK as a source of uncommon silicates with MK in the production of geopolymer concrete. For this purpose, MK was partially substituted with PDK at ratios of 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60% by weight. The compressive strength was determined by testing standard cubes at 7th and 28th day. The effect of PDK on the specific gravity, porosity and mechanical characteristics were studied. The presence of crystalline components, hydration and the internal structure were tested.

2. Experimental procedure

2.1 Materials

Metakaolin was prepared in ASCE laboratory, kaolin was supplied from south Sinai Quarries. Metakaolin was produced by thermal hydroxylation at 750 °C for 2 hr. and the PDK were collected from aluminum sulphate Co. of Egypt (ASCE). Fig. 1(a and b) show the thermogravimetric analysis (TG/DTG) of raw kaolin and MK, displaying the water released and the total mass loss (14.23 wt. %, 0.04% respectively) at the optimum temperature for calcination of kaolin (750 °C).

Aluminum oxide in PDK is significantly lower than corresponding value of MK due to the dealumination process that performed by sulphuric acid for formation of aluminum sulphate product. This lead to an appreciable increase of SiO₂/Al₂O₃ ratio (from 1.94 for average value in MK to 16.95 for average value in PDK). In mortar mixes, sand stone was used with density 2.5. Different conditioning procedures were also adopted for PDK before using it as an additive: PDK was adopted as amorphous silicate source after drying in oven at 100 °C for 12 h. The dry source was also used after further grinding; the ground source was also used after further dispersion as water slurry (ground-slurry). BET analysis revealed a high fineness for PDK (43 m²/g) and the density of 1.36. BET results of MK and PDK are plotted in Fig. 2 (a and b) which shows that 90% of MK diameter is ~8.6 µm and 10% is ~1.3 µm with an average diameter of ~4.5 µm. and 90% of PDK diameter is ~70.33 µm and 10% is ~4.3 µm with an average diameter of ~9.5 µm. The surface texture of PDK particles characterized by high roughness as already observed by [32]. PDK plays a significant role in simultaneous synthesis of sodium silicate during geopolymerisation process. The

reaction between PDK and NaOH increases the building up of strength of the fabricated geopolymer mortar by inducing the activation and speciation of siliceous aluminous ions of the raw materials, and self-formation of alkaline silicate compensate shortage of silicate in the geopolymerisation medium.

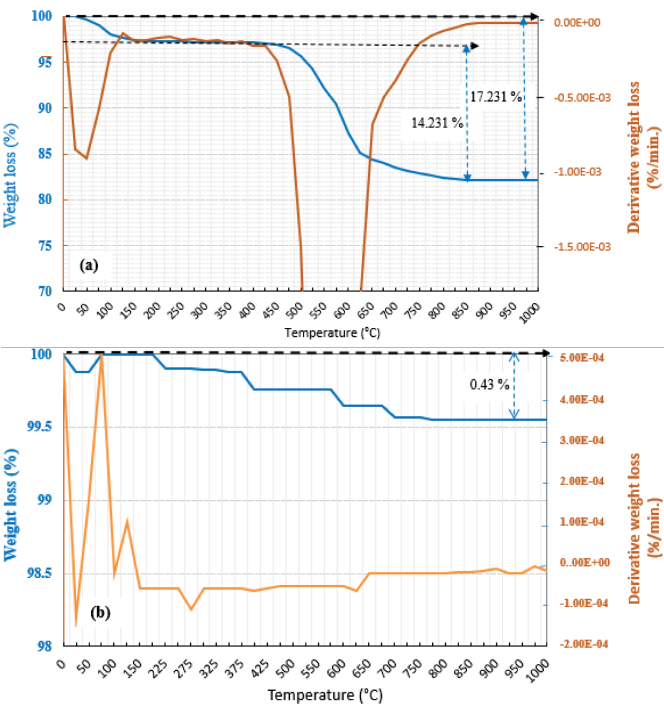


Fig. 1 Thermal gravimetric analysis (TGA / DTGA) of (a) raw kaolin and (b) calcined kaolin at 750 °C for 2 hrs. (MK)

1. ábra A nyers kaolin (a) és a 750 °C-on történő 2 órás hőkezelés után kaolin (b) termogravimetriás analízise (TGA/DTGA)

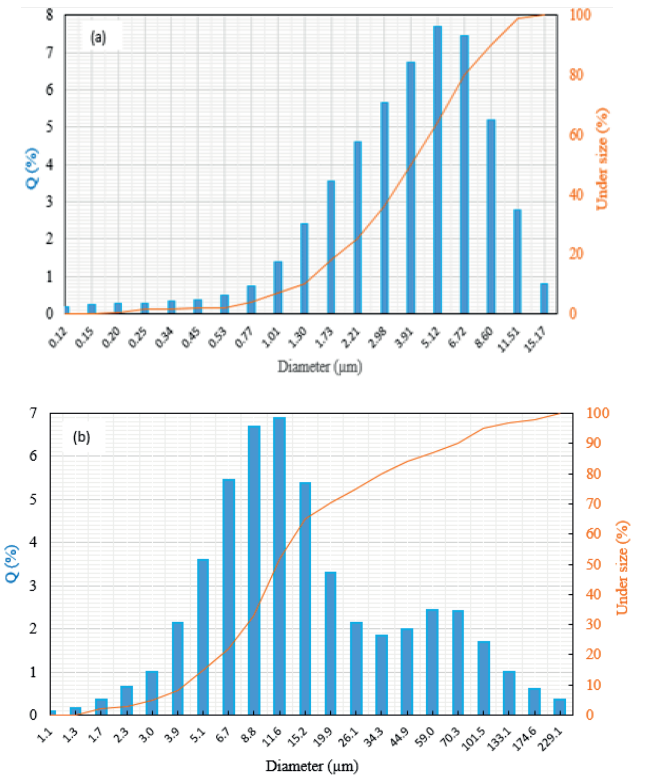


Fig. 2 Particle size distribution [(a) for MK and (b) for PDK]

2. ábra Az MK (a) és a PDK (b) szemcseméret-eloszlása

The chemical composition of (MK) and (PDK) are shown in Table 1. According to the percentages of SiO₂+Al₂O₃+Fe₂O₃ in DK is about, which fulfill the requirements of IS 3812:2003 this sample can be considered as a pozzolanic material. The mineralogical characteristics of MK and PDK are shown in Fig. 3 (a and b). XRD show that there is no mineral in the MK samples prepared, just only mullite resulted during calcination and quartz impurities derived from the source kaolin. XRD pattern of PDK shows quartz, kaolinite montmorillonite peaks and amorphous background.

Compound	Amount (weight %)		EN 450-1 Limits
	PDK	MK	
SiO ₂	82.83	52.2	Not less than 25%
SiO ₂ (active)	60 = 1.0 M	37.43 = 0.62 M	
Al ₂ O ₃	6.00 = 0.059 M	33 = 0.32 M	-
SiO ₂ /Al ₂ O ₃	16.95	1.94	
Fe ₂ O ₃	0.50	1.41	-
TiO ₂	3.20	2.2	-
MgO	0.09	0.19	Less than 4%
CaO	0.15	0.51	-
Na ₂ O	0.03	0.16	Less than 5%
K ₂ O	0.05	0.07	-
SO ₃	0.85	0.39	Less than 3%
P ₂ O ₅	0.01	0.12	Less than 5%
SrO	0.046	-	-
Cl-	0.06	0.11	Less than 0.1%
L.O.I	5.84	5.05	Category A: Not greater than 5.0% by mass / Category B: Not greater than: 7.0% by mass / Category C: Not greater than 9.0% by mass

Table 1 Chemical analysis of PDK and MK from ASCE
1. táblázat A PDK és az MK kémiai elemzése az ASCE-től

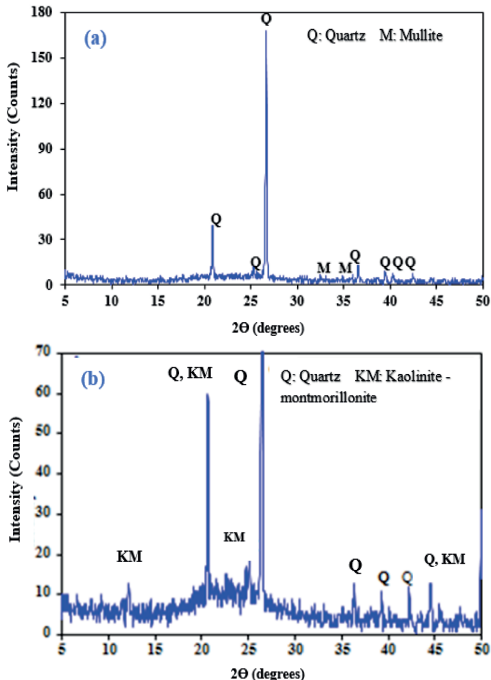


Fig. 3 XRD patterns of (a) MK and (b) PDK

3. ábra Az MK (a) és a PDK (b) XRD mintái

2.2 Geopolymerisation and curing

Geopolymer samples were prepared by added dry materials of PDK to MK in ratio of 0:100, 5:95, 10:90, 15:85, 20:80, 25:75, 30:70, 35:65, 40:60, 45:55, 50:50, 55:45 and 60:40 by weight, and alkali metal activating solutions (alkaline sodium hydroxide) and water in a 70-L pan mixer are given in Table 2. These different combinations of PDK and MK were used with two molar concentration of Na₂O (2.32 and 1.94) that have achieved two ranges of Na₂O/Al₂O₃ (0.83–0.96 M) and (0.70 – 0.80 M) respectively. NaOH was applied as an alkali metal activating solution in this research. Sodium hydroxide in platelet form was dissolved in distilled water to produce 12.26 M (Na₂O) sodium hydroxide solution.

Mix No.		Ratios of binder in geopolymer	
Na ₂ O (2.32 M)	Na ₂ O (1.94 M)	Partially De-aluminated metakaolin (PDK), weight %	Metakaolin (MK), weight %
Na ₂ O/Al ₂ O ₃ (0.83- 0.96 M)	Na ₂ O/Al ₂ O ₃ (0.70 – 0.80 M)		
M1	M14	0	100
M2	M15	5	95
M3	M16	10	90
M4	M17	15	85
M5	M18	20	80
M6	M19	25	75
M7	M20	30	70
M8	M21	35	65
M9	M22	40	60
M10	M23	45	55
M11	M24	50	50
M12	M25	55	45
M13	M26	60	40

Table 2 The mix combinations between PDK and MK
2. táblázat A PDK és az MK keverékösszetételei

For improvement of the workability of geopolymer pastes, the suitable amount of water needed for geopolymer mixing was determined, normal consistency was measured applying Humboldt Vicat's apparatus [40, 41]. The dry components of the precursors were blended firstly and the alkali activating solution were then added into the pan and mixed thoroughly for about 4 min until the mixture became glossy and well blended. The mixture was then poured into 5 cm³ cubic moulds, vibrated for perfect compaction and insulated with a cover to prevent loss of water as most as possible. All blends were kept undisturbed for curing at the ambient temperature for (24 hrs.), demolded and then subjected to further curing at the room condition 23-25 °C, and then tested for the compressive strengths. The resulted fragments were then immersed in acetone for 24 h before being dried at 60 °C, and pulverized for analysis [42].

2.3 Methods of investigation

The total-porosity was done for the relatively higher compressive strength specimens (M1 – M13). It was measured by the same equation applied previously in [44, 45] as in Eq. (1):
The total porosity (%) = $\frac{W_1 - W_3}{W_1 - W_2} \times 100$, (1)

Whilst the percentage of absorbed water was recorded by:

$$\text{Water-absorption (\%)} = [(W_1 - W_3)/W_3] \times 100. \quad (2)$$

Where: W1: saturated-weight, W2: suspended-weight and W3: dried-weight at 105 ± 2 °C. FTIR used for illustration of the crystalline and the amorphous constituents of geopolymer structure using Jasco-6100 with the aid of KBr binder in the range from 400 to 4000 cm⁻¹ [46, 47].

The morphology and microstructure of hardened geopolymer composites was examined by SEM [Inspect S-FEI Company, Netherlands] equipped with EDX. Thermogravimetry conducted using DT-50 Thermal Analyzer (Shimadzu Co-Kyoto, Japan), where the samples were crushed, transferred immediately to an alumina crucible, held under isothermal conditions for 60 min at 40 °C to equilibrate in a nitrogen environment (N₂ flowing at 200 ml/min), and then heated to 1000 °C at 10 °C/min in the same gas environment.

3. Results and discussion

3.1 Total-porosity and water-absorption

Fig. 4 illustrates the total-porosity of the investigated specimens at 28 days. Generally, the total-porosity decreases with the older hydration age. This is related to the continuous hydration and accumulation of hydration-products that occupies the available micro-pores within the binder matrix causing a pore size decreasing and reducing the total-porosity as well. As it can be noticed from Fig. 4, the presence of 25 weight % PDK (M6) marginally decreases the total-porosity at 28 days as compared to the reference. This reduction refers to the filling and pozzolanic impact of the fine PDK particles. These fine-particulates and hydration products that precipitate in the pores of the solidified geopolymer blend and consequent increase in the bulk density. However, the presence more than 25 weight % PDK causes relative increase of the total-porosity. This result are expected, because if the amount of the finest particles is higher than the optimum packing arrangement, the packing density reduces due to the clustering, leaving fin holes in between the clusters.

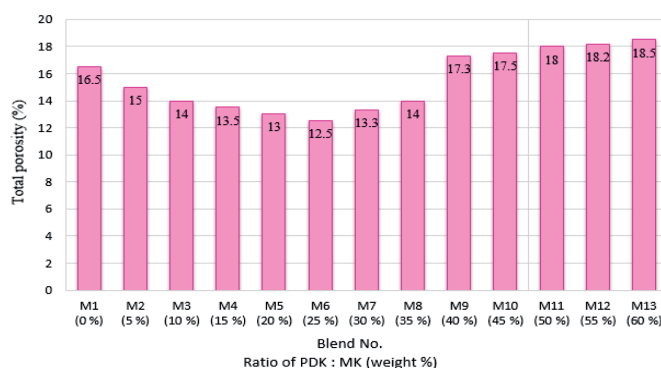


Fig. 4 Total porosity of the different combination of SiO₂ and Al₂O₃ at curing time of 28 days using constant Na₂O and the Na₂O/Al₂O₃ of 0.83 - 0.96

4. ábra A SiO₂ és Al₂O₃ különböző kombinációinak teljes porozitása 28 napos kikeményedési idő, állandó Na₂O és 0,83-0,96 Na₂O/Al₂O₃ értékek alkalmazásával

Fig. 5 illustrates the percentage of water-absorption for the tested specimens at 28 days. As expected, the trend of the water absorption is directly proportion with those of total-porosity.

The presence of 25 weight % PDK (M6) reduces the percentage of water-absorption at 28 days, whilst the presence more than or lower than 25 weight % increases it in a relative manner. So, it can be concluded that the preferred range of PDK is from 20 to 30 weight % and optimized at 25 weight %.

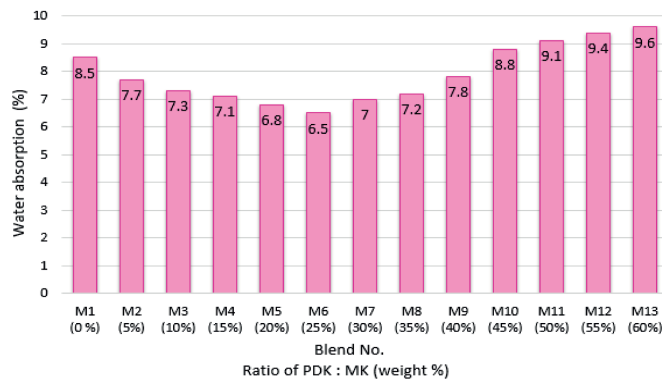


Fig. 5 Water absorption of the different combination of SiO_2 and Al_2O_3 at curing time of 28 days using constant Na_2O and the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 0.83 - 0.96

5. ábra A SiO_2 és az Al_2O_3 különböző kombinációinak vízfelvétele 28 napos kikeményedési idő, állandó Na_2O és 0,83-0,96 $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ arány alkalmazásával

3.2 Compressive strength

Variation of compressive strength with different combinations of SiO_2 and Al_2O_3 and different ratios of Na_2O are given in Tables 3, 4 and the results are also graphically illustrated as a function of curing period in Figs. 6, 7. The results reveal that the compressive strength increases with increasing hydration time (7 and 28 days) for all curing conditions due to continuous geopolymerisation and hydration reactions, also the compressive strength maximize at 25 weight % (M6) and then decreased with further addition up to 60 weight % (M13). It was found that the addition of PDK increase the compressive strength, it reach to a maximum value of 64 MPa at a percentage of 25 weight % PDK (M 6). It was found also that addition of PDK up to 55 weight % provide satisfactory compressive strengths at 7th and 28th days.

PDK was used as a source of active silica in the form of silicate of de-aluminated kaolinite along with metakaolin for manufacturing of geopolymer mortar. The effect of the three key ratios " $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{M}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{M}_2\text{O}$ " on the production of metakaolinite-based geopolymers, where M express the alkali metal ions (Na or K ion) was investigated. A total of 26 geopolymer pastes with different mole ratios $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}/\text{Na}_2\text{O}$ were prepared to examine their effects on the compressive strength. The gradation analysis of experimental results that were obtained revealed that $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ had significant impact on the compressive strength. The compressive strength increases up to 64 MPa with increasing in the quantity of PDK to reach maximum at $\text{SiO}_2/\text{Al}_2\text{O}_3=2.8$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.9$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 13.7$ these ratios were considered as fully reacted geopolymer mortar (Table 3, Fig. 6). Satisfactory results have been achieved at $\text{SiO}_2/\text{Al}_2\text{O}_3=2.8$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.75$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 13.7$ (Table 4, Fig. 7), but of lower compressive strength, so it is very important to optimize the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio to be in the range of 0.83-0.96 to get better mechanical characteristics of the geopolymer binder.

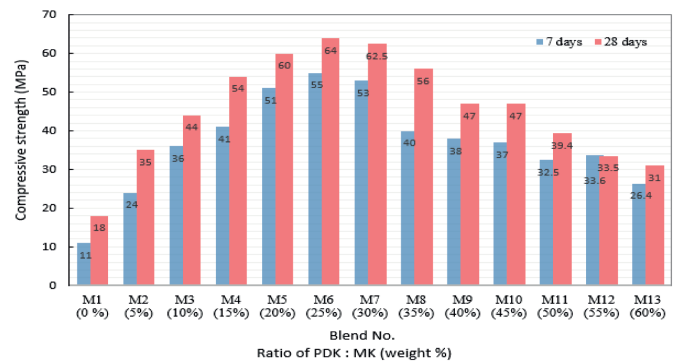


Fig. 6 Compressive strength of the different combination of SiO_2 and Al_2O_3 at curing time of 7 and 28 days using constant Na_2O that made the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ to be 0.83 - 0.96

6. ábra A SiO_2 és az Al_2O_3 különböző kombinációinak nyomószilárdsága 7 és 28 napos kikeményedési idő, állandó Na_2O és 0,83-0,96 $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ arány alkalmazásával

No.	PDK		H_2O Moles	NaOH Na_2O Moles	H_2O Total Moles	MK Molar ratio		$\text{SiO}_2/\text{Al}_2\text{O}_3$ Molar ratio	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ Molar ratio	$\text{H}_2\text{O}/\text{Na}_2\text{O}$ Molar ratio	Compressive strength, (MPa)	
	SiO_2 Moles	Al_2O_3 Moles				SiO_2 Moles	Al_2O_3 Moles				7 days	28 days
M1	0	0						1.90	0.96		11	18
M2	0.5	0.029						2.0	0.94		24	35
M3	1.0	0.058						2.28	0.93		36	44
M4	1.5	0.087						2.45	0.92		41	54
M5	2.0	0.116						2.60	0.91		51	60
M6	2.5	0.145						2.80	0.90		55	64
M7	3.0	0.174	23	2.32	31.8	4.68	2.43	2.95	0.89	13.7	53	62.5
M8	3.5	0.203						3.10	0.88		40	56
M9	4.0	0.232						3.26	0.87		38	47
M10	4.5	0.261						3.41	0.86		37	47
M11	5.0	0.290						3.56	0.85		32.5	39.4
M12	5.5	0.319						3.70	0.84		33.8	33.5
M13	6.0	0.348						3.84	0.835		26.4	31

Table 3 Compressive strength at the 28 day for a molar ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ between 0.83-0.96

3. táblázat 28 napos nyomószilárdság a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ 0,83-0,96 közötti moláris aránya esetén

No.	PDK		H ₂ O Moles	NaOH Na ₂ O Moles	H ₂ O Total Moles	MK		SiO ₂ /Al ₂ O ₃ Molar ratio	Na ₂ O/Al ₂ O ₃ Molar ratio	H ₂ O/Na ₂ O Molar ratio	Compressive strength, (MPa)	
	SiO ₂ Moles	Al ₂ O ₃ Moles				SiO ₂ Moles	Al ₂ O ₃ Moles				7 days	28 days
M14	0	0						1.90	0.80		8	12
M15	0.5	0.029						2.0	0.799		17	25
M16	1.0	0.058						2.28	0.78		32	44
M17	1.5	0.087						2.2.45	0.77		39	51
M18	2.0	0.116						2.60	0.76		41	52
M19	2.5	0.145						2.80	0.75		45	54
M20	3.0	0.174	22	1.94	26.7	4.68	2.43	2.95	0.74	13.7	33	44
M21	3.5	0.203						3.10	0.73		30	43
M22	4.0	0.232						3.26	0.73		30	40
M23	4.5	0.261						3.41	0.72		33	40
M24	5.0	0.290						3.56	0.71		28	35
M25	5.5	0.319						3.70	0.705		22	30
M26	6.0	0.348						3.84	0.70		16	22

Table 4 Compressive strength at the 28 day for a molar ratio of Na₂O/Al₂O₃ between 0.70-0.8
4 táblázat 28 napos nyomószilárdság a Na₂O/Al₂O₃ 0,83-0,96 közötti moláris aránya esetén

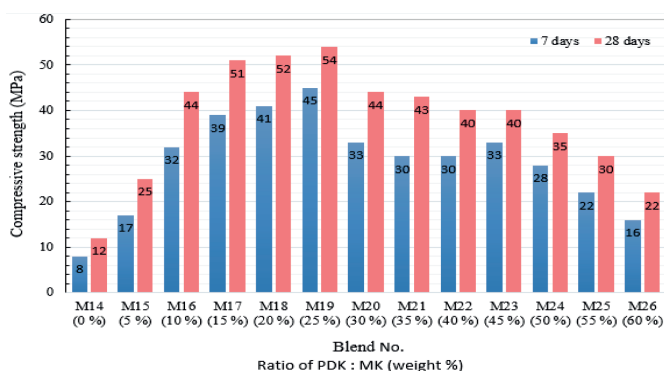


Fig. 7 Compressive strength of the different combination of SiO₂ and Al₂O₃ at curing time of 7 and 28 days using constant Na₂O that made the Na₂O/Al₂O₃ to be 0.70 – 0.80
7. ábra A SiO₂ és az Al₂O₃ különböző kombinációinak nyomószilárdsága 7 és 28 napos kikeményedési idő, állandó Na₂O és 0,70-0,80 Na₂O/Al₂O₃ arány alkalmazásával

3.3 Thermal analysis (TGA and DGA)

Figures 8, 9 show the differential thermogravimetric/thermo-gravimetric analysis (DTG/TG) for geopolymer composites with various ratio of PDK. Figure 8 shows the main endothermic peaks at about 80, 170, 450, and 700 °C whereas the first peak of the characteristic endotherm represents the free water released from the polymerization reactions, coined in macro pores of the geopolymer binder [48, 49], the second peak represents the dehydroxylation step of the strongly bound water in zeolite, as well as the dehydroxylation of strongly bound water in a calcium silicate hydrate (C-S-H gel) binder [50]. There are another endothermic peak at about 700 °C representative for calcium carbonate [51] resulting from the natural processes on the PDK after sample preparation. The figure illustrates the growth in the strength of endothermic peak at about 80 °C with curing time in mix M6 at 28 days as a results of continuous hydration and development of geopolymer reactions with aging, while there is a significant shifting in this endotherm to higher temperature informing the presence of aluminum silicate gel with strongly bound water within the geopolymeric chains in M6 rather than the other samples (Fig. 8). Through the examination of the effect of the added PDK, the endothermic peak for free water, increased

with PDK addition to about 25 weight % indicating the growth of amorphous geopolymer content with weakly bound free water. It can be witnessed that here is a clear endothermic peak for water escaped of C-S-H gel and aluminum silicate gel at 170 °C for which increased in strength with PDK addition up to 25 weight % (M6) as a results of the building up in geopolymerisation reactions which used the free silica in geopolymer production than in CSH aluminosilicate gel. A weak peak for M6 appeared at 700 °C, which refers to the destruction of carbonate salt into carbon dioxide [52]. There is wide peak in the carbonate endotherm at 650 - 700 °C, whereas the excess free alkali metal hydroxide that is not consumed in geopolymer formation as a result of early synthesis of Faujasite zeolite mineral formation which partially hinders geopolymerisation and this may cause efflorescence M1 and M5. Fig. 9 shows the weight loss of PDK based geopolymer mixes M1, M5, M6 and M7 at 28 days were 3.43, 4.5, 5.1 and 3.5%, respectively. It can be seen the total weight loss increases with PDK increase up to 25 weight % (M6) as an indication for relatively higher rate of geopolymerisation. The high water loss for M1 at a temperature greater than 800 °C displays that the early formed Faujasite zeolite beside geopolymer is destructed releasing the chemical bonded water.

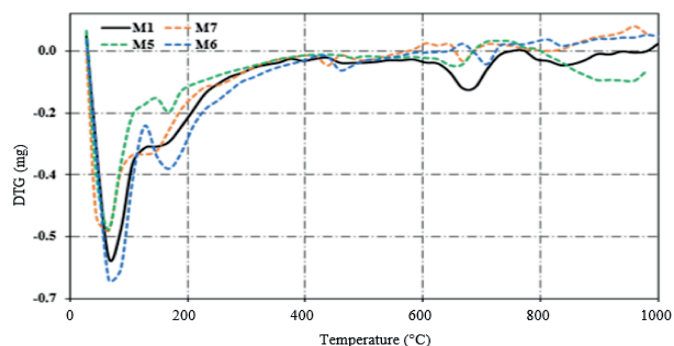


Fig. 8 Differential thermo-gravimetric analysis (DTGA) of the different combination of SiO₂ and Al₂O₃ at curing time of 28 days using constant Na₂O that made the Na₂O/Al₂O₃ to be 0.83-0.96
8. ábra A SiO₂ és az Al₂O₃ különböző kombinációinak differenciális termogravimetriás analízise (DTGA) 28 napos kikeményedési idő és állandó Na₂O alkalmazásával, a Na₂O/Al₂O₃ arány 0,83-0,96

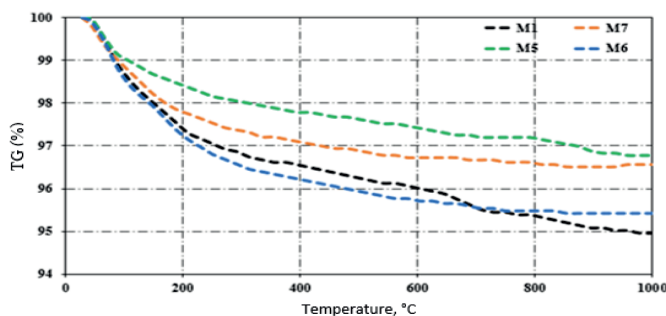


Fig. 9 Thermo-gravimetric analysis (TGA) curves of the different combination of SiO_2 and Al_2O_3 at curing time of 28 days using constant Na_2O that made the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ to be 0.83 - 0.96

9. ábra A SiO_2 és az Al_2O_3 különböző kombinációinak termogravimetriás (TGA) görbéi 28 napos kikeményedési idő és állandó Na_2O alkalmazásával, a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ arány 0,83-0,96

3.4 Fourier transforms infrared spectroscopy (FTIR)

FTIR spectra of the solidified geopolymer pastes which having different ratio of PDK are shown in Fig. 10. As can be seen, there are main wide bands of O-H stretching and bending located in the range of $3430\text{--}3460\text{ cm}^{-1}$ and 1650 cm^{-1} that characterize the water of crystallization of the hydrated compounds such as calcium silicate hydrate (C-S-H) and calcium aluminosilicate hydrate (C-A-S-H) [53]. The band intensities of the sample M6 is relatively bigger than the other blends. These confirm the higher strength of the M6 sample. The bands located between $1420\text{--}1460\text{ cm}^{-1}$ representative to stretching vibrations of O-C-O bond of carbonate compounds, which resulted from the reaction of carbon dioxide with the leached out alkali hydroxide [54]. The strongest band located at $950\text{--}1100\text{ cm}^{-1}$ is essentially resulted from the asymmetric stretching vibration of (T-O-Si), where T is tetrahedral silicon or aluminum. As seen, the bands featured for asymmetric stretching vibration of Si-O-T located at approximately 980 cm^{-1} are displaced to a lower frequency for M6 sample. This displacement is an evidence for the formation of amorphous aluminum silicate phases, indicating to new highly cross-linked geopolymer network [55]. The intensity of the band of M6 sample is higher than the other samples. The higher intensity of the band is an indication of increasing the mean chain length of aluminum silicate polymers [56]. Furthermore, the symmetric stretching vibration (Si-O-Si) in the region of 770 cm^{-1} and 690 cm^{-1} and bending vibration (Si-O-Si) and (O-Si-O) in the region of 500 cm^{-1} band intensities of M6 sample are relatively higher than other samples.

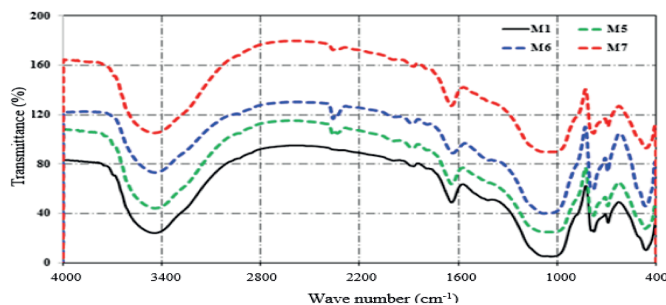


Fig. 10. FTIR spectra of the geopolymer pastes of different ratio of SiO_2 and Al_2O_3 at curing time of 28 days using constant Na_2O that made the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ to be 0.83 - 0.96

10. ábra A SiO_2 és Al_2O_3 különböző arányú geopolimer paszták FTIR spektrumai 28 napos kikeményedési időnél, állandó Na_2O alkalmazásával, a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ arány 0,83-0,96

3.5 Microstructure analyses

The micrographs of electron scanning microscope for geopolymer pastes at the 28th day which have having different ratio of DK are shown in Fig. 11. The micrograph for control blend M1 show micro-porous matrix formation with the distribution of both CSH and geopolymer within the matrix (Fig. 11a), while applying more DK up to 25% (M6) results in the generation of intensified homogenized geopolymer structure with growth of the amorphous (N-A-S-H) gel and the binding gels (C-A-S-H) that has advanced impact on the micro-structural characteristics forming compacted three-dimensional network from geopolymer strains (Fig. 11b). Adding more DK results in an increased dissimilarity with large spaces between its components causing reduction of the effectiveness of the reactions (Fig. 11c) as interpreted from the FTIR and DTG.

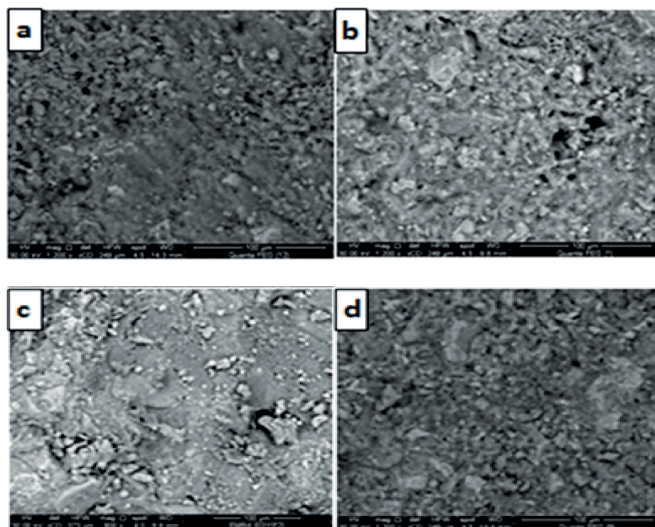


Fig. 11 SEM micrographs of the geopolymer pastes of different ratio of SiO_2 and Al_2O_3 at curing time of 28 days using constant Na_2O that made the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ to be 0.83 - 0.96 for the blends M1 (a), M5 (b), M6(c) and M7 (d).

11. ábra A SiO_2 és Al_2O_3 különböző arányú geopolimer paszták SEM mikroszkópos felvételei 28 napos kikeményedési idő és állandó Na_2O alkalmazásával, a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ arány 0,83-0,96 volt az M1 (a), M5 (b), M6(c) és M7 (d) keverékek esetében

4. Conclusions

The following items were concluded from the study the potentiality for using PDK as a siliceous material for manufacturing of geopolymer cement.

1. The geopolymer cement produced with different combination of MK and PDK are able to produce geopolymer cement (mortar) of high compressive strength (64 MPa) by self-curing mechanisms.
2. The influences of PDK on strength of geopolymer paste mixes were studied. It has been observed that the increasing the quantity of PDK increases the compressive strength of geopolymer to a certain limit of $\text{SiO}_2/\text{Al}_2\text{O}_3$.
3. The measured compressive strength of geopolymer mix is in the range from 18 MPa to 64 MPa and maximum of 64 MPa for $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.8 and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of 0.9 and $\text{H}_2\text{O}/\text{Na}_2\text{O}_3$ ratio of 13.7.

4. Sodium silicate has been prepared simultaneously during geopolymers synthesis by the reaction between PDK and NaOH that increased the building up strength of the fabricated geopolymeric mortar by inducing the activation and speciation of the siliceous and aluminum ions of the raw materials, and the self-preparation of silicates compensates shortage of silicate in the raw materials at the same time.
5. Apart from less energy intensiveness, the geopolymer concrete utilizes the industrial wastes for producing the binding system in concrete. There are both environmental and economic benefits of using MK and PDK.

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