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Solidification of Alum Industry Waste for Producing Geopolymer Mortar

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Abstract

This paper presents an experimental work, which carried out to test the feasibility of using dealuminated metakaolin (DaMK) as an additive to metakaolin (MK) in the production of geopolymer concrete. DaMK is produced as a byproduct from the aluminum sulfate industry. The chemical composition and physical properties of DaMK were investigated in this study. Results showed that DaMK is a good pozzolan material, which added to MK by 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, and 70% in producing geopolymer concrete. The compressive strength was measured by testing standard cubes at 7 and 28 days. Satisfactory results are achieved by using 20, 25, 30, 35, and 40% of DaMK. It is recommended to use MK with added proportions of DaMK up to 40% of MK to produce an ecofriendly and economic geopolymer concrete.

Keywords: *Dealuminated metakaolin, Metakaolin, Pozolan, Compressive Strength.*

Introduction

Geopolymer is an aluminosilicate amorphous material, which can interact with alkaline solutions by forming polymeric Si-O-Al-O bonds with high structural strength [1, 2]. Cement (Pozzolan/Portland) is the primary ingredient in the production of concrete, which largely utilized in the foundation and structure of buildings and bridges [3]. However, cement production releases gases, dust and consumes high quantities of energy and thus it affects the ecosystems. Heating of limestone releases CO_2, while burning fossil fuels for kilns leads to greenhouse gases. Therefore, many studies are being investigating ecofriendly alternatives for cement [4].

Geopolymers have distinct characteristics in civil engineering applications, physical and chemical properties, in terms of high compressive strength, durability, anticorrosive material, acid resistance, fire resistance, electrical insulation, thermal stability, immobilization of heavy metals and biological compatibility [5, 6, 7, 8, 9, 10]. Accordingly, geoploymers have been used in many special tasks such as radioactive waste encapsulation, fireproof construction, military engineering, aircrafts parts, decorative components, restoration of monuments medicinal applications, and even as biomaterials [11-14].

Geopolymers are being manufactured, with less consumption of energy [15], from cheap natural raw materials such as clay minerals as silico-aluminate materials (e.g. kaolinite, montmorillonite, smectite, illite etc.) [16-19]. In addition, geopolymers can be fabricated from industrial wastes (e.g. coal ash, slag, etc.) by converting the original waste into a useful product [8, 20-23].

Metakaolin (MK) is the most common in the geopolymer production at the laboratory scale, which can be obtained from the thermal activation of clay minerals (e.g. kaolinite) at a temperature between 500

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and 800 °C, resulting in the dehydroxylation of clay minerals [24]. The octahedral sheet loses water and dissolves into a disordered Meta state in case of collapsing clay minerals [25, 26, 27]. The Meta state of collapsing clay is generally known to be reactive as pozzolan [28, 29]. Firing clays to higher temperatures leads to forming new phases such as spinel, mullite and quartz particles that fill the micro-pores as micro-aggregates [30-32].

Dealuminated metakaolin (DaMK) is a byproduct of aluminum sulfate industry and it derives from acid leaching of MK (e.g. calcined kaolin, $Al_2O_3 \cdot 2SiO_2$). As result of the dealumination process, the SiO_2/Al_2O_3 ratio and B.E.T values are increased. The increasing of specific surface observed as consequence of acid attack due to the increasing of the pore volume without an appreciable increasing of the mean pore size distribution [33, 34]. It is reported that DaMK shows an appreciable pozzolanic activity using isothermal calorimetric tests [35]. The investigation of DaMK confirmed presence of quartz and highly amorphous silica with a high surface area indicating high reactivity. The mean effect of acid attack on metakaolin is the dissolution of aluminum forms from octahedral and tetrahedral sites and forming free silica. Accordingly, aluminum ions are removing from the lattice without disturbing its structure and revealing sites for substitution by other metal ions [36].

In this study, a geopolymer concrete was manufactured by using mixes of metakaolin (MK) and dealuminated metakaolin (DaMK), which is a waste derived from Aluminum Sulfate industry in Egypt. DaMK is currently using in land filling practices in which it may poses environmental threats. Therefore, this waste is grinded and then used in manufacturing of an ecofriendly and economic geopolymer concrete. In this paper, we tested several compressive strengths of geopolymer mixes with DaMK, which added in percentages to MK, to produce a workable, high strength and durable geopolymer concrete.

Materials and Methods

MK and DaMK samples were obtained from the Aluminum Sulfate Co. (ASCE) in Egypt. Both samples have undergone conditions for the polymerization process, starting with fine grinding and then drying at 105 °C for 24 hours to eliminate the humidity/water content.

The grain size distribution of the studied MK and DaMK samples was identified by laser diffraction particle size analyzer model NICOMP 380 ZLS Dynamic light scattering (PSS, Santa Barbara, CA, USA), at the Nanomaterial Investigation Laboratory, National Research Centre (NRC), Cairo, Egypt. Samples were prepared by 0.2g/5ml Millipore water and sonication for 5 minutes.

The mineral composition of MK and DaMK samples was determined from X-Ray Diffraction (XRD) analysis using PANalytical X'Pert PRO instrument. The chemical composition of MK and DaMK samples was determined using Philips X-ray fluorescence (XRF) spectrometer Model PW/2404. Both XRD and XRF analyses were performed in the central laboratories of the Egyptian Mineral Resources Authority (EMRA) at Cairo, Egypt.

Different ratios of MK and DaMK are mixed with sand, added as aggregates, for 5 minutes in a mixer to ensure its homogeneity. Then the mixer was stopped and the mixture was activated by adding NaOH and mixed for an additional 5 minutes. The final mixture then molded into 5 cm^3 cubes, whereby the compression test was carried out using a mortar handle.

Compressive strength test is the most important test for assuring the engineering quality of a building material [37]. Compressive strengths of the MK/DaMK geopolymer cubes were measured after 7 and 28 days of curing according to the ASTM C 109 Method [38]. The compressive test was carried out using Non-Automatic Compression Range 200 KN-Hoek Cell Machine in the material test laboratory of NRC at Cairo, Egypt.

Scanning Electron Microscopy (SEM) was applied on selected samples in order to study the microstructural components of the MK/DaMK geopolymer.

Whereas, Energy Dispersive Analysis X-Ray (EDAX) technique was used to identify the chemical characterization of the selected samples. Both SEM and EDAX were carried out by model Quanta FEG EMRA, in the central laboratories of EMRA at Cairo, Egypt.

Results and Discussion

The particle size distribution of MK and DaMK samples is shown in Fig. 1, indicating that MK particles are mostly in a range of 226 – 388 nm with a mean of 306 nm.While DaMK particles are mostly in a range of 188 – 514 nm with a mean of 366 nm.The analysis shows that MK particles are closely like those of DaMK, however MK particles are slightly finer and spherical and DaMK particles are irregular in shape [39].

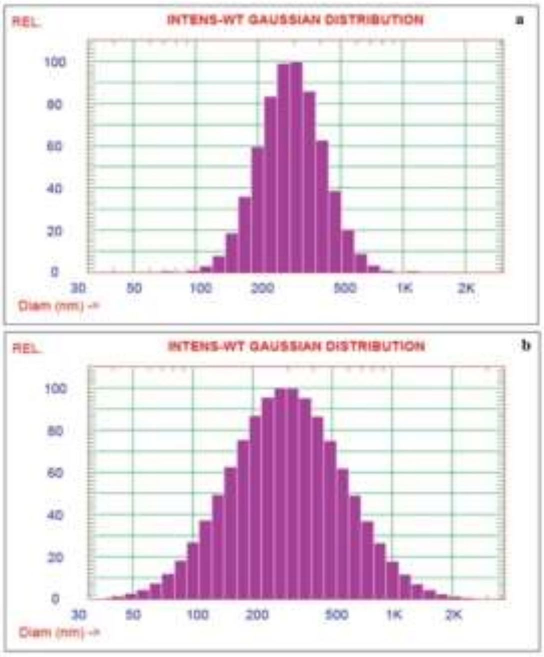

Fig. 1. The particle size distribution of MK (a) and DaMK (b) samples.

Table 1 summarizes the chemical composition of MK and DaMK samples as analyzed using XRF to check whether the materials are a pozzolan and if it can be used in the production of geopolymer concrete. The analysis shows that total amount of the major components (SiO_2, Al_2O_3 and Fe_2O_3) in MK are 85.06% while CaO and SO_3 contents are 4.16% and 2.09%, respectively. In the other hand, total amount of the major components in DaAK are SiO_2 (82.83%) and Al_2O_3 (6%). Therefore, according to the European specification and criteria, this can be used as a pozzolan material [40, 41].

Kaolinite is the raw material in the manufacture of MK and DaMK after several successive operations that are carrying out in the ASCE, where kaolinite is cracked, grinded and then calcined at 700 °C for two hours to form MK, then react with concentrated sulfuric acid to extract alumina and forming DaMK [42]. The mineral characteristics of MK and DaMK samples, that determined by XRD, are shown in Fig. 2. The analysis shows that MK samples consist of mainly amorphous humps with peaks of minor crystalline inclusions of quartz, gypsum and nontronite (Fig. 2a). While DaMK samples consist of amorphous humps with peaks of mineral components of quartz, anatase and sillimanite (Fig. 2b).

The value of specific gravity of aggregate and filler is very important in determining the quantity, which required in the mix proportioning. Hence, this test must be done for the aggregate. The specific gravity of sand, which used in this study, was 2.35 and carried out using laboratory tests [43, 13].

The mix combinations were carried out by adding DaMK to MK in percentages of 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, and 80% by weight and are tabulated in Table 2. The compressive strengths of these mixes were determined. While different mix combinations are going to be casted and tested in a further study.

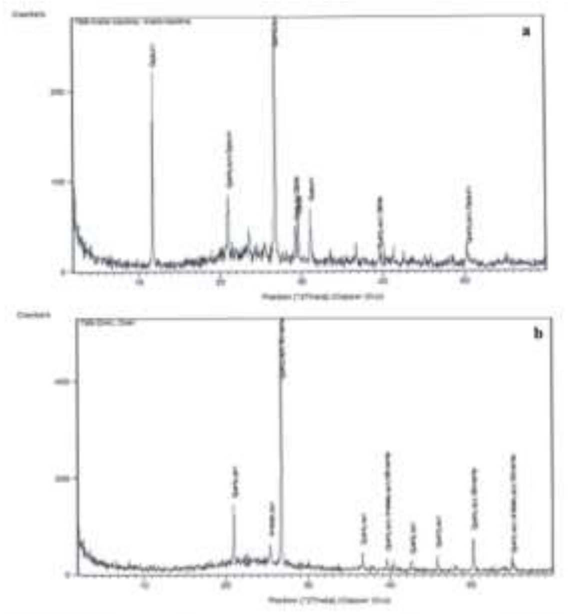

Fig. 2. XRD pattern of MK (a) and DaMK(b) samples.

Table 1. Chemical analysis of MK and DaMK samples.

Parameter	Value % (mass)		EN 450-1 Limits
	MK	DaMK	
SiO_2	52.12	82.83	Not less than 25%
Al_2O_3	31	6.00	-
Fe_2O_3	1.96	0.50	-
SiO_2+ Al_2O_3 + Fe_2O_3	85.06	89.33	Not less than 70%
TiO_2	2.33	3.4	Less than 4%
MgO	0.88	0.09	-
MnO	0.02	0.01	
CaO	4.16	0.15	Less than 5%
Na_2O	0.07	0.03	-
K_2O	0.09	0.05	Less than 3%
SO_3	2.09	0.85	Less than 5%
P_2O_5	0.06	0.01	-
Cl^-	0.13	0.06	Less than 0.1%
Loss of Ignition (L.O.I)	4.8	5.84	Category A: Not greater than 5% by mass Category B: Not greater than: 7% by mass Category C: Not greater than 9% by mass
Total	99.69	99.82	

Table 2. The mix combinations between MK and DaMK that casted and tested in this study.

Mix No.	Ratios of binder in geopolymer	
	Metakaolin (MK)	Dealuminated MetaKaolin (DaMK)
1	5	1
2	5	1.25
3	5	1.50
4	5	1.75
5	5	2
6	5	2.25
7	5	2.5
8	5	2.75
9	5	3
10	5	3.25
11	5	3.5
12	5	3.75
13	5	4

Table 3 Compressive strength at 7th and 28th days for different mixes.

Mix No.	Metakaolin + Dealuminated metakaolin SiO_2 /Al_2O_3	Na_2O/ Al_2O_3	H_2O/ Na_2O	Compressive strength (MPa)	
				7th day	28th day
1	20% DaMK 5.72 / 1.57 = 3.64	1.2	10	16.872	19.163
2	25% DaMK 6.07 / 1.59 = 3.81			29.837	36.440
3	30% DaMK 6.41 / 1.61 = 3.98			31.126	41.502
4	35% DaMK 6.76 / 1.62 = 4.17			38.154	50.649
5	40% DaMK 7.10 / 1.64 = 4.33			41.388	51.287
6	45% DaMK 7.45 / 1.65 = 4.52			34.530	46.041
7	50% DaMK 7.69 / 1.67 = 4.60			29.587	39.45
8	55% DaMK 8.14 / 1.68 = 4.85			21.471	28.252
9	60% DaMK 8.49 / 1.70 = 4.99			17.431	22.638
10	65% DaMK 8.83 / 1.71 = 5.16			15.345	20.461
11	70% DaMK 9.18 / 1.73 = 5.31			12.295	17.528
12	75% DaMK 9.52 / 1.74 = 5.47			10.909	14.742
13	80% DaMK 9.87 / 1.75 = 5.64			10.416	13.888

Fig.3. 5 cm^3 cubes casted for testing.

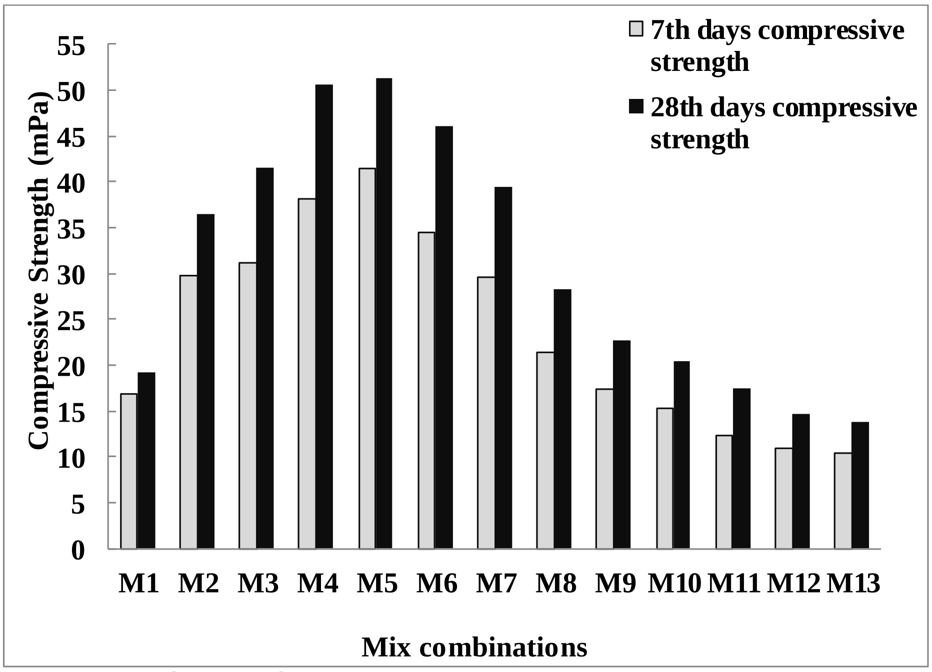

Fig. 4. Variation of 7th and 28th days compressive strengths with different mix combinations.

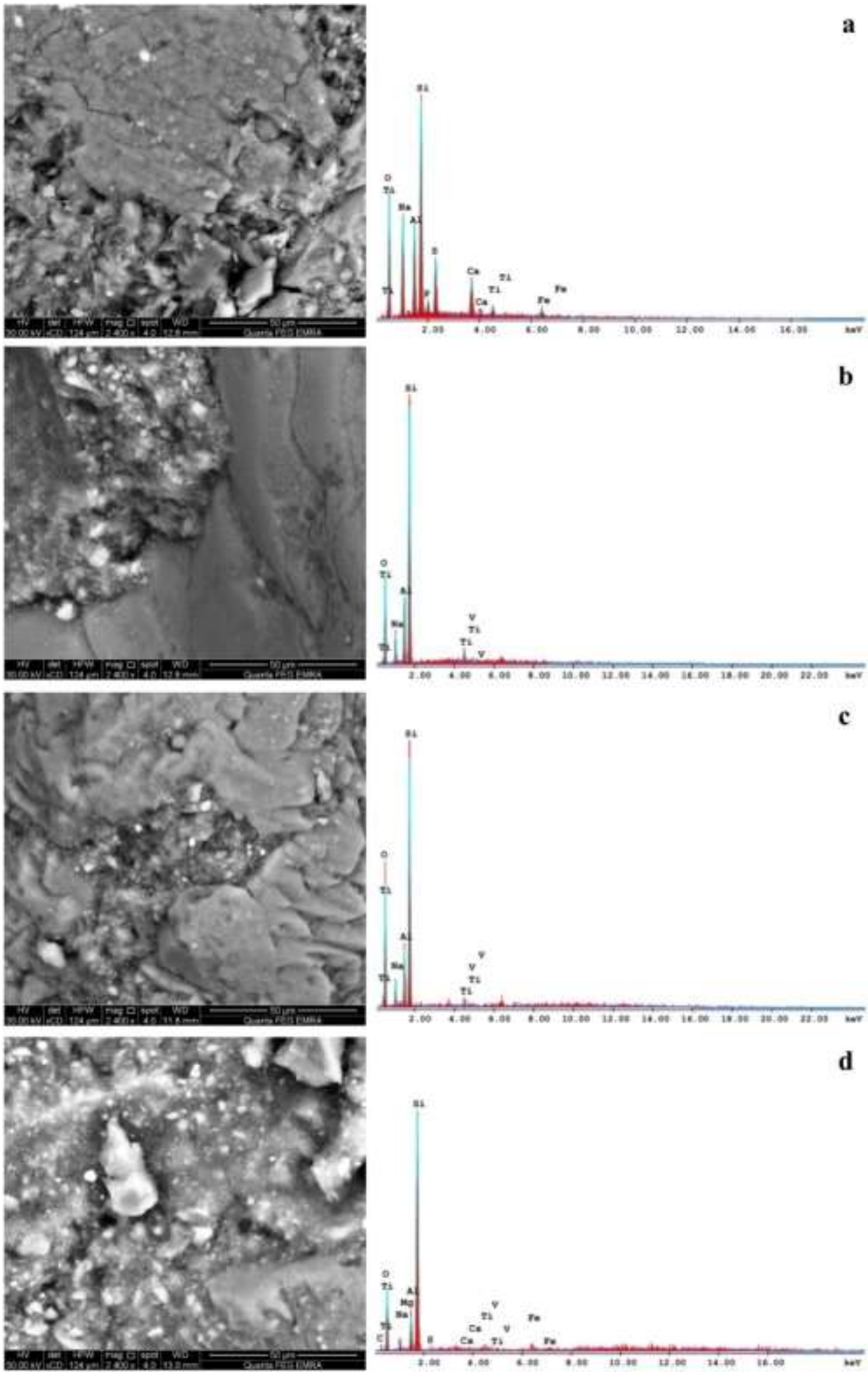

Fig. 5. SEM images (left) and EDAX charts (right) for the studied Geopolymer Mixes 1 (a), 5 (b), 6 (c) and 13 (d).

We figured out that there are no Egyptian standard specifications available for designing the mix of geopolymer concrete. Therefore, the design of geopolymer mix is done in this study using available literatures and the aggregateis taken as 75% of entireconcrete mix by mass. This value is like that used in Ordinary Portland Cement concrete (OPC) which is in a range of 75-80% of the entire concrete mix by mass [44, 45]. The average density of metakaolin geopolymer concrete is about 2200 kg/m^3 [46]. Knowing the density of concrete, the combined mass of alkaline solution and metakaolin can be calculated. The ratio of alkaline solution to metakaolin is assumed 0.25; mass of metakaolin and mass of alkaline solution are estimated. The concentration of NaOH solution, which used in this study, is 12.5 M. The proportioning for MK: DaMK: aggregates: water [47] is reported in Table 3.

Workability is the ability of a fresh concrete mix to fill the mold properly with required vibration and without reducing the quality of concrete [48]. Workability depends on water content, aggregate (shape and size distribution), cementitious content and age (level of hydration), which can be modified by adding chemical admixtures, like super-plasticizer [49]. Trial cubes were casted using mold size of 5 cm^3 for initial testing (Fig.3). These cubes were cured at normal temperature and were set after 6 hours from casting. Then the cubes were casted manually using trowel and manual mixing. There was no need for oiling the mold because it was made of Formica and then the cubes were dried in an open area without heating [50].

After curing at the ambient condition (at 22-25℃), the compressive strength of the cubes was measured at the 7^{th} and the 28^{th} days [51] and reported in Table 3.

A total of 13 mixtures with different molar ratios SiO_2/Al_2O_3, $Na_2O/\ Al_2O_3$ and H_2O/Na_2O were designated to investigate the effects on mechanical strength. The gradation analysis of experimental results revealed that Na_2O/Al_2O_3 and H_2O/Na_2O had significant impact on the compressive strength [52].

DaMK, a solid waste derived after dealumination process for producing aluminum sulfate which is a coagulant used in water treatment in Egypt, was used as a source of active silica along with MK for manufacturing of the geopolymer concrete. It is noted that Na_2SiO_3 is self-prepared inside the mixture by reacting NaOH with DaMK. We noticed that the compressive strength starts to develop at 20% added DaMK to MK (Mix 1). Then further addition of DaMK increases the compressive strength up to a maximum value of 51 MPa at a percentage of 35% and 40% of DaMK (Mixes 4 and 5). We also noticed that addition of DaMK up to 55% provides satisfactory compressive strengths at 7^{th} and 28^{th} days. The variation in the compressive strengths with mix combinations is indicated in Fig. 4.

Results of this study show that the compressive strength increases with increasing the quantity of DaMK reaching the maximum at SiO_2/Al_2O_3 = 4 into 4.5, Na_2O/Al_2O_3 = 1.2 and H_2O/Na_2O = 10. The mechanical properties of the geopolymers depends on amounts of active aluminum silicates in the starting material, the type of activator and the processing temperature [53].

The SEM images and EDAX analysis for the studied Mixtures (1, 5, 6 and 13, Table 3) are shown in Fig. 5. The cementitious products bind MK and DaMK particles then fill up the pore spaces and forming a dense matrix. These images obviously show the morphology of particles in the geopolymerization process [54, 55] (Fig. 5). We noticed that the Mix1 (Fig. 5a) shows a lower compressive strength (19 MPa) due to the low ratio of $SiO_2/Al_2O_{3,}$ which is in sufficient to form the cementitious geopolymer product. Therefore, we can see some cracks and caves in the SEM image of Mix 1 (Fig. 5a). The Mix 5 has the optimum ratio of SiO_2/Al_2O_3 (which equals 3) in the DaMK/MK geopolymer mixes produced in this study with a maximum strength of 51 MPa at 28 days. This obviously can be seen in the consistent and smooth surface of the geopolymer without cracks and caves (Fig. 5b). Moreover by increasing the SiO_2/Al_2O_3 ratio (more than 3) in Mix 6, the strength of the mix starts to decrease (46 MPa), but the geopolymer surface still consistent and smooth (Fig. 5c). The Mix 13 has the lowest compressive strength (13.88 MPa) in the produced geopolymer mixes which shows a loose and rough surface full of caves and pits (Fig. 5d).

The EDAX analysis shows that the ratios of SiO_2/Al_2O_3 and Na_2O/Al_2O_3 in the geopolymer mixes (Fig. 5) have similar behavior like those calculated and reported in Table 3.

Ensuring the usability of metakaolin as starting material for geopolymers, Qhatani and Moatafa (2010) stated that curing metakaolin at ambient temperature might delay the strength development. Accordingly, we suggest that there is no need for curing at higher temperatures as activation was preceded properly. The geopolymer concrete produced in this study shows higher compressive strengths without the need of adding sodium silicate, which formed during the activation process because of the chemical reaction between activated silicate in DaMK and the amount of sodium hydroxide. The geopolymer concrete has very low workability at the nominal blends. Therefore, super-plasticizer of any type or little excess water must be added to facilitate workability [56, 57]. The chemistry of geopolymers depends on the activators. Based on the findings of this study, NaOH, water glass and mixture of NaOH and water glass can be used independently as activator for producing geopolymer concrete [24].

Conclusions

The geopolymer produced in this study from different mix combinations of MK and DaMK, can produce high-grade structural concrete (more than 40 MPa) using self-curing mechanisms.

The influence of DaMK on strength of the geopolymer mixes was investigated as well. Its noticed that by increasing quantity of DaMK, the compressive strength of geopolymer mixes increases. The measured compressive strength of the geopolymer mixes is in a range of 40-51 MPa up to the maximum strength of 51 MPa for 40% of DaMK at 7th and 28th days respectively.

Water glass can be prepared during the production of geopolymers by the reaction between DaMK and NaOH. This reaction increases the rate of strength development of the produced geopolymers, by accelerating the hydrolysis of silicate and aluminum components and compensates the shortage of silicates in the raw materials.

The geopolymer concrete produced from industrial wastes (MK and DaMK) has ecofriendly and economic benefits with less energy consumption.

References

[1] Davidovits, J., 2008. "Geoplolymer chemistry and application". Institute Geopolymer Saint-Quentin, France, 2nd Ed, pp. 32.

[2] Ng, C., Alengaram, U. J., Wong, L. S., Mo, K. H., Jumaat, M. Z., and Ramesh, S. 2018. A review on microstructural study and compressive strength of geopolymer mortar, paste and concrete. Construction and Building Materials, 186, 550–576. https://doi.org/10.1016/j.conbuildmat.2018.07.075.

[3] Ali, M.M., 2001. Evolution of concrete skyscrapers: from Ingalls to Jinmao. ElectronicJournal of Structural Engineering, 1(1), 2-14.

[4] Kumar, T.P., Sudheesh. C. &Sasi Kumar. S., 2015. "Strength characteristics of saw dust ash based geopolymer concrete". International Journal of ChemTech Research, 8(2), 738-745.

[5] Sathia, R., Babu, K. G., and Santhanam, M., 2008. "Durability study of low calcium fly ash geopolymer concrete". In Proceedings of the 3rd ACF International Conference-ACF/VCA. https://www.researchgate.net/profile/Ko_Ganesh_babu/publication/237643013

[6] Thokchom, S., Ghosh, P. and Ghosh, S., 2010. "Performance of fly ash based geopolymer mortars in sulphate solution". Journal of Engineering Science and Technology Review, 3(1), 36-40. https://core.ac.uk/download/pdf/25919565.pdf

[7] Davidovits, J., 2011. 'Geopolymer Chemistry and Applications'. Institute Geopolymer, France. http://refhub.elsevier.com/S0169-1317(17)30261-2/rf0050.

[8] Provis, J.L. and Van Deventer, J.S. eds., 2013. Alkali activated materials: state-of-the-art report, RILEM TC 224-AAM (Vol. 13). Springer Science & Business Media. DOI: 10.1007/98-94-007-7672-2

[9] Zhang, Z.H., Zhu, H.J., Zhou, C.H. and Wang, H., 2016. Geopolymer from kaolin in China: an overview. Applied Clay Science, 119, 31-41. https://doi.org/10.1016/j.clay.2015.04.023

[10] Aguirre-Guerrero, A.M., Robayo-Salazar, R.A. and de Gutiérrez, R.M., 2017. A novel geopolymer application: Coatings to protect reinforced concrete against corrosion. Applied Clay Science, 135, 437-446. https://doi.org/10.1016/j.clay.2016.10.029

[11] Barsoum, M.W., Ganguly, A. and Hug, G., 2006. "Microstructural evidence of reconstituted limestone blocks in the Great Pyramids of Egypt". Journal of the American Ceramic Society, 89(12), 3788-3796. **https://doi.org/10.1111/j.1551-2916.2006.01308.x**

[12] Fernandes, H.R., Gaddam, A., Rebelo, A., Brazete, D., Stan, G.E. and Ferreira, J.M., 2018. Bioactive glasses and glass-ceramics for healthcare applications in bone regeneration and tissue engineering. Materials, 11(12), 2530; doi:10.3390/ma11122530.

[13] Chakravorty, A., Khatri, R., Tejkuvarba, Parmar, A., 2014. 'Effect of aggregate size and silica fume on the workability of geopolymer concrete' Int. J. Res. Eng. Technology, 3 (4). http://refhub.elsevier.com/S0169-1317(17)30261-2/rf0030.

[14] Damilola, O.M., 2013. Syntheses, characterization and binding strength of geopolymers: A review. Int. J. Mat.

Sci. Applications, 2, 185-193. doi: 10.11648/j.ijmsa.20130206.14

[15] McLellan, B.C., Williams, R.P., Lay, J., Van Riessen, A. and Corder, G.D., 2011. Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement. Journal of cleaner production, 19(9-10), 1080-1090. https://doi.org/10.1016/j.jclepro.2011.02.010

[16] Van Jaarsveld, J.G.S., Van Deventer, J.S.J. and Lukey, G.C., 2004. A comparative study of kaolinite versus metakaolinite in fly ash based geopolymers containing immobilized metals. Chemical Engineering Communications, 191(4), 531-549. https://www.tandfonline.com/doi/abs/10.1080/00986440490277974

[17] Van Jaarsveld, J.G.S., Van Deventer, J.S.J. and Lukey, G.C., 2002. The effect of composition and temperature on the properties of fly ash-and kaolinite-based geopolymers. Chemical Engineering Journal, 89(1-3), 63-73. https://doi.org/10.1016/S1385-8947(02)00025-6

[18] Skorina, T., 2014. Ion exchange in amorphous alkali-activated aluminosilicates: Potassium based geopolymers. Applied Clay Science, 87, 205-211. https://doi.org/10.1016/j.clay.2013.11.003

[19] El-Eswed, B.I., Yousef, R.I., Alshaer, M., Hamadneh, I., Al-Gharabli, S.I. and Khalili, F., 2015. Stabilization/solidification of heavy metals in kaolin/zeolite based geopolymers. International Journal of Mineral Processing, 137, 34-42. https://doi.org/10.1016/j.minpro.2015.03.002

[20] Wang, S., Li, L. and Zhu, Z.H., 2007. Solid-state conversion of fly ash to effective adsorbents for Cu removal from wastewater. Journal of Hazardous Materials, 139(2), 254-259. https://doi.org/10.1016/j.jhazmat.2006.06.018

[21] Zboon, K., Harahsheh, M.S. and Hani, F.B., 2011. Fly ash-based geopolymer for Pb removal from aqueous solution. Journal of Hazardous Materials, 188(1-3), 414-421. DOI: 10.1016/j.jhazmat.2011.01.133

[22] Yunsheng, Z., Wei, S., Qianli, C. and Lin, C., 2007. Synthesis and heavy metal immobilization behaviors of slag based geopolymer. Journal of Hazardous Materials, 143(1-2), 206-213. doi: 10.1016/j.jhazmat.2006.09.033.

[23] Suksiripattanapong, C., Kua, T.A., Arulrajah, A., Maghool, F. and Horpibulsuk, S., 2017. Strength and microstructure properties of spent coffee grounds stabilized with rice husk ash and slag geopolymers. Construction and Building Materials, 146, 312-320.

[24] Li, C., Sun, H. and Li, L., 2010. A review: The comparison between alkali-activated slag (Si+ Ca) and metakaolin (Si+ Al) cements. Cement and concrete research, 40(9), 1341-1349. https://doi.org/10.1016/j.cemconres.2010.03.020

[25] Baronio, G. and Binda, L., 1997. “Study of the pozzolanicity of some bricks and clays”. Construction and Building Materials, 11(1), 41-46. https://doi.org/10.1016/S0950-0618(96)00032-3

[26] Fernandez, R., Martirena, F. and Scrivener, K.L., 2011. The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite. Cement and Concrete Research, 41(1), 113-122. https://doi.org/10.1016/j.cemconres.2010.09.013

[27] Chen, L., Wang, Z., Wang, Y., and Feng, J., 2016. Preparation and properties of alkali activated metakaolin-based geopolymer. Materials, 9(9), 1–12. https://doi.org/10.3390/ma9090767.

[28] He, C., Makovicky, E. and Osbaeck, B., 2000. “Thermal stability and pozzolanic activity of raw and calcined mixed-layer mica/smectite”. Applied Clay Science, 17(3-4), 141-161. https://doi.org/10.1016/S0169-1317(00)00011-9

[29] Kakali, G., Perraki, T.H., Tsivilis, S. and Badogiannis, E., 2001. “Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity”. Applied clay science, 20(1-2), 73-80. https://doi.org/10.1016/S0169-1317(01)00040-0

[30] Mendelovici, E., 1997. “Comparative study of the effects of thermal and mechanical treatments on the structures of clay minerals”. Journal of Thermal Analysis and Calorimetry, 49(3), 1385-1397. https://doi.org/10.1007/bf01983697

[31] McManus, J., Ashbrook, S.E., MacKenzie, K.J. and Wimperis, S., 2001. “^{27}Al multiple-quantum MAS and ^{27}Al {^{1}H} CPMAS NMR study of amorphous aluminosilicates”. Journal of Non-Crystalline Solids, 282(2-3), 278-290. https://doi.org/10.1016/S0022-3093(01)00313-1

[32] Lee, W.E., Souza, G.P., McConville, C.J., Tarvornpanich, T. and Iqbal, Y., 2008. Mullite formation in clays and clay-derived vitreous ceramics. Journal of the European Ceramic Society, 28(2), 465-471. https://doi.org/10.1016/j.jeurceramsoc.2007.03.009

[33] Mohamed, M.A., Kassim, M.E. and El-Katatny, E.A., 1998. Optimization of the extraction of aluminum sulfate and ammonium aluminum sulfate alums from aluminum dross tailings. Journal of materials research, 13(4), 1075-1083. https://doi.org/10.1557/JMR.1998.0149

[34] Aderemi, B.O., Edomwonyi-Otu, L. and Adefila, S.S., 2009. A new approach to metakaolin dealumination. Australian Journal of Basic and Applied Sciences, 3(3), 2243-2248.

[35] Mostafa, N.Y., El-Hemaly, S.A.S., Al-Wakeel, E.I., El-Korashy, S.A. and Brown, P.W.,2001. “Characterization and evaluation of the pozzolanic activity of Egyptian industrial by-products: I: Silica fume and dealuminated kaolin”. Cement and Concrete

Research, 31(3), 467-474. https://doi.org/10.1016/S0008-8846(00)00485-3

[36] Nigussie, W., Zewge, F. and Chandravanshi, B.S., 2007. Removal of excess fluoride from water using waste residue from alum manufacturing process. Journal of Hazardous Materials, 147(3), pp.954-963. https://doi.org/10.1016/j.jhazmat.2007.01.126

[37] Krishnan, P. and Jewaratnam, J., 2017. Recovery of Water Treatment Residue into Clay Bricks. Chemical Engineering Transactions, 56, 1837-1842. https://doi.org/10.3303/CET1756307

[38] ASTM C109 / C109M-16a (2016), Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens), ASTM International, West Conshohocken, DOI: 10.1520/C0109_C0109M-16A

[39] KenneDiffo, B.B., Elimbi, A., Cyr, M., Dika Manga, J. and TchakouteKouamo, H., 2015. Effect of the rate of calcination of kaolin on the properties of metakaolin-based geopolymers. Journal of Asian Ceramic Societies, 3(1), 130-138. https://doi.org/10.1016/j.jascer.2014.12.003

[40] EN 450-1, 2012. Fly ash for concrete. Part 1: Definition, and specifications and criteria. European Committee for Standardisation CEM, Brussels.

[41] Szarek, Ł., and Wojtkowska, M., 2018. Properties of fly ash from thermal treatment of municipal sewage sludge in terms of EN 450-1. Archives of Environmental Protection, 44, 63-69. DOI: 10.24425/118182

[42] Das, B.R., Dash, B., Tripathy, B.C., Bhattacharya, I.N. and Das, S.C., 2007. Production of η-alumina from waste aluminium dross. Minerals engineering, 20(3), 252-258. https://doi.org/10.1016/j.mineng.2006.09.002

[43] Pan, Z., Sanjayan, J.G. and Kong, D.L., 2012. Effect of aggregate size on spalling of geopolymer and Portland cement concretes subjected to elevated temperatures. Construction and Building Materials, 36, 365-372. https://doi.org/10.1016/j.conbuildmat.2012.04.120

[44] Basheer, L., Basheer, P.A.M. and Long, A.E., 2005. Influence of coarse aggregate on the permeation, durability and the microstructure characteristics of ordinary Portland cement concrete. Construction and Building Materials, 19(9), 682-690. https://doi.org/10.1016/j.conbuildmat.2005.02.022

[45] IS 383,1970.Indian standard specification for Coarse and Fine Aggregates from Natural Sources for Concrete. https://archive.org/details/gov.in.is.383.1970/page/n3.

[46] Cheng-Yong H., Yun-Ming L., Abdullah M.M., Hussin K., 2017. "Thermal Resistance Variations of Fly Ash Geopolymers: Foaming Responses." Scientific Reports, 7, 45355, doi:10.1038/srep45355.

[47] Vijai, K., Kumutha, R., and Vishnuram, B., 2010. Effect of Types of curing on strength of geopolymer concrete. International Journal of Physical Sciences 5(9), 1419-1423. Doi.org/10.5897/IJPS.9000200

[48] Gencel, O., Brostow, W., Datashvili, T. and Thedford, M., 2011. Workability and Mechanical performance of steel fiber-rainforced self-compacting concrete with fly ash. Composite Interfaces, 18(2), 169-184.

[49] Nazari, A., Riahi, S., Shamekhi, S. and Khademno, A., 2010. Influence of Al_2O_3nano-particles on the compressive strength and workability of blended concrete. Journal of American Science, 6(5), 6-9.

[50] Naik, T.R., Kumar, R., Ramme, B.W. and Canpolat, F., 2012. Development of high-strength, economical self-consolidating concrete. Construction and Building Materials, 30, 463-469 https://doi.org/10.1016/j.conbuildmat.2011.12.025

[51] Komnitsas, K.A., 2011. Potential of geopolymer technology towards green buildings and sustainable cities. Procedia Engineering, 21, 1023-1032. https://doi.org/10.1016/j.proeng.2011.11.2108

[52] Yunsheng, Z., Wei, S. and Zongjin, L., 2010. "Composition design and microstructural characterization of calcined kaolin-based geopolymer cement". Applied Clay Science, 47(3-4), 271-275. https://doi.org/10.1016/j.clay.2009.11.002

[53] Qhatani, M. and Mostafa, N.Y., 2010. "Investigating the possibility of utilizing low kaolinitic clays in production of geopolymer bricks". Ceramics-Silikaty, 54(2), 160-168. http://www.ceramics-silikaty.cz/2010/2010_02_160.htm

[54] Cheng, T.W., Lee, M.L., Ko, M.S., Ueng, T.H. and Yang, S.F., 2012. The heavy metal adsorption characteristics on metakaolin-based geopolymer. Applied Clay Science, 56, 90-96. https://doi.org/10.1016/j.clay.2011.11.027

[55] Javadian, H., Ghorbani, F., Tayebi, H.A. and Asl, S.H., 2015. Study of the adsorption of Cd (II) from aqueous solution using zeolite-based geopolymer, synthesized from coal fly ash; kinetic, isotherm and thermodynamic studies. Arabian Journal of Chemistry, 8(6), 837-849. https://doi.org/10.1016/j.arabjc.2013.02.018

[56] Kirschner, A. and Harmuth, H., 2004. "Investigation of geopolymer binders with respect to their application for building materials". Ceramics-Silikaty, 48(3), 117-120.

[57] Ferone, C., Colangelo, F., Roviello, G., Asprone, D., Menna, C., Balsamo, A., Prota, A., Cioffi, R. and Manfredi, G., 2013. "Application-oriented chemical optimization of a metakaolin based geopolymer". Materials, 6(5), 1920-1939. **https://doi.org/10.3390/ma60519**